“Quat-Primer” polymers based on b-PEI and their application in composites

Von der Fakultät für Mathematik, Informatik und Naturwissenschaften der RWTH Aachen University zur Erlangung des akademischen Grades eines Doktors der Naturwissenschaften genehmigte Dissertation

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Publcations and Posters:

Publications: *'Quat-Primer' Polymers Bearing Cationic and Reactive Groups: Synthesis, Characterization, and Application.* Vishal Goel, Uwe Beginn, Ahmed Mourran, Martin Möller. *Macromolecules* **2008**, *41*, 8187-8197.

Adsorption of single molecules of functionalized polyethylenimine onto HOPG. Vishal Goel, Ahmed Mourran, Uwe Beginn, Martin Möller. *In preparation.*

Systematic study of adsorption of polyethylenimine bearing cationic and long alkyl groups and its application. Vishal Goel, Ahmed Mourran, Uwe Beginn, Martin Möller. *In preparation.*

Posters: *"New Technologies with Water"* Vishal Goel, Mi Ran Yu, Helga Thomas, Martin Möller, Uwe Beginn, Bio and Polymers, Aachen, September 28th – 30th **2008**.

"Advance Textile Technologies for Global Competition" Vishal Goel, Mi Ran Yu, Helga Thomas, Metodi Bozukov, Martin Möller 2nd Aachen Dresden International Textile Confrence, **2008** Germany.

Contents

List of Abbreviations:

Chemicals

$CDCl_3$	deuterated chloroform
CH_2Cl_2	dichloromethane
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DMF	N,N-dimethylformamide
DMSO	dimethylsulfoxide
EGDMA	ethylene glycol dimethacrylate
Et_2O	diethylether
HCl	hydrochloric acid
MeOH	methanol
Na_2SO_4	sodium sulphate
m-CPBA	3-chloroperoxybenzoic acid
b-PEI	branched polyethyleneimine
THF	tetrahydrofuran
TMS	tetramethylsilane

Units, Symbols and General

^{o}	degree
^oC	degree celsius
AFM	atomic force microscopy
bp	boiling point
C	concentration
d	diameter
d	doublet (NMR)
DLS	dynamic light scattering
DSC	differential scanning calorimetry
GPC	gel permeation chromatography
h	hours
Hg	mercurry
HOPG	highly oriented pyrolytic graphite
Hz	hertz

IR	infra red spectroscopy
J	coupling constant
L_n	number average countor length
L_w	weight average countor length
m	multiplet (NMR)
mL	millilitre
mm	milimeter
M_n	number average molecular weight
M_w	weight average molecular weight
n.d.	not determined
NMR	nuclear magnetic resonance
nm	nanometer
PDI	polydispersity index
ppm	parts per million
q	quartet (NMR)
R_h	hydrodynamic radius
RT	room temperature (21^{o}C)
s	singlet (NMR)
SFM	scanning force microscopy
t	time
t	triplet (NMR)
TLC	thin-layer chromatography
TGA	thermogravimetric analysis
T_g	glass transition temperature
T_m	melting temperature
UV	ultraviolet light
wt %	weight percent
δ	chemical shift (NMR)
μm	micrometer
λ	wavenumber
σ_f	tensile strength
τ_C	interfacial shear strength

Chapter 1

Introduction:

Despite of the tremendous success of carbon fibre composites in light weight construction, high performance parts and in electromagnetic shielding, there is still a need to improve certain fundamental properties, notably transverse and inter-laminar performances. The desired mechanical properties of polymer composites are achieved only when the optimal stress transfer from the compliant matrix material to the stiff reinforcing fibres is ensured.[1,2,3] It is therefore necessary to modify the non-polar carbon fibre surface to improve the adhesion between the polymeric matrix and carbon fibres. The interfacial bond between the carbon filaments and the resin matrix can be enhanced by increasing the surface area, for instance roughening of the surface, or by enhancing the physicochemical interaction between the components.[4,5,6,7] It is well established that increasing the level of surface oxygen and the surface roughness by oxidative treatment result only in moderate improvement of the interfacial bond indicating that van der Waals interactions alone are insufficient.[8,9] It would be profitable to pre-coat the carbon fibre surface with a thin chemically active protective polymer layer that guarantees cohesive adhesion between the fibre and the matrix. This interfacial polymeric layer would provide sufficient mobility for the chains to deform under load and therefore retain polymer and interphase toughness. The primer should bear two functionalities (i) quaternary ammonium groups which could bind to oxidized carbon fibre via van der Waals force and, (ii) reactive groups which can copolymerize with epoxy resin during cross linking. To prepare such polymeric primer, hyperbranched polymer e.g. poly(ethylene imine) b-PEI was selected as a functional polymer. It offers flexibility (mobility, elasticity) with large number of end groups ready to interact and react with the fibre as well as with the matrix. The primary, secondary and tertiary amino groups present could be selectively modified with different bifunctional couplers by polymer analogous reactions.

Content of the thesis:

The thesis is concerned with the synthesis of functionalized cyclic carbonates, epoxides, photoinitiators and their reaction with branched polyethylenimine. The adsorption behaviour of these modified polymers onto highly oriented pyrolytic graphite (HOPG) is studied by scanning force microscopy (SFM). Furthermore application of the functionalized polymers in the field of composites and UV curable coatings has also been investigated. **Scheme 1.1** is the general scheme representing functionalization of polyethylenimine.

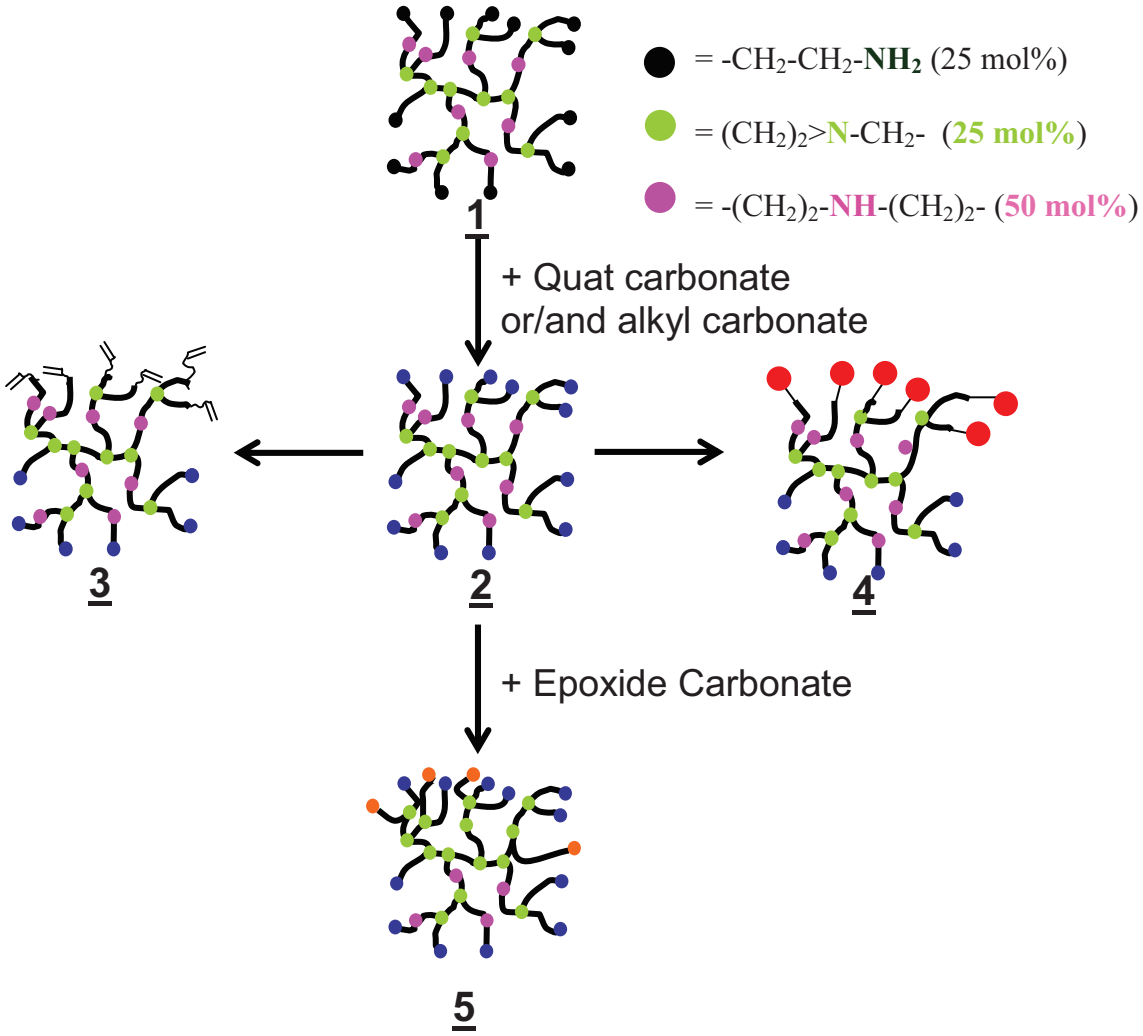
Chapter 1 (the present chapter) gives a short introduction of the thesis and presents the content of this work.

In chapter 2, the state of the literature is summarized regarding the objective of this thesis relating to bifunctional couplers, chemistry of epoxides and cyclic carbonates, structure of polyethylenimine, carbon fibres and sizing.

Chapter 3 displays the synthesis of functional couplers based on 5-membered cyclic carbonates and epoxides. The reactivity of cyclic carbonates and epoxides towards primary and secondary amine are investigated. Model reactions of some of the couplers with amines are also discussed.

Chapter 4 deals with the synthesis of Quat-Primer polymers bearing quaternary ammonium groups and cyclic carbonate groups (**2** and **5**). The synthesis starts with the branched polyethylenimine (**1**) as depicted in the S**cheme 1.1**. These modified polymers are subsequently characterized by with respect to structure, composition and molecular weight. Furthermore, application of these functionalized polymers in the field of carbon fibre – epoxy resin composites is also dealt with.

Chapter 5 describes the synthesis of polymers (**2**) bearing long alkyl chain (**C16**). The adsorption of these functionalized polymers onto HOPG in form of sub-monolayer coverage is studied by means of SFM. Moreover, from the SFM studies the structure of functionalized b-PEI is established.



Scheme 1.1: *Overview of the planned synthesis of primers based on technical polyethylenimine (**1**), ●,● =tertiary and secondary amino groups (-N< and –NH-) in the polymer skeletton, ● =quartenary ammonium - endgroups (-$NR_3^{\oplus}$)(QI) or alkyl side chains ● = cyclic carbonate groups , ●— = covalently fixed photoinitiator, =/ = terminal vinyl groups.*

Chapter 6 describes the synthesis of polymers (**2** and **5**) bearing long alkyl chain (**C8, C14 and C16**) quaternary ammonium groups (**QI**), and cyclic carbonate groups. It also provides the systematic study of adsorption behaviour of functionalized b-PEI onto HOPG by varying (i) length of alkyl chain, and (ii) ratio of cationic groups to alkyl groups. Furthermore, application of the polymers in the field of composites is presented.

Chapter 7 presents the synthesis of polymers bearing allyl groups, methacrylate groups and photoinitiator groups (**3** & **4**). These photoactive-quat primers can be used as initiators to polymerize various monomers under ultraviolet light.

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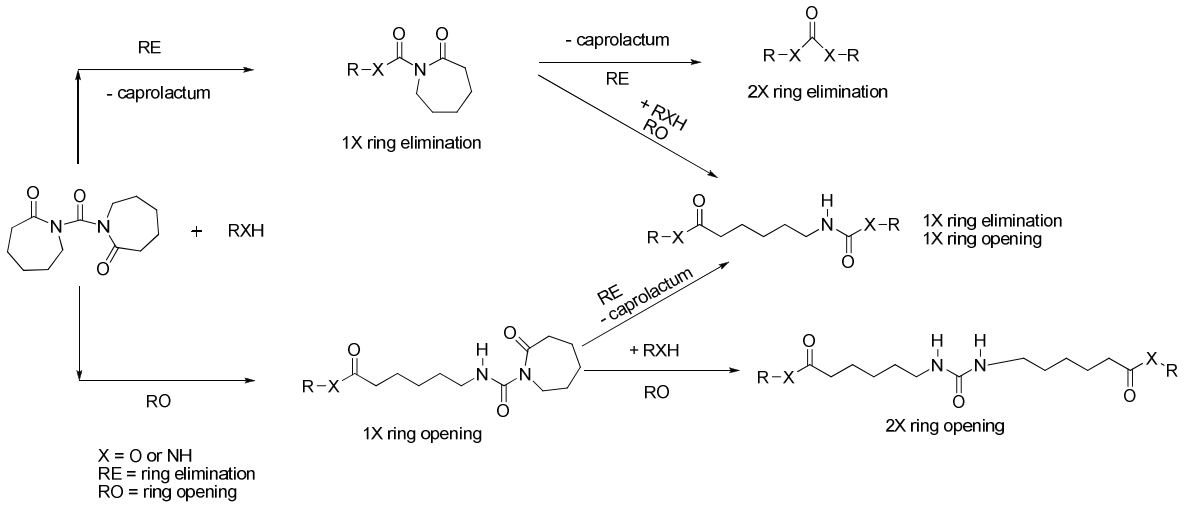
Chapter 2: Literature Review

Bifunctional Couplers:

Post- synthetic modification of polymers and functionalization of various surfaces is an important scientific topic and important for industrial applications. One of the procedures applied to prepare multifunctional polymers is based on couplers. There are many such examples but here only few of them will be discussed. A bifunctional coupling agent having an oxazoline and an oxazinone groups has been reported. [1] The oxazoline groups reacts with carboxylic acid groups whereas an oxazinone group reacts with amino or hydroxyl groups. Thereby, different polymers such as carboxy-terminated poly(propylene) and amino terminated polyamide have been coupled.

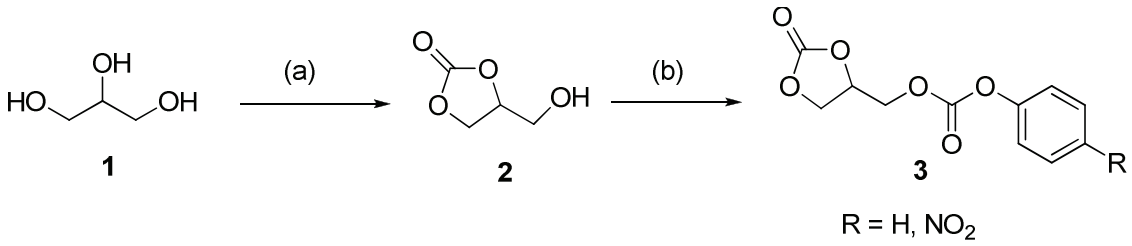
Another example of coupler is carbonylbis(caprolactam) (CBC). It reacts with amines and alcohols by ring elimination (RE) or ring opening (RO) mechanism as demonstrated in Scheme 2.1.[2,3] The quantitative CBC conversion with functional building blocks containing an amine end group occurs in bulk at 100 ^{o}C in the absence of catalysts, yielding N-carbonyl caprolactam terminated oligomers and caprolactam (RE pathway). Reaction with building blocks bearing hydroxyl end groups occur at 100 -150 ^{o}C in presence of catalysts such as magnesium bromide or dibutyltindilaurate (DBTL), yielding N-carbonyl caprolactam end groups via nucleophilic attack of the hydroxyl group at one of the CBC ring and subsequent ring opening (RO pathway) (cf. Scheme 2.1).



Scheme 2.1. Reaction of carbonylbiscaprolactam (CBC) with nucleophiles.

Another class of couplers is based on five membered cyclic carbonates. Five membered cyclic carbonates scarcely polymerize as a result of the stable five membered rings, whereas they efficiently react with primary amines to afford corresponding hydroxyl urethanes.[4]

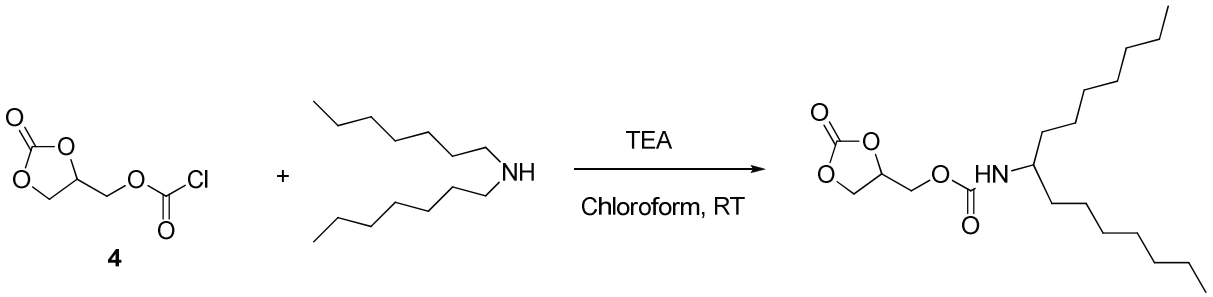
These couplers possess an ethylene carbonate moiety and an activated group showing different reactivity towards primary amines. An example of this type of bifunctional coupler is (2-oxo-1,3-dioxolan-4-yl)methyl phenyl carbonate (**3**).[5] The synthesis of coupler **3** is a two step procedure (cf. Scheme 2.2)



Scheme 2.2. Synthesis of bifunctional coupler 2-oxo-1,3-dioxolan-4-yl)methyl phenyl carbonate. (a) dimethyl carbonate. DABCO, 75 ^{o}C; (b) phenyl chloroformate, pyridine, 0 ^{o}C, RT, THF.

In the first step glycerol (**1**) is reacted with dimethyl carbonate to yield glycerol carbonate (**2**). Conversion of glycerol carbonate (**2**) with phenyl chloroformate leads to the dicarbonate coupler **3**. This dicarbonate coupler has two reactive sites. At low temperature a primary amine groups can react with the coupler releasing the phenyl ester group in a substitution reaction, whereas at higher temperature a second primary amine will react with the five membered ring via ring opening. Based on this principle, the use of this coupler in polycondensation reactions with diamine to prepare polyurethanes bearing pendant primary and secondary hydroxyl groups is reported.[4]

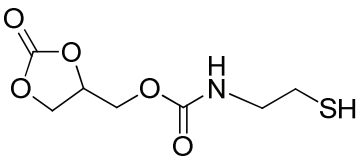
Glycerol carbonate chloroformate (**4**) is another example of bifunctional coupler.[6] It has also two reactive sites. As dicarbonate linker **3**, the chloroformate linker **4** has an ethylene carbonate ring, but instead of phenyl ester carbonate it has a more reactive chloroformate



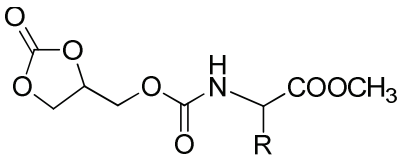
Scheme 2.3. Reaction of chloroformate linker (**4**) with secondary amines.

groups which could react with primary amine and as well as secondary amines. The substitution of chloroformate with an amine leads to the formation of elimination product (HCl). To trap HCl an additional reactant like triethylamine (TEA) is required in order to obtain full conversion (cf. Scheme 2.3).

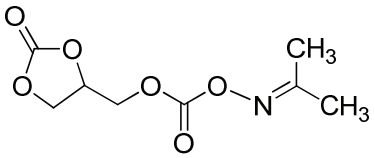
Other types of bifunctional couplers based on cyclic carbonated reported in literature[7] are mentioned in Scheme 2.4.



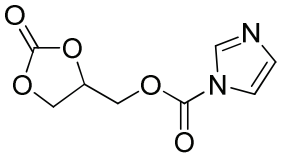
thiol functional coupler



α–amino acids functional coupler



acetone oxime functional coupler

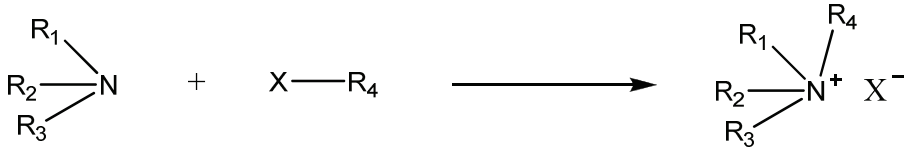


imidazole functional coupler

Scheme 2.4. Bifunctional Couplers based on five membered cyclic carbonates.

Quaternization of ammonium groups

Amines react with alkyl halides or certain esters attaining a higher degree of alkylation. The quaternization of amines by alkyl halides is known as the Menschutkin reaction[8] and was first reported over a hundred years ago. Significant steric effects were noted in these original small-molecule studies, with tertiary amines reacting much more slowly than secondary or primary amines. Primary and secondary amine gives, usually, mixture of amines and ammonium salts while tertiary amines undergo one-step reaction (cf. Scheme 2.5**),** the product of which is easy to separate and purify.



---- Eq. 2.1

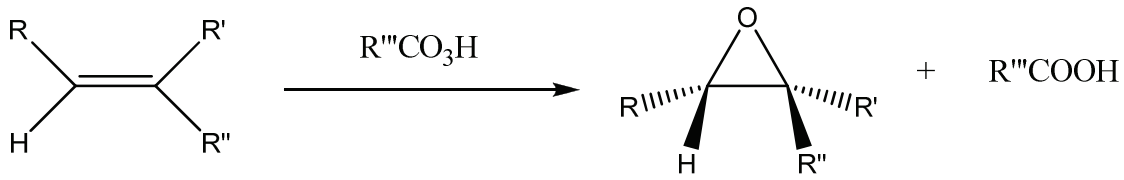
Scheme 2.5. Quaternization of tertiary amines with alkyl halides.

Quaternization reactions can be carried out with alkyl halides such as methyl iodide[9,10], and esters of strong acids such as 2,4-dinitobenzenesulphonate[11], methyl p-toulenesulphonate[12],

methyl picrate[13], and methyl sulphate.[14] The reaction can take place with or without solvent and at a wide range of temperatures ranging from room temperature up to that of reflux. The net effect of any such nucleophilic substitution on carbon is the gain of electron pair by the covalent iodine atom to form iodide ion. The quaternization will run well in polar solvents. Strong donor solvents like nitrobenzene will form weak hydrogen bonds with the alkyl groups. This donation will be inductively transmitted to the C → I bond, making the electron pair to shift towards iodine. This mechanism partly accounts why the reaction run over 1000 time faster than in hexane. Quaternary ammonium salts are commonly used as disinfectants, surfactants, fabric softeners, and as antistatic agents. These salts are most effective against gram-positive bacteria.

Chemistry of epoxides:

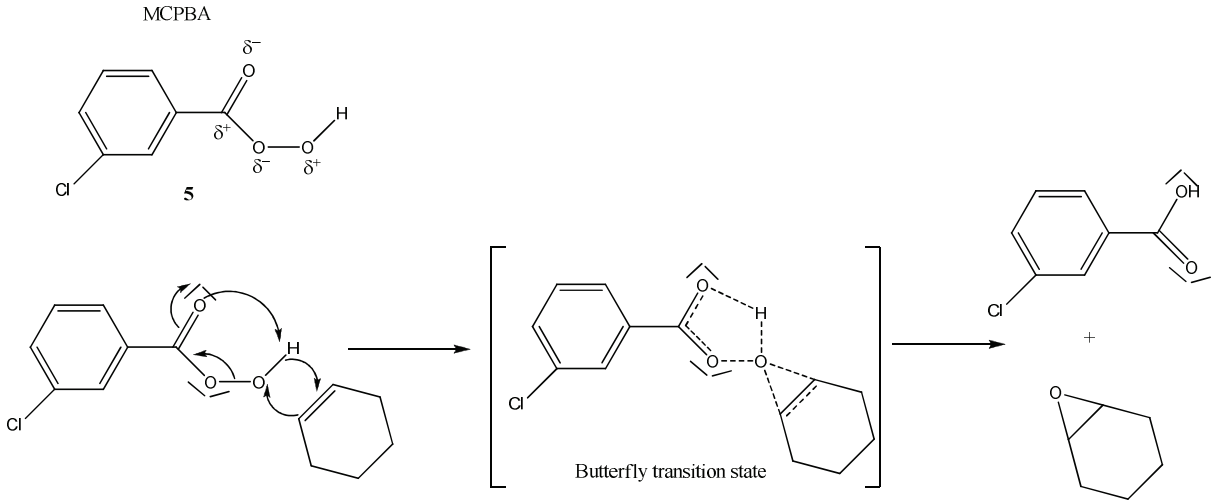
An epoxide is a cyclic ether with only three ring atoms. The ethylene oxide is also called "epoxyethane" or "oxirane". This ring is approximately an equilateral triangle which makes it highly strained. The strained ring makes epoxides more reactive than other cyclic ethers especially towards nucleophiles. The most general reagents for conversion of simple alkenes to epoxides are peroxycarboxylic acids.[15] This reaction is also known as "Prilezhaev reaction" (Scheme 2.6).[16] The most frequently used reagent for oxidation is m-chloroperoxybenzoic acid[17] (MCPBA).



Scheme 2.6. General reaction of alkenes with peracids - Prilezhaev reaction

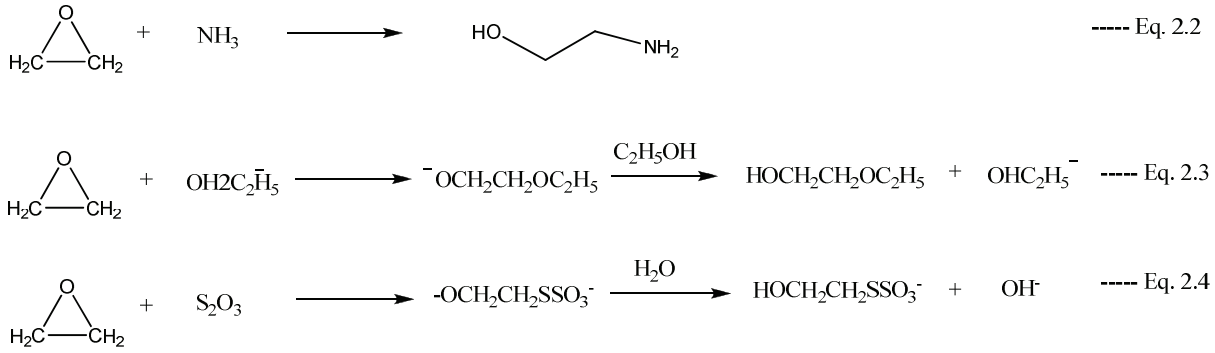
The other reagents used for epoxidation are magnesium salt of monoperoxyphthalic acids[18], potassium hydrogen peroxysulphate [19] , peroxyacetic acid, peroxybenzoic acid and peroxytrifluoroacetic acid. The mechanism of the reaction of an alkene with peracid to give an oxirane was first proposed by Bartlett[20] and Pausacker.[21]

Peracids tend to adopt an intramolecularly hydrogen-bonded conformation in solution, and the high degree of polarisation results in an electrophilic oxygen atom (**5**) that is able to add to alkenes. The transition state, in which oxygen is added and the proton is shifted simultaneously, resembles a butterfly and hence mechanism is known as the "Butterfly Mechanism" (Scheme 2.7).



Scheme 2.7. Mechanism of epoxidation – butterfly mechanism

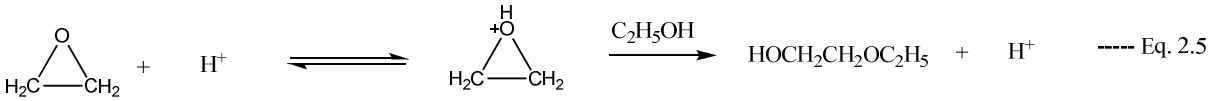
The majority of epoxide reactions have been studied in solution involving the opening of the epoxide ring and the addition of a reactant molecule of (Scheme 2.8, Eq. 2.2)



Scheme 2.8. Ring opening reaction of oxirane.

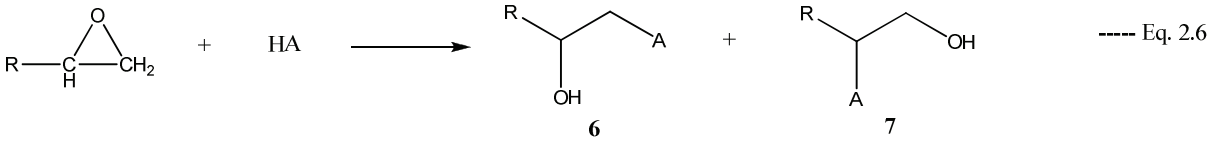
If the solvent is an anion for example ethanol then the reaction is completed by the solvent (Eq. 2.3). In this reaction the ethoxide ion is not consumed, so it is referred as base-catalyzed addition of ethanol. A similar reaction is observed in the addition of thiosulphate in water, where hydroxide ion is produced (Eq. 2.4). All these reaction are carried out under basic or neutral conditions and involve the ring opening by the attack of nucleophile on one of the epoxide carbon atom.

The ring opening reactions of epoxide can also be carried out under acidic conditions. The addition of most nucleophiles is accelerated by acids and this is due to reversible formation of the more reactive conjugate acids of epoxide (Scheme 2.9, Eq. 2.5).



Scheme 2.9. Lewis – acid catalyzed ring opening of oxirane.

Ring opening reaction of epoxides take place via ionic mechanisms. The reactions are generally carried out in the polar solvents and the bond which is broken is the highly polar carbon-oxygen bond. In the general case of reaction with an unsymmetrically substituted epoxide two isomeric product are possible (**6** & **7**) as shown in Scheme 2.10.

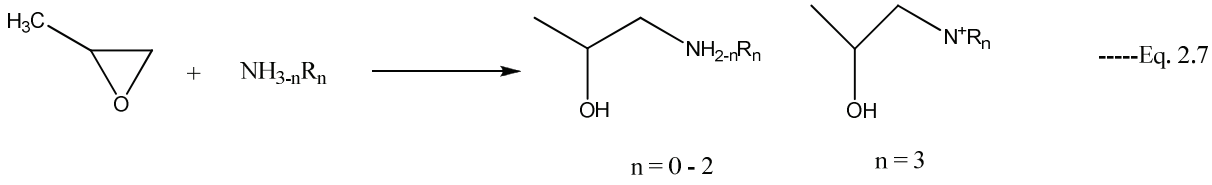


Scheme 2.10. Ring opening reaction of epoxide – formation of isomers

Krassuky[22,23] studied the ring opening reaction with ammonia and summarized in a rule which stated that "when ammonia adds to unsymmetrical olefin oxides, the amino group attaches itself to carbon atom bearing the greater number of free hydrogen atoms." Thus according to this rule the product **6** is termed as normal whereas product **7** is abnormal. Under basic or neutral conditions the normal isomer corresponding to attack on the least substituted carbon atom is nearly always the major or only isolated product.[24,25] The reaction observed is a single step reaction in accordance to the S_N2 mechanism. In the case of reaction under acidic conditions there is tendency towards the formation of abnormal products, and the mechanism of the reaction is in accordance to the S_N1-mechanism. The reactivity of the epoxide ring and amino groups depends on following parameters:

i. Reaction conditions whether basic, neutral or acidic.
ii. The basiticity of the amine nucleophile.
iii. The steric hindrance due to substituents at the amine nitrogen atom.

Among the series of amines ammonia (NH_3), primary amine (R-NH_2), secondary amine (R_2-NH) and tertiary amine (R_3N), the basiticity increases from ammonia to tertiary amine, but since the sterical hindrance grows with enhanced number of substituents, secondary amines are found to be most reactive. The reactivity ratios obtained from reaction rates of propylene oxide with alkyl amines (Scheme 2.11, Eq. 2.7) are tabulated in Table 2.1.[26]



Scheme 2.11. General reaction of propylene oxide with primary, secondary and tertiary amine.

The reaction between various amines and propylene oxide was carried at 20 ^{o}C. As seen from the table the reactivity of amines increases drastically from methylamine to trimethylamine. This could be explained by the fact that small methyl groups do not cause strong sterical hindrance. In the case of the ethylamine series (Table 2.1, R = C_2H_5), the reactivity decreases when compared to the methylamine series and exhibit a maximum in the case of diethylamine (1.8 times greater than ethylamine).

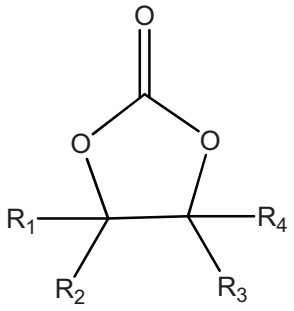
Table 2.1. Reactivity ratios of the reaction between propylene oxide and various amines. (all values are normalised to R_{NH3} = 0.0046 l^2/mol^2)

R	**NH_3**	**R-NH_2**	**R_2-NH**	**R_3-N**
-CH_3	1	8.04	36.96	57.83
-C_2H_5	1	2.61	4.56	0.84
-C_3H_7	1	5.87	n.d.	n.d.

In contradiction to the cited results, it has been reported that primary amine groups with bulky substituents may react one order of magnitude faster than secondary amines.[27] Charlesworth[28] also reported a higher reactivity of primary amines due to the sterical hindrance of secondary amino groups. This is especially true for amino polymers such as branched polyethylenimine (b-PEI).

Chemistry of five membered cyclic carbonates

Cyclic carbonates have received much attention as aprotic polar solvents.[29] Five membered cyclic carbonates (1,3-dioxolan-2-ones) are of the general structure depicted in Scheme 2.12. The cyclic carbonates can be synthesised from the reaction of carbon dioxide with oxiranes using lewis acids, transition metal complexes, organometallic compounds or poly(siloxanes) – supported metal halides as catalysts under high pressure.[30,31] Nishikubo et al.[32] reported the synthesis of cyclic carbonates by the addition reaction of oxiranes with carbon dioxide using insoluble polystyrene beads containing pendant quaternary ammonium catalysts at atmospheric pressure.



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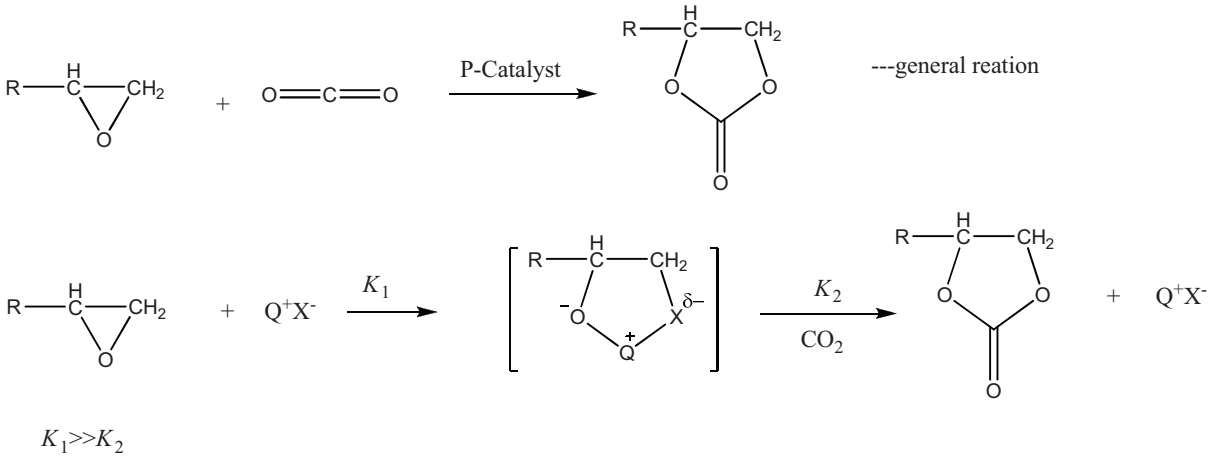
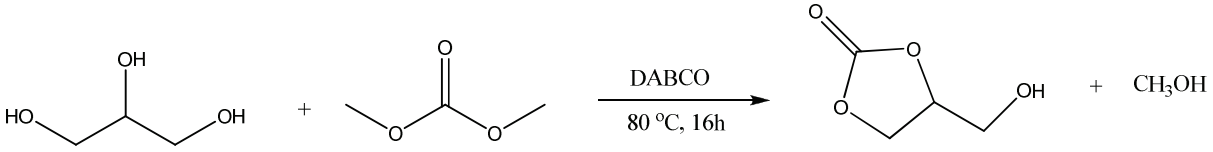
Scheme 2.12. General structure of five membered cyclic carbonates.

The reaction of oxiranes with carbon dioxide proceeded smoothly catalyzed by 1 – 2 mol % of polymer supported quaternary ammonium salts to give corresponding cyclic carbonates in high yields at 80 – 90 ^{o}C. The reaction is shown in Scheme 2.13.



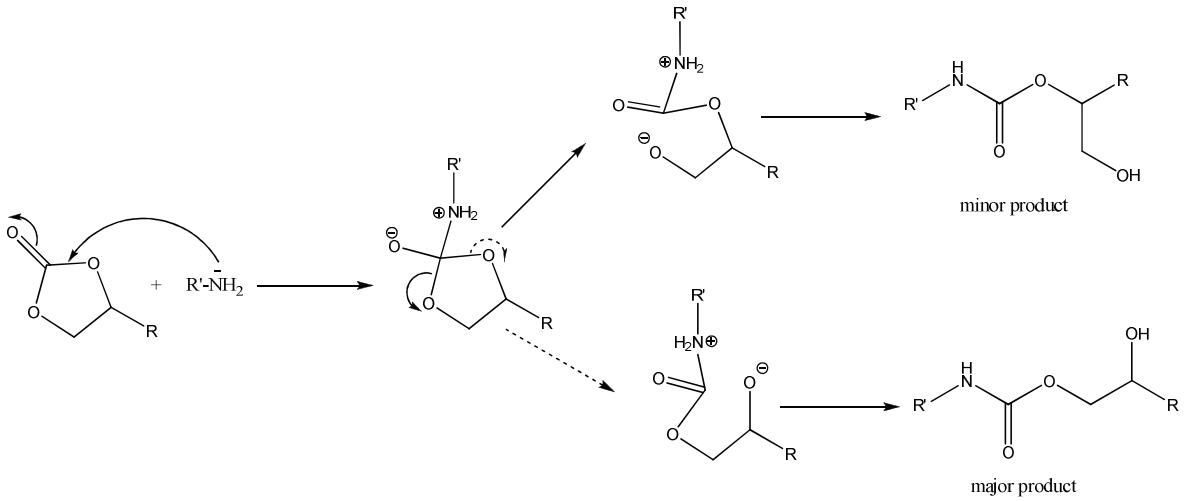
Scheme 2.13. Reaction of oxirane with carbon dioxide by polymer – supported catalysts.

The other synthetic routes for the synthesis of cyclic carbonates starts from 1,2- and 1,3-diols. Burk et al.[33] reported the synthesis of cyclic carbonates from diols with triphosgene in dichloromethane and pyridine at 70 ^{o}C. It can also be prepared by reacting glycerol with dimethyl carbonate using 1,4-diazabicyclo[2.2.2]octane (DABCO) as a catalyst at 80 ^{o}C (Scheme 2.14)[34,35]



Scheme 2.14. Synthesis route to cyclic carbonates from glycerol.

This five membered cyclic carbonate ring can react with aliphatic and aromatic amines, thiols and carboxylic acids. In this part only the reaction of cyclic carbonates with primary amines and water will be discussed. The primary amine reacts with the carbonyl group of the cyclic carbonate by ring opening and formation of urethane group and hydroxyl group. Two positional isomeric products (regioisomers) are obtained (cf. Scheme 2.15.), the ratio of which depends on the reaction conditions, the functional group attached to the cyclic carbonate and the substituents on the aliphatic amine.



Scheme 2.15. Ring opening of cyclic carbonate with aliphatic primary amine.

Table 2.2. Reaction of Five membered cyclic carbonates with n-hexylamine at 70 ^{o}C.

S.No	R of cyclic carbonate	Solvent	Time (days)	Conversion (%)	Rate constant, k (L/mol . h)	Product Ratio
1	CF_3	Toulene	1h	100	-	100:0
2	CF_3	DMSO-d_6	1h	100	64	100:0
3	$PhOCH_2$	Toulene	12	96	-	83:17
4	$PhOCH_2$	DMSO-d_6	17	92	0.42	81:19
5	Ph	Toulene	21	94	-	69:31
6	Ph	DMSO-d_6	17	92	0.38	68:32
7	H	Toulene	31	93	-	n.d.
8	H	DMSO-d_6	31	91	0.23	n.d.
9	Me	Toulene	50	75	-	55:45
10	Me	DMSO-d_6	50	75	0.05	55:45

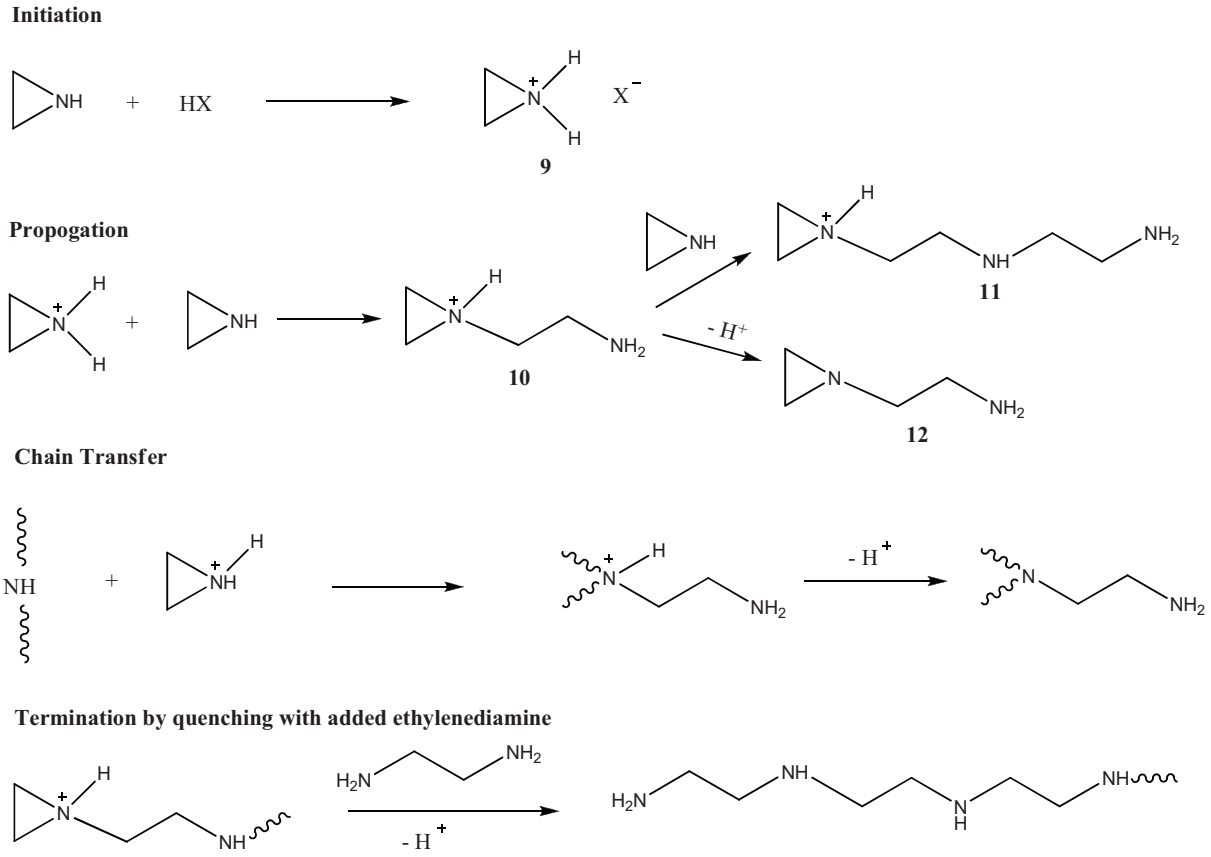
The major product is always the isomer bearing a secondary hydroxyl group, demonstrating a distinct regioselectivity.[36] The reaction rate constant obtained from the reaction of functional five-membered cyclic carbonates (with different substituents) with n-hexylamine are tabulated in Table 2.2.[37] As seen from the table the formation of urethanes with a secondary hydroxyl group increased with introduction of stronger electron withdrawing group into the corresponding cyclic carbonate. Moreover, the isomer with secondary hydroxyl group was major product in all the cases. Pasquier et al.[35] studied the model reaction of a quaternary ammonium functional cyclic carbonate with propylamine in water. The reaction was completed in 3 h at room temperature and the rate of reaction with propylamine was found to be much greater than rate of hydrolysis. However, when the reaction was carried out in methanol instead of water under the same conditions, the hydrolyzed compound was the major product. The stability of the functional cyclic carbonate against hydrolysis was investigated in water at room temperature and at 100 ^{o}C. It was reported that after 2 days at room temperature only 16% of the reactant was hydrolyzed, whereas at 100 ^{o}C, 73 % of the hydrolyzed product was obtained.

Branched Polyethylenimine (b-PEI):

The properties of the dendrimers and hyperbranched polymers are very different from the linear polymers. By comparison to the ideally perfectly branched dendrimers, hyperbranched polymers possess a randomly branched topology, i.e. branching is not achieved for every monomer unit incorporated and additional linear units are present. The lack of entanglements results in a lower viscosity, and the large extent of end functional groups cause higher solubility in various solvents for hyperbranched polymers compared with linear structure at a given molecular weight For example, natural polymers like glycogen, dextran and amylopectine are hyperbranched polymers.

b-PEI is a well known polymer obtained by ring opening polymerization of aziridine, commercially available in large ranges of molecular weights.[38, 39] The mechanism of polymerization involves addition of proton acid to aziridine to produce the corresponding aziridinium ion (**9**) (Scheme 2.16). The first propagation step is the ring opening of (**9**) by a nucleophilic attack of the monomer. The formed dimer (**10**) can react in two ways: a new ring opening of the aziridinium ion by monomer leads to trimer (**11**) while the second possibility is that (**10**) transfers its proton to another amino function present in the reaction mixture thus forming uncharged dimer N-(2-aminoethyl)-aziridine (**12**). The branching process occurs

right from the early stages of polymerization. An intramolecular reaction (back – biting reaction) has been proposed as a termination step. In order to control the molecular weight, the polymerization can be quenched with ethylene diamine.



Scheme 2.16. Mechanism of aziridine polymerization.

Lot of work has been put in to estimate the degree of branching in b-PEI. The difficulty to determine structure of b-PEI is caused by its polydispersity and its chain isomerism. In 1941, Kern and Brenneisen had already shown that benzoylation of b-PEI is incomplete and deduced that 20 – 30 % of amino groups were tertiary. Many methods were used but the best analytical method to study the structure is by ^{13}C-NMR spectroscopy.[40,41]

Lukovkin et al.[40] observed the ^{13}C-NMR spectrum to contain 8 lines (Figure 2.1b) which were attributed to methylene groups having primary, secondary or tertiary amino groups in **α** and **β** position. The eight major peaks have been assigned according to the different combination of amine nearest neighbours as listed in Table 2.3. From the integration of different signals, ratios of primary, secondary and tertiary amine groups being 31:40:29, and 31:38:31 respectively have been determined in $CDCl_3$ solution for b-PEIs with molecular weight, $<M_w>$ of 25000 and 750000 g/mol.[27] These results are different compared to the well established data which were 25:50:25.[38]

Table 2.3. ^{13}C-NMR characterization of PEI 25000

Structral Unit in b-PEI	δ (ppm)	Integrals
N-^{1}**CH$_2$**-CH$_2$-NH$_2$	57.2	1.00
N-^{2}**CH$_2$**-CH$_2$-NH-	54.3	2.12
N-^{3}**CH$_2$**-^{3}**CH$_2$**-N	52.5	2.75
-NH-^{4}**CH$_2$**-CH$_2$-NH$_2$	52.0	1.10
-NH-^{5}**CH$_2$**-^{5}**CH$_2$**-NH-	49.0	2.03
-NH-^{6}**CH$_2$**-CH$_2$-N	47.1	2.16
NH$_2$-^{7}**CH$_2$**-CH$_2$-NH-	41.3	1.06
NH$_2$-^{8}**CH$_2$**-CH$_2$-N	39.4	1.03

The difference can be explained due to following factors: (i) b-PEI is commercially available polymer in large range of molecular weight while earlier it was prepared in lab scale. (ii) The use of different catalysts, quenching agents and process parameters, and (iii) The sensitivity of NMR instruments increased dramatically since last 30 years enabling now more accurate measurements. Salah et. al.[42] assigned methylenic signals using ^{1}H-^{1}H correlation spectroscopy and ^{1}H-^{13}C hetronuclear multiple quantum correlation (HMQC). . The ^{1}H-NMR indicates the broad signal at 1.8 ppm and the methylenic signals overlap between 2.4 and 2.9 ppm (Figure 2.1a).

The b-PEI is soluble in water, alcohol and many polar solvents like DMF, DMSO, THF and $CHCl_3$. Due to its unique structure and properties b-PEI has been used in medicinal chemistry as transfection agents[43] and part of gene delivery system[44], water treatment[45], preparation of multilayers with embedded vesicles[46], pressure sensitive adhesives, paper production, laminated packaging films and primers for fibres.[35]

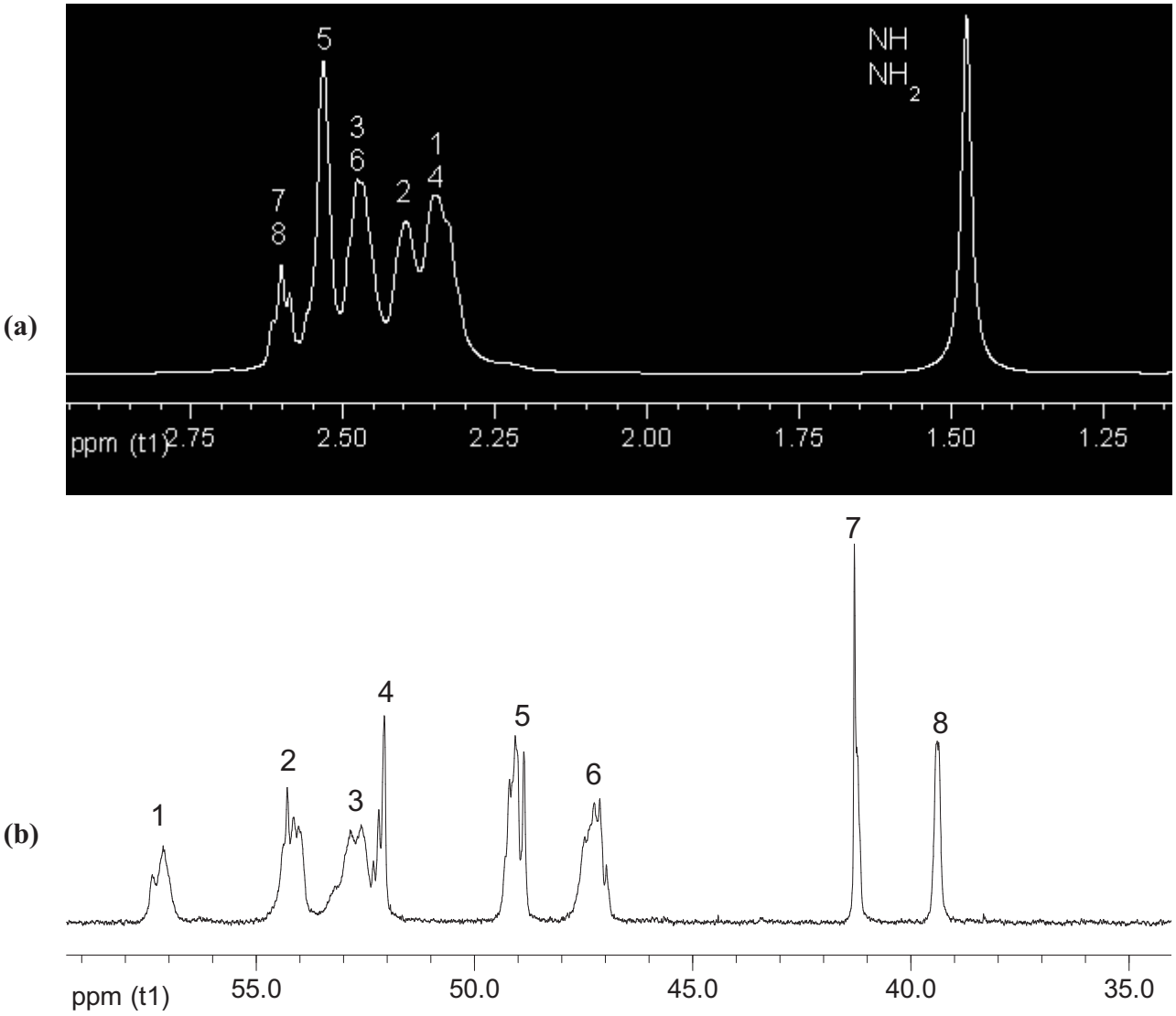
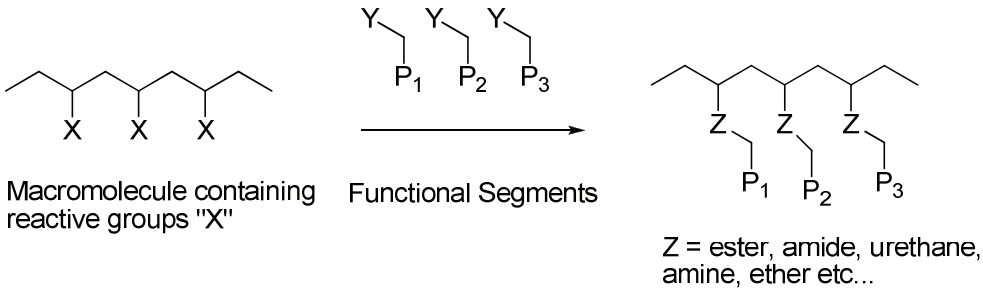


Figure 2.1. Spectra of PEI (M_w – 25000 g/mol) in $CDCl_3$ (a) ^{1}H-NMR, (b) ^{13}C-NMR.

Polymer analogous reactions:

A polymer analogous reaction represents any chemical reaction modifying a macromolecule without changing its degree of polymerization. It is assumes that the reactivity of the functional group in a macromolecule has to be same as one in low molecular weight compound. But often, this assumption is not true and the reactivity of the functional groups in the macromolecules depends on diffusional mobility of the reactants, intermediates and products in the reaction mixture, steric hindrance to the approach of reagents to the functional group, secondary structures, influence of neighbouring groups and solvation.[47] The key step is the step growth reaction in which a covalent bond is formed between polymer reactive groups and functional segments (cf. Scheme 2.17).



