

# Phase behavior and hydrogen bonding in biomembrane mimicing polyurethanes with long side chain fluorinated alkyl phosphatidylcholine polar head groups attached to hard block

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Received 14 March 2005; received in revised form 29 May 2005; accepted 13 June 2005

Available online 14 July 2005

## Abstract

To achieve a good biocompatibility, two sets of novel segmented polyurethanes, namely, poly(ether urethane)s and poly(carbonate urethane)s, with long side chain fluorinated alkyl phosphatidylcholine polar head groups attached to hard block have been synthesized recently in our laboratory by using a new diol with a long side chain fluorinated alkyl phosphatidylcholine polar head group 2-[2-[2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-hexadecafluoro-10-ethoxy-decyloxy]-*N*-(2-hydroxy-1-hydroxymethyl-1-methyl-ethyl)-acetamide] phosphatidylcholine, HFDAPC as an extender. These novel polyurethanes have shown a potential to be used as bio-membrane mimicry. In this article we investigated the phase behavior of these materials by Instron, DSC, DMA, and AFM because the phase behavior has a great effect on the surface properties thus the biological-related perspective.  $T_g$  decreases first then increases for the poly(carbonate urethane)s, but increases first then decreases for the poly(ether urethane)s with an increasing in fluorinate phosphatidylcholine content. On the other hand, the tensile modulus was found decrease for the poly(carbonate urethane)s but increase for the poly(ether urethane)s with an increasing in fluorinate phosphatidylcholine content. It was found via AFM that the phase separation increases in poly(ether urethane)s but phase mixing increases in poly(carbonate urethane)s, with increasing content of fluorinated phosphatidylcholine side chain. The interaction between hard and soft segment, particularly, the hydrogen bonding was investigated by FTIR. The effect of fluorinated phosphatidylcholine side group on the phase separation of polyurethane was discussed and compared with that of fluorinated polyurethanes containing only fluorinated side chains. Our result demonstrated how the phase behavior of polyurethanes could be controlled by tailoring the interaction between hard and soft segment. © 2005 Elsevier Ltd. All rights reserved.

**Keywords:** Phase behavior; Hydrogen bonding; Fluorinated phosphatidylcholine polyurethane

## 1. Introduction

Polyurethanes (PUs) are widely used as biomedical materials because of their excellent mechanical properties and good blood compatibility [1]. However, the long-term biostability and biocompatibility of polyurethanes are still major problems in vitro application [2,3], due to mainly adsorb protein on the materials surface and activate platelets to amplify coagulation. Recently considerable attention has been paid to biomedical polyurethanes containing phospholipid functionality, and particularly to those with the

phosphatidylcholine group, which is a major component of the extracellular surface of the phospholipid bilayer. It is believed that polymers containing this group can provide biomembrane mimicry and should be more compatible with human body. Nevertheless, these phosphatidylcholine polar head groups cannot easily migrate to the surface. Thus, in order to achieve a phosphatidylcholine polar head groups onto the surface, one has to use a large amount of phosphatidylcholine chain extender to synthesize the polyurethanes for high water adsorption rate in bulk. More than 16 wt% phosphatidylcholine chain extender was reported to prepare phosphatidylcholine polyurethanes, and this, consequently, results in poor mechanical properties as usual [4,5]. In order to obtain biomedical polyurethane with excellent biocompatibility and biostability as well as good mechanical properties, a novel chain extender with long fluorinated side chain phosphatidylcholine and a series

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of fluorinated phosphatidylcholine polyurethanes attached on the hard block were designed and synthesized recently in our group [6]. Our goal is to bring the phosphatidylcholine polar head groups onto the surface or sub-surfaces with the help of migration of fluorinated side chains. Thus only small amount of phosphatidylcholine is needed to realize the good biocompatibility. The surface and biocompatibility of these novel polyurethanes have been reported in our previous work [7]. In this article we focused on the phase behavior of these novel fluorinated phosphatidylcholine polyurethanes, because the phase behavior has a great effect on the surface properties thus the biological-related perspective.

It has been established that the desirable bulk properties of polyurethane mainly derive from the two-phase structure of hard and soft domains: Hard domains, composed of aromatic (or aliphatic) urethane or urea segments, and soft domains, composed of aliphatic polyether, polycarbonate, polyester or poly(methylsiloxane) segments [8,9]. Factors that control the phase separation include composition, such as the symmetry of diisocyanate, the type of chain extender, the number of carbons in linear low molecular weight chain extender [10], the type and the chain lengths of soft segments [8,10–12], crystallizability of either segment [13], the thermal history of the polyurethanes [11,14,15] and the method of synthesis [16]. In our previous work, we reported the synthesis and surface mobility of segmented polyurethanes with only fluorinated side chain attached on hard block [17]. We found that the fluorinated side chain can easily migrate onto the surface even it is attached on the hard block of polyurethane due to its low surface free energy [17]. It was found that the phase separation in both bulk and surface increases in fluorinated poly(carbonate urethane)s but phase mixing increases in fluorinated poly(ether urethane)s, with increasing amounts of fluorinated side chain. The increased degree of hydrogen bonding between hard segments and soft segments was observed by FTIR for fluorinated poly(ether urethane), which is believed to result in the enhanced phase mixing, and the enhanced association of domains with long-range order (hydrogen bonding) between hard segments was evident for fluorinated poly(carbonate urethane)s, which may correspond to the enhanced phase separation [18]. The overall objective of this research is to further investigate the effect of fluorinated phosphatidylcholine side chain attached on hard segment on the phase behavior and hydrogen bonding involved in. Very interestingly, it was found that the phase separation increases in poly(ether urethane)s but phase mixing increases in poly(carbonate urethane)s, with increasing amounts of fluorinated phosphatidylcholine side chain. This result is exactly contradictory with that obtained for polyurethanes containing only fluorinated side chain [18]. The effect of fluorinated phosphatidylcholine side group on the phase separation of polyurethanes was discussed and compared with that of fluorinated polyurethanes containing only fluorinated side chains. Our work demonstrated the

interplay of hydrogen bonding and inductive force in determining the phase behavior of polyurethanes.

