Low Surface Energy Polymeric Films from Novel Fluorinated Blocked Isocyanates

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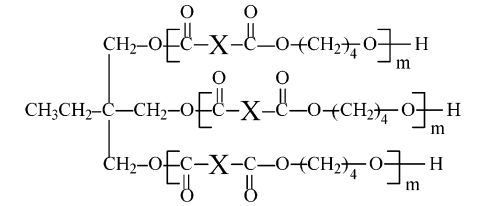
ABSTRACT: Polymeric films with surface energies as low as 10 mN/m were prepared from a mixture of a hydroxyl-end-capped solventless liquid oligoester (SLO), a blocked polyisocyanate, and a novel fluorinated blocked isocyanate (F_nB-NCO; the ratio of the fluorinated tail and the caprolactam blocking group: 1:1), with less than 4 wt % of fluorine in the films. The curing temperature demonstrated a significant effect on the reaction rate and the film wettability: a higher curing temperature led to a less significant surface enrichment of fluorine, especially at a low F content (<2 wt %), due to the fast immobilization of the cross-linked networks. The mixtures had excellent stability below the deblocking temperature (∼ 140 °C) of the blocked isocyanates, which allowed the determination of the diffusion coefficients of fluorinated species in the reaction mixtures by pulsed field gradient (PFG) NMR. The well-defined F_nB-NCOs enabled an easy and accurate adjustment of the fluorine concentration, making this approach practically attractive and efficient to prepare low surface energy films by using small amounts of fluorinated species.

Introduction

Fluoropolymers offer a wide range of interesting properties, such as low wettability (water/oil repellency) and low coefficients of friction.[1] These properties are basically surface properties, and it is, therefore, unnecessary to have the expensive fluorine in the bulk. The good water/oil repellency is especially due to the low surface energy of the fluorinated films, and there has been a considerable amount of interest to prepare fluorinated films.[2] Self-stratification strategies provide an excellent opportunity to create coatings in which desired surface and bulk properties are well-balanced. In such an approach, only a very small quantity of fluorinated species is needed to provide a surface with low surface energy. The fluorinated species would migrate toward the air/film interface to minimize the interfacial energy.[2b,c,e,f]

We have recently developed low surface energy cross-linked films on the basis of a partially fluorinated hydroxyl-end-capped solventless liquid oligoester (SLO, Scheme 1), either thermally cured[3] with a polyisocyanate or photocured[4] after the introduction of acrylic double bonds. The addition of 1−1.5 wt % of fluorine could reduce the surface energy from 45 to 20−30 mN/m.[3,4] Much stronger surface segregation of fluorinated species was obtained by using partially fluorinated polyisocyanates (the lowest surface energy reaching 10 mN/m), owing to the enhanced diffusivity of fluorinated polyisocyanates in comparison with fluorinated oligoesters.[5,6] During the partial fluorination,[3,5,7] the non-fluorinated components were in large excess compared to the fluorinated molecules, limiting the maximum amount of fluorine that can be incorporated into the films to relatively low levels; the low levels of fluorine content may not sustain the low film wettability in applications where mechanical abrasion is present. Another weak point in the partially fluorinated oligoesters/polyisocyanates systems is that the extent of fluorination for individual molecules cannot be accurately controlled. Besides, because of the high reactivity between isocyanate and hydroxyl groups, the stability of the reaction mixtures is another issue to be improved, as far as any practical applications are concerned.

Scheme 1



In this paper we report a convenient yet novel way of synthesizing fluorinated blocked isocyanates with a well-defined structure, which allowed an easy and accurate approach to prepare low surface energy films on the basis of polyurethane systems. The cross-linking reactions were monitored by attenuated total reflectance (ATR) FTIR. Diffusion coefficients of the fluorinated species in the reaction mixtures were measured by PFG NMR. The fluorine enrichment in the top surface of the films was examined by contact angle measurements and X-ray photoelectron spectroscopy (XPS). Temperature

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effects on both cross-linking and film wettability were investigated.

