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Liquid Crystal Polymer Brush with Hydrogen Bonds: Structure and Orientation Behavior

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ABSTRACT: The structure and properties of the H-bonded liquid crystalline (LC) polymer grafted onto fluorocarbon polymer substrate were studied by the FTIR spectroscopy technique. The grafted LC polymer brush was prepared via "grafting from" polymerization of 4-(6-acryloyloxyhexyloxy)benzoic acid initiated from the surface of UV-irradiated FEP substrate. The orientation under the uniaxial mechanical stress and the temperature behavior of LC brush stabilized by H-bonds were studied. Substantial changes of the structure and orientation of the LC brush were observed upon increase in temperature. The grafting of the LC layer provides the reversible destruction and restoration of the macroscopic orientation. In contrast to the homopolymer, the orientation behavior of grafted H-bonded LC layer is controlled by the fluorocarbon substrate.

Introduction

New developments in the field of modern polymer science include modification of surfaces with polymers having particular properties like adhesion, lubricity, wettability, chemical affinity, and biocompatibility.[1−3] This approach allows for expanding the area of applications toward microelectronics, smart surfaces, information storage, and medical devices. Surface treatment and modification techniques include plasma polymerization,[4] ion-beam-assisted deposition,[5] and surface grafting.[6] During the past 10 years vacuum-ultraviolet (VUV)-assisted modification of polymer surface has been successfully applied for creating environmentally friendly and biologically active surfaces and surfaces with controlled orientability.[7,8] The latter is considered to be particularly useful for modification of permeability properties and sensing of target molecules. It is especially effective in the case of fluorine-containing polymers. The treatment of such polymers with VUV radiation in the presence of oxygen generates radicals and unstable carboxyl-terminated fluorocarbon chains located on the surface of substrate.[7] The subsequent annealing leads to decomposition of the above products and produces active centers capable of initiating radical polymerization of typical acrylic monomers. Such grafting from initiation occurs when the monomers[7] are placed onto the "active" polymer surface. We have succeeded in creating surface grafted liquid crystal (LC) polymer brushes, forming micron thick layers and possessing properties similar to that of bulk polymers.[7,8] The main objective of this paper is to show the role of the grafting of the LC polymer on its structure and orientation behavior. We here describe an LC H-bonded polymer (poly[4-(6-acryloyloxyhexyloxy)benzoic acid]) covalently grafted onto Teflon FEP film. The choice of Teflon FEP as a support for graft polymerization was dictated by two reasons. The first one is the mechanical

and thermal stability of this polymer ($T_m = 260−280$ °C) which allows one to study the orientation behavior of the grafted brush layer in the wide temperature range. The second one pertains to its ability to form highly stable long-lived active centers upon UV irradiation in the form of oxygen-containing species such as $-CF_2C(O)F$ or peroxy radicals RO−OR that can initiate polymerization of acrylic monomers at elevated temperatures.[7]

Results and Discussion

The polymerization of the mesogenic monomer, 4-(6-acryloyloxyhexyloxy)benzoic acid (BA-6A), from the surface of Teflon FEP film results in the formation of the composite material. The IR spectrum (Figure 1) confirms the presence of both components of the composite material. The major spectral bands in spectrum 3 at 1731 cm^{-1} (ester, $\nu_{C=O}$), 1681 cm^{-1} (H-bonded $\nu_{C=O}$ in COOH), 1608 and 1514 cm^{-1} ($\nu_{C=C}$ in benzene rings), 775 and 850 cm^{-1} (out-of-plane δ_{CH} in benzene rings), 1426 cm^{-1} (δ_{CH_2}), and 2940 cm^{-1} (ν_{CH_2})[9] coincide with those in spectrum 1 of nongrafted poly(4-(6-acryloyloxyhexyloxy)benzoic acid) (PA-6BA).[10] At the same time several more bands, namely, 2370 cm^{-1} (ν_{CF} in CF$_2$), 1100−1300 cm^{-1} (δ_{CF} in CF$_2$), and 983 cm^{-1} (δ_{CC} in CCF$_3$), are apparent in spectrum 3, which can be attributed to Teflon FEP (spectrum 2).

