

SYNTHESIS AND PHASE BEHAVIOR OF POLYURETHANES END-CAPPED WITH FLUORINATED PHOSPHATIDYLCHOLINE HEAD GROUPS*

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Abstract A series of fluorinated phosphatidylcholine polyurethane macromolecular additives were synthesized by solution polymerization using methylenebis(phenylene isocyanates) (MDI) and 1,4-butanediol (BDO) as hard segments, a new phosphorylcholine, 2-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-hexadecafluoro-10-(2-hydroxyethoxy)decyloxy) ethyl phosphorylcholine (HDFOPC) as end-capper, and four polydiols, poly(tetramethylene glycol)s (PTMG), polydimethylsiloxane (PDMS), poly(1,6-hexyl-1,5-pentylcarbonate) (PHPC) and poly(propylene glycol) (PPG) as soft segments, respectively. The chemical structures of the synthesized polyurethanes were characterized by ¹H-NMR and FTIR. DSC and DMA were employed to study the phase behavior of these novel polyurethanes due to their great influences on the surface properties, and hence their interactions with bio-systems. The results showed that phase separation of the fluorinated phosphatidylcholine end-capped polyurethanes was increased in comparison with that of normal polyurethanes. The effect of fluorinated phosphatidylcholine end-capped groups on the phase behavior was further demonstrated by analyzing the degree of hydrogen-bonding between hard and soft segments.

Keywords: Polyurethanes; Phosphorylcholine; Synthesis; Phase behavior.

INTRODUCTION

Polyurethanes are among the important classes of thermoplastic elastomers and have been widely used for various clinical applications because of their favorable mechanical properties and fairly good biocompatibility^[1, 2]. However, their long-term biocompatibility is still a major concern during interfacing with physiological media as artificial organs^[3], due to protein's preferential adsorption on the material surface and activation of platelets to amplify coagulation.

Rendering polyurethanes surface biocompatibility *via* surface modification approaches has been extensively studied. One interest and efficient approach is that of incorporating phosphatidylcholine or its derivatives into polymers^[4–8]. Previous researches have shown that the phosphatidylcholine (PC) moiety is the main head group of the lipid component of red blood cell membranes^[9]. Polymers containing PC groups have a surface similar in structure to the outer surface of the cell membranes. Such biomimetic surfaces can resist protein adsorption^[10, 11] and limit other biological response^[6, 12, 13]. Recently, some polyurethanes containing phosphatidylcholine head groups (PC) in side chains were developed^[14, 15]. Nevertheless, the PC group cannot

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easily migrate to the surface because these monomers have only a short alkyl side chain. In order to achieve a PC group surface, one has to use a large amount of phosphatidylcholine chain extender to synthesize the polyurethanes that will cause high water adsorption in the bulk, and consequently result in poor mechanical properties^[14, 16, 17]. In our previous studies, we have successfully prepared a novel diol containing fluorinated phosphatidylcholine head group and the corresponding polyurethanes with fluorinated phosphatidylcholine side chains attached to hard blocks^[15]. With the help of migration of the fluorinated side chains, the PC groups can easily penetrate to the surface. Thus, only 5%–12.5% phosphatidylcholine is needed to improve the hemocompatibility for polyurethanes and achieve a better mechanical properties than literature values^[18]. Another legitimate method to altering the surface chemistry and thereby improving their blood compatibility is by use of additives. For example, Santerre *et al.* synthesized a series of polyurethanes tailored with fluorinated end groups (which were termed as surface-modification macromolecules (SMMs)) and blended with base polymers for surface modification^[19–21]. It was found that the surface energy of the polymer mixture appeared to be almost identical to that of polytetrafluoroethylene (Teflon) and showed reduced platelet adhesion with addition of less than 5 wt% of SMMs^[21–24]. Moreover, the bulk properties of the base polymer remained relatively unchanged.

To develop new polyurethane biomaterials, in this work, we designed and synthesized a series of novel polyurethanes end-capped with fluorinated phosphatidylcholine groups, which could be used as macromolecular additives for polyurethanes to improve the blood compatibility. The polyurethanes were prepared by solution polymerization using MDI and BDO as hard segments, a new phosphorycholine, 2-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-hexadecafluoro-10-(2-hydroxyethoxy)decyloxy) ethyl phosphorycholine (HDFOPC) as end-capper, and four polydiols: PTMG, PDMS, PHPC, PPG as soft segments, respectively. It is expected that the PC groups are more easily transferred to the outer surface of the materials forming biomimetic surface, due to the stronger activity of the end groups and lower surface energy of the long fluorinated alkyl chain. In addition, the chemical structure and molecular weight of these macromolecular additives can be easily controlled for different requirements.

The focus of this work is to verify the effect of chemical structure and fluorinated phosphatidylcholine end groups on phase behaviors of these novel phospholipid polyurethanes. Since some studies showed that the phase separation in polyurethanes had a great effect on the surface properties and its interactions with bio-system^[25]. Changing monomer chemistry^[26–28], such as the symmetry of diisocyanate, the type of chain extender and soft segment, polydiol molecular weight and the reaction stoichiometry in the process of the polyurethane synthesis can change the phase separation. Our previous work have reported that a novel diol containing fluorinated phosphatidylcholine head group together with 1,4-butanediol was used as chain extender for preparing a series of polyurethanes^[15]. We 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. Very interestingly, compared to that of normal polyurethanes, the phase separation was found to increase for all phospholipids polyurethanes prepared disregarding the soft segments used in the current study.