Scheme 2.17. Polymer analogous reaction – General scheme

In this study polymer analogous reaction refers to the reaction of electrophilic groups (carboxylic acids, acid chloride, anhydrides, carbonates, epoxides, alkyl halides etc.) with the polymer bearing nucleophilic groups (amines and alcohols). Lydie et. al. studied the reaction of amino groups present in b-PEI with palmitic acid at 140 ^{o}C in toluene for 21 hours.[48] The maximum degree of amidation calculated from ^{1}H-NMR was 70%. Other amidation of b-PEI includes reaction with palmitic acid chloride[49] and methyl palmitate.[50] The addition reaction of primary amino groups in b-PEI with substituted 5-membered cyclic carbonates to yield urethane groups and hydroxyl has also been reported.[51,52,35] The functionalized polymers were obtained in good yield (75 – 85%) and the functionalization was limited to 25 % with respect to total amino groups in b-PEI.

Carbon Fibres

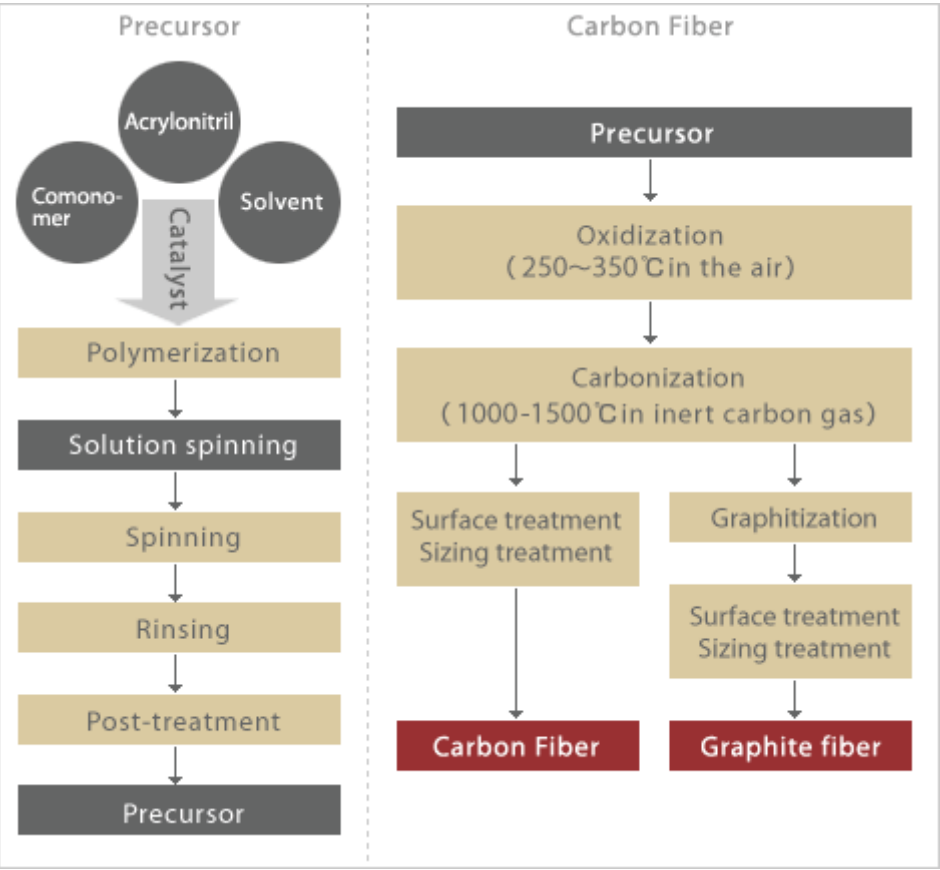
Carbon fibres are high strength, high modulus reinforcing fibres used in the manufacture of advanced composite materials. They are black fibres used as yarns, felt or powder-like short filaments with diameter smaller than 10 μm. These fibres are made by pyrolytic degradation of a fibrous organic precursor. In this process, an organic polymer fibre is heated under tension in an inert atmosphere to a very high temperature to drive off volatile constituents. The residual carbon atoms tend to orient themselves along the fibre axis into graphitic crystallites to form a high strength, high modulus fibres. The final properties of carbon fibre depend on the composition of the precursor and the time – temperature history of the fibre. In general, as the processing temperature to which the fibre is exposed is increases, the extent of crystallite orientation parallel to fibre axis increases and hence modulus increases. Because of greater sensitivity to flaws, the increase in modulus is generally accompanied by a decrease in strength.

The ideal requirements of the precursor are:

- The chemical structure should favour the formation of an aligned graphitic carbon structure during pyrolysis.

- ❖ A high carbon fibre yield should be obtained.
- ❖ The fibre should be strong enough to be handled during all phases of pyrolysis process.
- ❖ It should be inexpensive and readily available from various commercial sources.

Many type of precursor has been used to produce carbon fibres. The main precursors used are (i) Polyacrylonitrile, (ii) Cellulose precursor – rayon based and, (iii) Pitch based. Other forms of precursor such as vinylidene chloride and phenolic resin have been investigated but they are not commercially viable. In this chapter, literature survey on PAN based carbon fibres is presented.

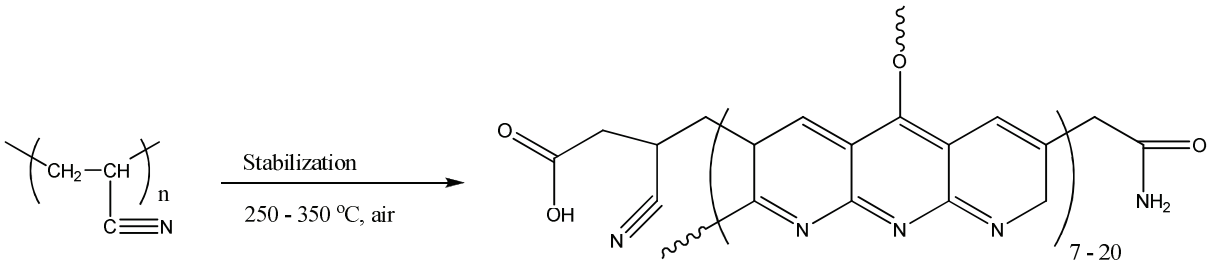


Scheme 2.18. Schematic diagram – production of carbon fibre.

The history of PAN based carbon fibres started in 1950 with the observation of R. C. Houtz[53] that polyacrylonitrile fibres are converted into black, flameproof material by heat treatment at 300 ^{o}C in air. In 1960 the process to produce a flameproof fibre, starting with Dupont's AF Orlon fibre and commercialized as Black Orlon was reported by Vosburgh.[54] The precursor fibre can be spun as a homopolymer or more commonly a co- or terpolymer composition. The typical commoners are methyl acrylate, methyl methacrylate and itaconic anhydride, methacrylic acid, methyl acrylate and methacrylic acid. The use of relatively low (0.5 – 5%)

concentrations of comonomers, improves the dissolution and stability of polymer solution and facilitates spinning. Polymer fibres can be spun by melt, wet and dry spinning processes. In the case of PAN as a carbon fibre precursor, the wet spinning is the most important. Dimethylacetamide and dimethylformamide are usually preferred solvents for wet spinning. The fibre is highly drawn in the spinning process to align the molecular chains. The precursor fibres are normally drawn to relatively small filament diameters of 6 – 15 μm. Contaminants in the precursor can lead to surface defects, voids or inclusions that seriously reduce the strength of the fibre. The process used in the production of carbon fibre is summarized in Scheme 2.18.

In the stabilization step, the precursor fibre is converted to thermally stable structure capable of withstanding high temperature processing at high rated with good yield. The stabilization step is carried out at 250 – 350 ^{o}C in air for 30 – 120 minutes, the structure is changed from a linear polymer system to highly condensed cyclized (ladder) structure of stacked, partially hydrogenated naphthyridine rings with conjugated C=N (Scheme 2.19). Although the stabilization chemistry of PAN is complex, it is clear that the presence of oxygen, chain scission, cross-linking, dehydrogenation and cyclization take place. During this step, heat is generated which must be controlled to avoid overheating the fibres. Commercially, the stabilization process uses a variety of equipment and techniques.

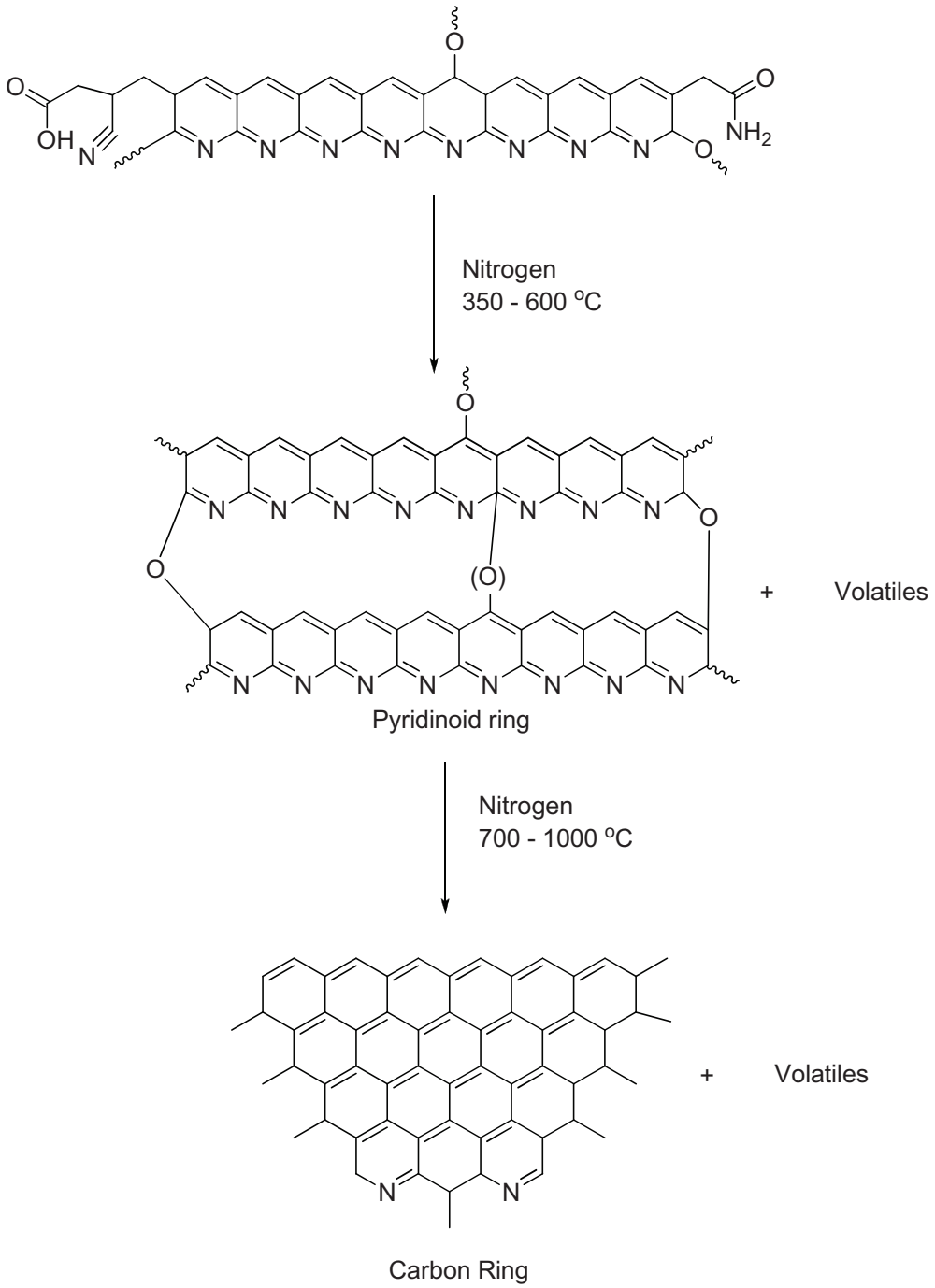


Scheme 2.19. Stabilization step of precursor PAN fibre.

In some processes, the fibres are drawn through a series of heated chambers or passed over hot rollers and through beds of lose material held in suspension by a flow of hot air. In this process, an overall weight loss of 5 – 8% occurs because of dehydrogenation reactions that evolve water, decarboxylation reaction and due to the fact that some nitrile groups do not take part in cyclization but are evolved as hydrogen cyanide (HCN). During the reaction the fibres carbon content slightly decreases from 68% to 62 – 65%.

The carbonization step involves a rapid thermal pyrolysis in an inert environment at 1200 – 2000 ^{o}C. The lack of oxygen prevents the fibre from burning at the very high temperatures. In the temperature region of 350 – 1300 ^{o}C a thermally stable pyridinoid structure is formed

which subsequently collapses into a stacked ring carbon structure to form carbon fibres (cf. Scheme 2.20). The yield of the fibres is 50% based on the precursor. Almost all the non-carbon elements are eliminated as volatiles, only a low nitrogen concentration remains. The volatiles include HCN, ammonia, nitrogen, water with lesser amount of carbon dioxide, carbon monoxide, hydrogen and methane.



Scheme 2.20. Condensation reactions occurring in carbonization of PAN

In the graphitization step, an additional heat treatment normally at temperatures above 2500 ^{o}C for short periods in argon or nitrogen further improves the preferred crystallite orientation and order and can lead to ultra high modulus fibres (>500 GPa).

Since graphitic carbon fibres show only modest degree of adhesion to various matrices, surface treatments are normally applied immediately subsequent to the carbonization or graphitization step. These treatments consist of controlled oxidation of the fibre and are applied from the gaseous or liquid phase over wide range of conditions depending on the method. The performance of the carbon fibre composites depends strongly on the degree of adhesion between the fibre and the matrix. When the load is applied to the composite, the stress is transferred from one carbon filament to another via the matrix resin. If a weak fibre – resin bond is present, then it will result in poor mechanical properties. Oxidative gas – phase treatment are typically carried out by heating the carbon fibre in air[55] or mixture of air and oxygen diluted with an inert gas like nitrous oxide, ozone or steam[56,57] at 350 – 1100 ^{o}C. The liquid phase oxidizing agents[58,59] used to surface treat carbon fibres are HNO_3, NaOCl, $KMnO_4$, $NaClO_3$, $Na_2Cr_2O_7$, and $NaIO_4$. Other methods used for surface treatment of carbon fibres include aniodic oxidation[60] and plasma treatment.[61] The various surface treatments differ substantially in severity, time and temperature conditions. Extensive oxidation can generate surface flaws and reduce the fibre strength. The objective of the treatment is to etch the surface, removing any weakly bonded carbon debris and other impurities, leaving back polar hydrophilic oxygen containing groups on the surface, increasing its wettability and bond-ability to the resin matrix. Drzal et al[62] examined Hercules untreated and proprietary treated A, HT and HM fibres using epoxy matrix and suggested a two part mechanism. Initially, a weak defect laden surface layer is removed, enabling higher shear loads to be supported and then surface oxygen groups are added, which can interact with polar epoxy resin. Wright has summarized the possible effects of surface treatment (i) there is little change in surface area irrespective of the fibre type, (ii) The reason is the removal of weak surface layer, (iii) chemical modification of the surface occurs and following groups have been detected: -OH, =O, =C=O, -COOX, $-CO_3$, and lactone, (iv) there is increase in polar surface free energy but no significant improvement in fibre wetting out due to presence of these surface groups, and (v) various workers are undecided whether chemical bonding occurs between these groups and the bulk resins.[58]

A final surface modification step consists of the application of thin layer of finish or size. The application of coating onto fibre is normally termed as size or finish. The function of sizing is to improve inter-filamentary adhesion, aids in wetting of the fibre in the resin matrices and act

as a lubricant to prevent fibre damage during subsequent textile processing. The sizing could be achieved in different ways (i) deposition from a polymer solution, (ii) deposition of a polymer onto fibre surface by electrodeposition, (iii) deposition of a polymer onto fibre surface by electro-polymerization, and (iv) plasma polymerization. Among these the most common method of sizing is the *deposition from solution of polymer* onto the fibre surface. The selection of polymeric size depends on the resin matrix. Thus, sizes of epoxy resins are generally used for epoxy matrices. To obtain the desired properties, applied sizes must not be tacky or brittle and can be obtained by selecting an epoxy resin with suitable molecular weight. Some workers believe that a flexible interlayer of size is preferable but other prefers a more brittle system with modulus between that of fibre and matrix. Drzal et al[63,64] termed the vicinity of fibre and the matrix as a graded three dimensional region as interphase. The proposed structure for the interphase is that since sizes contain no hardener, some will diffuse from the matrix into the size layer and hence will contain less than stoichiometric amount of curing agent. In another paper, Drzal[65] studied the possible effects of this curing agent deficiency by measuring Young's modulus, tensile strength and fracture toughness of series of composites. He reported that when applying less than stoichiometric amine, the system had higher modulus, lower strength and lower toughness. Hence coating does not prevent from fibre damage and does not improve the wetting of the fibre by matrix resin. Thus, the resulting interphase is a more brittle material and promotes better stress transfer, resulting in higher interfacial shear strength, but because of lower toughness, the failure mode changes from interfacial to matrix. Jones et al[66] have investigated epoxy sizes for polyethersulphone (PES) matrix and found that when using a brominated diglycidyl ether of bisphenol-A (DGEBA) size, the PES matrix penetrated the size and formed an interphase region, whereas with an epoxy matrix, a strongly bound DGEBA was formed, which appeared to create an weak interface between sizing resin and matrix.

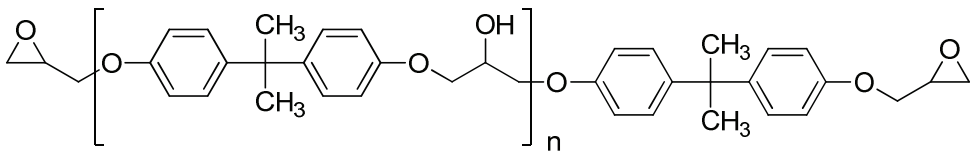
Other method of applying size includes deposition of *polymer onto fibre surface by electro deposition*. A performed polymer with an ionized group is said to be electrodeposited when, under an applied voltage, the polymer is attracted to the oppositely charged carbon fibre in an electrolytic cell. Subramanian et al[67,68] used batch and continuous methods and typical operating conditions were 10V applied for 1 min using a 2.5 % solution of polymer like butadiene-maleic acid co-polymer, pyrrole and poly(ethylenecoacrylic acid).

Deposition by *electro polymerization* enables the polymerization of monomers in an electrolytic cell, where carbon fibres can be made the anode or cathode. The solvent used to dissolve the monomer must act as an electrolyte and be sufficiently conducting to permit a

uniform non-conducting layer of polymer to be applied onto the carbon fibre at a controlled deposition rate. Harris and co-workers[69] studied different systems and found best results with o-diaminobenzene/$LiClO_4$, yielding a 46% improvement in interfacial shear strength with respect to an untreated fibre.

Epoxy Resins:

Epoxy resins have gained wide acceptance in protective coatings and electrical and structural applications because of their exceptional combinations of properties such as toughness, adhesion, chemical resistance and superior electrical properties. These resins are characterized mainly by the presence of three – membered cyclic ethers groups commonly known as epoxy groups. The most widely used epoxy resins are diglycidyl ethers of bisphenol A (DGEBA) derived from bisphenol A and epichlorohydrine (cf. Scheme 2.21).[70]



---- Eq. 2.8

Scheme 2.21. Structure of DGEBA.

The outstanding performance characteristics (i.e. toughness, rigidity and elevated temperature performance) of these resins are imparted by the bisphenol A group, ether linkage (chemical resistance) and hydroxyl and the epoxy groups (adhesive properties and reactivity with a wide variety of chemical curing agent). Conventional epoxy resins range from low viscosity liquids to solid resins. These resins are generally prepared by condensation of bisphenol-A and epichlorohydrine using a alkaline catalyst by a two sep reaction known as Taffy process.[71,72] The reaction initially consists of the formation of dichlorohydrine of bisphenol-A, followed by dehydrohalogenation of the intermediate product with a stoichiometric amount of alkali. Extent of formation of high molecular weight resin is reduced by using large excess of epichlorohydrine. Epoxy resins are characterized by *epoxide equivqlent weight*, which is equivalent weight in grams of resin containing one epoxide group.

Curing of an epoxy resin to give a cross-linked, three dimensional, infusible structure is brought about by using hardener or curing agent, sometimes with the accelerator to open the epoxide ring.[73] There are many curing agents like aliphatic amines, aromatic amines, anhydrides, dicyandiamide, substituted urea, BF_3 complex and imidazoles which have been used to cure epoxy resins. While selecting a curing agent following points should be considered: (i) temperature of cure, (ii) compatibility of hardener with the resin, (iii) pot life

of the hardener, (iv) volatility of hardener, (v) physical properties of the cured resin, and (vi) cost. The optimum proportions of the resin and curing agent are such that the cured material will have the highest softening temperature and the best combination of mechanical properties. To achieve the stoichiometric amount of curing agent and the epoxy resin, it is necessary to know the amine hydrogen equivalent weight (AHEW).

$$\text{AHEW} = \frac{\text{Molecular weight of amine}}{\text{Number of active hydrogens}} \quad \text{---- Eq. 2.9}$$

The active hydrogen corresponds to those directly bonded to the nitrogen in the curing agent. The parts per hundred of resin (phr) of the amine is determined from:

$$\text{phr of amine} = \frac{\text{AHEW} \cdot 100}{\text{Epoxide equivalent weight of resin}} \quad \text{----- Eq. 2.10}$$

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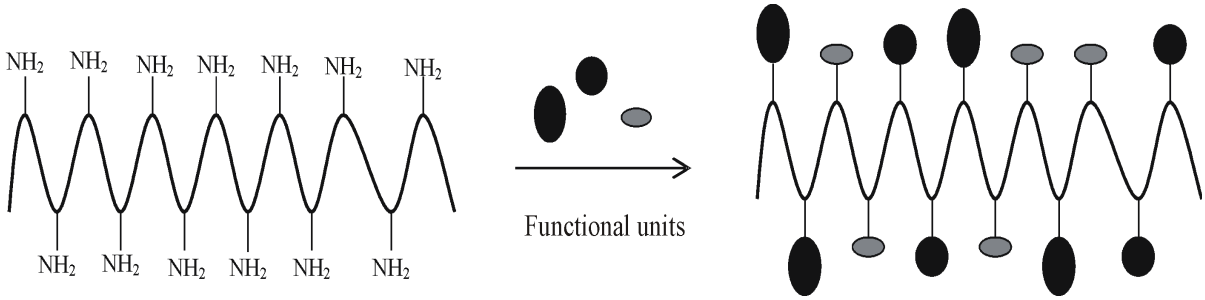
Chapter 3: Synthesis and Characterization of functional couplers.

Introduction:

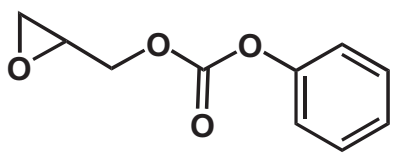
Post-synthetic modification of polymers and functionalization of surfaces is an important scientific topic and important for industrial applications. The use of e.g. functionalized b-PEI in cellulose reinforced polypropylene composites lead to remarkable increase in tensile properties.[1] The post modification of polymers can be done by polymer analogous reaction of reactive groups present in a polymer with the reactive groups of the functional couplers. In this way different functionalities can be incorporated in a macromolecule and hence can be tailored made for specific applications (Scheme 3.1). An interesting group of the polymers are polyamines like branched polyethylenimine (b-PEI). At low pH the b-PEI becomes protonated in aqueous solutions and is a positively charged polyelectrolyte.[2] To improve the ionic interaction further and make the charge of the polymer independent of pH, reactive molecules containing quaternary ammonium groups could be permanently fixed to the polymer. Due to the cooperative effect of the large number quaternary ammonium groups present in a single macromolecule, a strong interaction between negatively charged substrate and polymer coating should be obtained.[3,4] These cationic polymers could in particular strongly interact with the surface bearing groups like hydroxyl and carboxyl anion that are present at the graphitic surface of oxidised carbon fibres. Recently the synthesis of a cyclic carbonates[3] as well as the use of epoxide based couplers containing a quaternary ammonium end group[5] has been reported for covalent bonding of quaternary ammonium functions to polyamines.



Scheme 3.1. Polyamine containing multifunctional groups.

It is well known from the previous studies that the epoxy ring can be opened with primary, secondary and tertiary amines[6] whereas five membered cyclic carbonate rings only reacts with primary amines. Thus, a X-Y coupler consisting of a cyclic carbonate ring and epoxide ring would be of special interest, because of the selective reaction of its reactive units towards different types of amino groups.

X-Y **X-A$^{\oplus}$**



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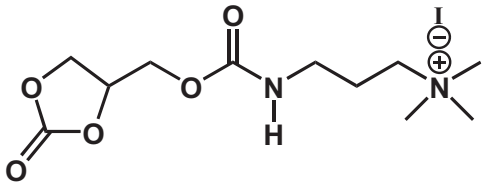

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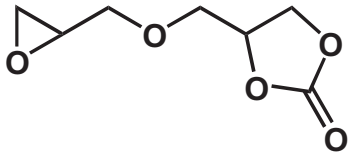

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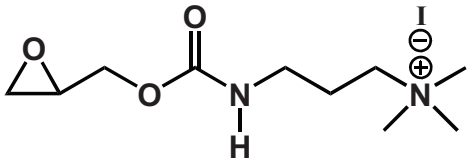


2

Scheme 3.2. Structures of the investigated cationic modifiers X-A$^{\oplus}$ (**2**, **5**) and bifunctional linker molecules X-Y (**1**, **6**).

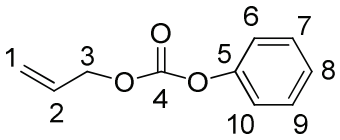
This chapter reports the synthesis of various couplers which can be bonded to polyamines to improve the interfacial properties of the carbon fibre used to reinforce epoxy resin composites. The aim was to prepare low molecular weight reactive compounds that either bear one amino-reactive and a positively charged group ('X-A$^{\oplus}$ modifiers') or two amino-reactive group of different reactivity ('X-Y linkers'). Scheme 3.2 summarizes the structures of the aimed reactive molecules. Moreover, model reactions of coupler (**6**) with primary, secondary and tertiary amines are also discussed.

Materials and Methods

Materials

Glycidol (Acros, 96%), phenyl chloroformate (Acros, 99%), pyridine (Aldrich, 99.8%), allyl alcohol (Aldrich, 99+%), 1,4-diazabicyclo[2.2.2]octane (DABCO, Aldrich, 98%), allyl amine (Aldrich, 98%), 3-chloroperoxybenzoic acid (Acros, 70-75%, MCPBA), *N*,*N*-dimethylpropane-1,3-diamine (Aldrich, 99%), iodomethane (Acros, 99%), epichlorohydrine (Aldrich, 99%), 4-(hydroxymethyl)-1,3-dioxolan-2-one (Aldrich) were used as received. All solvents were distilled before using.

Allyl phenyl carbonate[7]



In a three – necked round bottomed flask equipped with mechanical stirrer and condenser a mixture of allyl alcohol (3.89 g, 66.97 mmol), pyridine (6.55 g, 83.97 mmol) and 15 ml dichloromethane (CH_2Cl_2) was cooled down to 0^oC. Phenyl chloroformate (10.56 g, 67.45 mmol) was dropped in over a period of 1 hour and the reaction mixture was stirred for additional 3 hours at room temperature. 20 ml water was added to mixture and the product was extracted with 50 ml ether. The ether phase was washed twice with 1% HCl solution (2 X 20 ml), dried over Na_2SO_4 and concentrated in vacuum. The crude product was distilled in vacuum to give colourless oil, bp 68-72$^oC/10^{-2}$ mm Hg.

Yield : 11.3 g (95 % of theory)

Anal. calcd. for $C_{10}H_{10}O_3$: C 67.41, H 5.61, N 0.00 %; found: C 66.78, H 5.59, N 0.62 %.

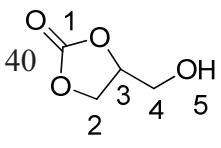
^{1}*H-NMR (*$CDCl_3$*):* δ = 4.69 (td, ^2J = 5.73 Hz, ^3J = 1.24 Hz, ^3J = 1.24 Hz, 2H, H^3), 5.22-5.45 (m, 2H, H^1), 5.88-6.05 (m, 1H, H^2), 7.16-7.39 (m, 5H, phenyl) ppm.

^{13}*C-NMR(*$CDCl_3$*):* δ = 69.1(C^3), 119.3(C^1), 121.0(C^6&C^{10}), 126.0(C^8), 129.5(C^7&C^9), 131.2(C^2), 151.2(C^5), 153.5(C^4) ppm.

IR (KBr pellet) = 3078, 2952, 2888, 1762, 1649, 1592, 1494, 1457, 1364, 1293, 1242, 1211, 1164, 1101, 1045, 949, 832, 776, 719, 687, 501 /cm^{-1}

m/z = 77.1 (76.8), 78.1 (25.4), 79.1 (8.2), 94.1 (83.8), 105.1 (14.9), 119.1 (37.45), 134 (100) 178.1($M^{+\cdot}$)

(Hydroxymethyl)-1,3-dioxolan-2-one[3]



Glycerol (25.0 g, 271 mmol), dimethyl carbonate (DMC) (72.76g, 813 mmol) and DABCO (291 mg, 2.71 mmol) were mixed and heated at 75°C for 10 h. After distillation of MeOH and excess DMC under vacuum, glycerol carbonate was used without further purification for the synthesis of the dicarbonate.

Yield : 24.96 g (78 % of theoretical)

Anal. calcd. for $C_4H_6O_4$: C 40.68, H 5.12, N 0.00 %; found: C 40.75, H 5.59, N 0.00 %.

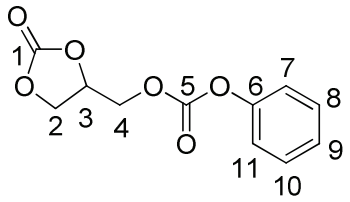
^{1}*H-NMR(DMSO-*d_6*):* δ = 3.51 (ddd, ^2J = 12.7 Hz, ^3J = 5.6 Hz, ^3J = 3.3 Hz, 1H, H^4), 3.67 (ddd, ^2J = 12.7 Hz, ^3J = 5.4 Hz, ^3J = 2.8 Hz, 1H, H^4), 4.29 (dd, ^2J = 8.2 Hz, ^3J = 5.8 Hz, 1H, H^2), 4.50 (dd, $^2J \approx {}^3J \approx$ 8.3 Hz, 1H, H^2), 4.80 (dddd, ^3J = 8.6 Hz, ^3J = 5.8 Hz, $^3J \approx {}^3J$ = 3.0 Hz, 1H, H^3), 5.26 (dd, $^3J \approx {}^3J \approx$ 5.4-5.6 Hz, 1H, OH) ppm.

^{13}*C-NMR (DMSO*d_6*):* δ = 60.6 (C^4), 65.8 (C^2), 77.0 (C^3), 155.2 (C^1) ppm.

IR (KBr pellet) = 3404, 2929, 2881, 1786, 1552, 1481, 1402, 1338, 1279, 1178, 1085, 1053, 983, 943, 856, 775, 716, 576 / cm^{-1}

m/z = 77.1 (5.1), 87.1 (100), 90.1 (6.4), 94.1 (83.8), 119.1($M^{+\cdot}$)

(2-Oxo-1,3-dioxolan-4-yl)methyl phenyl carbonate[3]



dicarbonate

In a three – necked round bottomed flask glycerol carbonate (64.47 g, 546 mmol) and pyridine (47.46 g, 600 mmol) were dissolved in 660 ml tetrahydrofuran (THF) under nitrogen atmosphere. The solution was cooled to 0°C. A solution of phenylchloroformate (93.94 g, 600 mmol) in 120 ml THF was slowly added and the temperature was maintained around 0°C. The reaction mixture was stirred at this temperature for 2 hours and then stirred at room temperature for 14 hours. Precipitated pyridine hydrochloride was removed by filtration. The filtrate was diluted with 200 ml diethyether and was washed with equal volume (300 ml each) of water, 0.1% hydrochloric acid, 0.1% sodium hydroxide and 5% brine solution. The organic phase was dried over sodium sulphate and the solvent was removed in rotary vacuum evaporator (20 mbar, 40°C). The crude product formed was recrystallized from 350 ml chloroform at 40°C and a fine colourless powder was obtained.

Yield : 97.5 g (75 % of theory)

Anal. calcd. for $C_{11}H_{10}O_6$: C 55.47, H 4.23, N 0.00 %; found: C 55.45, H4.20, N 0.00 %.

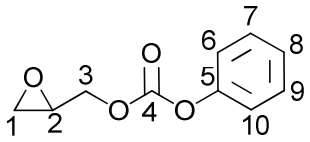
^{1}H NMR (DMSO-d6): δ = 4.39 (dd, ^{2}J = 8.7 Hz, ^{3}J= 6.0 Hz, 1H, H^{2}), 4.46 (dd, ^{2}J = 12.4 Hz, ^{3}J = 4.9 Hz 1H, H^{4}), 4.53 (dd, ^{2}J = 12.4 Hz, ^{3}J =2.6 Hz, 1H, H^{4}), 4.62 (dd, ^{2}J = 8.7 Hz, ^{3}J = 8.7 Hz, 1H, H^{2}), 5.11-5.18 (m, 1H, H^{3}), 7.25-7.45 (m, 5H, phenyl) ppm.

^{13}C NMR (DMSO-d6): δ = 65.7 (C^{2}), 67.5 (C^{4}), 74.0 (C^{3}), 121.2 (2C, C^{7}), 126.3 (C^{9}), 129.6 (2C, C^{8}), 150.6 (C^{6}), 152.7 (C^{5}), 154.6 (C^{1}) ppm.

IR (KBr pellet) = 1798, 1762, 1749, 1592, 1496, 1457, 1396, 1319, 1285, 1265, 1217, 1194, 1169, 1097, 1082, 1022, 770, 717, 690, 505. /cm^{-1}

m/z = 77.1 (66), 87.1 (12.6), 90.1 (30), 94.1 (100), 107.1 (10.9), 121.1 (4.9), 141.1 (7.6), 169.1 (3.4), 194.1 (2.4), 214.1 (9.2), 238.1($M^{+\cdot}$)

Oxiran-2-ylmethyl phenyl carbonate (**1**)



1

A) Allyl phenyl carbonate (2.6 g, 14.59 mmol) and 3-chloroperoxybenzoic acid (6.29 g, 36.46 mmol) (MCPBA) were dissolved in 30 ml dichloromethane (CH_2Cl_2) and the solution was stirred for 48 hours at room temperature. The precipitated m-chlorobenzoic acid was filtered off and the filtrate was diluted with 20 ml dichloromethane. 6 g of potassium carbonate was added to the organic phase and stirred for 15 minutes. The salt was removed by filtration and the filtrate was concentrated in a rotary vacuum evaporator at 500 mbar, 40^{o}C. The distillation (0.1 mbar, 95 ^{o}C) of the crude product resulted in the desired product.

Yield: 2.0 g (71% of theory).

Anal. calcd. for $C_{10}H_{10}O_4$: C 61.85, H 5.28, N 0.00 %; found: C 62.15, H 5.28, N 0.64 %.

^{1}H-NMR ($CDCl_3$): δ = 2.70 (td, ^{2}J = 13.27 Hz, ^{3}J = 6.64 Hz, ^{3}J = 6.64 Hz, 1H, H^{1}), 2.90(t, 1H, H^{1}), 3.25- 3.31(m, 1H, H^{2}), 4.10(dd, ^{2}J = 12.08 Hz, ^{3}J = 6.17 Hz, 1H, H^{3}), 4.51 (dd, ^{2}J = 12.08 Hz, ^{3}J = 3.08 Hz, 1H, H^{3}), 7.16-7.39 (m, 5H, phenyl) ppm.

^{13}C-NMR($CDCl_3$): δ = 44.5(C^{1}), 48.9(C^{2}), 68.9(C^{3}), 121.1(2C, C^{6} & C^{9}), 126.2(C^{8}), 129.5(2C, C^{7} & C^{10}), 151.0(C^{5}), 153.5(C^{4}) ppm.

m/z = 77.1 (39.8), 94 (100), 107 (15.8), 120 (2.9), 194.1($M^{+\cdot}$).

IR (KBr pellet) = 3063, 3005, 2957, 2296, 2038, 1950, 1765, 1592, 1487, 1456, 1387, 1348, 1244, 1211, 1164, 1057, 1023, 989, 947, 914, 865, 833, 775, 713, 688, 613, 565, 505 /cm^{-1}

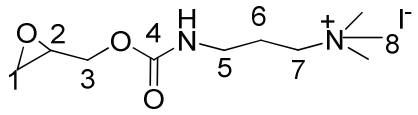
B) In a three – necked round bottomed flask glycidol (5 g, 67.50 mmol), and pyridine (5.886 g, 74.25 mmol) were dissolved in 70 ml tetrahydrofuran (THF) under nitrogen

atmosphere. The solution was cooled to 0°C. A solution of phenyl chloroformate (11.62 g, 74.25 mmol) in 15 ml THF was slowly added and the temperature was maintained around 0°C. The contents were stirred at this temperature for 2 hours and then stirred at room temperature for 14 hours and pyridine hydrochloride formed was removed by vacuum filtration. The filtrate was diluted with 10 ml diethylether and was washed with equal volumes (5 ml) of water, 0.1% hydrochloric acid, 0.1% sodium hydroxide and brine solution. The organic phase was dried over sodium sulphate and the solvent was removed in rotary vacuum evaporator (20 mbar, 40°C). The product was purified by column chromatography on silica gel (Ø – 2cm, column length – 50cm) (ethyl acetate/*n*-hexane, 2:4) to afford a colourless liquid.

Yield: 3.90 g (30% of theory).

Characterization same as *Method A.*

N,N,N-trimethyl-3-{[(oxiran-2-ylmethoxy)carbonyl]amino}propan-1-ammonium iodide (**2**)



2

In a three-necked flask equipped with a thermometer, dropping funnel and condenser, a solution of oxiran-2-ylmethyl phenyl carbonate (**1**, 1 g, 5.15 mmol) was dissolved in 10 ml THF and cooled down to 0 °C. The solution of *N*,*N*-dimethylpropane-1,3-diamine (0.55 g, 5.41 mmol) in 6 ml dry THF was slowly added with the help of dropping funnel and temperature was maintained around 0 °C. The reaction was stirred for 16 hours at room temperature. Then the solution of iodomethane (1.46 g, 10.28 mmol) in 8 ml dry THF was dropped in the solution of oxiran-2-ylmethyl [3-(dimethylamino)propyl]carbamate, phenol and THF at room temperature over a period of 2 hours. The reaction was stirred for additional 2 hours at room temperature and the product was filtered and subsequently washed with 5 ml THF three times. The crude product was dried under vacumm (10^{-2} mbar) to yield white solid.

Yield: 1.6 g (90% of theory).

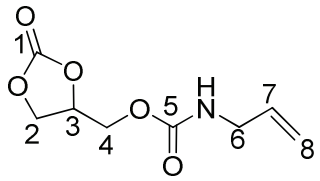
Anal. calcd. for $C_{10}H_{21}IN_2O_3$: C 35.00, H 5.87, N 8.16 %; found: C 34.10, H 6.34, N 7.95 %.

^{1}H-NMR (DMSO-d_6): δ = 1.74-1.95 (m, 2H, H^6), 2.62 (t, 1H, H^1), 2.78 (t, ^3J = 3.61 Hz, ^3J = 3.61 Hz,1H, H^1), 3.00-3.20 (m, H^8, H^5, H^2, 12H), 3.25-3.45 (t, 2H, H^7), 3.72 (dd, ^2J = 10.96 Hz, ^3J = 6.61 Hz, 1H, H^3), 4.32 (d, ^2J = 12.25 Hz, 1H, H^3), 7.41(s, 1H, NH) ppm.

^{13}C-NMR (DMSO-d_6): δ = 23.1 (C^6), 37.4 (C^5), 43.8 (C^1), 49.4 (C^2), 52.3 (C^8), 63.3 (C^7), 64.9 (C^3), 155.9 (C^4) ppm.

IR (KBr pellet) = 3400, 3080, 2956, 2933, 1716, 1519, 1485, 1434, 1408, 1338, 1279, 1239, 1142, 1128, 1091, 1072, 1027, 964, 934, 912, 900, 854, 775 /cm^{-1}.

(2-Oxo-1,3-dioxolan-4-yl)methyl allylcarbamate (**3**)



3

In a two- necked 250 ml round bottomed flask, (2-oxo-1,3-dioxolan-4-yl)methyl phenyl carbonate (20 g, 84.02 mmol) was dissolved in 200 ml dry THF. The solution was cooled to 0^{o}C and a solution of allyl amine (5.74 g, 100 mmol) in 40 ml dry THF was slowly added using a dropping funnel and the temperature was maintained around 0^{o}C. The reaction was stirred at this temperature for 2 hours and then stirred at room temperature for 14 hours. The crude product was concentrated under vacuum and was purified by column chromatography over silica gel (Ø – 5cm, column length – 50cm) (ethyl acetate/n-hexane, 1:1) to afford a white solid.

Yield : 16.2 g (96 % of theory).

Anal. calcd. for $C_8H_{11}NO_5$: C 47.49, H 5.47, N 6.96 %; found: C 47.65, H 5.49, N 6.89 %.

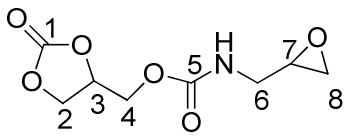
^{1}H-NMR ($CDCl_3$): δ = 3.78 (t, ^3J = 5.64 Hz, 2H, H^6), 4.20-4.65 (m, 4H, H^2 & H^4), 4.88 - 5.03 (m, 1H, H^3), 5.05 - 5.30 (m, 2H, H^8), 5.60 (s, 1H, NH), 5.70 – 5.90 (m, 1H, H^7) ppm.

^{13}C-NMR ($CDCl_3$): δ = 43.4 (C^6), 63.5 (C^2), 66.1 (C^4), 74.6 (C^3), 116.1 (C^8), 134.1 (C^7), 154.9 (C^5), 155.6(C^1) ppm.

m/z = 70.4 (11.03), 84 (94.8), 96.1 (25.3), 100 (100), 111 (6.4), 126.1 (9.8), 140.1 (26.8), 174.1 (7.4), 201.1(M^+).

IR (KBr pellet) = 3328, 3080, 3016, 2979, 2925, 2780, 1815, 1782, 1692, 1645, 1536, 1480, 1458, 1420, 1388, 1345, 1250, 1182, 1153, 1089, 1047, 989, 958, 923, 865, 773, 712, 645, 458 /cm^{-1}.

(2-Oxo-1,3-dioxolan-4-yl)methyl (oxiran-2-ylmethyl)carbamate (**4**)



4

Allyl dicarbonate (**3**, 5 g, 24.85 mmol) and 3-chloroperoxybenzoic acid (m-cPBA) (7.3 g, 42.31 mmol) were dissolved in 60 ml CH_2Cl_2. The reaction mixture was stirred for 24 hours at room temperature and then diluted with 50 ml CH_2Cl_2. Solid potassium carbonate (7 g) was added to the solution to convert the formed m – chlorobenzoic acid in the potassium salt. The solution was filtered off from the precipitated salt, and the filtrate was rotary evaporated to dryness to give a light yellow residue. The product was purified by column chromatography on silica gel (Ø – 5cm, column length – 30cm) (ethyl acetate) to afford a white solid.

Yield: 4.10 g (75.4 % of theory).

Anal. calcd. for $C_8H_{11}INO_6$: C 44.23, H 5.06, N 6.45 %; found: C 44.13, H 5.27, N 6.41 %

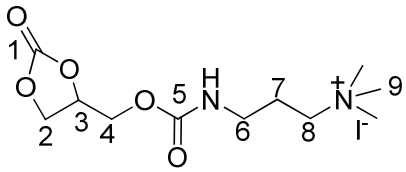
^{1}*H-NMR (*$CDCl_3$*)*: δ = 2.62 (dd, ^3J = 4.62 Hz, ^3J = 2.63 Hz,1H, H^8), 2.81 (t, ^3J = 4.3 Hz, 1H, H^8), 3.12 (dd, ^2J = 7.37 Hz, ^3J = 4.03 Hz,1H, H^7), 3.18 -3-32 (m,1H, H^6), 3.61(ddd, ^2J = 14.63 Hz, ^3J =6.17 Hz, ^3J = 3.13 Hz,1H, H^6), 4.20-4.42 (m, 3H, H^2 & H^4), 4.57(t, ^3J = 8.6 Hz, 1H, H^2), 4.88 - 5.03 (t, 1H, H^3), 5.47 (s, 1H, NH) ppm.

^{13}*C-NMR (*$CDCl_3$*)*: δ = 42.4 (C^6), 45.1(C^8), 50.4 (C^7), 63.6 (C^2), 65.9 (C^4), 74.2 (C^3), 154.6 (C^5), 155.7(C^1) ppm.

m/z = 70.3 (100), 86 (42.1), 100 (30), 116 (47.7), 130 (9.6), 142 (69.9), 156 (14.8), 174 (99.2), 188 (80.7), 218.2(M^+).

IR (KBr pellet) = 3352, 3064, 2998, 2931, 1793, 1724, 1536, 1481, 1398, 1334, 1250, 1174, 1090, 1054, 910, 849, 773, 714, 597 /cm^{-1}.

N,N,N-trimethyl-3-({[(2-Oxo-1,3-dioxolan-4-yl)methoxy]carbonyl}amino)propan-1-amonium iodide (**5**)



5

In a two- necked 250 ml round bottomed flask, (2-oxo-1,3-dioxolan-4-yl)methyl phenyl carbonate (10 g, 42.01 mmol) was dissolved in 100 ml dry THF.[3] The reactants were cooled to 0^{o}C and the solution of 3-dimethylamino-1-propylamin (4.29 g, 42.01 mmol) in 21 ml dry

THF was slowly added using a dropping funnel and the temperature was maintained around 0°C. The reaction were stirred at this temperature for 2 h and then stirred at room temperature for 14 h. Then the solution of iodomethane (11.92 g, 84 mmol) in 60 ml dry THF was dropped slowly to the above mentioned reaction for 2 hours. The reaction mixture was stirred at this temperature for 2 h and then stirred for an additional 1 h at 50 °C. The product was filtered and subsequently washed with THF (10 ml X 3) times. The crude product was dried under high vacuum 10^{-2} mbar to afford light yellow solid.

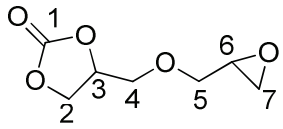
Yield: 15.5 g (95% of theory).

^{1}H-NMR(DMSO-d_6): δ = 1.74-1.95 (m, 2H, H^7), 3.00 - 3.20 (m, 11H, H^6, H^9), 3.25 - 3.45(t, 2H, H^8), 4.10-4.34(m, 3H, H^2,, H^4), 4..59 (t, ^{2}J = 8.54 Hz, 1H, H^2), 4.96-5.14 (m, 1H, H^3), 7.39(t, ^{3}J = 5.6 Hz, 1H, NH) ppm.

^{13}C-NMR(DMSO-d_6): δ = 22.9 (C^7), 37.3 (C^6), 52.3 (C^9), 63.2 (C^8), 66.1 (C^2), 66.9 (C^4), 74.7(C^3), 154.7 (C^5), 155.6 (C^1) ppm.

IR (KBr pellet) = 3265, 3013, 2950, 1785, 1716, 1516, 1493, 1446, 1395, 1348, 1272, 1241, 1182, 1139, 1095, 1050, 1026, 1010, 966, 910, 875, 770, 712, 615, 457 /cm^{-1}

4-[(Oxiran-2-ylmethoxy)methyl]-1,3-dioxolan-2-one (**6**)



6

Glyceryl carbonate (4 g, 33.87 mmol) was dissolved in 18 ml dry THF and sodium hydride (0.975 g, 40.64 mmol) was added under nitrogen atmosphere. The reaction mixture was stirred for 1 h and the formed hydrogen was released under nitrogen atmosphere to avoid an explosion. Then epichlorohydrine (7.83 g, 84.64 mmol) was added and the reaction was heated under reflux at 60°C for 16 hours. The sodium chloride formed was filtered off and washed with 10 ml THF. The combined organic filtrates were rotary evaporated to dryness and subsequently the product was purified by column chromatography on silica gel (Ø – 2cm, SiO_2 Length – 50cm) with ethyl acetate/chloroform : 1/1 vol:vol.

Yield: 1.8 g (30.56% of theory).

Anal. calcd. for $C_7H_{10}O_5$: C 48.28, H 5.79, N 0.00 %; found: C 48.12, H 5.78, N 0.34 %.

^{1}H-NMR($CDCl_3$): δ = 2.57-2.66 (m, 1H, $H^{7'}$, H^7), 2.78 - 2.84 (m, 1H, H^7, $H^{7'}$), 3.12 - 3.20 (m, 1H, H^6, $H^{6'}$), 3.38 (dd, ^{2}J = 11.76 Hz, ^{3}J = 6.43 Hz, 0.40H, H^5), 3.48 (dd, ^{2}J = 11.94 Hz, ^{3}J = 5.70 Hz, 0.60H, $H^{5'}$), 3.68 (dd, ^{2}J = 11.12 Hz, ^{3}J = 3.65 Hz, 0.6H, $H^{4'}$), 3.77 (d, ^{2}J =

3.65, 0.8H, H^4), 3.84 (dd, ^2J = 11.12 Hz, ^3J = 3.88 Hz, 0.60H, $H^{4'}$), 3.90 (dd, ^2J = 11.86 Hz, ^3J = 2.45 Hz, 0.60H, $H^{5'}$), 3.94 (dd, ^2J = 11.73 Hz, ^3J = 2.37 Hz, 0.40H, H^5), 4.35 - 4.57 (m, 2H, H^2, $H^{2'}$), 4.78-4.90 (m, 1H, H^3) ppm.

^{13}C-NMR($CDCl_3$): δ = 43.8 (C^7), 43.8 ($C^{7'}$), 50.6, 50.7 (C^6, $C^{6'}$), 66.1 (C^2), 70.2 (C^4), 70.3 ($C^{4'}$), 71.9 ($C^{5'}$), 72.6 (C^5), 75.0 (C^3), 154.9 (C^1) ppm.

m/z = 71 (14.8), 73 (70), 83 (7.7), 87 (100), 100 (8.9), 113 (5), 117 (7.3).

IR (KBr pellet) = 3565, 3062, 2998, 2923, 2506, 2340, 1789, 1549, 1480, 1397, 1337, 1309, 1255, 1172, 952, 908, 850, 773, 713, 611, 577, 534, 487, 416 / cm^{-1}.

Measurements

^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker DPX-300 FT-NMR spectrometer at 300 MHz and 75 MHz respectively. Chloroform-d ($CDCl_3$) and dimethylsulfoxide-d_6 (DMSO-d_6) were used as solvents, and tetramethylsilane (TMS) was used as internal standard.

The infrared spectra were measured on a Thermo Nicolet Nexus 470 spectrometer with a resolution of 4 cm^{-1}. The samples were prepared as KBr pellets for the measurement in transmission mode.

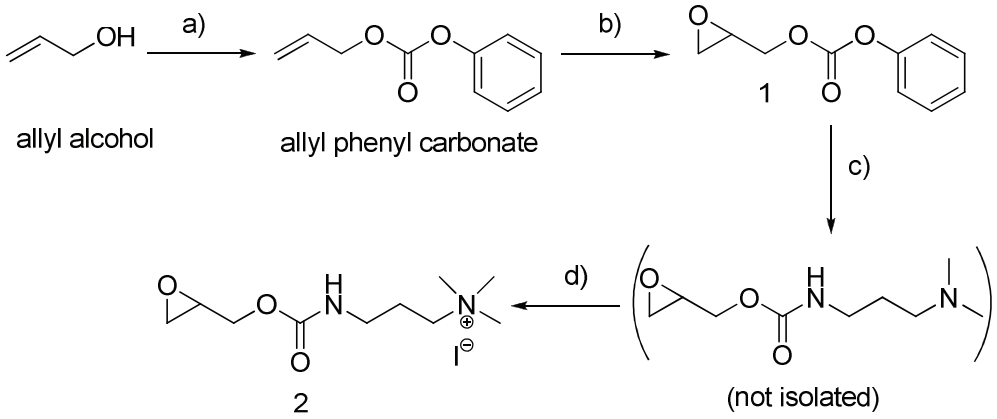
Carbon, hydrogen and nitrogen elemental analyses were performed on a Hearaeus CHN-O Rapid Elementar Vario El instrument.

Mass Spectroscopy was carried on Finnigan MAT 95 high resolution mass spectrometer. The samples were mixed with 3-Nitrobenzylalcohol matrix and were injected into the spectrometer.

Results and Discussions:

Synthesis of couplers

In a first attempt to prepare the epoxy/phenyl carbonate coupler **1** (Scheme 3.3), glycidol was reacted with phenyl chloroformate in the presence of pyridine as acid scavenger.[8] The desired product was only obtained in 30 % yield, because of an epoxide ring opening side reaction. A more successful route started with allyl alcohol which was first converted to allyl phenyl carbonate by means of phenyl chloroformate and pyridine.[7] Subsequently the allyl phenyl carbonate was epoxidized with m-chloroperbenzoic acid (MCPBA)[9] to yield oxiran-2-ylmethyl phenyl carbonate (**1**) in nearly quantitative yield. The formation of the epoxide ring can be demonstrated from ^{1}H-NMR and ^{13}C-NMR (Figure 3.1). The signals at δ = 44.5 ppm and 48.9 ppm (see Figure 3.1b) are characteristic for epoxide rings, indicating that the epoxidation was successful.



Scheme 3.3. Synthesis of the epoxy/carbonate linker **1** and the epoxy-quat modifier **2** (a) C_6H_5N, PhOCOCl, CH_2Cl_2, 0°C, b) MCPBA, CH_2Cl_2, room temperature, c) *N*,*N*-dimethyl-propane-1,3-diamine, THF, 0 °C, d) CH_3I, THF, room temperature.

