

Synthesis and Characterization of Novel Polyurethane Crosslinked by Linear Oligo[bis-(phenoxy)_{1.8}(4-hydroxybutaneoxy)_{0.2} Phosphazene]

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ABSTRACT: Linear oligo [bis-(phenoxy)_{1.8}(4-hydroxybutaneoxy)_{0.2} phosphazene] (OPHBP) was synthesized and characterized by Fourier transform infrared spectroscopy, nuclear magnetic resonance, and GPC. The obtained oligo [bis-(phenoxy)_{1.8}(4-hydroxybutaneoxy)_{0.2} phosphazene] was used as crosslinker to prepare a series of novel polyurethanes. Their structure and properties were measured through Fourier transform infrared spectroscopy, thermogravimetric anal-

ysis, differential scanning calorimetry, and water contact-angle measurement. Compared with conventional polyurethane, novel polyurethanes exhibited better thermal stability, low temperature resistance, and hydrophobicity. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 473–478, 2009

Key words: polyphosphazenes; polyurethanes; crosslinking; thermal properties

INTRODUCTION

Polyurethane (PU) elastomers are a class of versatile engineering materials¹ with high abrasion resistance,² excellent flexibility,³ chemical resistance,⁴ high impact strength,⁵ and damping ability.⁶ However, traditional PU elastomers exhibit poor heat stability, for example, the acceptable mechanical properties (strength, modulus, etc.) disappear at temperatures greater than 80°C and thermal degradation occurs at temperatures greater than 200°C, which has limited their applications.⁷

To improve thermal stability, a variety of approaches has been attempted. Among them, chemical crosslinking is one of the most popular techniques. Chemical crosslinking of PU has many configurations, containing triols or higher functional polyols,⁸ isocyanates with functionalities greater than two,⁹ NCO/OH ratios greater than one,¹⁰ or combinations thereof.¹¹ Another accepted approach is the introduction of high thermal stable groups into PU, such as imide,¹² siloxane,¹³ triazine,¹⁰ and phosphazene (PPZ).¹⁴ PPZs are a class of inorganic-backbone polymers resulting from the repetition of the —P=N— monomer unit in the backbone and exhibit a number of useful features for practical devices.¹⁵

In recent years, many studies on PPZ-modified PUs have been reported and performed by the use of various approaches. For example, bifunctional

hydroxylated or diamined cyclotriphosphazenes were used as chain extenders to prepare poly (cyclotriphosphazene-urethane)s.^{16,17} Another approach was the introduction of PPZ into the PU network.^{18,19} Recently, we discovered that linear oligo-phosphazene containing hydroxyl modified PU as crosslinker.

In this work, we synthesized linear oligo [bis-(phenoxy)_{1.8}(4-hydroxybutaneoxy)_{0.2} phosphazene] (OPHBP), whose structure and characteristics were characterized by Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), and GPC. A series of novel polyurethanes (PUOs) were prepared with different contents of OPHBP as crosslinker. PUO structure and properties were characterized by FTIR, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and water contact-angle measurements.

EXPERIMENTAL

Materials

All the preparations were conducted under nitrogen unless otherwise stated. NH₄Cl was dried in a desiccator over P₂O₅. PCl₅ was purified by sublimation. Tetrahydrofuran (THF) was dried over and distilled from Na alloy under an atmosphere of dry nitrogen in the presence of benzophenone. Toluene diisocyanate (TDI) was used as received from Mitsui Takeda Chemicals (Tokyo, Japan). Poly (tetramethylene glycol) (PTMG; DuPont, Wilmington, DE), with a molecular weight of 1000, and 1,4-butanediol (BDO) were dried in vacuum at 100°C for 2 h to remove

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trace water. Trimethylolpropane (TMP) and petroleum ether (60–90°C) were received from the Shanghai Chemical Reagent Corp. (Shanghai, China) and used without further purification. All glassware was dried overnight in an oven under vacuum before use.

Synthesis

Synthesis of OPHBP

A solution of sodium phenoxy (17.98 g, 155 mmol) (prepared from phenol [14.57 g, 155 mmol] and sodium hydride [6.20 g, 155 mmol] in THF [100 mL]) was added via addition funnel into a round-bottom flask that contained a stirred solution of linear oligo[bis (chloro) phosphazene] (10.00 g) in 50 mL of THF at 25°C. The addition took place during the course of 1 h. The mixture was stirred and refluxed for 12 h.