EXPERIMENTAL

Materials

2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-Hexadecafluoro-1,10-decandiol (HDFDOL) was purchased from Aldrich (97% purity). 2-Chloro-1,3,2-dioxaphospholane-2-oxide (COP, ACROS), sodium hydrogen (60%), bromoacetic acid and dimethyl sulfoxide (DMSO) were used as received. Isobutyl chlorocarbonate (*i*BuOCOC_l) and acetyl chloride were distilled under atmospheric pressure. *N*-methylmorpholine was distilled under atmospheric pressure in the presence of acetic anhydride. Methylenebis(phylene isocyanates) (MDI) and 1,4-butanediol (BDO) were distilled under vacuum. Poly(tetramethylene glycol)s (PTMG, $M_w = 1000$, obtained from Dupont), poly(propylene glycol) (PPG, $M_w = 1000$, obtained from Sinopec Shanghai GaoQiao Petrochemical Corporation, China), hydroxy alkyl polydimethylsiloxane (TEGOMER H-SI 2111, $M_w = 1000$, obtained from

Degussa, Germany) were dehydrated at 100°C for 4 h under vacuum before use. Poly(1,6-hexyl-1,5-pentylcarbonate) diol (PHPC, $M_n = 1058$) was synthesized in our laboratory and dehydrated under reduced pressure at 100°C for 4 h^[29]. *N,N*-dimethylacetamide (DMAc) was dried over CaH₂ for 2 days at room temperature, distilled under vacuum and stored in the presence of 0.4 nm molecular sieves. The other reagents were used as received.

Synthesis of 2-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-Hexadecafluoro-10-(2-hydroxy ethoxy)decyloxy) Ethanol (HDFOOL)

A detailed preparation for CHFA has been reported in reference^[15]. A solution of CHFA (2.0 g, 3.46 mmol) and *N*-methylmorpholine (0.95 mL, 8.65 mmol) in anhydrous tetrahydrofuran (30 mL) was cooled to −15°C, then isobutyl chlorocarbonate (0.95 mL, 7.3 mmol) was added. After the mixture was stirred for 15 min, NaBH₄ (0.39 g, 10.38 mmol) was added. The reaction mixture was stirred for 2 h at room temperature, and then the excessive NaBH₄ was decomposed by adding distilled water. The solution was concentrated under reduced pressure to give solid residue, and the solid residue was dissolved in ethyl acetate. The solution was washed with dilute HCl, saturated NaCl, H₂O, dried over Mg₂SO₄, filtered under vacuum and evaporated in vacuum to give crude HDFOOL. The crude HDFOOL was purified by silica gel column chromatography using gradient petroleum ether/EtOAc to yield 1.25 g of HDFOOL (64.7%). Synthesis route is shown in Fig. 1.

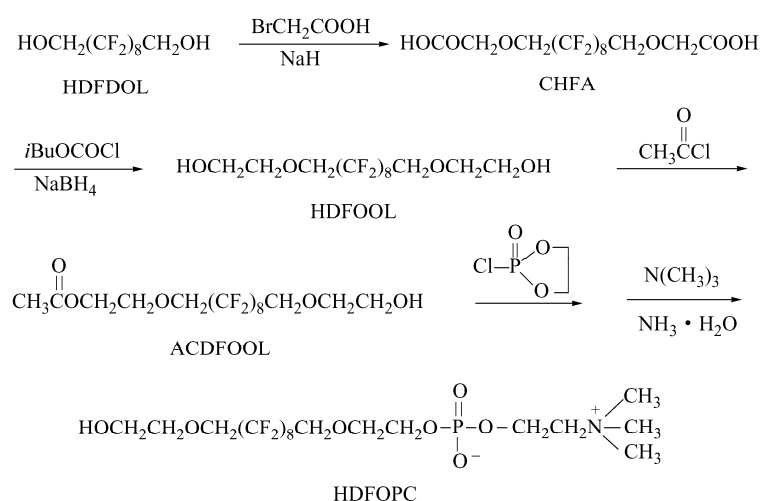


Fig. 1 Synthesis route of HDFOPC

IR (KBr): 3348 (—OH), 2938 (—CH₂—), 1202 (—CF₂—), 1147 (C—O—C); APCI ms (positive) *m/z* theoretical 550 g/mol, observed 551 g/mol; ¹H-NMR (CDCl₃, TMS, 400 MHz) δ : 3.73–3.79 (m, 8H, —CH₂CH₂—), 3.99–4.06 (m, 4H, —CH₂CF₂—).

Synthesis of 2-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-Hexadecafluoro-10-(2-hydroxy ethoxy)decyloxy) Ethyl Acetate (ACDFOOL)

A solution of HDFOOL (4.0 g, 7.3 mmol) and triethylamine (1.10 mL, 8.0 mmol) in anhydrous tetrahydrofuran (60 mL) was cooled to 0°C, acetyl chloride (0.95 mL, 7.3 mmol) was dropwise added to the stirred solution. The reaction mixture was stirred for 4 h at room temperature, and then filtered under vacuum, the filtrate was concentrated under reduced pressure to give solid residue, and the solid residue was dissolved in ethyl acetate. The solution was washed with dilute HCl, saturated NaCl, H₂O, dried over Mg₂SO₄, filtered under vacuum and evaporated in vacuum to give crude ACDFOOL. The crude ACDFOOL was purified by silica gel column chromatography using gradient petroleum ether/EtOAc to yield 2.07 g of ACDFOOL (48%). Synthesis route is shown in Fig. 1.

