Macromolecules **2008**, *41*, 8187−8197

'Quat-Primer' Polymers Bearing Cationic and Reactive Groups: Synthesis, Characterization, and Application

Vishal Goel, Uwe Beginn,* Ahmed Mourran, and Martin Möller

DWI an der RWTH Aachen e.V. and Institut für Technische and Makromolekulare Chemie der RWTH Aachen, Pauwelsstrasse 8, D-52056 Aachen, Germany

Received May 13, 2008; Revised Manuscript Received September 4, 2008

ABSTRACT: Subsequent treatment of branched poly(ethylene imine) with *N*,*N*,*N*-trimethyl-3-({[(2-oxo-1,3-dioxolan-4-yl)methoxy]carbonyl}amino)propan-1-ammonium iodide and either (2-oxo-1,3-dioxolan-4-yl)methyl-(oxiran-2-ylmethyl)carbamate or 4-[(oxiran-2-ylmethoxy)methyl]-1,3-dioxolan-2-one yielded 'quat-primer polymers' bearing quarternary ammonium and cyclic carbonate groups covalently linked to the macromolecule. ^{1}H and ^{13}C NMR spectroscopy with model reaction mixtures and the macromolecular products revealed that the quaternary ammonium groups were selectively attached to the primary amino groups of the polymeric educt. The new functional macromolecules were characterized further by means of DSC and TGA. Upon spin coating the cyclic carbonate groups containing cationic polymers on oxygen/argon plasma-pretreated highly oriented pyrolytic graphite (HOPG), scanning force microscopy revealed the presence of a 3 nm thick film covering the substrate. This ultrathin coating was persistent against extraction with methanol, demonstrating the adherence of the polymer on the substrate. Applied on carbon fibers the polymer layer improved the interfacial shear strength between the carbon fiber and an epoxy resin matrix by 35% with respect to nontreated carbon fibers as demonstrated by single-fiber fragmentation tests.

Introduction

Carbon fibers have become one of the most important reinforcing materials, being characterized by extremely high strength and modulus. Carbon fiber−epoxy composites are being used in numerous aerospace, marine, and recreational applications. The interface between reinforcing fibers 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 fiber. However, carbon fiber surface which has lower wettability and chemical activity causes the weak adhesion with epoxy matrix. A universal method to increase the surface polarity of carbon fibers is their surface modification, which increases the hydrophilicity of the fiber.[5] The oxidative methods for modification of carbon fiber surfaces includes oxidation in different plasmas,[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 fibers and concluded that the contribution to interfacial adhesion of covalent bonds formed between carboxylic groups present on the oxidized fiber surfaces and epoxide groups in the 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 an improvement in the interfacial strength the failure mode is no longer interfacial.[15] To have good adhesion between fiber and matrix, fibers 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 a wetting promotion function but is particularly important for facilitating fiber handling during composite manufacture, acting as a lubricant to prevent fiber damage.

Highly oriented pyrolytic graphite (HOPG) was used as a model substrate due to the structural similarity of the carbon fiber and HOPG. HOPG consists of a two-dimensional solid 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 the HOPG surface; 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, which allows variation of roughness in a well-defined way.[21−23] Surface functionalization of HOPG, using a low-energy plasma environment, was done in such a way that the treatment resulted in chemical groups being introduced at the outer layers of the surface. Scanning force microscopy (SFM) was used for surface characterization of primer-coated HOPG.

This study presents quat-primer functional polymers prepared by ring-opening reaction of functional five-membered cyclic carbonates with poly(ethylene imine).The function of the primer polymers is to (i) bind to the surface of carbon fibers via electrostatic forces of interactions and (ii) 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 has two electrophilic sites with different reactivity. At low temperatures (0−25 °C) the phenyl ester carbonate reacts with the first amine whereas the cyclic carbonate 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 over HOPG was studied by SFM, and the interfacial adhesion between functionalized carbon fiber-sized with quat-primer polymers and the epoxy matrix was carried out using the fragmentation test.

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%), *N*,*N*-dimethylpropane-1,3-diamine (Aldrich, 99%), iodomethane (Acros,

---

* To whom correspondence should be addressed. Present address: Institut für Chemie, Barbarastrasse 7, D-49069 Osnabrück. Phone: +49 451 969 2814. E-mail: ubeginn@uni-osnabrueck.de.

10.1021/ma801064e CCC: $40.75

99%), epichlorohydrine (Aldrich, 99%), 4-(hydroxymethyl)-1,3-dioxolan-2-one (Aldrich), 1,6-dibromo hexane (Aldrich, 96%), 4-hydroxybenzophenone (Ardrich, 98%), poly(ethylene imine) (PEI, $M_w \approx 25\,000$ by light scattering (LS), $M_n \approx 10\,000$ by gel permeation chromatography (GPC), water free, Aldrich), and tetraethylenepentamine (TEPA, Aldrich) were used as received. All solvents were distilled before use.

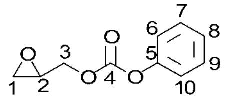
ZYB-grade high-ordered pyrolytic graphite was obtained from Advance Ceramics, Inc. Substrates were obtained by cleavage from adhesive tape just prior to plasma treatment.

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

Allyl Phenyl Carbonate.[27] In a three-necked round bottomed flask equipped with a 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 of dichloromethane (CH_2Cl_2) was cooled to 0 °C. Phenyl chloroformate (10.56 g, 67.45 mmol) was dropped in over a period of 1 h, and the reaction was stirred for an additional 3 h at room temperature. Twenty milliliters of water was added to the mixture, and the product was extracted with 50 mL of ether. The ether phase was washed twice with 1% HCl solution (2 × 20 mL), dried over Na_2SO_4, and concentrated in vacuum. The crude product was distilled in vacuum to give a colorless oil, bp 68−72 °C/10^{-2} mmHg. 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.

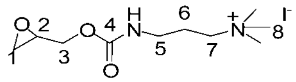
(2-Oxo-1,3-dioxolan-4-yl)methyl Phenyl Carbonate.[26] In a three-necked round bottomed flask glycerol carbonate (64.47 g, 546 mmol) and pyridine (47.46 g, 600 mmol) were dissolved in 660 mL of tetrahydrofuran (THF) under a nitrogen atmosphere. The solution was cooled to 0 °C. A phenylchloroformate (93.94 g, 600 mmol) solution in 120 mL of THF was slowly added, and the temperature was maintained around 0 °C. The reaction mixture was stirred at this temperature for 2 h and then stirred at room temperature for 14 h. Precipitated pyridine hydrochloride was removed by filtration. The filtrate was diluted with 200 mL of diethyl ether and washed with an 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 sulfate, and the solvent was removed by a rotary vacuum evaporator (20 mbar, 40 °C). The crude product formed was recrystallized from 350 mL of chloroform at 40 °C, and a fine colorless powder was obtained.



1

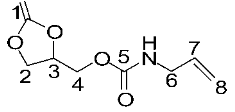
Oxiran-2-ylmethyl Phenyl Carbonate (1). Allyl phenyl carbonate (2.6 g, 14.59 mmol) and *m*-cPBA (6.29 g, 36.46 mmol) were dissolved in 30 mL of dichloromethane (CH_2Cl_2), and the solution was stirred for 48 h at room temperature. The precipitate of *m*-chlorobenzoic acid was filtered, and the filtrate was diluted with 20 mL of dichloromethane. Six grams of potassium carbonate was added to the organic phase and stirred for 15 min. The salt was removed by filtration, and the filtrate was concentrated by a rotary vacuum evaporator (500 mbar, 40 °C). Distillation (0.1 mbar, 95 °C) of the crude product resulted in the desired product. Yield: 2.0 g (71% of theoretical). 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. *m*/*z* = 77.1 (39.8), 94 (100), 107 (15.8), 120 (2.9), 194.1 ($M^{+\cdot}$). ^{1}H NMR ($CDCl_3$): δ 2.70 (td, ^2J = 13.27 Hz, ^3J = 6.64 Hz, ^3J = 6.64 Hz, 1H, H^1), 2.90 (t, 1H, H^1), 3.25−3.31 (m, 1H, H^2), 4.10 (dd, ^2J = 12.08 Hz, ^3J = 6.17 Hz, 1H, H^3), 4.51 (dd, ^2J = 12.08 Hz, ^3J = 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.