Coupler **1** contains two electrophilic sites of different reactivity towards nucleophiles, where the phenyl ester carbonate is much more reactive then the epoxy ring. At low temperature (0 – 25 °C) the phenyl ester carbonate selectively reacts with primary amines and forms a urethane linkage under simultaneous release of phenol. The epoxide ring reacts only at higher temperature (room temperature) with amines and only after consumption of the more reactive phenyl ester carbonate.

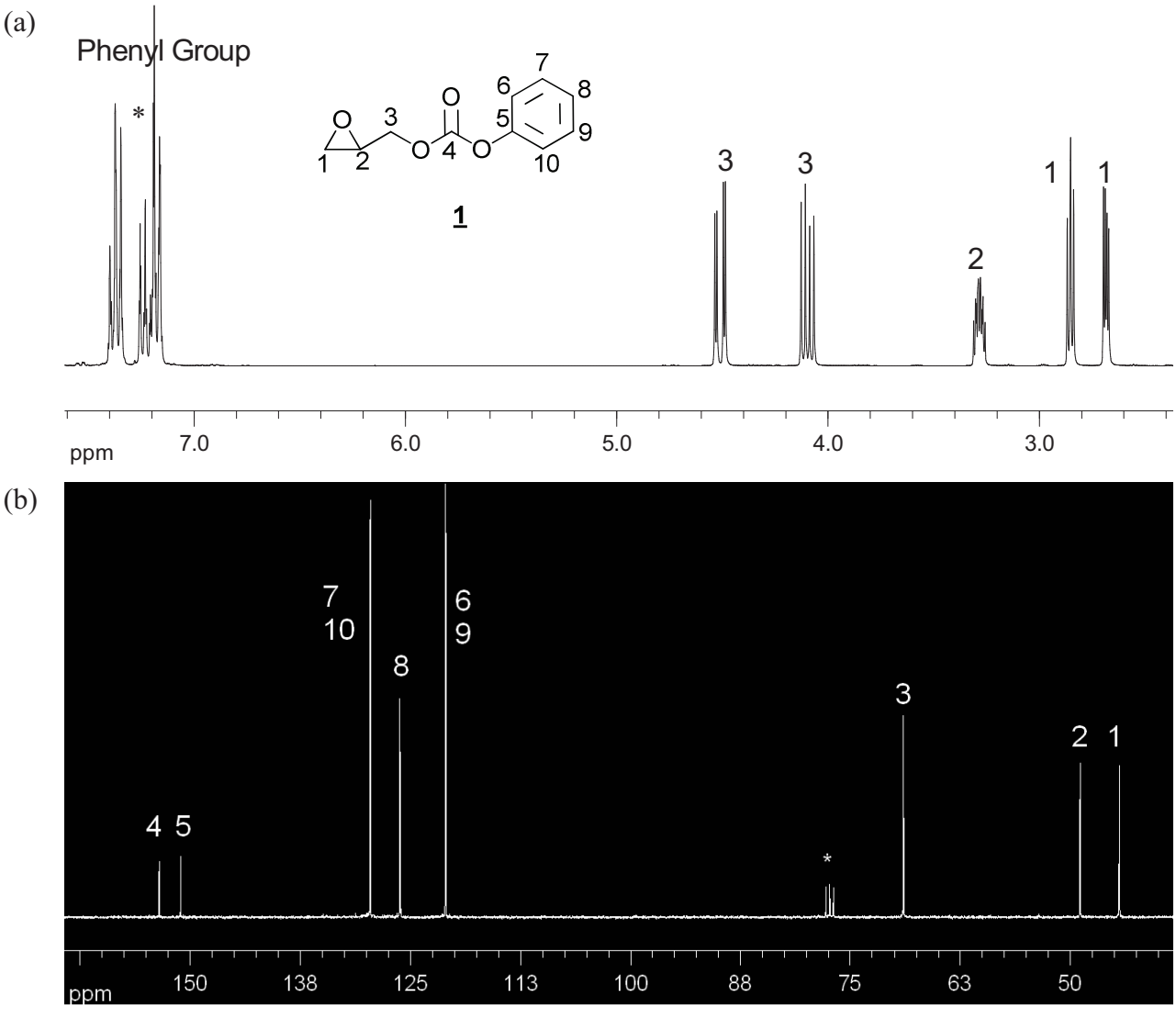


Figure 3.1. (a)^{1}H-NMR, (b) ^{13}C-NMR spectra with signal assignments of the epoxy-carbonate linker (**1**) in $CDCl_3$ (*)

Using this principle, the epoxy/quat modifier **2** was obtained from compound **1** by addition of *N*,*N*-dimethylpropane-1,3-diamine and subsequent quarternization of the adducts secondary amino group with methyl iodide. The two steps could be carried out in a one-pot synthesis by avoiding the isolation of the intermediate oxiran-2-ylmethyl 3-(dimethylamino)propylcarbamate (cf. Scheme 3.3). Note, that upon isolation of the intermediate the epoxy ring can be opened by phenol in the presence of tertiary amines.[10] The absence of signals caused by phenol (formed as a side product) in the NMR spectra and the presence of signals coming from quaternary ammonium methyl groups (3.1 ppm, signal 8) and urethane groups (NH) at δ = 7.40 ppm indicates that coupler **2** was successfully obtained (cf. Figure 3.2).

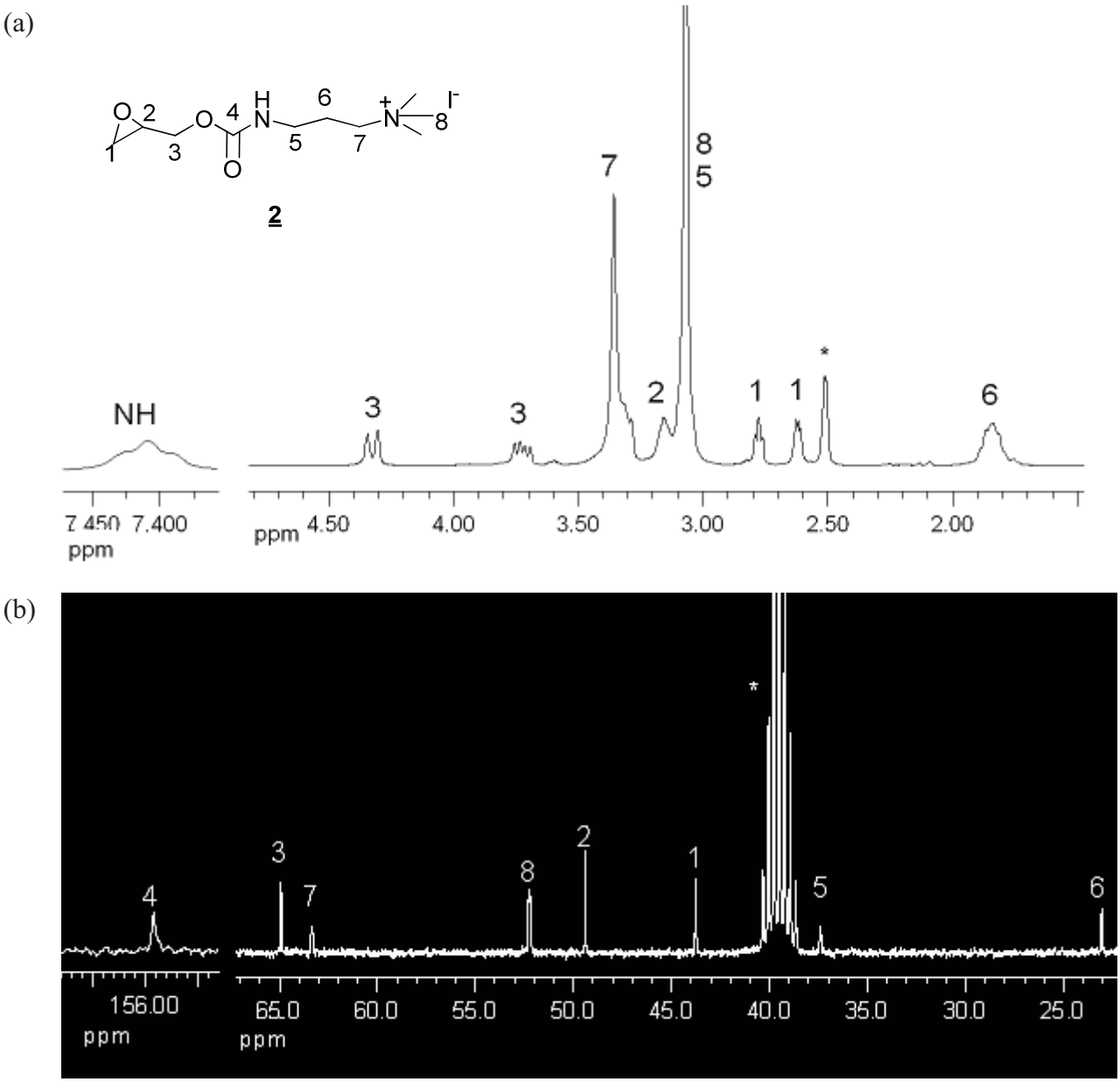
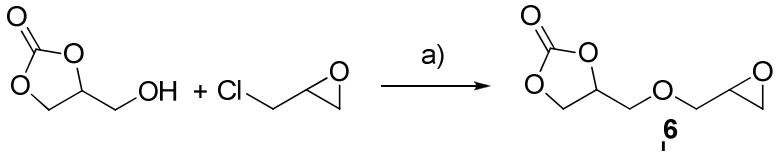


Figure 3.2. (a)[1]H-NMR, (b) [13]C-NMR spectra with signal assignments of the linker **2** in DMSO (*)

Glyceryl carbonate and epichlorohydrine were used as the starting material for the synthesis of the epoxy/cyclocarbonate linker **6** using the Williamson ether synthesis (**Scheme 3.4**) with sodium hydride as a base.

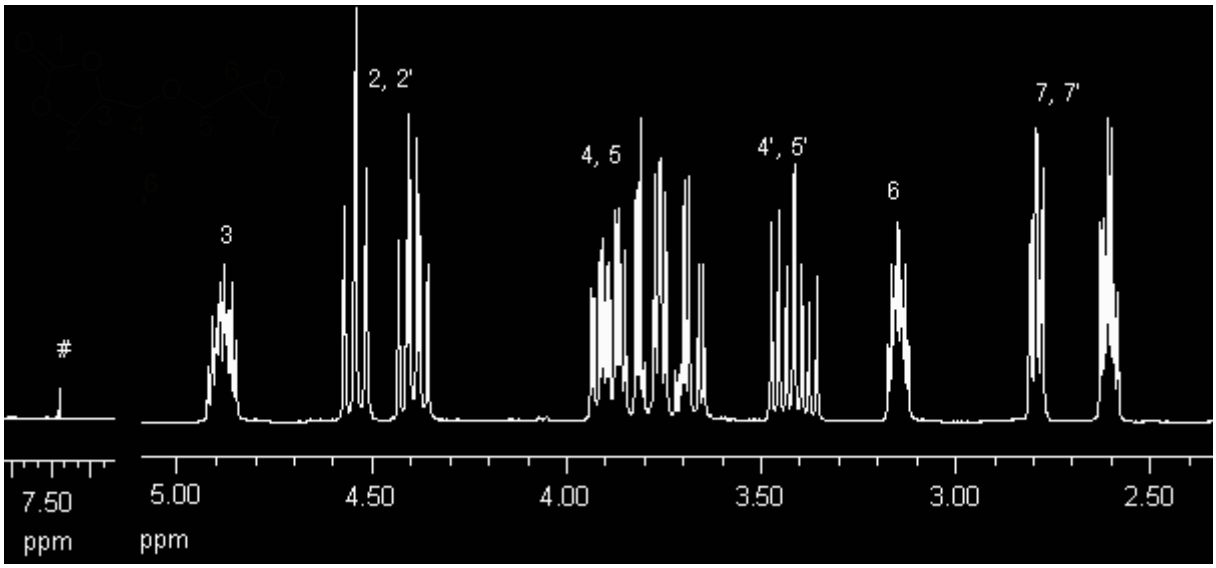


Scheme 3.4. Synthesis of epoxy/cyclic carbonate linker **6** (a) NaH, THF, 60 °C

From ^{1}H-NMR spectra of the reaction mixture the educt conversion was found to be 70%, however, the yield of the product **6** was around 30 % as the product is water soluble and thus difficult to isolate.

The ^{1}H-NMR and ^{13}C-NMR spectra of linker **6** are depicted in Figure 3.3.

a)



b)

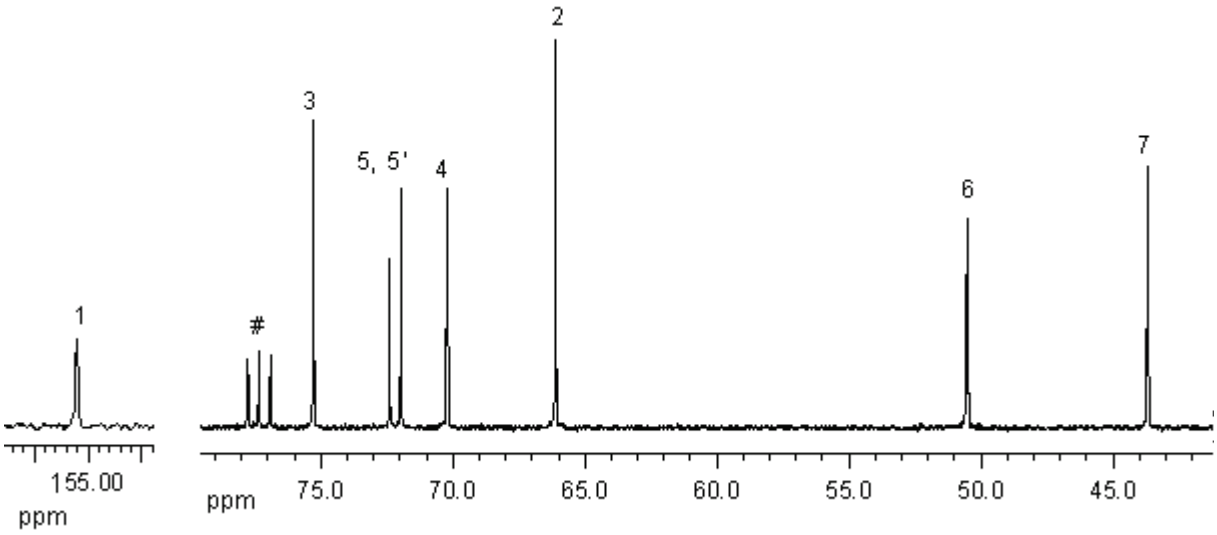


Figure 3.3. (a) ^{1}H-NMR- (b) and ^{13}C-NMR spectra with signal assignments of the epoxy/cyclo-carbonate linker **6** in $CDCl_3$ (#)

The compound possesses two stereogenic carbon atoms (C3 and C6, cf. Figure 3.3) and was obtained in form of a mixture of two pairs of enantiomers, since the synthesis was not stereoselective. The four stereoisomers can be grouped in two pairs of diastereomers that can be distinguished by NMR spectroscopy in a non-chiral environment. Consequently the NMR

spectra showed the presence of two isomers by splitting of the signals of the respective stereogenic centres (cf. Figure 3.3). The protons attached to position 4, 4', 5 and 5' exhibited geminal and vicinal coupling with protons attached to positions 3 and 6, respectively, resulting in a complex signal pattern between δ = 3.3 and 4.0 ppm.

Model Reactions:

(a) Model reactions were carried with compound **6** to investigate the selectivity of primary amino groups towards the epoxide and the cyclic carbonate ring.

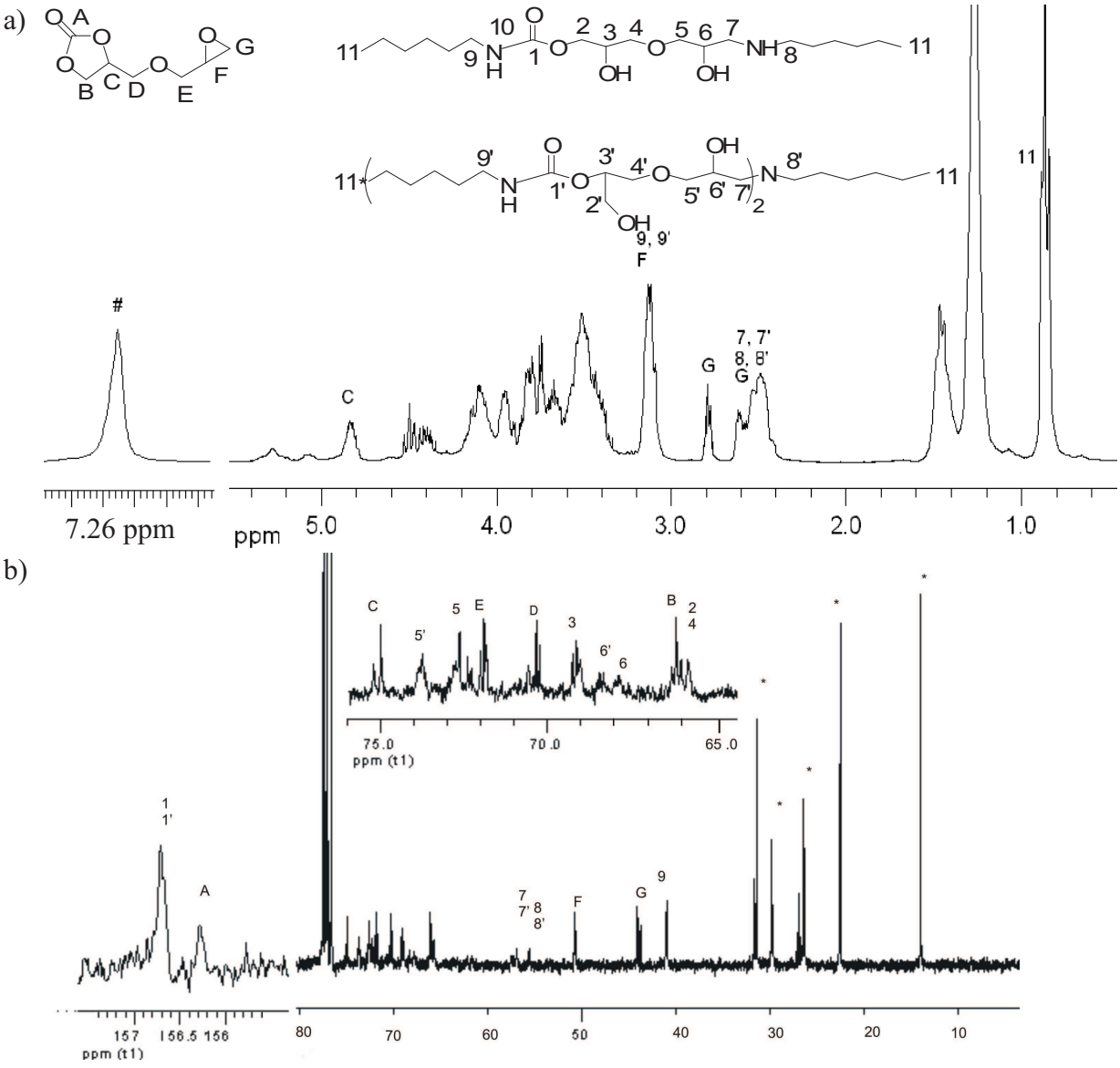


Figure 3.4. ^{1}H-NMR (a) and ^{13}C-NMR (b) spectra of the product resulting from the model reaction between linker **6** and hexyl amine(**6** : $C_6H_{13}NH_2$ = 1:1 mol:mol) (* = alkyl signals of hexylamine, # = $CDCl_3$)

One mole of compound **6** was reacted with one mole of hexylamine in $CDCl_3$ as the solvent at 0 ^oC for 4 hours and subsequently at room temperature. ^{1}H-NMR and ^{13}C-NMR were measured at the different time intervals and the analysis of the spectra was performed when all the hexylamine was consumed as indicated by ^{1}H-NMR. Note that the resulting product was a complicated mixture of at least 10 reaction products, because (i) the linker **6** consisted of a mixture of diastereomers, (ii) the carbonate ring can be opened in two different ways and (iii) any bifunctional compound AB can inherently yield three addition products (R-AB, R-BA and R-AB-R). The relative reactivity of the epoxide- and the carbonate ring towards amine addition was calculated using the proton signals corresponding to carbon atoms C, D, 7, 7', 8, 8', 9 and 11 (cf. Figure 3.4). The ^{1}H-NMR revealed that the primary amino groups did not distinguish between an epoxide- and the carbonate ring. The spectral data also indicated that the hexylamine became attached to the carbon atom G of linker **6**, being the carbon atom of the three-membered ring bearing no other substituent. Since further two moles of oxirane reacted with one mole of hexyl amine at room temperature, these results are in agreement to the well known chemistry of epoxides.[6]

(b) The reaction products from the above reaction were further analyzed by reacting the product mixture with excess of diallylamine in $CDCl_3$ as a solvent. The diallylamine was used as the reactant because allyl signals are in the range of 5 -6 ppm and there is no overlapping with other signals in ^{1}H-NMR. Since the cyclic carbonate has no reactivity towards the secondary amine, only epoxide ring could react with the diallylamine. The reaction was carried out at 50 ^oC and was monitored by ^{13}C-NMR spectroscopy until all the epoxide has been consumed. The obtained product was dried under vacuum to remove excess of diallylamine. The ^{1}H-NMR (see Figure 3.5) confirms that all the epoxide groups have reacted and integral of proton attached to carbon C (1 proton) was comparable to integral of protons attached to allyl groups and it justifies the calculation done in the model reaction (a).

(c) The model reaction of 1 mole of coupler **6** with 1 mole of dihexylamine was carried out at 60 ^oC for 16 h in chloroform as solvent. Since cyclic carbonate ring does not have any reactivity towards secondary amines, the signals of the cyclic carbonate could be well seen in the ^{13}C spectra (cf. Figure 3.6). The signals due to ring opening of epoxide ring by secondary amine could also be identified (carbon 6 and 7).

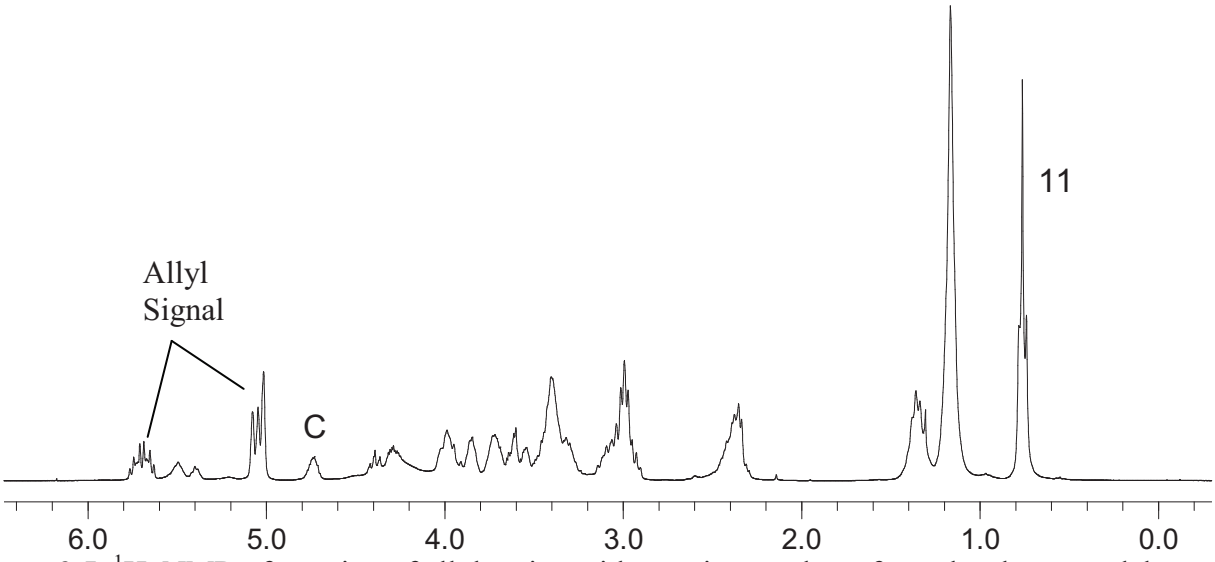


Figure 3.5. ^{1}H–NMR of reaction of allyl amine with reaction products from the above model reaction.

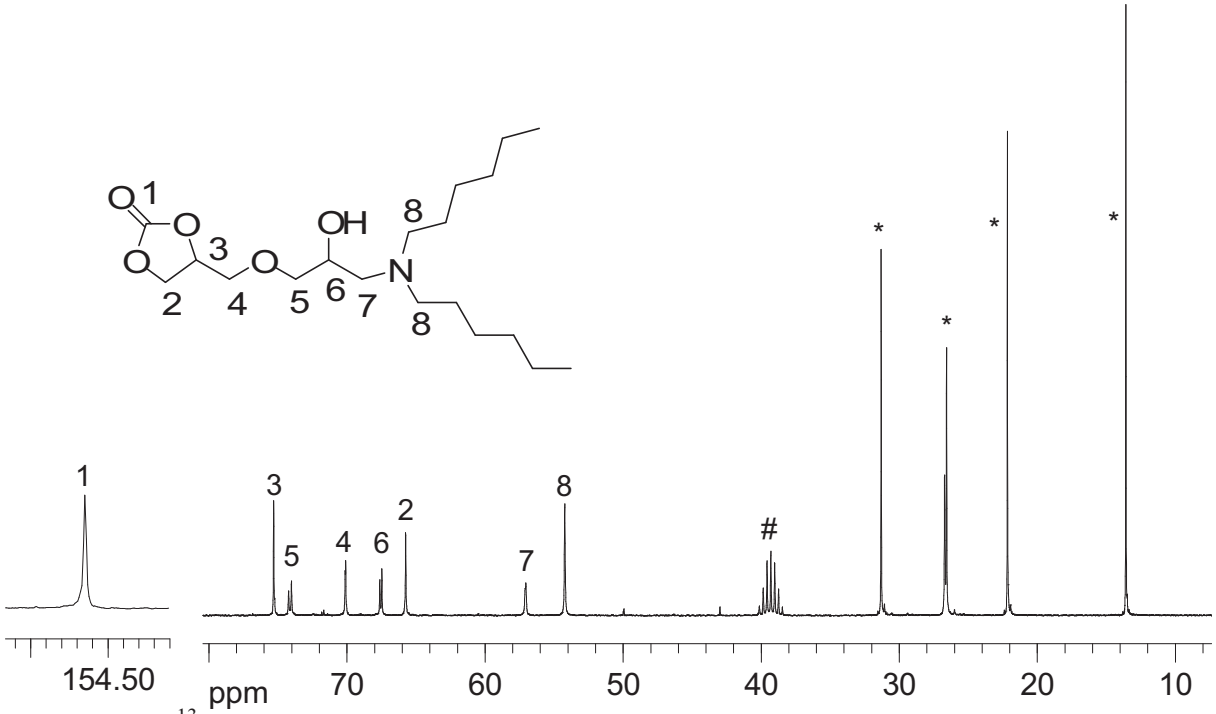


Figure 3.6. ^{13}C-NMR - Model reaction between linker 6 and dihexylamine. (# = DMSO, * = alkyl chain signals)

(d) The model reaction of compound 6 with equimolar trihexylamine was carried out in $CDCl_3$ at 80 ^oC for 24 h. Due to low reactivity of epoxide towards tertiary amine; the reaction did not go to completion. Furthermore, ring opening of cyclic carbonate ring with trihexylamine was not observed. The mixture of product was characterized by ^{1}H-NMR and ^{13}C-NMR (cf. Figure 3.7). The unreacted compound could be well seen in the spectra. Due to formation of cationic group in the product, there was shift in the carbon 3 from δ = 75.2 ppm to δ = 76.9 ppm.

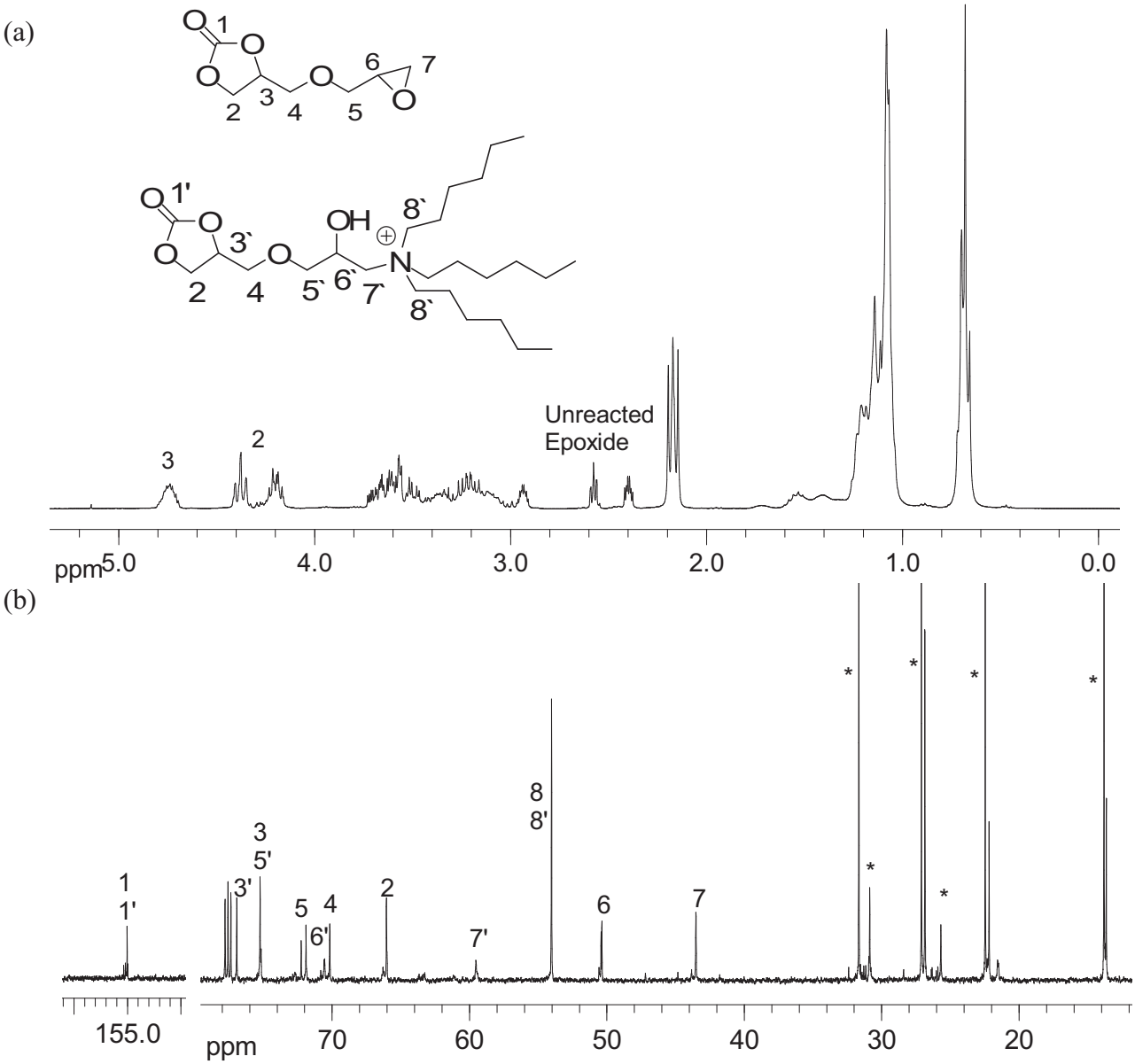


Figure 3.7. Reaction of 1 mole of linker 6 with 1 mole of trihexylamine (a) ^{1}H-NMR, (b) ^{13}C-NMR. (* = alkyl groups of trihexylamine)

The results of the model reactions are summarized in Table 3.1. The cyclic carbonate ring does not react with the secondary and tertiary amines under the mentioned reaction conditions, whereas the epoxide ring reacts with all the amino groups as mentioned in the literature.[11] Furthermore, the reactivity of hexylamine towards the epoxide and the cyclic carbonate ring was observed to very similar ($R_{EH} \sim R_{CH}$). When reacted with a polyamine exclusively bearing secondary and tertiary amino groups, coupler **6** can be used to introduce the cyclic carbonate functionality in the macromolecule. Hence, in case of b-PEI care must be taken to either protect or to permanently block $-NH_2$ groups.

Table 3.1. Summary of model reactions: reaction of coupler **6** with various amines.

	Epoxide Ring (E)	**Cyclic Carbonate Ring (C)**
hexylamine (H)	Ring opening (R_{EH})	Ring opening (R_{CH})
dihexylamine	Ring opening	No Ring opening
trihexylamine	Ring opening	No Ring opening

Note - R_{EH} = rate of reaction of epoxide ring towards hexyl amine, R_{CH} = rate of reaction of cyclic carbonate ring towards hexyl amine.

Conclusions:

An epoxide and a cyclic carbonate reactive "Quat modifier" as well as two X-Y couplers combined cyclic carbonate and epoxide functionality were successfully synthesized and characterized. The reactivity of the 5-membered cyclic carbonates and epoxides towards primary amines was found to be same. The model reactions of the compound **6** with different amines were successfully characterized by NMR spectroscopy. Couplers like **6** are of special interest for e.g. reaction with linear polyethylenimine (secondary amino groups) will lead to a polymer bearing cyclic carbonate groups.

The reactions of various couplers with polyamines will be described in **Chapter 4** and structural characterization of the macromolecular products will be based on these model reactions.

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Chapter 4: Quat-Primer' Polymers bearing cationic and reactive groups: synthesis, characterization and application.

Introduction:

Carbon fibres have become one of the most important reinforcing materials, being characterized by extremely high strength and modulus. Carbon fibre – epoxy composites are used in numerous aerospace, marine and recreational applications. The interface between reinforcing fibres and polymeric matrices in composite materials is the controlling factor in obtaining optimum mechanical properties.[1-4] The function of the interface is to transmit stress from the matrix to the reinforcing fibre. But the carbon fibre surface which is characterized by low wettability and chemical activity exhibits weak adhesion to an epoxy matrix. A universal method to increase the surface polarity of carbon fibres is to modify their surface to increase the hydrophilicity of the fibre.[5] The oxidative methods for the modification of carbon fibre surfaces include oxidation in different types of plasma[6-8], oxidation in air[9], electrochemical oxidation[10] and wet chemical methods, such as immersing in phosphoric acid or boiling[11,12] in nitric acid and intercalation[13]. Drzal et al. studied the effect of oxidizing surface treatments on carbon fibres and concluded that contribution to interfacial adhesion of covalent bonds formed between carboxylic groups present on the oxidized fibre surfaces and epoxide groups in the epoxy matrix was very small.[14] They also studied the effect of epoxy based coatings on the interfacial shear strength and concluded that although there is improvement in the interfacial strength but the failure mode is no longer interfacial.[15] To have good adhesion between fibre and matrix , fibres are generally oxidized and coated with thin monomeric films (100 – 200 nm thick) or coated with thin polymeric films from solutions.[16,17] Sizing has an adhesion and wetting promotion function but is particularly important for facilitating fibre handling during composite manufacture or acting as a lubricant to prevent fibre damage.

In the present study highly oriented pyrolytic graphite (HOPG) was used as model substrate, due to structural similarity of the carbon fibre and HOPG. HOPG consists of two dimensional solid layers with strong covalent bonding within each layer and only weak van der Waals interactions between neighboring layers.[18] Several studies have shown that nanometer to

micrometer sized surface pits may form on HOPG surface upon oxidation; the pit size, its number density, and its shape are dependent on the plasma gas mixture, temperature, pressure and treatment time.[19-20] Rabe et al. studied the thermal oxidation of the basal plane of graphite in the presence of molecular oxygen allowing the variation of surface roughness in a well defined way.[21-23] Surface functionalization of HOPG, using low-energy plasma environments was performed to attach chemical groups at the top most layer of the surface Scanning force microscopy (SFM) was used for surface characterization of treated HOPG.

This study deals with the interaction of Quat-Primer functional polymers and HOPG. The primers were prepared by ring opening reaction of functional five-membered cyclic carbonates with poly(ethylene imine). The function of the primer polymers is (i) to bind to the surface of carbon fibres via electrostatic interactions and (ii) to supply epoxy- or cyclic carbonate groups that can copolymerize with the amine components of epoxy resins during the curing step. The concept was to couple two different amines via the dicarbonate linker (2-oxo-1,3-dioxolan-4-yl)methyl phenyl carbonate.[24-26] This carbonate coupler posesses two electrophilic sites of different reactivity. At low temperatures (0 - 25 ^{o}C), the phenyl ester carbonate reacts with a first amine whereas the cyclic carbonate only reacts with a second amine under ring opening at elevated temperature after full consumption of the phenyl ester carbonate. The surface morphology of the polymers covered HOPG was studied by SFM and the interfacial adhesion between functionalized carbon fibre sized with Quat-Primer Polymers and the epoxy matrix were investigated using the Kelley – Tyson fragmentation test.

Materials and Methods:

Materials

Poly(ethylene imine) (b-PEI, Mw approx. 25000 g/mol by light scattering (LS), Mn approx. 10000 g/mol by gel permeation chromatography (GPC), water free, Aldrich), tetraethylenepentamine (TEPA, Aldrich), were used as received. The couplers prepared in *Chapter 3* are used to functionalize b-PEI. All solvents were distilled before using.

ZYB grade high ordered pyrolytic graphite (HOPG) was obtained from advance ceramics; Inc. Substrates were obtained by cleavage from adhesive tape just prior to plasma treatment.

The carbon fibre was a high modulus PAN based sized carbon fibre, UTS-5631 from Tenax (nominal tensile strength = 4800 MPa, nominal fibre diameter is 7μm, 12.000 fibres/bundle).

The epoxy resin was DER 331 from Dow Chemical co. (bisphenol-A based liquid epoxy resin, average equivalent weight = 186 – 192 g/equivalent, mixed with curing agent DEH 226 (tetraethylenepentamine, amine hydrogen equivalent weight = 27 g/equivalent.

The couplers listed in Scheme 4.1 were used in functionalization of branched polyethylenimine. The synthesis of these couplers is already described in Chapter – 3.

General procedure for the reaction of b-PEI with cationic carbonate- or cationic epoxy compounds.

At 50 ^{o}C the respective amounts of carbonate **2** or **5** (see Table 4.1) were added to a solution of 1.0 g (23.25 mmol) b-PEI in 10 ml DMF. After stirring the solution at 50 ^{o}C for 48 hours the polymer was precipitated in a 1:1 (vol : vol) mixture of hexane and diethylether. The polymer was re-dissolved in 10 ml methanol, stirred vigorously for 15 min and re-precipitated in the above mentioned non-solvent. After repeating the cycle for 3 times the solvent was distilled off and the product was dried (room temperature, 24 h) at 1.3 Pa to yield a white solid.

Table 4.1. Educt composition and yields in the preparation of polymers **PEI-2** and PEI-5

	Reactants (mg)			**Yield**
	b-PEI	**2**	**5**	
PEI-2	1000	4180	-	4.4 g, 85%
PEI-5	1000	-	2705	3.2 g, 88%

*General procedure to functionalize modified **b-PEI** with (2-oxo-1,3-dioxolan-4-yl)methyl (oxiran-2-ylmethyl)carbamate (**4**) or 4-[(oxiran-2-ylmethoxy)methyl]-1,3-dioxolan-2-one (**6**)*

To a solution of 1000 mg of modified **PEI -5** in 10 ml DMF the required amount of the epoxy- or cyclic carbonate linker (**4** or **6**) was added (see Table 4.2) and stirred at 50 ^{o}C for 48 hours and was precipitated in a 1:1 (vol : vol) mixture of hexane and diethylether.

Table 4.2. Educt composition and yields in the preparation of polymers **PEI-54** and **PEI-56**

Polymer	**Reactants (mg)**			**Yield**
	PEI-5	**4**	**6**	
PEI-54	1000	812	---	1.5 g, 86 %
PEI-56	1000	---	621	1.3 g, 81%

The polymer was re-dissolved in 10 ml methanol, stirred vigorously for 15 min and re-precipitated in the above mentioned non-solvent. After repeating the cycle for 3 times the solvent was removed and the product was dried (room temperature, 24 h) at 1.3 Pa to yield a white solid.

Measurements:

^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker DPX-300 FT-NMR spectrometer at 300 MHz and 75 MHz respectively. Chloroform-d ($CDCl_3$) and dimethylsulfoxide-d6 (DMSO-d6) were used as solvents, and tetramethylsilane (TMS) was used as internal standard.

The infrared spectra were measured on a Thermo Nicolet Nexus 470 spectrometer with a re-solution of 4 cm^{-1}. The samples were prepared as KBr pellets for the measurement in trans-mission mode.

Viscosity measurements were carried out with polymer concentrations varying from 0.5 g/dl to 1.5 g/dl in 0.5M sodium nitrate solution using a Ostwald capillary viscometer (Schott, Type 509 03) at 25 ^{o}C. The intrinsic viscosity [η] was calculated by means of the Huggins equation

$\eta_{red} = [\eta] + [\eta]^2 \cdot k_H \cdot c$ (ηred = reduced viscosity, $[\eta]$ = intrinsic viscosity = 'Staudinger Index', k_H = Huggins constant, c = polymer concentration).

The hydrodynamic diameter of the macromolecules was determined on a Zetasizer NanoZS ZEN3500 dynamic light scattering system. The concentration of the polymer was 1 – 10 g/L in 0.5M sodium nitrate solution.

Differential scanning calorimetry (DSC) was performed with a Netzsch DSC 204 under nitrogen atmosphere with a heating rate of 10°C/min. Calibration was achieved using indium standard samples, the sample mass was kept between 5 – 15 mg.

Thermogravimetric analyses (TGA) were performed on a Netzsch TG 209C thermobalance with a TA System Controller TASC 414/4. The measurements were performed under nitrogen atmosphere with a heating rate of 10°C/min. The sample mass was kept between 5 – 15 mg.

The surface modification of HOPG samples was carried out in a microwave plasma discharge system, AK 330 Roth & Rau, using argon or oxygen/argon mixtures. The sample was placed inside the chamber and became evacuated to a pressure of 10^{-3} bar. The treatment of HOPG was done in two ways (i) in an argon atmosphere and (ii) in a mixture of argon and oxygen (Ar : O_2 – 1:1) atmosphere. The following process parameters were used: O_2 and Ar gas flow, 30 ft^3 / min each; working pressure, 0.4 mbar; power, 150W; treatment time 2 min.

The surface morphology of thin polymer films was investigated by atomic force microscopy (AFM) at room temperature using a Solver SFM (NTMDT, Zelenograd, Moscow). Imaging was done in the tapping mode using standard silicon cantilevers: Nanoworld Pointprobe NCH f0 (330 kHz). The thin films were prepared by spin coating a volume of 40 µL from solutions of the polymers, containing 0.04 wt% to 0.004 wt% of polymer in pure methanol at a rotation rate of 2000 rpm.

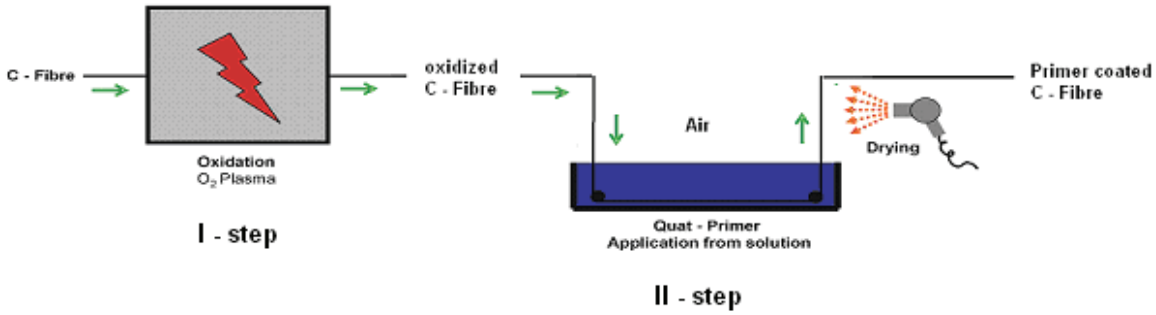
Fabrication of Composite Specimens

(a) Fabrication of Steel and Rubber Molds

First, a mild steel master of dogbone-shape was machined with a length of 16 mm, a width of the core of 2 mm and a height of 2 mm. Silicone rubber (Rhodorsil RTV 3450A, Rhodia Silicon GmbH) was used for transferring the masters shape to a mould with a cavity of 16 x 2 x 2 mm^3.

(b) Preparation of carbon fibre samples

Non-sized carbon fibre samples were prepared by extracting (1g) of the commercially obtained carbon fibre in a Soxhlet extractor with acetone for 5 hours.



Scheme 4.1. Schematic diagram – sizing of carbon fibre.

To prepare Quat-Primer sized carbon fibres the commercially obtained carbon fibre roving was treated with a continuous oxygen plasma machine (c.f. Scheme 4.1) The fibre was put on a roller (length : 35 cm, Ø – 9 cm) and evacuated in a plasma discharger, AK 550 Roth and Rau to a pressure of 10^{-3} bar. The following parameters were used: O_2 gas flow, 100 ft^3 / min; working pressure = 1 mbar, microwave power = 150 W, motor speed = 4 m/min. Immediately after the plasma treatment, the fibres were dip-coated in a solution of **PEI-56** (0.1 wt% polymer) in methanol (weight of fibre : volume of polymer solution - 300 mg : 15 mL) and were dried under vacuum (14 h, 50 ^oC, membrane pump).

(c) Preparation of single carbon fibre/epoxy resin specimens

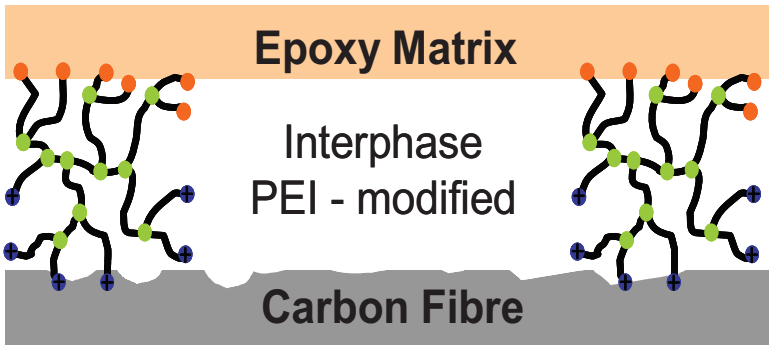
A single filament was picked from the fibre bundle and was aligned axially on the silicone rubber mould. To straighten the filament, two weights of 100 mg each were hanged at both ends of the fibre. The liquid epoxy resin was heated for about 1 h at 40 ^oC to reduce the viscosity, and then degassed for 10 hours in vacuum at room temperature. The resin was then briefly heated up again at 40 ^oC and mixed thoroughly with a stoichiometric amount of the curing agent. Subsequently a 10 min degassing step was follows until all trapped air was evacuated. Prior to filling in the mould, the mixture was again heated to 40 ^oC. Curing of the sample was performed subsequently according to following schedule: 3h at 80 ^oC and 1h at 110 ^oC and then slow cooling to room temperature. After cooling down the silicone mould was removed from the specimen parallel to the fibre to prevent fibre damage.

d) Tensile and Photoelastic Measurements

The carbon single fibre / epoxy specimen were clamped in a Rheometric Scientific 'minimat' tensile testing device, mounted under a Zeiss Stemi – 2000c polarizing microscope, equipped with a camera (Nikon Cooplix 4500, 4 mega pixels) facility mounted at the top. The images were analyzed using Microsoft Photo Editor Software.

Results and Discussions:

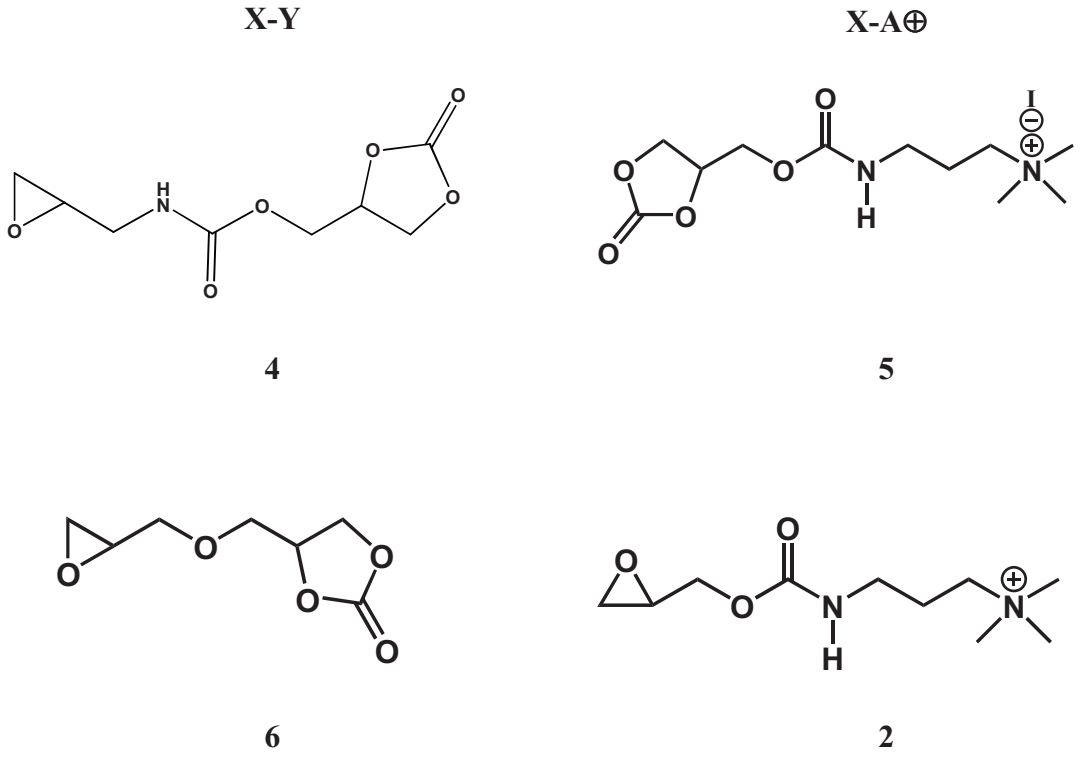
The objective of this study was to prepare cationic primer polymers ('Quat-Primer Polymers') which permanently bind to the surface of carbon fibres via electrostatic interactions (cf. Scheme 4.2). Furthermore the polymer should bear epoxy- or cyclic carbonate groups that can copolymerize with the amine components of epoxy resins during the curing step. Conceptually such primer polymers should allow controlling the chemical and mechanical properties of an interface layer between the carbon fibre and the surrounding epoxy resin matrix with a thickness comparable to the polymers radius of gyration (~ 1 – 4 nm).



Scheme 4.2. Schematic diagram of **b-PEI** modified interphase in carbon fibre epoxy resin composites.

The synthetic strategy was to prepare the required 'Quat-Primer Polymers' by polymer analogous reaction between a polyamine and low molecular weight reactive compounds that either bear one amino-reactive and a positively charged group ('X-A⊕ modifiers') or two amino-reactive group of different reactivity ('X-Y linkers'). Scheme 4.3 summarizes the structures of the aimed reactive molecules.

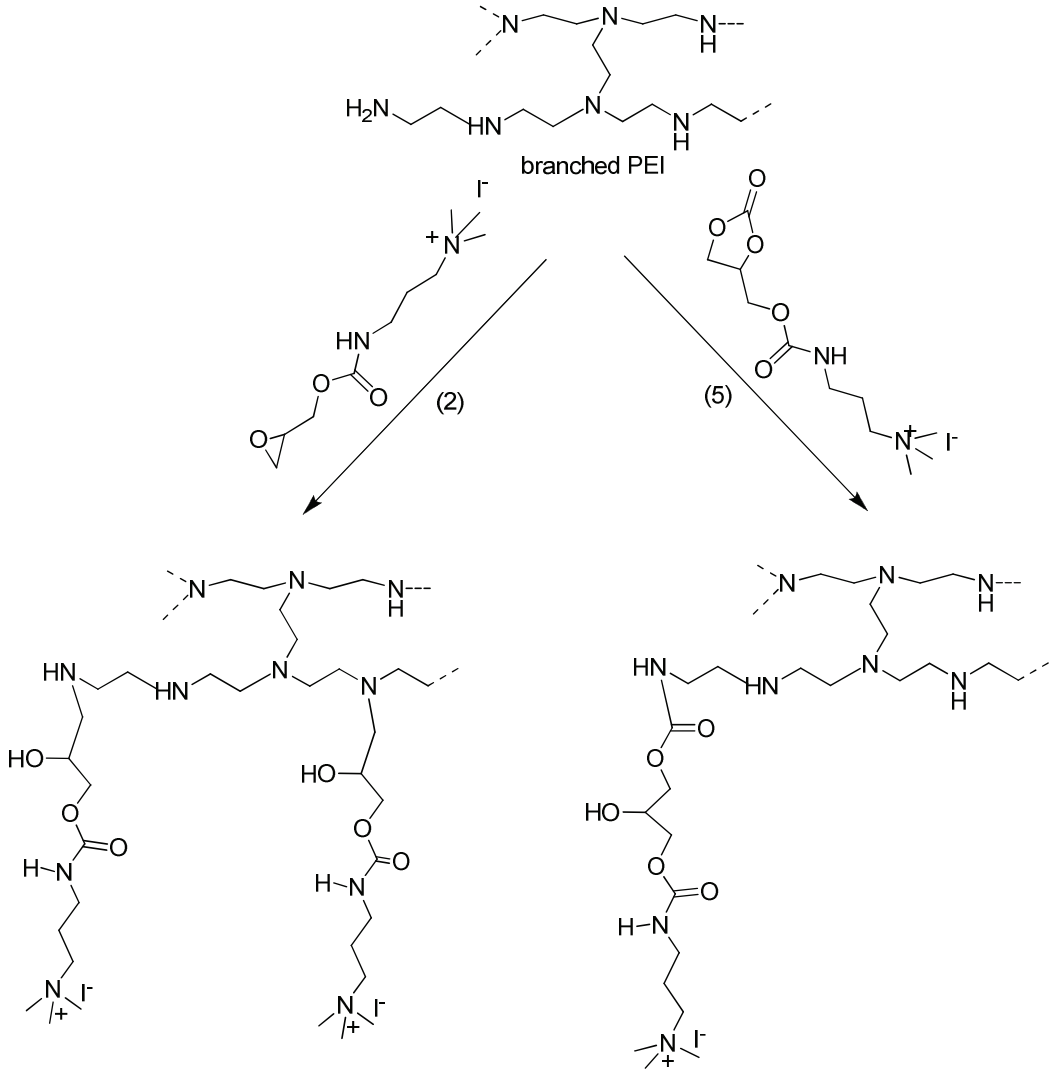
Branched poly(ethylene imine) (b-PEI) containing 25 mol% primary, 50 mol% secondary and 25 mol% tertiary amino groups with number average molecular weight of M_n = 10,000 g/mol was used as the starting material. This branched polymer was first reacted with the trimethylammonium functionalized carbonate coupler molecules **2** or **5** (Scheme 4.4) and subsequently reacted further with couplers **4** or **6**.