## 2. Experimental

### 2.1. Synthesis of materials

To obtain fluorinated phosphatidylcholine polyurethanes, a new diol with a long side chain fluorinated alkyl phosphatidylcholine polar head group 2-[2-[2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-hexadecafluoro-10-ethoxy-decyloxy]-N-(2-hydroxy-1-hydroxymethyl-1-methyl-ethyl)-acetamide] phosphatidylcholine, (HFDAPC) was first synthesized and characterized. Then a series of poly(carbonate urethane)s containing long side chain fluorinated alkyl phosphatidylcholine polar head group were synthesized using methylenebis(phenylene isocyanate) (MDI), poly(1,6-hexyl-1,5-pentylcarbonate) diol (PHPCD,  $M_n$ : 1058) and polytetramethyleneoxide (PTMO,  $M_n$ : 1000), 1,4-butandiol (BDO) and HFDAPC as a chain extender with two-step solution polymerization in DMAc. The feed ratios are shown in Table 1. MDI was added to the stirred DMAc solution of PHPCD under a dry nitrogen atmosphere at 50 °C, and stirred for 1 h at 55–60 °C. Chain extender (BDO, HFDAPC) and 1%<sub>o</sub> stannous octoate were added to the reaction solution while the temperature was kept at 65–70 °C for 20 min, and then the stirring was continued at 80–90 °C for 5 h. Stirring continued at 100–110 °C for 1 h. The detailed synthesis of the materials has been described in Refs. [6,7], and the information of these samples is listed in Table 1, including molecular weight and distribution. The structure is shown in Fig. 1.

Table 1  
Composition, molecular weights and molecular weight distribution of segmented poly(ether urethane)s and poly(carbonate urethane)s with various amounts of fluorinated phosphatidylcholine chain extender

Sample	Molar ratio MDI/chain extender/polydiol <sup>a</sup>	Chain extender BDO, FPC <sup>b</sup> (mol)	$M_w$ ( $\times 10^{-4}$ ) <sup>c</sup>	$M_w/M_n$
PEU	2:1:1	1.0, 0.0	16.439	1.8521
FPCPEU5	2:1:1	0.95, 0.05	6.2569	2.2276
FPCPEU20	2:1:1	0.8, 0.2	2.0986	1.9141
FPCPEU50	2:1:1	0.5, 1.5	2.0624	1.7229
PCU	2:1:1	1.0, 0.0	9.9543	1.5249
FPCPCU5	2:1:1	0.95, 0.05	2.4842	1.9119
FPCPCU20	2:1:1	0.8, 0.2	3.6612	2.0529
FPCPCU50	2:1:1	0.5, 0.5	3.7415	2.0642

<sup>a</sup> PTMO (or PHPCD).

<sup>b</sup> HFDAPC.

<sup>c</sup> The molecular weights and molecular weights distribution were determined by GPC using polystyrene standards and THF as the mobile phase.

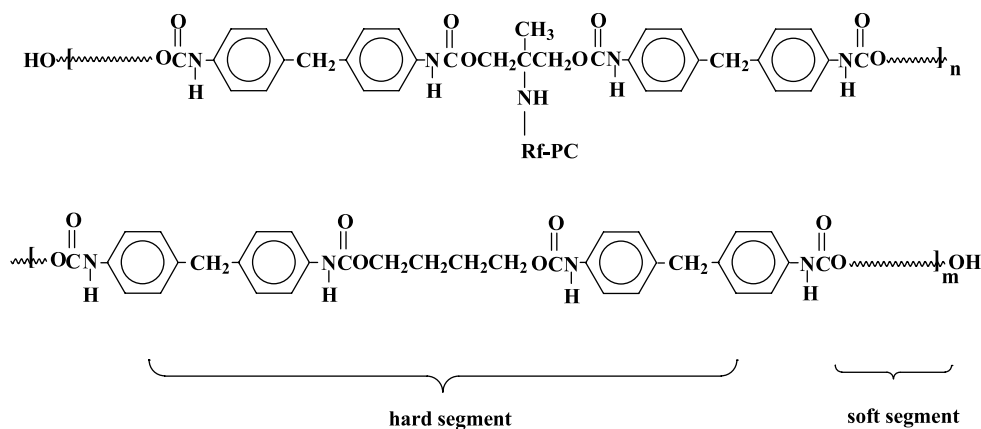


Fig. 1. Structure of fluorinated phosphatidylcholine polyurethanes.  $R_f = \text{OCH}_2\text{CH}_2\text{OCH}_2(\text{CF}_2)_8\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}$ ;  $n = 1, 2, 3, \dots$ ,  $m = 0, 1, 2, 3, \dots$ . Soft segment

is PTMO or PHPCD; PC:  $\begin{array}{c} \text{O} \\ \parallel \\ -\text{P}-\text{O}-\text{CH}_2\text{CH}_2-\text{N}-\text{CH}_3 \\ | \\ \text{O}^- \\ | \\ \text{CH}_3 \end{array}$ .

## 2.2. DSC measurements

The polymer samples (17–20 mg) were cut off from the films prepared by casting the polymer onto a clean glass disk from 5% (w/v) DMAc, putting into oven at 40 °C for 24 h, 50 °C for 12 h and 60 °C for 3 days under vacuum. The DSC heating data was collected at 10 °C/min from –100 to 80 °C by TA instrument 2910 thermal analyzer.

## 2.3. Dynamic mechanical analysis (DMA)

Dynamic mechanical properties were measured on a dynamic mechanical thermal analyzer (DMTA IV Rheometric Scientific Ltd) using rectangular test film specimens ( $45 \times 10 \times 0.2 \text{ mm}^{-3}$ ) prepared as described above. The testing was done at a heating rate of 5 °C/min and at a frequency of 10 Hz.

## 2.4. Tensile testing

Tensile testing was carried out with an Instron 4302 Model Universal Testing machine at 23 °C and relative humidity of 50%. The crosshead speed was 500 mm/min. Each sample was cast to form film from 10% (w/v) THF or mixture solvent of THF and DMAc (5:1). They were cut into dumbbells of 5 cm in length and 1 cm in width; the narrow section was  $2 \times 0.5 \text{ cm}^2$  in area and 0.3 mm in thickness. The results reported are the mean values for five replicates.

## 2.5. Fourier transform infrared spectroscopy (FTIR)

Each sample for infrared analysis was prepared by casting the polymer onto a clean potassium bromide disc from a single drop of 1% DMAc. These samples were put into an oven at 40 °C for 24 h, 50 °C for 12 h, and 60 °C for 24 h under vacuum to completely remove the solvent.