After that, NaOCH₂CH₂CH₂CH₂OH (1.93 g, 17.2 mmol) (prepared from BDO [1.55 g, 17.2 mmol] and sodium hydride [0.69 g, 17.2 mmol] in THF [50 mL]) was added dropwise into the mixture at 25°C for 24 h. The polymer was then precipitated from THF into deionized water and ethanol three times respectively. The desired product was dried under vacuum.

Synthesis of PUOs

TDI (3.48 g, 20 mmol) was charged into round-bottom flask and the PTMG1000 (10.00 g, 10 mmol) was added dropwise. The reaction was maintained at 70°C for 2 h to obtain isocyanate (NCO)-terminated PU prepolymer.

According to the –NCO content (determined by dibutylamine titration) of PU prepolymer, the exact amount of BDO and OPHBP were calculated on from the following equations:

$$[-\text{NCO}]_{\text{TDI}} = [-\text{OH}]_{\text{PTMG1000}} + [-\text{OH}]_{\text{BDO}} + [-\text{OH}]_{\text{OPHBP}} \quad (1)$$

$$[-\text{OH}]_{\text{OPHBP}} = m_{\text{OPHBP}}/1151 \quad (2)$$

where [] defines the mole values and 1151 represents gram values per mole hydroxyl of OPHBP. They were heated to 70°C and then added into PU prepolymer in drops. Subsequently, the mixture was intensively stirred for several minutes and was vacuum degassed for 10 min. Afterward, the mixture was poured into Teflon mold held in an 80°C oven for 6 h. Finally, PUO was placed into a 110°C oven for 3 h. Conventional polyurethane (CPU) based on TMP as crosslinker was prepared with a polymerizing process similar to PUO. All PUs were stored at room temperature for 7 days for the measurement of their properties.

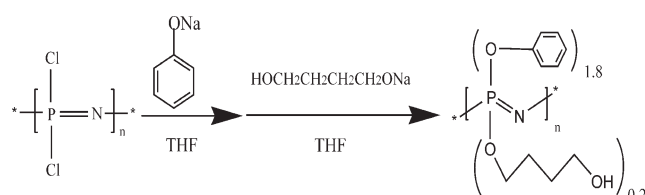
Measurements

The FTIR spectra were recorded on a Paragon 1000 instrument (PerkinElmer, Wellesley, MA) over the range of 4000–500 cm⁻¹. ¹H-NMR (400 MHz) and ³¹P-NMR (161.9 MHz) spectra were recorded on a Varian DRX 400 NMR spectrometer (Varian NMR Instruments) with the operating frequency at 400 MHz. GPC was obtained with the use of a PE Series-200 instrument (PerkinElmer). Sample (15–20 mg) was solved in DMF (5 mL) for molecular weight determination and calibrated with narrow-distributed polystyrene standards. TGA of the PUs was performed on a TGA 7 instrument (PerkinElmer) thermal analysis system from 40 to 800°C at a heating rate of 20°C/min under N₂ flow. The weight of sample was about 2–4 mg. DSC analysis was conducted on a PYRIS DSC analyzer (PerkinElmer) under a dry nitrogen purge. The PUs were first heated from room temperature to 150°C to counteract the thermal history; 3 min later, the temperature was reduced to –70°C and then increased to 150°C at a heating rate of 10°C/min. The weight of sample was 10–15 mg. The water contact angle was measured at 25°C using a sessile drop method (OCA 20 contact angle system, Dataphysics Instruments GmbH, Filderstadt, Germany). The results were the mean value of five data.

RESULTS AND DISCUSSION

Preparation and characterization of OPHBP and PUOs

The synthesis of OPHBP is illustrated in Scheme 1. Linear oligo [bis (chloro) phosphazene] was synthesized after a procedure described in the literature.²⁰ It is a simple and convenient one-pot synthesis method. Co-substituted OPHBP were accomplished by the introduction of phenoxy first, followed by excess NaOCH₂CH₂CH₂CH₂OH in an attempt to generate an ~ 9 : 1 molar ratio of substituent and in a 30.8% yield. These oligomers have good solubility in organic solvents, such as tetrahydrofuran, dimethyl sulfoxide, dimethylformide, and *N,N*-dimethylacetamide, etc. OPHBP was characterized by means of FTIR, multinuclear (¹H, ³¹P) NMR, and GPC.



