New Copoly(urethane-methacrylate)s Obtained by Adjusting the Content of the Poly(1,2-propanediol *ortho*-phthalate): Transparent, Thermal, and Mechanical Properties

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ABSTRACT: A series of new crosslinked copoly(urethane-methacrylate)s (CPUAs) were synthesized by the polymerization of new urethane–methacrylate macromonomers with double bonds at the end of the chain, which were prepared from isophorone diisocyanate, β-hydroxyethyl methacrylate, different content of poly(1,2-propanediol *ortho*-phthalate) (PPP), and poly(ethylene glycol) 600. The properties of CPUAs were measured by dynamic mechanical analysis, thermogravimetric analysis, wide-angle X-ray diffraction, water uptake, and optical properties testing, and mechanical performance measurements. The results revealed that the greater PPP contents in the CPUAs lead to the higher glass transition temperature, hardness, lower thermal stability, and water uptake. Obtained CPUAs present the good transparence. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 128: 3900–3905, 2013

INTRODUCTION

Polyurethanes (PU) can vary from rubbery materials to glassy thermoplastics and from linear polymers to thermosetting plastics.[1] PU can be used in extensive applications, including optics,[2–5] automotive parts,[6] optoelectronics,[7–12] and biocompatible materials[13] for its outstanding properties, such as transparence in a wide wavelength range, strong damage resistance for laser irradiation, chemical stability, good dimensional stability, etc.

Traditional PU are usually obtained by condensation polymerization method.[14,15] This type of PU requires a certain amount of chain extenders to form high molecular weight polymers in the postprocessing. The PU in this article were prepared by the macromonomer technique. The macromonomer is a kind of monomer with a reactivity site consisting of vinyl group at the end of the chain, so relatively high molecular weight PU are obtained without any chain extender.

In the earlier studies, we have produced poly(urethane-methacrylate) (PUA) elastomers[16–19] without any chain extenders in order to obtain moderate molecular weights which had better mechanical properties than the conventional PU and optic plastics. A kind of PUA (PUA-1),[19] which was prepared from polyethylene glycol 600 (PEG600), presents the good thermal stability and transparence, meanwhile, the another kind of PUA (PUA-6),[19] which was synthesized from poly(1,2-propanediol *ortho*-phthalate) (PPP), owns the high glass transition temperatures (T_g) and mechanical properties. However, insufficient thermal stability of PUA-6 and low T_g of PUA-1 limited their practical application in a wide range. In order to improve the performance of products, PPP was used as the additive to introduce benzene rings into the main chains of PUA-1.

In this article, we have synthesized four new kinds of co-PUAs (CPUAs) using IPDI, HEMA, and different content of PPP and PEG600 by the macromonomer technique. The structure–property relationships of the CPUAs are investigated. Modified CPUAs exhibit good thermal stability, high T_g, and mechanical properties.

EXPERIMENTAL SECTION

Materials

Phthalic anhydride (PA) and 2,2′-azobis(isobutyronitrile) (AIBN) are purchased from Tianjin Fuchen Chemical Reagants Factory. 1,2-Propanediol (PDO) and PEG600 are purchased from Tianjin Kermel Chemical. Isophorone diisocyanate (IPDI) was provided by Shanghai NCM Hersbit chemical. 2-Hydroxyethyl methacrylate(HEMA) is purchased from Tianjin Chemical Reagent Research Institute. Dibutyltin dilaurate (DBTL) is

Table I. Chemical Composition of CPUAs Using Different Content PPP and PEG600

| Sample code | Diol (mol) | | HEMA (mol) | IPDI (mol) |
	PPP	PEG600		
PUA-1	0.00	0.25	0.50	0.50
PUA-2	0.05	0.20	0.50	0.50
PUA-3	0.10	0.15	0.50	0.50
PUA-4	0.15	0.10	0.50	0.50
PUA-5	0.20	0.05	0.50	0.50
PUA-6	0.25	0.00	0.50	0.50

purchased from Shanghai Far Navigation Chemical Reagent Factory. AIBN was recrystallized from alcohol and dried by vacuum distillation. Other materials were standard laboratory reagents and were used as received.