IR (KBr): 3428 (—OH), 2950 (—CH₂—), 1740 (—C=O), 1204 (—CF₂—), 1147 (C—O—C); APCImS (positive) m/z theoretical 592 g/mol, observed 593 g/mol; ¹H-NMR (CDCl₃, TMS, 400 MHz) δ : 2.08 (s, 3H, —CH₃), 3.74–3.78 (m, 4H, —CH₂O—), 3.82–3.94 (t, 2H, —CH₂OH), 3.97–4.06 (m, 4H, —CH₂CF₂—), 4.23–4.25 (t, 2H, —COOCH₂—).

Synthesis of 2-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-Hexadecafluoro-10-(2-hydroxy ethoxy)decyloxy)ethyl Phosphorycholine (HDFOPC)

ACDFOOL (7.6 g, 12.8 mmol) and triethylamine (1.97 mL, 14.1 mmol) were dissolved in a mixture of 40 mL anhydrous diethyl ether and 20 mL dry acetonitrile. After cooling the solution down to –15°C, COP (1.83 g, 12.8 mmol) dissolved in anhydrous diethyl ether (10 mL) was added slowly to the stirred solution under nitrogen over 20 min. The temperature of the reaction mixture was maintained at –15°C for 1 h and allowed to slowly warm up to the room temperature. Triethylammonium chloride precipitate was filtered off and washed with diethyl ether. The filtrate was evaporated under vacuum to give residue as colorless oil. Then the residue was dissolved in 60 mL dry acetonitrile and transferred to a 100 mL glass pressure bottle. After the pressure bottle was cooled to –18°C, excessive trimethylamine was rapidly added to the solution. The pressure bottle was then sealed and maintained at 60°C for 24 h, subsequently the solution was evaporated under vacuum to produce viscous liquid. The viscous liquid was dissolved in methanol, and excessive ammonia was added with stirring for 24 h at room temperature. The solution was concentrated under reduced pressure to give crude HDFOPC. Finally, the crude HDFOPC was purified by C18 reverse silica gel column chromatography using water/methanol to yield 8.2 g of HFDAPC (90%). Synthesis route is shown in Fig. 1.

IR (KBr): 3372 (—OH), 2946 (—CH₂—), 1204 (—CF₂—, P=O), 1147 (C—O—C), 1061 (P—O—CH₂); APCI ms (positive) m/z theoretical 715 g/mol, observed 716 g/mol; ¹H-NMR (DMSO, TMS, 400 MHz) δ : 3.13 (s, 9H, —N⁺(CH₃)₃), 3.49–3.54 (m, 4H, —CH₂O—, —CH₂N⁺), 3.60–3.63 (t, 2H, —CH₂OH), 3.70–3.73 (t, 2H, —OCH₂C—), 3.74–3.77 (m, 2H, —CH₂OP—), 4.01–4.02 (s, 1H, —OH), 4.15–4.24 (m, 4H, —CH₂CF₂—), 4.86–4.88 (t, 2H, —POCH₂—); ¹³C-NMR (DMSO, TMS, 400 MHz) δ : 53.2 (s, 3C17), 58.5 (d, C15), 60.2 (s, C1), 63.5 (d, C16), 65.6 (s, C13), 66.8–67.4 (m, C3, C12), 72.3 (d, C14), 74.1 (s, C2), 107.9 (m, C5, C10), 110.7 (m, C6, C9), 113.5 (m, C7, C8), 116.1 (m, C4), 118.6 (m, C11).

Synthesis of Fluorinated Phosphatidylcholine Polyurethanes

Four polydiols were used for the synthesis: PTMG, PPG, PDMS, PHPC. All polyurethanes were synthesized by similar methods using solution polymerization based on MDI, polydiol, chain extender (BDO) and end-capper HDFOPC (FPC) in DMAc. The feed ratios are shown in Table 1. In the first reaction step: MDI was added to the stirred DMAc solution of polydiol under a dry nitrogen atmosphere at 40°C. The reaction was maintained within a range of 60–65°C for 2 h. Chain extender (BDO) and 0.1% stannous octoate were added to the reaction solution, while the temperature was kept at 65–70°C for 1 h. Following this, the FPC dissolved in DMSO was added to the products of the first step and the mixture stirred at 80°C for 1 h, at 85–90°C for 4 h, and then at 100–110°C for 1 h. The solution was then cooled down to room temperature and stored for 1 week. The polymer was precipitated in methanol/distilled water mixed solvent (*V/V* = 1/5) to remove any residual FPC and the low molecular weight fraction, then dried in oven at 50°C for 24 h. This step was repeated two times.

Table 1. Theoretical composition, molecular weights and molecular weight distribution of fluorinated phosphatidylcholine polyurethanes and normal polyurethanes

Samples	Stoichiometry		Fluorine atom (%)	Phosphorus atom (%)	$M_w \times 10^{-4}$	M_w/M_n
	MDI/(polydiol +BDO)/FPC ^a	MDI/polydiol/BDO				
PTMG-FPC	3:2:2		11.60	0.72	3.59	2.02
PDMS-FPC	3:2:2		13.70	0.85	5.05	2.51
PHPC-FPC	3:2:2		11.30	0.71	5.49	2.29
PPG-FPC	3:2:2		13.60	0.85	4.61	2.64
PTMG-PU		3:2:1			12.54	2.25
PDMS-PU		3:2:1			11.76	2.81

^a FPC: HDFOPC, F and P are expected theoretical elemental bulk composition;

The polydiol/BDO molar ratio was kept at 9/1 for every FPC containing polyurethanes.

