Grafted Carbon Fibers and Their Physico-Chemical Properties. Part II. Grafting of Liquid Crystalline Methacrylic Monomers onto Carbon Fibers and the Influence of an Applied Voltage to the Carbon Fiber Embedded in a Liquid Crystalline Matrix

A. BISMARCK, M. PFAFFERNOSCHKE, B. SONG, J. SPRINGER

Technische Universität Berlin, Institut für Technische Chemie, Fachgebiet Makromolekulare Chemie, Sekr. TC6, Strasse des 17, Juni 135, 10623 Berlin, Germany

Received 20 March 1998; accepted 16 August 1998

ABSTRACT: Results of grafting reactions of a liquid crystalline (lc) monomer onto carbon fiber surfaces are presented and compared with results of noncovalently bonded lc polymer, which is proved reproducible by scanning electron microscopy. Electro-optical investigations under a polarizing microscope hints of the possibility of changing lc polymer and lc low molecular mass matrix molecules properties by applying a certain voltage to the carbon fibers. Wetting and electrokinetic measurements were performed and correlated with grafting reaction parameters. Those investigations revealed a nearly complete coverage of the carbon fiber surfaces by lc polymers. These measurements are suitable to characterize carbon fibers modified by grafted or coated polymers. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1893–1904, 1999

Key words: grafting reaction; carbon fiber; liquid crystalline monomer and polymer; contact angle; zeta-potential

INTRODUCTION

As described in part I of this article,¹ grafting of methacrylic acid onto carbon fibers can be easily achieved by radically initiated bulk polymerization. The influences on modification prior to grafting and the influences on the amount of initiator to the behavior of the resulting surfaces were studied.

Besides non-lc monomers and polymers, lc material was also grafted onto carbon fibers. This was accomplished by 1,3-dicyclohexylcarbodiimide-activated esterification of acidic surface groups present on the carbon fiber with lc monomers and polymers.²

Herein, we extend the introduced grafting method of methacrylic monomers onto lc monomers.

We used the well-known lc monomer [4-methoxyphenyl-4'-(6-methacryloyl-oxyhexyloxy)-benzoate (\mathbf{A})]^{3,4} (Scheme 1). Additionally, we present results obtained from electro-optical investigations on these grafted fibers. Surface properties were studied by ζ -potential and contact-angle measurements to prove the results described in Part I.

EXPERIMENTAL

Grafting Reactions

Based on parameters fitted to grafting of methacrylic acid onto various carbon fibers, now

Correspondence to: J. Springer.

Journal of Applied Polymer Science, Vol. 71, 1893-1904 (1999)

^{© 1999} John Wiley & Sons, Inc. CCC 0021-8995/99/111893-12



we only used in oxygen plasma-modified $(OP)^5$ [10 min, 1.5 mbar, reactor power: 16.5 W, gas flow: 4.5 mL (STP) min⁻¹], high-tensile, polyacrylonitrile-based carbon fibers from Sigri Carbon (Sigrafil C320.00A). The amount of initiator azodiisobutyronitrile (AIBN) was in all cases 5 mol %, and the results were studied by scanning electron microscopy (SEM).

The monomer (**A**) was synthesized after a procedure described by Finkelmann and colleagues.³ Additionally, flush chromatography was applied to the monomer, because reprecipitation and recrystallization were not enough to purify it. Without flush chromatography, the monomer tends to crosslink in the polymerization.

The monomer and the initiator AIBN were dissolved in dichloromethane to ensure a homogeneous distribution of the components. Then, the solvent was evaporated (25°C, 100 mbar), and the dry mixture was placed on oxygen plasma-modified fibers (C320.00A) and flushed with nitrogen for 20 min. Bulk polymerization was initiated by heating the reaction vessel up to 85°C for 15 min. Longer reaction times lead to branching and crosslinking, which had to be suppressed.

After removing the resulting composite from the reactor, it was extracted with dichloromethane for 7 days to remove all unreacted monomer and polymer not bound to the fibers. Finally, the samples were dried at 40°C and 1 mbar.

