

Note

SELF-ASSEMBLED MICRO-DOMAINS ON THE UPPERMOST SURFACE OF FLUORINATED POLY(CARBONATE URETHANE)S WITH FLUORINATED SIDE CHAIN ATTACHED ON HARD SEGMENTS*

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Abstract The surface phase separated structure of polyurethanes is always desired due to the advantage of better biocompatibility, compared with the homogeneous one. The key issue is how to control and characterize the surface morphology. In this work, we report the uppermost surface morphology of fluorinated poly(carbonate urethane)s with fluorinated side chains attached to hard segments as studied by AFM, XPS and contact angle measurement. A self-assembled micro-domain with the fluorinated side chain standing up on the uppermost surface has been proposed for polyurethane with higher fluorinated content, based on the result obtained

Keywords Fluorinated poly(carbonate urethane), Surface morphology, AFM

INTRODUCTION

Poly(carbonate urethane)s are used as biomedical materials for long-term implants because their biostability and moderate biocompatibility are similar to those of poly(ether urethane)s^[1]. The moderate biocompatibility of polyurethanes is derived from the hard segment microdomains at the surface which can keep protein in the native or near-native state on adsorption because of similar size^[2]. The microdomains lie underneath the uppermost surface layer (about 10 nm near the surface) and were mostly investigated by AFM using moderate force tapping^[3–5]. The hard segment domains on the uppermost surface of polyurethanes is believed to arise from the surface structural rearrangements of polyurethane, which may be induced by hydration of the polymer surface^[2]. It was reported that fluorinated side chains can easily enrich at the air-polymer surface in semifluorinated fluorocarbon diblock copolymers^[6] and form a self-assembled liquid crystalline phase for a family of monodisperse polystyrene semifluorinated alkyl ester side chain block copolymers^[7]. However, for fluorinated polyurethanes, the situation may be different due to the effect of fluorine side chain on the hydrogen bonding between the hard segments and soft segments. For surface study, AFM is one of the most useful techniques to investigate the surface morphology. In general, the phase images are dramatically affected by the tip-sample force interaction, which can be adjusted by the ratio of amplitude to the free air amplitude^[8–10]. Light force tapping in which the ratio of the amplitudes is in the range of 0.75–0.9, gives information of surface morphology about 0–5 nm below the surface. And moderate force tapping in which the ratio of amplitude is in the range of 0.4–0.7, resolves domains lying underneath the uppermost surface layer (about 10 nm near the surface). A new applicable ultra-light tapping technique has been developed, which derives its chemical resolution from hydrophilicity differences of the phases at the surface^[10]. The change of hydrophilicity will modify the water meniscus forces on

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the scanning tip and allow indirect assignment of domains assigned according to different hydrophilicities in cases where there are no prior stiffness assignments of the different domains. In this work, we report the uppermost surface morphology of poly(carbonate urethane) with fluorinated side chains attached to hard segments, as revealed by AFM, XPS and contact angle measurement. A self-assembled nano-structure has been proposed based on the results obtained.

EXPERIMENTAL

Materials and Film Preparation

Poly(carbonate urethane) (PHPCPU) and fluorinated poly(carbonate urethane) (FPHPCPU) were synthesized using two-step solution polymerization. The structure of FPHPCPU was showed in Fig. 1. PHPCPU, FPHPCPU20, FPHPCPU50, FPHPCPU100 samples were synthesized from the reaction of MDI with poly(1,6-hexyl-1,5-pentylcarbonate) diol (PHPCD), 1,4-butandiol (BDO) and 3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-octyloxy)-propane-1,2-diol (PFOPDOL), respectively. Their molecular details are listed in Table 1. The sample films were prepared by casting 5% (W/V) DMAc polymer solution onto clean glass disks. The disks were put into an oven at 40°C for 24 h, 50°C for 12 h, and 60°C for 3 days under vacuum.