The structure of the LC brush is sensitive to changes in temperature, which can be easily traced by FTIR. The increase in temperature up to 160 °C leads to a strong decrease in the intensity of absorption bands at 1681 and 2550 cm^{-1}, corresponding to the hydrogen-bonded carboxyl groups. The change in absorption at 1690−1700 cm^{-1} and the appearance of a broad absorption band at 3200−3400 cm^{-1} indicate the formation of free COOH groups. As illustrated in Figure 2, the transition of the LC grafted layer to the isotropic state is accompanied by considerable drop in the relative optical density of the 1681 cm^{-1} spectral band. Thus, the transformation of the micron thick layer of the grafted

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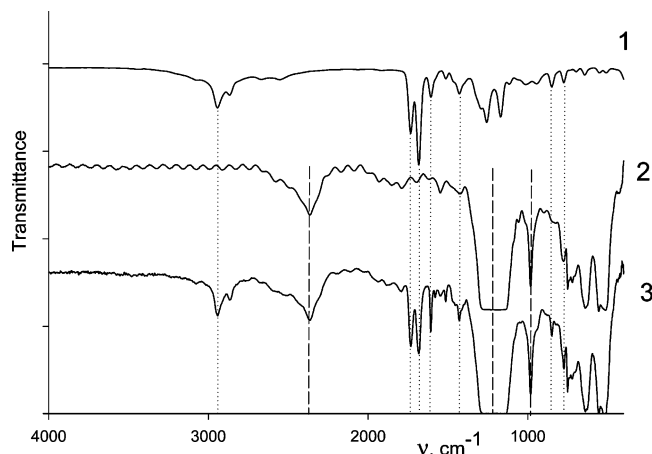[‡] A.V. Topchiev Institute of Petrochemical Synthesis.

Figure 1. FTIR spectra of the PA-6BA polymer film (1), Teflon FEP support (2), and composite grafted polymer (3).
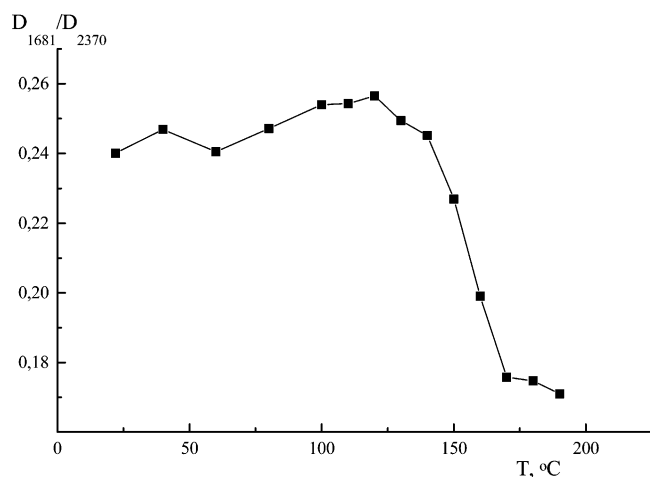

Figure 2. Relative optical density corresponding to the H-bounded C=O groups in the grafted PA-6BA polymer vs temperature.
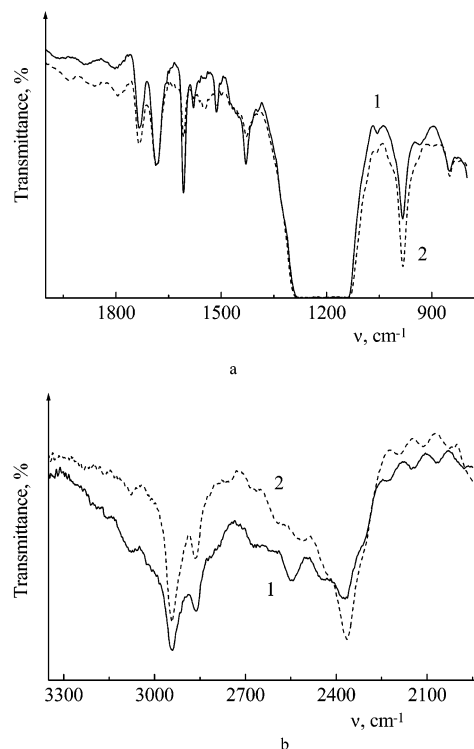

Figure 3. FTIR spectra of the oriented composite film (PA-6BA grafted on Teflon FEP) in the middle- (a) and high-frequency (b) regions measured with parallel (1) and crossed (2) polarizers.