Additionally, we used the pure polymer (\mathbf{P}_{A}), obtained from monomer **A**. \mathbf{P}_{A} was synthesized in a solution of dimethylformamide with 2 mol % AIBN at 70°C for 24 h. This procedure generally yields a polymer with $1.1 \cdot 10^{5}$ g mol⁻¹.

Two low molecular mass liquid crystals [4-methoxybenzylidene-4'-*n*-butylaniline (MBBA)⁶ and 4-cyano-4'-octyl-biphenyl $(8CB)^7$] were also used to study the wetting behavior of the fibers. These substances were used as purchased without further purification. The polymer was synthesized by precipitation polymerization in tetrahydrofurane as described elsewhere⁴ (Scheme 2).

Mesophase and Electro-optical Characterization

The lc properties of the composites were characterized by differential scanning calorimetry (DSC



8CB (K24 Merck) C 21°C SmAd 32.5°C N 40.5°C I



MBBA (Aldrich) C 22°C N 47°C I Scheme 2 .

7, Perkin-Elmer), X-ray diffraction (monochromatic CuK_{α} radiation, flat-plate polaroid camera), and polarizing microscopy (Olympus BHS).

Because the lc domains in the polymer composites were very small, birefringence can be observed, but no typical liquid crystalline textures were formed. However, an interesting aspect was discovered, when a small voltage was applied to the fibers of up to ± 50 V peak to peak, 0.005-0.5Hz). The fibers were used as current carrying conductors that produce a concentric magnetic field around the fibers. This magnetic field should cause an orientation of the mesogens, due to their magnetic susceptibility. Further details are described in "Results and Discussion." Samples for electro-optical investigations were prepared as follows: 1–6 fibers, or a fiber rowing were taped to a glass plate and contacted to a wire with conductive paint. Then, the liquid crystals were spread over the fibers. In the case of monomers, polymerization was conducted as described. Samples were contacted with banana plugs to an AC/DC amplifier connected to a function generator.

In case of low molecular liquid crystals, only six fibers were used, and the substance was simply spread over the fibers and analyzed *via* polarizing microscopy. With these liquid crystals (MBBA and 8CB), phase characterization was easily possible, because textures were established rather fast.

Surface Morphology

All treated fibers were analyzed by SEM to show eventual changes in the surface morphology. Fibers were investigated with a Hitachi S-2700 scanning electron microscope. Grafted fibers were sputtered with gold before microscopic analysis, because the polymer is nonconducting.

To check the difference between grafted and nongrafted, but polymer-coated carbon fibers, the polymer $\mathbf{P}_{\mathbf{A}}$ was dissolved in dichloromethane, the solution was poured over the carbon fibers, and the solvent evaporated at 40°C (1 mbar). In another experiment, carbon fibers were immersed into a melt of polymer $\mathbf{P}_{\mathbf{A}}$ and removed again.

Contact-angle Measurements

Experimental procedures and the theories for contact angle- as well as ζ -potential measurements, which were applied in this study, are extensively outlined in Part I¹ and in the general literature (i.e., see refs. 8, 9, and 21). Therefore it is not mentioned herein.

The contact angles of all fibers under investigation were measured *vs.* water and diiodomethane using the modified Wilhelmy technique,¹⁰ and fiber surface tensions were calculated from the obtained contact-angle values, as described in Part I.

As described elsewhere,¹¹ a reliable and convenient contact-angle determination method for drop-on-fiber systems on the basis of our computer-aided pendant-drop method^{12,13} was developed. To calculate the contact angle from the extracted drop profile, we have extended the concept of the common maximum drop height-length (KL) method^{14,15} and introduced a so-called generalized drop height-length (KLy) method. The droplets on fibers were prepared by dipping the fibers, which were taped onto a metal frame and covered with aluminum foil into MBBA, followed by pulling out into the air. To study the influence of the voltage-induced reorientation of MBBA and its effect on the contact angle, fibers prepared in this way were connected to the power supply unit. Then, a voltage of 16 V was applied to the fibers and the contact angle was measured. The voltage was switched off and contact angle was measured again. This procedure was repeated 19 times to check the reproducibility of the obtained effect. Additionally another experiment was performed by increasing the applied voltage stepwise from 16 to 30 V. To measure the temperature dependence of the MBBA contact angle on carbon fibers these were placed on a hot stage (TH 600 Linkam Scientific Instruments Ltd., UK) and the temperature was increased with a rate of 1 K min^{-1} .