Scheme 4.3. Structures of the investigated cationic modifiers X-A⊕ (2, 5) and bifunctional linker molecules X-Y (4, 6).

The couplers **2** and **5** contains one quaternary ammonium group on one side and an epoxy ring (**2**) or carbonate ring (1,3-dioxolan-2-one) (**5**) on the other side respectively. As seen from Scheme 4.4, the carbonate ring can react only with primary amine to form stable urethane linkage and a hydroxyl group whereas the epoxy ring can react to primary and secondary amine.[27]

The aim was to convert all the primary amine groups of the b-PEI with coupler **5** (bearing a carbonate ring) and then to react the secondary amines of the modified b-PEI with the epoxy ring of couplers **4** or **6**. Hence polymers containing quaternary ammonium groups at the end groups and 5–membered ring carbonates along the linear chain units will be obtained.



Scheme 4.4. Synthesis of b-PEI based amino – Quat Primer macromolecules by polymer analogous reaction of b-PEI with couplers **2** and **5**.

Synthesis of functionalized poly(ethylene imine)

The commercial b-PEI used in the experiments was a branched polymer of molecular weight 10000 g/mol, with a molar ratio of primary, secondary and tertiary groups to be 25:50:25. The aim was to obtain the polymers having (i) quaternary ammonium groups which impart adhesion to the carbon fibre and (ii) reactive groups which could react with epoxy resin ring during cross-linking with amine. Therefore, b-PEI was modified with the different linkers in two steps. In the first it was aimed to convert all the primary amino groups (25 % of all amino units) of the b-PEI. Thus the secondary and tertiary amines will remain unreacted. In the second step the unreacted secondary amines of the functionalized b-PEI become converted.

Based on the above principle b-PEI was first reacted with the cyclic carbonate **5**. Hence the primary amino groups in b-PEI (25% of all amino units) have been modified to 25 mol% of quaternary ammonium groups (**PEI-5**). In the next step secondary amino groups in functionalized b-PEI have been modified with carbonate linkers **4** or **6** to yield a degree of functionalization of 75 % (with respect to all amino units in b-PEI) in **PEI-54** and **PEI-56**, letting only the tertiary amino groups of the branching units in the polymer backbone unreacted.

All functionalized polymers were prepared in DMF at 60 ^{o}C reacting for 48 hours according to the experimental procedure and using the amounts given in Table 4.1 and Table 4.2.

Characterization of functionalized poly(ethylene imine)s

The structures of the functionalized PEI's were investigated by means of ^{1}H-NMR, ^{13}C-NMR and IR spectroscopy. The NMR spectra of **PEI-2**, **PEI-5** and **PEI-56** and are shown in Figures 4.1 - 4.3.

The ^{13}C-NMR spectra of **PEI-2** (Figure 4.1) shows the characteristics peak of the hydroxyl propyl moiety arising from the reacted oxirane ring (signals 9, 10 and 11).

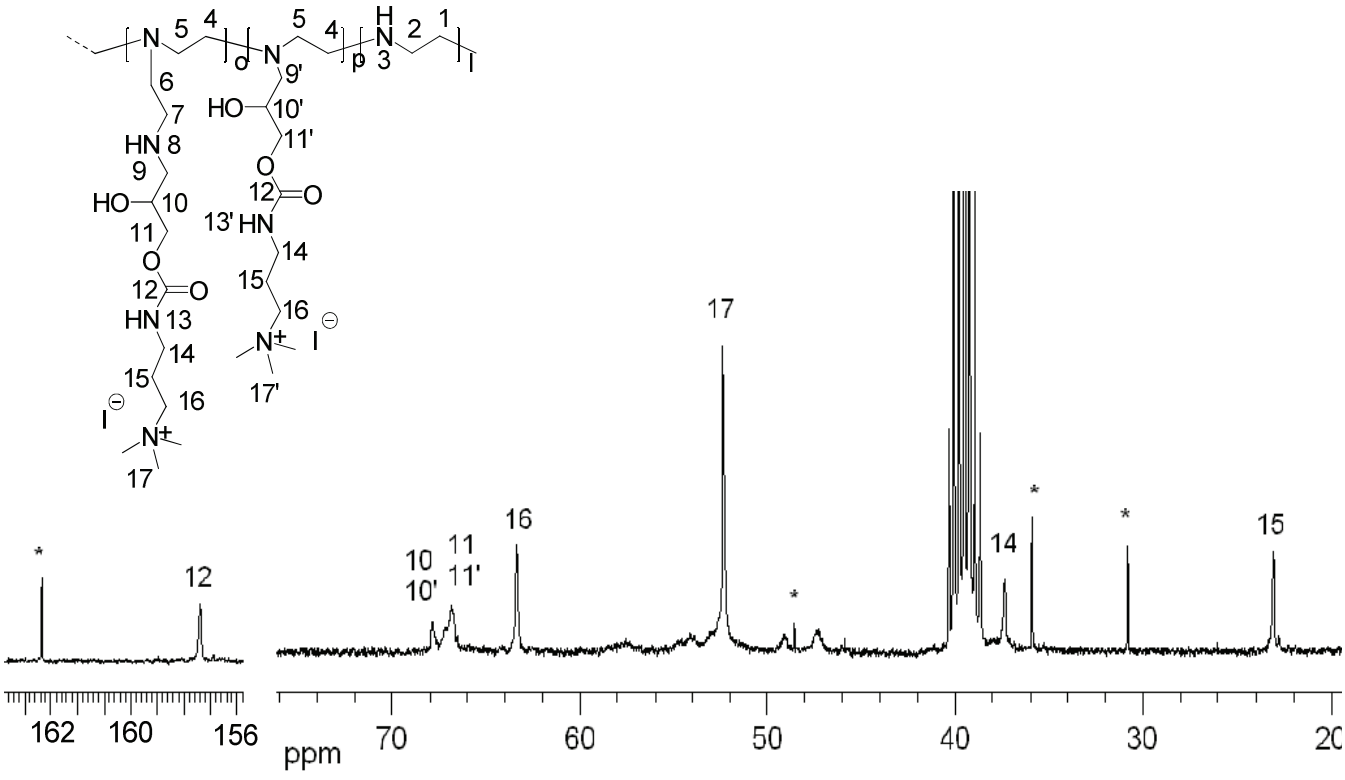


Figure 4.1. ^{13}C-NMR spectra of **PEI-2** in DMSO-d6 (* = residual solvent, # = DMSO)

The assignment was done based on the model reaction done between one mole each of compound **2** and hexyl amine (cf. Chapter 3). Furthermore, the absence of the characteristic peaks of oxirane ring indicates that the conversion is complete.

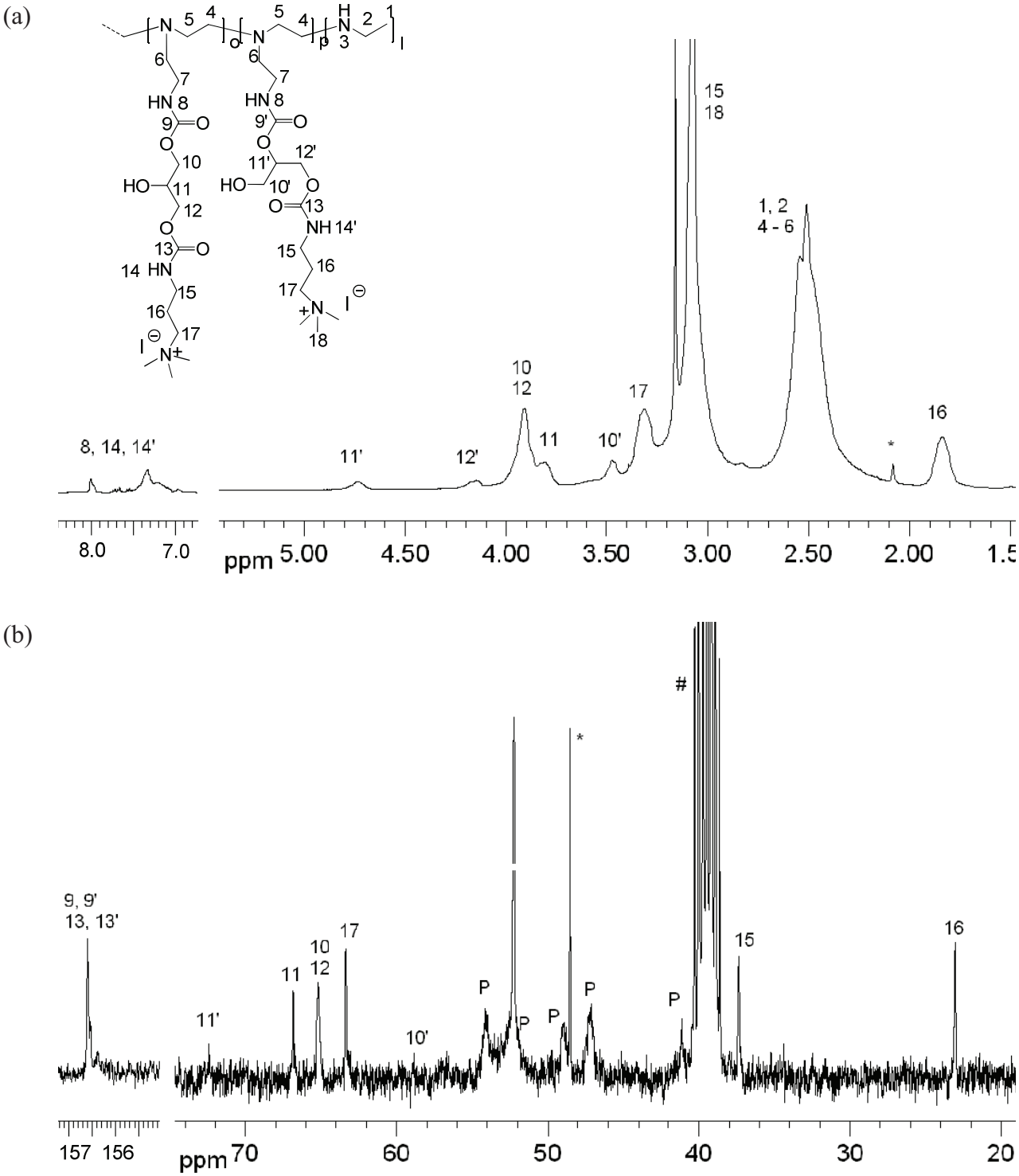


Figure 4.2. NMR spectra of **PEI-5** in DMSO-d6 : (a) ^{1}H-NMR and (b) ^{13}C-NMR (P = b-PEI backbone, # = DMSO, * = Methanol)

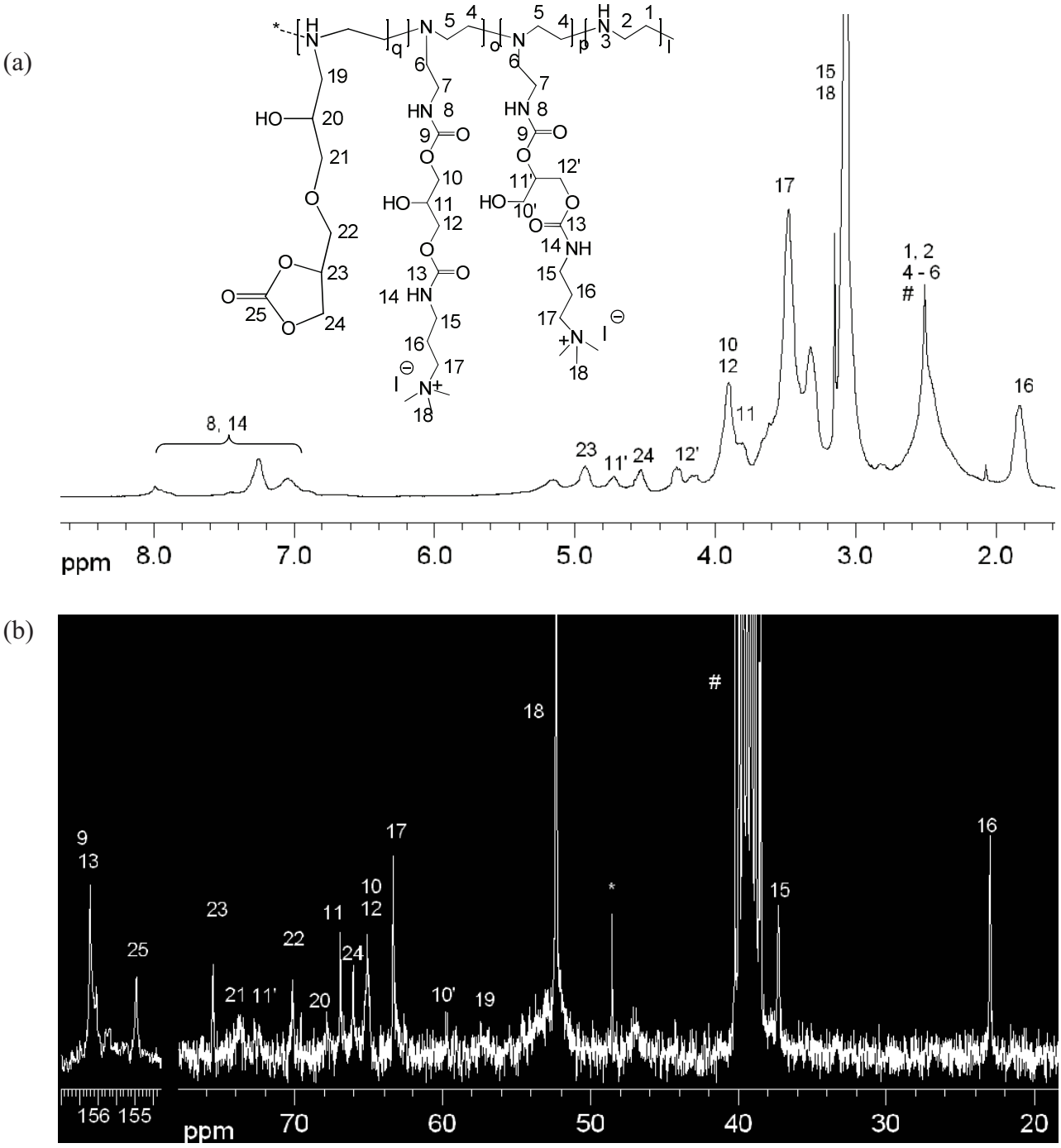


Figure 4.3. NMR spectra of **PEI-56** in DMSO-d6 : (a) ^{1}H-NMR and (b) ^{13}C-NMR (# =DMSO).

In **PEI-5**, the attachment of the quaternary carbonate to the polymer can be seen from ^{1}H-NMR (cf. Figure 4.2). The additional urethane signal 8 caused by the reaction was observed between 7 – 8 ppm which overlapped with the signal 14. Ring opening of the ethylene carbonate ring can occur in two different ways and leads to two isomers with pendant primary or secondary hydroxyl groups are formed as shown in Figure 4.2. The ratio of two isomers was calculated from ^{1}H-NMR taking into account the protons 10a, 11a, 12a, 11'a and 12'a and was found to be 79.8 : 20.2. In addition the ^{1}H-NMR spectra doesn't show the characteristic signals of the carbonate ring proving that conversion is complete.

The ^{1}H-NMR of **PEI-56** (Figure 4.3) was difficult to interpret due to overlapping of signals but the ^{13}C-NMR showed the characteristic peaks of the carbonate ring (position 23, 24 and 25), while the characteristic peaks for oxirane ring were not observed indicating that the conversion is complete.

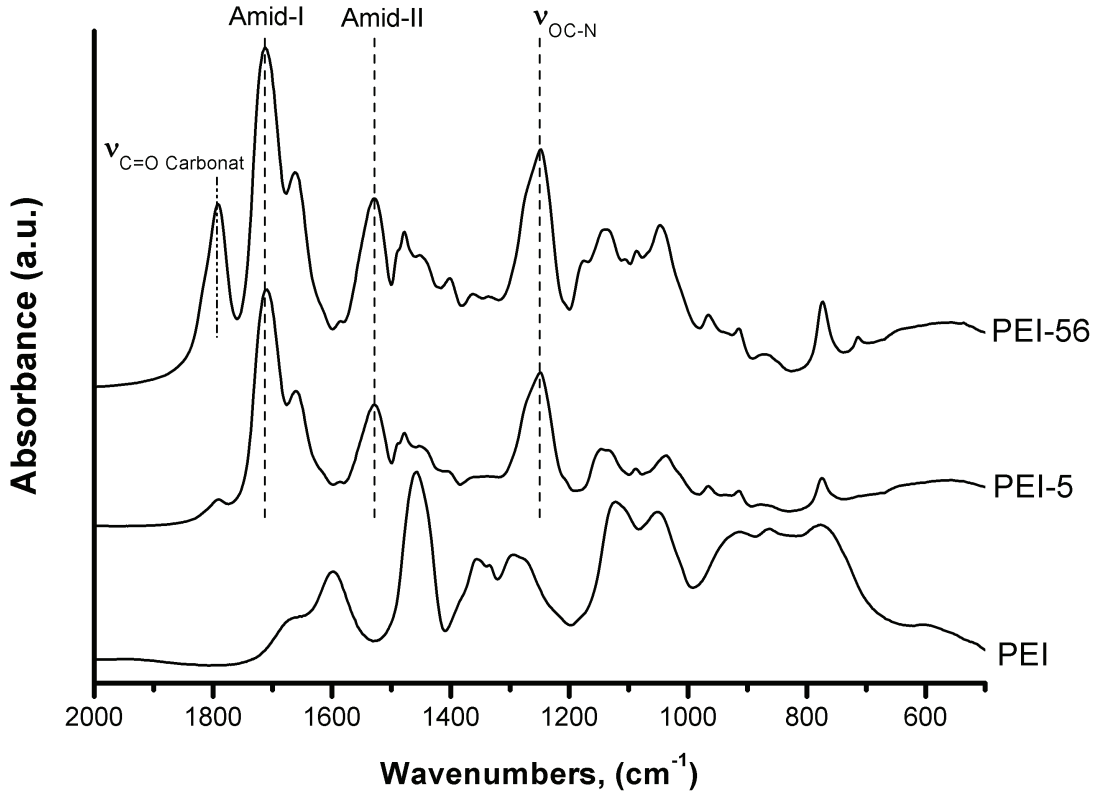


Figure 4.4. Infrared spectra of **b-PEI**, **PEI-5**, and **PEI-56** ($\nu_{C=O}$,Carbonat = 1792 cm^{-1}, ν_{Amid-I} = 1713 cm^{-1}, νAmid-II = 1530 cm^{-1}, ν_{OC-N} = 1248 cm^{-1}).

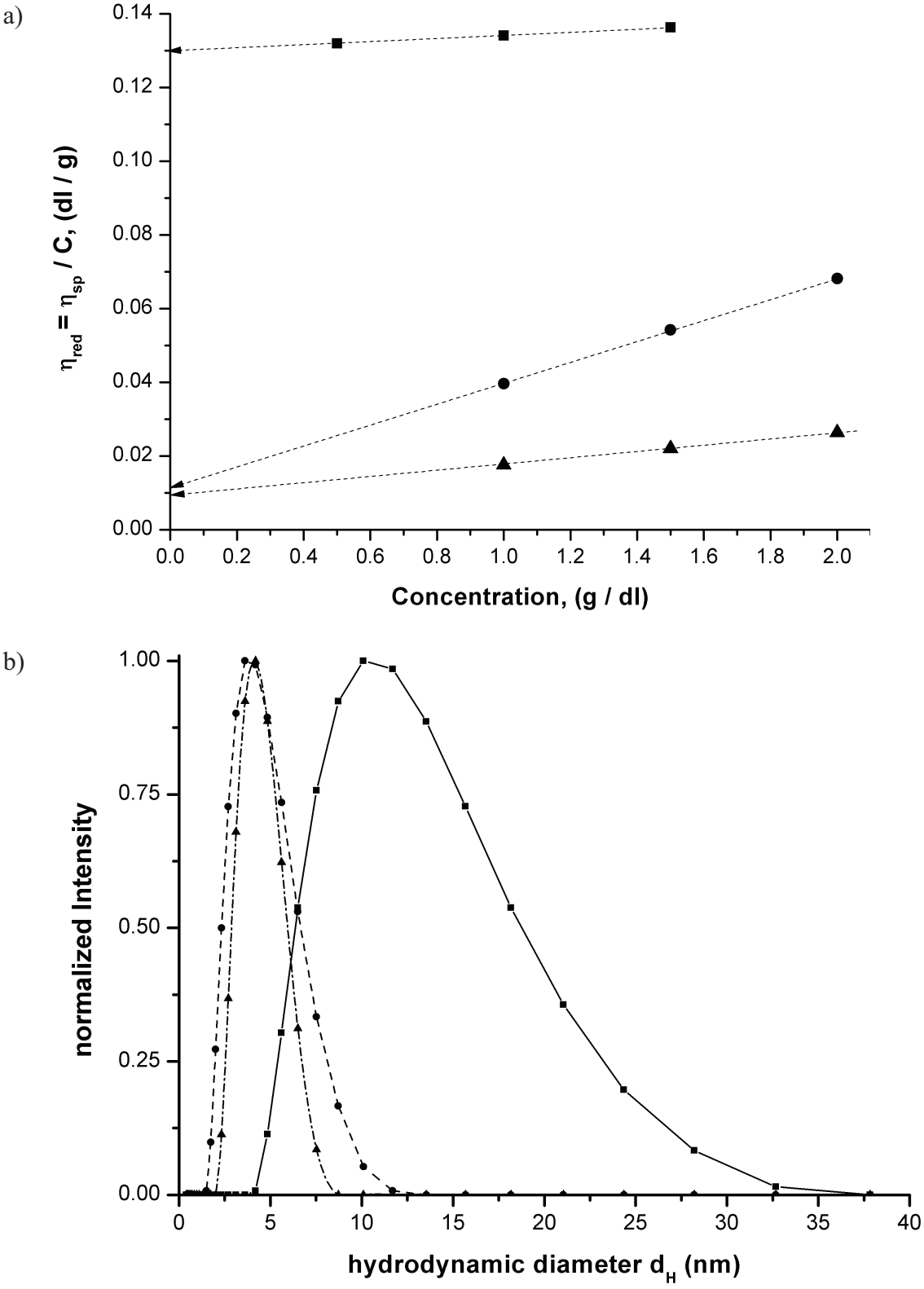


Figure 4.5. (a) Huggins plot of solution viscosimetry data, and (b) hydrodynamic diameter distribution from dynamic light scattering of **b-PEI** (■), **PEI-56** (●), and **PEI-5** (▲), measured at 25 °C in 0.5 M aqueous $NaNO_3$ solution.

Comparing the infrared spectra of PEI, PEI-5, and PEI-56 (see Figure 6) confirmed the presence of amide groups (PEI-5, PEI-56) and cyclic carbonate units (PEI-56) in the macromolecules. The bands at 1248 cm^{-1} (OC-N - stretch), 1530 cm^{-1} (Amide-I) and 1660 cm^{-1} (Amide-II) are characteristic for –CO-NH- groups, while the band at 1791 cm^{-1} that appeared only in PEI-56 was attributed to the >C=O stretching vibration of the cyclic carbonate ring.

Since the polymer analogous reaction started with b-PEI of $<M_n>$ = 10000 g/mol, the spectroscopically measured degree of modifications inferred a molecular weight of $<M_n> \approx$ 25000 g/mol with **PEI-5** and $<M_n> \approx$ 45000 g/mol with PEI-56. Figure 4.5a depicts the results from viscosimetric measurements, performed in 0.5 M aqueous $NaNO_3$ solution to screen the Coulomb interaction and to avoid polyelectrolyte effects.

While an intrinsic viscosity of $[\eta]$ = 0.13 dL/g was measured for the educt b-PEI the modified products yielded intrinsic viscosities that were smaller for one order of magnitude (**PEI-5**: $[\eta]$ = 0.011 dL/g, **PEI-56**: $[\eta]$ = 0.009 dL/g). This finding was supported by dynamic light scattering measurements of the hydrodynamic diameter in the same solvent system (cf. Figure 4.5b) The measured hydrodynamic diameter d_H of **b-PEI**, **PEI-5**, and **PEI-56** were 10.5 nm, 4.2 nm, and 3.7 nm, respectively (cf. Table 4.3). Note, that the intrinsic viscosities are proportional to approximately the third power of the hydrodynamic diameter ($\log[\eta] = -3.56\pm0.07 + 2.6\pm0.2 \cdot \log d_H$).

Since it is well known that the employed ring-opening modification reactions cannot cleave the polymer backbone, the observed reduction of the hydrodynamic diameter was not caused by depolymerization or polymer degradation. It was hence assumed that strong, but short ranged intramolecular interactions contract the modified macromolecules below the typical radius of non-modified b-PEI. The interactions must be of short range, because at the applied polymer concentrations (1 – 10 g/L) corresponding to average intermolecular distances in the solutions of 12 – 25 nm, the intermolecular interactions were not sufficiently large to cause association or precipitation. The sodium nitrate should have screened the Coulomb interaction and impede the polyelectrolyte typical ion association. For these reasons it is assumed that intramolecular hydrogen bonds between the introduced urethane-, and hydroxyl groups as well as the macromolecular amine groups cause the observed contraction. Obviously this contraction will bring all molecular weight determination methods to the fail that relay on determination of molecular size parameters, like viscometry or, in particular, size exclusion chromatography.

Thermal properties of the cationic polymers

Differential scanning calorimetry was used to measure the glass transition temperatures T_g of the polymers **b-PEI**, **PEI-2**, **PEI-5**, and **PEI-56** (see Figure 4.6a). All the polymers were found to be amorphous and the glass transition temperature was found to increase with growing degree of substitution (cf. Table 4.3). b-PEI exhibited the lowest glass transition temperature of -53 ^{o}C, while the glass transition temperature of **PEI-2** was found to be higher than other polymers (63 ^{o}C) because of its lower flexibility in the side chains.

Thermogravimetry (TGA) measurements were performed under nitrogen atmosphere at a heating rate of 10 ^{o}C/min. The TGA curves (Figure 4.6b) of the modified b-PEI compounds showed two weight loss steps, the onset of the first step was located at 156 °C, indicating that the modified PEI's were stable up to ~ 150 ^{o}C which was less stable than unmodified b-PEI (onset: ~ 270 °C). The second decomposition process – not well separated from the first process - started with all modified polymers above ~ 290 °C and could be attributed to the decomposition of urethane groups.[26]

Table 4.3. Glass transition temperatures, intrinsic viscosities and hydrodynamic diameter of PEI and the primer polymers **PEI-2**, **PEI-5**, and **PEI-56**.

	Glass Transition Temperature T_g (^{o}C)	**Intrinsic Viscosity [η] (dl/g)**	**Hydrodynamic diameter d_H (nm)**
PEI	- 53	0.119	10.5
PEI-2	61	n.d.	n.d.
PEI-5	60	0.009	4.2
PEI-56	54	0.011	3.7

n.d. = not determined

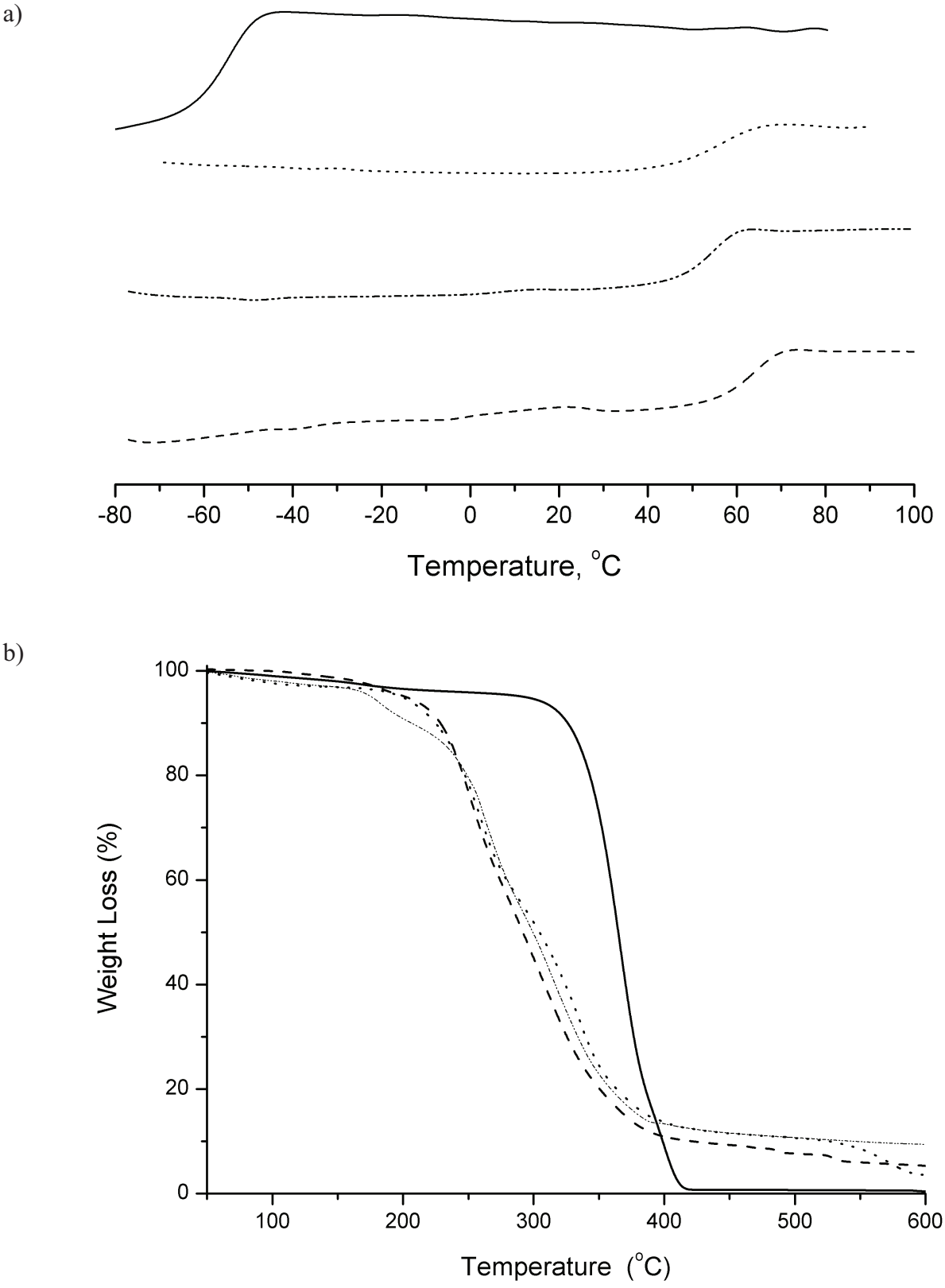


Figure 4.6. (a) Differential Scanning Calorimetry, and (b) Thermo Gravimetry Scans under N_2 atmosphere of **b-PEI** (—), **PEI-2** (----), **PEI-5** (·····), and **PEI-56** (-·-·) (dT/dt = 10 K/min).

Adsorption on graphitic surfaces

In a first series of experiments thin films of **PEI-56** were spin coated on highly oriented pyrolytic graphite (HOPG) as a model substrate. Although the interior of PAN-based carbon fibres consist of turbostratic carbon instead of graphite, it is generally accepted that non-surface modified carbon fibres are covered by a thin sheath of graphitic basal plane structure ('Onion Skin' model).[28] HOPG consist of layers of two-dimensional sheets with strong covalent bonds with in each layer (Young modulus in-plane: 1 TPa[29]) and only weak van-der-Waals interactions between stacked layers (Young modulus perpendicular to plane: 34.6 GPa[30]). Because of the structural similarity between HOPG and the surface of non-modified carbon fibres, in addition to its close to perfect planarity, HOPG was selected as a suitable and easy to investigate model substrate.

Figure 4.7a depicts a scanning force micrograph of **PEI-56** coated from a 0.04 wt% solution in methanol on non-treated, freshly cleaved HOPG. The polymer virtually did not spread but formed isolated irregular shaped droplets and islands with non-uniform diameters from 40 to about 400 nm. These droplets could be removed by a single washing step with methanol. In a second series of experiments **PEI-56** was coated under identical conditions on HOPG that was pre-treated for 2 minutes with low-energy argon plasma. The plasma treatment conditions were adjusted such way that any surface modification was limited to the topmost layers of the surface.[18] On this substrate the polymer became deposited in the form of small, partially interconnected droplets with a more uniform size distribution of an average size around 50 - 60 nm (see Figure 4.7b). Figure 4.7c shows the scanning force image of **PEI-56** coated from a 0.004 wt% solution in methanol onto a HOPG-substrate that has been pre-treated with oxygen – argon plasma. In this picture the polymer film is hard to see; however, the steps originally present at the HOPG surface can be recognized. The picture demonstrates that an ultra thin polymer film was formed. Detailed scanning force investigations revealed the presence of a continuous film of the polymer on the substrate with a thickness of 3 nm.

Subsequent to these measurements the sample depicted in Figure 4.7c was extracted for 2 hours with methanol in a Soxhlet extractor. No difference in film morphology and thickness was found by means of scanning force microscopy after the extraction step (cf. Figure 4.7d), indicating that the polymer became strongly bond to the substrate.

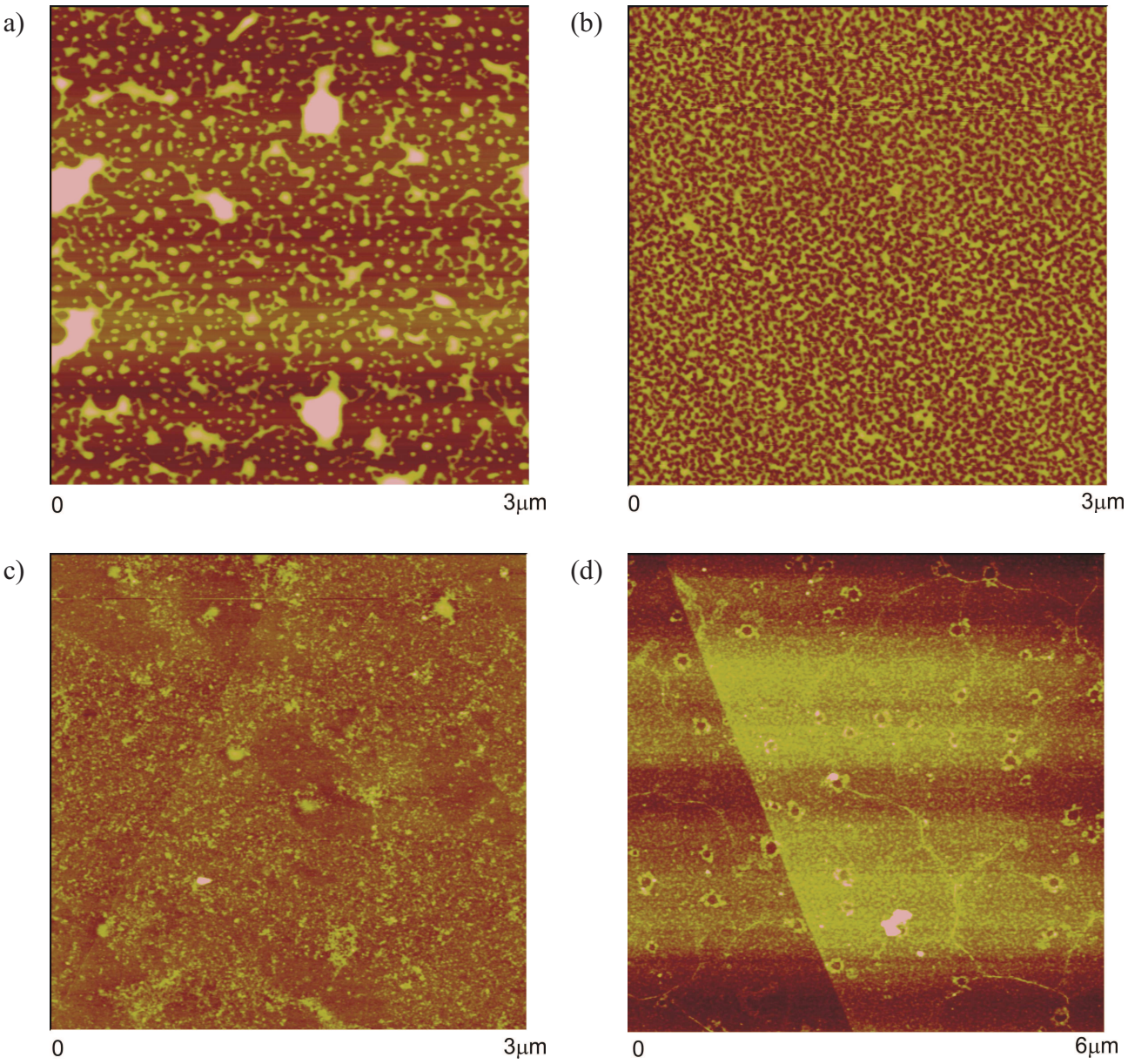


Figure 4.7. Scanning force micrographs of HOPG surfaces spin coated with methanolic **PEI-56** solutions. (a) Non-treated HOPG (0.04 wt% **PEI-56**), (b) argon plasma treated HOPG (0.04 wt% **PEI-56**), (c) argon / oxygen plasma treated HOPG (0.004 wt% **PEI-56**), (d) sample picture (c) after extraction with methanol.

Obviously the highly polar **PEI-56** polymer did neither wet, nor adhere well to the non-polar HOPG surface. It is well documented that argon plasma treatment creates grooves with uniform spacing and congruent alignment at HOPG surfaces[21,22] and that the edges of graphite layers are more reactive than the damage-free basal planes. The argon plasma treatment improved the wetting behaviour of **PEI-56**, possibly because the plasma increased the surface

roughness and allowed for a certain degree of oxidation when the sample was exposed to air prior to the polymer coating. An argon / oxygen plasma not only generates structural defects, but also produces oxygen containing species like ≡C-OH, >C=O and –COOH covalently bound to the edges of the defects.[31] These groups will increase the surface energy of the substrate, create negative (partial) charges at its surface and allow for hydrogen bonding. The combination of these effects seemed to cause a nearly perfect spreading of the positively charged **PEI-56** on the substrate and considerably improved the interaction between the polymer and the HOPG surface. The model experiments showed that PEI-based 'Quat-Primer Polymers' strongly adhered to roughened graphite surfaces bearing covalently fixed negatively charged oxygen species. Since commercial carbon fibres become anodic oxidised subsequent to the carbonisation step and prior to seizing,[32,33] strong adhesion of these polymers on carbon fibres can also be expected.

High performance fibre/matrix composites can only be obtained if the matrix is effectively able to transfer mechanical stress to the fibre. Hence, the strength at break of such composites is highly dependent on the fibre matrix adhesion. Since on one hand the Quat-Primer Polymers are expected to adhere well to carbon fibre surfaces and since on the other hand epoxy resins are known to bind covalently to polyamines, the PEI based Quat-Primer polymers conceptually offer a simple and rational mean to control the properties of the carbon fibre / epoxy resin interface.

Carbon-Fibre / Epoxy Model Resins

To investigate the suitability of PEI based Quat-Primer Polymers as carbon fibre surface modification agents, carbon fibre / epoxy resin composites were prepared from (i) de-seized carbon fibres and (ii) from carbon fibres that were plasma treated to remove the size and subsequently coated with a Quat-Primer Polymer. Single filaments were taken from a carbon fibre bundle and embedded in a technically used epoxy resin system (cf. Experimental Part).

There are three main micromechanical tests which have been developed to evaluate interfacial shear strength of single fibre composites namely single fibre pull out test[34-36], fragmentation test[37-43]and microbond test.[44,45] The different techniques are based on specific sample configurations and loading geometries, and thus involve different stress states at the interface. The fibre pull out test is the most extensively used because of its simplicity but there are some inherent drawbacks. The main problem with the pull out test is that the resin meniscus formed on fibre makes the determination of embedded fibre length difficult. Moreover, since in pull

out tests the interfacial debonding force is directly related to embedded fibre length, there is maximum embedded fibre length which permits the fibre to be pulled out without breakage. The maximum embedded length is usually very short in case of composite system having strong interfacial bonding. For example, the maximum embedded fibre length for carbon fibre epoxy matrix system in generally less than 200 μm, which causes difficulties in making specimen.[46] The pull out test is best suited for glass fibres and is difficult to use with thin carbon fibres. The microbond test method, which is a modified pull-out test, was developed by Miller et al.[44] This method is a revision to the single-fibre pull-out test to eliminate the meniscus effect during elevated-temperature curing and the potential rupture of the meniscus before debonding. This test is also difficult to perform because of the very small embedded length and the condition that the fibre should be normal to the mould.[47] The single fibre fragmentation test is a technique that involves the critical fragment length and the single fibre strength distribution. There is limitation to this test that the failure strain of the matrix should be three times the failure strain of the fibres to meet the needs of achieving a saturated fragmentation test. The obtained composites were investigated by means of a modified Kelley-Tyson fragmentation test.[37] A single carbon fibre was aligned axially in the cavity of a dog bone shaped silicone mould, covered with the liquid epoxy resin, followed by thermal curing of the specimen.

When stretching the specimen parallel to the fibre axis the fibre starts to break at a certain elongation, since the maximum strain of the fibre is lower than that of the matrix. Upon further stretching the fibre fractures into smaller fragments until a minimum critical length l_c is reached. The fragments length is limited to l_c, because the matrix transfers the tensile stress to the fibre via shear stresses along the fibres axis,- when the fragments become shorter than l_c a stress larger than the tensile strength σ_f can no longer be transferred. The mathematical treatment of this situation yielded equation (1), relating the interfacial shear yield stress τ_C to the tensile strength σ_f, the diameter d of the fibre as well as the critical fragments length l_c.

$$\tau_C = \sigma_f \cdot d / 2 \cdot l_C \qquad \text{(Eq. 1)}$$

(τ_C = interfacial shear yield stress, σ_f = tensile strength, d = fibre diameter, l_C = critical fragments length)

The stretching process was monitored by means of a polarization microscope in polarized light, allowing simultaneously detecting the occurrence of stress induced birefringence and measuring of the fragment lengths.

Figure 4.8 compares typical fracture length vs. elongation curves obtained from composites with non-coated (dotted curve in Figure 4.8) and with **PEI-56** coated (solid curve) carbon fibrils / epoxy resins. In the presence of **PEI-56** at the fibre/matrix interface the fibre fragmentation starts at an elongation ($\varepsilon \cong 0.043$) that is about 19% below that of the sample without Quat-Primer Polymer ($\varepsilon \cong 0.055$) and the critical fragment length becomes reduced for 20 % (no primer: $l_c = 410 \pm 5$ μm, with **PEI-56**: $l_c = 330 \pm 10$).

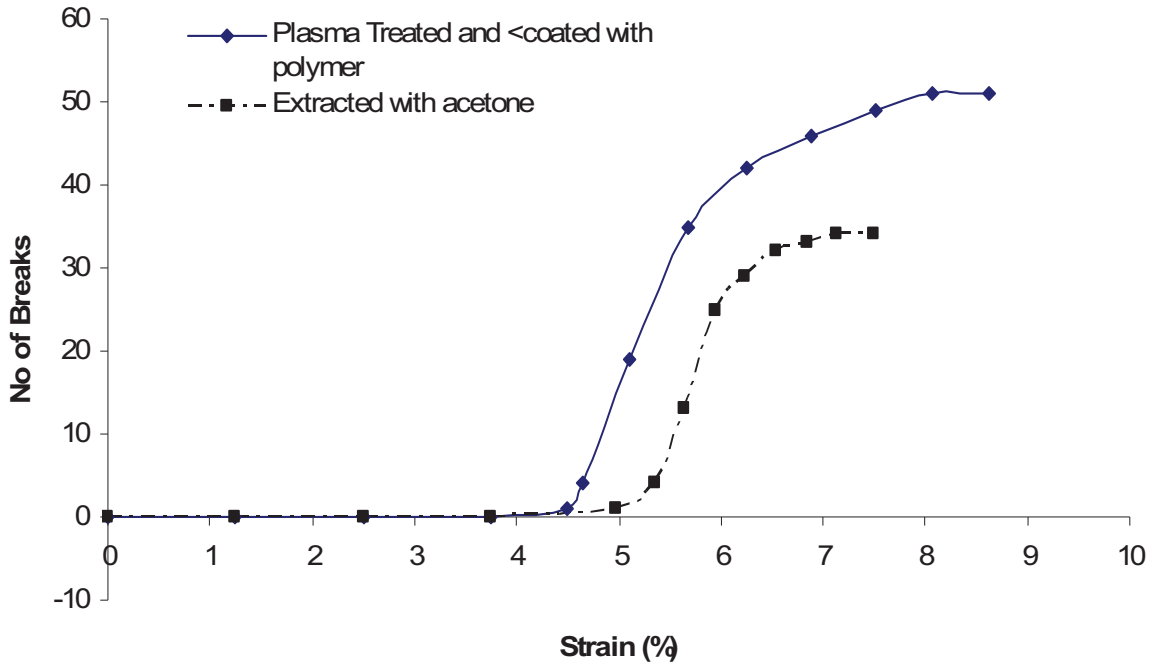


Figure 4.8. Number of breaks versus strain of a carbon fibre embedded in epoxy resin cured by tetraethylenepentamine curing agent (14:1, wt:wt), gauge length of specimen = 16mm.

The average values of the critical fragment length as obtained from all investigated specimens are summarized in Table 4.4. It was assumed that the tensile strength τ_C at the critical fibre length is the same for untreated and treated carbon fibres. The use of **PEI-56** coated carbon fibre fibrils increased the interfacial shear yield stress τ_C for ~ 25 % from 40.9±3 to 51±3 MPa.

The fragmentation of the epoxy resin embedded fibres was associated with the development of characteristic birefringence patterns that developed at each break point. In the present experimental situation these patterns are caused by the interfacial shear and frictional stresses and strains at the fibre/matrix interfaces. The stress birefringence patterns generated during the experiment were recorded photographically with increasing strain.

Table 4.4. Average values of the critical number of fibre fractures N_C, the critical fibre length l_c/d and of the interfacial shear strength τ_C obtained from Kelley/Tyson fragmentation tests with carbon fibre / epoxy resins using non-sized and **PEI-56** sized single carbon fibre.

Sample	**Critical Fragment Length, l_c [µm]**	**Average Number of Fragments, N_c**	**l_c/d**	**Interfacial Shear Strength, τ, [MPa]**
Unsized Carbon Fibre	410 ± 5	33 ± 3	58.6 ± 1	40.9 ± 1
Quat-Primer Sized Carbon Fibre	330 ± 10	49 ± 2	47.1 ± 2	51.0 ± 1

(a) The diameters of the unsized and the sized filaments were assumed to be 7 µm .

Figure 4.9 depicts typical examples of the observed birefringence patterns in the loaded state. In the vicinity of any fragment tip an intense photoelastic region developed, resulting in the shown stress pattern with alternating dark and light areas. The birefringence pattern was usually symmetric at both sides of the fibre ends. As expected no new fibre breaks occurred once the critical fragment length was reached, even if the applied tensile load was continuously increased further. According to Figure 4.9 marked differences were observed with the two different specimen types. The gap between the birefringence nodes at the fragmented ends was larger in the case of composite systems using the unsized carbon fibre than for the **PEI-56** treated fibrils, indicating that the fibre fragmentation was associated with interfacial debonding.[42]

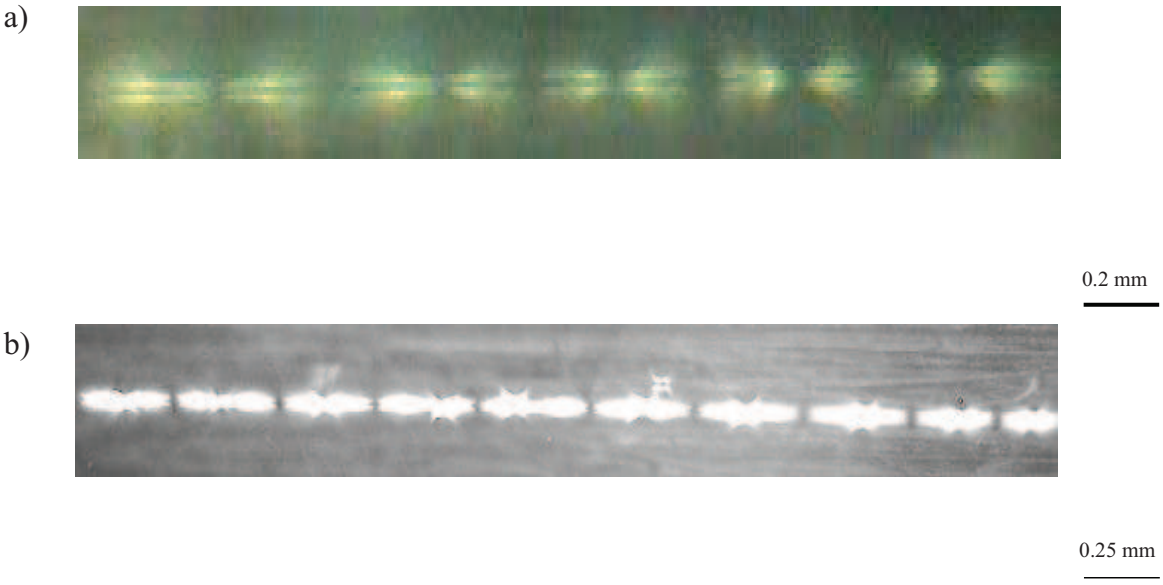


Figure 4.9. Optical micrographs of birefringence patterns observed upon stretching of carbon single fibre / epoxy resin composites to the fragmentation saturation level. a) Unsized, b) **PEI-56** sized carbon fibre composite system.

Conclusions:

The primary and secondary amino groups of poly(ethylene imine) have been functionalized with quaternary carbonates and various carbonate couplers using mild conditions in an aprotic solvent. The polymers were successfully characterized with the help of model reaction by NMR spectroscopy. The hydrodynamic diameter of the functionalized polymers was found to be smaller compared to unmodified b-PEI. The cationic polymer is suitable for coating application on oxidized graphitic surfaces and the coating is permanent due to strong electrostatic force of attraction. The sizing of carbon fibre with epoxy reactive quaternary primers leads to the improvement in fibre matrix adherence.

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Chapter 5: Intra - and intermolecular self assembly of branched polyethylenimine on graphite.

Introduction:

Since Flory's theoretical report in 1952 on polycondensation of AB_f monomers to generate high branching densities polymer without passing a gel point,[1] to date continuous effort in synthesis, characterization and theory[2,3, 4,5] have made possible to deliberately "tune" polymer architecture.[6] This has generated interest in understanding the role of the architecture on the interfacial properties and offered new possibility for single molecule manipulation and structure formation. Although hyperbranched polymers do not have perfectly defined structures, they retain many of the important features of dendritic macromolecules (i.e., multiple end groups, high solubility, and reduced viscosities relative to their linear counterparts).

Polyethylenimines (PEI) represents important class of readily available, highly branched molecules (cf. Scheme 5.1), water-soluble and widely used in paper industry,[7] food industries,[8] cosmetic[9] and pharmaceutical industries.[10,11,12,13,14] b-PEI is also known for its high capability in forming a number of different complexes with metal ions,[15] anionic polyelectrolytes[16,17] and surfactants.[18] For instance, complexation of b-PEI with n-alkyl carboxylic acids results in ionic complexes that self assemble into defined mesophase structures,[19] while in solution the complex lead to unimolecular micelles "nanocapsules".[20] Moreover, b-PEI adsorbs readily on variety of surfaces like muscovite mica, silica[21,22] and it is frequently used as primer coating.[23] Schneider et al. studies represent one of the few reports that addressed the adsorption behaviour of b-PEI form single molecules to continuous layer.[24,25] In particular on hydrophobic graphite surface (HOPG), it has been shown that the shape and the distance between individual b-PEI chains are controlled by degree of protonation of the amine groups.

In this study terminal primary amino groups present in b-PEI has been modified with hexadecane cyclic carbonate coupler (**C16**) via polymer analogous reaction.[26,27] The adsorption of such functionalized b-PEI from chloroform solution onto HOPG has been studied by scanning force microscopy (SFM) with sub molecular resolution. HOPG has been selected as model substrate because of the epitaxial adsorption of alkyl chain through Van der Waals interaction; in addition graphite represents an idealized surface of carbon fibres wherein b-PEI serves as primer coating.[23] The main issues are: (i) how the aliphatic tail and the molecular weight influence the adsorption and the two dimensional structure of the hyperbranched polymer, (ii) effect of solution concentration on the adsorption and self assembly.

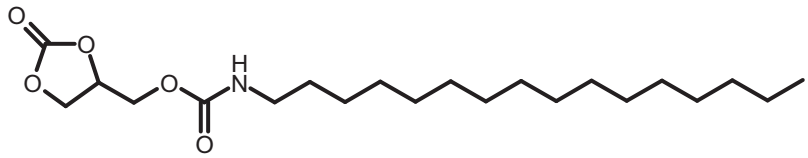
Materials and Methods

Materials

Poly(ethylene imine) (b-PEIs) with two molecular weights have been used : PEI -25K (water free, M_w (LS) = 2.5 X 10^4 g/mol, Aldrich) and PEI 750K (Lupasol P, ~ 50% aqueous solution, M_w = 7.5 X 10^5 g/mol, BASF). All PEIs were freeze dried for 2 days prior to use.