Finally, the polymer was dried under vacuum at 60°C for 48 h to remove trace solvent. Synthesis of the normal polyurethanes has been described in detail previously^[29, 30]. The sample name, taking PTMG-FPC (or PU) as an example, where PTMG represents the soft segment, FPC represents the end capter HDFOPC and PU represents the normal polyurethanes without end-capping. In addition, the molar ratio of PDMS/PHPC which was used as mixed soft segments in PDMS system polyurethanes was kept at 4/1.

Characterization

Instrumentation for confirming the chemical structure of the intermediates and HDFOPC

¹H-NMR and ¹³C-NMR data were collected on a Bulker-400 spectrometer (400 MHz). Mass spectra of these compounds were obtained on an HP1100-LC/MSD with atmosphere pressure chemical ionization (positive mode). Infrared analysis was performed on a Nicolet-560 spectrophotometer between 4000 cm⁻¹ and 400 cm⁻¹ at the resolution of 4 cm⁻¹.

Molecular weight determination

Gel permeation chromatography was carried out on an HP1100 using two PLgel columns (10 μ 10³ nm, 10 μ 50 nm). Molecular weights are relative to monodisperse polystyrene standards. The mobile phase was THF. Sample concentration was 1.000 g/L. The detector was RID and the flow rate was 1.000 mL/min.

Differential scanning calorimetry (DSC) measurements

Thermal transition of the polyurethanes was measured on a NETZSCH DSC 204 differential scanning calorimeter with a low-temperature measuring head and a liquid nitrogen-cooled heating element. Films of the polymers were cast onto a clean glass disk from 100 g/L polymer in DMAc. The solvent was evaporated in an oven at 50°C for 24 h, and the films were further dried in a vacuum at 60°C for 3 days. The films were approximately 0.2 mm thick. The 5–6 mg samples were cut from these films for DSC analysis.

Dynamic mechanical analysis (DMA)

Dynamic mechanical properties were measured on a dynamic mechanical thermal analyzer (Q800, TA Instruments-Waters LLC) using rectangular test film specimens (40 mm × 5 mm × 0.2 mm) prepared as described above. The testing was done at a heating rate of 5 K/min and a frequency of 10 Hz.

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 50°C for 24 h, and 60°C for 48 h under vacuum to completely remove the solvent. Infrared data was obtained with a Nicolet-560 spectrophotometer between 4000 cm⁻¹ and 600 cm⁻¹ in the resolution of 4 cm⁻¹. Fifty scans were taken for average for each sample. The analysis was performed to fit a Gaussian curve by Origin Pro 7.0 software.

RESULTS AND DISCUSSION

Synthesis of HDFOPC Used as an End-capper for Polyurethanes

The HDFOPC containing a fluorinated alkyl phosphatidylcholine polar group was synthesized according to Fig. 1. In copolymers, fluorinated segments are usually enriched at the surface because of their low surface free energy. This fact is the basis for introducing the long fluorinated alkyl chain to this novel end capter so that the phosphatidylcholine polar head group can transfer to the polyurethanes surface. HDFOOL prepared from HDFDOL and bromoacetic was reacted with isobutyl chlorocarbonate in the presence of NaBH₄. Subsequently, ACDFOOL synthesized from HDFOOL and acetyl chloride was reacted with COP and trimethylamine. The method of HDFOPC synthesis with trimethylamine in dry acetonitrile is according to the Nakaya method^[31]. Figure 2(a) is an ¹H-NMR spectrum of the HDFOPC, and there are multiplets at $\delta = 4.15\text{--}4.24$ ascribed to CH₂—CF₂— originating from HDFDOL, and single at $\delta = 3.13$ assigned to —N⁺(CH₃)₃ of phosphatidylcholine polar group. Peaks of an *O*-methylene proton and *N*-methylene proton, both of which originated from the phosphatidylcholine group, were also observed at $\delta = 4.01\text{--}4.02$ and $\delta = 3.49\text{--}3.54$, respectively. In addition, the

multiplets at $\delta = 4.86$ – 4.88 were assigned to $-\text{OH}$ because these peaks disappeared in ^1H -NMR spectrum after exchanging with D_2O . ^{13}C -NMR spectrum (Fig. 2b) of HDFOPC exhibited the similar series of signals between $\delta = 107.9$ and 118.6 assigned to $\text{C}-\text{F}$ as that of HDAOL^[15], thus confirming the presence of a fluorinated carbon chain in the molecular structure. The signals at $\delta = 66.8$ – 67.4 , 53.2 and 60.2 were ascribed to CH_2-CF_2- , $-\text{N}^+(\text{CH}_3)_3$ and $-\text{CH}_2\text{OH}$, respectively. The structures of HDFOOL and ACDFOOL were also confirmed by ^1H -NMR, MS and IR. The typical peaks of CH_2-CF_2 are also observed in ^1H -NMR spectra of HDFOOL and ACDFOOL at $\delta = 3.99$ – 4.06 , 3.97 – 4.06 , respectively. The results of MS and IR revealed similarly that the HDFOOL and ACDFOOL were also synthesized in this route.