Scheme 1 Synthesis of OPHBP.

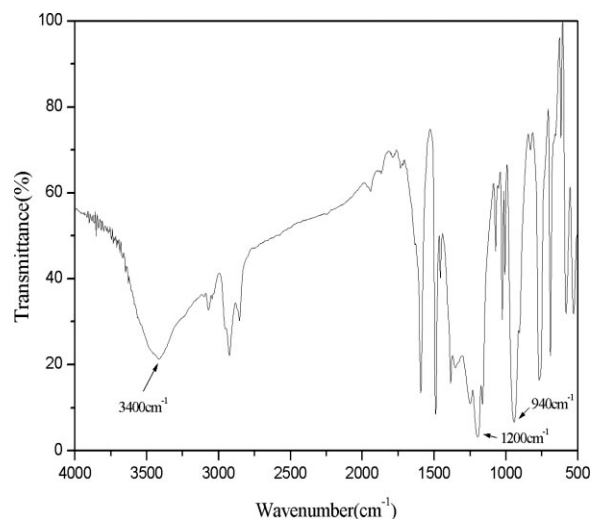


Figure 1 FTIR spectrum of OPHBP.

The FTIR spectrum of OPHBP was shown in Figure 1. The characteristic peaks for OH, P=O, and P—O—Ph can be seen at 3400, 1220, and 940 cm^{-1} , respectively. The $^1\text{H-NMR}$ spectrum of OPHBP is shown in Figure 2. $^1\text{H-NMR}$ spectroscopy showed aromatic protons at $\delta = 6.81\text{--}7.19$ ppm (t, 45H), $-\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$ protons at $\delta = 1.09\text{--}1.41$ ppm (d, 6H), P—O— CH_2 protons at $\delta = 3.17\text{--}3.43$ ppm (s, 2H), and OH protons at $\delta = 4.41\text{--}4.48$ ppm (s, 1H). In addition, the integration data indicated the OPHBP structure was the same as designed.

The ^{31}P spectrum of OPHBP is shown in Figure 3. The spectrum of OPHBP showed three broad peaks, at $\delta = -18.8$ and -13.3 ppm corresponding to the phosphorous atom with fully substituted phenoxy and 4-hydroxybutaneoxy as side groups, respectively, in addition, at $\delta = -16.0$ ppm indicating to the occurrence of mixed substitution. The average

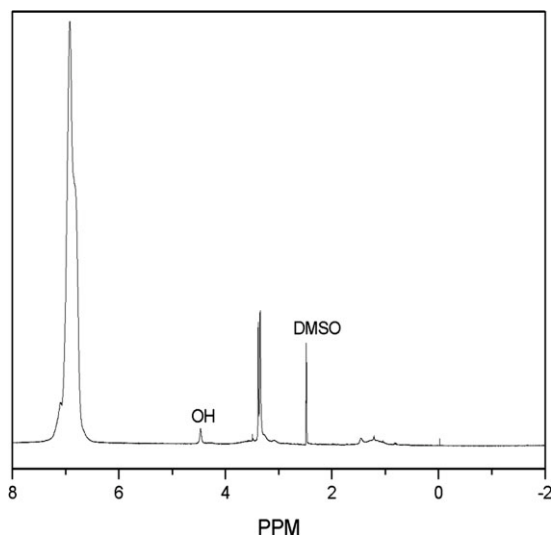


Figure 2 $^1\text{H-NMR}$ spectrum of OPHBP.