Electrical Conductivity Measurements

To eliminate problems of the contact resistance, the 4-point-method to estimate the electrical conductivity of a single filament was applied.¹⁶ Precondition is that the input resistance of the voltage measuring device used is much higher than the resistance R of the filament. All measurements were performed at room temperature (20°C). The current I was taken from the power supply-type Gossen Konstanter T4 33 2 and measured with a Fluke 45 Dual Display Multimeter. The input resistance of this is 200 T Ω . The voltage U was determined by a Keithley 617 programmable electrometer. A constant current of 100 μ A was applied. The specific resistance of a single filament ρ was calculated under consideration of the fiber length l (l = 2 cm) and the fiber diameter $d \ (d \approx 7 \ \mu \text{m}, \text{ estimated by SEM micrographs})$ using the following equation:

$$\rho = \frac{R \cdot \pi \cdot d^2}{4l} = \frac{U \cdot \pi \cdot d^2}{I \cdot 4 \cdot l} = \frac{1}{\kappa}$$

 κ is specific conductivity. All measurements were repeated on 10 samples of each fiber type to get average values.

ζ-Potential Measurements

 ζ -Potentials were determined with the electrokinetic analyzer EKA (Anton Paar KG, Graz, Austria) based on the streaming potential method. Details of the ζ -potential measuring technique are reported elsewhere.¹⁷

RESULTS AND DISCUSSION

Grafting Reactions and SEM Investigations

Investigations of lc polymer-grafted carbon fibers revealed similar results like the methacrylic acidgrafted carbon fibers.¹ In contrast to the methacrylic acid-grafted carbon fibers, the lc polymer-grafted carbon fibers are polymer-coated, and polymer cylinders point away like "stalagmites" from the carbon fiber surface (Fig. 1), which can be understood, if the different polarities of polymer and carbon fiber are taken into account. After the oxygen plasma treatment, the carbon fiber surface became polar, although P_A is not as polar. The nongrafted, but polymer-sized carbon fibers (Fig. 2 and 3), show incomplete wet-



Figure 1 P_A grafted 10 min OP C320.00A.

Figure 3 10 min OP C320.00A sized with molten P_A.

ting and no stalagmite-like polymers away from the fiber surface.

Liquid Crystalline (LC) Properties of Composites

As reported in previous papers,⁴ the homopolymer ($\mathbf{P}_{\mathbf{A}}$) of the lc monomer (\mathbf{A}) exhibits a smectic A monolayer and a nematic phase, so we also expected them in the composites. The glass tran-



Figure 2 10 min OP C320.00A P_A solution sized.

sition temperature on heating is 47°C, a smectic A-nematic transition is observed at 72°C, the clearing temperature is 111°C, as determined by differential scanning calorimetry (DSC). Unfortunately, the ratio of lc polymer/fiber was very small, so the DSC traces were difficult to obtain (Fig. 4). However, we were able to detect the same mesomorphic behavior in the composites (T_g : 46°C, T_{s-n} : 74°C, T_{n-i} : 112°C) as in the linear homopolymer, even though the phase transition enthalpies were much smaller.

"Electro-optical" Investigations

LCP auf CF aufgeschmolzen

The application of an AC voltage to the grafted carbon fibers should orient the mesogens in a magnetic field and influence the birefringence of the lc textures between crossed polarizers. We observed that the texture becomes isotropic if a certain threshold voltage is exceeded. If the voltage is removed or reversed, the sample becomes birefringent again. With increased voltage, the isotropic areas became larger. This might be caused by a homeotropic alignment of the mesogens, causing a black appearance between crossed polarizers, or simple by a thermal effect, caused by the amount of heat dissipated from the carbon fibers, because they also work as electrical resistance.