Infrared data was obtained with the Nicolet-560 spectrophotometer between 4000 and 600  $\text{cm}^{-1}$  in the resolution of 4  $\text{cm}^{-1}$ . Fifty scans were averaged for each sample. The analysis was performed to fit the combination of Lorentzian and Gaussian curve by Peakfit version 4.0.

## 2.6. Atomic force microscopy (AFM)

Sample films were prepared by casting the poly(ether urethane)s onto clean glass disks from 5% (w/v) DMAc. 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. The AFM measurements were performed on SPA400 with an SPI3800N controller, Seiko Instruments Industry, Co., Ltd 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. For our study, the ratio of amplitude was adjusted to 0.4–0.7 of the free air amplitude for all the images. Since fluorinated phosphatidylcholine polyurethane contains both hydrophobia fluorinated chain and

Table 2

The storage modulus at  $T_g + 50$  °C, dissipation factor and glass transition temperature of fluorinated phosphatidylcholine polyurethanes in DMA and glass transition temperature in DSC

Sample	$T_g$ (°C)	$\tan \delta$	$E'$ (MPa) $T_g + 50$ °C	Soft segment $T_g$ (°C) <sup>a</sup>
PEU	–57.35	0.31	7.6	–45.7
FPCPEU5	–5.0	0.47	15.7	–43.4
FPCPEU20	–36.0	0.32	30.0	–47.6
FPCPEU50	–49.0	0.22	24.5	–52.2
PCU	24.5	0.57	6.39	–3.6
FPCPCU5	–6.0	0.54	14.0	–16.4
FPCPCU20	27.0	0.43	4.94	–14.3
FPCPCU50	30.0	0.41	2.54	–9.4

<sup>a</sup> DSC results.

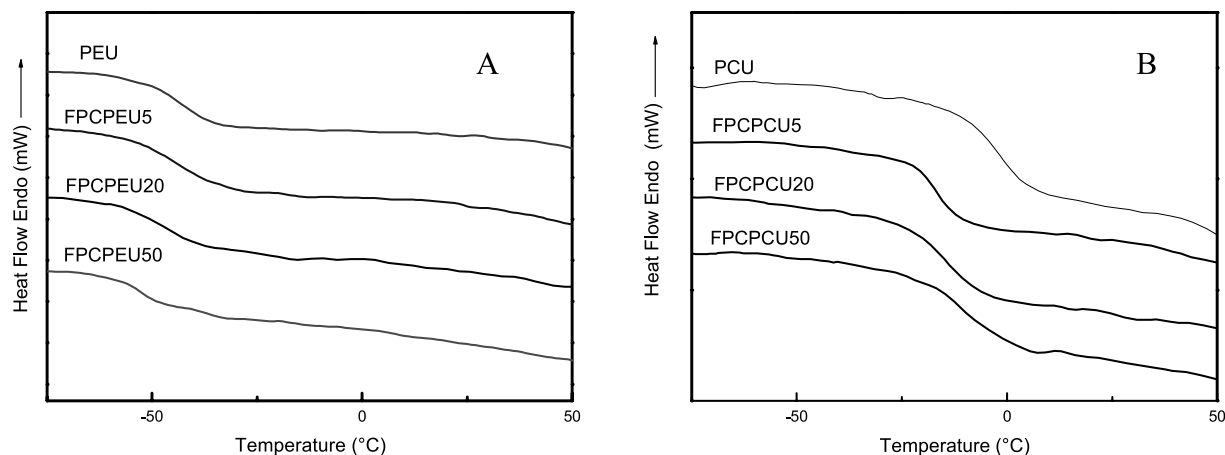


Fig. 2. DSC thermograms of fluorinated phosphatidylcholine polyurethanes and polyurethanes. (A) Poly(ether urethane)s series. (B) Poly(carbonate urethane)s series.

hydrophilic phosphatidylcholine group, the moderate tapping mode was used to investigate the difference of surface stiffness between hard and soft segment of polyurethane [19–21].

### 3. Results and discussion

#### 3.1. DSC analysis

The DSC heating curves of these fluorinated phosphatidylcholine polyurethanes are shown in Fig. 2(A). In the poly(ether urethane) system, the  $T_g$  is found to increase first then decreases with an increasing of fluorinate phosphatidylcholine content (Table 2). The change in  $T_g$  of the soft segment has been used as an indicator of the degree of phase separation [12]. The change of  $T_g$  of poly(ether urethane)s with an increasing of fluorinated phosphatidylcholine content indicates that the phase separation is getting less at small content but enhanced at higher content of poly(ether

urethane)s with fluorinated phosphatidylcholine attached on hard block. For the fluorinated phosphatidylcholine poly(carbonate urethane)s, on the other hand, the  $T_g$  is found to decrease first then increases with an increasing in fluorinated phosphatidylcholine content (Fig. 2(B), Table 2). The change of  $T_g$  of poly(carbonate urethane)s suggests an enhanced phase separation at small content but a phase mixing at higher content of fluorinated phosphatidylcholine attached on hard block. The endotherm of these fluorinated phosphatidylcholine polyurethanes was not found at higher temperature region in DSC curves. This can be understood as due to the interruption of crystallization by introducing fluorinated phosphatidylcholine on the hard segment [4].

#### 3.2. Dynamic mechanical analysis

Dynamic mechanical analysis provides information on glass transition and the mechanical behavior of a polymer. The dynamic mechanical properties of the fluorinated