LC polymer to the isotropic state is accompanied by the partial dissociation of hydrogen-bonded dimers in the LC polymer brush. The decrease in the amount of hydrogen-bonded dimers can be quantified by the decrease of relative optical density at the 1681 cm^{-1} band. According to the data shown in Figure 3, the transformation to the isotropic state is followed by $\approx$30% decrease in hydrogen-bonded COOH groups. Note that the relative decrease in the concentration of hydrogen-bonded dimeric structures upon isotropization for micron-thick grafted LC polymer layers is about the same as for bulky polymer we studied before.[10]

The stretching of the composite film results in the anisotropic optical properties with IR spectra recorded in two polarizations: parallel and perpendicular to the stress axis (Figure 3). The dichroism value $D < 1$ was observed for the IR band at 983 cm^{-1}, corresponding to the $-C-C-$ vibration in the side-chain groups $C-CF_3$, thus suggesting the orientation of the main chains of fluorocarbon chains along the deformation axis. The band at 1731 cm^{-1} attributed to the ether carbonyl C=O groups in the side chains of LC polymer did not exhibit a noticeable dichroic ratio, whereas the absorption band at 1681 cm^{-1} attributed to the hydrogen-bonded carboxylic groups of the mesogenic fragment displayed a weak dichroic ratio of $D_{1683} \approx 1.2-1.3$ (Figure 3a). Such a difference in orientation behavior is probably due to the fact that the ester C=O group

undergoes free rotation around the axis of the polymer side chain while the mobility of the acid C=O group of oriented mesogenic fragment is limited by hydrogen bonding. The IR spectrum of the grafted LC polymer at room temperature did not exhibit any absorption corresponding to the free OH groups in the wavelength region from 3200 to 3400 cm^{-1}; however, the band at 2550 cm^{-1} with a noticeable dichroism corresponding to the hydrogen-bonded COOH group[11] was observed (Figure 3b). The most pronounced effect of stretching is seen for the absorption bands at 1608, 1580 (ν_{as} Ph), and 1514 cm^{-1} (ν_s Ph) attributed to the phenyl rings located along the mesogenic fragments. They exhibit much higher dichroism $D > 1$. The orientation function of mesogen groups in grafted PA-6BA calculated from the dichroic ratio of the band at 1514 cm^{-1} measured at 20 °C is given in Figure 4 as a function of strain. The orientation degree becomes higher with the increase in strain and reaches the plateau at the $\Delta l/l = 1$ (Figure 4, curve 1). Such behavior is in good agreement with the orientation dependence observed for the homopolymer (Figure 4, curve 2). These data indicate the preferable orientation of mesogen groups along the stress axis. However, the homopolymer BA-6PA is known to have a smectic C_A structure, and when oriented under stretching it arranges smectic layers parallel to the film plane in which H-bonded mesogenic groups are tilted in an alternating fashion.[12,13] Taking into account the tilted Sm C_A structure of the LC polymer, the value of dichroism and related orientation degree of the grafted BA-6PA imply that the mechanical field produces alignment not of the LC director itself, but rather its projection in the film plane (Figure 5).