ZYB grade high ordered pyrolytic graphite (HOPG) was obtained from advance ceramics, Inc.

*(2-oxo-1,3-dioxolan-4-yl)methyl hexadecylcarbamate (**C16**)*[28]



C16

In a two- necked 1 L round bottomed flask, (2-Oxo-1,3-dioxolan-4-yl)methyl phenyl carbonate (20 g, 84 mmol) was dissolved in 400 ml dry chloroform. The solution was cooled to 0^{o}C and a suspension of hexadecylamine (20.28 g, 84 mmol) in 240 ml dry chloroform was slowly added using a dropping funnel and the temperature was maintained around 0^{o}C. The reaction was stirred at this temperature for 2 hours and then stirred at room temperature for additional 14 hours. The **C16** coupler was purified by recrystallization from $CHCl_3$/Et_2O (1:1, v:v, 800 ml) to yield a colorless powder

Yield : 26.20 g (81% of theory)

^{1}H-NMR(DMSO-d_6): δ = 0.85 (t, 3H, CH_3), 1.10-1.32 (s, 26H, CH_2^{alkane}), 1.30-1.45 (m, 2H, $NHCH_2CH_2$), 2.96 (dt, 2H, $NHCH_2$), 4.10-4.29 (m, 3H, $OCOOCH^aH^b$, $NHCOOCH_2$), 4.55 (dd, 1H, $OCOOCH^aH^b$), 4.93-5.05 (m, 1H, OCH), 7.33 (t, 1H, NH) ppm.

^{13}C-NMR(DMSO-d_6): δ = 13.9 (CH_3), 22.0 (CH_2CH_3), 26, 28.5-29.2 (12C, CH_2^{alkane}), 31.2 ($NHCH_2CH_2$), 40.2 ($NHCH_2$), 62.9 ($NHCOOCH_2$), 65.8 ($OCOOCH_2$), 74.8 (OCH), 154.6 (OCOO), 155.5 (OCONH) ppm.

General Procedure for the functionalization of b-PEI's with various functional cyclic carbonates[26,27]

The polyethylenimine (**b-PEI**) is a commercial hyperbranched polymer with primary, secondary and tertiary amine in the molar ratio of 31:39:30 respectively. The primary amino groups present in b-PEI's were selectively modified with the functionalized cyclic carbonate coupler (**C16**). The secondary and tertiary amino groups remained unmodified. At 50 ^{o}C the respective amounts of cyclic carbonate (cf. Table 5.1) were added to a solution of freeze dried b-PEI (1.0 g) in 10 ml DMF. After stirring the solution at 50^{o}C for 72 hours the polymer was precipitated in a 2:1 (vol : vol) mixture of hexane and diethylether. The polymer was re-dissolved in 10 ml methanol, stirred vigorously for 15 min and re-precipitated in the above mentioned non-solvent. After repeating the cycle for 3 times the solvent was distilled off and the product was dried (room temperature, 24 h) at 1.3 Pa to yield a slightly yellow solid.

The absence of characteristic peaks of the cyclic carbonate in ^{1}H-NMR and ^{13}C-NMR indicates that all the cyclic carbonate has reacted with b- PEI.

In the subsequent text the index of **b-PEI** indicates its molecular weight in kD, while the extension **$C16_{25}$** denotes a b-PEI where 25 mole% of the primary amino groups have been reacted with hexadecyl – carbonate coupler (**C16**).

Table 5.1. Composition of the polymers after reaction of PEI's with cyclic carbonate coupler.

Polymer	**b-PEI – 25 KDa**	**b-PEI – 750 KDa**	**Coupler C16**	**Yield**
	mg	**mg**	**mg**	
PEI_{25K}-$C16_{25}$	1000	----	1120	1.6 g, 78 %
PEI_{750K}-$C16_{25}$	----	1000	1120	1.7 g, 82 %

Number average molecular weight for **PEI_{25K}-$C16_{25}$** and **PEI_{750K}-$C16_{25}$** corresponds to 33 KDa and 970 KDa respectively (theoretically calculated from the molecular weight of unmodified b-PEI).

Measurements

^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker DPX-300 FT-NMR spectrometer at 300 MHz and 75 MHz respectively. Chloroform-d ($CDCl_3$) and dimethylsulfoxide-d_6 (DMSO- d_6) were used as solvents, and tetramethylsilane (TMS) was used as internal standard.

The infrared spectra were measured on a Thermo Nicolet Nexus 470 spectrometer with a resolution of 4 cm^{-1}. The samples were prepared as KBr pellets for the measurement in transmission mode.

The hydrodynamic radius of the macromolecules was determined on ALV 5000 dynamic light scattering system. The concentration of the polymer was 1 – 10 g/L in chloroform solution. The data was analyzed on ALV correlator software version 3.0. The date was fitted by using DLS-exponential (g2(t)) fit to obtain the mass average hydrodynamic radii.

The surface morphology of the monofilms was investigated by atomic force microscopy (AFM) at room temperature using a Nanoscope IIIa. Imaging was done in the tapping mode using standard silicon cantilevers: Nanoworld Pointprobe NCH 330 or 75 kHz and supersharp tips from µ-Masch. The deposition was done by spin coating a volume of 40 µL from solutions of the polymers, containing 10^{-3} wt% to 10^{-4} wt% of polymer in pure chloroform onto freshly cleaved HOPG at a rotation rate of 2000 rpm. The same samples were also imaged with Molecular Imaging as it allowed us to investigate single molecules conformation in different atmosphere. First, the coated substrates were imaged in situ under nitrogen atmosphere for 2 h. Then the imaging was carried out in situ under atmosphere of water and ethanol (1:1) for 8 h. Finally, the samples were dried and imaged again under flux of nitrogen.

The molecular weight of the islands was measured from the AFM images using Nanoscope 5.12 r5 software. The function called "particle analyses" was used to estimate the volume of molecule from the surface area and height of the each island. The volume of the island multiplied by the Avogadros number (N_A) leads to the molecular weight. Thus, molecular weight distribution diagram is obtained by plotting molecular weight of islands against the amount of polymer with given molecular weight.

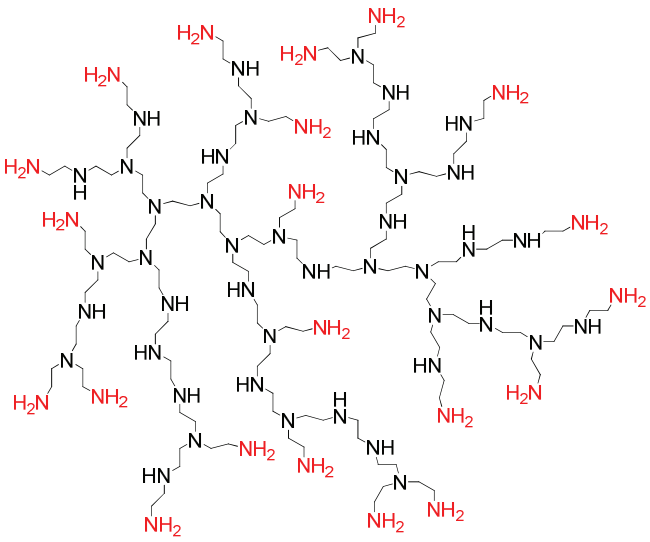
The amount of polymer adsorbed (Γ, mg/m^2) onto graphite (from AFM images) was calculated using "bearing" function in the Nanoscope 5.12 r5 software. The bearing area (%) of AFM image times the average height of the molecules and density of the polymer leads to the amount of polymer adsorbed onto graphite.

Result and Discussions:

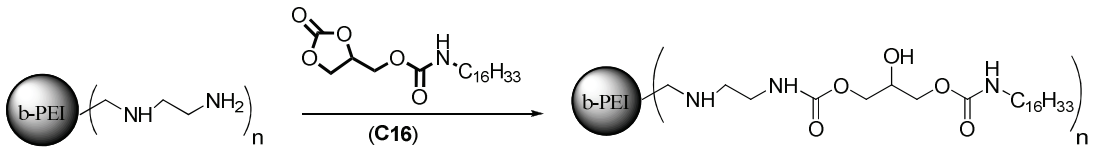
Structural and Molecular Characterization of functionalized poly(ethylene imine)s

Scheme 5.1 displays the general synthetic concept for selective functionalization of terminal primary amino groups with hexadecyl-carbonate coupler (**C16**). The reaction proceeds via ring opening of cyclic carbonate ring with primary amine.

(a)



(b)



Scheme 5.1. (a) Structure of hyperbranched polyethylenimine (b-PEI) – degree of branching: 60 %. The relative amount of the terminal primary (in red), secondary and tertiary amine groups (31:39:30) in the polymer have been already estimated by inverse gated ^{13}C NMR spectroscopy.[29,30] , (b) Polymer analogous reaction of primary amino groups in b-PEI with C16 coupler.

Figure 5.1 displays the infrared spectra of **PEI_{25K}**, **PEI_{25K}-$C16_{25}$**, and **PEI_{750K}-$C16_{25}$** , the bands characteristic for –CO-NH- groups at 1248 cm^{-1}, 1530 cm^{-1} and 1707 cm^{-1} are the stretching frequency of OC-N, Amide-II and Amide-I respectively. The opening of five – membered cyclic carbonate ring with primary amine leads to the formation of urethane linkage. The presence of amide groups inferred from the IR spectra and absence of band at $\nu_{C=O,Carbonat}$ = 1792 cm^{-1} (carbonyl group of cyclic carbonate) suggests selective functionalization of b-PEI with the **C16** coupler.

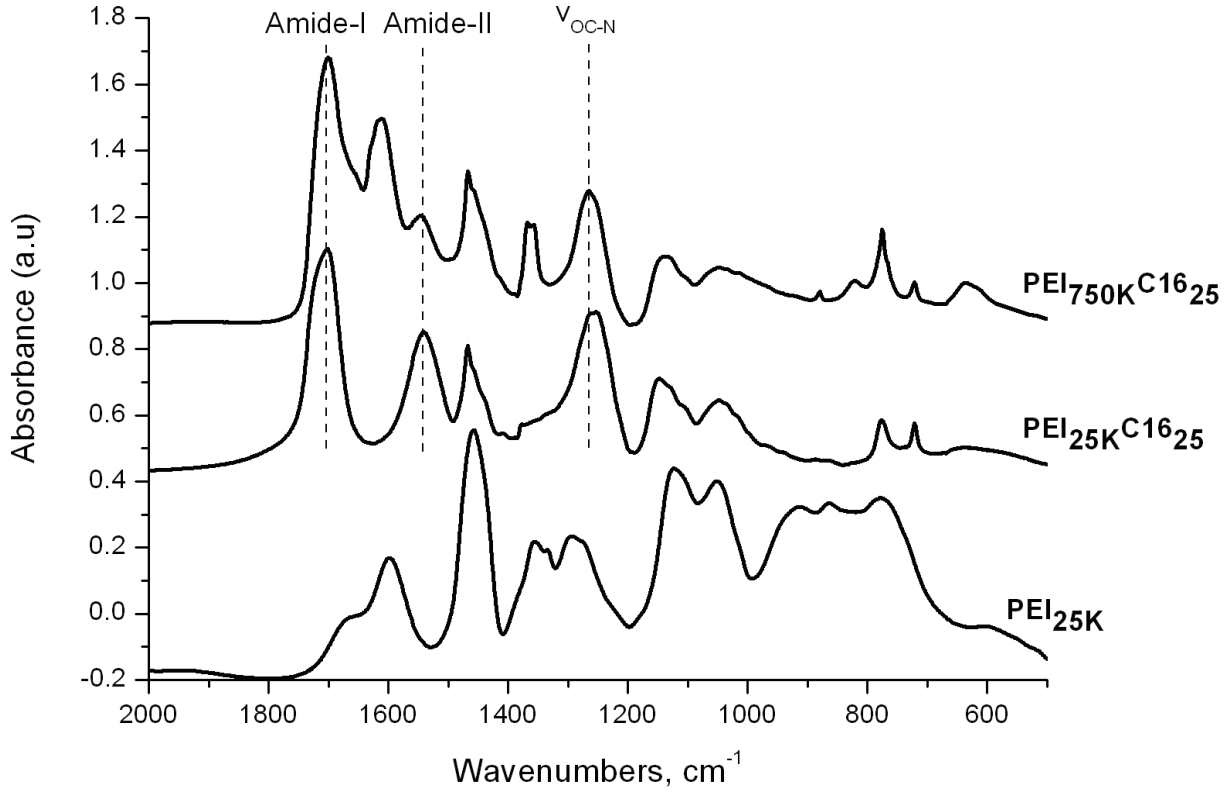


Figure 5.1. Infrared spectra of **PEI_{25K}**, **PEI_{25K}-$C16_{25}$**, and **PEI_{750K}-$C16_{25}$**($\nu_{C=O,Carbonat}$ = 1792 cm^{-1}, ν_{Amid-I} = 1713 cm^{-1}, $\nu_{Amid-II}$ = 1530 cm^{-1}, ν_{OC-N} = 1248 cm^{-1}).

Table 5.2. Hydrodynamic Radius (R_H) of unmodified and functionalized b-PEI's in chloroform.

Concentration (g /L)	**b-PEI - Mw = 25 KDa**	**Functionalized PEI_{25K}-$C16_{25}$**	**b-PEI - Mw = 750 KDa**	**Functionalized PEI_{750K}-$C16_{25}$**
	R_H (nm)	**R_H (nm)**	**R_H (nm)**	**R_H (nm)**
1	-	4.09	35.8	33.4
5	5.28	5.28	35.9	33.6
10	5.35	5.28	--	--

Dynamic light scattering investigation of the polymers in chloroform showed that **PEI_{25K}** and **PEI_{750K}** has hydrodynamic radius (R_H) of 5.3 nm and 35.9 nm respectively whereas after modification there was little difference in hydrodynamic radii (cf. Table 5.2). These data agrees with the literature report and basically shows that the DLS, as an average method, will

not be sensitive to small changes of relatively polydisperse samples.[20,31] Actually, the DLS analysis also shows particle with R_H ~ 100 nm given that the adsorption study (see below) did not indicates presence of large particle and because their amount was less than 1% regardless the molecular weight, they were simply discarded from further analysis.

Adsorption Studies

SFM investigation of the conformation of single macromolecules on the surface requires statistically relevant number of isolated chains. Therefore, the deposited amount was studied depending on the concentration. Figure 5.2 shows that the casting process from solution of 10^{-4} to 10^{-3} weight % eads to twofold increase in the surface coverage which correspond to 1 molecule / 10^4 nm^2 and 6 molecules/10^4 nm^2 respectively.

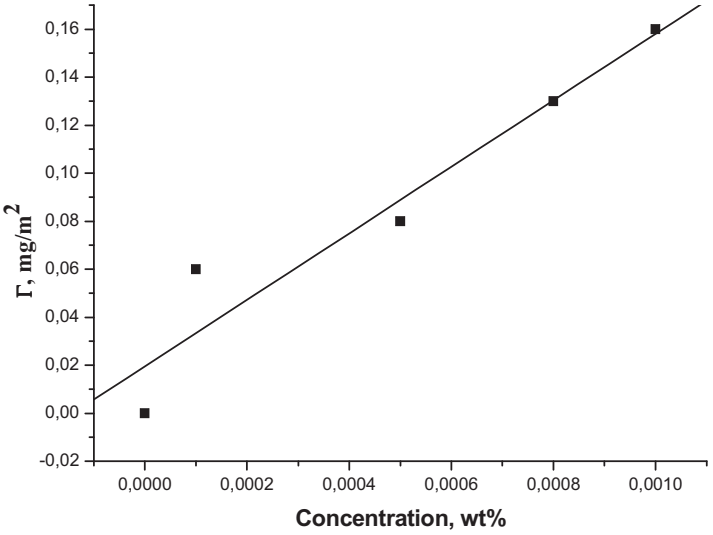


Figure 5.2. Variation of the surface density (adsorbed amount) onto HOPG depending on the concentration of **PEI_{750K}-$C16_{25}$** in chloroform solution.

Figure 5.3a is the height image of the as cast **PEI_{750K}-$C16_{25}$** sample, the film consisted of an array of islands with mean height distribution around 1.3 nm suggesting mono-molecular layer. The difference in islands diameter may indicate the parent polydispersity of the polymer.

Quantitatively, the average molecular weight was calculated from the surface area and height of each island. Figure 5.3b displays the mass distribution of 220 islands assuming density of 1.03 g/cm^3 for **PEI_{750K}-$C16_{25}$**, the number average mass was then estimated to be ca. 720 kDa which is comparable to the molecular weight of the polymer (M_n = 970 KDa). Hence, it can

be concluded that at low concentration **PEI_{750K}-$C16_{25}$** adsorb onto graphite surface as isolated molecules.

Yet, low drive amplitude of the scanning cantilever enhance the material contrast and reveals that each island "molecule" enclose an assembly of rods with variable length (Figure 5.3c and 5.3d). Most important is the relative arrangement of the rods, as indicated by arrows in Figure 3d, which reflects the branched structure of b-PEI. We assign the rods to the self assembly of alkyl chains on HOPG.

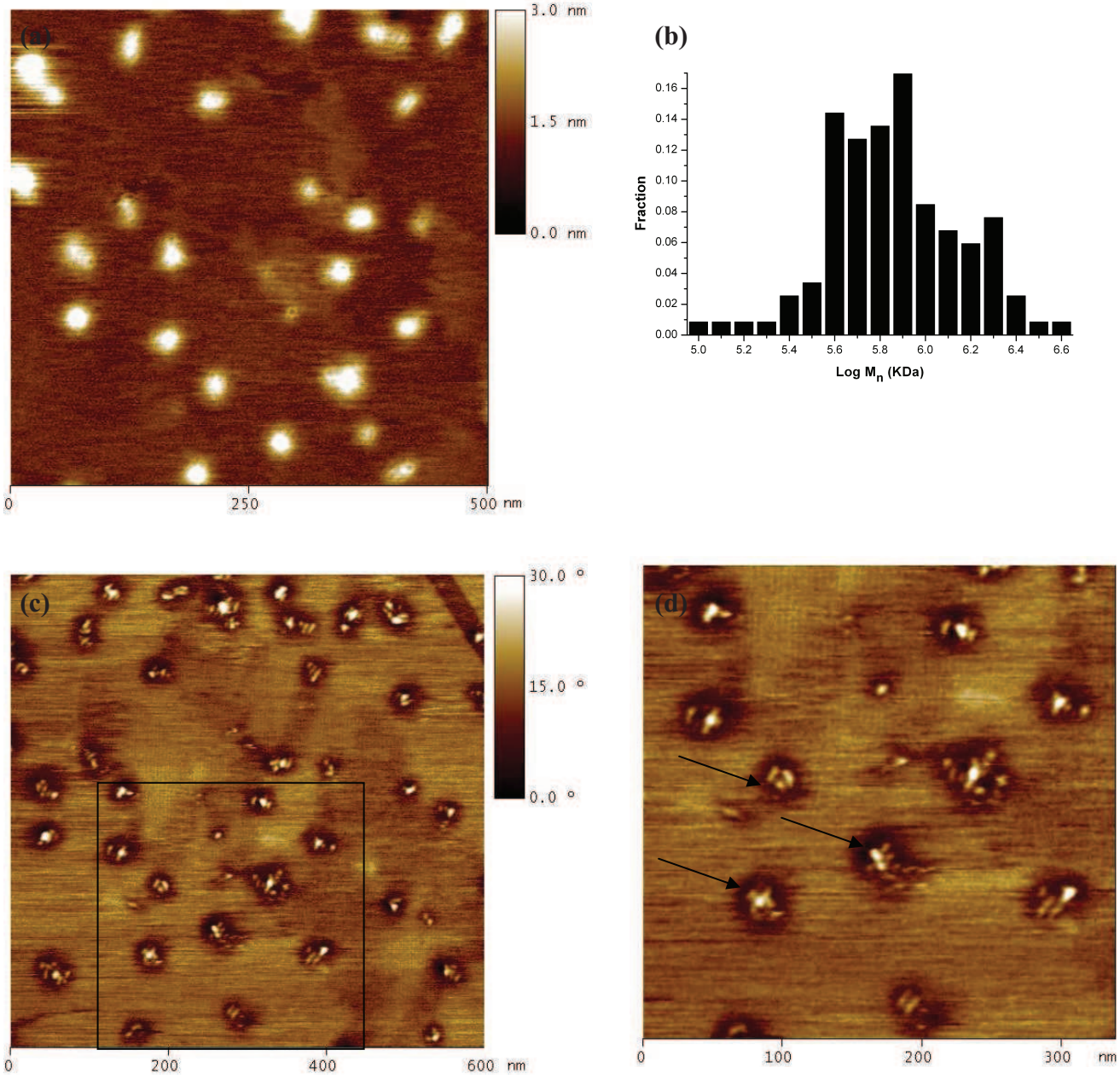
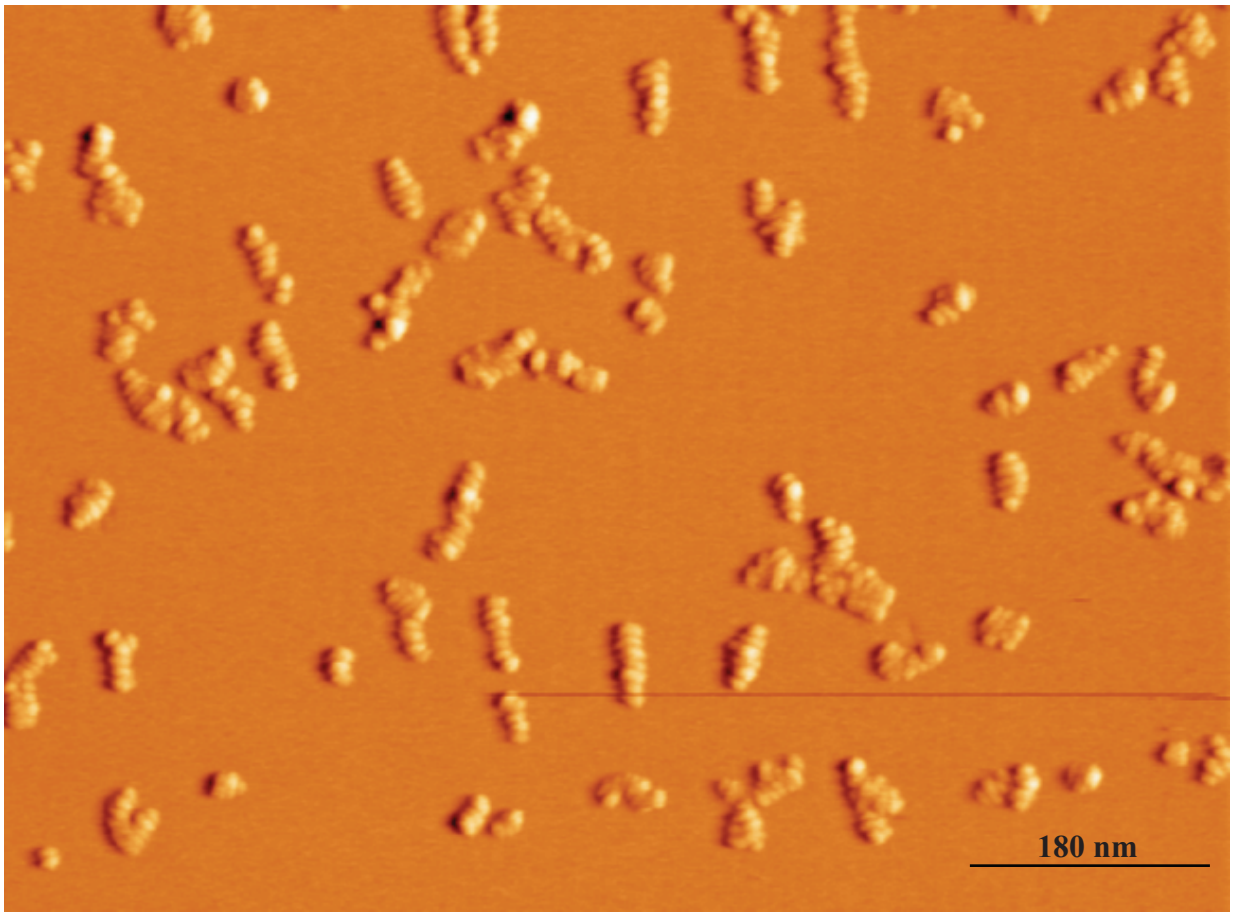


Figure 5.3. SFM images of **PEI_{750K}-$C16_{25}$** molecules adsorbed on HOPG from chloroform (10^{-4} wt %) (a) as cast height at low force; (b) molecular weight distribution; (c) As cast phase image at high force; (d) high magnification image of (c).

(a)



(b)

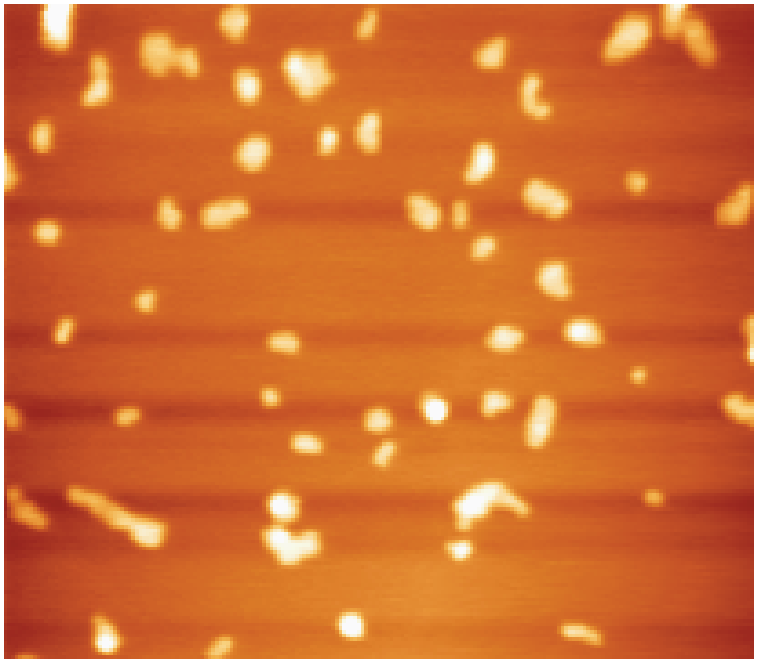


Figure 5.4. (a) Topography image of **PEI_{750K}-$C16_{25}$** – as cast from 5. 10^{-4} wt% chloroform solution, (b) sample from Figure (a) exposed to water – ethanol mixture for 8 h.

To understand how these rods evolves from the "hyperbranched backbone", first increase of the surface coverage from 6 10^{-2} to 8.0 10^{-2} mg/m^2 leads to the ordering of the rods as seen in Figure 5.4a. Secondly, while scanning the surface, the sample environment was saturated with a vapors mixture of water / ethanol (1:1) for 8h. As a consequence the average height of the molecules increase by 50 % and the rod substructure vanishes (cf. Figure 5.4b). Apparently, the b-PEI has affinity towards these solvents; as it reduce the adsorption strength and induce change in their conformation.

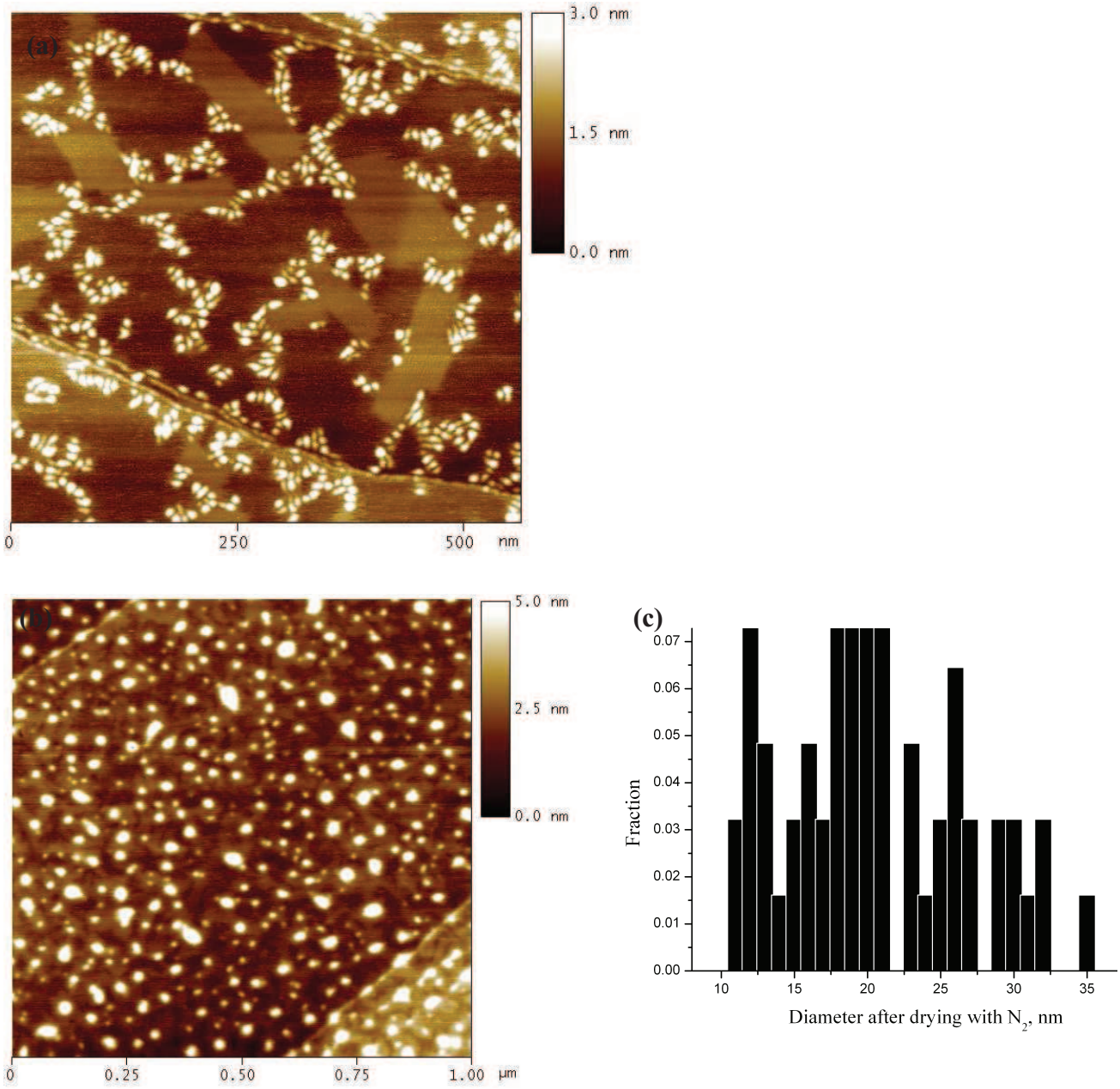


Figure 5.5. AFM images of **PEI_{750K}-$C16_{25}$** from chloroform – 8.10^{-3} wt % (a) as cast height image, (b) height image obtained after exposing sample (a) to the 1:1 water – ethanol mixture and finally drying with nitrogen. (c) is the size distribution of the nanodroplets

Although the average height of layer was 1.2 nm as the surface density increase to 13 10^2 mg/m^2, it becomes difficult to identify the single molecules (cf. Figure 5.5a). Nevertheless, exposing the sample to the mixture of water and ethanol (1:1), induce collapse of the layer into nano-droplet with an average height of 2.6 nm but broad diameter distribution ranging from 20 nm to 60 nm. Subsequent drying with nitrogen reduce the height to $h_{average}$= 2.2 nm with noticeable narrowing of the diameter ca. 24 nm (cf. Figure 5.5b). Once more an estimate of the number molecular weight average leads to approximately 650 KDa within the expected range**.**

This result suggests that even at relatively high surface coverage the **PEI_{750K}-$C16_{25}$** self assemble on HOPG and their conformation may be altered without aggregation. However to recover the initial self assembled pattern a long annealing time (solvent vapour or thermal) is needed. This may be due to steric hindrance of the branching junction or intramolecular interactions like hydrogen bonding which retard their reorganization.

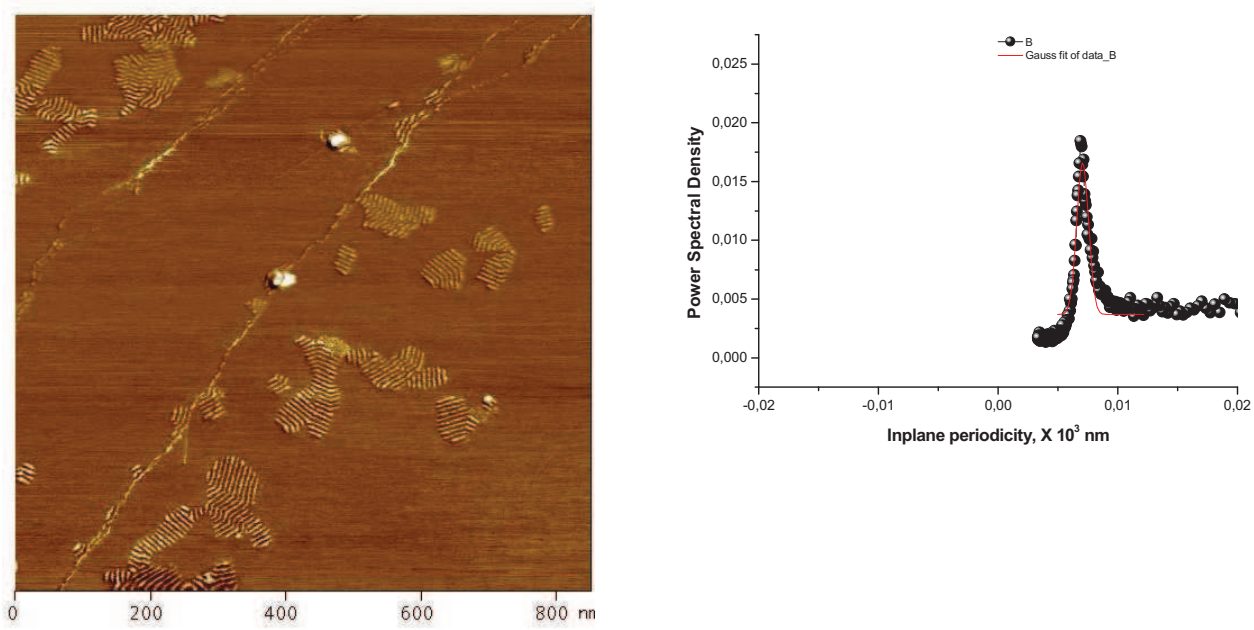


Figure 5.6. (a) Phase image of **$PEI_{750K}C16_{25}$** cast from chloroform solution 5 10^{-4} wt% and exposed to ethanol for 2h. (b) is the power spectral density of the image which shows a pick at 6.8nm± (half width from Gaussian fits) indicating defined in-plane periodicity.

The Figure 5.6a shows the phase image of the spin coated **PEI_{750K}-$C16_{25}$** onto HOPG exposed to ex-situ to ethanol for 2 hours. The rods grow in the length and remarkable alignment was observed. This image was used to accurately measure the inter rod distance, the power

spectral density indicates defined peak at 6.8 nm (Figure 5.6b). While the as cast sample shows that the inter rod distance was 7.5 nm.

Similar adsorption pattern was observed with low molecular weight polyethylenimine modified with 25 mole % of **C16** coupler. For instance, at low concentration **PEI_{25k}-$C16_{25}$** adsorb on HOPG as discrete assembly of rods (cf. Figure 5.7a). Assuming that single molecule is an assembly of rods with mean height of 1.3 nm, leads to an average volume of 200 nm^3; which correspond to number average molecular weight of 125 KDa. Figure 5.7b displays the mass distribution of the molecules ranging from 25 KDa to 630 KDa which is larger that the parent polymer $<M_n> \approx$ 33 KDa. Hence, it can be concluded that some aggregates may be present.

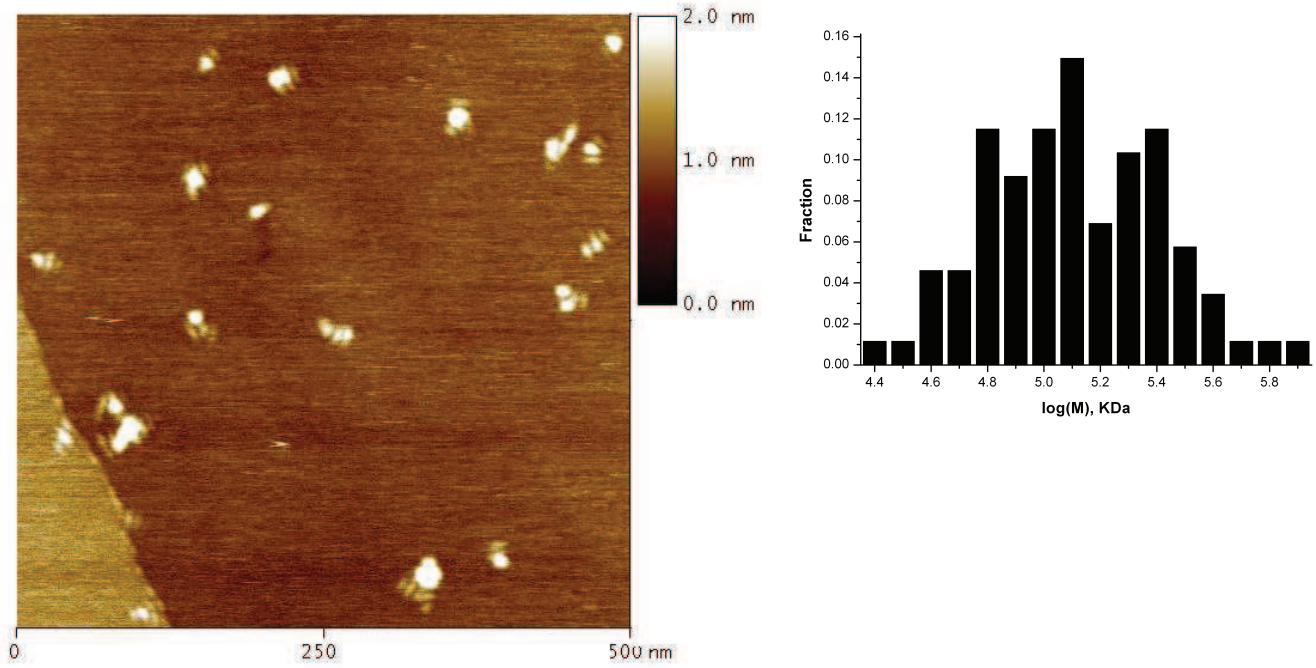


Figure 5.7. (a) Height image of **PEI_{25K}-$C16_{25}$** molecules adsorbed on HOPG from chloroform (10^{-4} wt %). (b) molecular weight distribution estimated over 110 molecules.

The experiments provide evidence that the aliphatic chain drives the adsorption of b-PEI whereas formation of rods and their alignment results from their self assembly and epitaxies: registration of hexadecane chains to the graphite lattice.

Yet if one assume that the width of the rods is defined by the length of the hexadecane chain i.e. two alkyl chains arranged in tail to tail, the length of the hexadecane chain in all-trans

conformation is 2.2nm, will leads to 4.4nm. It is less than the inter-rods distance 6.8nm but it reflects the steric hindrance that arises from the branched polymer backbone and their terminal groups to which the aliphatic tails are anchored. It has been shown that in the bulk the branched topology of the PEI polymer does not prevent self assembly of the alkyl chain but rather reduce their ordering and crystallinity within the layered structure[32].

Perfect dendrimer has degree of branching of 100% while b-PEI is 60%[29,30] which are distributed within a Gaussian sphere with hydrodynamic diameter of 70nm[20]. Upon adsorption, the conformation of the molecules will result from the interplay between the polymer substrate interactions: i) spreading increase the contact area monomers/substrate and ii) long range van der Waals interaction may be repulsive or attractive all depends on the sign of the Hamaker, and iii) the elastic cost due to the intramolecular interactions. Their relative magnitude depends on the system in consideration.

That leads to the model depicted in Figure 5.8 which correlates the single chain conformation to the surface density.

Conclusions:

In good solvent chloroform the modification of the terminal groups of the b-PEI with hexadecane chains does not influence their hydrodynamic radius R_H = 35nm.

Upon deposition on HOPG their conformation is controlled by surface coverage and by the two dimensional self-assembly of the "stickers" aliphatic chains. At low surface density, the alkyl chain organize within single macromolecules which turn it reduce the overall contact area by 50% relative to their size in chloroform.

Close to the monolayer coverage highly ordered structure evolves with characteristic distance controlled by the length of the hexadecane chains and the steric hindrance of the branched backbone.

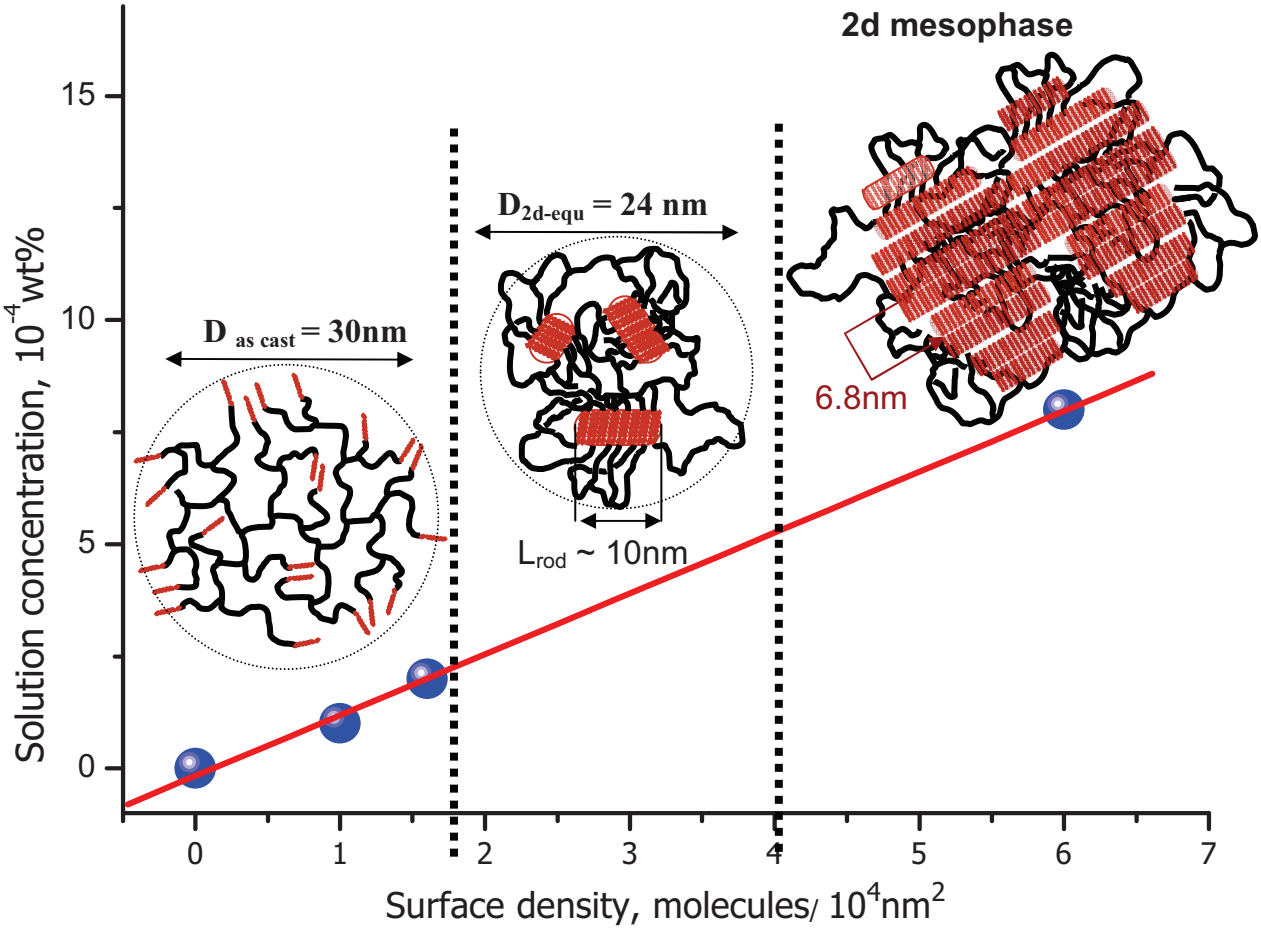


Figure 5.8. The schemes illustrate the conformational changes of hyperbranched molecules depending on the surface density. The proposed model shows how the rod evolves upon adsorption and reorganization from single molecules to 2D mesophase. The scheme is appropriate for the adsorption on HOPG of the high molecular weight b-PEI 750KDa modified with hexadecane chain at the terminal groups.

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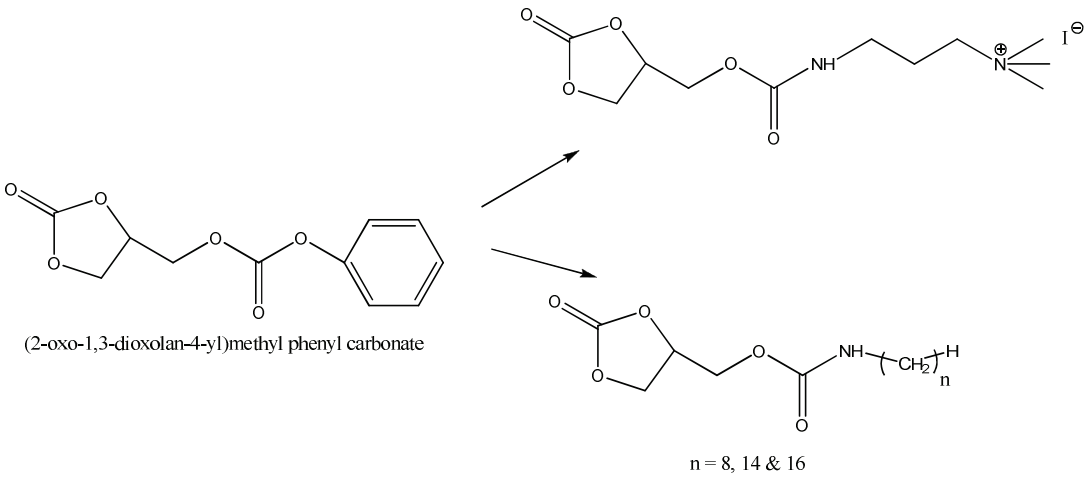
Chapter 6: Adsorption behaviour of functionalized branched polyethylenimine onto graphite : Effect of charge and alkyl chain.

Introduction

Highly branched polymers like hyperbranched polyethylenimine (b-PEI) have gained widespread attention due their unique properties, which differ significantly from their linear counterparts e.g. the large number of terminal functional groups, the intrinsic globular structure and possibility to accumulate small molecules within the macromolecule. Compared to dendrimers hyperbranched macromolecules are characterized by lower degree of branching, but definitely possess non-linear architecture and a high number of reactive end groups. Adsorption of charged polymers i.e. polyelectrolytes on surfaces and interfaces has been under extensive theoretical and experimental study for the last four decades.[1,2] The adsorption of the weak polyeletrolyte b-PEI from diluted polymer solutions of all pH values onto high ordered pyrolytic graphite surfaces (HOPG) has been studied. It was found that single molecules of b-PEI are adsorbed on hydrophobic and uncharged graphite depending on the pH of the solution.[3] Recently investigation on complexes of b-PEI and n-alkanoic acids with lamellar mesophorous structures has been reported.[4] The long period of the complex bulk structure and the tendency of the tail chains to crystallize were found to depend on the tail length of the physically bound n-alkanoic acids. It is well known that molecules containing long alkyl chain can self assemble on suitable surfaces like graphite, giving rise to highly ordered structures.[5] The interaction of polyelectrolyte complexes is of fundamental interest in wetting and adhesion.[6] The adsorption of macromolecules at the interface generally affects the conformation of the polymers. The size distribution of polymers in solutions and adsorbed on the surfaces can be very different.[7] Optical reflectometer studies on the adsorption characteristics of polymers containing different PEO/charge ratios along their backbones on silica as the substrate revealed the degree of adsorption increases with the increase in charge density of the polymer. [8]

In most published studies the adsorption and distribution of the polymer over the substrate was estimated by means of macroscopically averaging methods such as optical reflection, scattering techniques or quartz crystal microbalance (QCM) studies. In contrast, scanning probe techniques offers the unique possibility to look at the adsorption on nano-meter scale.

SFM provides the opportunity for direct observation or visualization of polymers on atomic flat substrates with sub-molecular resolution. In this work the behaviour of b-PEI modified with different ratios of alkyl chains and quaternary ammonium groups along the backbone upon adsorption on highly oriented pyrolytic graphite (HOPG) is studied by means of scanning force microscopy (SFM). The functionalized polymers were prepared by polymer analogous reaction between b-PEI and different functionalized carbonate modifiers.[9,10,11] The synthesis of most of the functional carbonates starts from (2-oxo-1,3-dioxolan-4-yl)methyl phenyl carbonate and the corresponding amines (Scheme 6.1)[12]. One or two desired functionalities were introduced in b-PEI by one step addition of primary amine groups with functional cyclic carbonates.



Scheme 6.1. Synthesis of functional cyclic carbonates.

Furthermore, the application of one of the polymers as a primer in carbon fibre – epoxy resin matrix system is investigated. Due to poor wetting of non polar carbon fibres in the epoxy matrix, interfacial adhesion is poor. Therefore, it would be profitable to pre-coat the carbon fibre surface with a thin chemically active protective polymer layer that guarantees cohesive adhesion between the fibre and the matrix. This interfacial polymeric layer would provide sufficient mobility for the chains to deform under load and therefore retain polymer and interphase toughness.

This chapter deescribes the adsorption behaviour of b-PEI modified with different cation/alkyl chain ratios on graphite as a model system for carbon fibres. Subsequently the interfacial shear strength of the primer modified carbon fibres embedded in epoxy resins are investigated by means of the well known Kelley - Tyson Fragmentation Test.[13]

Materials and Methods

Materials

1-Hexadecylamine (Aldrich, 98%), 1-tetradecylamine (Aldrich, 9%), 1-octylamine (Aldrich, 99.5%), *N*,*N*-dimethylpropane-1,3-diamine (Aldrich, 99%), iodomethane (Acros, 99%), 3-(allyloxy)propane-1,2-diol (Aldrich, 99%), 1,4-diazabicyclo[2.2.2]octane (DABCO, Aldrich, 98%), dimethyl carbonate (Aldrich, 99%), 3-chloroperoxybenzoic acid (Acros, 70-75%, MCPBA), (Different Poly(ethylene imine) (b-PEIs) corresponding to various molecular weights have been used : PEI 25K (water free, M_w (LS) = 2.5 .10^4 g/mol, Aldrich) and PEI 750K (Lupasol P, ~ 50% aqueous solution, M_w = 7.5 .10^5 g/mol, BASF). All b-PEIs were freeze dried for 2 days prior to use. All solvents were distilled before using.

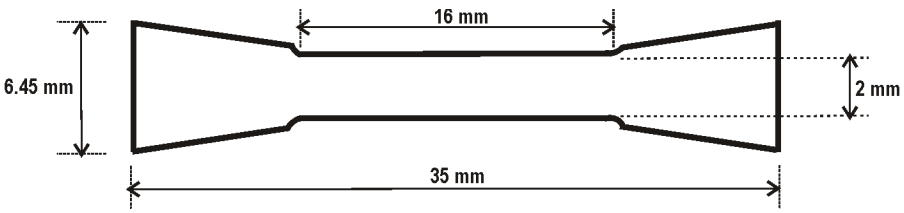
The carbon fibre was a high modulus PAN based sized carbon fibre, UTS-5631 from Tenax (nominal tensile strength = 4800 MPa, nominal fibre diameter is 7μm, 12000 fibres/bundle).

The epoxy resin was DER 331 from Dow Chemical co. (bisphenol-A based liquid epoxy resin, average equivalent weight = 186 – 192 g/equivalent, mixed with curing agent DEH 226 (tetraethylenepentamine), amine hydrogen equivalent weight = 27 g/equivalent
ZYB grade high ordered pyrolytic graphite (HOPG) was obtained from advance ceramics, Inc.

Fabrication of Composite Specimens

(a) Fabrication of Steel and Rubber Molds

First, a "mild steel" master of dogbone-shape was machined with a length of 16 mm, a width of the core of 2 mm and a height of 2 mm (cf. Scheme 6.2). Silicone rubber (Rhodorsil RTV 3450A, Rhodia Silicon GmbH) was used for transferring the masters shape to a mould with a cavity of 16 x 2 x 2 mm^3.



Scheme 6.2. Dogbone shaped specimen for fragmentation test.

(b) Preparation of carbon fibre samples

Non-sized carbon fibre samples were prepared by extracting 1g of the commercially obtained carbon fibre in a Soxhlet extractor with acetone for 5 hours.

To prepare Quat-Primer sized carbon fibres, two types of samples were prepared:

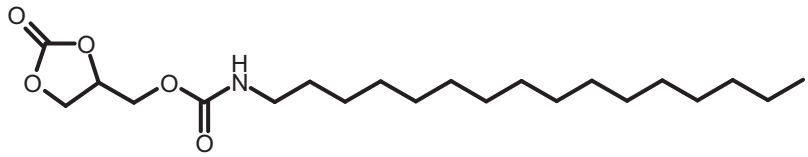
(i) The commercially obtained carbon fibre roving was treated with continuous oxygen plasma machine. The fibre was put on a roller (length : 35 cm, Ø – 9 cm) and evacuated in a plasma discharger, AK 550 Roth and Rau to a pressure of 10^{-3} bar. The following parameters were used: O_2 gas flow, 100 ft^3 / min; working pressure = 1 mbar, microwave power = 150 W, motor speed = 4 m/min. Immediately after the plasma treatment, the fibres were dip-coated in a solution of **PEI_{25K}-$C16_{15}$-QI_{15}–EC_{30}** (0.1 wt % polymer) in chloroform (weight of fibre : volume of polymer solution = 300 mg : 15 mL) and were dried under vacuum (14 h, 50 ^oC, membrane pump).