Experimental Section

Materials, Synthesis, and Film Preparation. The synthesis of a solventless liquid oligoester (SLO, Scheme 1) was detailed elsewhere.[3,7] The M_n for this oligoester was estimated to be 914 from ^{1}H NMR. The molar amount of hydroxyl groups in 1 g of the oligoester was 3.56×10^{-3} mol as determined by titration. The majority of the cross-linker was Desmodur BL-3272 (hexamethylene diisocyanate polyisocyanurate blocked by caprolactam) from Bayer.

The perfluoroalkyl-end-capped caprolactam-blocked isocyanates (F_nB-NCO) were synthesized via a one-step reaction[8,9] between *N,N′*-carbonyl biscaprolactam (CBC, ALLINCO, a gift from DSM Research) and an equal molar amount of a perfluoroalkyl alcohol, $F(CF_2)_nCH_2CH_2OH$ ($n = 6$ or 8, gifts from Clariant GmbH), under a dry N_2 atmosphere at 125 °C for 5 h and catalyzed by $MgBr_2$ (1% of the total weight of the reactants). The obtained F_nB-NCOs were purified by recrystallization in ethyl acetate. The structures of F_nB-NCOs were examined by ^{1}H, ^{19}F, and ^{13}C NMR on a Varian 400 spectrometer at 25 °C with $CDCl_3$ as the solvent.

In the reaction mixtures comprising SLO, F_nB-NCO, and BL-3272, the overall OH/blocked-NCO molar ratio was maintained slightly greater than 1 to ensure the complete conversion of the blocked NCO groups. The ratio of F_nB-NCO to BL-3272 was varied to obtain different fluorine contents in the films. These mixtures did not undergo any reactions below 140 °C. Thin films were applied on clean aluminum panels and then cured at 150−200 °C for 1−3 h. The thickness for dry films was found to be about 20 μm, as measured using a Twin-Check thickness gauge by List-Magnetic GmbH.

Techniques. Contact angles were measured with deionized water and hexadecane (>99%, Merck) on a contact angle microscope (G10, Krüss, Hamburg). In-situ IR spectra were recorded under dry N_2 atmosphere on a BioRad Excalibur spectrophotometer equipped with a mercury−cadmium−telluride (MCT) detector, a MKII Golden Gate heated diamond 45° ATR top plate (Specac Ltd., England), and a 3000 series high stability temperature controller (Specac). Reactive mixtures of BL-3272 and SLO were deposited on the diamond unit and cured at elevated temperatures. Spectra (eight scans per spectrum at a resolution of 4 cm^{-1}) were collected each minute until the completion of the cross-linking reaction. XPS measurements were performed on a VG-Escalab spectrometer using an aluminum anode (Al Kα = 1486.3 eV) operating with a background pressure of 2×10^{-9} mbar. A takeoff angle of 90° (between the film surface and the axis of the analyzer lens) was used, corresponding roughly to a sampling depth of ~8 nm.[10] Spectra were recorded within 2 min in order to minimize radiation damage of the sample. Curve fitting was done with CasaXPS version 2.19 software.

The diffusion coefficients (D_c) of fluorinated species in the reaction mixture of SLO, F_nB-NCO, and BL-3272 at 60, 80, and 100 °C (below the deblocking temperature, ca. 140 °C, of blocked isocyanates) were determined by pulsed field gradient (PFG) NMR.[11−13] Special coaxial NMR tubes were used to separate the locking agent (DMSO-d_6) from the reaction mixture to be analyzed. ^{19}F NMR spectra were recorded on a Varian 500 spectrometer. The peak at −85.8 ppm (C**F**$_3$, Figure 2) was chosen for further analysis. A series of magnetic field gradient pulses G_i (T/m) were applied on the sample, resulting in attenuated signal intensities $S(G_i)$. The relation between D_c and attenuated signal intensities is as follows:

$$\ln \frac{S(G_i)}{S(G_0)} = -D_c\gamma^2\delta^2(\Delta - \delta/3)(G_i^2 - G_0^2) \qquad (1)$$

where $S(G_i)$ is the signal intensity at G_i, G_i the strength of the field gradient, γ the gyromagnetic ratio, δ the length of the diffusion gradient, and Δ the gradient pulse interval. D_c can be determined from (1). The use of ^{19}F NMR allows the exclusive analysis of D_c of F_nB-NCOs.