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 of tetrahydrofuran (THF) under a nitrogen atmosphere. The solution was cooled to 0 °C. A phenyl chloroformate (11.62 g, 74.25 mmol) solution in 15 mL of THF was slowly added, and the temperature was maintained around 0 °C. The contents were stirred at this temperature for 2 h and then stirred at room temperature for 14 h, and pyridine hydrochloride that was formed was removed by vacuum filtration. The filtrate was diluted with 10 mL of diethyl ether and 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 sulfate, and the solvent was removed by a rotary vacuum evaporator (20 mbar, 40 °C). The product was purified by column chromatography on silica gel (Ø, 2 cm; SiO_2 length, 50 cm) (ethyl acetate/*n*-hexane, 2:4) to afford a colorless liquid. Yield: 3.90 g (30% of theoretical).



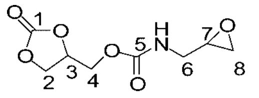
2

***N,N,N*-Trimethyl-3-{[(oxiran-2-ylmethoxy)carbonyl]amino}-propan-1-ammonium Iodide (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 of THF and cooled to 0 °C. The solution of *N,N*-dimethylpropane-1,3-diamine (0.55 g, 5.41 mmol) in 6 mL of dry THF was slowly added with the help of a dropping funnel, and the temperature was maintained around 0 °C. The reaction was stirred for 16 h at room temperature. Then the solution of iodomethane (1.46 g, 10.28 mmol) in 8 mL of 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 h. The reaction was stirred for an additional 2 h at room temperature, and the product was filtered and subsequently washed with 5 mL of THF three times. The crude product was dried under vacumm (10^{-2} mbar) to yield a white solid. Yield: 1.6 g (90% of theoretical). 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}.



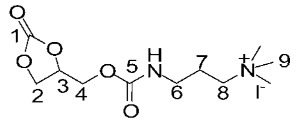
3

(2-Oxo-1,3-dioxolan-4-yl)methyl Allylcarbamate (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 of dry THF. The solution was cooled to 0 °C; a solution of allyl amine (5.74 g, 100 mmol) in 40 mL of dry THF was slowly added using a dropping funnel, and the temperature was maintained around 0 °C. The reaction was stirred at this temperature for 2 h and then stirred at room temperature for 14 h. The crude product was concentrated under vacuum and purified by column chromatography over silica gel (Ø, 5 cm; SiO_2 length, 50 cm) (ethyl acetate/*n*-hexane, 1:1) to afford a white solid. Yield: 16.2 g (96% of theoretical). 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}.



4

(2-Oxo-1,3-dioxolan-4-yl)methyl (oxiran-2-ylmethyl)carbamate (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 of CH_2Cl_2. The reaction mixture was stirred for 24 h at room temperature and then diluted with 50 mL of 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, 5 cm; SiO_2 length, 30 cm) (ethyl acetate) to afford a white solid. Yield: 4.10 g (75.4% of theoretical). Anal. Calcd for $C_8H_{11}NO_6$: 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}.



5

***N,N,N*-Trimethyl-3-({[(2-oxo-1,3-dioxolan-4-yl)methoxy]carbonyl}amino)propan-1-amonium Iodide (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 of dry THF. The reactants were cooled to 0 °C; the solution of 3-dimethylamino-1-propylamine (4.29 g, 42.01 mmol) in 21 mL of dry THF was slowly added using a dropping funnel, and the temperature was maintained around 0 °C. The reaction was 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 of dry THF was dropped slowly to the above-mentioned reaction for 2 h. 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 × 3) times. The crude product was dried under high vacuum, 10^{-2} mbar, to afford a 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, ^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.

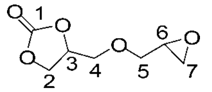
Table 1. Educt Composition and Yields in the Preparation of Polymers PEI-2 and PEI-5

	reactants (mg)			
	PEI	2	5	yield
PEI-2	1000	4180		4.4 g, 85%
PEI-5	1000		2705	3.2 g, 88%

Table 2. Educt Composition and Yields in the Preparation of Polymers PEI-54 and PEI-56

	reactants (mg)			
polymer	**PEI-5**	**4**	**6**	yield
PEI-54	1000	812		1.5 g, 86%
PEI-56	1000		621	1.3 g, 81%

4-[(Oxiran-2-ylmethoxy)methyl]-1,3-dioxolan-2-one (6). Glyceryl carbonate (4 g, 33.87 mmol) was dissolved in 18 mL of 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 a 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 h. The sodium chloride formed was filtered off and washed with 10 mL of THF. The combined organic filtrates were rotary evaporated to dryness, and subsequently the product was purified by column chromatography on silica gel (Ø, 2 cm; SiO_2 length, 50 cm) with ethyl acetate/chloroform: 1/1 vol:vol. Yield: 1.8 g (30.56% of theoretical). 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, ^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. *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}.



6

General Procedure for the Reaction of PEI with Cationic Carbonate or Epoxy Compounds. At 50 °C the respective amounts of carbonate **2** and **5** (see Table 1) were added to a solution of 1.0 g (23.25 mmol) of PEI in 10 mL of DMF. After stirring the solution at 50 °C for 48 h the polymer was precipitated in a 1:1 (vol: vol) mixture of hexane and diethyl ether. The polymer was redissolved in 10 mL of methanol, stirred vigorously for 15 min, and reprecipitated in the above-mentioned nonsolvent. After repeating the cycle for 3 times the solvent was distilled off and the product dried (room temperature, 24 h) at 1.3 Pa to yield a white solid.

General Procedure To Functionalize Modified 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 of DMF the required amount of the epoxy or cyclic carbonate linker (**4** or **6**) was added (see Table 2) and stirred at 50 °C for 48 h and precipitated in a 1:1 (vol: vol) mixture of hexane and diethyl ether. The polymer was redissolved in 10 mL of methanol, stirred vigorously for 15 min, and reprecipitated in the above-mentioned nonsolvent. After repeating the cycle 3 times the solvent was removed and the product 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 and 75 MHz, respectively. Chloroform-*d* ($CDCl_3$) and dimethyl sulfoxide-d_6 (DMSO- d_6) were used as solvents, and tetramethylsilane (TMS) was used as internal standard.

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 measurement in transmission mode.

Viscosity measurements were carried out with polymer concentrations varying from 0.5 to 1.5 g/dL in 0.5 M sodium nitrate solution using a Ostwald capillary viscometer (Schott, type 509 03) at 25 °C. The intrinsic viscosity $[\eta]$ was calculated by means of the Huggins equation $\eta_{red} = [\eta] + [\eta]^2 k_H c$ (η_{red} = 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 0.5 M sodium nitrate solution.

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

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

Surface modification of HOPG samples was carried out in a microwave plasma discharge system, AK 330 Roth and Rau, using argon or oxygen/argon mixtures. The sample was placed inside the chamber and became evacuated to a pressure of 10^{-3} bar. 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, 150 W; treatment time 2 min.