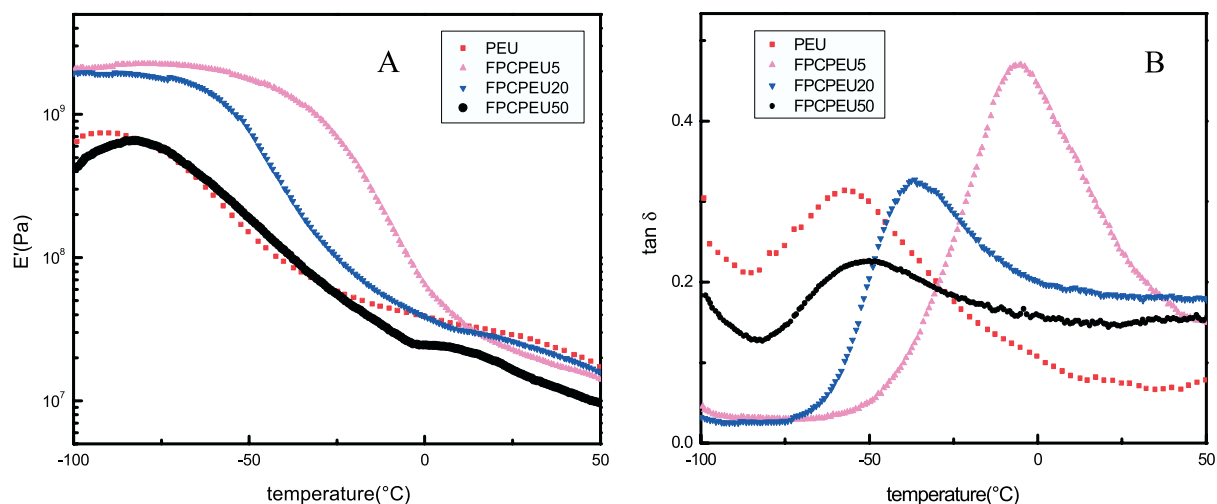


Fig. 3. Dynamic-mechanical spectra for fluorinated phosphatidylcholine poly(ether urethane)s and poly(ether urethane)s samples. (A)  $E'$  vs.  $T$ , (B)  $\tan \delta$  vs.  $T$ .

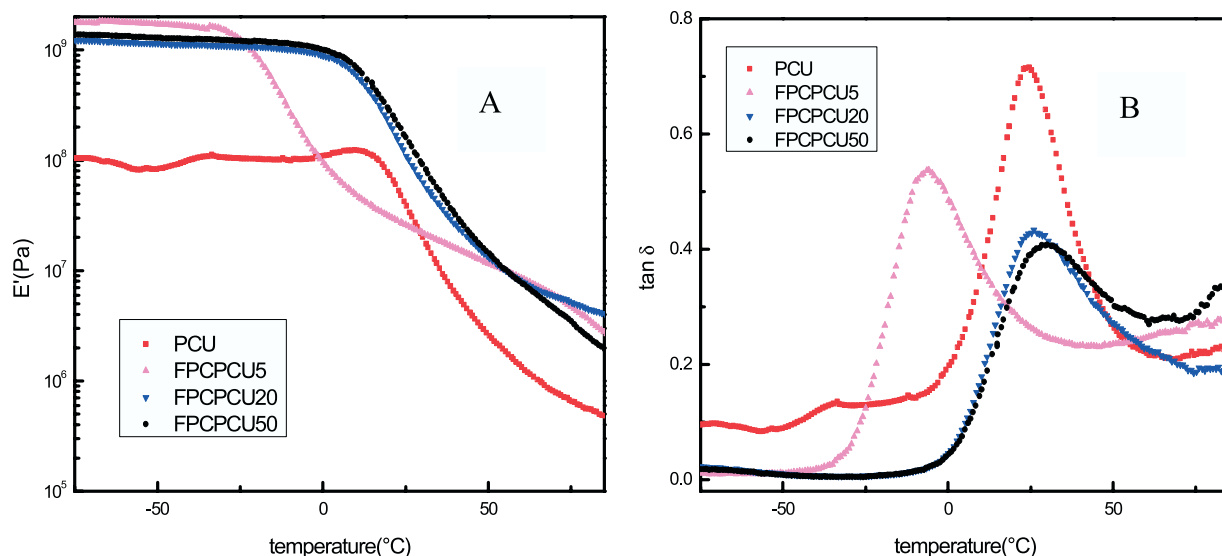


Fig. 4. Dynamic-mechanical spectra for fluorinated phosphatidylcholine poly(carbonate urethane)s and poly(carbonate urethane)s samples. (A)  $E'$  vs.  $T$ , (B)  $\tan \delta$  vs.  $T$ .

phosphatidylcholine poly(ether urethane)s series are shown in Fig. 3. From the storage modulus ( $E'$ ) vs. temperature curves (Fig. 3(A)), the storage modulus is seen increase in the glass plateau region for poly(ether urethane)s with low fluorinated phosphatidylcholine content compared with that PEU. On the other hand, the loss peak ( $T_g$ ) of poly(ether urethane)s is shifted toward higher temperature then back to lower temperature as increasing of fluorinated phosphatidylcholine content (Fig. 3(B)). Fig. 4 shows the dynamic mechanical properties of the fluorinated phosphatidylcholine poly(carbonate urethane)s series. The storage modulus in the glass plateau region is seen also to increase for fluorinated phosphatidylcholine poly(carbonate urethane)s series compared with that of PCU (Fig. 4(A)), and the loss peak, however, is shifted toward lower temperature first then back to higher temperature as increasing of fluorinated phosphatidylcholine content (Fig. 4(B)). Numerical DMA data of all polyurethanes are reported in Table 2, including the  $T_g$  obtained by DSC for comparison. The  $T_g$ s obtained via DSC and DMA are quite different, but the trend is exact the same, that is:  $T_g$  decreases first then increases for the poly(carbonate urethane)s, but increases first then decreases for the poly(ether urethane)s with an increasing in fluorine phosphatidylcholine content. In order to better understand the effect of fluorinated phosphatidylcholine side chain attached on hard segment on the phase separation, the rubber plateau modulus (at temperature  $T_g + 50$  °C) is particularly listed in Table 2 [22]. One observes an increased rubber plateau modulus for poly(ether urethane)s series but a decreased rubber plateau modulus for poly(carbonate urethane)s series as increasing of fluorinated phosphatidylcholine content. The change in poly(ether urethane)s series is appropriately in reverse to that in poly(carbonate urethane)s series. The increase in storage

modulus of fluorinated phosphatidylcholine poly(ether urethane)s indicates that the hard-segment acts as reinforcing agent more efficiently via enhanced phase separation [22]. On the other hand, the decreased storage modulus of fluorinated phosphatidylcholine poly(carbonate urethane)s indicates enhanced phase mixing as increasing of fluorinated phosphatidylcholine content.