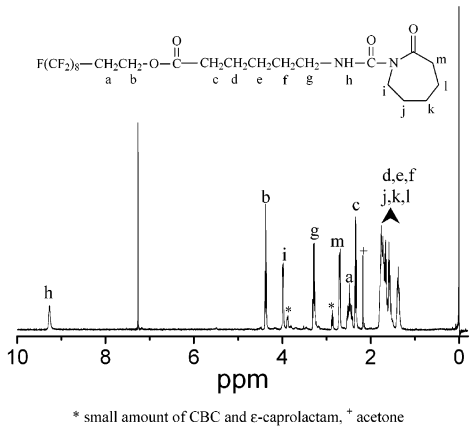

Figure 1. ^{1}H NMR spectrum of F_8B-NCO.

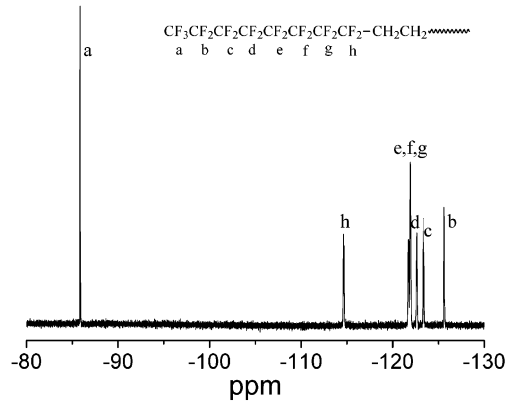

Figure 2. ^{19}F NMR spectrum of F_8B-NCO.

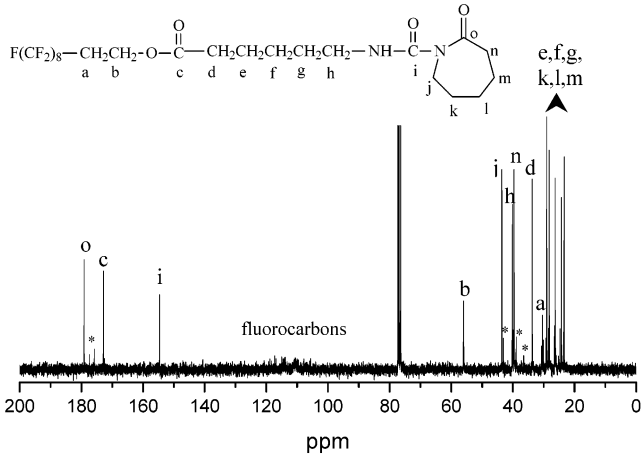

Figure 3. ^{13}C NMR spectrum of F_8B-NCO.

Results and Discussion

Synthesis of F_nB-NCOs. The F_nB-NCOs were synthesized via a one-step reaction between CBC and an equal molar amount of $F(CF_2)_nCH_2CH_2OH$ in high yields.[8,9] The structure of F_nB-NCOs, with a perfluoroalkyl group on one end and a caprolactam blocking group on the other, was confirmed by NMR analyses. Shown in Figures 1−3 are ^{1}H, ^{13}C, and ^{19}F NMR spectra for F_8B-NCO, which correspond well to its molecular structure. For instance, in Figure 1, the integrals of peaks *b* and *m* (or *i*) are the same, indicating a 1:1 ratio

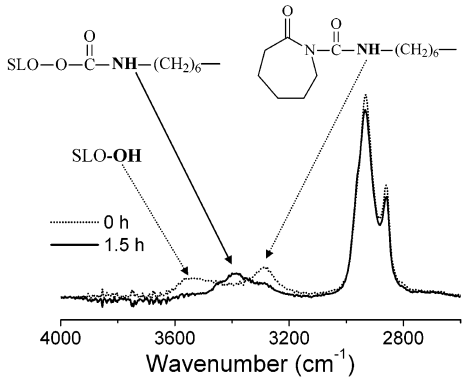

Figure 4. IR spectra of the reaction mixture of SLO and BL-3272 at the beginning of the reaction and after 1.5 h reaction at 160 °C.