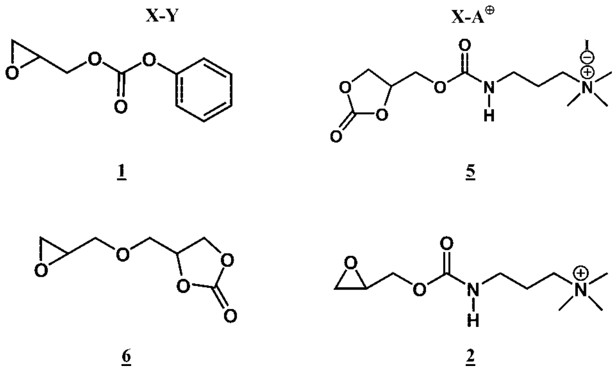
The surface morphology of thin polymer films was investigated by atomic force microscopy (AFM) at room temperature using a Solver SFM (NTMDT, Zelenograd, Moscow). Imaging was done in the tapping mode using standard silicon cantilevers: Nanoworld Pointprobe NCH f0 (330 kHz). The thin films were prepared by spin coating a volume of 40 μL from solutions of the polymers containing 0.04−0.004 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 mold with a cavity of $16 \times 2 \times 2$ mm^3.

b. Preparation of Carbon Fiber Samples. Nonsized carbon fiber samples were prepared by extracting 1 g of the commercially obtained carbon fiber in a Soxhlet extractor with acetone for 5 h.

To prepare quat-primer-sized carbon fibers the commercially obtained carbon fiber Roving was treated with a continuous oxygen plasma machine. The fiber 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/s. Immediately after the plasma treatment the fibers were dip coated in a solution of PEI-56 (0.1 wt % polymer) in water (weight of fiber:volume of polymer solution = 300 mg:15 mL) and dried under vacuum (14 h, 50 °C, membrane pump).

Scheme 1. Structures of the Investigated Cationic Modifiers X−A$^\oplus$ (2, 5) and Bifunctional Linker Molecules X−Y (1, 6)



c. Preparation of Single Carbon Fiber/Epoxy Resin Specimens. A single filament was picked from the fiber bundle and aligned axially on the silicone rubber mold. To straighten the filament, two weights of 100 mg each were hanged at both ends of the fiber. The liquid epoxy resin was heated for about 1 h at 40 °C to reduce the viscosity and then degassed for 10 h in vacuum at room temperature. The resin was then briefly heated again at 40 °C 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 mold, the mixture was again heated to 40 °C. Curing of the sample was performed subsequently according to the following schedule: 3 h at 80 °C and 1 h at 110 °C and then slow cooling to room temperature. After cooling the silicone mold was removed from the specimen parallel to the fiber to prevent fiber damage.

d. Tensile and Photoelastic Measurements. The carbon single-fiber/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

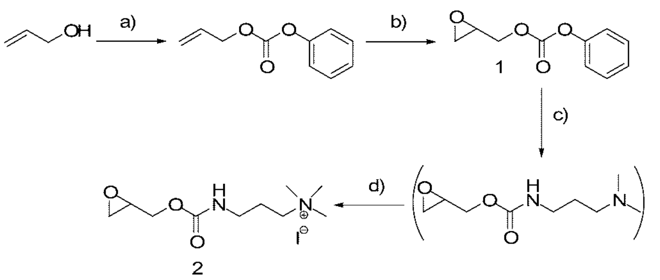
The objective of this study was to prepare cationic primer polymers ('quat-primer polymers') which permanently bind to the surface of carbon fibers via electrostatic interactions. Furthermore, the polymer should bear epoxy or cyclic carbonate groups that can copolymerize with the amine components of 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 fiber and the surrounding epoxy resin matrix with a thickness comparable to the polymers radius of gyration (∼1−4 nm).

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 positively charged group ('X−A$^\oplus$ modifiers') or two amino-reactive groups of different reactivity ('X−Y linkers'). Scheme 1 summarizes the structures of the aimed reactive molecules.

In a first attempt to prepare the epoxy/phenyl carbonate coupler **1** (Scheme 2) glycidol was reacted with phenyl chloroformate in the presence of pyridine as acid scavenger.[28] 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.[27] Subsequently, the allyl phenyl carbonate was epoxidized with *m*-chloroperbenzoic acid (MCPBA)[29] to yield oxiran-2-ylmethyl phenyl carbonate (**1**) in nearly quantitative yield.

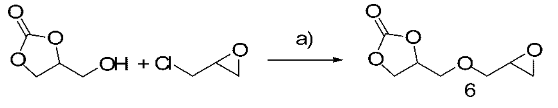
Coupler **1** contains two electrophilic sites of different reactivity toward nucleophiles, where the phenyl ester carbonate is much more reactive then the epoxy ring.[30] At low temperature

Scheme 2. Synthesis of the Epoxy/Carbonate Linker 1 and the Epoxy-Quat Modifier 2[a]



[a] (a) C_6H_5N, PhOCOCl, CH_2Cl_2, 0 °C, (b) MCPBA, CH_2Cl_2, room temperature, (c) *N*,*N*-dimethylpropane-1,3-diamine, THF, 0 °C, (d) CH_3I, THF, room temperature.

Scheme 3. Synthesis of Epoxy/Cyclocarbonate Linker 6[a]



[a] (a) NaH, THF, 60 °C.

(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 with amines (room temperature) and only after consumption of the more reactive phenyl ester carbonate. 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 isolation of the intermediate oxiran-2-ylmethyl 3-(dimethylamino)propylcarbamate (cf. Scheme 2). Note that upon isolation of the intermediate the epoxy ring can be opened by phenol in the presence of tertiary amines.[31]

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) with sodium hydride as a base. From ^1H 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 extract.

The ^1H and ^{13}C NMR spectra of linker **6** are depicted in Figure 1. The compound possesses two stereogenic carbon atoms (C3 and C6, cf. Figure 1) and was obtained in the 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 nonchiral environment. Consequently, the NMR spectra showed the presence of two isomers by splitting of the signals of the respective stereogenic centers (cf. Figure 1). The protons attached to positions 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 $\delta = 3.3$ and 4.0 ppm.

Model reactions were carried with compound **6** to investigate the selectivity of primary amino groups toward the epoxide and cyclic carbonate ring. One mole of compound **6** was reacted with 1 mol of hexylamine in $CDCl_3$ as the solvent at 0 °C for 4 h and subsequently at room temperature. ^1H and ^{13}C NMR were measured at different time intervals, and analysis of the spectra was performed when all of the hexylamine was consumed as indicated by ^1H 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 carbonate ring toward amine addition was calculated using the proton signals corresponding to carbon atoms C, D, 7, 7′, 8, 8′, 9, and 11 (Figure 2). ^1H NMR revealed that the primary amino groups did not distinguish between the epoxide and the carbonate ring. The spectral data also indicated that the hexylamine became attached to the carbon atom G of linker **6**, the carbon atom of the three-membered ring bearing no other substituent. Since an additional 2 mol of oxirane reacted with 1 mol of hexyl amine at room temperature, these results are in agreement to the well-known chemistry of epoxides.[32]

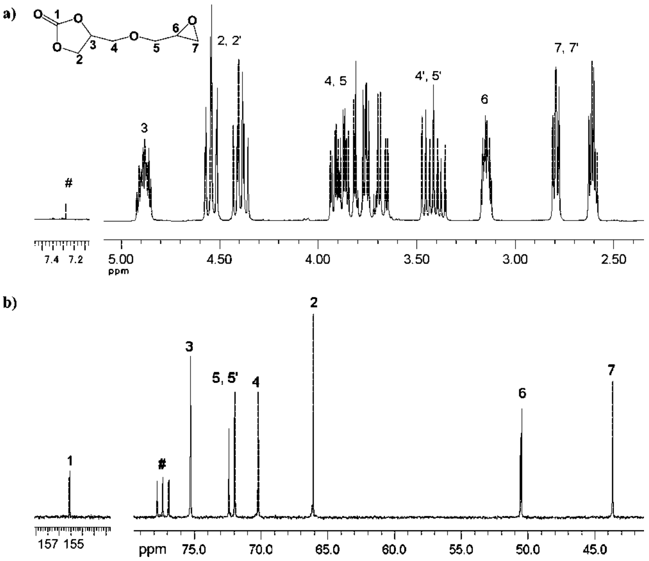


Figure 1. ^1H (a) and ^{13}C NMR (b) spectra with signal assignments of the epoxy/cyclocarbonate linker **6** in $CDCl_3$ (#).