### 3.3. Tensile properties

The changed degree of phase separation or mixing can be also reflected from tensile properties, since the tensile strength (or modulus) is remarkably affected by the two-phase structure of polyurethanes. Fig. 5(a) shows the typical engineering stress–strain curves of the series of fluorinated phosphatidylcholine poly(ether urethane)s. One observes a decreased ultimate tensile strength and elongation at break but a increased tensile modulus (the slope) after introducing fluorinated phosphatidylcholine side chain on the hard block of poly(ether urethane)s. Since there exists difference in molecular weight among the samples, due to the likely low reactivity of HFDAPC in comparison with BDO in the process of polyurethanes synthesized, tensile strengths cannot be compared straightly. The general trend is the tensile modulus increase as increasing of the side chain content. Fig. 5(b) shows the typical stress–strain curves of the series of fluorinated phosphatidylcholine poly(carbonate urethane)s. One observes a decreased ultimate tensile strength and modulus (the slope) but a increased elongation at break after introducing fluorinated phosphatidylcholine side chain on the hard block of poly(carbonate urethane)s. The tendency in this case is the tensile strength and modulus decreases as increasing of the side chain content. From above DSC and DMA result, the increased tensile modulus in the fluorinated phosphatidylcholine poly(ether urethane)s

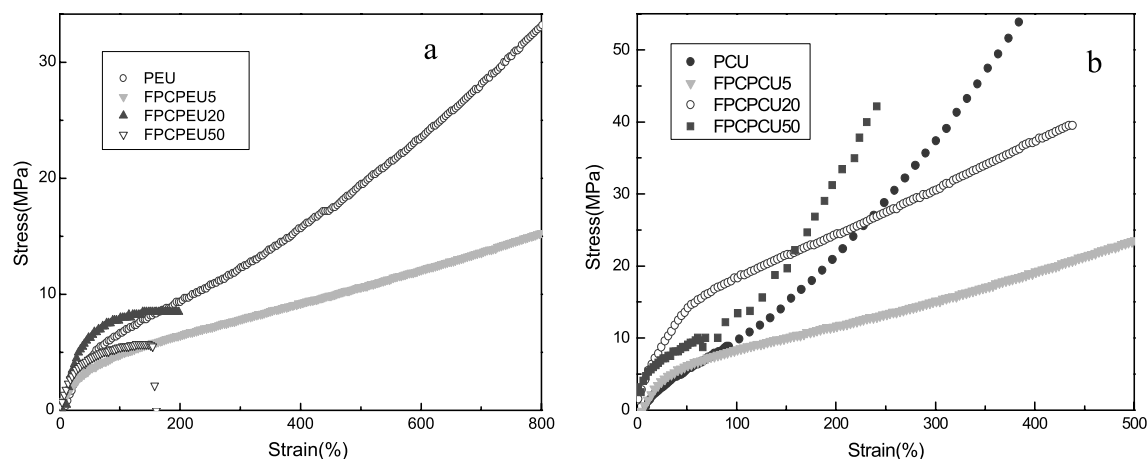


Fig. 5. Stress–strain curves of fluorinated phosphatidylcholine polyurethanes and polyurethanes. (a) Poly(ether urethane)s series. (b) Poly(carbonate urethane)s series.

series can be understood as due to the increased phase separation, and the decreased tensile strength and modulus in the fluorinated phosphatidylcholine poly(carbonate urethane)s series is due to the increased phase mixing. One may concern the mechanical properties of these polymers in water. For this reason, these polymers were kept in water at room temperature for 24 h and the same tensile experiment was repeated. Not much change of tensile properties was found. This may be due to the relatively lower water adsorption rate in bulk (2.0%).

Since the chemical structure will significantly affect the stress strain behavior, it is expected that some of these materials will crystallize and some may not during stretching. To understand the deformation behavior and explain the observed differences in the stress strain behavior, future work is needed to focus on the strain induced-crystallization of these samples by capturing the samples at different stretch levels and simultaneous measurement of WAXS.

### 3.4. AFM measurement

AFM technique was used to study the microdomains of polyurethanes lying underneath the upper most surface layer by moderate force tapping [19,20,23], and the phase imaging at moderate tapping of the ratio (amplitudes with range 0.4–0.7) provides information about surface stiffness variation related to changes in Young's modulus [21,23]. While, the phase imaging at light force tapping of the ratio of amplitudes with range 0.8–0.9 derives the chemical resolution from hydrophilicity differences of the phase at the surface [21,24,25]. For polyurethanes containing only fluorinated side chain, the surface morphology can be characterized via AFM at light force tapping from hydrophilicity difference, since the fluorinated side chain attached on hard block can migrate onto the surface to form the hydrophobic area [18]. However, for polyurethane containing both hydrophobic fluorinated chain and

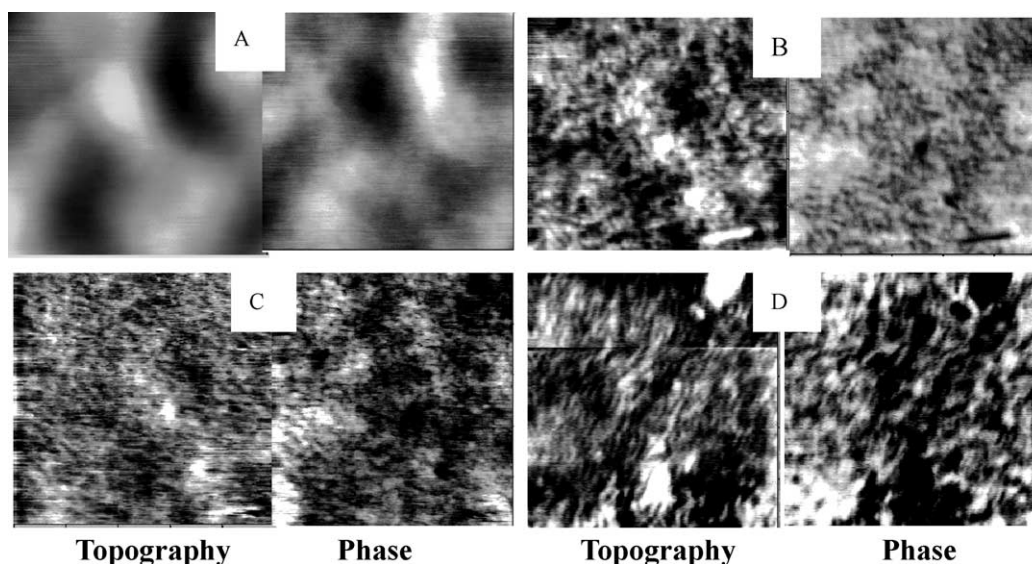


Fig. 6. Topography and phase images of PEU (A), FPCPEU5 (B), FPCPEU20(C), FPCPEU50 (D) at 500 nm scan sizes.