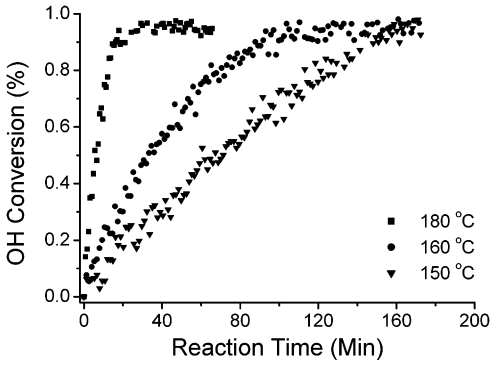

Figure 5. Temperature effects on the OH conversion during the reaction between SLO and BL-3272 from ATR−FTIR studies.

between the perfluoroalkyl group and the caprolactam blocking group in F_8B-NCO.

The well-defined structure of the fluorinated blocked isocyanates enabled an easy and accurate adjustment of the fluorine content in the films. The majority of the cross-linker was a nonfluorinated blocked polyisocyanate cross-linker (Desmodur BL-3272). The blocked (poly)-isocyanates rendered the reaction mixtures stable up to 140 °C, which in turn would allow the determination of diffusion coefficients of the fluorinated species in the mixture of F_nB-NCO, BL-3272, and SLO at a temperature below 140 °C, as shown below.

Reactions between SLO and Blocked Polyisocyanate. The reactions between caprolactam-blocked isocyanates and hydroxyls lead to the formation of a urethane (carbamate) linkage via an addition−elimination mechanism while releasing ϵ-caprolactam, which has been well documented in literature.[14] The cross-linking reactions between the hydroxyl groups of SLO and BL-3272 were monitored by ATR−FTIR at 150, 160, and 180 °C. IR spectra of the reaction mixture of SLO and BL-3272 at the beginning of the reaction and after 1.5 h at 160 °C are shown in Figure 4. The OH stretching peak (3530 cm^{-1}) from SLO and the NH stretching peak (3290 cm^{-1}) from BL-3272 disappeared or decreased significantly after 1.5 h reaction, and a new NH stretching peak (3400 cm^{-1}) emerged due to the formation of the urethane bond.

The disappearance of the OH stretching peak at 3530 cm^{-1} of the SLO was used as an indication of the extent of the reaction. The C═O peak at 1690 cm^{-1} of the isocyanurate ring remained unchanged and was thus taken as an internal reference. The conversion of OH could be derived from the decrease of the OH peak. Figure 5 shows the pronounced effect of the reaction temperature on the OH conversion: it took only 20 min at 180 °C while about 3 h at 150 °C to reach a similar extent of OH conversion (about 95%). The cure half-life time for the reactions at 150, 160, and 180 °C was found to be about 7.5, 33.3, and 64.5 min, respectively, according to an asymptotic regression exponential fitting for the data in Figure 5. The reaction at 200 °C would proceed even faster than at 180 °C (data were not collected due to the operation temperature limit for the ATR unit). The addition of a small amount of F_nB-NCO did not show significant effect on the cross-linking reactions.

Measurement of Diffusion Coefficient (D_c) of Fluorinated Species in the Reaction Mixture. Below the deblocking temperature (ca. 140 °C) of the blocked isocyanates used in this study, the reaction mixture of SLO, F_nB-NCO, and BL-3272 was stable, which allowed us to determine the D_c of the fluorinated species in the reaction mixture at a temperature below 140 °C by using PFG NMR. ^{19}F NMR was used to exclusively determine the D_c of the fluorinated species.

The attenuated signal of C**F**$_3$ (−85.8 ppm, Figure 2) of F_8B-NCO in a mixture of SLO, F_8B-NCO, and BL-3272 (containing 3.8 wt % of F) was collected at different temperatures. Figure 6 shows the attenuated signals of the C**F**$_3$ peak under different field gradients at 100 °C. D_c can be obtained from the slop of the plot of ln $[S(G_i)/S(G_0)]$ against $\gamma^2\delta^2(\Delta - \delta/3)(G_i^2 - G_0^2)$ (Figure 7). The D_c of F_8B-NCO in the reaction mixture at 60, 80, and 100 °C was determined to be 1.1×10^{-11}, 2.4×10^{-11}, and 5.3×10^{-11} m^2/s, respectively. As shown in Figure 8, these data follow an Arrhenius-type behavior

$$D_c(T) = A e^{-E_a/RT} \qquad (2)$$

where $D_c(T)$ is the D_c at temperature T, A a preexponential, E_a the activation energy, and R the gas constant.