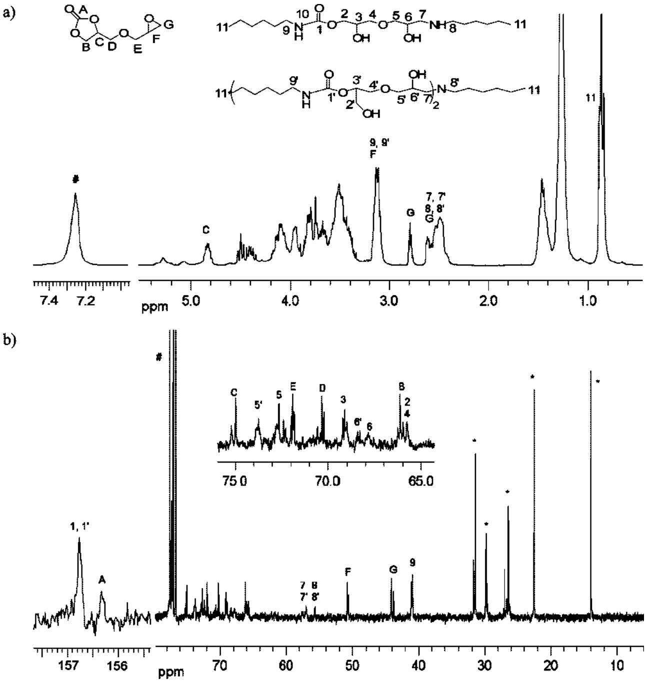
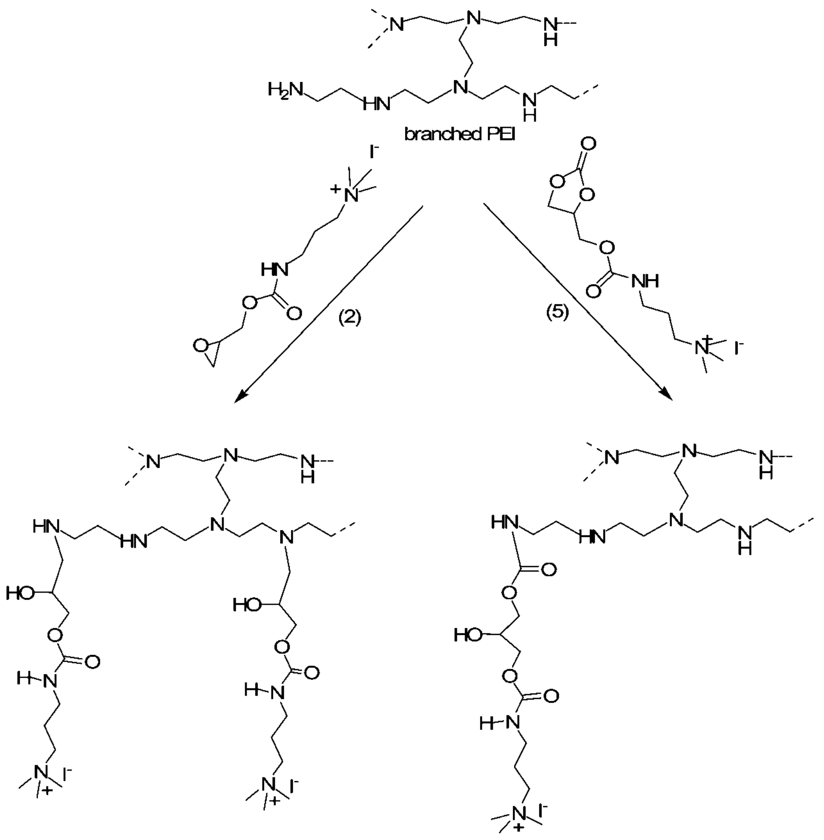


Figure 2. ^1H (a) and ^{13}C NMR (b) spectra of the product resulting from the model reaction between linker **6** and hexyl amine (**6**:$C_6H_{13}NH_2$ = 1:1 mol:mol) (* = alkyl signals of hexylamine, # = $CDCl_3$).

Scheme 4. Synthesis of PEI-Based Quaternary Carbonate Using Carbonate Couplers 2 and 5



Branched poly(ethylene imine) (PEI) containing 25 mol % primary, 50 mol % secondary, and 25 mol % tertiary amino groups with a 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) and subsequently reacted further with couplers **4** or **6**.

Couplers **2** and **5** contain one quaternary ammonium group on one side and an epoxy (**2**) or carbonate ring (1,3-dioxolan-2-one) (**5**) on the other side, respectively. As seen from Scheme 4, the carbonate ring can react only with primary amine to form a stable urethane linkage and a hydroxyl group whereas the epoxy ring can react to primary and secondary amine.[33]

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

Syntheis of Functionalized Poly(ethylene imine)

The commercial **PEI** used in the experiments was a branched polymer of molecular weight 10.000 g/mol with a molar ratio of primary, secondary, and tertiary groups of 25:50:25. The aim was to obtain polymers having (i) quaternary ammonium groups which impart adhesion to the carbon fiber and (ii) reactive groups which could react with epoxy resin ring during cross-linking with amine. Therefore, **PEI** was reacted 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 PEI. Thus, the secondary and tertiary amines will remain unreacted. In the second step the unreacted secondary amines of the functionalized PEI become converted.

On the basis of the above principle **PEI** was first reacted with the cyclic carbonate **5**. Hence, the primary amino groups in **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 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 PEI) in **PEI-54** and **PEI-56**.

All functionalized polymers were prepared in DMF at 60 °C reacting for 48 h according to the experimental procedure and using the amounts given in Tables 1 and 2.

Characterization of Functionalized Poly(ethylene imine)s. The structures of the functionalized PEIs were investigated by means of ^{1}H NMR, ^{13}C NMR, and IR spectroscopies. The NMR spectra of **PEI-2**, **PEI-5**,and **PEI-56** are shown in Figures 3−5.

The ^{13}C NMR spectra of **PEI-2** (Figure 3) show the characteristics peak of the hydroxyl propyl moiety arising from the reacted oxirane ring (signals 9, 10, and 11). The assignment was done based on the model reaction done between one mole each of compound **2** and hexyl amine. Furthermore, the absence

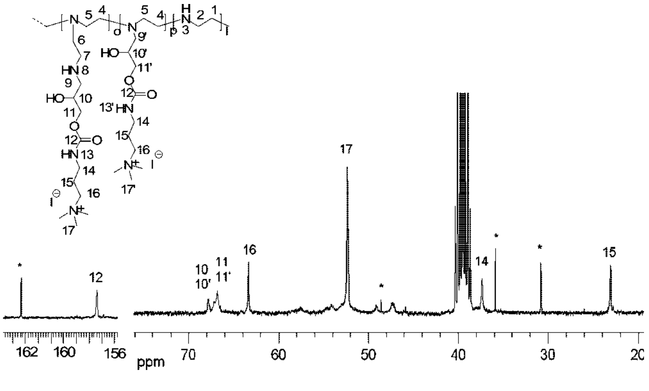


Figure 3. ^{13}C NMR spectra of **PEI-2** in DMSO-d_6 (* = residual solvent, # = DMSO).