hydrophilic phosphatidylcholine group, one has to use the moderate tapping mode to investigate the difference of surface stiffness between hard and soft segment of polyurethane. Fig. 6 shows the topographic and phase images of PEU, FPCPEU5, FPCPEU20 and FPCPEU50 samples at moderate mode in region of 500 nm scan. The phase data for the hard blocks are bright and the soft blocks are dark. For PEU a typical two phases structure is seen. For these fluorinated phosphatidylcholine poly(ether urethane)s, on the other hand, with increasing of fluorinated phosphatidylcholine content an apparent phase mixing at low fluorinated phosphatidylcholine content (FPCPEU5 and FPCPEU20 shown in Fig. 6(B) and (C)) but phase separation at high fluorinated phosphatidylcholine content (FPCPEU50 shown in Fig. 6(D)) are observed. These results show again directly that the degree of the phase separation increase with increasing content of fluorinated phosphatidylcholine attached on hard block for poly(ether urethane)s. It has to be mentioned the phase structures at the surface related to the fluorine rich domains may be different than that in the bulk and the observed domains maybe result from the excess of fluorine rich species at the surface. For poly(carbonate urethane)s series, however, the morphology changes from co-continuous-like of PCU to drop-like of fluorinated phosphatidylcholine poly(carbonate urethane)s, and the domain size decreases as increasing of fluorinated phosphatidylcholine content, as shown in Fig. 7. This result gives direct evidence that the phase mixing on the surface of fluorinated phosphatidylcholine poly(carbonate urethane)s is enhanced with increasing content of fluorinated phosphatidylcholine attached on hard block. The AFM result is in good agreement with DSC and DMA data.

### 3.5. FTIR analysis

It was found in our previous work that the phase separation in both bulk and surface increases in fluorinated poly(carbonate urethane)s and the phase mixing increases in fluorinated poly(ether urethane)s, with increasing amounts of fluorinated side chain. Now by introducing fluorinated phosphatidylcholine instead of only fluorinated side chain we find a totally opposite change, that is: (1) Tensile modulus and rubber plateau modulus increase in poly(ether urethane)s series but decrease in poly(carbonate urethane)s series as increasing of the side chain content, (2)  $T_g$  decrease in poly(ether urethane)s but increase in poly(carbonate urethane)s series, (3) phase separation increases in poly(ether urethane)s but decreases in poly(carbonate urethane)s series. This phenomenon is very interesting and worth to be further investigated. We also found that for fluorinated polyurethanes (containing only fluorinated alkyl side chain without phosphatidylcholine polar head group) the increased degree of hydrogen bonding between hard segments and soft segments for fluorinated poly(ether urethane)s results in the enhanced phase mixing [18], and the enhanced association of domains with long-range order (hydrogen bonding) between hard segments corresponds to the enhanced phase separation for fluorinated poly(carbonate urethane)s. It is logical to ask if the observed opposite effect in fluorinated phosphatidylcholine polyurethanes is directly connected with the different change of hydrogen bonding in these two systems. For this reason, FTIR experiments were carried out. Hydrogen bonding exists in polyurethanes, and involves the amide group (NH) as the donor, and the urethane carbonyl, the ether oxygen (in

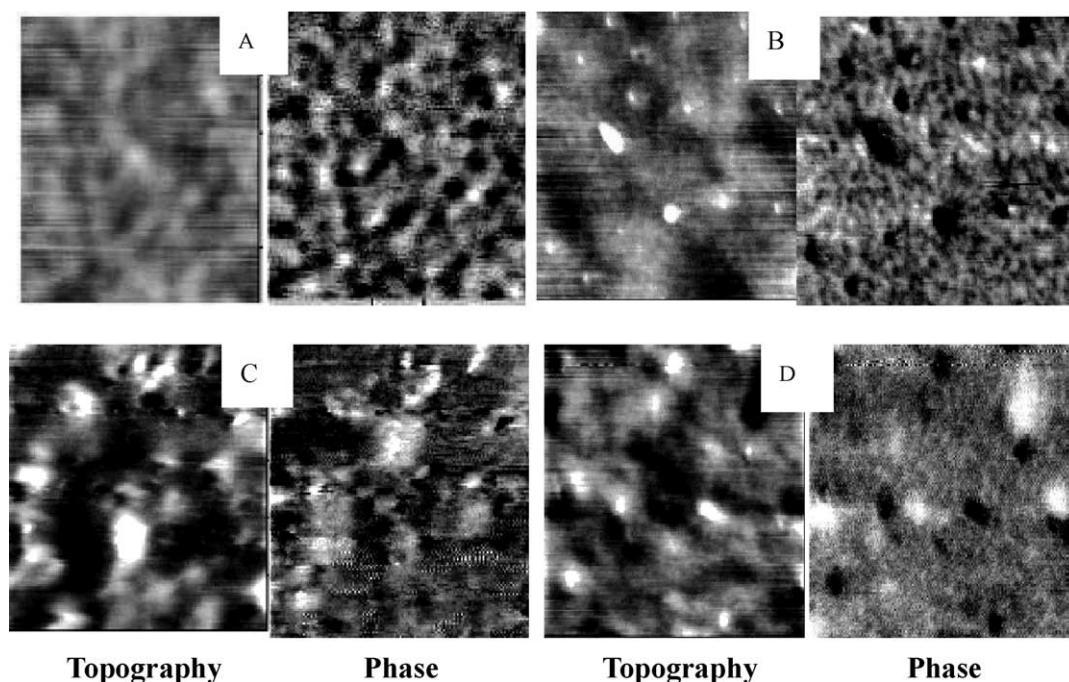


Fig. 7. Topography and phase images of PCU (A), FPCPCU5 (B), FPCPCU20(C), FPCPCU50 (D) at 500 nm scan sizes.