Although it is not possible to measure the D_c at a temperature higher than the deblocking temperature (ca. 140 °C) of the blocked isocyanates, an estimation of the D_c of F_8B-NCO as it would be at reaction temperatures (150−200 °C) can be obtained by extrapolating the D_c-T curve (Figure 8) to higher temperatures, according to (2). The "virtual" D_c for F_8B-NCO in the reaction mixture at 150 and 200 °C (assuming no reaction taking place) would be 2.5×10^{-10} and 8.4×10^{-10} m^2/s, respectively. Detailed investigations on the competition between the diffusion of fluorinated species and the immobilization of cross-linked networks are under way in our laboratory.

Film Wettability. The value of the contact angle of a liquid on a film is a direct reflection of the surface wettability. Advancing contact angles of water and static contact angles of hexadecane on films based on SLO, F_8B-NCO, and BL-3272 as a function of the added fluorine content in the films (calculated from the recipes by assuming complete reactions and no loss of the fluorinated species during heating) are shown in Figure 9. When the films were cured at 200 °C, the water contact angles increased steadily from 87° to 124° and the hexadecane contact angles increased from 0 (without fluorine present in the films, hexadecane spread over the surface, and a contact angle of 0 was assigned) to about 80°, as the added fluorine content in the films increased from 0 to 3.8 wt %. The contact angle data

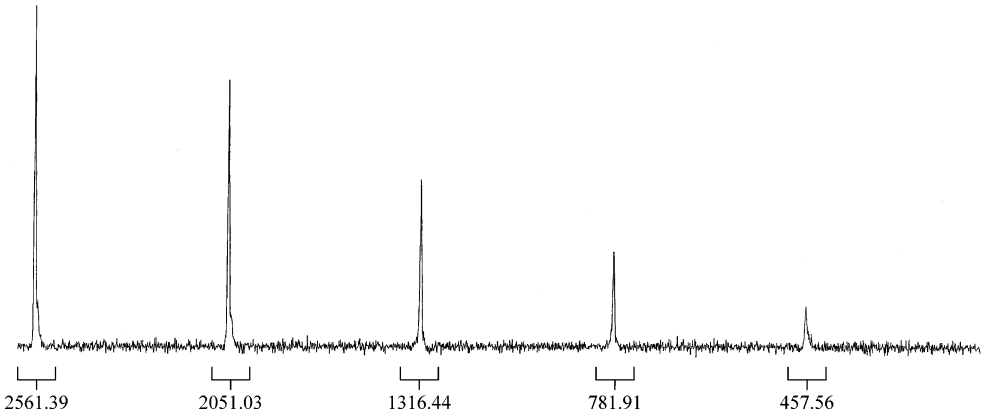

Figure 6. Attenuated signals $S(G_i)$ for a reaction mixture of F_8B-NCO, SLO, and BL-3272 (containing 3.8 wt % of F) under increasing field gradients at 100 °C. The applied field gradients (G_i) were (from left to right) 500, 10 000, 17 500, 25 000, and 32 000 T/m, respectively. $\Delta = 0.40$ s and $\delta = 0.001$ s.

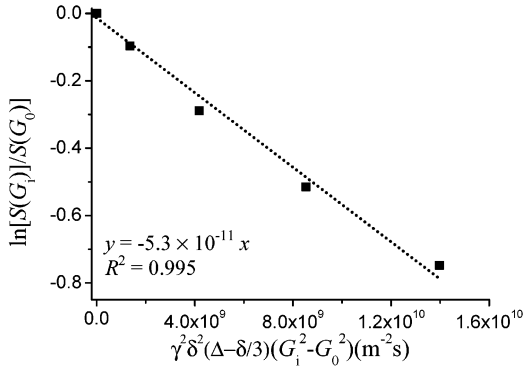

Figure 7. Determination of the D_c of F_8B-NCO in the reaction mixture (containing 3.8 wt % of F) at 100 °C; $D_c = 5.3 \times 10^{-11}$ m^2/s.