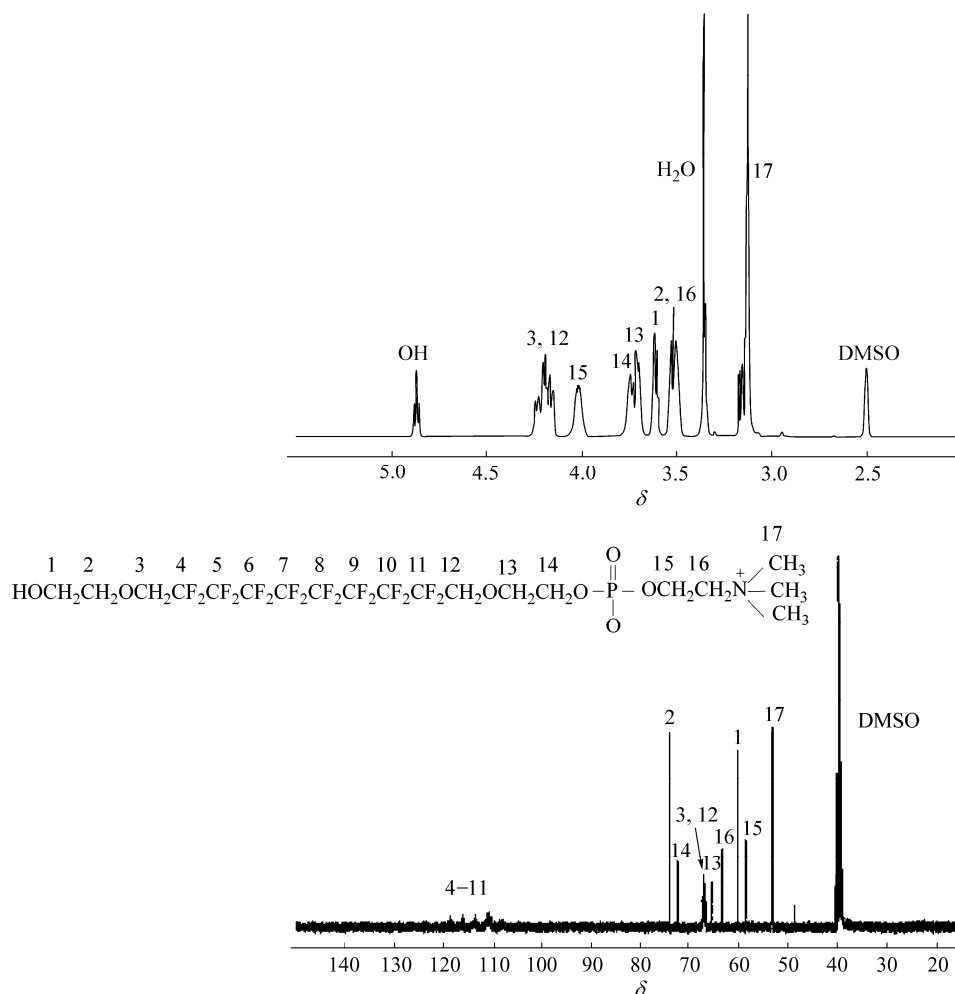


Fig. 2 NMR spectra of HDFOPC: (a) ^1H -NMR spectrum, (b) ^{13}C -NMR spectrum

Synthesis of Polyurethanes

A series of fluorinated phosphatidylcholine end-capped polyurethanes with various type of soft segments: PTMG, PPG, PDMS, PHPC were prepared using solution polymerization. The scheme structure of the fluorinated phosphatidylcholine polyurethanes is shown in Fig. 3. PTMG-PU and PDMS-PU without end-capping with HDFOPC were also synthesized for comparison. The theoretical fluorine contents in the bulk are in the range of 11.3%–13.7% (atomic percentage of fluorine), and the contents of phosphorus are from 0.71% to 0.85%. The ^1H -NMR spectra of the series of fluorinated phosphatidylcholine polyurethanes are shown in Fig. 4. A single peak at $\delta = 3.1$ ascribed to the methyl protons of the choline group was observed, and more confirming the HDFOPC covalently bonded to the polyurethanes chain. The molecular weights and polydispersity index

(M_w/M_n) of the novel polyurethanes were determined by GPC using polystyrene standards and THF as the mobile phase, and the results are listed in Table 1. All the polyurethanes are in same level of polydispersity, while it should be noted that the molecular weight of the fluorinated phosphatidylcholine polyurethanes was less than that of normal polyurethanes, for instance, PTMG-FPC (3.59×10^4) showed a molecular weight about 70% lower than that of PTMG-PU (12.54×10^4). This is because, during the chain extend procedure, just a little amount of BDO was used to control the prepolymer chain length of fluorinated phosphatidylcholine polyurethanes. However, these molecular weights of novel phospholipid polyurethanes are enough to be used as macromolecular additives for polyurethane system and will not be leached out of the polyurethane matrix because of their good compatibilities and strong hydrogen bonding interactions.

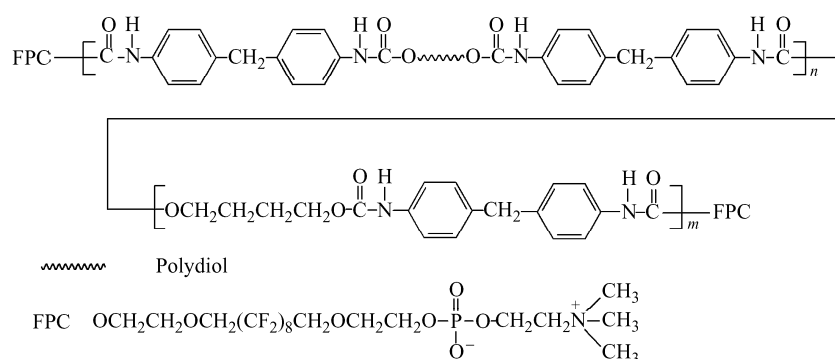


Fig. 3 Schematic structure of fluorinated phosphatidylcholine end-capped polyurethanes $n = 1, 2, 3, \dots$; $m = 1, 2, 3, \dots$