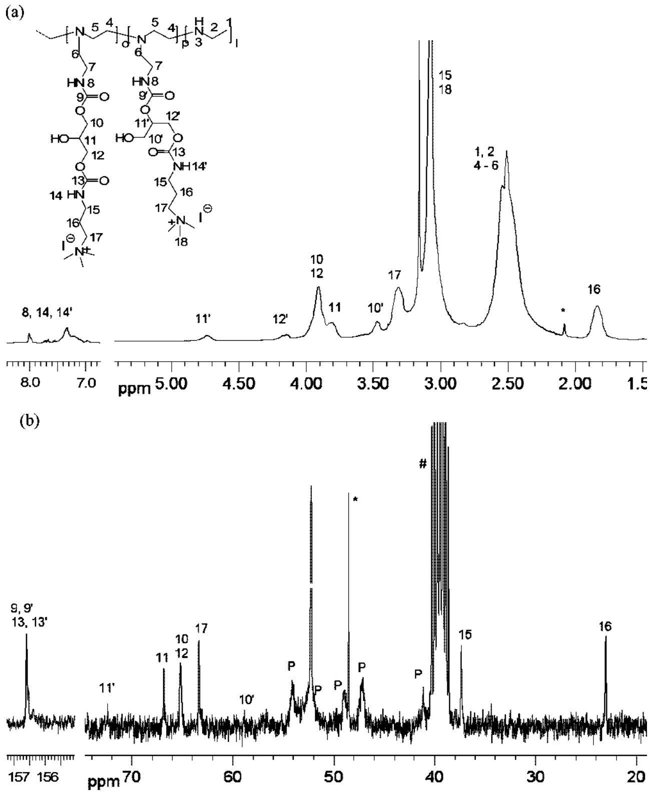


Figure 4. NMR spectra of **PEI-5** in DMSO-d_6: (a) ^{1}H and (b) ^{13}C NMR (*P* = PEI backbone, # = DMSO, * = methanol).

of the characteristic peaks of oxirane ring indicates the conversion is complete.

In **PEI-5** attachment of the quaternary carbonate to the polymer can be seen from ^{1}H NMR. The additional urethane signal 8 caused by the reaction was observed between 7 and 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, as shown in Figure 4. The ratio of two isomers was calculated from ^{1}H NMR taking into account 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 do not show the characteristic signals of the carbonate ring, proving that conversion is complete.

The ^{1}H NMR of **PEI-56** (Figure 5) was difficult to interpret, but the ^{13}C NMR showed the characteristic peaks of the carbonate ring (positions 23, 24, and 25), while the characteristic peaks for the oxirane ring were not observed, indicating that conversion is complete.

Comparing the infrared spectra of **PEI**, **PEI-5**, and **PEI-56** (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 (OC−N stretch), 1530 (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 PEI of $<M_n> = 10.000$ g/mol, the spectroscopically measured degree of modifications inferred a molecular weight of $<M_n> \approx 25.000$ g/mol with **PEI-5** and $<M_n> \approx 45.000$ g/mol with **PEI-56**. Figure 7a depicts the results from viscosimetric measurements, performed in 0.5 M aqueous $NaNO_3$ solution to screen the Coulomb interaction and avoid polyelectrolyte effects. While an intrinsic viscosity of $[\eta] = 0.13$ dL/g was measured for the educt PEI the modified products yielded intrinsic viscosities that were smaller for 1 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. The measured hydrodynamic diameters, d_H, of **PEI**, **PEI-5**, and **PEI-56** were 10.5, 4.2, and 3.7 nm, respectively (cf. Table 3). Note that the intrinsic viscosities are proportional to approximately the third power of the hydrodynamic diameter ($\log[\eta] = -3.56 \pm 0.07 + 2.6 \pm 0.2 \cdot \log d_H$).

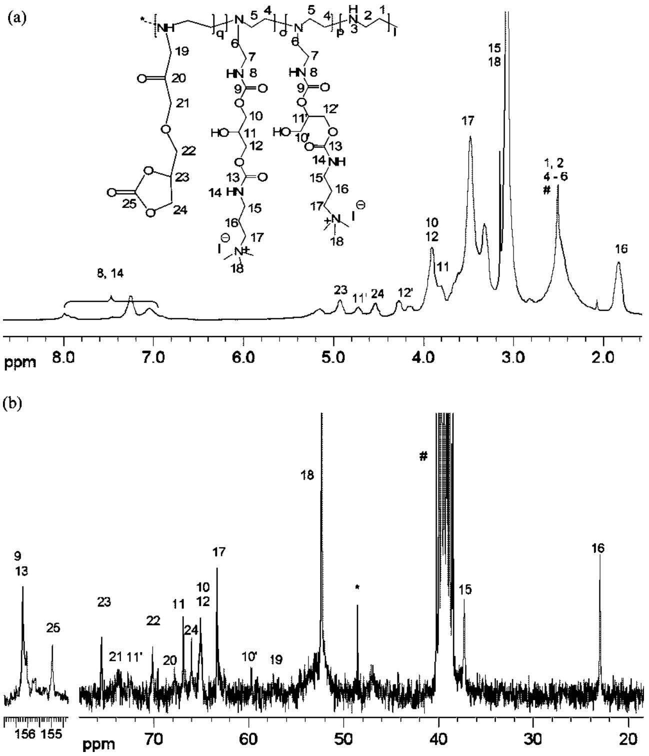


Figure 5. NMR spectra of **PEI-56** in DMSO-d_6: (a) ^{1}H and (b) ^{13}C NMR (# =DMSO).

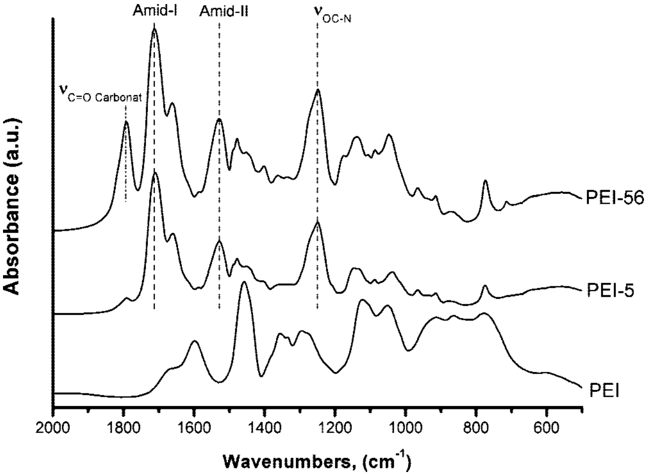


Figure 6. Infrared spectra of PEI, PEI-5, and PEI-56 ($\nu_{C=O,Carbonate} = 1792$ cm^{-1}, $\nu_{Amide-I} = 1713$ cm^{-1}, $\nu_{Amide-II} = 1530$ cm^{-1}, $\nu_{OC-N} = 1248$ cm^{-1}).

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-range intramolecular interactions contract the modified macromolecules below the typical radius of nonmodified PEI. The interactions must be of

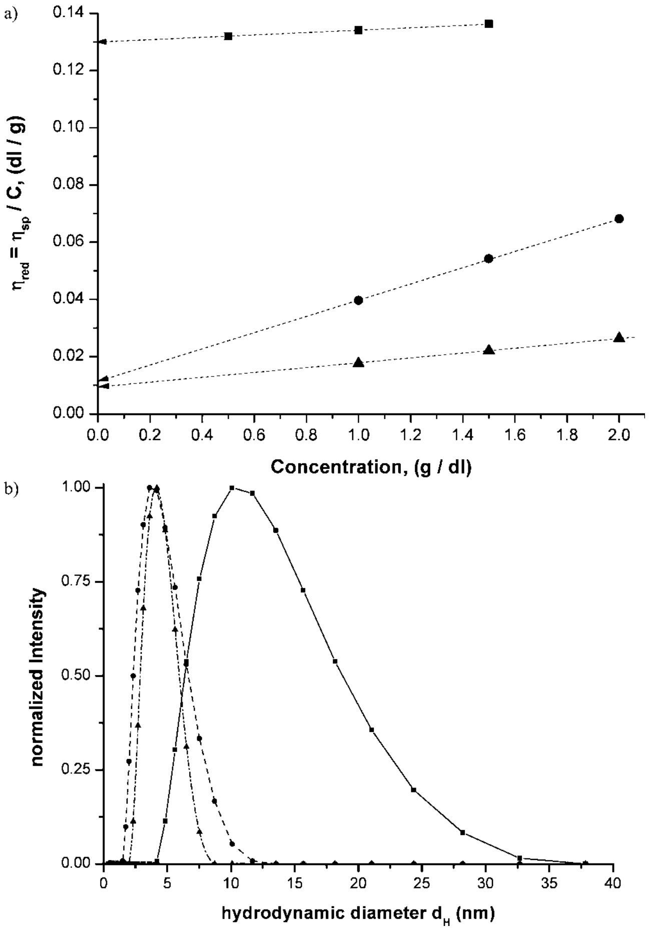


Figure 7. (a) Huggins plot of solution viscosimetry data and (b) hydrodynamic diameter distribution from dynamic light scattering of PEI (■), PEI-56 (●), and PEI-5 (▲) measured at 25 °C in 0.5 M aqueous $NaNO_3$ solution.