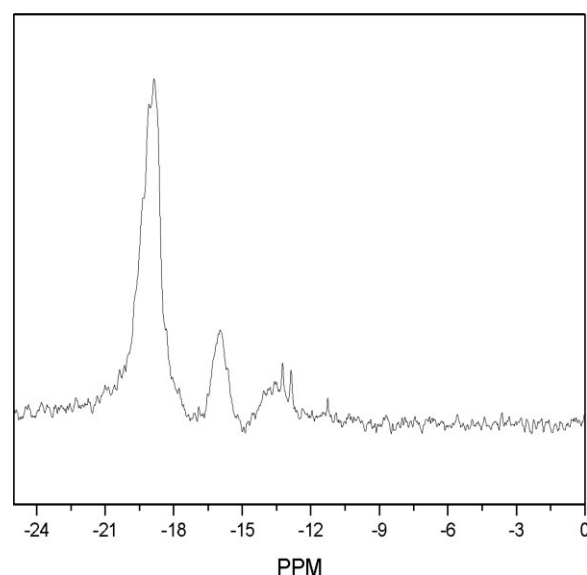
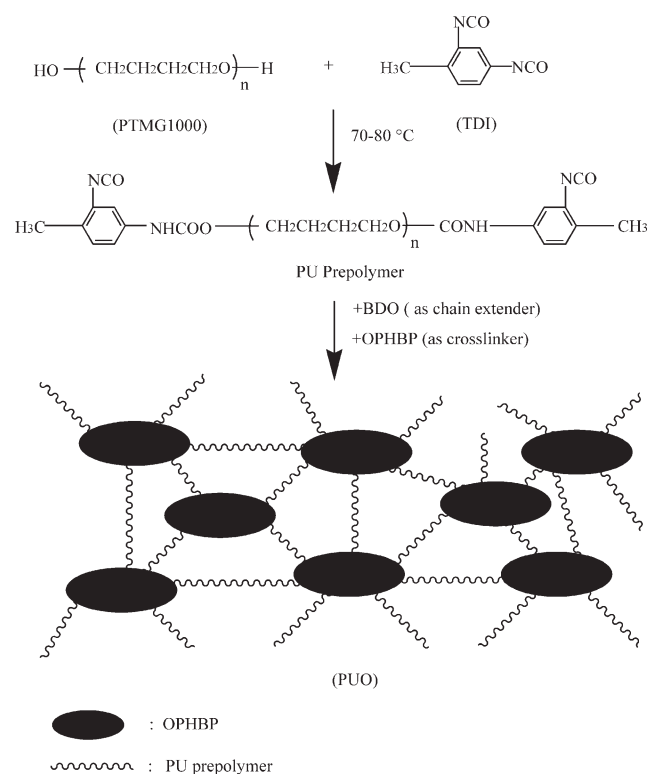


Figure 3 $^{31}\text{P-NMR}$ spectrum of OPHBP.

molecular weight of OPHBP was determined by GPC, detailed results including M_n (number average) $= 1.32 \times 10^4$ g/mol and M_w/M_n (polydispersity) $= 1.82$.

The preparation of PUOs is outlined in Scheme 2. At first, the NCO-capped PU prepolymer was synthesized, which subsequently chain extended by BDO and finally crosslinked by OPHBP to prepare PUOs. The chemical composition of PUs is listed in



Scheme 2 Preparation of PUOs crosslinked by OPHBP.

TABLE I
Chemical Composition of PUs

Polymer	TDI (g)	PTMG1000 (g)	BDO (g)	Crosslinker (g)
CPU	3.48	10.00	0.77	TMP (0.13)
PUO-1	3.48	10.00	0.88	OPHBP (0.50)
PUO-2	3.48	10.00	0.86	OPHBP (1.00)
PUO-3	3.48	10.00	0.83	OPHBP (1.50)

Table I. There are several advantages in using our method. First, the synthesis procedure of OPHBP is simple and an efficient one-spot approach to obtain a hydroxyl end-capped phosphazene crosslinker. Compared with traditional synthesis, for example, in Cui et al.'s studies,²¹ a hydroxyl end-capped cyclophosphazene is prepared in two steps by aldehyde groups followed by alcohol groups by the use of sodium borohydride, our method was simpler. Second, the PUOs are prepared through a two-step method, which is as simple as that of the preparation of conventional PU. In this study, TMP was selected as the contrast with OPHBP because TMP is a conventional crosslinker. PUs were held in a 110°C oven for 3 h so that the excess -NCO groups would react with urethane groups.