The heating of the grafted material strongly affects the macroscopic orientational order. Figure 6 shows the variation of the orientation functions of the fluorocarbon
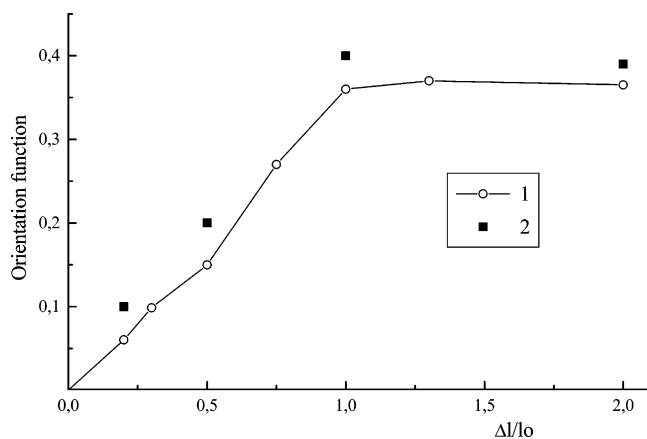
Figure 4. Orientation function vs relative elongation calculated from the dichroic ratio of the IR band at 1514 cm^{-1} for the grafted polymer PA-6BA (1) and homopolymer (2).
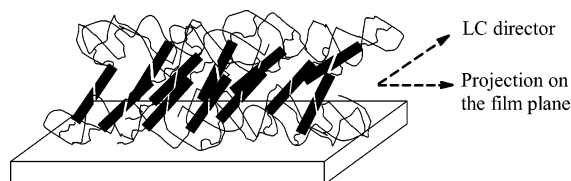

Figure 5. Schematic presentation of the structure of the grafted PA-6BA oriented under mechanical deformation.
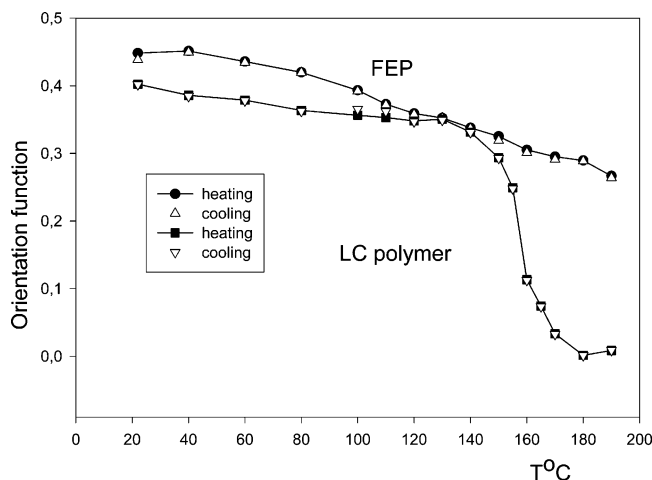

Figure 6. Orientation function vs temperature calculated from dichroic ratio of IR bands 1514 cm^{-1} (C=C Ph in grafted LC polymer) and 983 cm^{-1} (C−CF$_3$ in FEP support).

substrate and grafted BA-6PA with the temperature. The orientation function for the Teflon FEP copolymer substrate was calculated from the dichroism of the 983 cm^{-1} band. For the grafted LC polymer brush, the absorption band at 1608 cm^{-1} due to asymmetric in-plane C=C vibrations of the phenyl ring was used. The dipole moment corresponding to this vibration is directed along the axis of the mesogenic fragment. The heating leads to a noticeable decrease in the degree of orientation of the Teflon FEP substrate, which is probably due to an increase in the mobility of polymer chains and, as a result, to some disorientation of the stretched Teflon FEP support. The orientation function of the grafted LC polymer first slightly goes down with the decrease of orientation function of fluorocarbon substrate during heating from room temperature to 140 °C. The further increase in the temperature above 140 °C causes a significant decrease of the orientation function of grafted LC polymer down to zero in the
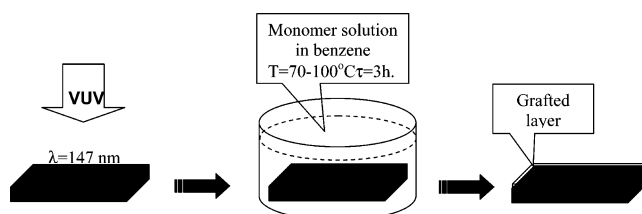

Figure 7. Schematic presentation of graft polymerization process induced by vacuum-ultraviolet irradiation.

vicinity of the LC−isotropic transition ($T_{LC-isotropic} = 160$ °C). The cooling of the sample results in the increase of the orientation degree and the restoration of the macroscopically oriented structure of the grafted layer (Figure 6).