To examine this behavior, samples were prepared where the polymer was not attached to the



Temperature (°C)

Figure 4 DSC trace of P_A grafted 10 min OP C320.00A (CA).

fiber. A solution of homopolymer $(\mathbf{P}_{\mathbf{A}})$ was poured over the fibers, and the solvent (dichloromethane) was allowed to evaporate. This sample was also investigated by polarizing microscopy. The main difference to the polymerized sample was the wetting behavior. No large polymer areas on carbon fibers were formed, but small domains were observed between the crossed polarizers. This is first of all due to the bad film formation properties of methacrylates. Additionally, repulsive interactions between polymer and fibers (Table I) have to be taken into consideration. Application of an AC voltage to this nongrafted sample yielded the same effect. But this time, it was not as pronounced, probably to the greater disorder of the polymer. So, an effect, deriving from the covalent attachment of the lc to the carbon fiber surface can be excluded.

When the monomer (\mathbf{A}) was polymerized onto the fibers, a much more homogeneous film resulted (see also Fig. 1), which can be reoriented by electro-magnetical fields. In a detailed study, various samples were prepared: a bulky sample with many fibers, a sample with just one fiber, and a sample with five fibers on 1 cm^2 . Generally speaking, the more fibers are used, the smaller the threshold voltage necessary to reorient the liquid crystals. If many fibers are used, the threshold voltage is at ~ 10 V; if only one fiber is embedded, the threshold is as high as 40–50 V. From the polymer behavior, it is not clear whether the lc becomes homeotropic or isotropic.

To gain a deeper understanding of the observed reorientation phenomena, we prepared samples with low molecular liquid crystals, such as MBBA and 8CB, also to decide whether the texture becomes homeotropic or isotropic.

When using MBBA, a fast reorientation process was observed after exceeding the threshold voltage of ~ 7 V. Decreasing of the voltage imme-

Table I Surface Tensions and Surface Polarities of the Investigated Materials

Material	$\gamma^p \ ({ m mN} \ { m m}^{-1})$	$\gamma^d \;({ m mN}\;{ m m}^{-1})$	$\gamma \ (mN \ m^{-1})$	X^p
C320.00A	9.95 ± 1.56	27.52 ± 1.74	34.47 ± 2.33	0.36
10 min OP C320.00A	53.35 ± 2.57	34.20 ± 2.45	19.15 ± 0.76	0.64
$\mathbf{P}_{\mathbf{A}}$ grafted 10 min				
OP C320.00A	20.76 ± 1.33	22.46 ± 0.91	43.22 ± 1.61	0.48
P _A	17.71 ± 1.83	22.68 ± 2.79	40.39 ± 3.34	0.44

diately lead to the formation of the nematic phase again, but still no decision could be made, whether reorientation leads to homeotropic orientation or to isotropization. The application of an AC voltage to a 8CB sample transforms the smectic A phase to a nematic phase and further to the isotropic phase. So, a homeotropic orientation can be excluded. From these results, we assume a thermal effect to be responsible for the texture change caused by the current applied to the fibers; in other words, the fibers heats up like an ohm resistance, if a voltage is applied to them. The temperature increase is hardly measurable on a macroscopic basis, but it is enough to transform lc phases into the isotropic phase. What is rather simple to understand for the low molecular liquid crystals due to their low transition temperatures is much more difficult for the polymer, because their transition temperatures are well above 130°C.

Further investigations concerning this feature are under way to gain better understanding of this phenomena.

Contact-Angle Measurements

Contact angle measured versus water fall from 82.5° for the untreated C320.00A to $\sim 50^\circ$ for the oxygen plasma-treated fiber, only to rise again to 65° for the oxygen plasma-treated and lc-grafted fiber. As a reference, we determined the contact angle of the pure $\mathbf{P}_{\mathbf{A}}$ by the sessile drop method¹² to 70°, which is in good correspondence to the lc-grafted fiber, if the different methods of contact-angle determination are taken into account. Against diiodomethane, we found an increase of the obtained contact-angle values from the untreated C320.00A to the oxygen plasma-treated fiber due to the disruption of the graphitic part of the fiber surface.⁵ The lc-grafted fibers and the pure polymer show the same wetting behavior versus the nonpolar liquid diiodomethane and have contact-angle values lower than the plasmamodified fiber.