Typical FTIR spectra of CPU and PUO-2 are displayed in Figure 4. In the spectra, typical polyurethane absorption bands include the following, at 3300 and 1160 cm^{-1} , which indicate the existence of N-H and C-O groups, respectively. Two bands at 1740 and 1750 cm^{-1} denote C=O groups because of the presence of intermolecular H-bonding.²²

In comparison with the spectrum of CPU, the spectrum of PUO-2 showed enhanced intensities at approximately 1220 and 940 cm^{-1} , which were attributed to P=N (1220 cm^{-1}) and P-O-Ph (940

cm^{-1}) absorptions, respectively. The spectrum of PUO-2 exhibited additional absorption band at 730 cm^{-1} , which was attributed to N-P transfiguration stretching vibrations. These indicated that OPHBP had been introduced into the PU network. In addition, no absorption at 2260–2280 cm^{-1} (-NCO) appeared in the spectra which indicated that -NCO groups in PU prepolymer had completely reacted with chain extender and crosslinker.

Thermal properties of PUOs

The thermal degradation investigation of polymers allows the determination of proper conditions for manipulating and processing and for obtaining high-performance products that are stable and free of undesirable byproducts. In addition, the use of TGA provides a method for accelerating the lifetime testing of polymers so that short-term experiments can be used to predict in-use lifetime.

Figure 5 shows the TGA and DTG curves of OPHBP, CPU, and PUOs, respectively. Detailed TGA results, such as T_{onset} , $T_{5\%}$, and $T_{50\%}$, which represented the initial temperature of decomposition, 5% weight loss temperature of degradation, and 50% weight loss temperature of degradation, respectively, were shown in Table II. In addition, $T_{\text{max}1}$ and $T_{\text{max}2}$, two temperature stages at maximum decomposition rate, also are listed in Table II.

According to Figure 5, both CPU and PUOs showed a two-stage decomposition pattern. W_1 values (Table II) indicated that the weight loss percentages of PUOs at first degradation stage were a little lower than that of CPU because the degradation of OPHBP occurs during the second stage. It is considered that the first stage of PU degradation is mainly

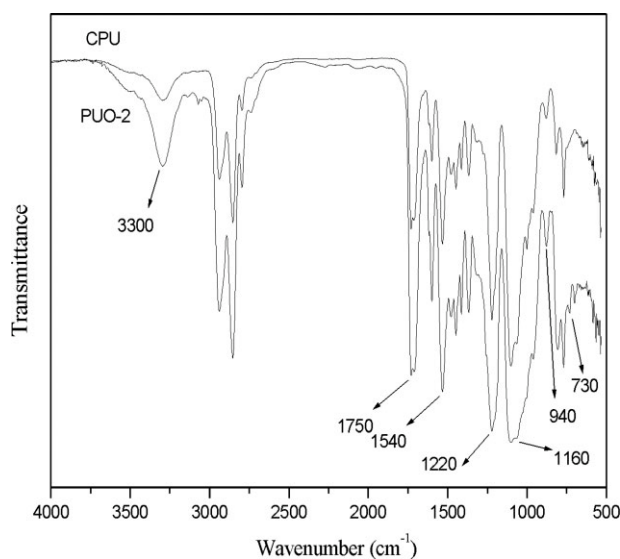


Figure 4 FTIR spectra of PUO-2 and CPU.

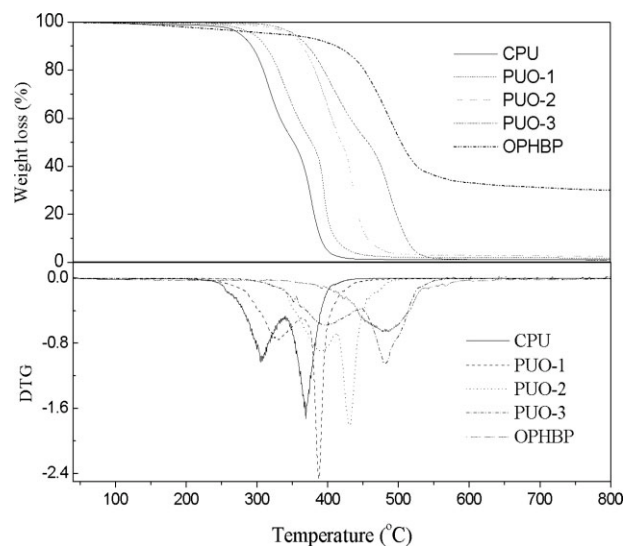


Figure 5 TG and DTG curves of OPHBP and PUs.