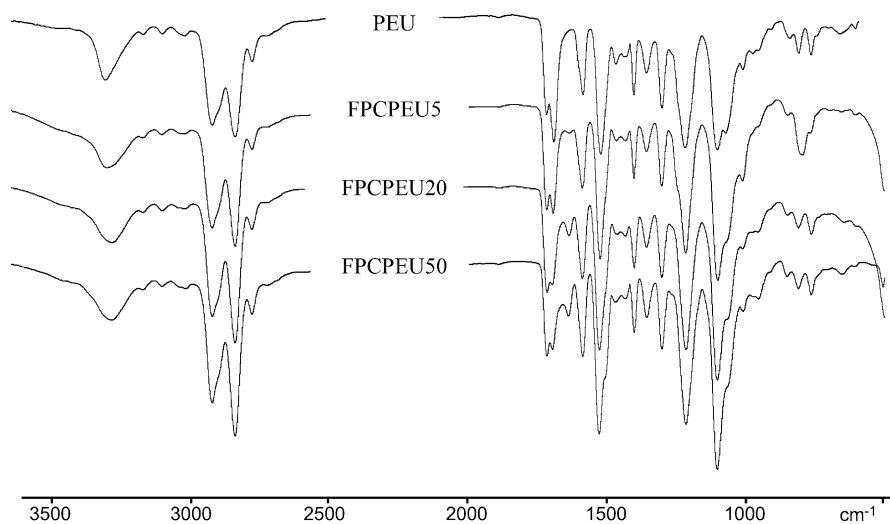


Fig. 8. IR spectra of fluorinated phosphatidylcholine poly(ether urethane)s and poly(ether urethane)s.

poly(ether urethane)s), or the carbonate carbonyl (in poly(carbonate urethane)s) as the acceptor. The FTIR spectra of sets of fluorinated phosphatidylcholine poly(ether urethane)s samples cast on KBr disc from DMAc are shown in Fig. 8. A single stretching band is observed near  $\sim 3300 \text{ cm}^{-1}$  corresponding to the hydrogen-bonded N–H stretching vibration [26]. The stretching band at  $\sim 1730 \text{ cm}^{-1}$  is due to the absorption of the free carbonyl of hard segments, and  $\sim 1700 \text{ cm}^{-1}$  is mainly caused by hydrogen-bonded carbonyl absorption between hard segments [26,27]. Table 3 lists the fraction of hydrogen-bonded carbonyl of urethane according to the relative area of the free carbonyl adsorption and the hydrogen-bonded carbonyl in urethane to calculation [16]. Fig. 9 shows the 1850–1650  $\text{cm}^{-1}$  region assigned to free carbonyl and hydrogen-bonded carbonyl absorption of the urethane in the fluorinated phosphatidylcholine poly(ether urethane)s. One observes almost constant carbonyl group absorption at  $\sim 1730 \text{ cm}^{-1}$ , accompanied with a decreasing of hydrogen-bonded carbonyl group absorption at  $\sim 1709 \text{ cm}^{-1}$ , with increasing fluorinated phosphatidylcholine content. This

result suggests that the degree of hydrogen bonding between hard segment and soft segment is decreased as the content of fluorinated phosphatidylcholine attached to hard block increases. This will result in an enhanced phase separation between soft and hard segments.

A different result is seen for fluorinated phosphatidylcholine poly(carbonate urethane)s, which is shown in Fig. 10. Here again, the amide groups in fluorinated phosphatidylcholine poly(carbonate urethane)s are mostly involved in hydrogen bonding. Fig. 11 shows the 1850–1650  $\text{cm}^{-1}$  region assigned to the urethane and carbonate C=O of the fluorinated phosphatidylcholine poly(carbonate urethane)s, the stretching band at the 1850–1650  $\text{cm}^{-1}$  region is overlapped by the stretching band at  $\sim 1743$ ,  $\sim 1720$ ,  $\sim 1710$  and  $\sim 1690 \text{ cm}^{-1}$  due to the absorption of the free carbonyl of PHPCD soft segments, hydrogen-bonded carbonyl in carbonate, free carbonyl of urethane and hydrogen-bonded carbonyl absorption of urethane, respectively [26–28]. With increasing of fluorinated phosphatidylcholine content, the hydrogen-bonded carbonyl adsorption of urethane decreases and adsorption of free carbonyl in

Table 3

Fraction of hydrogen-bonded carbonyl of urethane and hydrogen-bonded carbonyl of carbonate in FTIR analysis of fluorinated phosphatidylcholine polyurethanes and polyurethanes

	N–H stretching band		Urethane bonded C=O			Carbonate bonded C=O	
	$\nu \text{ (cm}^{-1}\text{)}$	$\Delta\nu^a$	Stretching band $\nu \text{ (cm}^{-1}\text{)}$	$\Delta\nu^a$	%	Stretching band $\text{(cm}^{-1}\text{)}$	%
PEU	3328	0	1702	–	72.5	–	–
FPCPEU5	3322	–6	1706	4	60.5	–	–
FPCPEU20	3304	–16	1709	7	59.3	–	–
FPCPEU50	3306	–18	1709	7	61.6	–	–
PCU	3337	0	1689 <sup>b</sup>	–	10.7	1723 <sup>b</sup>	25.2
FPCPCU5	3342	5	1695 <sup>b</sup>	6	6.8	1722 <sup>b</sup>	30.1
FPCPCU20	3344	7	1695 <sup>b</sup>	6	5.8	1723 <sup>b</sup>	19.7
FPCPCU50	3345	8	1693 <sup>b</sup>	4	2.8	1723 <sup>b</sup>	21.9

<sup>a</sup>  $\Delta\nu = \nu_{\text{FPCPU}} - \nu_{\text{PU}}$ .

<sup>b</sup> The peak position was obtained by curve fit.



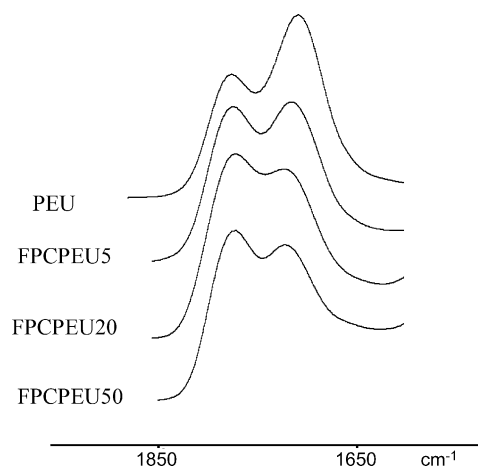


Fig. 9. Urethane C=O stretching region [A] of fluorinated phosphatidylcholine poly(ether urethane)s and poly(ether urethane)s.

carbonate at  $\sim 1720\text{ cm}^{-1}$  increases, and the peaks ( $1850\text{--}1650\text{ cm}^{-1}$ ) become sharper (Table 3, Fig. 11) [16,28]. These results suggest that the phase mixing is enhanced with increasing of fluorinated phosphatidylcholine content because the fraction of hydrogen-bonded carbonyl decreases and the fraction of free carbonyl in carbonate increases in this system.