Table 3. Glass-Transition Temperatures, Intrinsic Viscosities, and Hydrodynamic Diameter of PEI and the Primer Polymers PEI-2, PEI-5, and PEI-56[a]

	glass-transition temperature, T_g (°C)	intrinsic viscosity $[\eta]$ (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

[a] n.d. = not determined.

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 fail that relay on determination of molecular size parameters, like viscosimetry 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 **PEI**, **PEI-2**, **PEI-5**, and **PEI-56** (see Figure 8a). All polymers were found to be amorphous, and the glass-transition temperature was found to increase with growing degree of substitution (cf. Table 3). **PEI** exhibited the lowest glass-transition temperature of −53 °C, while the glass-transition temperature of **PEI-2** and **PEI-5** were found to be higher (60−61 °C) than that of **PEI-56** because of their lower flexibility in their side chains.

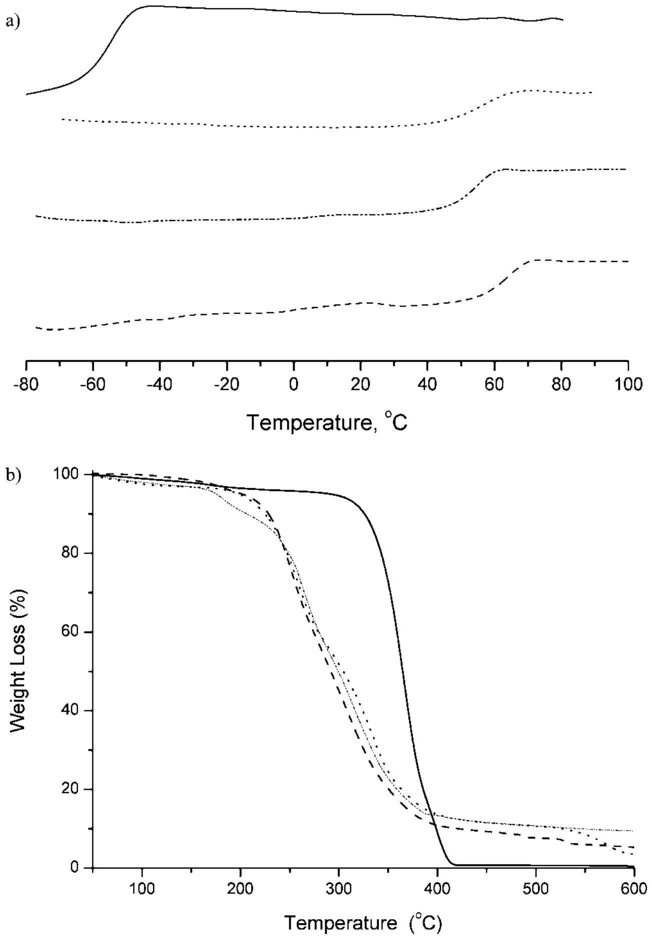


Figure 8. (a) Differential scanning calorimetry and (b) thermogravimetry scans under N_2 atmosphere of **PEI** (—), **PEI-2** (- - -), **PEI-5** (• • •), and **PEI-56** (- • -) (dT/dt = 10 K/min).

Thermogravimetry (TGA) measurements were performed under a nitrogen atmosphere at a heating rate of 10 °C/min. The TGA curves (Figure 8b) of the modified 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 °C, which was less stable than unmodified 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 decomposition of urethane groups.[26]

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 fibers consist of turbostratic carbon instead of graphite, it is generally accepted that nonsurface-modified carbon fibers are covered by a thin sheath of graphitic basal plane structure ('onion skin' model).[34] HOPG consist of layers of two-dimensional sheets with strong covalent bonds within each layer (Young modulus in-plane = 1 TPa[35]) and only weak van der Waals interactions between stacked layers (Young modulus perpendicular to plane = 34.6 GPa[36]). Because of the structural similarity between HOPG and the surface of nonmodified carbon fibers, in addition to its close to perfect planarity, HOPG was selected as a suitable and easy to investigate model substrate.

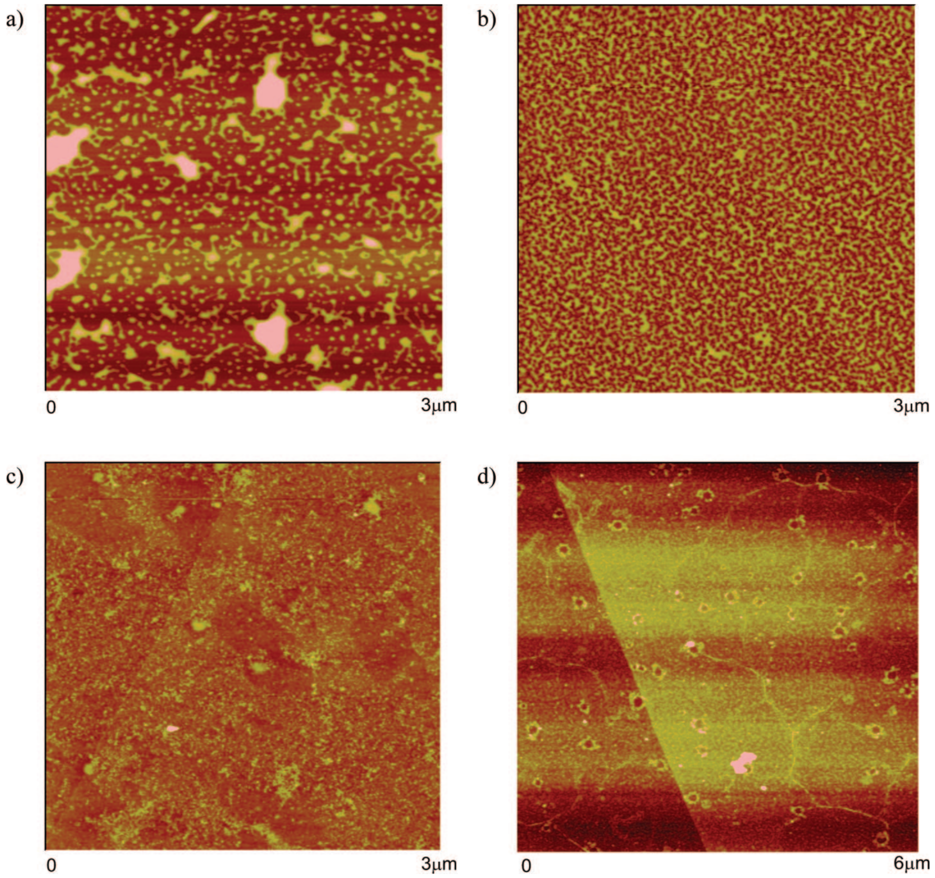


Figure 9. Scanning force micrographs of HOPG surfaces spin coated with methanolic **PEI-56** solutions: (a) nontreated HOPG (0.04 wt % **PEI-56**), (b) argon plasma-treated HOPG (0.04 wt % **PEI-56**), (c) argon/oxygen plasma-treated HOPG (0.004 wt % **PEI-56**), (d) sample picture, (c) after extraction with methanol.