Conclusions

In summary, the "grafting from" polymerization technique provides the possibility to synthesize the temperature stable macroscopically oriented composite LC polymer brush with SmC$_A$ structure with reversibly variable parameters. Heating and cooling of the sample near the LC−isotropic transition temperature lead to the reversible disappearance and recovery of hydrogen-bonded dimers that define the LC state. The grafting itself provides a well-pronounced memory effect, which is manifested in the restoration of the orientation of the LC layer after cooling the sample heated above LC−isotropic transition. It makes the grafted polymer layer much different from the corresponding homopolymer which completely loses its orientation after heating above the LC−isotropic transition and cooling below it. The reason for the latter is the perfluorinated polymer substrate that provides the orientation by keeping its stretched alignment in a wide temperature range, thereby allowing for the reversible restoration of the macroscopic monodomain structure of the LC polymer layer.

Experimental Section

The monomer, 4-(6-acryloyloxyhexyloxy)benzoic acid, was synthesized as previously described.[14] The yield of the monomer was 60%, melting temperature $T_m = 68$ °C, and clearing temperature $T_c = 98$ °C. The homopolymer was prepared by radical polymerization in benzene at 65 °C for 75 h. 2,2′-Azoisobutyronitrile (0.1% of the total weight of the monomer) was used as initiator. The polymer yield was 60%.

Figure 7 shows the scheme of graft polymerization process. To generate the active centers of graft polymerization, the samples of Teflon FEP (copolymer of tetrafluoroethylene with hexafluoropropylene, 85%:15%, 120 μm thickness, and 15 mm in diameter) were irradiated by a vacuum-ultraviolet (VUV) Xe lamp KsR-2A[15] (wavelength 147 nm, intensity of 3 × 10^{15} photons/(s cm^2)) in the vacuum chamber at 4 × 10^2 Pa air pressure and 20 cm^3 (STP)/min air flow rate and room temperature for 1 h. The low molecular weight products of photooxidation were then removed by chloroform in order to reduce the formation of homopolymer on the surface.

The graft polymerization was carried out by immersion the VUV-treated FEP film in the benzene solution at the temperature range 70−100 °C and monomer concentration 0.5−3 wt % for 3 h. The solution during graft polymerization was filled in with dry nitrogen to prevent inhibitory effect of dissolved oxygen on surface-active centers.

Homopolymer films and grafted specimens were oriented by uniaxial stretching with an "Instron-1122" instrument. The films (5 mm × 10 mm) were placed in a heat chamber and fixed in the crosshead grips. The deformation of the films was performed at 110 °C in the load range 1−50 N with the

deformation rate of 2 mm/min. The temperature dependence of IR absorption spectra, as well as the IR dichroic ratio for the absorption bands attributed to various functional groups of the homopolymer, grafted polymer and the substrate were measured using a FTIR spectrometer "Perkin-Elmer1720X". An optical attachment designed for this purpose made it possible to record transmission spectra in polarized-light for the oriented polymer specimens in the temperature range from 20 to 250 °C. An electronic control unit made on the basis of a modified temperature controller ensured the measurement and automated maintenance of specimen temperature accurate to 0.2 °C. The value of IR dichroic ratio was calculated as $D = I_{||}/I_{\perp}$ for the absorption bands corresponding to the Teflon FEP substrate: 2370 cm^{-1} (ν_{CF} CF$_2$) and 983 cm^{-1} (δ_{CC} CCF$_3$) as well as for the absorption bands at 1608, 1580 cm^{-1} (ν_{as} Ph), 1514 cm^{-1} (ν_s Ph), and 1430 cm^{-1} (δ_{CH} CH$_2$) attributed to the LC polymer. The degree of orientation S was calculated from the dichroic ratio as $S = (D - 1)/(D + 2)$ if the dipole moment corresponding to the absorption band was parallel to the axis of the oriented fragment and $S = -2(D - 1)/(D + 2)$ if the corresponding dipole moment was perpendicular to the axis of the oriented macromolecule or the mesogenic fragment.[16]

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MA0357164