Now another question arises that why fluorinated side chain and fluorinated phosphatidylcholine side chain can lead to totally different hydrogen bonding in the two polyurethane series? In poly(carbonate urethane) ('PCU'), there exist relatively vast numbers of 'hard-soft' hydrogen bonding linkage besides the 'hard-hard' linkage. In PEU without fluorinated phosphatidylcholine side chain, the 'hard-soft' linkage will be rare and can hardly play any significant roles since the hydrogen bond between the amide on hard blocks and the oxygen of polyether soft segments is weak and hard to form. For fluorinated phosphatidylcholine poly(ether urethane)s, however, we do see the possibility to form the 'hard-soft' linkage under the effect of the side

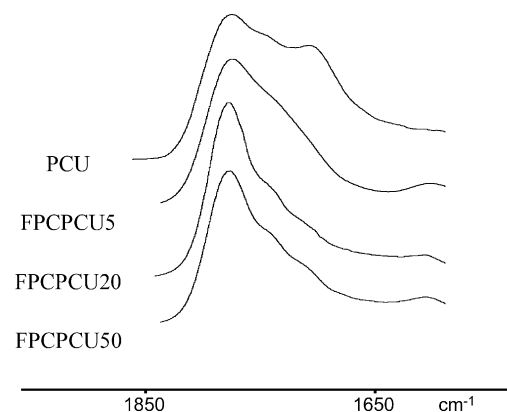


Fig. 11. Urethane C=O stretching region [A] of fluorinated phosphatidylcholine poly(carbonate urethane)s and poly(carbonate urethane)s.

group. To better understand the interaction between 'hard-hard' linkage or the 'hard-soft' linkage, the structure of two sets of polyurethanes containing only fluorinated side chain can be found in Ref. [18]. For polyurethanes with only fluorinated side chain, the phase separation in poly(carbonate urethane)s is due to the increased strength of carbonyl in urethane as an acceptor. And the phase mixing in poly(ether urethane)s is caused by the increased capability of the amide group as a donor [29]. In fluorinated phosphatidylcholine polyurethanes systems, however, the degree of hydrogen bonding between hard segments and soft segments is influenced not only by the chemical structure of main chain and side chain, but also by the zwitterionic phosphatidylcholine moieties [4]. The peak positions associated with hydrogen-bonded amide group, in poly(carbonate urethane) system, are shifted to higher frequencies, indicating a weakened donor strength. Thus the ability of forming hydrogen-bonding between hard segments is reduced (Table 3) [29]. On the other hand, the carbonate groups in polycarbonate diol chain are bonded with zwitterionic phosphatidylcholine through inductive

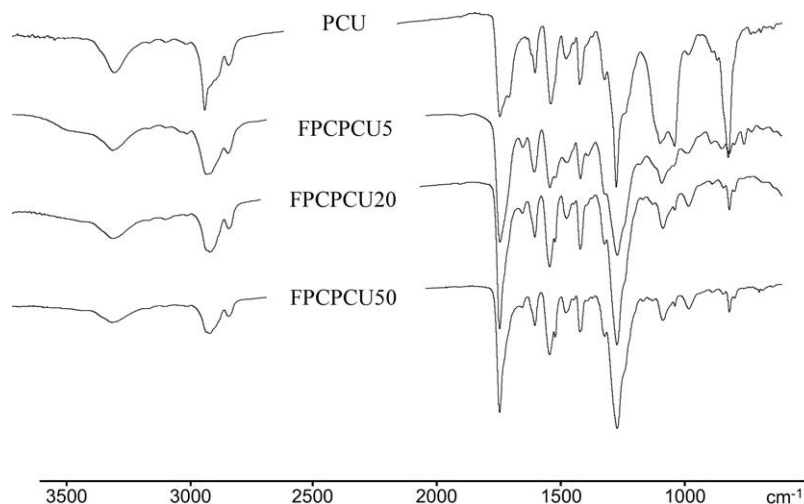


Fig. 10. IR spectra of fluorinated phosphatidylcholine poly(carbonate urethane)s and poly(carbonate urethane)s.

effect, due to asymmetric distributing of electron in the carbonate resonance structures. The rise in  $\tan \delta$  of poly(carbonate urethane)s seen in DMA (Table 2) is another evidence of inductive effect, which results in the decreased amount of hydrogen-bonded amide group and the enhanced interaction between hard segment and soft segment, as the content of fluorinated phosphatidylcholine increases.

In the poly(ether urethane)s, the peak position associated with hydrogen-bonded amide group is shifted to lower frequencies, indicating an enhanced ability as a donor, thus the ability of forming hydrogen-bonding between hard segments and soft segments is strengthened (Table 3) [29]. Also the inductive force between zwitterionic phosphatidylcholine and ether is very small and can be neglected in this case due to the symmetrical structure of ether. Meanwhile, the polarity difference between the hard and soft segments is enlarged in this system as the fluorinated phosphatidylcholine content increases. This will have additional contribution to the increased degree of microphase separation.

#### 4. Conclusion

In summary, DSC, DMA, AFM and tensile measurement measurements on fluorinated phosphatidylcholine poly(ether urethane)s and fluorinated phosphatidylcholine poly(carbonate urethane)s containing various amounts of chain extender of fluorinated phosphatidylcholine side chains clearly show that the phase mixing increases in poly(carbonate urethane)s and the phase separation increases in poly(ether urethane)s with increasing amounts of fluorinated phosphatidylcholine side chain on hard segment. The increased degree of hydrogen bonding between hard segments and soft segments is evident by FTIR for fluorinated phosphatidylcholine poly(carbonate urethane)s, and the enhanced association of domains with long-range order (hydrogen bonding) between hard segments for fluorinated phosphatidylcholine poly(ether urethane)s. The totally opposite change in these two systems is due to their ability of forming hydrogen bonding between hard segments and soft segments or among hard segments depending on the structure of main chain and side chain. This work suggests the importance of hydrogen bonding and inductive effect in determining the phase behavior of polyurethanes and, demonstrates how the phase behavior of polyurethanes can be controlled by tailoring the interaction between hard and soft segment via hydrogen bonding and inductive effect.

#### Acknowledgements

We would like to express our great thanks to the National Natural Science Foundation of China (50303014) for Financial Support. We also thank Mr Yunfei Tian, Center of Analysis, Sichuan University, for AFM measurement, Prof Aiming Zhang, and Mr Tao Zhou, State key Laboratory of Polymer Materials Engineering, Sichuan University, for curve fit of FTIR.

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