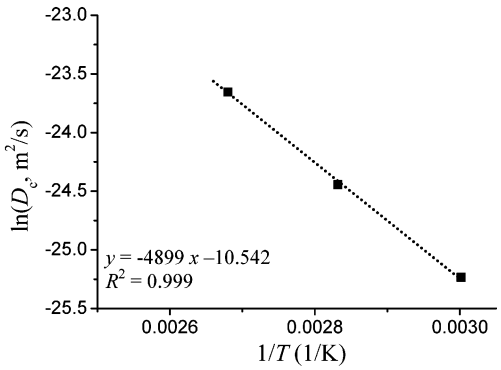

Figure 8. Temperature dependence of the D_c of F_8B-NCO in the reaction mixture.

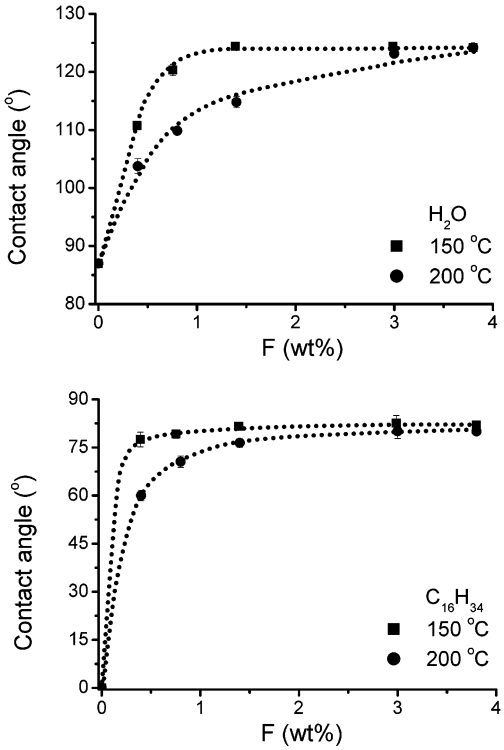

Figure 9. Contact angles of water and hexadecane as a function of the added F content on the films from SLO, F_8B-NCO, and BL-3272 cured at 150 and 200 °C, respectively.

reached similar levels as in our previous studies in which partially fluorinated nonblocked (poly)isocyanates were used.[5,6] These high contact angles (corresponding approximately to a surface energy of 10 mN/m) showed clearly that the surface of the films was significantly enriched in the fluorinated species.[5,6]

The low surface energy films were either rinsed by water or rubbed by acetone; the difference of the water advancing contact angles was less than 2° in comparison with the films as prepared, implying that the fluorinated tail was chemically bonded to the cross-linked films.

On the other hand, when the films were cured at 150 °C, the increase of both the water and hexadecane contact angles was much more pronounced upon the addition of a small amount of fluorinated species, as also shown in Figure 9. Both contact angles reached plateau values (water: 125°; hexadecane: 80°) at lower fluorine concentrations. Further increase of the fluorine content was feasible, which may result in thicker fluorine-enriched layers in the surface.[15] Apparently, when films were cured at a lower temperature, the surface enrichment of the fluorinated species was even stronger. As shown earlier from our FTIR studies in the previous section, the reaction between SLO and BL-3272 proceeded much faster at 180 °C than at 150 °C. At 200 °C even less time would be needed for the reaction to be complete. Therefore, at 200 °C the reactive mixture became immobilized in a very short period of time. The diffusion of fluorinated species would become very limited when the viscosity of the mixture was high. When the mixture was cured at 150 °C, the mixture would remain as a liquid in the first 1 h. Although the diffusion of F_8B-NCO at 150 °C was about 3 times slower than at 200 °C, as shown by the PFG NMR study,