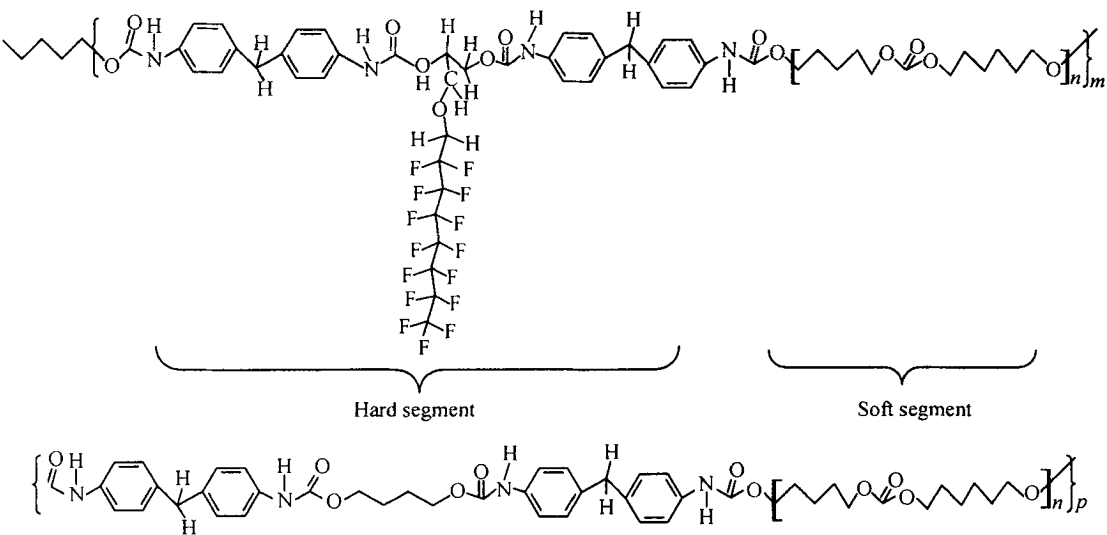


Fig. 1 Structure of fluoropolyurethanes
 $R_f = CH_2(CF_2)_6CF_3$; $n = 1, 2, 3, \dots$, $m = 0, 1, 2, 3, \dots$, $p = 0, 1, 2, 3, \dots$; Soft segment is PHPCD.

Table 1. Composition of poly(carbonate urethane)s with various amounts of fluorinated chain extender

Sample	Molar ratio MDI/chain extender/PHPCD	Chain extender BDO, PFOPDOL (mol)	Hard segment (wt%)	Fluorine atom (wt%)
PHPCPU	2:1:1	1.0, 0.0	35.8	0.00
FPHPCPU20	2:1:1	0.8, 0.2	38.7	3.3
FPHPCPU50	2:1:1	0.5, 0.5	42.5	7.7
FPHPCPU100	2:1:1	0.0, 1.0	47.9	14.0

Surface Characterization

The AFM measurements were performed with an SPA400 instrument equipped with SPI3800N controller (Seiko Instruments Industry), at room temperature, using the micro-fabrication cantilevers with force constant of approximately 13 N/m. In tapping mode, the topographic and phase data were recorded simultaneously. In our work, the ratio of amplitude was adjusted to 0.8–0.9 of the free air amplitude for all the images. Under these light force tapping conditions, phase data are sensitive to local hydrophilicity differences of the phase about 0–5 nm below the surface^[8–10]. X-ray photoelectron spectroscopy (XPS) was carried out on an XSAM-800 electron spectrometer. The spectrometer was equipped with a MgK α achromatic X-ray source (20 kV, 10 mA) and take-

off angles of 30° were used with the X-ray source. The analysis was performed to fit the combination of Lorentzian and Guassian curves by XPSPEAK version 1.05. Contact angles were measured on 3 μL of distilled water and diiodomethane with an Eyma contact angle goniometer at 20°C, and the results reported are the mean values for ten replicates. The critical surface tension was calculated with the harmonic mean equation^[11].

RESULTS AND DISCUSSION

The surface microheterogeneity sensitivity of contact angle measurement is about 0.5–1.0 nm on polymer surfaces^[2]. In order to study how the fluorinated side chains on the hard segment migrate to the surfaces of the poly(carbonate urethane)s, the measurement of contact angles with water and diiodomethane was carried out. The results are listed in Table 2. The increased water contact angle and low critical surface tension of the fluorinated poly(carbonate urethane)s show that the surfaces become significantly nonpolar, indicating that the fluorinated side chains on the hard segment have been enriched on the surface of the polyurethanes. To further examine the surface properties, XPS measurement was carried out. In the XPS measurement, the take-off angle is 30°, and the detection depth is then around 5 nm^[12]. The XPS results are listed in Table 3. It can be seen that all fluorinated poly(carbonate urethane) films have higher fluorine on the surface compared with that in the bulk. The content of nitrogen (which represents the hard segments of polyurethane) on the uppermost surface increases with the increase of fluorine content in the bulk of polymers, especially, the content of nitrogen of FPHPCPU50 and FPHPCPU100 almost equals or exceeds that in the bulk. This result also suggests that both the fluorinated side chains and the hard segments are enriched on the uppermost surface of the fluorinated poly(carbonate urethane)s. Very interestingly, the carbon ratio of CF₂ and CF₃ gradually reaches six with increasing fluorine content in the fluorinated poly(carbonate urethane)s, which is an indication that the –CF₂CF₃ group may stand up with CF₃ on the top of the surface. One may expect to see the micro-domain on the uppermost surface of the fluorinated poly(carbonate urethane) by using the light tapping mode AFM. Under these measurement conditions, the hydrophobic region is bright in phase images and dark in topography images^[10]. The AFM result is shown in