The difference between the advancing (θ_a) and receding (θ_r) contact angles, the so-called contact angle hysteresis, is only observed for wetting measurements *versus* water. For the investigated fibers, no significant hysteresis deviation was found versus water, and absolutely no hysteresis occurred against diiodomethane.

In both cases (water and diiodomethane), θ_a values for the lc-grafted fibers and the $\mathbf{P}_{\mathbf{A}}$ coincide very well, which means, that the carbon fiber surface is totally covered with polymer.

We calculated the solid surface tensions from the obtained θ_a values using the harmonic mean equation introduced by Wu¹⁸ (Table I). Again, it was found that the surface tensions for the lcgrafted fibers and the $\mathbf{P}_{\mathbf{A}}$ agree very well. Nevertheless, the rather nonpolar monomer \mathbf{A} could be grafted onto the carbon fiber surface, which is rather polar after the oxygen plasma treatment. This can be understood, if one considers the fact that the methacrylic group, where the polymerization process takes place, is polar. By contactangle measurements, only an integral polarity of the whole surface can be detected.

The temperature dependence of the contact angle of MBBA on C320.00A fibers (Fig. 5) shows that the contact angle passed a maximum value near the clearing temperature. This maximum value of the heating trace is shifted to a lower value on cooling. This shift from 46° to 42°C is due to a supercooling effect. The maximum of the contact angle of MBBA can be explained with the molecular ordering at the phase transition nematic—isotropic and the further decrease of the contact angle is due to the decrease of the surface tension of MBBA.¹⁹

We also performed contact-angle measurements on the same system, but we applied a voltage of 16 V to the fibers. We choose for this measurements a MBBA drop with an relative high contact-angle value. An increase of the contact angle was obtained while a voltage was applied to the fiber. The nematic phase was changed during this process into the isotropic state (Fig. 6). After disconnecting the fibers, the contact angle relaxed back to the starting value. This can also be seen in Figure 6(a,b), which show pictures of MBBA droplets with and without an applied voltage. In Figure 6(b), the droplet is in the lc state, and some sort of birefringence can be detected. Figure 6(a)shows the same droplet with an applied voltage. Here, it is transparent because it is above the clearing temperature. The applied voltage was enough to heat up the small drops (~ 40 μ m diameter) of MBBA above the clearing temperature (Fig. 7). When the voltage was switched off, the liquid crystal returned immediately into its nematic state.

In the experiment with subsequent increase of the applied voltage with return to 0 V after each measurement, the same trend as observed in the temperature-dependent contact-angle measurement was found (Fig. 8). When the voltage was applied, the contact-angle value increased and



Figure 5 Temperature dependence of the contact angle of MBBA on CA.

nearly returned to its initial value after voltage was switched off.

Electrical Conductivity Measurements

Conductivity measurements were performed to estimate the resistivity of modified and unmodi-

fied carbon fibers and to compare the results with well-known conductors [i.e., Konstantan alloy (Cu 60%, Ni 40%)].

The results of the electrical conductivity measurements are summarized in Table II. It seems that a slight plasma oxidation increases the con-



Figure 6 (a) MBBA droplet on C320.00A with applied voltage (16 V). (b) MBBA droplet on C320.00A with no voltage.



Figure 7 Voltage dependence of contact angle of MBBA on C320.00A (CA).

ductivity, compared with the unmodified hightensile carbon fibers. Assuming the carbon fibers are built of onion skin-ordered graphite layers,²⁰ the graphitic framework is relatively rigid and could resist intercalation or bulk oxidation.

This examination shows that carbon fibers are conductible enough to be used as current carrying conductors. Konstantan wire, a well-known resis-



Figure 8 Voltage dependence of contact angle of MBBA on CA.

tance alloy, has a conductivity of 20,000 S cm⁻¹, which is 2 orders of magnitude higher. This verifies the observed increase in temperature when a voltage is applied to the carbon fiber.

ζ-Potential Measurements

The time dependence of the ζ -potential (Fig. 9) of the $\mathbf{P}_{\mathbf{A}}$ powder shows that the ζ -potential values decrease in the beginning range. A constant plateau value is reached after ~ 435 min, but the ζ -potential values decrease only 4 mV. According to this effect, we used for all ζ -potential measurements only samples that were kept in double distilled water for 1 day.