(ii) The extracted carbon fibres were dip-coated in a solution of **PEI_{25K}-$C16_{15}$-QI_{15}–EC_{30}** (0.1 wt % polymer) in chloroform and were dried under vacuum (14 h, 50 ^oC, membrane pump).

(c) Preparation of single carbon fibre/epoxy resin specimens

A single filament was picked from the fibre bundle and was aligned axially on the silicone rubber mould. To straighten the filament, two weights of 100 mg each were hanged at both ends of the fibre. The liquid epoxy resin was heated for about 1 h at 40 ^oC to reduce the viscosity, and then degassed for 10 hours in vacuum at room temperature. The resin was then briefly heated up again at 40^oC and mixed thoroughly with a stoichiometric amount of the curing agent (epoxy resin : curing agent = 100:14 wt/wt). Subsequently a 10 min degassing step was follow until all trapped air was evacuated. Prior to filling in the mould, the mixture was again heated to 40^oC. Curing of the sample was performed subsequently according to the following schedule: 3h at 80^oC and 1h at 110^oC and then slow cooling to room temperature. After cooling to ambient temperature the silicone mould was carefully removed from the specimen parallel to the fibre to prevent fibre damage.

(2-oxo-1,3-dioxolan-4-yl)methyl hexadecylcarbamate (**C16**)[14]



C16

In a two- necked 1 L round bottomed flask, (2-oxo-1,3-dioxolan-4-yl)methyl phenyl carbonate (20 g, 84 mmol) was dissolved in 400 ml dry chloroform. The solution was cooled to 0^oC and a solution of hexadecylamine (20.28 g, 84 mmol) in 240 ml dry chloroform was slowly added using a dropping funnel while maintaining the temperature around 0^oC. The reaction was stirred at this temperature for 2 hours and then stirred at room temperature for

additional 14 hours. The C16 coupler was purified by recrystallization from $CHCl_3/Et_2O$ (1:1, v:v, 800 ml) to yield a colourless powder

Yield: 26.20 g (81% of theory)

^{1}H-NMR(DMSO-d_6): δ = 0.85 (t, 3H, CH_3), 1.10-1.32 (s, 26H, CH_2^{alkane}), 1.30-1.45 (m, 2H, $NHCH_2CH_2$), 2.96 (dt, 2H, $NHCH_2$), 4.10-4.29 (m, 3H, $OCOOCH^aH^b$, $NHCOOCH_2$), 4.55 (dd, 1H, $OCOOCH^aH^b$), 4.93-5.05 (m, 1H, OCH), 7.33 (t, 1H, NH) ppm.

^{13}C-NMR(DMSO-d_6): δ = 13.9 (CH_3), 22.0 (CH_2CH_3), 26, 28.5-29.2 (12C, CH_2^{alkane}), 31.2 ($NHCH_2CH_2$), 40.2 ($NHCH_2$), 62.9 ($NHCOOCH_2$), 65.8 ($OCOOCH_2$), 74.8 (OCH), 154.6 (OCOO), 155.5 (OCONH) ppm.

(2-Oxo-1,3-dioxolan-4-yl)methyl tetradecylcarbamate (**C14**)[14]

In a two- necked 1 L round bottomed flask, (2-oxo-1,3-dioxolan-4-yl)methyl phenyl carbonate (20 g, 84 mmol) was dissolved in 400 ml dry THF. The solution was cooled to 0 °C and a suspension of tetradecylamine (17.92 g, 84.01 mmol) in 230 ml dry THF was slowly added using a dropping funnel while maintaining the temperature around 0°C. The reaction was stirred at this temperature for 2 hours and then stirred at room temperature for additional 14 hours. Solvents were removed by distillation (~20 mbar, 40 °C). The cyclic carbonate **C14** was purified by recrystallization from $CHCl_3/Et_2O$ (7:3, v:v, 100 mL) to yield a colourless powder.

Yield: 21.1 g, (72 % of theory).

^{1}H NMR (DMSO-d6): δ = 0.86 (t, 3H, C*H*$_3$), 1.10-1.32 (s, 22H, C*H*$_2^{alkane}$), 1.30-1.45 (m, 2H, NHCH$_2$C*H*$_2$), 2.96 (dt, 2H, NHC*H*$_2$), 4.10-4.29 (m, 3H, OCOOC*H*^{a}H^b, NHCOOC*H*$_2$), 4.55 (dd, 1H, OCOOCH^a*H*^{b}), 4.93-5.05 (m, 1H, OC*H*), 7.33 (t, 1H, N*H*) ppm.

^{13}C NMR (DMSO-d6): δ = 13.8 (*C*H$_3$), 22.0 (*C*H$_2$CH$_3$), 26.2, 28.7-29.2 (10C, *C*H$_2^{alkane}$), 31.2 (NHCH$_2$*C*H$_2$), 40.3 (NH*C*H$_2$), 62.9 (NHCOO*C*H$_2$), 65.8 (OCOO*C*H$_2$), 74.8 (O*C*H), 154.6 (O*C*OO), 155.5 (O*C*ONH) ppm.

(2-Oxo-1,3-dioxolan-4-ylmethyl) octylcarbamate (**C8**)[14]

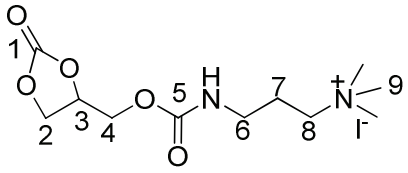
To a solution of (2-oxo-1,3-dioxolan-4-yl)methyl phenyl carbonate (20.0 g, 84.0 mmol) in 200 ml THF at 0°C was added a solution of octylamine (10.9 g, 84.0 mmol) in 100 ml THF and while maintaining the temperature below 5 °C. The reaction was stirred for 16 h at room temperature. Solvents were removed by distillation (~20 mbar, 40 °C). The cyclic carbonate **C8** was purified by recrystallization from warm $Et_2O/CHCl_3$ (5:1, v:v, 180 mL) to yield a colourless powder

Yield: 20 g, (85 % of theory).

^{1}H-NMR (CDCl$_3$): δ = 0.88 (t, 3H, C*H*$_3$), 1.20-1.39 (s, 10H, C*H*$_2^{alkane}$), 1.43-1.58 (m, 2H, NHCH$_2$C*H*$_2$), 3.17 (dt, 2H, NHC*H*$_2$), 4.22-4.40 (m, 3H, OCOOC*H*$_a$H$_b$, NHCOOC*H*$_2$), 4.55 (dd, 1H, OCOOCH$_a$*H*$_b$), 4.87-4.98 (m, 1H, OC*H*), 5.04-5.16 (m, 1H, N*H*) ppm.

^{13}C-NMR (CDCl$_3$): δ = 14.1 (*C*H$_3$), 22.6 (*C*H$_2$CH$_3$), 26.7, 29.2, 29.5, 29.8 (4C, *C*H$_2^{alkane}$), 31.8 (NHCH$_2$*C*H$_2$), 41.2 (NH*C*H$_2$), 63.3 (NHCOO*C*H$_2$), 65.9 (OCOO*C*H$_2$), 74.5 (O*C*H), 154.7 (O*C*OO), 155.5 (O*C*ONH) ppm.

N,N,N-trimethyl-3-({[(2-Oxo-1,3-dioxolan-4-yl)methoxy]carbonyl}amino)propyl-1-amonium iodide (**QI**)[9]



In a two- necked 250 ml round bottomed flask, (2-oxo-1,3-dioxolan-4-yl)methyl phenyl carbonate (10 g, 42.01 mmol) was dissolved in 100 ml dry THF. The reactants were cooled to 0^{o}C and the solution of 3-dimethylamino-1-propylamine (4.29 g, 42.01 mmol) in 21 ml dry THF was slowly added using a dropping funnel and the temperature was maintained around 0^{o}C. The reaction were stirred at this temperature for 2 h and then stirred at room temperature for 14 h. Then the solution of iodomethane (11.92 g, 84 mmol) in 60 ml dry THF was dropped slowly to the above mentioned reaction for 2 hours. The reaction mixture was stirred at this temperature for 2 h and then stirred for an additional 1 h at 50 ^{o}C. The product was filtered and subsequently washed with THF (10 ml X 3) times. The crude product was dried under high vacuum 10^{-2} mbar to afford light yellow solid. Yield: 15.5 g (95% of theoretical).

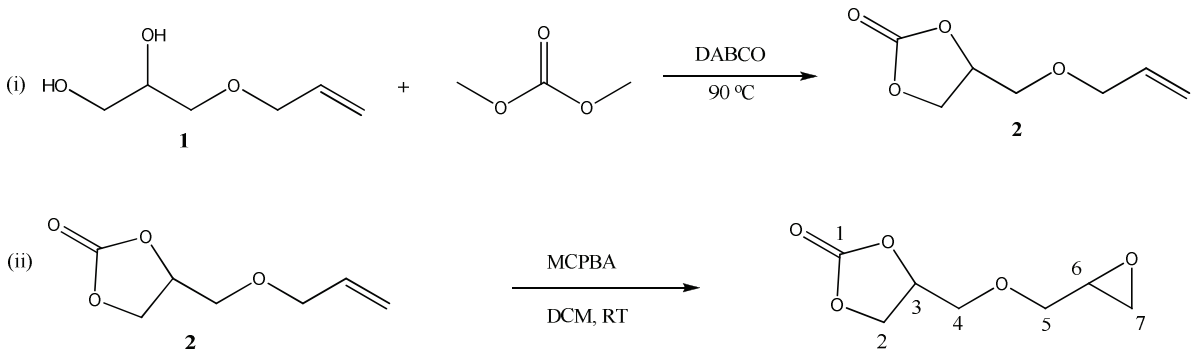
^{1}H-NMR(DMSO-d$_6$): δ = 1.74-1.95 (m, 2H, H^7), 3.00 - 3.20 (m, 11H, H^6, H^9), 3.25 - 3.45(t, 2H, H^8), 4.10-4.34(m, 3H, H^2,, H^4), 4..59 (t, ^{2}J = 8.54 Hz, 1H, H^2), 4.96-5.14 (m, 1H, H^3), 7.39(t, ^{3}J = 5.6 Hz, 1H, NH) ppm.

^{13}C-NMR(DMSO-d$_6$): δ = 22.9 (C^7), 37.3 (C^6), 52.3 (C^9), 63.2 (C^8), 66.1 (C^2), 66.9 (C^4), 74.7(C^3), 154.7 (C^5), 155.6 (C^1) ppm.

4-[(Oxiran-2-ylmethoxy)methyl]-1,3-dioxolan-2-one (**EC**)

This coupler was synthesized in two steps as shown in Scheme 6.3. In the first step 3-(allyloxy)propane-1,2-diol (**1**, 5.0 g, 37.8 mmol), dimethyl carbonate (DMC) (10.2 g, 113.4 mmol) and DABCO (420 mg, 0.37 mmol) were mixed in 250 ml round bottom flask and heated at 90 °C for 10 h. After distillation of MeOH and excess DMC under vacuum, 4-

(allyloxymethyl)-1,3-dioxolan-2-one (**2**) obtained was used without further purification for the second step of the synthesis.



Scheme 6.3. Synthesis of coupler (**EC**)

In the next step 4-(allyloxymethyl)-1,3-dioxolan-2-one (**2**, 5.85 g, 37.8 mmol) and 3-chloroperoxybenzoic acid (MCPBA) (10.8 g, 62.9 mmol) were dissolved in 100 ml CH_2Cl_2. The reaction mixture was stirred for 24 hours at room temperature and then diluted with 50 ml CH_2Cl_2. Solid potassium carbonate (7 g) was added to the solution to convert the formed m – chlorobenzoic acid in the potassium salt. The solution was filtered off from the precipitated salt, and the filtrate was rotary evaporated to dryness to give a light yellow residue. The product was purified by vacuum distillation at 170 ^oC, 10^{-2} mm Hg.

Yield: 4.5 g (70 % of theory).

^{1}H-NMR($CDCl_3$): δ = 2.57-2.66 (m, 1H, $H^{7'}$, H^7), 2.78 - 2.84 (m, 1H, H^7, $H^{7'}$), 3.12 - 3.20 (m, 1H, H^6, $H^{6'}$), 3.38 (dd, ^2J = 11.76 Hz, ^3J = 6.43 Hz, 0.40H, H^5), 3.48 (dd, ^2J = 11.94 Hz, ^3J = 5.70 Hz, 0.60H, $H^{5'}$), 3.68 (dd, ^2J = 11.12 Hz, ^3J = 3.65 Hz, 0.6H, $H^{4'}$), 3.77 (d, ^2J = 3.65, 0.8H, H^4), 3.84 (dd, ^2J = 11.12 Hz, ^3J = 3.88 Hz, 0.60H, $H^{4'}$), 3.90 (dd, ^2J = 11.86 Hz, ^3J = 2.45 Hz, 0.60H, $H^{5'}$), 3.94 (dd, ^2J = 11.73 Hz, ^3J = 2.37 Hz, 0.40H, H^5), 4.35 - 4.57 (m, 2H, H^2, $H^{2'}$), 4.78-4.90 (m, 1H, H^3) ppm.

^{13}C-NMR($CDCl_3$): δ = 43.8 (C^7), 43.8 ($C^{7'}$), 50.6, 50.7 (C^6, $C^{6'}$), 66.1 (C^2), 70.2 (C^4), 70.3 ($C^{4'}$), 71.9 ($C^{5'}$), 72.6 (C^5), 75.0 (C^3), 154.9 (C^1) ppm.

General Procedure for the functionalization of PEI's with functional cyclic carbonates[9]

At 50^{o}C the respective amounts of cyclic carbonate (see Table 6.1) were added to a solution of freeze dried b-PEI (1.0 g) in 10 ml DMF. After stirring the solution at 50 ^{o}C for 72 hours the polymer was precipitated in a 1:1 (vol : vol) mixture of hexane and diethylether. The polymer was re-dissolved in 10 ml methanol or chloroform, stirred vigorously for 15 min and re-precipitated in the above mentioned non-solvent. After repeating the cycle for 3 times the

solvent was distilled off and the product was dried (room temperature, 24 h) at 10^{-3} bar to yield a slightly yellow solid.

General Procedure for the functionalization of ***PEI_{25K}-$C16_{15}$-QI_{15}*** *with coupler* ***EC***[15]

To a solution of 1000 mg of **PEI_{25K}-$C16_{15}$-QI_{15}** in 10 ml DMF the required amount of the epoxy carbonate linker (**EC**) was added (see Table 6.2) and stirred at 50 ^{o}C for 48 hours. The product was precipitated in a 1:1 (vol : vol) mixture of hexane and diethylether. The polymer was re-dissolved in 10 ml methanol, stirred vigorously for 15 min and re-precipitated in the above mentioned non-solvent. After repeating the cycle for 3 times the solvent was removed and the product was dried (room temperature, 24 h) at 10^{-2} mbar to yield a white solid. The structural characterization of polymer is described in results and discussions.

Table 6.1. Composition and hydrodynamic radius of functionalized polymers obtained by reaction of PEIs with functionalized cyclic carbonate couplers

Functionalized Polymers	**Alkyl Chain (mole %)[a]**			**Cationic groups (mole %)[a]**	**Yield**
	C8	**C14**	**C16**	**QI**	
PEI_{25K}	-	-	-	-	-
PEI_{750K}	-	-	-	-	-
PEI_{25K}-$C16_{25}$*	-	-	25	0	2.7g, 84%
PEI_{25K}-$C14_{25}$	-	25	-	-	2.6g, 85%
PEI_{25K}-$C8_{25}$	25	-	-	-	2.2g, 85%
PEI_{25K}-$C16_{20}$-QI_{5}	-	-	20	5	2.7g, 84%
PEI_{25K}-$C16_{12.5}$-$QI_{12.5}$	-	-	12.5	12.5	2.6g, 80%
PEI_{25K}-$C16_{15}$-QI_{15}	-	-	15	15	3.0g, 81%
PEI_{25K}-$C16_{5}$-QI_{20}	-	-	5	20	2.3g, 82%
PEI_{25K}-QI_{25}	-	-	0	25	3.1g, 88%
PEI_{750K}-$C16_{25}$	-	-	25	-	2.8g, 88%

[a] Percentage of primary amine groups converted upon reaction with functional cyclic carbonates.

* PEI_a-$C16_b$-QI_c – 'a' refers to molecular weight of b-PEI and 'b', 'c' refers to degree of functionalization w.r.t all amino groups in b-PEI.

All the polymers were obtained in good yield (more than 80 % of theory). The ring opening of cyclic carbonate ring with the primary amino groups present in b-PEI leads to the formation of urethane linkages which could be seen in the region δ = 7 -8 ppm in the ^{1}H-NMR. Moreover the signals due to cyclic carbonate ring were not observed indicating that all the couplers have reacted with b-PEI. The polymers are described in details in results and discussion part.

Table 6.2. Educt composition and yields in the preparation of polymers **PEI_{25K}-$C16_{15}$-QI_{15}–EC_{40}**

Polymer	**Reactants (mg)**		**Yield**
	PEI_{25K}-$C16_{15}$-QI_{15}	**EC**	
PEI_{25K}-$C16_{15}$-QI_{15}–EC_{30}	1000	516	1288 mg, 85%

* PEI_a-$C16_b$-QI_c-EC_d – 'a' refers to molecular weight of b-PEI and 'b', 'c', 'd' refers to degree of functionalization w.r.t all amino groups in b-PEI.

Measurements

The elemental composition of the various carbon fibre samples was analyzed with the AXIS His, 165, Ultra device from Kratos Analytical. Elements of investigated surfaces were excited with monoenergetic aluminium $K_{1,2}$ irradiation with an energy of 1486.6 eV and a power of 150 W.

The infrared spectra were measured on a Thermo Nicolet Nexus 470 spectrometer with a resolution of 4 cm^{-1}. The samples were prepared as KBr pellets for the measurement in transmission mode.

The hydrodynamic radius of the macromolecules was determined on ALV 5000 dynamic light scattering system. The concentration of the polymer was 1 – 10 g/L in chloroform solution. The data was analyzed on ALV correlator software version 3.0. The date was fitted by using a DLS-exponential (g2(t)) fit delivering the mass average hydrodynamic radii.

The surface morphology of thin polymer films was investigated by atomic force microscopy (AFM) at room temperature using a Solver SFM (NTMDT, Zelenograd, Moscow). Imaging was done in the tapping mode using standard silicon cantilevers: Nanoworld Pointprobe NCH f0 (330 kHz). The deposition was done by spin coating a volume of 40 µL from solutions of the polymers, containing 0.001 wt% of polymer in pure chloroform or methanol onto freshly cleaved HOPG at a rotation rate of 2000 rpm.

The amount of polymer adsorbed (Γ, mg/m^2) on graphite (from AFM images) was calculated using "bearing" function in the Nanoscope 5.12 r5 software. The bearing area (%) of AFM image times the average height of the molecules and density of the polymer leads to the amount of polymer adsorbed onto graphite.

Differential scanning calorimetry (DSC) was performed with a Netzsch DSC 204 under nitrogen atmosphere with a heating rate of $10^{o}C$/min. Calibration was achieved using indium standard samples, the sample mass was kept between 5 – 15 mg.

Tensile and Photoelastic Measurements

The carbon single fibre / epoxy specimen were clamped in a Rheometric Scientific 'minimat' tensile testing device, mounted under a Zeiss Stemi – 2000c polarizing microscope, equipped with a Axiocam ICc3 and analyses was done using Axiovision software. The specimen was pulled at rate of 1 mm/min. The axial loading was continued until full fragmentation was reached or the specimen breaks.

Results and Discussions:

The goal of the study was to functionalize the b-PEI polymers to improve the interfacial adhesion between a polymer – cladded carbon fibre and its surrounding epoxy resin matrix system. The functionalized polymer should serve for two purposes. (i) It should contain quaternary ammonium groups or long alkyl chain groups which could adsorb on surface of carbon fibre and (ii) it should supply reactive groups which can copolymerize with epoxy groups present in epoxy resin during curing step. From the previous studies it is well known that polymer bearing quaternary ammonium groups spreads well on oxidized HOPG[15] and long aliphatic chains adsorbs well on graphite due to epitaxial adsorption.[16] In order to obtain such polymers branched polyethylenimine was selected for further functionalization. b-PEI has primary, secondary and tertiary amino groups in the molar ratio of 31:39:30 respectively[17,18] which can be selectively functionalized with different couplers. The study was divided into two parts. In the first part the various modified b-PEI's (Table 6.1) were adsorbed on HOPG and the degree of adsorption was estimated from SFM. In the second part one of the functionalized polymers which show good adsorption was selected and coated on oxidized and non-oxidized carbon fibre and interfacial shear strength between fibre and matrix was estimated from Kelley-Tyson fragmentation test.

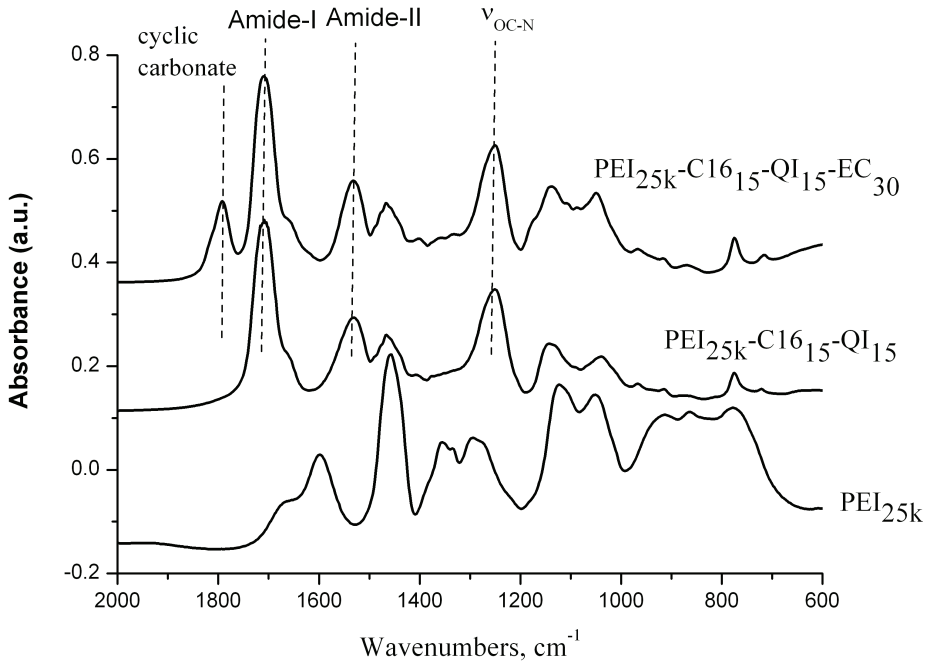


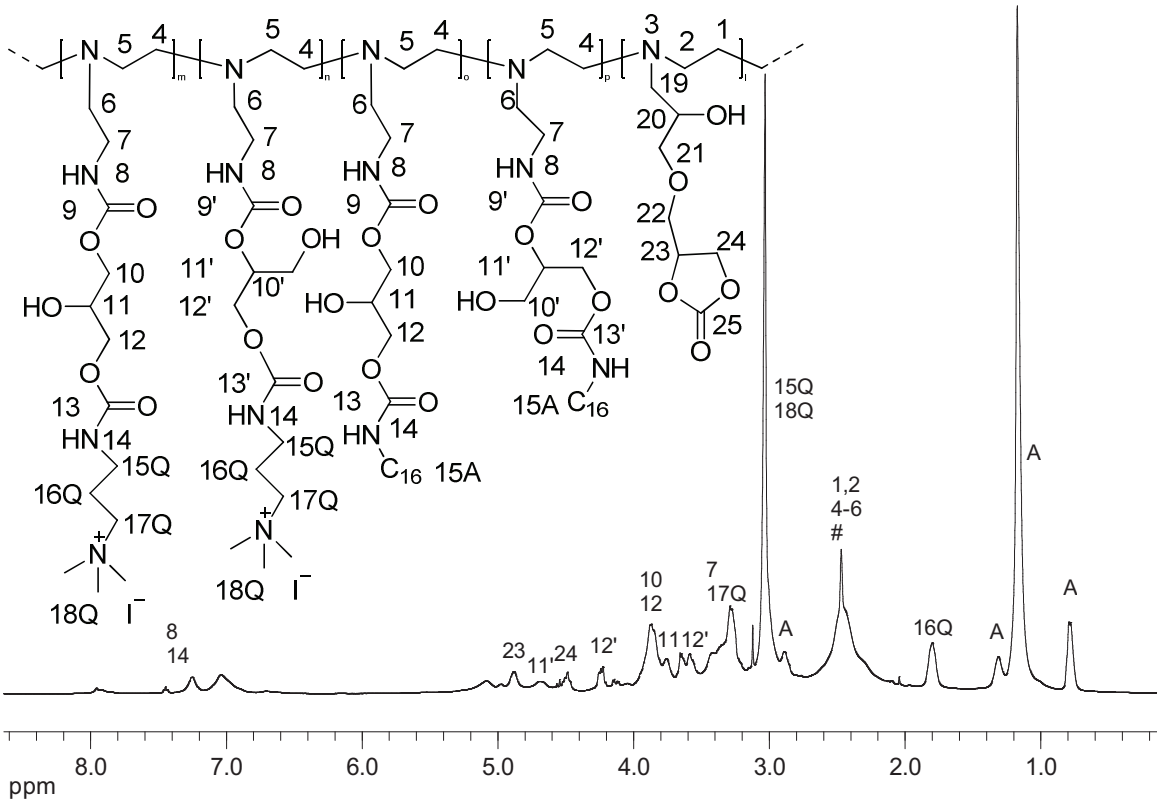
Figure 6.1. Infrared spectra of **PEI_{25K}**, **PEI_{25K}-$C16_{15}$-QI_{15}** and **PEI_{25K}-$C16_{15}$-QI_{15}–EC_{30}** ($\nu_{C=O,Carbonat}$ = 1792 cm^{-1}, ν_{Amid-I} = 1713 cm^{-1}, $\nu_{Amid-II}$ = 1530 cm^{-1}, ν_{OC-N} = 1248 cm^{-1}).

Structural and molecular characterization

Figure 6.1 compares the infrared spectrum of **PEI_{25K}**, **PEI_{25K}-$C16_{15}$-QI_{15}** and **PEI_{25K}-$C16_{15}$-QI_{15}–EC_{30}**. The bands at 1248 cm^{-1} (OC-N - stretch), 1530 cm^{-1} (Amide-I) and 1660 cm^{-1} (Amide-II) are characteristic for urethane groups, while the band at 1791 cm^{-1} that appeared only in **PEI_{25K}-$C16_{15}$-QI_{15}–EC_{30}** was attributed to the >C=O stretching vibration of the cyclic carbonate ring. Moreover, due to absence of band at 1791 cm^{-1} in **PEI_{25K}-$C16_{15}$-QI_{15}** indicates that all the cyclic carbonate has reacted with b-PEI.

Figure 6.2 displays the ^{1}H-NMR and ^{13}C-NMR of **PEI_{25K}-$C16_{15}$-QI_{15}–EC_{30}.** The ^{1}H-NMR was difficult to interpret due to overlapping signals caused by ring opening reaction of cyclic carbonate and epoxides rings. The ring opening of cyclic carbonate ring with primary amine leads to the formation of an urethane linkage which could be identified in the region δ = 7 – 8 ppm (signal 8 & 14). ^{13}C-NMR shows the characteristic peaks of the cyclic carbonate ring (signal 23, 24 and 25). Moreover, signals (10, 11, 12, 19, 20, 21) due to ring opening reaction could also be assigned. The absence of signals coming from an oxirane ring indicates that the coupler EC has completely reacted with functionalized b-PEI. Thus it can be concluded from the IR and NMR spectroscopy that a polymer bearing aliphatic tails, quaternary ammonium groups and cyclic carbonate groups was obtained.

(a)



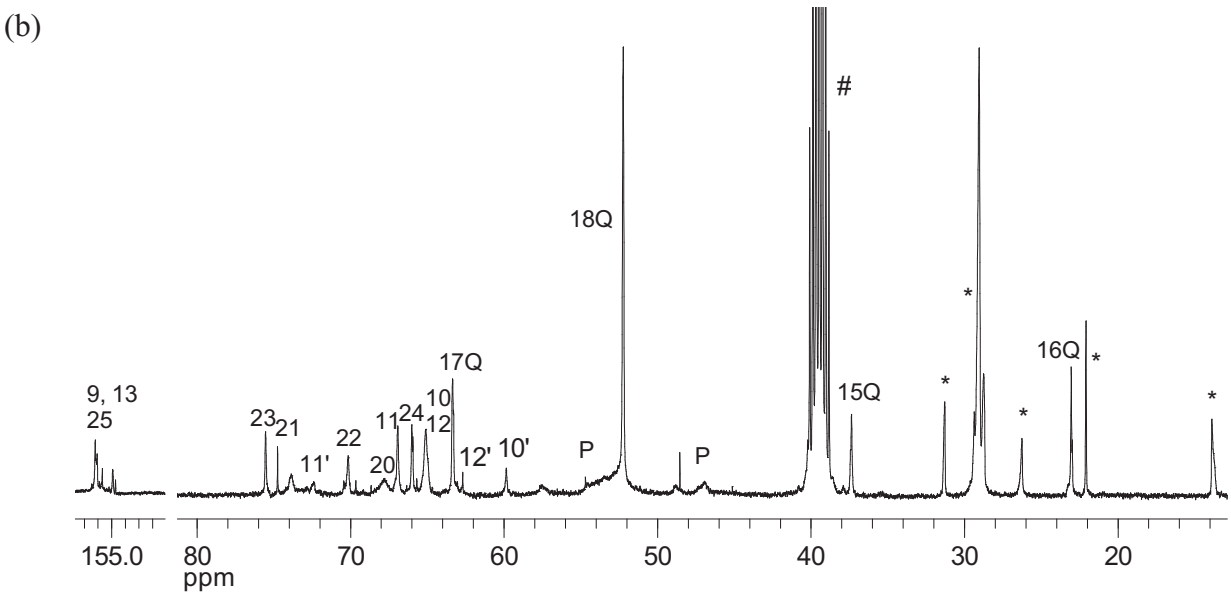


Figure 6.2. (a) ^{1}H-NMR and (b) ^{13}C-NMR of **PEI_{25K}-$C16_{15}$-QI_{15}–EC_{30}** in DMSO-d6.
P = polymer backbone, * = alkane signals and # = DMSO.

Dynamic light scattering investigation of polymers in chloroform showed that **PEI_{25K}** and **PEI_{750K}** have hydrodynamic radii of 5.3 nm and 35.9 nm respectively. Obviously, higher the molecular weight higher will be the size of the polymer. However, R_H of the functionalized polymers was comparable to that of the respective parent polymer (see Table 6.1). Replacement of C16 by QI has almost no effect on the hydrodynamic radius. In the previous study it was found that there was a considerable reduction in size of **$PEI_{25K}QI_{25}$** (R_H = 2.1 nm) when measured in sodium nitrate - water solution compared to the size of non modified b-PEI (R_H = 5.2 nm).[15] $NaNO_3$ was added to screen the Coulomb interaction and impede the polyelectrolyte typical ion association. The observed contraction could be explained due to intramolecular interaction forces in **$PEI_{25K}QI_{25}$** that leads to the compact structure. Obviously the introduction of long alkyl chains (for e.g. in **PEI_{25K}-$C16_{12.5}$-$QI_{12.5}$**) in the polymers impedes these interactions and hence the contraction is not observed.

Thermal properties of the polymer

The thermal properties of the polymers were characterized by differential scanning calorimetry (DSC). All the polymers investigated were found to be completely amorphous except **PEI_{25K}-$C16_{25}$** (see Figure 6.3 and Table 6.3). The glass transition temperature of unmodified PEI was -52.6 ^{o}C. The T_g of all the modified polymers were found to be in between 0 – 60 ^{o}C indicating the functionalization of polymers. The glass transition

temperature was found to increase with the increase in the amount of charge in the functionalized polymer.

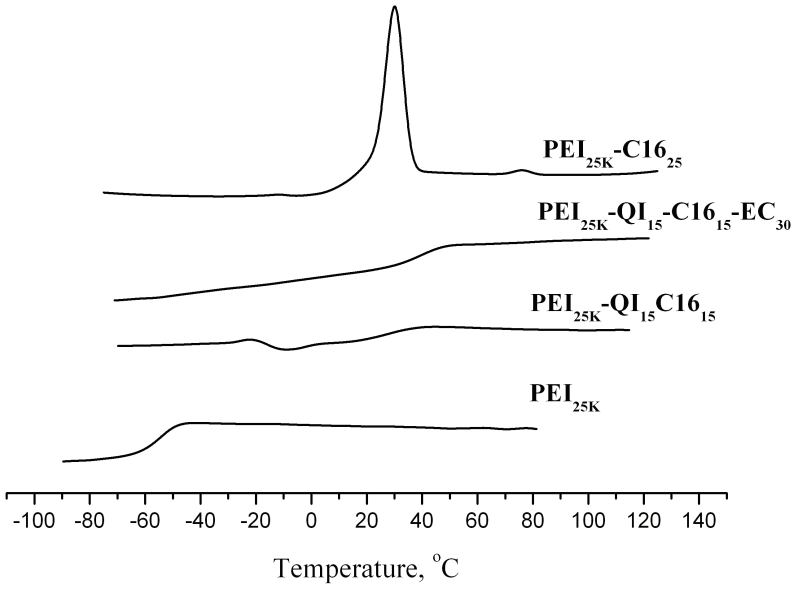


Figure 6.3. DSC trace of functionalized b-PEI's. The curves are vertically shifted to avoid overlapping. T_g is calculated as point of inflection.

Table 6.3. Glass transition and crystallization temperature of functionalized PEI's.

Polymers	Glass Transition Temperature, ^oC	Crystallization Temperature, ^oC	Hydrodynamic Radius, R_H, nm
PEI_{25K}	- 53.0	-	5.28
PEI_{750K}	n.d.	n.d.	33.4
PEI_{25}-$C8_{25}$	14.0	-	3.64
PEI_{25K}-$C14_{25}$	15.2	-	5.46
PEI_{25K}-$C16_{25}$	17.0	42.8	5.28
PEI_{25K}-QI_5-$C16_{20}$	19.2	-	5.68
PEI_{25K}-$C16_{12.5}$-$QI_{12.5}$	28.3	-	5.80
PEI_{25K}-$C16_{15}$-QI_{15}	30.5	-	5.85
PEI_{25K}-QI_{25}	58.9	-	n.d.
PEI_{25K}-$C16_{15}$-QI_{15}- EC_{30}	37.5	-	n.d.
PEI_{750K}-$C16_{25}$	n.d.	n.d.	33.4

The crystallization of **PEI_{25K}-$C16_{25}$** can be explained due to stiffening of polymer chains resulted from crystalline packing of bound C16 molecules, which hinders the mobility of polymer chain. The endothermic peak is at 42.8 ^{o}C which is due to melting of C16 alkyl chain crystals. The b-PEI modified with **C8** and **C14** were found to be amorphous because of the length alkyl chain and the flexibility of b-PEI backbone which makes them difficult to crystallize. The incorporation of charge (QI) into the polymers (**PEI_{25K}-QI_5-$C16_{20}$, PEI_{25K}-$C16_{15}$-QI_{15} and PEI_{25K}-QI_{25}**) hinders the crystalline packing of the bound **C16** molecules and hence found to be amorphous.

Adsorption Studies

To study the adsorption behaviour, the functionalized polymers were spin coated onto HOPG from dilute solution in chloroform or methanol and the surface topography was studied by SFM. The mono-layer coverage of the functionalized polymer was studied depending on (i) the length of the aliphatic tail (**C8**, **C14** and **C16**) and (ii) by varying the amount of quaternary ammonium groups and hexadecane side chains in the polymer (**QI** and **C16**).

(i) Effect of aliphatic chain length

b-PEI based functionalized polymers with varying length of alkyl chain **(PEI_{25K}-$C16_{25}$, PEI_{25K}-$C14_{25}$, PEI_{25K}-$C8_{25}$)** were adsorbed on HOPG from dilute polymer solution in chloroform (10^{-3} wt %.). The casting process allows the formation of uniform layers with monolayer coverage. As typical example Figure 6.4a shows an AFM height image of **PEI_{25K}-$C16_{25}$** which shows short rods like features with average rod length of 10.2 nm. As understood from previous studies (Chapter 4) that self assembly of rods leads to single molecule. At this coverage, the single molecules are difficult to isolate. Thus these rods like features were attributed to intermolecular and intra-molecular self assembly. A similar type of surface morphologies was obtained with **PEI_{25K}-$C14_{25}$** as indicated in Figure 6.4b. This image shows additional stripe patterns forming “rafts” as indicated by an arrow. The periodicity of the stripes calculated from AFM was 5.6 nm. These stripes can be assigned to unreacted alkyl chains (hexadecylamine) which are present as impurities in the polymer and forms an independent layer.

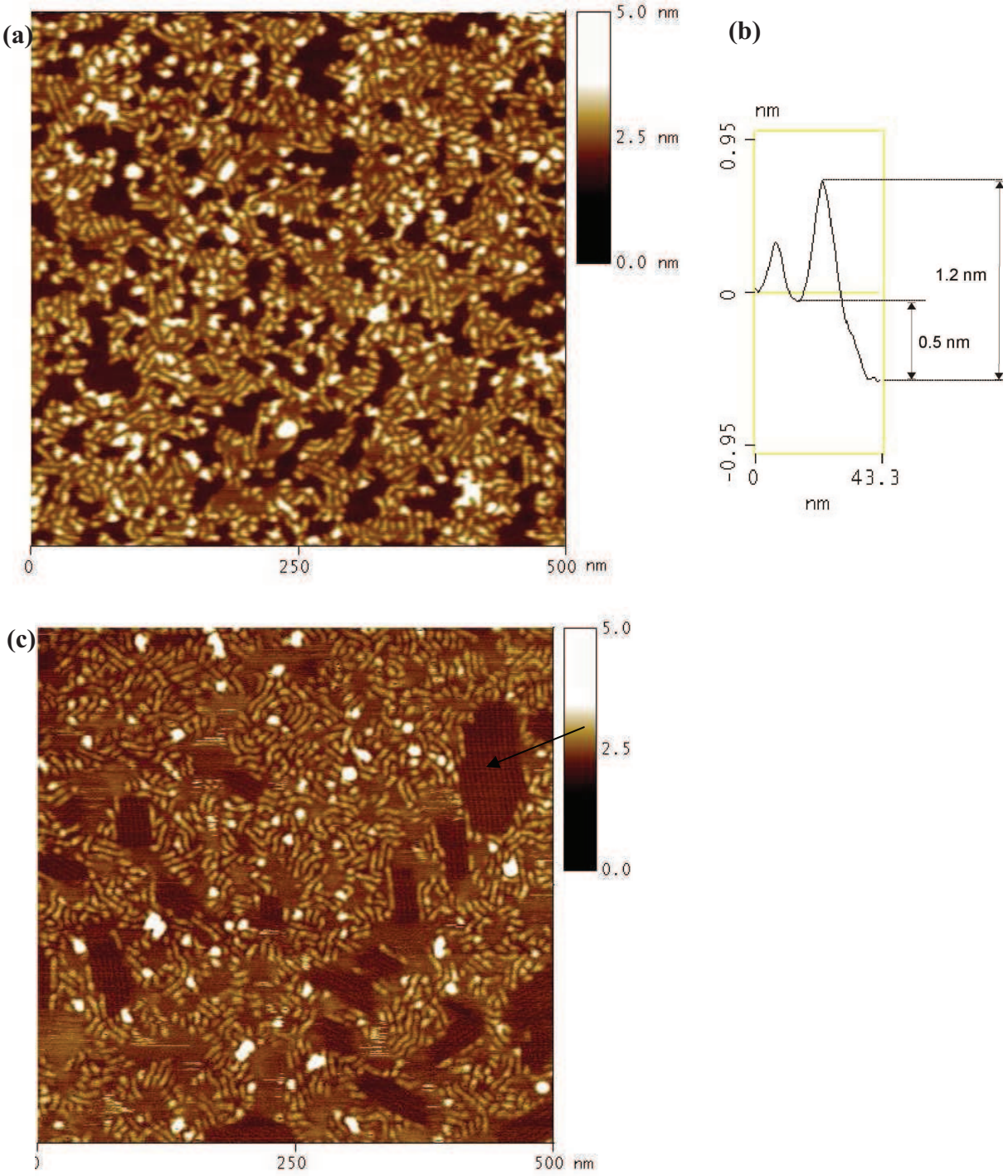


Figure 6.4. Height image of functionalized b-PEI molecules adsorbed onto HOPG (10^{-3} wt% chloroform). (a) **PEI_{25K}-$C16_{25}$**; (b) **PEI_{25K}-$C14_{25}$** and section analyses; (c) detailed profile of single rods which show two layer structure: monomeric thickness 0.5 nm and the hemicylindrical shape of rod profile h = 1.1 nm

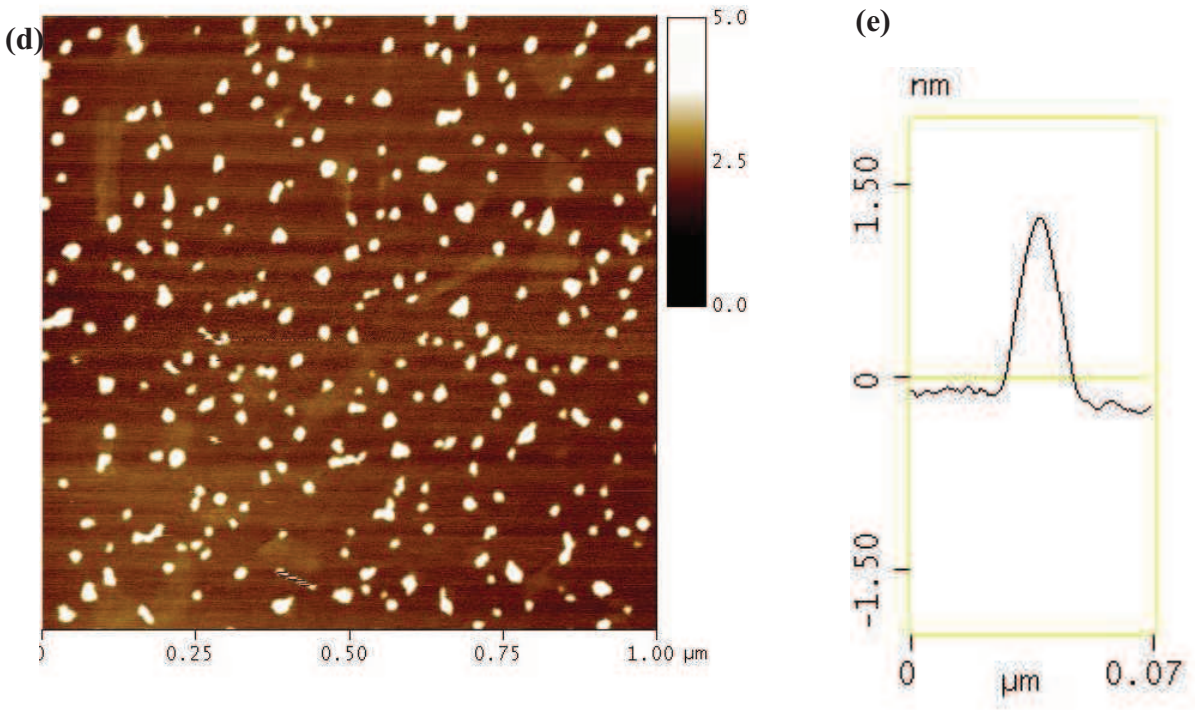


Figure 6.4. AFM image of functionalized b-PEI molecules adsorbed onto HOPG; (d) & (e) Topography of $\mathbf{PEI_{25K}\text{-}C8_{25}}$ and section analyses (concentration = 10^{-3} wt% in chloroform).

HOPG adsorbed $\mathbf{PEI_{25K}\text{-}C8_{25}}$ exhibited a distinctly different pattern (cf. Figure 6.4d). The molecules adopt three dimensional coiled conformations over HOPG which could be seen as spheres. This could be explained because intermolecular interactions are much smaller in **C8** compared to **C14** and **C16** which is responsible for the formation of an ordered two dimensional structure. Thus it can be concluded that the adsorption stability of polymer containing alkanes as side chain increases with the increasing chain length. The driving force for the formation of the observed surface structure are dominantly van der Waals interactions which drives the alkyl side chains to adsorb epitaxially onto graphite surface. Similar adsorption results have been observed during adsorption of poly(γ-L-glutamates) modified with long n-alkyl side chains on graphite.[19]

Figure 6.5a shows the adsorbed mass of the functionalized polymers versus the alkyl chain length for the same solution conditions (c.a. Experimental part). The curve shows that the degree of adsorption (Γ) of the polymer increases with the length of alkyl chain (n) and is at maximum in the case of $\mathbf{PEI_{25K}\text{-}C16_{25}}$ among the polymers studied**.** There was difference

when comparing the height of the adsorbed molecules of the various functionalized polymers on HOPG (see Figure 6.5b). The average height of the b-PEI modified with shorter alkyl chain **C8** (1 nm) is higher than the height of polymer molecules modified with **C14** and **C16**.

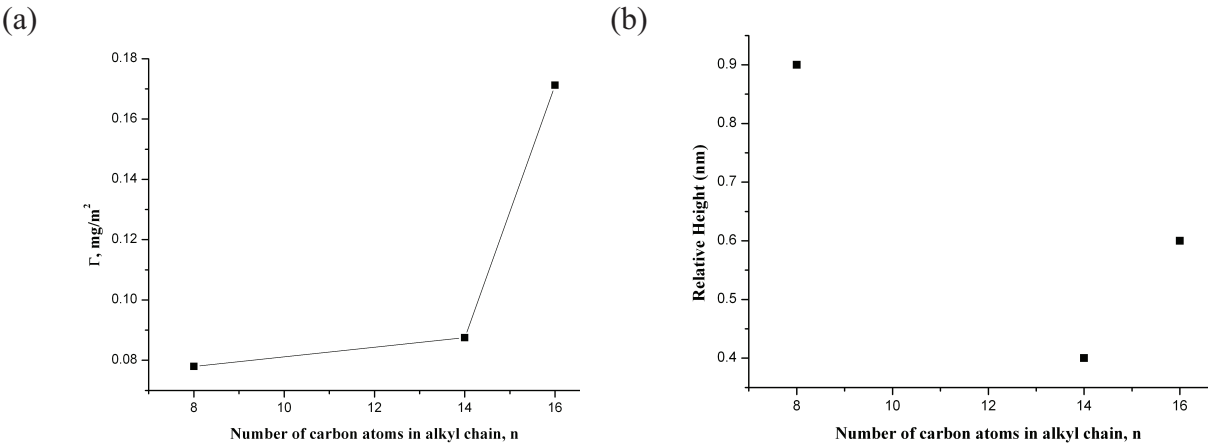


Figure 6.5. (a) Variation of adsorbed amount of functionalized b- PEI with different alkyl length. (b) Relative height of adsorbed polymers as a function of alkyl length.

The epitaxial interaction between the **C16** side chain and the graphite surface could be seen well in the case of **PEI_{750K}-$C16_{25}$** adsorbed onto HOPG (see Figure 6.6).

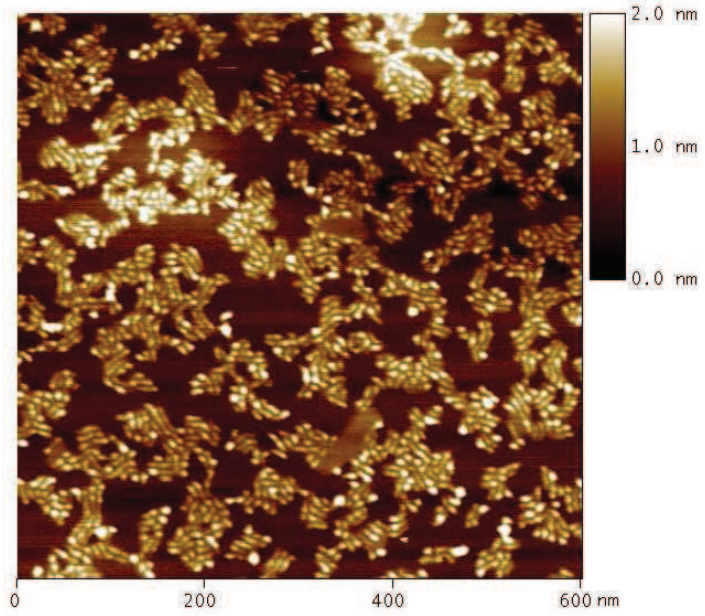


Figure 6.6. AFM height image of **PEI_{750K}-$C16_{25}$** (10^{-3} wt% in chloroform).

The assembly of molecules displayed a cross angle 60° between rods in different islands. The cross angle of 60° between different rods can be attributed to the crystallographic axes of the modelying of HOPG. Thus, long alkyl chain (**C16**) in the polymer adsorbs epitaxially due to affinity of hexadecane side chain towards the surface of graphite. The average length of rods estimated over the AFM image is 20 nm compared to 10 nm at lower surface coverage (10^{-4} wt%, Chapter 5).

(ii) Effect of charge

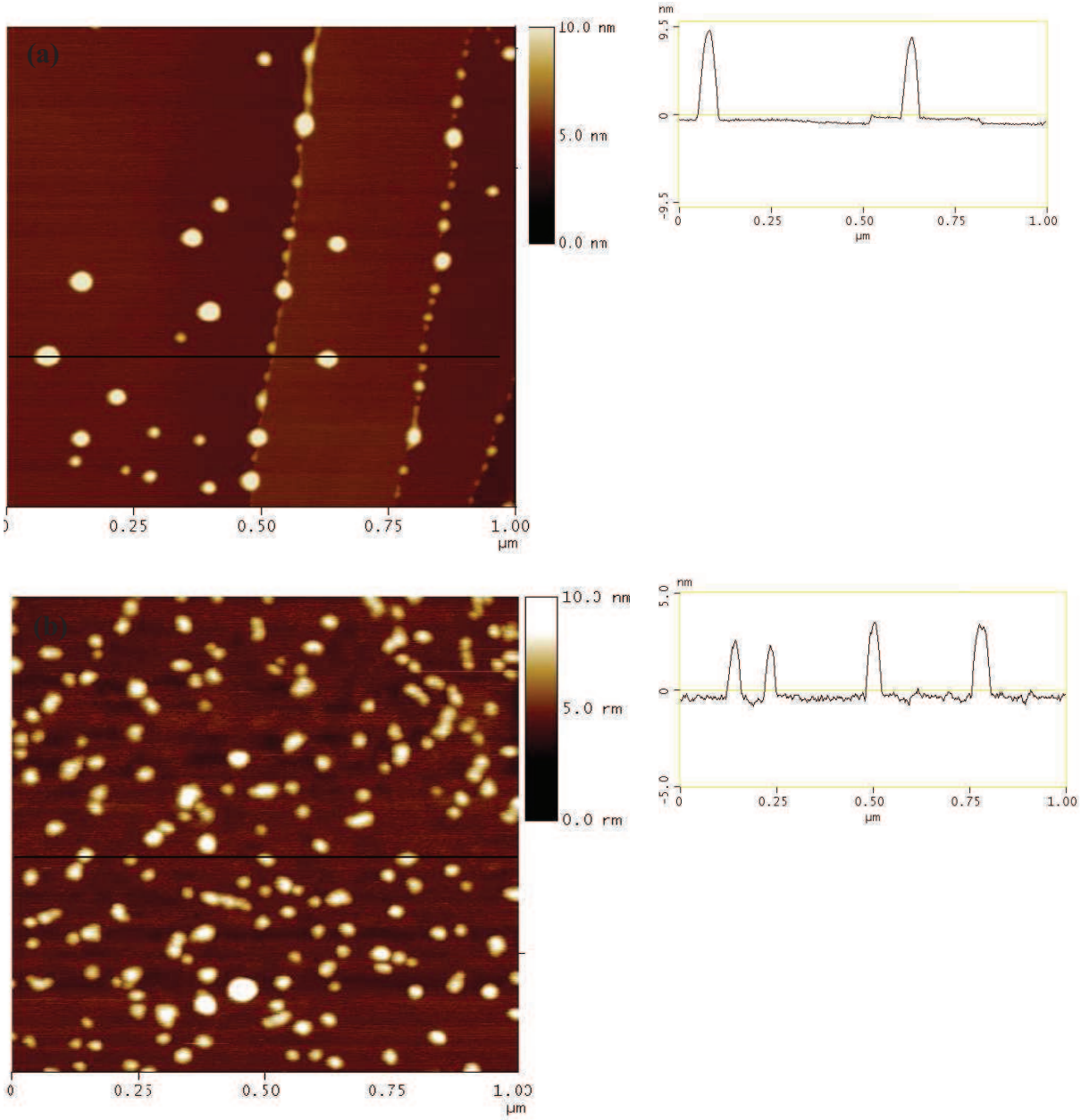


Figure 6.7. Micrograph displaying the topography of single functionalized PEI molecules. (a) **PEI_{25K}-QI_{25}** – spin coated from methanol, (b) **PEI_{25K}-$C16_5$-QI_{20}** – spin coated from methanol.