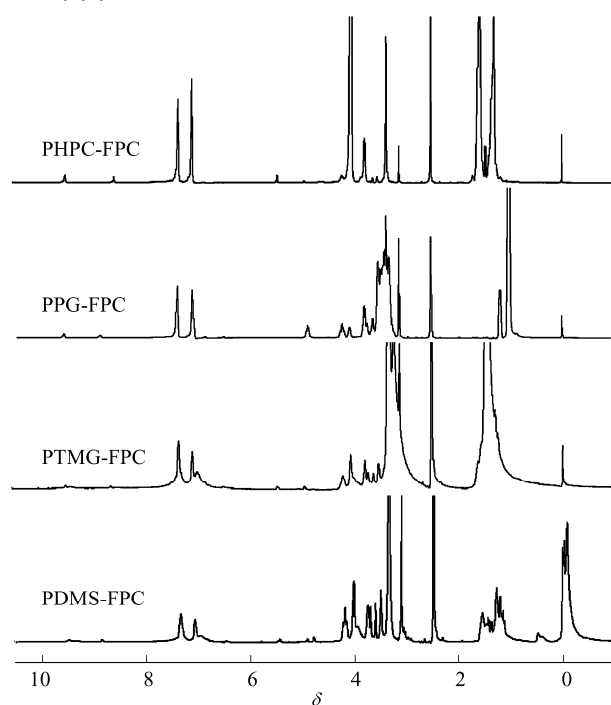


Fig. 4 ^1H -NMR spectra of fluorinated phosphatidylcholine polyurethanes

DSC Analysis

DSC was used to characterize the thermal transitions of the polyurethanes and to assess the state of microphase separation^[32]. The DSC heating curves from the first heating of the samples are shown in Fig. 5. Glass transition

temperatures (T_g) are reported as the midpoint of the transition process (Table 2). From the DSC results, the T_g value of PTMG-FPC is decreased compared with that of PTMG-PU. And the same decrease of PHPC-FPC T_g was also observed in comparison with that of pure polycarbonate polyurethanes (-3.6°C) reported in reference^[15]. In PDMS polyurethane system, PHPC and PDMS were used as mixed soft segments for improving the interaction between hard segments and soft segments. Nevertheless, just only one T_g ascribed to PHPC was observed on the DSC heating curve. The T_g of PDMS was not detected by DSC probably owing to less change of PDMS heat capacity. Furthermore, the T_g value of PDMS-FPC was slightly shifted to lower temperature compared to that of PDMS-PU. The change in T_g of the soft segment has been used as an indicator of the degree of phase separation: a lower T_g of the soft segment phase can suggest improvement in the extent of microphase separation^[33]. One has seen that the T_g values of all the phospholipid polyurethanes are decreased, which indicates that the phase separation is enhanced by introducing the fluorinated phosphatidylcholine group to polyurethanes.

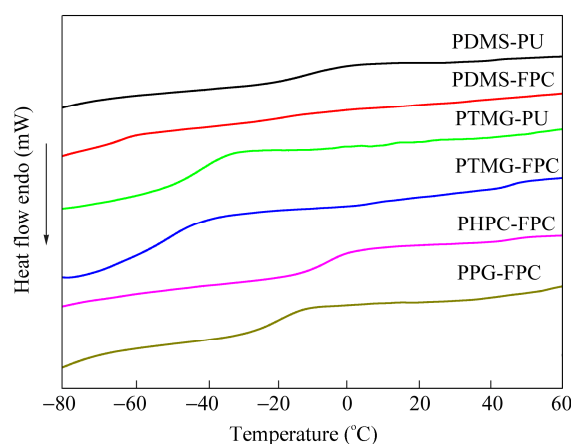


Fig. 5 DSC thermograms of fluorinated phosphatidylcholine polyurethanes and normal polyurethanes

Table 2. Glass transition temperature and dissipation factor of fluorinated phosphatidylcholine polyurethanes in DMA and glass transition temperature in DSC

Sample	T_g ($^\circ\text{C}$)		$\tan\delta$		Soft segment T_g^a ($^\circ\text{C}$)	
PTMG-FPC	-25.5		0.4184		-51.3	
PDMS-FPC	-89	6	0.0913	0.2757	—	-18.6
PHPC-FPC	15		0.636		-5.8	
PPG-FPC					-19.7	
PTMG-PU	-17		0.8183		-48.4	
PDMS-PU	-89.5	19	0.1173	0.4873	—	-10.7

^a DSC results

DMA Analysis

In order to further understand the phase separation of the fluorinated phosphatidylcholine end-capped polyurethanes, dynamic mechanical analysis was employed to study the thermal transitions of polyurethanes. The dynamic mechanical properties of polyurethanes are showed in Fig. 6. These DMA data of all polyurethanes are reported in Table 2. However, the DMA analysis of PPG-FPC could not be performed because of its low molecular weights and poor mechanical properties. To better understand the effect of fluorinated phosphatidylcholine groups in end-capper of polyurethanes on the phase separation, dissipation factor ($\tan\delta$) was also considered. As can be seen, the glass transition temperatures determined from the peaks of $\tan\delta$ curves are higher than those determined by DSC, which can be related to the heat transporting hysteresis for large scale samples in DMA. The PDMS containing polyurethanes showed clearly two T_g s due to the mixed soft segments of PDMS and PHPC, respectively. In addition, the first T_g at -89°C ascribed to PDMS almost kept constant,

undepending on the composition, indicating that the PDMS microphase completely separated from both the PHPC soft segment and hard segment phase. The second T_g assigned to PHPC shifted to lower temperature compared to PDMS-PU. The $\tan\delta$ peak of PTMG-FPC is also slightly shifted to lower temperatures compared to PTMG-PU. And the same change of $\tan\delta$ peak was observed in PHPC polyurethanes system. The decrease of glass transition temperatures determined from $\tan\delta$ indicates that interaction between hard segments and soft segments is reduced in fluorinated phosphatidylcholine polyurethanes^[34], which means that the phase separation is enhanced by introducing the fluorinated phoasphatidylcholine group. These DMA results are in good agreement with the DSC data.