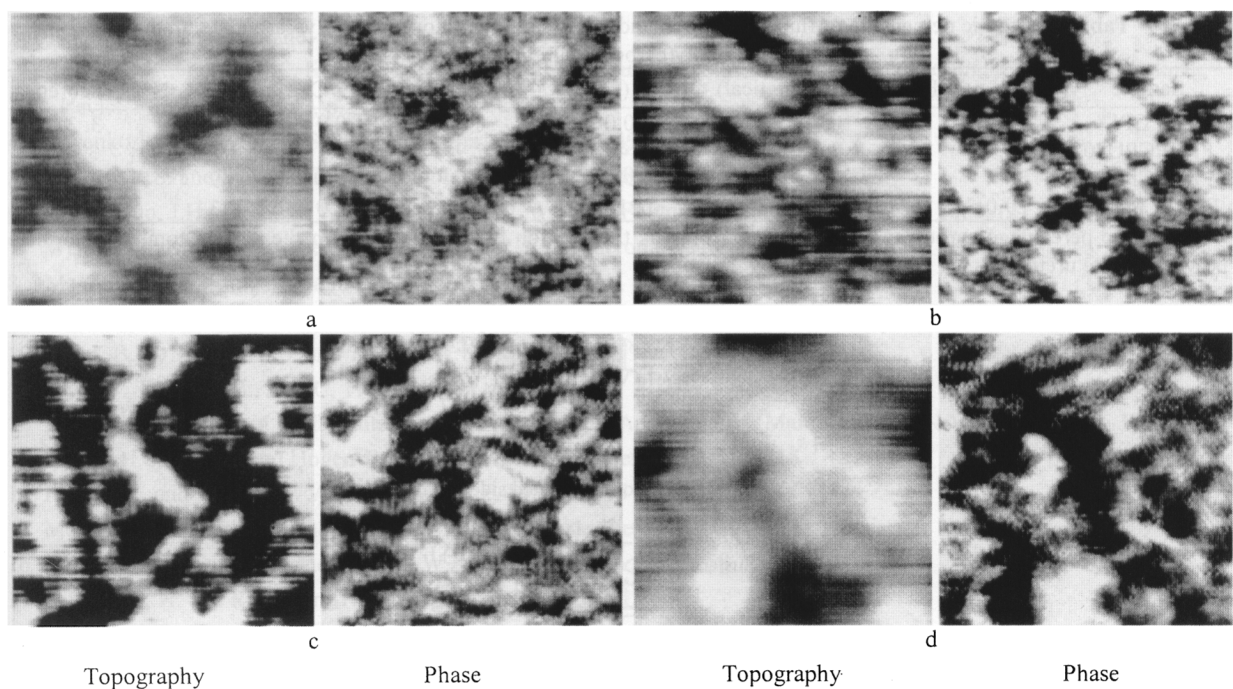


Fig. 2 Topography and phase images of PHPCPU (a), FPHPCPU20 (b), FPHPCPU50 (c), FPHPCPU100 (d) at 500 nm scan sizes.

Data obtained using light tapping mode in air. Z ranges are 5 nm, 9 nm, 6 nm, 18 nm in (a)–(d), respectively.

Fig. 1. For FPHPCPU50 and FPHPCPU100 samples, one observes apparent topography and phase images (worm-like shadow, 20 nm in width hydrophobic rich fluorine patches on their surfaces (Fig. 2c and d). For the FPHPCPU20 sample, there also exist the hydrophobic areas, but not very much distinct nanophase on the surface (Fig. 2b). The surface of PHPCPU sample without fluorine shows hydrophilic areas from topography and phase images (Fig. 2a).