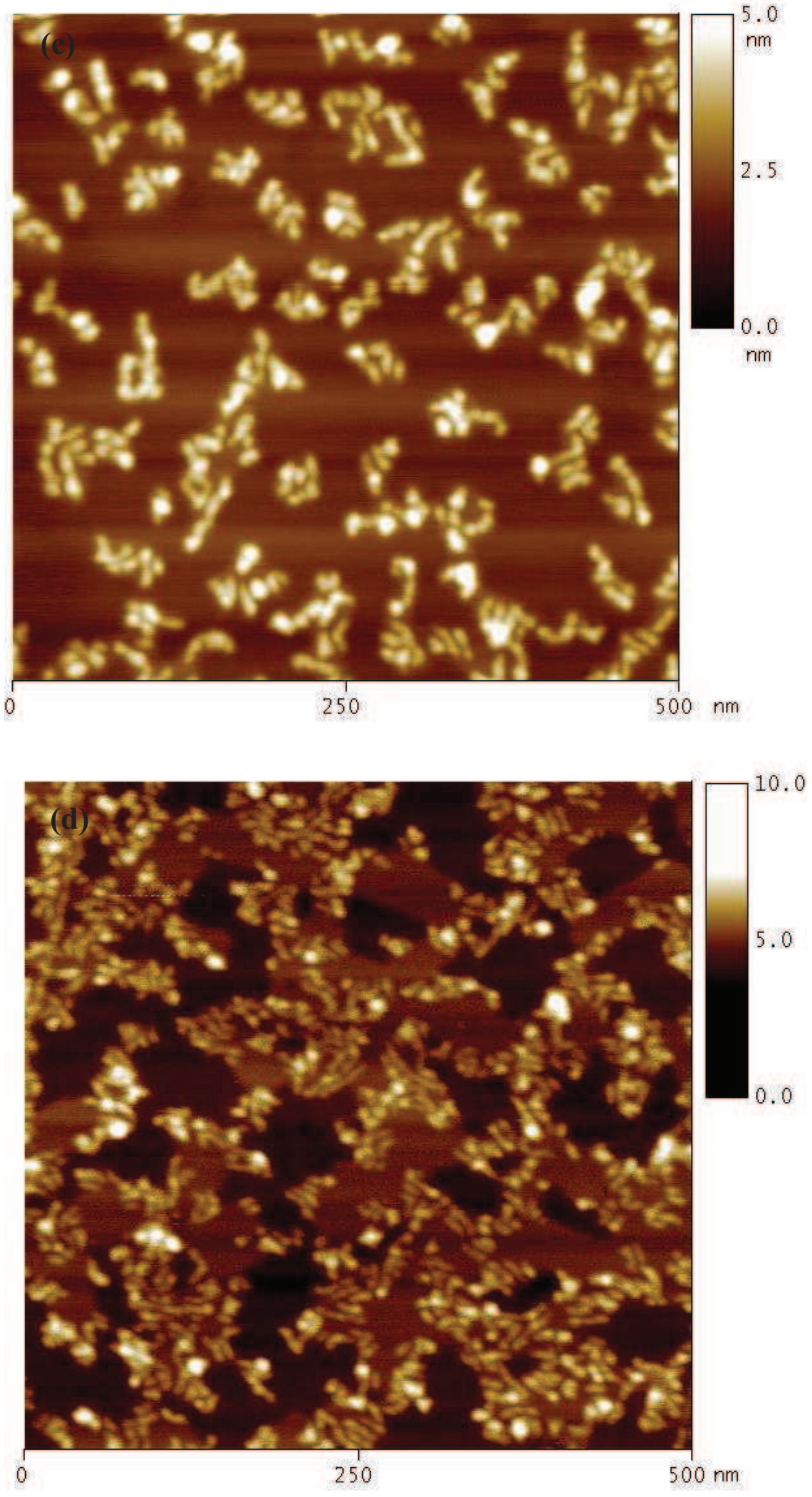


Figure 6.7. (contd.) Micrograph displaying the height of single functionalized b-PEI molecules 10^{-3} wt% in chloroform (c) **PEI_{25K}-$C16_{12.5}$-$QI_{12.5}$** : (d) **PEI_{25K}-$C16_{20}$-QI_5**

The effect of charge was studied by varying the composition of carbonate couplers **C16** and **QI** incorporated in the b-PEI. The total number of moles of **QI** and **C16** coupler in the polymer was kept constant to 25%. **C16** was selected as it has good adsorption compared to **b-PEI** modified with **C14** and **C8**.

Due to presence of quaternary ammonium groups the polymers (**PEI_{25K}-QI_{25}** and **PEI_{25K}-$C16_5$-QI_{20}**) are insoluble in non-polar solvent like chloroform. However, with the increase in amount of alkyl chain into the polymer, the polymers (**PEI_{25K}-$C16_{12.5}$-$QI_{12.5}$** and **PEI_{25K}-$C16_{20}$-QI_5**) become soluble in chloroform and insoluble in polar solvents. Figure 6.7a depicts the scanning force micrograph of **PEI_{25K}-QI_{25}** coated from methanol solution. The polymer did not spread but formed isolated spherical droplets with an average height of 4.3 nm. With an introduction of 5 mole % of C16 in the polymer (**PEI_{25K}-$C16_5$-QI_{20}**), the polymers spreads onto HOPG. Further increase of the **C16** content into the polymer reduced the height of the adsorbate leading to the structure with locally aligned rods (see Figure 6.7c and 6.7d).

It can be concluded that highly polar **PEI_{25K}-QI_{25}** polymer did neither wet, nor adhere well to HOPG surface. At the composition of 12.5 mole % of C16 into the polymer (**PEI_{25K}-$C16_{12.5}$-$QI_{12.5}$**), the effect of **C16** chain predominates and single molecules aligned due to van der Waals interaction which drives to adsorb the alkyl side chain epitaxially onto the graphite surface.

Figure 6.8a represents the adsorbed mass as a function of the cationic groups in the polymer.

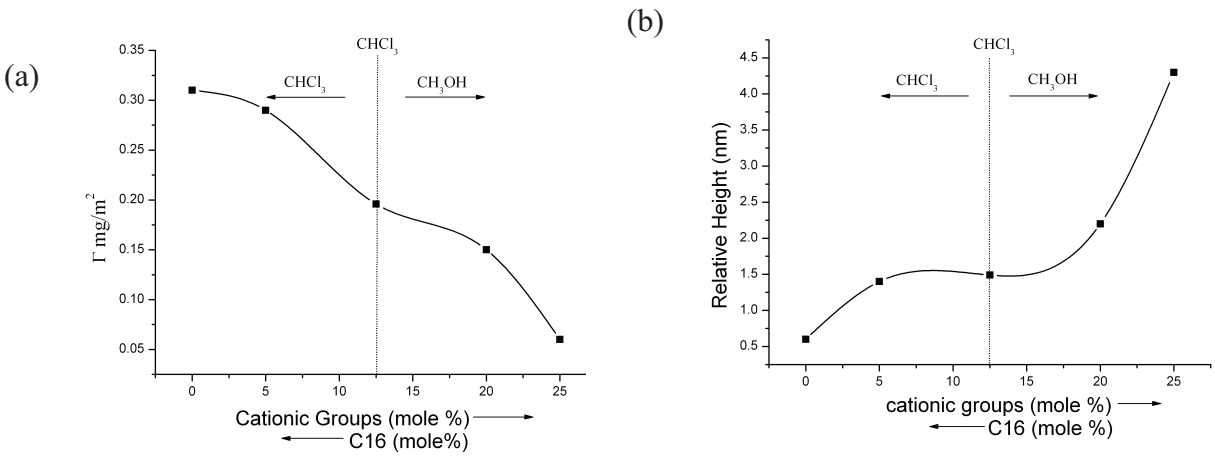


Figure 6.8. (a) Amount of polymer adsorbed Vs moles of cationic groups. (b) Relative height of single molecules in variation with charge.

As seen from the plot the degree of adsorption onto HOPG decreases with the increase of quaternary ammonium groups in the polymer. Furthermore, the increase in amount of charge in the polymer increases the relative height of polymer on the substrate (see Figure 6.8b).

Table 6.4. Length of the rods calculated from SFM

Polymer	**L_n (nm)**	**L_w (nm)**	**PDI = L_w/L_n**	**No. of Rods studied**
PEI_{25K}-$C16_{25}$	10.2 (5 – 25)	13.8	1.15	355
PEI_{25K}-QI_5C16_{20}	13.7 (6 – 38)	16.2	1.18	180
PEI_{25K}-$QI_{12.5}C16_{12.5}$	15.6 (7 – 43)	18.0	1.27	173

As seen from the Table 6.4 the length of the rods increases with the amount of charge present in the polymer. This could be explained because the cationic groups in the polymer try to repel each other. The higher steric hindrance of these longer side chains causes the length from 10.2 nm for **PEI_{25K}-$C16_{25}$** to 15.6 nm for **PEI_{25K}-$QI_{12.5}C16_{12.5}$**.

Adsorption of **PEI_{25K}-$C16_{15}$-QI_{15}–EC_{30}** on HOPG leads to formation of a mono-layer of 1.1 nm thick, containing rod like features with average length of 32 nm as illustrated in Figure 6.9. The role of this polymer on the interfacial adhesion between carbon fibre and epoxy matrix will be further demonstrated.

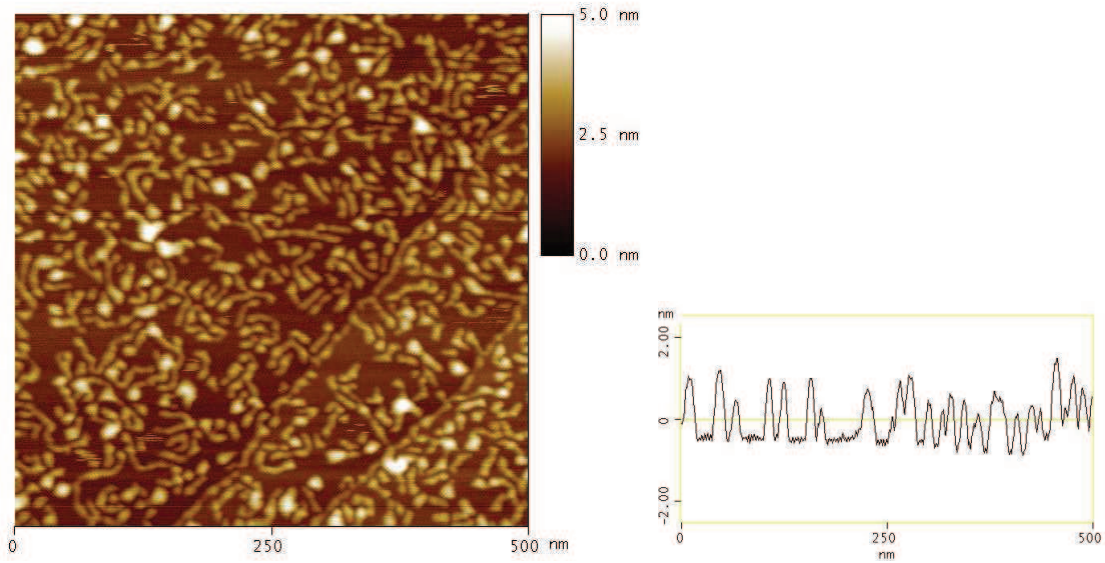


Figure 6.9. height image of **PEI_{25K}-$C16_{15}$-QI_{15}–EC_{30}** on HOPG (0.002 wt% solution in chloroform)

Carbon-Fibre / Epoxy Model Resins

Table 6.5 compares the surface composition obtained from XPS of different carbon fibre systems. The increase in nitrogen content for primer coated samples indicates that the coating was successful. The theoretical elemental composition of the **PEI_{25K}-$C16_{15}$-QI_{15}–EC_{30}** is C 68.9 % O 19.4% N 10.7% I 1% which is comparable to the elemental composition of coated fibres.

Table 6.5. XPS-analysis of elemental composition of different carbon fibre systems.

Samples	Elemental Composition (atom - %)			
	Carbon	**Oxygen**	**Nitrogen**	**Iodine**
Unsized carbon fibre extracted	83.4	16.6	0	0
Extracted carbon fibre & coated with primer.	72.0	18.7	8.9	.26
Plasma treated carbon fibre & coated with primer.	74.6	18.3	7.07	0

Effective degree of coverage could be obtained from XPS results and was estimated to 82 % ± 4 %. (based on carbon content = 79%, oxygen content = 86% and nitrogen content = 82%) (cf. Figure 6.10).

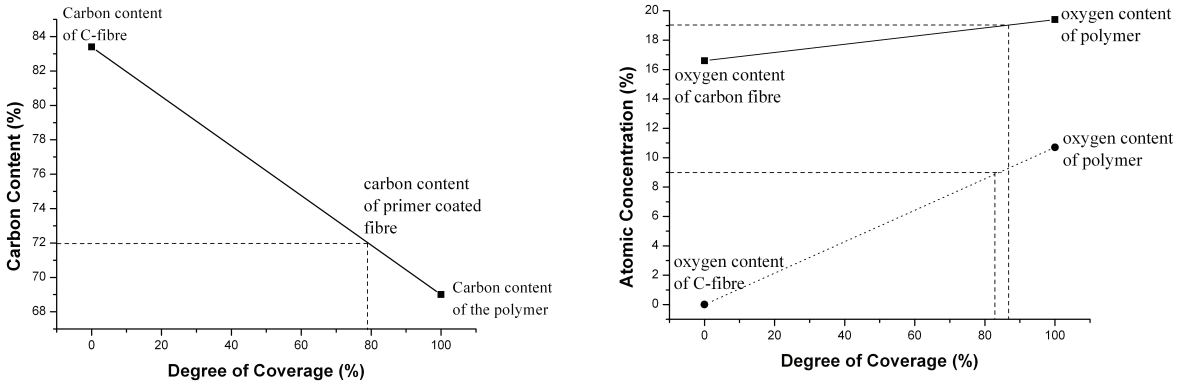


Figure 6.10. Degree of coverage on primer coated carbon fibre

To study the effect of primer coating on the interfacial properties of carbon fibre- epoxy resin composite systems following carbon fibre samples were studied. (i) as received sized

carbon fibre – UTS 5631 from Tenax, (ii) unsized carbon fibre obtained by extraction, (iii) carbon fibres were plasma treated to remove any sizing and then subsequently coated with **PEI_{25K}-$C16_{15}$-QI_{15}–EC_{30}** from solution and (iv) unsized carbon fibre coated with **PEI_{25K}-$C16_{15}$-QI_{15}–EC_{30}** from solution (no plasma oxidation). (cf. experimental Part). **PEI_{25K}-$C16_{15}$-QI_{15}–EC_{30}** was selected as a primer polymer because it adsorbs well on graphite to form monolayer. Moreover, coating this polymer onto non-oxidized and oxidized carbon fibre, effect of charge and alkyl chain on interfacial properties of the composites could be studied. In all the experiments, a single filament was aligned axially in the cavity of dog bone shape cavity mould, filled with the liquid epoxy resin, followed by thermal curing of the specimen. The obtained single filament composites were analyzed by Kelley Tyson Fragmentation Test.

On application of tensile load to a single fibre specimen in the fragmentation test, stress is transferred from the matrix to the fibre. The fibre begins to break at some stress and continues to break as the stress is increased. The fibre breaks can be easily observed using a polarized light allowing simultaneously detecting the occurrence of stress induced birefringence and measuring of the fragment lengths. Figure 6.11 shows the fibre breaks for carbon fibre at different strain during tensile loading in fragmentation test.

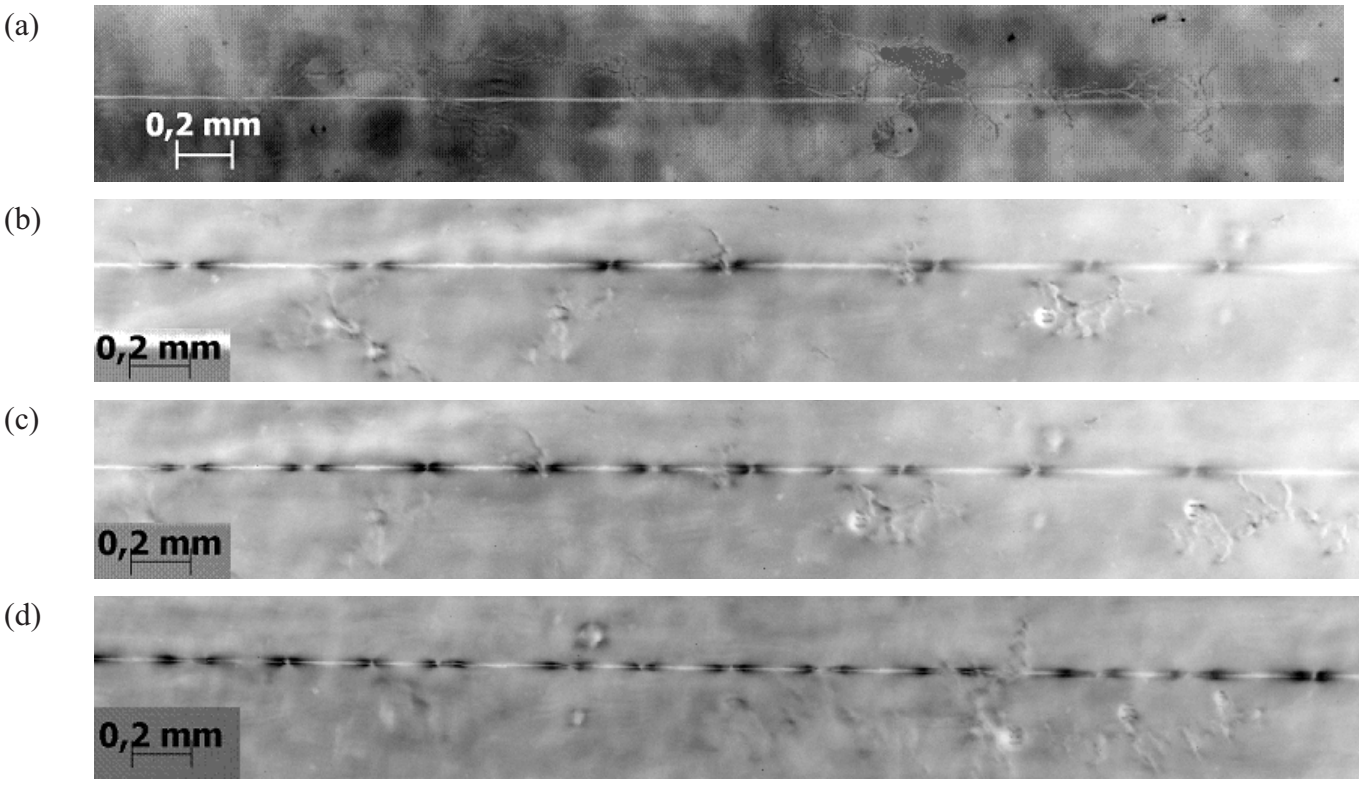


Figure 6.11. A single carbon fibre – as received during fragmentation test at different strain (ε). (a) before tensile loading, (b) ε = 5.3 %, (c) ε = 5.7 % and (d) ε = 6.9 %

As the applied stress is increased, the crack density i.e. number of break also increases. In other words, the fibre fragment become smaller and smaller with increase in force. Upon further stretching the fibre fractures into smaller fragments until a minimum critical length l_c is reached. The fragments length is limited to l_c, because the matrix transfers the tensile stress to the fibre *via* shear stresses along the fibres axis,- when the fragments become shorter than l_c a stress larger than the tensile strength σ_f can no longer be transferred. The mathematical treatment of this situation yielded equation (1), relating the interfacial shear yield stress τ_C to the tensile strength σ_f, the diameter d of the fibre as well as the critical fragments length l_c.

$$\tau_C = \sigma_f \cdot d / 2 \cdot l_C \qquad \text{(Eq. 1)}$$

Figure 6.12 depicts typical examples of the observed birefringence patterns in the loaded state for different systems.

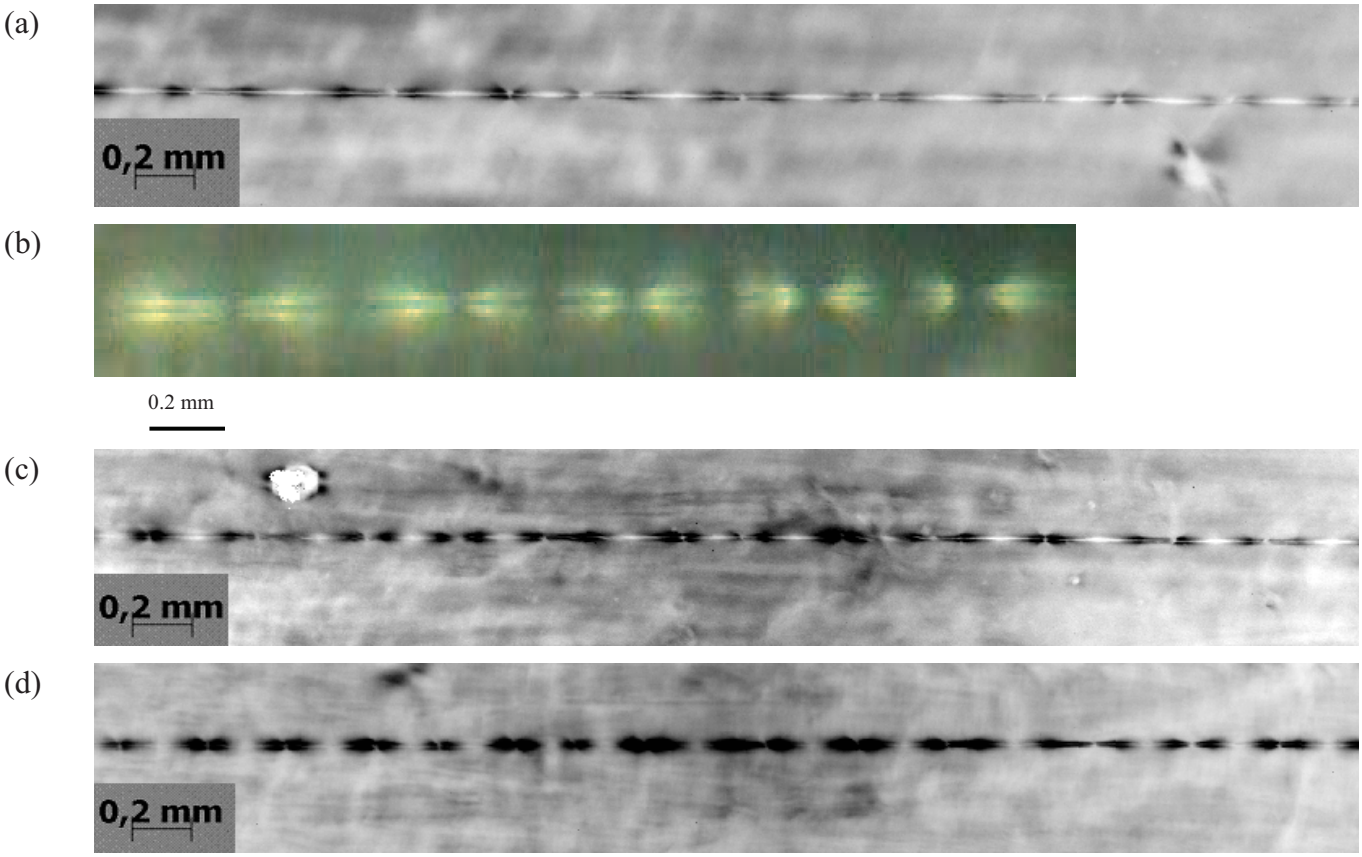


Figure 6.12. Optical micrographs of birefringence patterns observed upon stretching of carbon single fibre / epoxy resin composites to the fragmentation saturation level. a) As received - sized, b) Unsized carbon fibre – acetone extracted, c) Extracted carbon fibre & coated with primer and, (d) Plasma treated carbon fibre & coated with primer.

In the vicinity of any fragment tip an intense photoelastic region developed, resulting in the shown stress pattern with alternating dark and light areas. The birefringence pattern was usually symmetric at both sides of the fibre ends. As expected no new fibre breaks occurred once the critical fragment length was reached, even if the applied tensile load was continuously increased further. Figure 6.13 compares the crack density of different carbon fibre – epoxy resin systems in the single fibre fragmentation test.

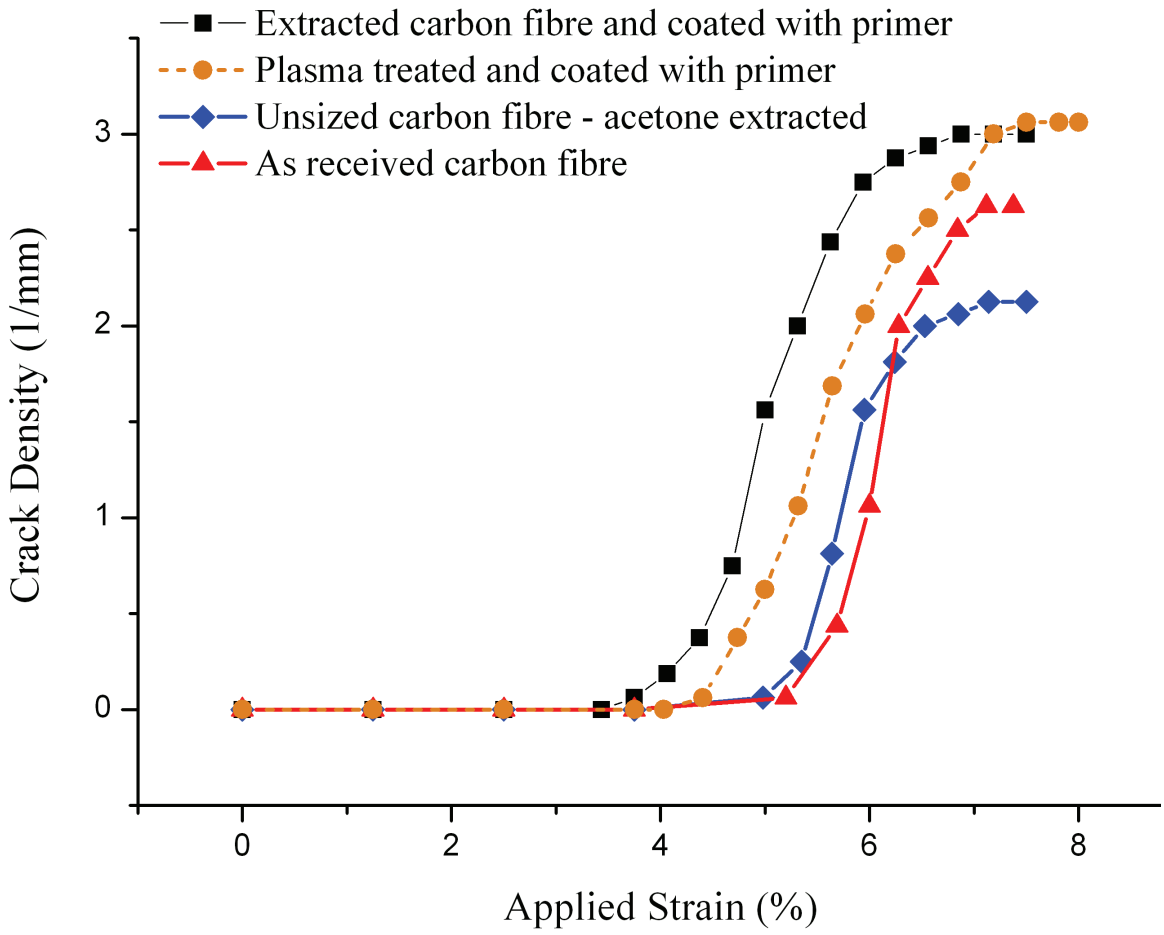


Figure 6.13. Crack density of different carbon fibre systems as a function of applied strain. * Crack density is equal to number of breaks at saturation divided by original gauge length of the specimen.

In the presence of polymer primer (**PEI_{25K}-$C16_{15}$-QI_{15}–EC_{30})** at the non-oxidized and oxidized carbon fibre/matrix interface the fibre fragmentation starts at an elongation (ε ≅

0.038) that is about 30 % below that of the unsized primer polymer sample ($\varepsilon \cong 0.055$). At elongation ($\varepsilon \cong 0.07$), crack density showed a plateau or saturation in all the studied samples.

Table 6.6. Average values of the critical number of fibre fractures N_C, the critical fibre length l_c and of the interfacial shear strength τ_C obtained from Kelley/Tyson fragmentation tests with different carbon fibre / epoxy resins systems.

Sample	Average Number of Fragments, N_c	Critical fragment length, l_c (μm)	l_c/d*	Interfacial Shear Strength, τ, [MPa]
Sized carbon fibre – as received	42 ± 2	370 ± 6	52.9 ± 1	45.4 ± 1
Unsized carbon fibre – acetone extracted	33 ± 3	410 ± 5	58.6 ± 1	40.9 ± 1
Extracted carbon fibre & coated with primer	47 ± 2	340 ± 5	48.5 ± 1	49.5 ± 1
Plasma treated carbon fibre & coated with primer	48 ± 3	330 ± 10	47.1 ± 2	51.0 ± 2

* Diameter of the single carbon fibre is assumed to be 7 μm.

The interfacial shear strength was calculated assuming that the tensile strength σ_f at critical fibre length is same for all the carbon fibre systems. There was marked improvement in the interfacial shear strength of primer coated carbon fibre samples ($\tau_C \sim 25$ % for non oxidized & coated with primer and $\tau_C \sim 21$ % for oxidized and coated with primer) compared to unsized carbon fibre system (cf. Table 6.6). Moreover, the interfacial shear strength of non-oxidized and oxidized carbon fibre samples (both samples are coated with primer **PEI_{25K}-$C16_{15}$-QI_{15}–EC_{30}**) was found to be same. The polymer primer consists of equal amount (moles) of alkyl chains and quaternary ammonium groups. It is well known that quaternary ammonium groups adsorbs well on oxidized carbon fibre system whereas they does not like to wet non polar

carbon fibre surfaces. Alkyl chains are known to adsorb epitaxialy onto non oxidized carbon fibre. Since, the interfacial strength obtained is similar for both the systems, it can be concluded that this primer polymer has enough alkyl (**C16**) chains which allows them to adsorb onto non – oxidized carbon fibres. The conclusion is further supported from the adsorption study of this polymer onto graphite (cf. Figure 6.9).
The similar test was carried out for as received carbon fibre systems from Toho Tenax. 13 % improvement in interfacial shear strength of primer sized carbon fibre system compared to the strength of the commercial fibres was observed.

Conclusions

A series of functional b-PEI containing alkyl and ammonium functionalities were successfully synthesized and characterized. The adsorption behaviour of the polymers was studied onto graphite demonstrating the formation of mono-layer coverage by means of atomic force microscopy. The amount of adsorbed material was found to increase with the length of the used alkyl chain and maximum adsorption was observed for the **C16** modified b-PEI. Furthermore, the degree of adsorption onto graphite decreased with the increase in amount of quaternary ammonium groups in the polymer. The incorporation of additional cyclic carbonate groups in a b-PEI bearing 15 mole % **C16** and 15 mole % **QI** groups did not considerably change the adsorption behaviour as indicated by AFM. **PEI_{25K}-$C16_{15}$-QI_{15}–EC_{30}** adsorbed well on carbon fibre as indicated by XPS measurements. When embedded in an epoxy matrix the adsorbed polymer caused an increase of the interfacial shear strength for about 35 % as compared to non sized embedded fibre.

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Chapter 7. Polymer bearing UV polymerizable groups.

Introduction:

The surface modification of textile fibres has been an active and important field of research and industrial development since the introduction of synthetic fibres. A large number of methods have been described in the literature, e.g. surface oxidation by oxygen plasma introduces hydroxyl, carboxyl and ketone groups, ammonia plasma introduces ammonium groups on the surfaces.[1,2,3] Other methods include surface coating with or without chemical bonding to the fibre surface. The objective of the treatments is to make the inert and hydrophobic fibre surface more hydrophilic. High energy radiations like γ ray and electron beams have been applied to change the fibre surface. [4] In presence of monomer and photoinitiator, the irradiation initiates the polymerization by free radical or ionic mechanisms. The limitation to this treatment is that the radiation penetrates the bulk polymer and affects the mechanical properties. Chemical methods are found to be better and more specific. Surface radicals on the fibres can be introduced by peroxide, redox or azo dye systems and can be subsequently reacted with monomers.[5,6] Oster and coworkers[7,8] and Stannett and coworkers[9,10] were first to introduce the photochemical methods for polymer modification. In most of the photo-initiated surface modification, the grafting efficiency is low and irradiation time usually too long for industrial applications.[11,12] Photo-grafting has proven to be highly effective and attracted attention due to its significant advantages: easy and controllable operations, low cost, mild reaction conditions, potentially reducing or even avoiding negative effects on the bulk polymer. In 1983, Ranby et al. developed two new approaches for photo-initiated surface grafting, (i) a batch process for films where the initiator and monomer are transferred through vapour phase during UV irradiation[13], and (ii) a continuous process[14] for films, fibres and yarns of any polymer where the substrate is pre-soaked in a solution of monomer and initiator and then UV irradiated in an inert atmosphere. The grafting takes place in the thin layer of solution on the surface of the substrate.

The prepolymer concept is a widely used for preparation of crosslinked materials. The advantage of prepolymer is (i) polymerization and crosslinking are independent steps; (ii) it does not contain any toxic monomers and can therefore be handled under less stringent conditions; and (iii) the properties of the prepolymer can be tailored offering potential for applications like coatings. In the present study a prepolymer containing cationic and photo-polymerizable groups will be prepared by polymer analogous reaction of a branched

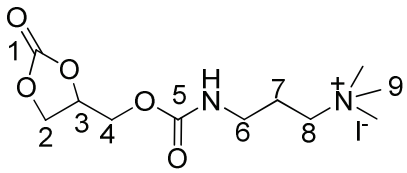
polyethylenimine (b-PEI) with amino reactive couplers.[15,16,17] It is well known that polymer containing quaternary ammonium groups adsorb well on carbon fibres due to electrostatic forces.[18] Furthermore, photo-grafting onto the prepolymer coated oxidized carbon fibre using continuous method will be described.

Materials and Methods:

Materials

Allylamine (Aldrich, 98%), diallylamine (Aldrich, 99%), dodecylamine (Aldrich 96%), triethylamine (Aldrich, 99.5%), 4-hydroxybenzophenone (Aldrich, 98%), 1,6 dibromohexane (Aldrich, 98%), heptadecafluorodecyl methacrylate (Aldrich, 97%), (2-Oxo-1,3-dioxolan-4-yl)methyl phenyl carbonate (Chapter – 3), oxiran-2-ylmethyl phenyl carbonate (Chapter -3), Poly(ethylene imine) (b-PEI, M_w approx. 25000 by light scattering (LS), M_n approx. 10,000 by gel permeation chromatography (GPC), water free, Aldrich). All solvents were distilled before using.

*N,N,N-trimethyl-3-({[(2-Oxo-1,3-dioxolan-4-yl)methoxy]carbonyl}amino)propan-1-amonium iodide (**QI**)*[17]



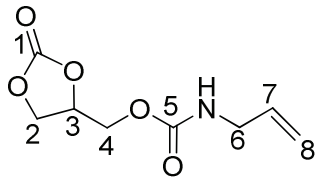
In a two- necked 250 ml round bottomed flask, (2-oxo-1,3-dioxolan-4-yl)methyl phenyl carbonate (10 g, 42.01 mmol) was dissolved in 100 ml dry THF. The reactants were cooled to 0^oC and the solution of 3-dimethylamino-1-propylamine (4.29 g, 42.01 mmol) in 21 ml dry THF was slowly added using a dropping funnel and the temperature was maintained around 0^oC. The reaction were stirred at this temperature for 2 h and then stirred at room temperature for 14 h. Then the solution of iodomethane (11.92 g, 84 mmol) in 60 ml dry THF was dropped slowly to the above mentioned reaction for 2 hours. The reaction mixture was stirred at this temperature for 2 h and then stirred for an additional 1 h at 50 ^oC. The product was filtered and subsequently washed with THF (10 ml X 3) times. The crude product was dried under high vacuum 10^{-2} mbar to afford light yellow solid.

Yield: 15.5 g (95% of theory).

^{1}H-NMR(DMSO-d_6): δ = 1.74-1.95 (m, 2H, H^7), 3.00 - 3.20 (m, 11H, H^6, H^9), 3.25 - 3.45(t, 2H, H^8), 4.10-4.34(m, 3H, H^2,, H^4), 4..59 (t, ^2J = 8.54 Hz, 1H, H^2), 4.96-5.14 (m, 1H, H^3), 7.39(t, ^3J = 5.6 Hz, 1H, NH) ppm.

^{13}C-NMR(DMSO-d_6): δ = 22.9 (C^7), 37.3 (C^6), 52.3 (C^9), 63.2 (C^8), 66.1 (C^2), 66.9 (C^4), 74.7(C^3), 154.7 (C^5), 155.6 (C^1) ppm.

*(2-Oxo-1,3-dioxolan-4-yl)methyl allylcarbamate (**AA**)*



In a two- necked 250 ml round bottomed flask, (2-Oxo-1,3-dioxolan-4-yl)methyl phenyl carbonate (20 g, 84.02 mmol) was dissolved in 200 ml dry THF. The solution was cooled to 0 ^{o}C and a solution of allyl amine (5.74 g, 100 mmol) in 40 ml dry THF was slowly added using a dropping funnel and the temperature was maintained around 0^{o}C. The reaction was stirred at this temperature for 2 hours and then stirred at room temperature for 14 hours. The crude product was concentrated under vacuum and was purified by column chromatography over silica gel (Ø – 5cm, SiO_2 Length – 50cm) (ethyl acetate/n-hexane, 1:1) to afford a white solid. Yield : 16.2 g (96 % of theory).

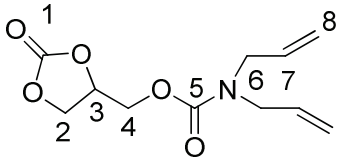
Anal. calcd. for $C_8H_{11}NO_5$: C 47.49, H 5.47, N 6.96 %; found: C 47.65, H 5.49, N 6.89 %.

^{1}H-NMR ($CDCl_3$): δ = 3.78 (t, ^3J = 5.64 Hz, 2H, H^6), 4.20-4.65 (m, 4H, H^2 & H^4), 4.88 - 5.03 (m, 1H, H^3), 5.05 - 5.30 (m, 2H, H^8), 5.60 (s, 1H, NH), 5.70 – 5.90 (m, 1H, H^7) ppm.

^{13}C-NMR ($CDCl_3$): δ = 43.4 (C^6), 63.5 (C^2), 66.1 (C^4), 74.6 (C^3), 116.1 (C^8), 134.1 (C^7), 154.9 (C^5), 155.6(C^1) ppm.

IR (KBr pellet) = 3328, 3080, 3016, 2979, 2925, 2780, 1815, 1782, 1692, 1645, 1536, 1480, 1458, 1420, 1388, 1345, 1250, 1182, 1153, 1089, 1047, 989, 958, 923, 865, 773, 712, 645, 458 /cm^{-1}.

*(2-oxo-1,3-dioxolan-4-yl)methyl diallylcarbamate (**2**)*



In a two neck 100 ml round bottom flask, diallyl amine (2.15 g, 22.2 mmol) and triethylamine (TEA) (2.24 g, 22.2 mmol) were dissolved in 22 ml chloroform. The solution of (2-oxo-1,3-dioxolan-4-yl)methyl carbonochloridate (4.0 g, 22.2 mmol) in 16 ml chloroform was slowly added using dropping funnel at room temperature and stirred for 3 hours. The solid formed during the reaction was filtered off and the obtained filtrate was extracted with 1 % HCl solution (3 X 20 ml) and finally with the brine solution. The organic phase was dried over

anhydrous Na_2SO_4. After removal of solvents under vacuum, the diallyl carbonate coupler was obtained as colorless oil.

Yield : 4.4 g (85 % of theory).

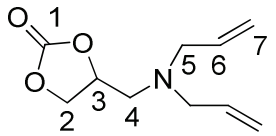
Anal. calcd. for $C_{11}H_{11}NO_5$: C 54.77, H 6.27, N 5.81 %; found: C54.35, H 6.23, N 5.80 %.

^{1}H-NMR ($CDCl_3$): δ = 3.85 (t, ^3J = 5.64 Hz, 4H, H^6), 4.20-4.65 (m, 4H, H^2 & H^4), 4.90 - 5.00 (m, 1H, H^3), 5.05 - 5.30 (m, 4H, H^8), 5.70 – 5.90 (m, 2H, H^7) ppm.

^{13}C-NMR ($CDCl_3$): δ = 48.7, 49.5 (C^6), 64.1 (C^2), 65.9 (C^4), 74.3 (C^3), 116.8, 117.6 (C^8), 132.8 (C^7), 154.5 (C^5), 155.1 (C^1) ppm.

IR (KBr pellet) = 3328, 3080, 3016, 2979, 2925, 2780, 1815, 1782, 1692, 1645, 1536, 1480, 1458, 1420, 1388, 1345, 1250, 1182, 1153, 1089, 1047, 989, 958, 923, 865, 773, 712, 645, 458 /cm^{-1}.

*4-((diallylamino)methyl)-1,3-dioxolan-2-one (**3**)*



In a two-necked 100 ml flask equipped with a condenser, oxiran-2-ylmethyl phenyl carbonate (2 g, 10.30 mmol) and diallyl amine (2 g, 20.60 mmol) were dissolved in 15 ml THF and the reaction was carried out for 24 hours at 60 ^oC. The crude product was extracted with 1 % HCl solution (5 ml X 3 times) and once with brine solution. The organic phase was dried over Na_2SO_4. After removal of solvents under vacuum, the functionalized coupler was obtained as colorless oil.

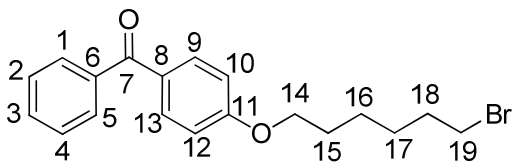
Yield : 1.4 g (70 % of theory).

Anal. calcd. for $C_{10}H_{15}NO_3$: C 60.90, H 7.67, N 7.10 %; found: C 61.20, H 7.82, N 7.05 %.

^{1}H-NMR ($CDCl_3$): δ = 3.85 (t, ^3J = 5.64 Hz, 4H, H^5), 4.20-4.60 (m, 4H, H^2 & H^4), 4.90 - 5.00 (m, 1H, H^3), 5.05 - 5.30 (m, 4H, H^7), 5.70 – 5.90 (m, 2H, H^6) ppm.

^{13}C-NMR ($CDCl_3$): δ = 48.7, 49.4 (C^5), 64.1 (C^2), 66.0 (C^4), 74.3 (C^3), 116.7, 117.5 (C^7), 132.8 (C^8), 154.5 (C^5), 155.0 (C^1) ppm.

*{4-[(6-Bromohexyl)oxy]phenyl}(phenyl)methanone (**PI**)*



A 3-necked round-bottomed flask equipped with a mechanical stirrer and a reflux condenser was charged with 500 ml cyclohexanone. The apparatus was flushed with nitrogen, and under

vigorous stirring 4-hydroxybenzophenone (50.00 g, 250 mmol) and 1,6 dibromohexane (125 g, 512 mmol) were added and dissolved in the solvent. Subsequently potassium iodide (1 g) and potassium carbonate (52 g, 375 mmol) were added with vigorous stirring. The viscous solution was refluxed at 190^{o}C for 5 h. The reaction was monitored with the help of TLC (KG-60 silica gel plate, hexane: ethyl acetate-6:1). The solid was separated by hot filtration and the solvent was removed from the filtrate in the rotary vacuum evaporator to give a viscous solution. The photoinitiator was purified by recrystallization from ethanol (1:5l) to yield white solid.

Yield: 65.8 g (71% of theory).

Anal. calcd. for $C_{19}H_{21}BrO_2$: C 63.17, H 5.86, N 0.00 %; found: C 63.08, H 5.53, N 0.01 %.

^{1}H-NMR ($CDCl_3$): δ = 1.44-1.60 (m, 4H, H^{16}& H^{17}), 1.75-1.96 (m, 4H, H^{15}& H^{18}), 3.42 (t, ^{2}J = 6.75 Hz, 2H, H^{19}), 3.42 (t, ^{2}J = 6.37 Hz, 2H, H^{14}), 6.80 – 7.80 (m, 9H, phenyl) ppm.

^{13}C-NMR ($CDCl_3$): δ = 25.2 (C^{16}), 27.8 (C^{17}), 28.9 (C^{18}), 32.6 (C^{15}), 33.7 (C^{19}), 67.9 (C^{14}), 113.9 (2C, C^{12}, C^{10}), 128.1 (2C, C^{2}, C^{4}), 129.6 (2C, C^{1}, C^{5}), 129.9 (C^{8}), 131.8 (C^{3}), 132.5 (2C, C^{9}, C^{13}), 138.2 (C^{6}), 162.7 (C^{11}), 195.4 (C^{7}) ppm.

IR (KBr pellet) = 3433, 2938, 2861, 1651, 1600, 1576, 1507, 1445, 1419, 1316, 1281, 1255, 1173, 1149, 1114, 1027, 938, 923, 846, 794, 741, 701, 637, 624 / cm^{-1}.

*Reaction of photoinitiator (**PI**) with **b-PEI*** **(PEI_{25K}-PI)**

In a two - neck round bottom flask equipped with the condenser, 1 g of b-PEI was reacted with photoinitiator (83 mg, 0.23 mmol) in 10 ml DMF for 16 h under nitrogen atmosphere. After addition of 40 ml of hexane, the formed two phase system was stirred vigorously for 15 min. The upper layer consisting of hexane and DMF was removed by decantation. The procedure was repeated many times until bottom layer became viscous. The polymer was dried under vacuum and was obtained as viscous liquid. The reaction was monitored by TLC using chloroform as a solvent. Note, that **b-PEI** is UV inactive whereas **PI** is UV active. At the start of the reaction, two different spots could be seen on TLC plate. As the reaction proceeded, the UV active spot due to **PI** disappeared and spot due to **b-PEI** turned UV active indicating that **PI** was covalently bonded to the polymer. Yield: 830 mg (84% of theory).

*Reaction of N,N,N-trimethyl-3-({[(2-Oxo-1,3-dioxolan-4-l)methoxy]carbonyl}amino)propan-1-amonium iodide (**QI**), (2-Oxo-1,3-dioxolan-4-yl)methyl allylcarbamate (**AA**) and photoinitiator (**PI**) with **b-PEI*** **(PEI_{25K}-QI_{15}-AA_8-PI_1)**

In a two-neck flask equipped with the condenser, **b-PEI** (2.58 g), **QI** (3.49 g, 9 mmol), **AA** (0.96 g, 4.8 mmol) and **PI** (216 mg, 0.60 mmol) were dissolved in 70 ml DMF and the reactants were stirred at 50 ^{o}C for 18 h. The crude product was precipitated in a 1:1 (vol : vol) mixture of hexane and diethylether (500 ml). The polymer was re-dissolved in 10 ml methanol, stirred vigorously for 15 min and re-precipitated in the above mentioned non-solvent. After repeating the cycle for 3 times the solvent was removed and the product was dried (room temperature, 24 h) at 1.3 Pa to yield a white solid.

Measurements

^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker DPX-300 FT-NMR spectrometer at 300 MHz and 75 MHz respectively. Chloroform-d ($CDCl_3$) and dimethylsulfoxide-d_6 (DMSO- d_6) were used as solvents, and tetramethylsilane (TMS) was used as internal standard.

The infrared spectra were measured on a Thermo Nicolet Nexus 470 spectrometer with a re-solution of 4 cm^{-1}. The samples were prepared as KBr pellets for the measurement in trans-mission mode.

The hydrodynamic diameter of the macromolecules was determined on a Zetasizer NanoZS ZEN3500 dynamic light scattering system. The concentration of the polymer was 1 – 10 g/L in 0.5M sodium nitrate solution.

Differential scanning calorimetry (DSC) was performed with a Netzsch DSC 204 under ni-trogen atmosphere with a heating rate of 10^{o}C/min. Calibration was achieved using indium standard samples, the sample mass was kept between 5 – 15 mg.

Carbon, hydrogen and nitrogen elemental analyses were performed on a Hearaeus CHN-O Rapid Elementar Vario El instrument.

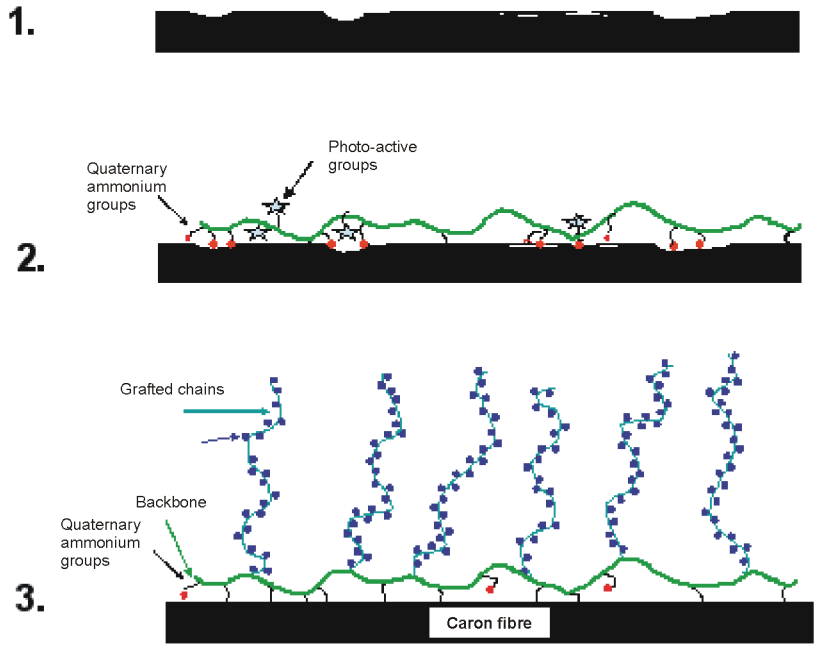
The elemental composition of the various carbon fibre samples was analyzed with the AXIS His, 165, Ultra device from Kratos Analytical. Elements of investigated surfaces were excited with monoenergetic aluminium $K_{1,2}$ irradiation with an energy of 1486.6 eV and power of 150W.

To prepare Quat-Primer sized carbon fibres the commercially obtained carbon fibre roving was treated with continuous oxygen plasma machine. The fibre was put on a roller (length : 35 cm, Ø – 9 cm) and evacuated in a plasma discharger, AK 550 Roth and Rau to a pressure of 10^{-3} bar. The following parameters were used: O_2 gas flow, 100 ft^3 / min; working pressure

= 1 mbar, microwave power = 150 W, motor speed = 4 m/min. Immediately after the plasma treatment, the fibres were dip-coated in a solution of **PEI_{25K}-QI_{15}-AA_8-PI_1** (0.1 wt% polymer) in methanol (weight of fibre : volume of polymer solution - 300 mg : 15 mL) and were dried under vacuum (14 h, 50 ^{o}C, membrane pump).

Results and Dsicussions:

The goal of the study was to prepare a universal primer system for carbon fibres. The primer should be polymeric compound and should bear (i) quaternary ammonium groups which bind by multiple ionic interactions onto oxidized carbon fibre surfaces, and (ii) unsaturated and (iii) photo-active groups. On application of the primer on the carbon fibre, a subsequent photochemical modification step can be accomplished at any later time and thus, different monomers or polymeric compounds could be grafted, depending on the intended application (Scheme 7.1).



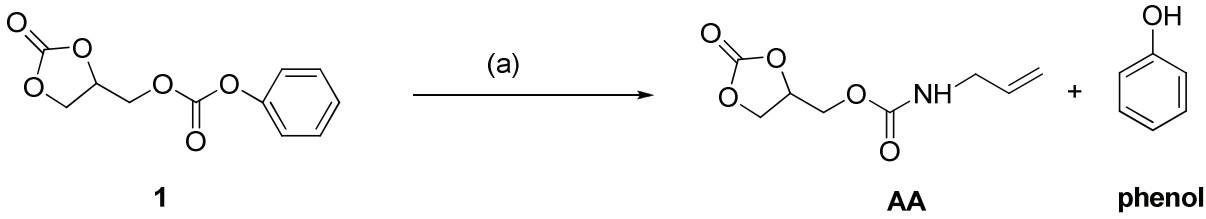
Scheme 7.1: Schematic representation of the primer system. In the first step (**1.**) the carbon fibres surfaces are slightly oxidised by an oxidative treatment (O_2 plasma). In the second step (**2.**) a cationic polymer compound is applied, which contains unsaturated and / or photo-active groups beside the quaternary ions. In the third step (**3.**) a ultra thin monomer/polymer layer isgenerated, which is covalent bound to the primer sublayer after exposure to ultra violet radiation.

The synthetic strategy was to prepare the required polymers by polymer analogous reaction between a polyamine and low molecular weight reactive compounds. To prepare such polymeric primers hyperbranched polyethylenimine (b-PEI) was selected as a functional polymer for post functionalization. It consists of primary, secondary and tertiary amino groups which could be selectively functionalized with different couplers.[19] The synthesized

couplers should bear amino reactive groups and quaternary ammonium groups or unsaturated groups.

Synthesis of couplers

The synthesis of such couplers containing unsaturated groups started from (2-oxo-1,3-dioxolan-4-yl)methyl phenyl carbonate (**1**). The reaction was carried out on the principle already described in the literature.[17] The dicarbonate coupler (**1**) contain two electrophilic sites with different reactivities. At low temperature (0 – 25 ^{o}C), a highly reactive phenyl ester carbonate reacts with one mole of amine whereas the five – membered cyclic carbonate ring remains unreacted. Based on this principle, the dicarbonate (**1**) was reacted with equimolar amount of allyl amine to obtain allyl – cyclic carbonate linker (**AA**) in nearly quantitative yield (cf. Scheme 7.2). Note, that this reaction releases phenol as a side product. It was possible to remove phenol by washing with 1% HCl solution and subsequent extraction of the product with diethylether but the yield of the desired product was 50% as the coupler 2 is water soluble. To obtain compound **AA** in the good yield, it was purified by column chromatography as explained in the experimental procedure.



Scheme 7.2. Synthesis of allyl – cyclic carbonate linker **2.** (a) allylamine, THF, 0 ^{o}C, 16h.

Figure 7.1 shows the ^{1}H-NMR and ^{13}C-NMR spectra of coupler **AA**. The signals due to allyl groups in the region δ = 5 – 6 ppm and due to formation of urethane groups (δ = 7.2 – 7.5 ppm) indicate that the coupler was synthesized successfully. Moreover, no signal originating from phenol which is formed as a side product during the reaction was observed.
The above mentioned strategy from coupler **1** is limited to primary amines. Moreover, it is difficult to obtain the product in good yield by extraction techniques. Another approach is to start from (2-oxo-1,3-dioxolan-4-yl)methyl chloroformate. This coupler also contains a five membered cyclic carbonate ring but instead of the phenyl ester carbonate it bears the more reactive chloroformate group which can react with primary as well as secondary amines. At room temperature the chloroformate reacts with a secondary amine leaving the cyclic

carbonate ring unreacted. In this method an auxiliary base has to be added to trap HCl which is formed during reaction.