Table II Resistance (R), Electrical Conductivity (κ), and Resistivity (ρ) of Carbon Fibers

Fiber	$egin{array}{c} R \ (\Omega) \end{array}$	$(S \text{ cm}^{-1})$	$\stackrel{\rho}{(m\Omega\ cm^{-1})}$
C320.00A	7,325	530	1.89
C320.00A Konstantan alloy	6,384 —	639 20,000	$\begin{array}{c} 1.56 \\ 0.05 \end{array}$



Figure 9 Time dependence of the ζ -potential of **P**_A.

For all investigated materials, the pH dependence of the ζ -potential (Fig. 10) shows a striking plateau range in the alkaline part. The dissociation of the acidic surface groups causes this plateau range. The unmodified carbon fiber (C320.00A) contains oxygen-containing surface groups due to the manufacturing process, which were formed in air at unsaturated carbon atoms at the basal plane edges. These groups are acidic functional surface groups. At lower pH values, the adsorption of protons, which are potential determining ions, is the predominant mechanism that leads to a change of the surface charge. Modification of the carbon fiber surfaces in oxygen plasma also forms acidic surface groups; the pH dependence of the ζ -potential shows also a plateau area in the alkaline part; the sign of the ζ -potential is also negative, but compared with the unmodified carbon fiber the isoelectrical point is shifted to more acidic values through the higher surface functionalization. But, these high acidic values are not measurable because the proton concentration is too low; a high ion strength of the electrolyte solution would cause a decrease of the ζ -potential. On the other hand, the plateau value of the ζ -potential of 10 min in oxygen plasma-modified fibers is the same as C320.00A.⁵ This change of surface morphology also effects the value of the ζ -potential.²¹ This modification leads to a plateau ranging from pH 5 to 9 ($\zeta_{Plateau} = 25.5 \text{ mV}$). Compared with the unmodified carbon fiber, this plateau area is broader, caused by a repress of the dissociation of those acidic surface functional groups.



Figure 10 pH dependence of the ζ -potential of the investigated materials.

 $\mathbf{P}_{\mathbf{A}}$ shows an analogous trend as described, but its acidic plateau value of the ζ -potential (ζ_{Plateau} = -13 mV) is much lower than that of the investigated carbon fibers. In difference to carbon fibers, this plateau is not caused through dissociation of acidic surface groups, because the polymer does not contain acidic groups according to the synthesis. The measured acidic ζ -pH course might be caused through a saponification of the ester groups. Two of them are present in the lc side group of the polymer. This reaction leads to a separation of the side groups from the polymer backbone or splits the ester function between the phenyl rings, which produced free carboxylic and hydroxy groups. In the acidic range, an adsorption mechanism is also predominant, but the i.e.p. of this $\mathbf{P}_{\mathbf{A}}$ is much lower (i.e.p. = 3.6), compared with the C320.00A fiber (i.e.p. = 4.2). This indicates that the polymer is more acidic than the carbon fiber C320.00A.

Both $\mathbf{P}_{\mathbf{A}}$ -grafted carbon fibers (extracted with dichloromethane and nonextracted) show nearly the same trend. In the acidic range, the adsorption mechanism is also predominant, but no i.e.p. is observable because of its shift to higher acidic values. The observed adsorption behavior is within the same error range as oxygen plasma-modified carbon fibers. In difference to the plasma-modified fibers, the plateau starts at pH 6.7. The relatively high value of the plateau ($\zeta_{\text{Plateau}} = -34 \text{ mV}$) might be caused by the acidity evoked through plasma modification and saponification of the present ester functions of the grafted polymer.