For our poly(carbonate urethane)s with fluorinated side chain attached to the hard segment, it has been demonstrated from water contact angle and surface tension measurements that the surfaces became significantly nonpolar, indicating that the fluorinated side chains on the hard segment indeed migrate to the surface of the polyurethanes (Table 2), due to the low surface energy of fluorine atoms attached on them. At lower fluorine concentrations, fluorinated side chains will most likely exist in a dissociated form with high mobility. They are relatively homogeneously distributed on the surface, and randomly oriented when in contact with a high surface tension liquid, leading to a large critical surface tension. Therefore, the distinct micro-domains on the uppermost surface of FPHPCPU20 are not observable by AFM (Fig. 2b), and the carbon ratio of CF_2 and CF_3 is lower than six (Table 3). With increasing fluorine content, fluorinated side chains may exist in an aggregated form (even R_F domain) with low mobility, as seen in the case of one ended perfluorinated PEG derivatives^[13]. This aggregation structure could be simply maintained on the domains of hard segments and does not allow an easy deformation, due to the strong interaction among the R_F domain. Hence, we could observe the micro-domains of fluorinated

Table 2. Contact angles and surface tension results of fluorinated poly(carbonate urethane)s and poly(carbonate urethane)s

Sample	CH_2I_2 (°)	H_2O (°)	Surface tension $\times 10^{-2}$ (N/m)
PHPCPU	49.5 ± 0.9	49.5 ± 0.9	4.01
FPHPCPU20	84.3 ± 1.9	101.6 ± 1.0	2.07
FPHPCPU50	88.6 ± 1.6	106.8 ± 0.8	1.85
FPHPCPU100	94.5 ± 0.7	113 ± 1.4	1.55

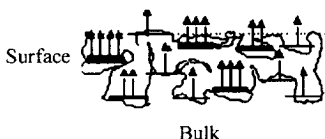
Table 3. Atomic percentage of fluorine, carbon and nitrogen in the fluorinated poly(carbonate urethane)s and poly(carbonate urethane)s

Sample	F%	F% Bulk (Theoretical)	C% (CF_2)*	C% (CF_3)*	CF_2/CF_3	N%	N% (Theoretical)
PHPCPU	0	0.0	0.0	0.0	0.0	2.1	3.3
FPHPCPU20	26.4	2.4	14.8	2.9	5.1	2.7	3.2
FPHPCPU50	36.4	5.7	24.7	4.2	5.9	2.9	3.0
FPHPCPU100	29.0	10.5	21.5	3.6	6.0	3.3	2.8

* The atomic percentage carbon in CF_2 and CF_3 groups is the fraction of these carbons in the carbon total of fluorinated poly(carbonate urethane)s.



Low content of fluorinated side chain



High content of fluorinated side chain

Fig. 3 Schematic diagram of the molecular associations of fluorinated side chains

— hard segment; — soft segment; ↑ R_F ; — hard segment domain

side chains attached to hard segments on the uppermost surfaces for FPHPCPU50 and FPHPCPU100 by AFM (Fig. 2c and d). The R_f side chains in the domains should stand vertically on the surface, which makes the carbon ratios of CF_2 and CF_3 nearly equal to six (Table 3). From the surface tension and water contact angle point of view, the fluorinated side chains should orient towards air and are close-packed on the uppermost surface. For examples, poly(tetrafluoroethylene) (CF_2 packing) has a critical surface tension (CST) of $1.85 \times 10^{-2} \text{ N/m}^{[14]}$, the water contact angle is 109° ^[15], and a monomolecular film of perfluorododecanoic acid on platinum (close-packed CF_3) has a CST of $5.6 \times 10^{-3} \text{ N/m}^{[16]}$, and the water advancing contact angle is 112° – 120° ^[17]. The lower critical surface tensions and higher contact angle of many fluorinated surfaces reflect the concentration of CF_3 groups^[16, 17]. Fluorinated poly(carbonate urethane)s with higher fluorine concentration, such as FPHPCPU50 and FPHPCPU100, have also shown lower critical surface tensions and higher water contact angles, especially, FPHPCPU50 ($1.80 \times 10^{-2} \text{ N/m}$, 107°) and FPHPCPU100 ($1.55 \times 10^{-2} \text{ N/m}$, 113°) (Table 2), indicating that there are more CF_3 groups on the outermost surface. To understand the surface structures of these fluorinated poly(carbonate urethane)s, the graphic representation of fluorinate side chains attached to hard segments of self-assembled nanophase on the uppermost surfaces is shown in Fig. 3. Since the glass transition temperature of hard segments is over the room temperature, it is not possible to form self-assembled nanophase in the solid state because the hard segments will freeze at room temperature. The self-assembled nanophase is most likely formed during the process of film casting and evaporation of solvent.

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