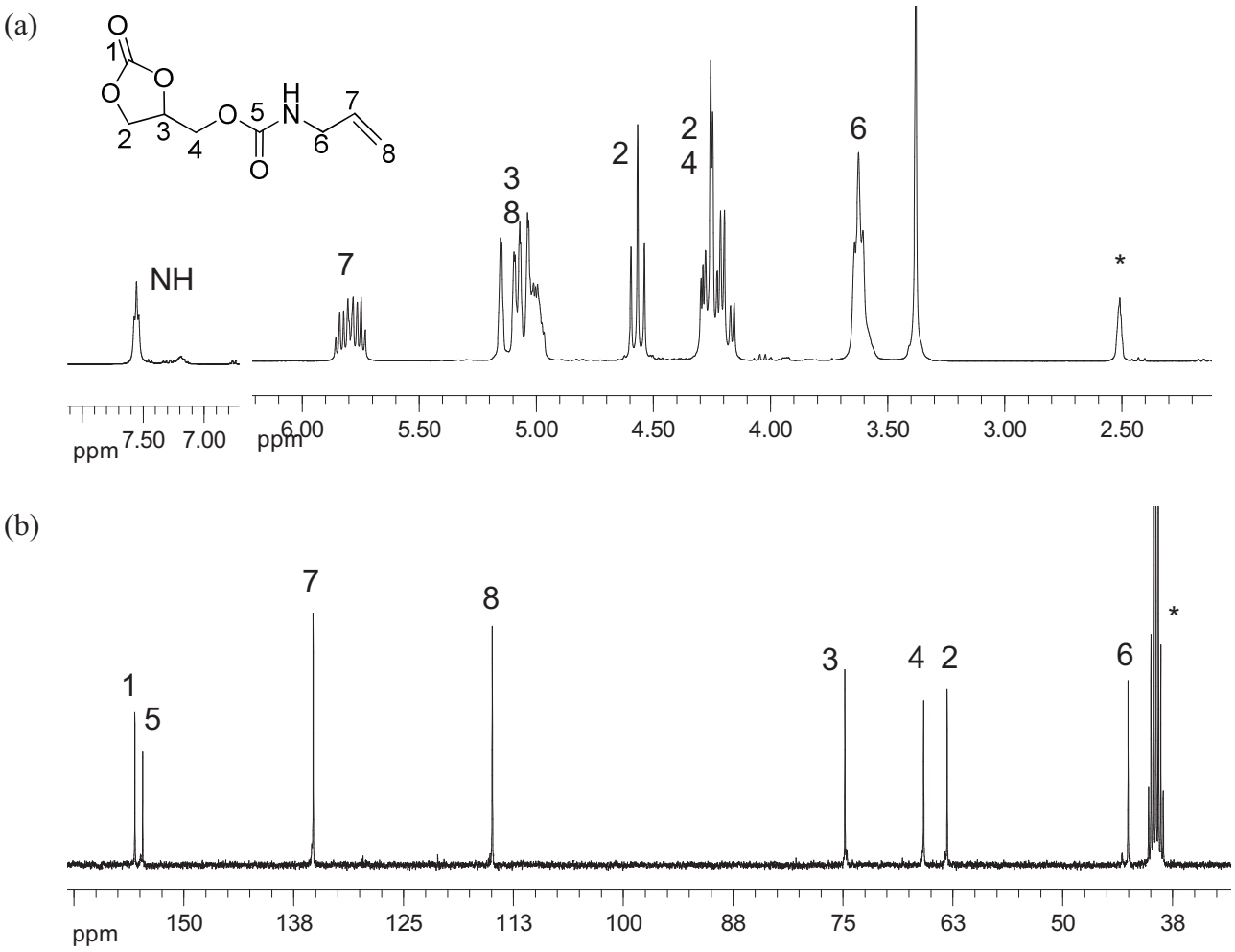
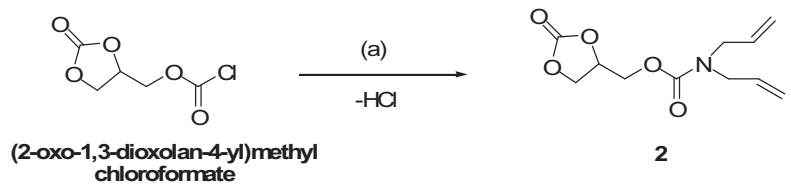


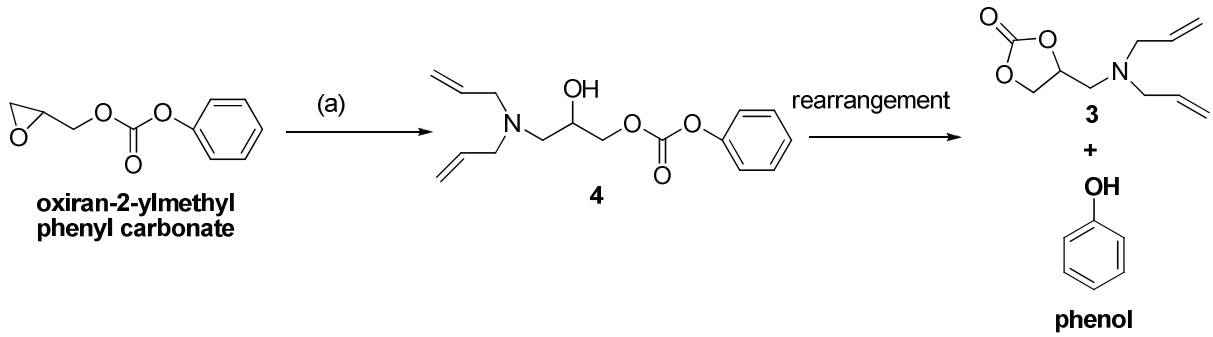
Figure 7.1. (a)^{1}H-NMR and (b)^{13}C-NMR spectra of allyl – cyclic carbonate coupler (**AA**).



Scheme 7.3. Synthesis of diallyl – cyclic carbonate coupler **2**. (a) diallylamine, TEA, THF, R.T., 16 h.

Based on the above mentioned principle the chloroformate was reacted with equimolar amount of diallylamine and triethylamine (TEA) (cf. Scheme 7.3). The crude product was purified by filtration and extraction and the coupler **2** was obtained in good yield (85% of theory). Thus, using this route two allyl groups could be introduced per cyclic carbonate ring. The signals in the ^{1}H-NMR and ^{13}C-NMR spectra of coupler **2** were similar to that of coupler **AA**.

Another synthetic route to couplers having unsaturated groups starts from oxiran-2-ylmethyl phenyl carbonate. This coupler bears an epoxy and a phenyl ester group. It is well known that epoxy groups can react with primary, secondary and tertiary amines whereas the reactivity of phenyl ester carbonate is limited to primary amines. Based on this difference in reactivity, oxiran-2-ylmethyl phenyl carbonate was reacted with an excess amount of diallylamine (Scheme 7.4). The amine was used in excess to drive the reaction to completion. It was desired to obtain coupler **4** which contains two allyl and a phenyl carbonate group. Instead, due to the presence of a hydroxyl group, a rearrangement was observed (from ^{1}H-NMR and ^{13}C-NMR – Figure 7.2) which lead to the cyclization and formation of five membered cyclic carbonate ring. The signals for carbon 2, 3 and 4 are characteristic of cyclic carbonate ring. Phenol was formed as a side product. The coupler **3** was obtained by extraction from water as described in the experimental part.



Scheme 7.4. Synthesis of coupler **3**. (a) diallyl amine, THF, 60 ^{o}C, 24 h.

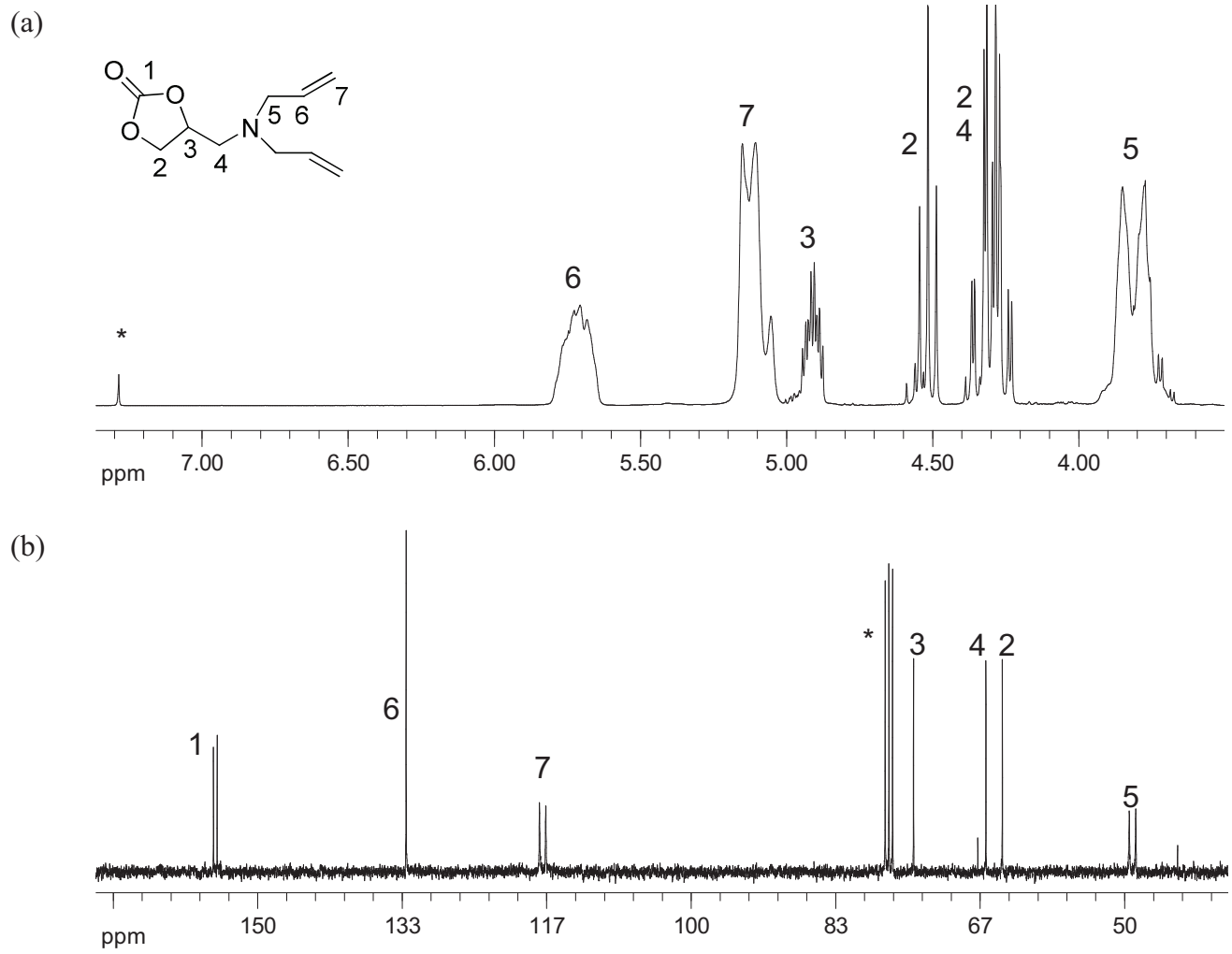
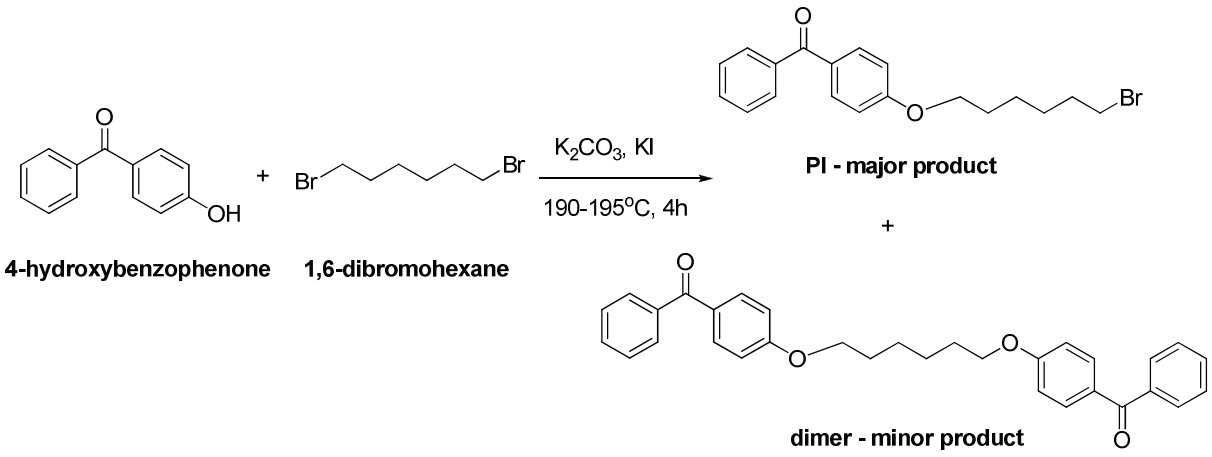


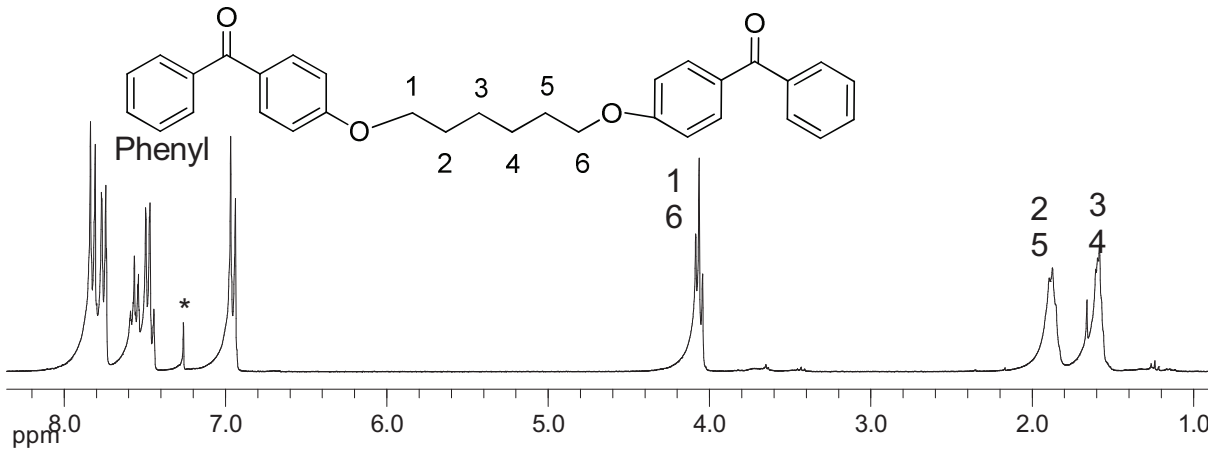
Figure 7.2. (a) ^{1}H-NMR and (b)^{13}C-NMR spectra of diallyl – cyclic carbonate coupler (**3**).

The photoinitiator (**PI**) was synthesized by reaction of 4-hydroxybenzophenone with an excess of 1,6-dibromohexane in the presence of K_2CO_3 and KI in the boiling cyclohexanone as a solvent at 190 – 195 ^{o}C for 4 hours (Scheme 7.5). The excess of 1,6-dibromohexane was added to limit the formation of 1,6-disubsituted hexanes ("dimmer"). The solution of the crude product was separated from inorganic salts by filtration and the purification of the obtained crude product was done by crystalliitzion from ethanol. At 0 ^{o}C the dimer crystallized, whereas at – 20 ^{o}C the crystals of photoinitiator (**PI**) were obtained.

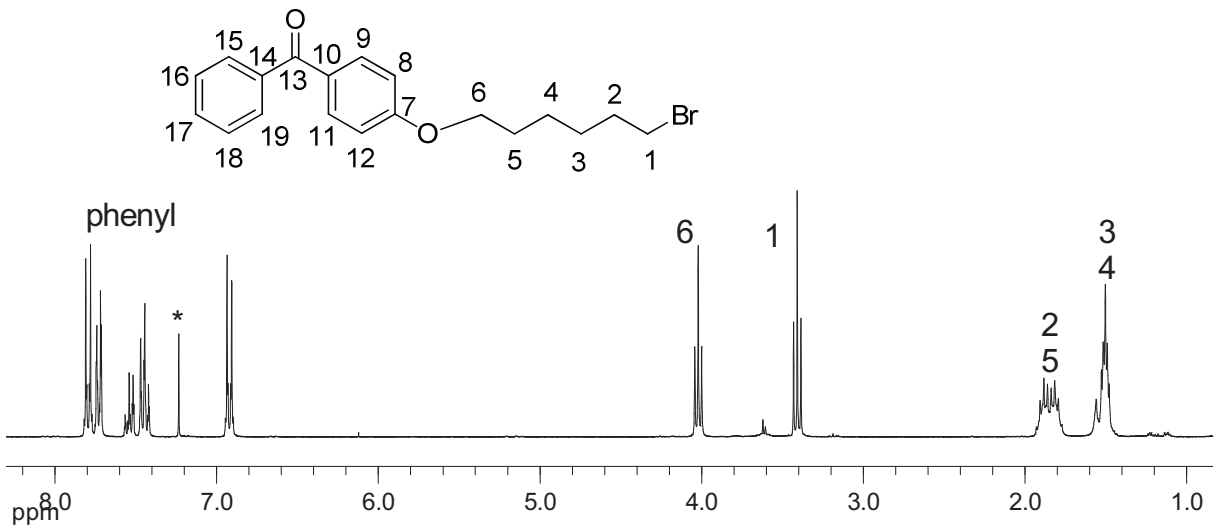


Scheme 7.5. Synthesis of photoinitiator (**PI**)

(a)



(b)



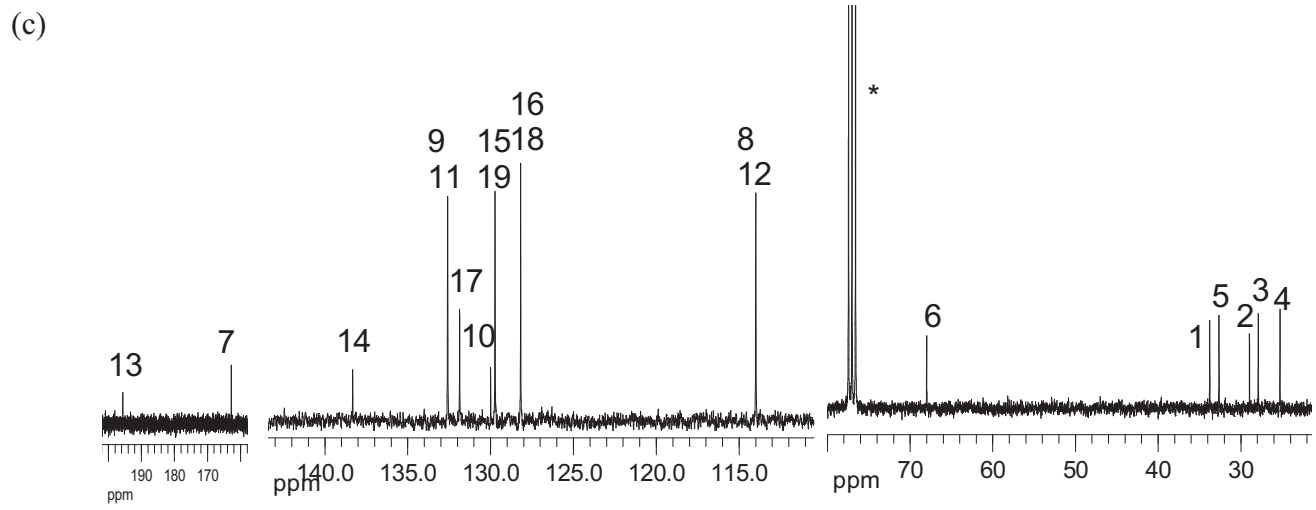


Figure 7.3. (a) ^{1}H-NMR of dimer, (b) ^{1}H-NMR and (b)^{13}C-NMR spectra photoinitiator (**PI**)

Figure 7.3a shows the ^{1}H-NMR spectra of the obtained dimer. The protons attached to carbon 1 and 6 exhibited only one signal (δ ~ 4 ppm) indicating that the dimer was formed, whereas in the ^{1}H-NMR of **PI**, two distinct signal of methylene groups 1 and 6 (δ ~ 3.3 and 4 ppm respectively) were found (Figure 7.3b).

Model Reaction

The aim was to covalently link the photoinitiator to the polyamine. Therefore a model reaction of the photoinitiator (**PI**) with equimolar amount of dodecylamine was carried out at 80 ^{o}C in ethanol for 16 hours. The crude product was purified by the crystallization from ethanol at – 20 ^{o}C. In Figure 7.4, ^{1}H-NMR of the product is illustrated.

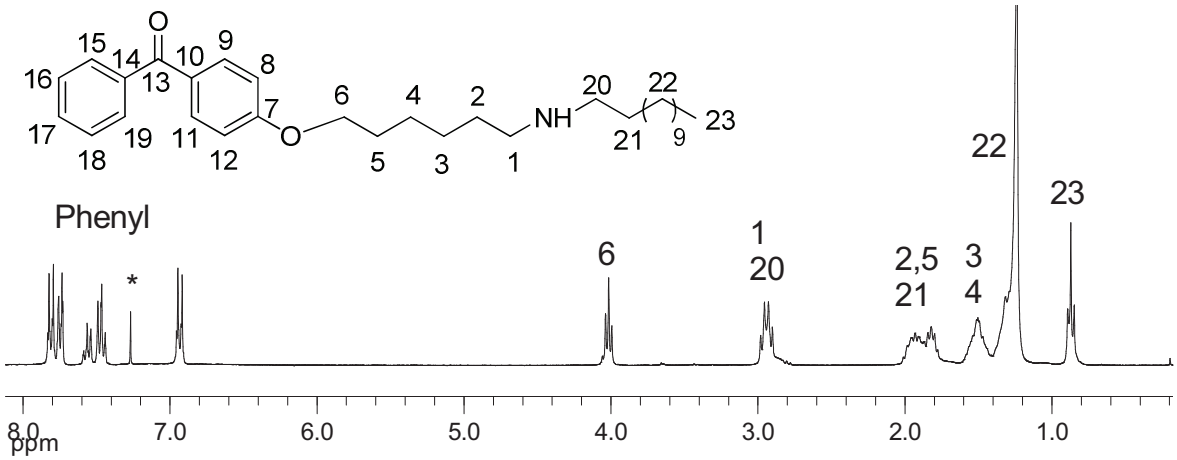


Figure 7.4. ^{1}H-NMR -model reaction of one mole of **PI** with dodecylamine at 80^{o}C in ethanol.

The shift in the frequency of hydrogen attached to carbon 1 of the alkyl amine (δ ~ 3.3 to 3.0 ppm) indicated the covalent linking of photoinitiator to the dodecylamine (Figure 7.4). The yield (70 % of theory) indicated that this reaction can be used to functionalize b-PEI with **PI** – moieties.

Structural Characterization of functionalized b-PEI

The terminal primary amino groups in b-PEI were modified with different carbonate couplers via polymer analogous reactions as described in the experimental part. The structure of **PEI_{25K}-QI_{15}-AA_8-PI_1** was investigated by means of ^{1}H-NMR, ^{13}C-NMR, IR and Raman spectroscopy. In the region of b-PEI backbone, two main signals were observed at δ = 2.5 ppm and 3.1 ppm in the ^{1}H-NMR spectrum (Figure 7.5a). The signal at δ = 2.5 ppm corresponds to the protons of the polymer backbone and to the protons of the methylene group in α and β positions of unreacted amine groups. The signal at δ = 3.1 ppm corresponds to protons of methylene groups in α position of the reacted amines. The ring opening reaction of cyclic carbonate ring with primary amines leads to the formation of urethane linkage. The signals (-NH- = 8, 8', 14, 14') could be seen well in the spectra. The ring opening reaction of cyclic carbonate with primary amine can lead to the formation of two isomers and their signals (10, 11, 12, 10', 11' and 12') could be easily identified in ^{1}H-NMR and ^{13}C-NMR (see Figure 7.5b). The signals at δ = 5.1 and 5.8 ppm (^{1}H-NMR) and δ = 117 and 135 ppm (^{13}C-NMR) corresponds to allyl groups present in polymer. The signals due to photoinitiator (**PI** – 1mole %) could also be identified in the ^{13}C-NMR spectra. It was difficult to calculate the degree of functionalization from the ^{1}H-NMR because of overlapping of the signals due to b-PEI backbone with DMSO. As mentioned, the polymer was obtained by precipitating into 1:1 mixture of diethyl ether and hexane. The coupler **QI** is also insoluble in this mixture of solvent and hence unreacted QI would precipitate along with the polymer. But, the signals due to unreacted cyclic carbonate ring were not observed; hence it was assumed that all the coupler has reacted with b-PEI. Moreover, by comparing the integrals (^{1}H-NMR) of signals 17A (**AA**) and 16Q (**QI**), the molar ratio of **QI** groups and **AA** groups was found to be 2:1 which is same as the feed molar ratio. Hence, it can be concluded that all the couplers have reacted with **b-PEI**.

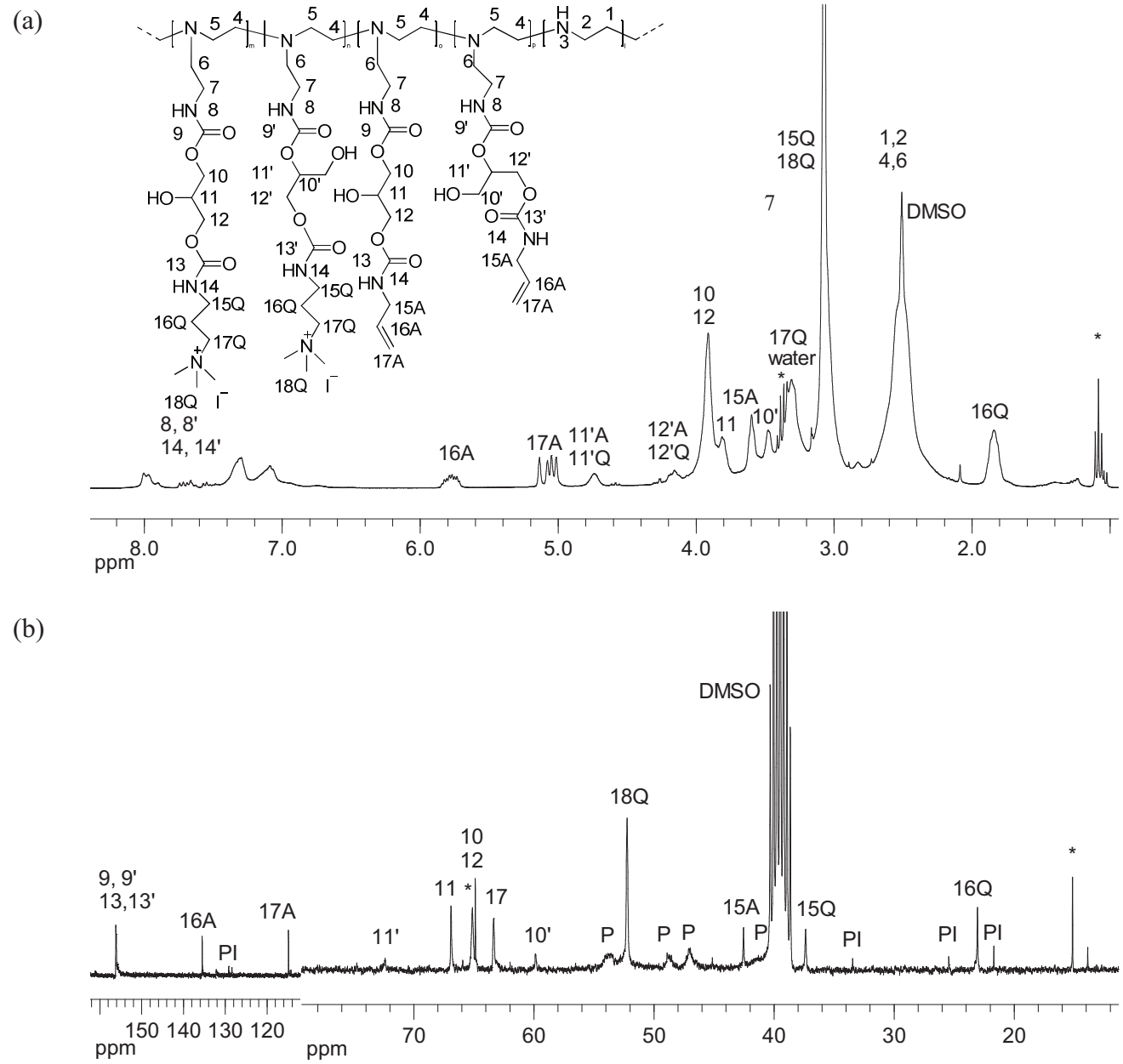


Figure 7.5. NMR spectra of **PEI_{25K}-QI_{15}-AA_8-PI_1** in DMSO-d6 (a) ^{1}H-NMR, (b) ^{13}C-NMR. (P = b-PEI backbone, PI = photoinitiator groups, * = diethyl ether

Figure 7.6 compares the infrared spectrum of **b-PEI** and **PEI_{25K}-QI_{15}-AA_8-PI_1.** The assignment of various peaks in b-PEI is presented in Table 7.1. The reaction of primary amino groups present in b-PEI with cyclic carbonate ring leads to the formation of urethane linkages. The band at 1709 cm^{-1} (amide-I), 1526 cm^{-1} (amide-II) and 1248 cm^{-1} (OC-N stretch) are characteristics of urethane linkage. Moreover, the band at 1791 cm^{-1} which is attributed to cyclic carbonate was found to be absent indicating that the couplers have reacted with b-PEI. **PEI_{25K}-QI_{15}-AA_8-PI_1** contains 8 mole % allyl groups but the peak could not be seen the IR spectra due to strong absorbance of carbonyl groups.

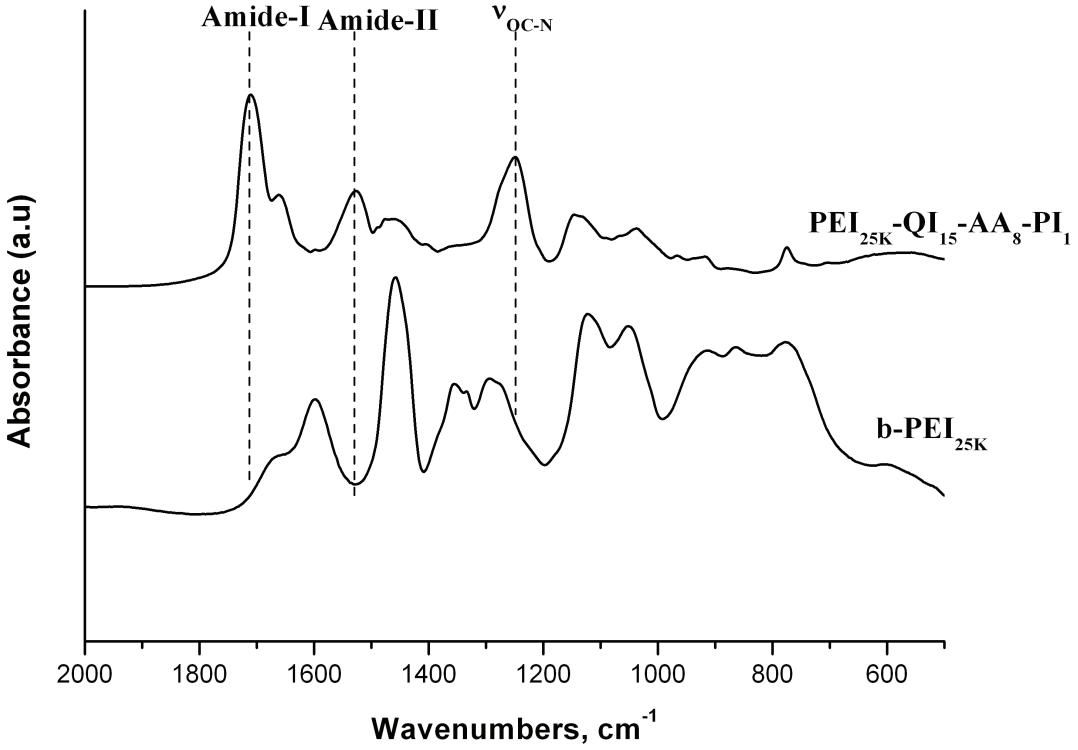


Figure 7.6. Infrared spectrum of **b-PEI** and **PEI_{25K}-QI_{15}-AA_8-PI_1.**

Table 7.1. Assignment of IR spectrum of **b-PEI**[20]

Wavenumber (cm^{-1})	**Assignment**
3300	OH, NH stetch
2940, 2861	CH stretch
1653	NH_2 bend
1598	NH bend
1457	CH_2 bend
1352, 1293	CH bend
1120, 1048	C-C, C-N stretch

Figure 7.7 shows the Raman spectra of **PEI_{25K}-QI_{15}-AA_8-PI_1**. The band at 3009 cm^{-1} (C-H stretch in unsaturated groups) and 1644 cm^{-1} (-C=C- stretch) confirms the presence of

unsaturated groups in the polymer. The band at 1597 cm^{-1} corresponds to the aromatic C=C stretch in **PI**.

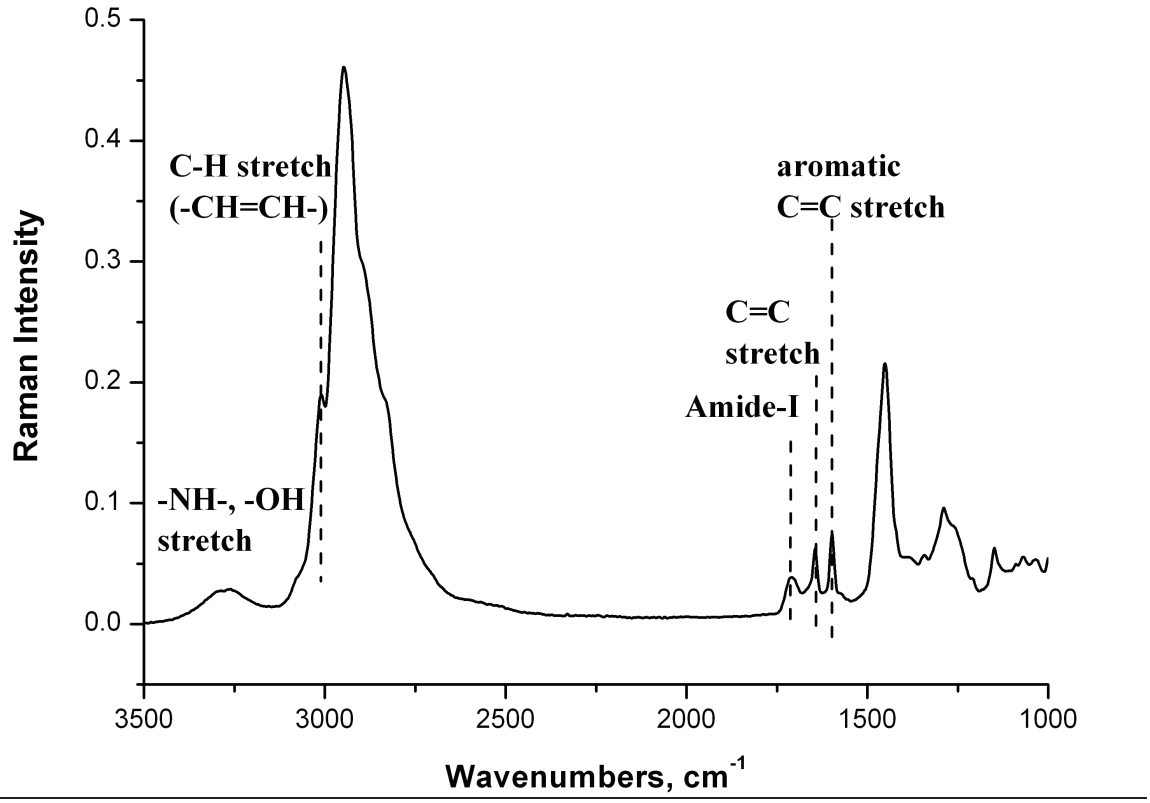


Figure 7.7. Raman spectra of $\mathbf{PEI_{25K}\text{-}QI_{15}\text{-}AA_8\text{-}PI_1}$.

Molecular Characterization of functionalized b-PEI

Figure 7.8 depicts the hydrodynamic diameter measurement performed in 0.5 M aqueous $NaNO_3$ solution to screen the coulomb interaction and to avoid polyelectrolyte effects. The measured hydrodynamic diameters were 10 nm and 4.3 nm for **b-PEI** and $\mathbf{PEI_{25K}\text{-}QI_{15}\text{-}AA_8\text{-}PI_1}$ respectively. Moreover, the width of peak in case of b-PEI was broader compared to the functionalized polymer. It is assumed that intramolecular hydrogen bonds between the introduced urethane-, and hydroxyl groups as well as the macromolecular amine groups cause the observed contraction.

Thermal Properties

DSC diagram of **b-PEI** and $\mathbf{PEI_{25K}\text{-}QI_{15}\text{-}AA_8\text{-}PI_1}$ displayed only glass transition temperature (Figure 7.9). The glass transition temperature of unmodified **b-PEI** was observed at – 53 ^oC whereas the T_g of $\mathbf{PEI_{25K}\text{-}QI_{15}\text{-}AA_8\text{-}PI_1}$ was found at 39.4 ^oC indicating that the polymer was successfully functionalized.

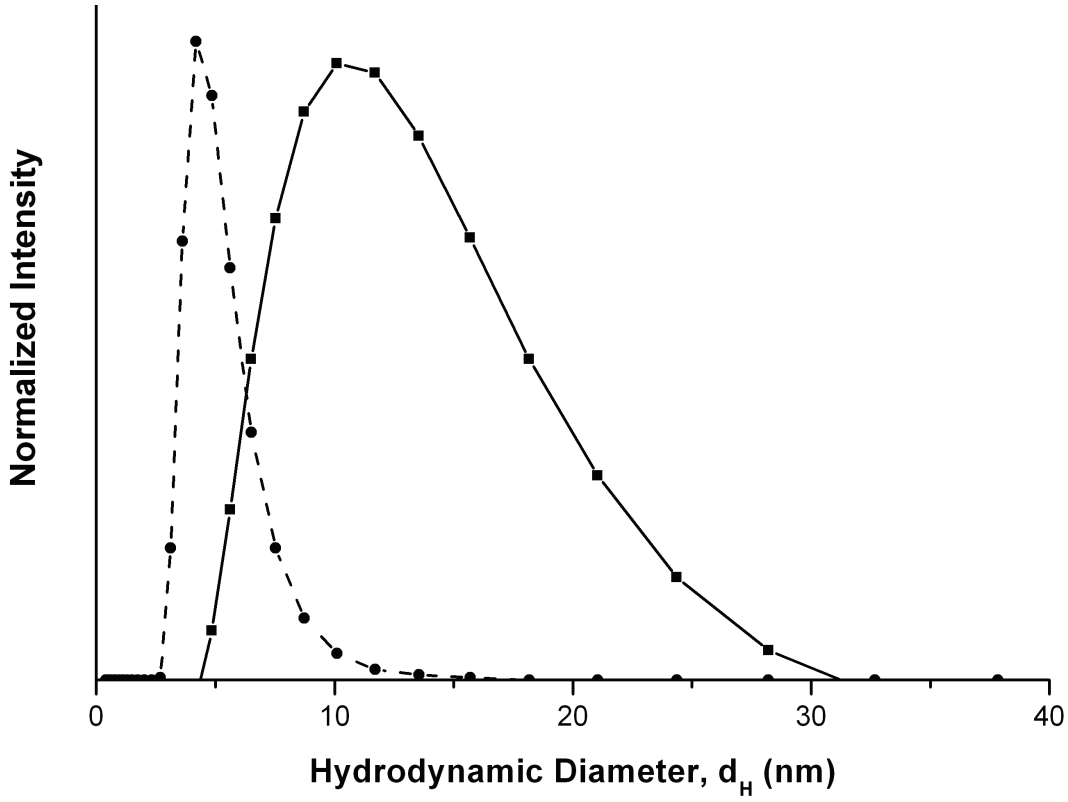


Figure 7.8. Hydrodynamic diameter distribution from dynamic light scattering of **b-PEI** (■) and **PEI_{25K}-QI_{15}-AA_8-PI_1** (●) measured at 25 °C in 0.5 M aqueous $NaNO_3$ solution.

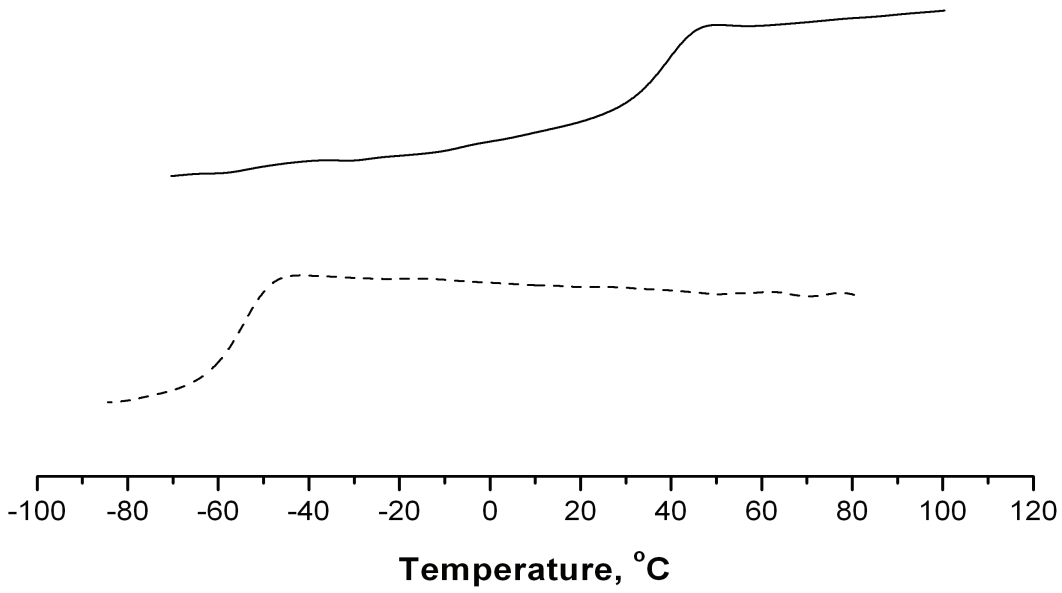


Figure 7.9. Differential Scanning Calorimetry under N_2 atmosphere of **b-PEI** (----and **PEI_{25K}-QI_{15}-AA_8-PI_1** (—)).

Cross-linking Experiments

PEI_{25K}-QI_{15}-AA_8-PI_1 contains 15 mole% of quaternary ammonium groups, 8% allyl groups and 1% photoinitiator groups. The obtained functionalized polymer was cross-linked photochemically in presence of ultra-violet light. It is known from previous studies that in a photochemical cross-linking, the extent of cross-linked material can be greatly increased on addition of a small amount of a low molecular weight cross-linking agent like diethyleneglycol dimethacrylate (DegDMA).[21] Therefore, the polymer (**PEI_{25K}-QI_{15}-AA_8-PI_1**), cross-linker (DegDMA) and photoinitiator (**PI**) (if more than 1 % is required, **PI** was added externally) were dissolved in methanol in different proportions and after evaporation of the solvent, the remaining film was irradiated for 8 h at a distance of 15 cm from the UV lamp. After UV irradiation the obtained polymer was washed with methanol to dissolve the uncross-linked part and the insoluble part was dried and weighed. The cross-linking results obtained as expressed by the yield of the gel phase are presented in Figure 7.10.

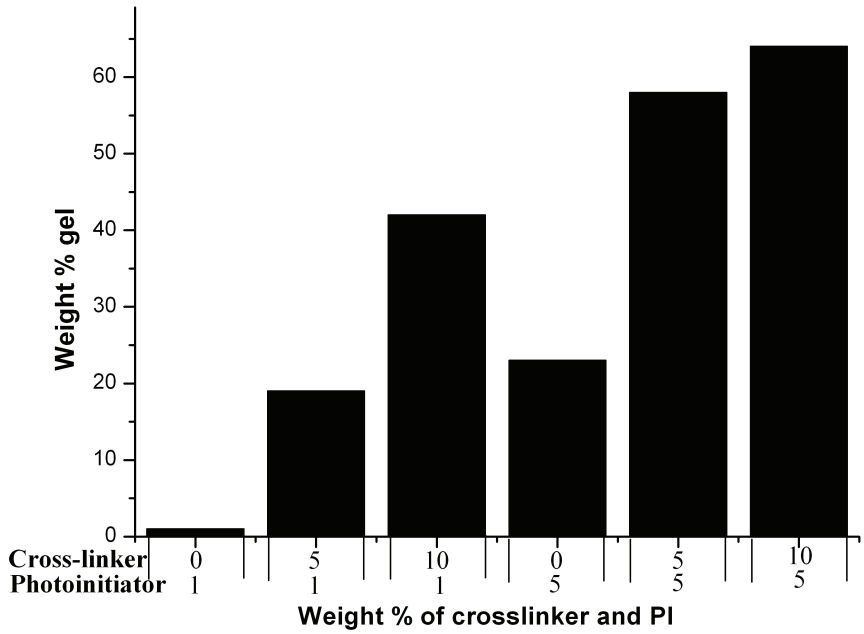


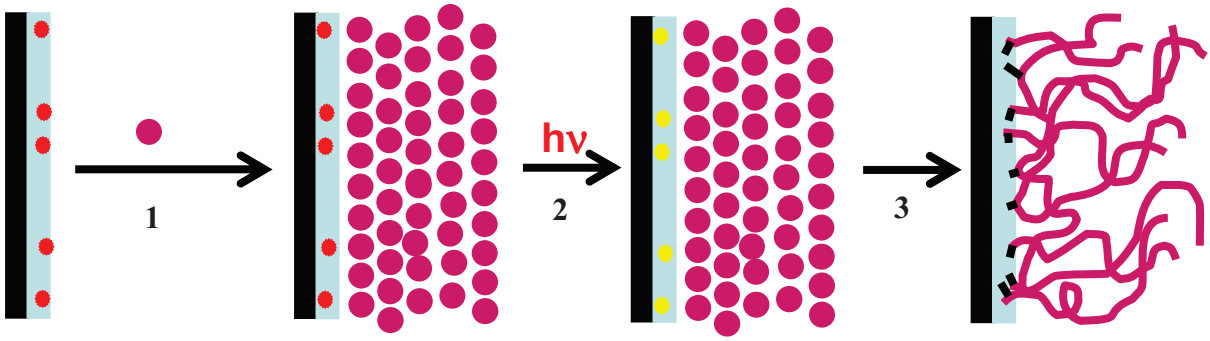
Figure 7.10. Photochemical cross-linking of **PEI_{25K}-QI_{15}-AA_8-PI_1** (15 mole % **QI**, 8 mole% **AA** and 1 mole% **PI**) using variable concentration of photoinitiator and low molecular weight cross-linking agent (DegDMA), irradiation time – 8h, wt % of DegDMA and **PI** are w.r.t mass of pre-polymer, weight % gel corresponds to total mass of cross-linked polymer.

In absence of DegDMA, 1% gel was formed by UV irradiation of **PEI_{25K}-QI_{15}-AA_8-PI_1**. An increase in concentration of photoinitiator from 1 to 10 wt % leads to an increase in the

amount of cross-linked gel. The maximum percentage of gel yield (63%) was observed when a mixture of the polymer with 10 wt% DegDMA and 5 wt% **PI** was irradiated under UV light. Due to autoinhibition of α olefins the homo-polymerization of allyl groups is difficult, thus irradiation of the polymer in the absence of a methacrylate cross-linker leads to a low degree of cross-linking. This particular fact is advantageous as oxidized carbon fibres can be coated with this polymer and can subsequently be stored or transported without danger of unwanted cross-linking. The cross-linking can be done at any stage whenever desired. This polymer can be used in the field of carbon fibre – epoxy resin composites. It is known from the previous experiments that there is strong adhesion between the polymer containing quaternary ammonium groups and oxidized carbon fibres. The **PEI_{25K}-QI_{15}-AA_8-PI_1** coated carbon fibres can be used to cross-link epoxy acrylate resin under UV light and the obtained composite should have improved interfacial properties.

Grafting Experiment

The objective was to graft a monomer or polymer onto the primer coated carbon fibre. The carbon fibres were oxidized and coated with **PEI_{25K}-QI_{15}-AA_8-PI_1** as described in the experimental part. The primer coated fibres were dipped into the solution of PI (1wt % w.r.t monomer), DegDMA (5 wt % w.r.t monomer) and heptadecafluorodecyl methacrylate (20 wt % solution in Freon) and were irradiated under UV 366 nm for 8h. The obtained fibres were washed in the Freon and dried.



Scheme 7.6. Grafting of polymer onto primer coated carbon fibre. (**1**) Oxidized carbon fibre coating with primer (**PEI_{25K}-QI_{15}-AA_8-PI_1**) is dipped into solution of monomer (methacrylate) and cross-linker. (**2**) UV irradiation – activation of **PI** groups. (**3**) polymerization of monomer which is covalently linked to primer.

Table 7.2. XPS-analysis of elemental composition of different carbon fibre systems.

Sample	Surface atomic concentration (%)				
	carbon	**oxygen**	**nitrogen**	**iodine**	**Fluorine**
Oxidized carbon fibre coated with **PEI_{25K}-QI_{15}-AA_8-PI_1**.	61.84	16.59	19.43	2.1	0
Grafting with heptadecafluorodecyl methacrylate	42.57	11.47	0	0	45.96

Table 7.2 compares the surface atomic concentration of primer coated carbon fibre and the carbon fibre obtained after grafting experiment. The presence of 19 % nitrogen and 2 % iodine indicates the presence of primer coating onto oxidized carbon fibre. In case of carbon fibre sample obtained after grafting experiment, the nitrogen and iodine were found to be absent whereas fluorine content was found to be 46 %.

Therefore, different monomers can be grafted onto primer coated fibres depending on the desired application. Moreover, the cross-linking should start from the bulk of the primer coating since the primer polymer contains covalently linked allyl and photoinitiator groups.

Conclusions:

The couplers containing allyl groups were successfully synthesized and characterized. The primary amino groups of poly(ethylene imine) have been functionalized with different couplers. A photoinitiator covalently linked to b-PEI was also obtained which acts as a macro-initiator that initiated polymerization under UV irradiation.

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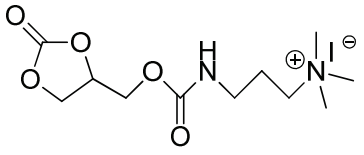
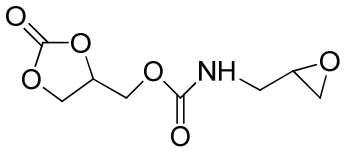
Summary:

The thesis is concerned with the synthesis of functionalized polymers prepared by ring opening reaction of various functionalized five-membered cyclic carbonates and epoxides couplers with branched polyethylenimine (b-PEI). Furthermore, depending on the functionality introduced in the polymer, the application of these modified polymers (i) as primers in carbon fibre - epoxy resin composite and (ii) UV curable coatings were also investigated.

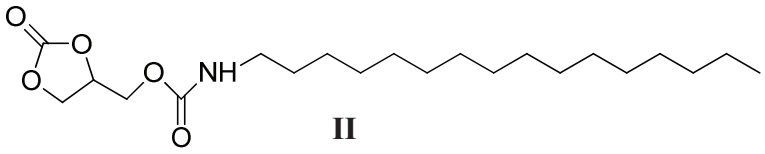
The primer polymers to be used in carbon fibre epoxy resin composites should serve two functionalities (i) to bind to the surface of carbon fibres via electrostatic forces of interactions or epitaxial adsorption or both and (ii) to supply cyclic carbonate groups that can copolymerize with the amine components of epoxy resins during the curing step.



I



III



II

Branched Polyethylenimine has primary, secondary and tertiary amino groups in the molar ratio of 31:39:30 respectively. The primary and secondary amines present in b-PEI can be selectively modified with different couplers. The strategy followed was based on difference in reactivity of secondary amine towards five-membered cyclic carbonate and epoxide ring. Five-membered cyclic carbonate reacts only with primary amine whereas epoxide ring can react with all primary, secondary and tertiary amine. The synthesis of the primer polymers is a two step process. In the first step all the primary amino groups in b-PEI were selectively

modified with coupler **I** or **II** or both. In the next step the secondary amine in modified b-PEI opens the epoxide ring present in the coupler **III** to obtain the desired functional polymers.

Due to structural similarity of the carbon fibre and graphite, highly oriented pyrolytihc graphite (HOPG) was used as model substrate. In order to study the adsorption behaviour of modified b-PEI's onto HOPG different parameters were varied: (i) length of alkyl chain (C8, 14 and C16), (ii) the molar ratio of cationic/alkyl groups and (iii) molecular weight of b-PEI. The adsorption behaviour of these polymers onto HOPG was studied by Scanning Force Microscopy (SFM). Upon deposition on HOPG rod like structure was observed and their confirmation was controlled by the surface coverage and by the two dimensional self-assembly of aliphatic chains. The amount of adsorbed material was found to increase with the length of the used alkyl chain and maximum adsorption was observed for the **C16** modified b-PEI. Furthermore, the degree of adsorption onto graphite decreased with the increase in amount of quaternary ammonium groups in the polymer.

These primer coatings were applied to carbon fibre and interfacial adhesion between carbon fibre and epoxy resin was demonstrated by well known Kelley Tyson Fragmentation test. The use of primer coating increased the interfacial shear strength by 25 % with respect to unsized fibre.

U.V. curable coatings prepared were also prepared based on b-PEI. These coatings can be obtained in one step synthesis by polymer analogous reaction with different kind of functional carbonates containing allyl groups with b-PEI.