TABLE II
Chemical Composition of PUs

Polymer	$T_{d5\%}$ (°C)	$T_{d50\%}$ (°C)	T_{max1} (°C)	T_{max2} (°C)	W_1 (%)
OPHBP	274.3	498.2	480.1	–	–
CPU	265.8	343.0	305.0	369.5	50.2
PUO-1	284.5	369.0	326.7	388.7	49.3
PUO-2	338.6	412.0	386.1	426.9	48.8
PUO-3	343.6	450.3	398.8	493.3	47.6

$T_{d5\%}$ = decomposition temperature at 5 wt % weight loss; $T_{d50\%}$ = decomposition temperature at 50 wt % weight loss; T_{max} = maximum decomposition temperature; and W_1 = weight loss percentage at the first stage.

attributed to the less-stable PU, which can be decomposed to form alcohol and isocyanate groups. The second stage of the degradation, which takes place in the temperature range, may be attributed to the residual material. In this step, the product will be further decomposed to form nitrogen and carbon volatiles.²³

The typical temperature values of PUOs, such as $T_{d5\%}$ and $T_{d50\%}$, were greater than those of CPU. Moreover, the T_{max1} and T_{max2} values of PUOs were greater than those of CPU, although the initial weight loss percentage of OPHBP was greater than that of PUs because oligophosphazene contained a few low molecule weight polymers. From the aforementioned details, we can conclude that the heat resistance of PUOs was greater than that of CPU.

The thermal properties of PUOs and CPU were determined by DSC analysis. The DSC thermograms are presented in Figure 6. It is clear that CPU exhibits two glass transition temperatures (T_g), suggesting that CPU are microseparation. It is well-known that PU consists of a hard segment and soft segment (AB)_n type block structure. The hard segments can interact with each other, for example, through

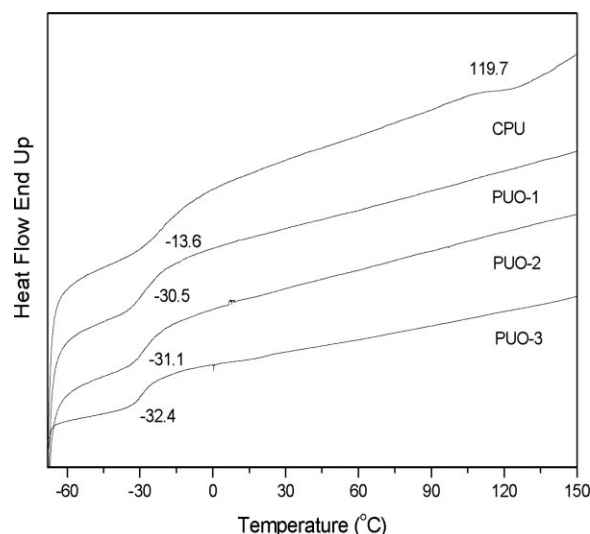


Figure 6 DSC curves of PUs.

hydrogen bonds or through dispersion influences of polar urethane groups, which contributes to agglomeration of those groups and formation of a compact rigid phase. That phase is hardly miscible with the soft phase which has been formed with the use of much less polar soft segments. If the hard phase and soft phase within PU become completely immiscible, two separate phase transition points can be frequently observed as two clearly different glassy temperatures. But only one T_g was observed in each PUO curve which indicated good compatibility between the soft and hard segments, after the introduction of OPHBP. This may be attributed to flexible oligophosphazene as crosslinker.

According to Figure 6, it could be seen that T_g values of PUOs were lower than that of CPU. It is probably due to polyphosphazene backbone is one of the most flexible known, being comparable to silicone polymers. The decrease of T_g caused that PUOs could have better low temperature resistance. From TGA and DSC results, we could conclude that PUO could be used in a broader range of temperature.