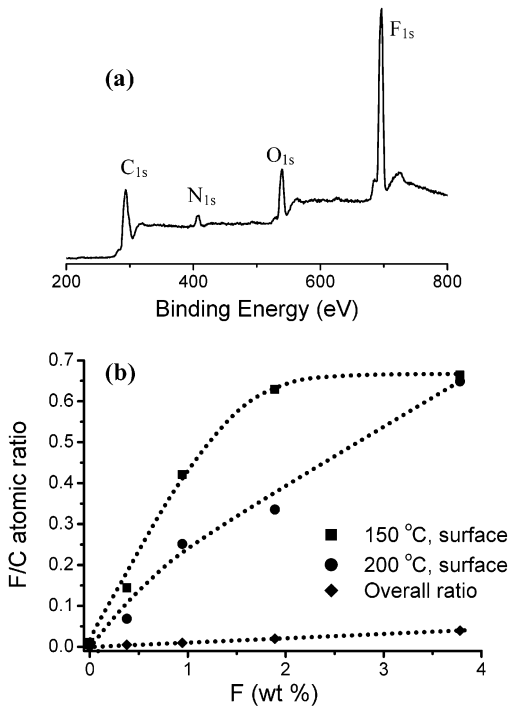

Figure 10. (a) XPS spectrum of a film containing 0.9 wt % F from SLO, F_8B-NCO, and BL-3272 cured at 150 °C. (b) F/C atomic ratio at the surface (about 8 nm deep) in the films on the basis of SLO, F_8B-NCO, and BL-3272 cured at 150 and 200 °C, respectively (the overall F/C ratio was estimated from the recipe of the reaction mixtures).

there was obviously much more time allowed for the fluorinated species to migrate toward the air/film interface, leading to the more pronounced surface enrichment of the fluorinated species.

The contact angles on the films from SLO, F_6B-NCO, and BL-3272 showed a similar trend to the films from F_8B-NCO as the fluorine content increased, but the plateau values for both water and hexadecane contact angles were lower. Similarly, a higher curing temperature also led to a less significant surface enrichment of the fluorinated species.

Surface Composition at the Film Surfaces. In addition to the contact angle measurements, XPS was used to reveal the fluorine enrichment at the surface. In a typical wide-scan spectrum (Figure 10a), peaks corresponding to F_{1s}, C_{1s}, O_{1s}, and N_{1s} are shown. The N_{1s} signal was presumably due to the carbamate linkage in the cross-links formed during the film formation (indicated in Figure 4); this signal would be less likely due to the residual ϵ-caprolactam since ϵ-caprolactam was supposed to leave the films during curing. The F/C atomic ratio was calculated from the XPS spectra by comparing the F_{1s} and C_{1s} peak intensities (in combination with the sensitivity factors for C and F). In Figure 10b, the F/C atomic ratio at the surface is given as a function of the added fluorine content in the films on the basis of F_8B-NCO. The overall F/C atomic ratio (estimated from the recipes by deducting the amount of ϵ-caprolactam) in the films was lower than 0.04, but in the surface (about 8 nm deep) of the films much more fluorine-containing species segregated, with the F/C ratio reaching 0.65. The XPS data were in agreement with the contact angle data but showed not exactly the same trend. For the contact angle data, the plateau values were reached at lower F levels than for XPS data. This is reasonable since XPS probes much deeper layers than contact angle measurements. The curing temperature also showed a strong influence on the F/C atomic ratio: a lower curing temperature facilitated the surface enrichment of the fluorinated species, especially at a low F content (less than 2 wt %).

Conclusions

By using a novel fluorinated blocked isocyanate, together with a conventional blocked polyisocyanate and a hydroxyl-functionalized oligoester, polymeric films with surface energies as low as 10 mN/m were readily prepared. The curing temperature demonstrated a significant effect on both the cross-linking reaction and the wettability of the films: a higher curing temperature led to a lesser surface enrichment of fluorine especially at a low F content (less than 2 wt %) because of the fast immobilization of the cross-linked networks. Because of the well-defined F_nB-NCOs, the fluorine content in the films can be easily and accurately adjusted, making this approach practically attractive and efficient to prepare low surface energy polymeric films by using small amounts of fluorinated species.

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