Figure 9a depicts a scanning force micrograph of **PEI-56** coated from a 0.04 wt % solution in methanol on nontreated, freshly cleaved HOPG. The polymer virtually did not spread but formed isolated irregular-shaped droplets and islands with nonuniform 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 pretreated for 2 min with low-energy argon plasma. The plasma treatment conditions were adjusted in such a 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 9b). Figure 9c shows the scanning force image of **PEI-56** coated from a 0.004 wt % solution in methanol onto a HOPG substrate that has been pretreated with an 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. Since the presence of the **PEI-56** was checked by independent tests, the picture demonstrates that an ultrathin 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 9c was extracted for 2 h with methanol in a Soxhlet extractor. No difference in film morphology and thickness was found by scanning force microscopy after the extraction step (cf. Figure 9d), indicating that the polymer became strongly bond to the substrate.

Obviously the highly polar **PEI-56** polymer did not wet nor adhere well to the nonpolar 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 behavior 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 $\equiv$C−OH, >C=O, and −COOH covalently bound to the edges of the defects.[37] These groups will increase the surface energy of the substrate, create negative (partial) charges at its surface, and allow for hydrogen bonding. 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 fibers become anodic oxidized subsequent to the carbonization step and prior to seizing,[38,39] strong adhesion of these polymers on carbon fibers can also be expected.

High-performance fiber/matrix composites can only be obtained if the matrix is effectively able to transfer mechanical stress to the fiber. Hence, the strength at the break of such composites is highly dependent on the fiber matrix adhesion. Since, on one hand, the quat-primer polymers are expected to adhere well to carbon fiber 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 means to control the properties of the carbon fiber/epoxy resin interface.

Carbon-Fiber/Epoxy Model Resins. To investigate the suitability of PEI-based quat-primer polymers as carbon fiber surface modification agents, carbon fiber/epoxy resin composites were prepared from (i) deseized carbon fibers and (ii) carbon fibers that were plasma treated to remove the size and subsequently coat with a quat-primer polymer. Single filaments were taken from a carbon fiber bundle and embedded in a technically used epoxy resin system (cf. Experimental Section).

There are three main micromechanical tests which have been developed to evaluate the interfacial shear strength of single-fiber composites, namely, single fiber pull-out test,[40−42] fragmentation test,[43−49]and microbond test.[50,51] The different techniques are based on specific sample configurations and loading geometries and thus involve different stress states at the interface. The fiber pull-out test is 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 fiber makes determination of the embedded fiber length difficult. Moreover, since in pull-out tests the interfacial debonding force is directly related to the embedded fiber length, there is a maximum embedded fiber length which permits the fiber to be pulled out without breakage. The maximum embedded length is usually very short in the case of a composite system having strong interfacial bonding. For example, the maximum embedded fiber length for carbon fiber epoxy matrix system is generally less than 200 μm, which causes difficulties in making specimens.[52] The pull-out test is best suited for glass fibers and difficult to use with thin carbon fibers. The microbond test method, which is a modified pull-out test, was developed by Miller et al.[50] This method is a revision to the single-fiber pull-out test to eliminate the meniscus effect during elevated temperature curing and the potential rupture of the meniscus before debonding. This test is difficult to perform because of the very small embedded length, and the fiber should be normal to the mold.[53] The single-fiber fragmentation test is a technique that involves the critical fragment length and single fiber strength distribution. There is limitation to this test that the failure strain of the matrix should be three times the failure strain of the fibers to meet the needs of achieving a saturated fragmentation test. The obtained composites were investigated by means of a modified Kelley−Tyson fragmentation test.[43] A single carbon fiber was aligned axially in the cavity of a dog bone-shaped silicone mold, covered with the liquid epoxy resin, followed by thermal curing of the specimen.

When stretching the specimen parallel to the fiber axis the fiber starts to break at a certain elongation since the maximum strain of the fiber is lower than that of the matrix. Upon further stretching the fiber 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 fiber via shear stresses along the fibers 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 eq 1, relating the interfacial shear yield stress τ_C to the tensile strength σ_f, the diameter d of the fiber, as well as the critical fragments length l_c.

$$\tau_C = \sigma_f d / 2 l_C \tag{1}$$

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 10 compares typical fracture length vs elongation curves obtained from composites with noncoated (dotted curve in Figure 10) and **PEI-56**-coated (solid curve) carbon fibrils/epoxy resins. In the presence of **PEI-56** at the fiber/matrix interface the fiber 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 37% (no primer $l_c = 470$ μm; with **PEI-56** $l_c = 296$ μm).

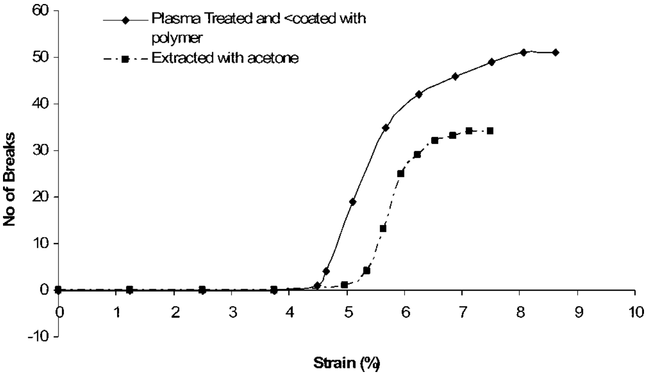


Figure 10. Number of breaks versus strain in carbon fiber embedded in epoxy resin cured by tetraethylenepentamine curing agent; gauge length of specimen = 16 mm.

Table 4. Average Values of the Critical Number of Fiber Fractures, N_C, Critical Fiber Length, l_c/d, and Interfacial Shear Strength τ_C Obtained from Kelley/Tyson Fragmentation Tests with Carbon Fiber/Epoxy Resins Using Unsized and PEI-56-Sized Single Carbon Fiber

sample	fiber diameter, d^a[μm]	average number of fragments, N_c	critical fragment length, l_c/d	interfacial shear strength, τ [MPa]
unsized carbon fiber	6.5 ± 0.5	33 ± 3	61.5 ± 3	39.0 ± 3
quat-primer-sized carbon fiber	7.5 ± 0.5	49 ± 2	45.3 ± 3	53.0 ± 3

[a] The diameters of the unsized and sized filaments were determined with SEM.

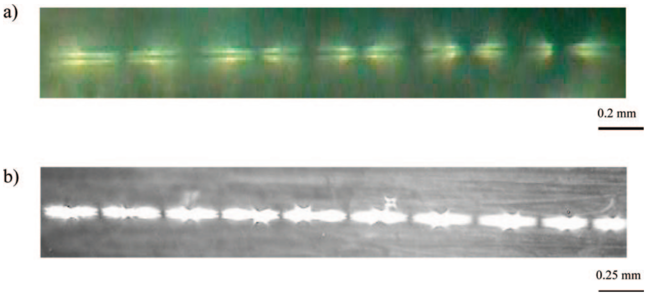


Figure 11. Optical micrographs of birefringence patterns observed upon stretching of carbon single fiber/epoxy resin composites to the fragmentation saturation level: (a) unsized and (b) **PEI-56**-sized carbon fiber composite system.

The average values of the critical fragment length as obtained from all investigated specimens are summarized in Table 4. It was assumed that the tensile strength τ_C at the critical fiber length is the same for untreated and treated carbon fibers. Use of **PEI-56**-coated carbon fiber fibrils increased the interfacial shear yield stress τ_C for ~36% from 39 ± 3 to 53 ± 3 MPa.