Water contact-angle measurement

The surface hydrophobicity of the PUs, as characterized by water contact angle, is summarized in Table III. The water contact angle for CPU was 74.8°, and for PUOs, they gradually increased to 94.6°. With an increasing amount of OPHBP incorporated into PU structure, a significant increase in water contact angle was observed. It is probably because aryloxy-phosphazene is hydrophobic.²⁴

CONCLUSIONS

In this study, OPHBP containing hydroxyl was successfully synthesized. The composition and structure were characterized by FTIR, NMR, and GPC.

TABLE III
Water Contact Angle of PUOs and CPU

Polymer	CPU	PUO-1	PUO-2	PUO-3
Water contact angle (°)	74.8	87.5	90.8	94.6

A series of novel PUOs were prepared in a two-step way in which PU prepolymer was crosslinked by OPHBP substituting for TMP. FTIR analysis showed that OPHBP had been introduced into PUOs. Compared with CPU, PUOs presented better thermal stability and low-temperature resistance. According to water contact-angle measurements analysis showed PUOs were more hydrophobic than CPU.

References

1. Piotr, K. *Prog Mater Sci* 2007, 52, 915.
2. Poomali, S. S.; Siddaramaiah, A.; Leed, J. H. *Mater Sci Eng A* 2008, 492, 486.
3. Hynek, B.; Jiri, R.; Petr, H.; Hana, S.; Jiri, K.; Zdenek, H. *Polym Adv Technol* 2007, 18, 149.
4. Kumar, M. N. S.; Manjula, K. S.; Siddaramaiah, A. *J Appl Polym Sci* 2007, 105, 3153.
5. Han, J. L.; Lin, S. P.; Ji, S. B.; Hsieh, K. H. *J Appl Polym Sci* 2007, 106, 3298.
6. Lohe, M.; Cook, M.; Klippstein, A. H. *Macromol Symp* 2002, 187, 493.
7. Zuo, M.; Takeichi, T. *Polymer* 1999, 40, 5153.
8. Spirkova, M.; Matejka, L.; Hlavata, D.; Meissner, B.; Pytela, J. *J Appl Polym Sci* 2000, 77, 381.
9. Desai, S.; Thakore, I. M.; Sarawade, B. D.; Devi, S. *Eur Polym J* 2000, 36, 711.
10. Semsarzadeh, M. A.; Navarchian, A. H. *J Appl Polym Sci* 2003, 90, 963.
11. Buckley, C. P.; Prisacariu, C.; Caraculacu, A. *Polymer* 2007, 48, 1388.
12. Mishra, A. K.; Chattopadhyay, D. K.; Sreedhar, B.; Raju, K. V. S. N. *J Appl Polym Sci* 2006, 102, 3158.
13. Chuang, F. S.; Tsen, W. C.; Shu, Y. C. *Polym Degrad Stab* 2004, 84, 69.
14. Allcock, H. R. *J Inorg Organometal Polym Mater* 2006, 16, 277.
15. Gleria, M.; Jaeger, R. D. *Top Curr Chem* 2005, 250, 165.
16. Dez, I.; Jaeger, R. D. *J Appl Polym Sci* 2003, 89, 1925.
17. Dez, I.; Mitjaville, J. L.; Grützmacher, H.; Gramlich, V.; Jaeger, R. D. *Eur J Inorg Chem* 1999, 1673.
18. Reed, C. S.; Taylor, J. P.; Guigley, K. S.; Coleman, M. M.; Allcock, H. R. *Polym Eng Sci* 2000, 40, 465.
19. Wang, P. S.; Chiu, W. Y.; Chen, L. W.; Denq, B. L.; Don, T. M.; Chiu, Y. S. *Polym Degrad Stab* 1999, 66, 307.
20. Carriedo, G. A.; Alonso, F. J. G. A.; Paloma, G.; Fidalgo, J. I.; Alvarez, J. L. G.; Presa, A. S. *Chem Eur J* 2003, 9, 3833.
21. Cui, Y.; Ma, X.; Tang, X.; Luo, Y. *Eur Polym J* 2004, 40, 299.
22. Goddard, R. J.; Cooper, S. L. *Macromolecules* 1995, 28, 1390.
23. Bajsic, E. G.; Rek, V. *J Appl Polym Sci* 2001, 79, 864.
24. Allcock, H. R.; Steely, L. B.; Anurima, S.; Singh, A. *Polym Int* 2006, 55, 621.