The concentration dependence [Fig. 11(a)] of the $\mathbf{P}_{\mathbf{A}}$ indicates that the K^+ and Cl^- ions, which the electrolyte solution contains, were not specifically adsorbed. The electrochemical double layer, which might be formed by in water-solved carbon dioxide, will be destroyed through the increase of the electrolyte concentration so the negative ζ -potential values decrease. A parabolic curve-like trend was found for all investigated carbon fibers as expected for the concentration dependence. In difference to P_A , the carbon fibers will adsorb these ions specifically. As compared with C320.00A, the maximum ζ -potential (ζ_{max}) (Table III) values shift for oxygen plasma-treated fibers and $\mathbf{P}_{\mathbf{A}}$ -grafted carbon fibers, as well as extracted fiber to lower concentration values and higher negative ζ_{max} values. Only the $\mathbf{P}_{\mathbf{A}}$ -grafted fiber has a lower negative ζ_{max} value as the C320.00A at the same electrolyte concentration. This is mainly evoked by the more or less complete sizing by $\mathbf{P}_{\mathbf{A}}$, and this trend is caused by an indifferent

adsorption behavior. ζ -potential versus concentration curves and surface conductance-corrected¹ curves [Fig. 11(b)] show nearly the same tendency. There is no shift from the maximum ζ -potential to other observable concentration values. According to Davies and Rideal,²² the correction of surface conductance should shift the maximum values to other concentration values. The adsorption potentials of K⁺ and Cl⁻ (Table III) indicate that Cl⁻ is preferably adsorbed on all investigated carbon fibers. An increase of the K⁺ and Cl⁻ adsorption was determined for plasma-modified C320.00A and P_A -grafted extracted fibers. The indifference in the adsorption behavior of $\mathbf{P}_{\mathbf{A}}$ causes a decrease of the K^+ and Cl^- adsorption for grafted, but unextracted fiber surfaces. Only the correction of ζ -potential values obtained from concentration dependence for pure $\mathbf{P}_{\mathbf{A}}$ show a large difference in ζ -potential values measured at low ion concentrations. Wagenen and $\mathrm{Androde}^{23}$ described that correction of surface conductance is insignificant at ion concentrations $> 10^{-3}$ mol L^{-1} . Surface conductance is caused in a capillary or a diaphragm, like fiber bundles by: (1) the liquid layer at the interface of the solid that has a higher ion concentration than the bulk liquid or (2) the different amount of anions and cations that causes no charge compensation at the interface; this makes current conduction possible.²⁴ The large difference between corrected and uncorrected ζ -potential values for $\mathbf{P}_{\mathbf{A}}$ might be caused by various effects, such as solved carbon dioxide or adsorbed water, but the present ions $(K^+$ and Cl^{-}) are indifferent for P_A . The plateau values from the pH dependence and the shift of the i.e.p. to more acidic values can be explained by a polarization effect. The decrease of surface polarity on lc-grafted carbon fibers is also indicated by pH dependence. Both investigations give the same tendency, but are based on different mechanisms on the material surface or in the electrical double layer. Changes of the ζ -potential value measured in double distilled water indicates that a modification of carbon fiber surfaces causes differences in the concurrence mechanism between water adsorption and specific ion adsorption.

CONCLUSIONS

We extended our grafting method to lc methacrylic monomer and showed how the surface morphology and polarity can be influenced by grafting this monomer onto the carbon fiber sur-



Figure 11 (a) Concentration dependence of the ζ -potential of the investigated materials. (b) Concentration dependence of the ζ -potential (surface conductance corrected) of the investigated materials.

Material	$\zeta_{\rm max}~({\rm mV})$	$c_{\max} \ (\text{mol } \mathbf{L}^{-1})$	$\Phi_+ ~(\mathrm{kJ}~\mathrm{mol}^{-1})$	$\Phi_{-}~(kJ~mol^{-1})$
C320.00A	-28.35 ± 0.10	0.006	-9.86 ± 0.45	-15.33 ± 0.01
10 min OP C320.00A	-37.73 ± 0.50	0.003	-10.66 ± 0.20	-17.93 ± 0.19
P_A grafted 10 min OP C320 004	-26.70 ± 0.60	0.003	-11.73 ± 0.41	-16.88 ± 0.92
P. grafted and extracted	20.10 ± 0.00	0.005	11.75 ± 0.41	10.00 ± 0.22
10 min OP C320.00A	-36.13 ± 0.71	0.0006	-14.77 ± 0.13	-21.74 ± 0.27

Table III ζ_{max} , C_{max} Values and Adsorption Potentials for K⁺ and Cl⁻ (Φ_+ , Φ_-)

face. SEM micrographs indicate that polymeric substance is present and most likely covalently bonded to the carbon fiber surface after extraction in an appropriate solvent for a long period of time. These grafted polymers display a bottle brushlike structure; on the other hand, noncovalently bonded polymer that was brought in contact with oxygen plasma-modified carbon fibers gives incomplete and poor sizing of those carbon fibers.