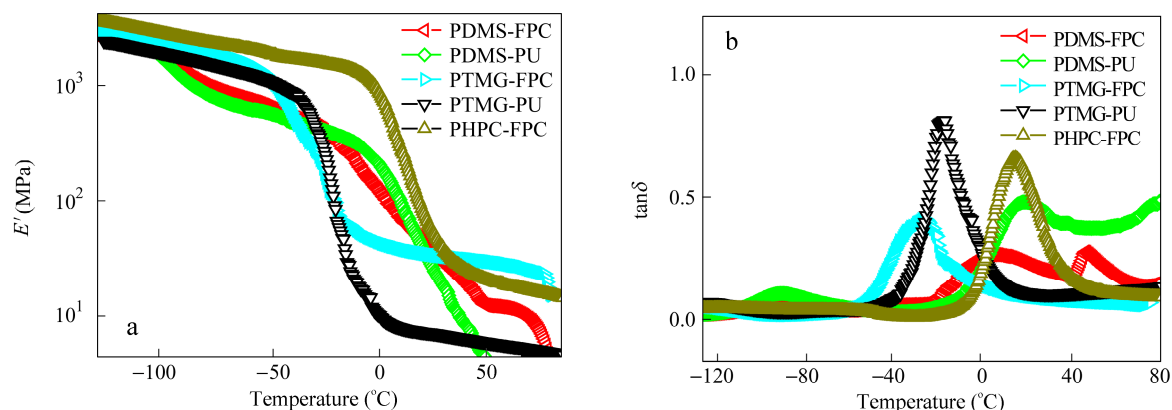


Fig. 6 Dynamic-mechanical spectra of fluorinated phosphatidylcholine polyurethanes and normal polyurethanes: (a) E' versus T , (b) $\tan\delta$ versus T

FTIR Analysis

Polyurethanes are an intriguing class of polymers whose properties are determined by the phase-separated hard and soft segments that usually define their microstructure. Crystallization of the hard segments is one of the major factors in phase separation, while hydrogen bonding between hard segments is an additional driving force for phase separation. Infrared spectroscopy is very sensitive to hydrogen bonding, and this technique has been extensively applied to characterize phase separation in polyurethanes^[35, 36]. Here we will apply this technique to investigate the hydrogen bonding structure in the bulk polyurethanes. The hydrogen bonding was constituted by the NH group being as donor, and the urethane carbonyl, the ether oxygen, or the carbonate carbonyl as acceptors.

The FTIR spectra of a series of fluorinated phosphatidylcholine polyurethanes are shown in Fig. 7. The spectra show almost a single broad stretching band at *ca.* 3300 cm^{-1} corresponding to H-bonded N—H stretching vibration^[37]. The IR peaks in the region of $1680\text{--}1750\text{ cm}^{-1}$ were assigned to the urethane and carbonate C=O stretching. Table 3 lists the fraction of hydrogen-bonded carbonyl of urethane and hydrogen-bonded carbonyl of carbonate according to the relative area of the free carbonyl adsorption and that of the hydrogen-bonded carbonyl in urethane^[38, 39]. In PTMG containing polyurethanes (Fig. 8a), the stretching band at *ca.* 1730 cm^{-1} is assigned to the absorption of the free C=O of hard segments, and *ca.* 1700 cm^{-1} is related to the H-bonded C=O absorption between hard segments^[37, 39]. One can observe that the fraction of H-bonded C=O absorption of PTMG-FPC at *ca.* 1706 cm^{-1} is increased by introducing the fluorinated phosphatidylcholine group (Table 3). This result indicates that the degree of hydrogen bonding between hard segments is increased and it gives rise to an enhanced phase separation between hard and soft segment. For PDMS containing polyurethanes, PDMS and PHPC were taken as mixed soft segments to synthesize these polyurethanes. Figure 8(b) shows the stretching band at the $1850\text{--}1650\text{ cm}^{-1}$ region is overlapped by the stretching bands at *ca.* 1740 , *ca.* 1720 , *ca.* 1710 , *ca.* 1690 cm^{-1} ascribed to the absorption of the free C=O of PHPC soft segments, H-bonded C=O in carbonate, free C=O of urethane and H-bonded C=O absorption of urethanes, respectively^[27, 37, 40]. As can be seen, H-bonded C=O absorption of urethanes increases while absorption of H-bonded C=O in

carbonate sharply decreases, and the peak at *ca.* 1740 cm^{-1} ascribed to the free C=O of carbonate becomes ambiguous. These results indicated that phase separation of the polyurethanes was enhanced by introducing fluorinated phosphatidylcholine end-capping groups into polyurethanes.

Table 3. Fraction of hydrogen-bonded carbonyl urethane and hydrogen-bonded carbonyl of carbonate in FTIR analysis of fluorinated phosphatidylcholine polyurethanes and normal polyurethanes

Sample	N—H stretching band	Urethane bonded C=O ^a		Carbonate bonded C=O ^a	
	ν (cm^{-1})	ν (cm^{-1})	%	ν (cm^{-1})	%
PTMG-PU	3322	1705	45.1	—	—
PTMG-FPC	3305	1706	56.6	—	—
PDMS-PU	3332	1689	31.6	1722	30.5
PDMS-FPC	3333	1695	59.8	1723	1.8
PHPC-FPC	3344	1695	52.8	1723	1.7
PPG-FPC	3298	1704	49.2	—	—

^a The peak position of hydrogen-bonded carbonyl was obtained by curve fit.