Fragmentation of the epoxy resin embedded fibers 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 fiber/matrix interfaces. The stress birefringence patterns generated during the experiment were recorded photographically with increasing strain.

Figure 11 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 fiber ends. As expected no new fiber breaks occurred once the critical fragment length was reached, even if the applied tensile load was continuously increased further. According to Figure 11 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 fiber than for the **PEI-56**-treated fibrils, indicating that the fiber fragmentation was associated with interfacial debonding.[48]

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 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 fiber with epoxy reactive quaternary primers leads to an improvement in fiber matrix adherence.

References and Notes

(1) Bourgeois, P.; Davidson, T. *J. Adhes.* **1994**, *45*, 73.
(2) Drzal, L. T. *Advances in Polymer Science 75-Epoxy Resins and Composites II*; pp 3−30.
(3) Zou, Y. L.; Netravali, A. N. *J. Adhes. Sci. Technol.* **1995**, *9*, 1505.
(4) Yumitrori, S.; Wang, D.; Jones, F. R. *Composites* **1994**, *25*, 698.
(5) Pittman, U. C.; Jiang, W.; He, G. R.; Gardner, S. D. *Carbon* **1998**, *36*, 25.
(6) Morra, M.; Ochiello, E.; Garbassi, F.; Nicolais, L. *Compos. Sci. Technol.* **1991**, *42*, 361.
(7) Yuan, L. Y.; Chen, C. S.; Shyu, S. S.; Lai, J. Y. *Compos. Sci. Technol.* **1992**, *45*, 1.
(8) Da, Y.; Wang, D.; Sun, M.; Chen, C.; Yue, J. *Compos. Sci. Technol.* **1987**, *30*, 119.
(9) Park, S. J.; Kim, M. H. *J. Mater. Sci.* **2000**, *35*, 1901.
(10) Park, S. J.; Park, B. *J. Mater. Sci. Lett.* **1999**, *18*, 47.
(11) Fjeldy, A.; Olsen, T.; Rysjedal, J. H.; Berg, J. E. *Composites, Part A* **2001**, *32*, 373.
(12) Ramanathan, T.; Bismarck, A.; Schluz, E.; Subramanian, K. *Compos. Sci. Technol.* **2001**, *61*, 599.
(13) Toyoda, M.; Katoh, H.; Inagaki, M. *Carbon* **2001**, *39*, 2231.
(14) Drzal, L. T.; Rich, M. J.; Lloyd, P. M. *J. Adhes.* **1982**, *16*, 1.
(15) Drzal, L. T.; Rich, M. J.; Koenig, M. F.; Lloyd, P. M. *J. Adhes.* **1983**, *16*, 133.
(16) Cooke, T. F. *J. Polym. Eng.* **1987**, *7*, 197.
(17) Vassoudevane, L. B.; Samuel, I. S. *Chem. Mater.* **1994**, *6*, 1880.
(18) Yang, D. Q.; Sacher, E. *Chem. Mater.* **2006**, *18*, 1811.
(19) Chang, H.; Bard, A. J. *J. Am. Chem. Soc.* **1991**, *113*, 5588.
(20) Chu, X.; Schmidt, L. D. *Carbon* **1991**, *29*, 1251.
(21) Tracz, A.; Wegner, G.; Rabe, J. P. *Langmuir* **1993**, *9*, 3033.
(22) Stabel, A.; Eichhorst, K.; Rabe, J. P.; Gonzalez-Elipe, A. R. *Langmuir* **1998**, *14*, 3033.
(23) Stabel, A.; Eichhorst, K.; Rabe, J. P.; Gonzalez-Elipe, A. R. *Langmuir* **1998**, *14*, 7324.
(24) Moeller, M.; Beginn, U.; Keul, H.; Thomas, H. European Patent, **2006**.
(25) Ubaghs, L.; Fricke, N.; Keul, H.; Höcker, H. *Macromol. Rapid Commun.* **2004**, *25*, 517.
(26) Pasquier, N.; Keul, H.; Moeller, M. *Des. Monomers Polym.* **2005**, *8*, 679.
(27) Pittelkow, M.; Lewinsky, R.; Christensen, J. B. *Synthesis* **2002**, *15*, 2195.
(28) Jansen, J. F. G. A.; Dias, A.; Dorschu, M.; Coussens, B. *Macromolecules* **2003**, *36*, 3861.
(29) Ruano, J. L. G.; Fajardo, C.; Fraile, A.; Mart1n, M. R. *J. Org. Chem.* **2005**, *70*, 4300.
(30) Pasquier, N.; Keul, H.; Heine, E.; Moeller, M. *Biomacromolecules* **2007**, *8*, 2874.
(31) Stephenson, O. *J. Chem. Soc.* **1954**, 1571.
(32) Parker, R. E.; Isaacs, N. S. *Chem. Rev.* **1959**, *59*, 737.
(33) Graham, A. R.; Millidge, A. F.; Young, D. P. *J. Chem. Soc.* **1954**, 2180.
(34) Lee, R. N. Carbon Fiber Surface Properties. In *International Encyclopedia of Composites*; Lee, S. M., Ed.; VCH Publishers: New York, 1990; Vol. 1, p 241−253.
(35) Piper, E. L. *Soc. Min. Eng. AIME Prepr.* **1973**, *73*, H14.
(36) Blakeslee, O. L.; Proctor, D. G.; Seldin, E. J.; Spence, G. B.; Weng, T. J. *Appl. Phys.* **1970**, *41*, 3373.
(37) Tracz, A.; Wegner, G.; Rabe, J. P. *Langmuir* **2003**, *19*, 6807.
(38) Peebles, L. H. *Carbon Fibres Formation Structures & Properties: Formation, Structure and Properties*; CRC Press Inc.: Boca Raton, 1994.
(39) Riggs, J. P. Carbon Fibres. In *International Encyclopedia of Composites*; Lee, S. M., Ed.; VCH Publishers: New York, 1990; Vol. 1, p 197.
(40) Fuli, Z.; Grubb, D. T. *J. Mater. Sci.* **1984**, *29*, 189.
(41) Wells, J. K.; Beaumont, P. W. R. *J. Mater. Sci.* **1985**, *20*, 1275.
(42) DiFrancia, C.; Ward, T. C.; Claus, R. O. *Composites* **1996**, *27A*, 597.
(43) Kelley, A.; Tyson, W. R. *J. Mech. Phys. Solids* **1965**, *13*, 329.
(44) Scherf, J.; Wagner, H. D. *Polym. Eng. Sci.* **1992**, *32*, 298.
(45) Melanitis, N.; Galiotis, C.; Tetlow, P. L.; Davies, C. K. L. *J. Compos. Mater.* **1992**, *26*, 574.
(46) Kim, B. W.; Nairn, J. A. *J. Compos. Mater.* **2002**, *36*, 1825.
(47) Yavin, B.; Gallis, H. E.; Scherf, J.; Eitan, A.; Wagner, H. D. *Polym. Compos.* **1991**, *12*, 436.
(48) Huang, Y.; Young, R. J. *Composites* **1995**, *26*, 541.
(49) Zhou, X. F.; Wagner, H. D.; Nutt, S. R. *Composites Part A* **2001**, *32*, 1543.
(50) Miller, B.; Muri, P.; Rebenfeld, L. *Compos. Sci. Technol.* **1987**, *28*, 17.
(51) Marshall, D. B. *J. Am. Ceram. Soc.* **1984**, *67*, 259.
(52) Deng, S.; Ye, L.; Mai, Y. U. *Adv. Compos. Mater.* **1998**, *7*, 169.
(53) Wu, H. F.; Claypool, C. M. *J. Mater. Sci. Lett.* **1991**, *10*, 269.

MA801064E