Electro-optical investigations show the possibility of influencing a polymer and low molecular mass lc matrix by applying a voltage to the carbon fibers.

The wetting behavior and surface energy are primarily influenced by the grafted monomer and equals that of the polymer. In contrast to wetting properties, electrokinetic characteristics of such grafted fibers are affected by a combination of both: the grafted substance and the original fiber surface.

Financial support from Deutsche Forschungsgemeinschaft, Sfb 335, and the Fonds der Chemischen Industrie is gratefully acknowledged. We are indebted to Dipl. Ing. J. Nissen (ZELMI, TU Berlin) for recording the SEM micrographs, and we thank Dr. A. Beer (TU Berlin) for valuable comments and helpful suggestions.

REFERENCES

- 1. Bismarck, A.; Pfaffernoschke, M.; Springer, J. J Appl Polym Sci, to appear.
- Le Bonheur, V.; Stupp, S. I. Chem Mater 1993, 5, 1287.
- Finkelmann, H.; Ringsdorf, H.; Wendorff, J. Macromol Chem 1978, 179, 273.
- Ruhmann, R.; Rübner, J.; Rodekirch, G.; Zschuppe, V.; Gnauck, R.; Netopilik, M.; Wolff, D. Acta Polym 1990, 41, 493.

- 5. Bismarck, A.; Kumru, M. E.; Springer, J.; Song, B. J Adhesion, to appear.
- Demus, D.; Demus, H.; Zaschke, H. Flüssige Kristalle in Tabellen; VEB Deutscher Verlag für Grundstoffindustrie; Leipzig, 1974.
- Demus, D.; Zaschke, H. Flüssige Kristalle in Tabellen II; VEB Deutscher Verlag für Grundstoffindustrie: Leipzig, 1984.
- Garbassi, F.; Morra, M.; Occhiello, E. Polymer Surfaces: From Physics to Technology; J. Wiley & Sons: New York, 1994.
- Jacobasch, H.-J.; Simon, F.; Werner, C.; Bellmann, C. Technisches Messen 1996, 63, 439.
- 10. Neumann, A. W. Chemie-Ing-Techn 1970, 15, 969.
- Song, B.; Bismarck, A.; Tahhan, R.; Springer, J. J Colloid Interf Sci 1998, 197, 68.
- 12. Song, B.; Springer, J. J Colloid Interf Sci 1996, 184, 64.
- Song, B.; Springer, J. J Colloid Interf Sci 1996, 184, 77.
- Yamaki, J.; Katayama, Y. J Appl Polym Sci 1975, 19, 2897.
- 15. Carroll, B. J. J Colloid Interf Sci 1976, 57, 488.
- 16. DIN 53 482 (Methods of Test for Materials for Electrical Purposes; Measuring of Electrical Resistance of Non-metallic Materials).
- 17. Tahhan, R. Doctoral Thesis, TU Berlin, 1997.
- Wu, S. Polymer Interface and Adhesion; Marcel Dekker, Inc.: New York, 1982.
- 19. Chen, G.-H.; Springer, J. Mol Cryst Liq Cryst, to appear.
- 20. Ruland, W. Adv Mater 1990, 2, 528.
- 21. Jacobasch, H.-J. Oberflächenchemie faserbildender Polymere; Akademie-Verlag: Berlin, 1984.
- 22. Davies, J. T.; Rideal, E. K. Interfacial Phenomena; Academic Press: New York, 1961.
- Wagenen, R. A.; Andrade, J. D. J Colloid Interf Sci 1980, 76, 305.
- 24. Bikerman, J. Kolloid-Z 1935, 72, 100.