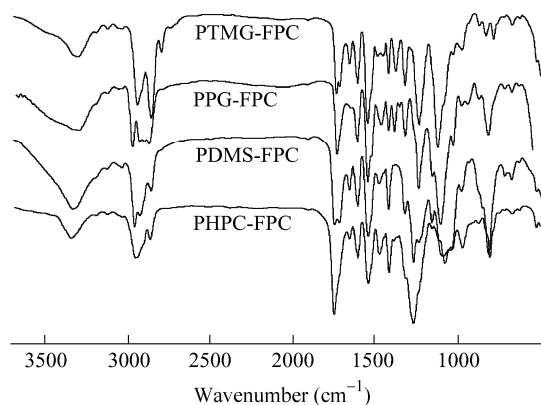


Fig. 7 IR spectra of fluorinated phosphatidylcholine polyurethanes

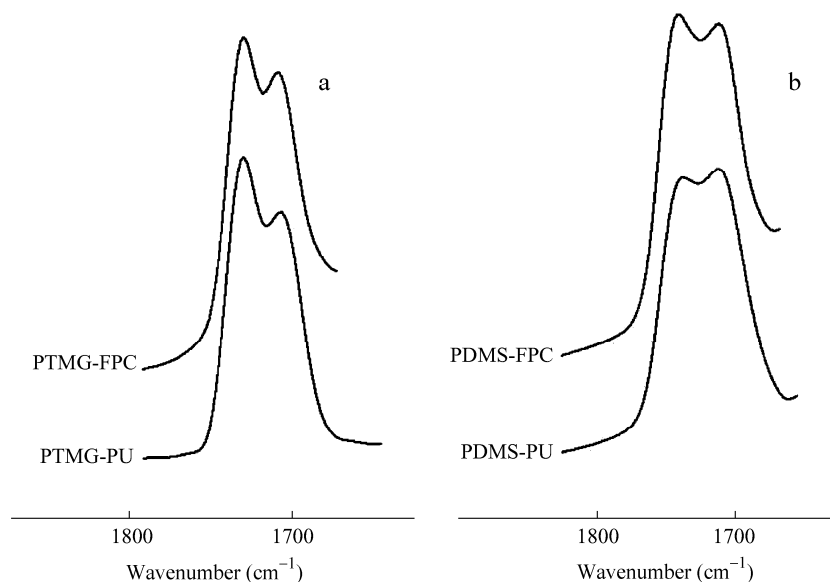


Fig. 8 Carbonyl stretching region of fluorinated phosphatidylcholine polyurethanes: (a) PTMG system, (b) PDMS system

In our previous studies^[41], we found that phase separation was getting less at small content but enhanced at higher content of poly(ether urethane) with fluorinated phosphatidylcholine groups attached to hard block. Nevertheless, a completely opposite trend of phase separation was observed in poly(carbonate urethane) system. Here, the fluorinated phosphatidylcholine end groups in these polyurethanes lead to improving the degree of microphase separation of polyurethanes. Therefore, a logical explanation is necessary. For PTMG-containing polyurethanes, the peak position associated with hydrogen-bonded NH groups is shifted to lower frequencies (from 3322 cm⁻¹ to 3305 cm⁻¹, shown in Table 3), indicating an enhanced ability as a donor^[42], thus the ability of forming hydrogen-bonding between hard segments is enhanced. For PDMS-containing polyurethanes, one of the soft segment PDMS is almost completely separated from the hard segment and the other soft segment PHPC as indicated by DMA, thus only the carbonyl groups of carbonate ascribed to the PHPC soft segment have the possibility to form the “hard-soft” hydrogen-bonding linkage. Table 3 shows that the peak position associated with H-bonded NH groups is almost not changed, indicating a constant donor strength. In addition, the more obvious peak at *ca.* 1740 cm⁻¹ ascribed to free C=O absorption of carbonate in PDMS-FPC roughly indicates the decreased hydrogen-bonding between hard and soft segments in comparison with PDMS-PU (Fig. 8b). Besides the reason mentioned above, the specific dipole-dipole interaction between the zwitterionic phosphatidylcholine groups could be another possible explanation for the increased phase separation in fluorinated phosphatidylcholine end capped polyurethanes^[43, 44]. The self-assemblies (dipole-dipole interaction) of phosphatidylcholine groups, which are attached to the hard blocks, may enhance the interaction between hard segments. This interaction may lead to an additional contribution to increase the degree of phase separation.

CONCLUSIONS

In summary, we have successfully synthesized a series of fluorinated phosphatidylcholine end-capped polyurethanes with four different soft segments. DSC and DMA results clearly show that the phase separation of these novel polyurethanes is enhanced by introducing the fluorinated phosphatidylcholine groups. The increased hydrogen-bonding between hard segments is confirmed by FTIR measurements for fluorinated phosphatidylcholine polyurethanes. Our work demonstrated that the interaction between hard segments was improved by introducing the fluorinated phosphatidylcholine end groups into polyurethanes. This research showed the promising prospect to blend these macromolecular additives with normal medical polyurethanes to alter the surface chemistry of polyurethanes, simultaneously getting polymer mixtures with good compatibility and stability. It is anticipated that the surface chemistry of the polymer mixtures will close to that of the macromolecular additive, thereby altering their biocompatibility. Now, this study is in progress in our laboratory.

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