Synthesis of CPUAs

CPUAs were synthesized in a multistep reaction that contains the preparation and curing of urethane-methacrylate macromonomer. The synthesis of PUA-2 is described in latter section as an example.

The appropriate amount of 14.12 g (0.05 mol) PPP, which was obtained by the reaction of 60.87 g (0.80 mol) 1,2-propanediol(PDO) and 59.25 g (0.40 mol) phthalic anhydride (PA),[19] 120.00 g (0.20 mol) PEG600 and 111.15 g (0.50 mol) IPDI were mixed for 5 min in a 500-mL three-necked flask equipped with a mechanical stirrer and a nitrogen inlet valve. Totally, 0.13 g (0.202 mmol) DBTL was added as a catalyst. Then the temperature was held at 28°C for 70–90 min. The prepolymer was obtained. After that, 65.07 g (0.50 mol) HEMA was added in the flask and stirred for 70 min. Then the urethane–methacrylate macromonomer was produced. 0.38 g (2.33 mmol) AIBN was added into the obtained urethane–methacrylate macromonomer and stirred at 28°C for 30 min. The mixture was poured into a preheated glass grinding apparatus of a certain thickness (3 mm) at room temperature and cured at 40°C for 2 h, and then heated to 60°C for 3 h. After that, the mixture was cured at 80°C for an additional 8 h. Finally, the PUA-2 sheet with certain thickness (3 mm) was obtained during this thermosetting molding process. The synthesis of PUA-1, PUA-3, PUA-4, PUA-5, and PUA-6 was the same as PUA-2 (Table I).

Characterization

The ^{1}H-NMR spectra were obtained on a DPX-400 (400 MHz) (Bruker) using DMSO-d6 as the solvent. ^{1}H-NMR spectra were obtained at room temperature using tetramethylsilane as the internal standard.

WAXD measurements were made using a Bruker D8 ADVANCE X-ray diffractometer. The angular 2θ diffraction range was between 3° and 80°. The data were collected with an angular step of 0.04° at 0.5 s per step. Cu Kα radiation was obtained from a copper X-ray tube operated at 40 kV and 30 mA. Transparencies were measured using WGT-S Ubest-35 spectrometer according to GB 2410-80 with a white halogen light. The dimension of samples is $50 \times 50 \times 3$ mm^3.

A Perkin-Elmer Diamond TG/DTA thermogravimeter was used to measure the weight loss of samples under a nitrogen atmosphere (100 mL/min). The samples were heated from room temperature to 650°C at a heating rate of 10°C/min. Generally, 5–10 mg samples were used for the TGA.

Stress-strain measurements were performed at room temperature using a CMT 6104 tensile testing machine. Samples for tensile tests were applied dumb-bell geometry with dimension of $150 \times 10 \times 3$ mm^3. The used cross head speed was 50 mm/min. At least six identical dumb-bell shaped specimens for each sample were tested, and their average mechanical properties are reported. Unnotched freely supported beam impact strength of each sample was tested conforming to ISO 179-1982 with XJJ-5 apparatus. All samples tested were unnotched so they would be more sensitive to the transition between ductility and brittleness. Specimens with dimension of $80 \times 10 \times 3$ mm^3 were tested at ambient temperature. At least six specimens were tested for each of the samples to ensure the accuracy of the results. Rockwell hardness was tested with XHR-150 apparatus. Rockwell hardness was performed according to ISO 2039/2-1981. Specimen thickness is 3 mm. At least six specimens were tested for each of the samples to ensure the accuracy of the results. The dynamic mechanical behavior of the specimens was determined using a dynamic mechanical analyzer (TA instrument DMA Q800) with tensile mode at 1 Hz and a heating rate of 3°C/min in the temperature range from 30°C to 250°C. Specimens with a typical size of about $35 \times 12.5 \times 3$ mm^3 (length × width × thickness) were used.

The hydrophilicity of the PU was quantified by the measurement of the amount of water that each polymer absorbed at 25°C. The dry samples ($50 \times 50 \times 3$ mm^3) were weighed and then immersed in distilled water and were kept at room temperature for 24 h. The samples were removed from water at predetermined time, wiped gently with filter paper, and weighed with an analytical balance. The water uptake was defined as follows: water uptake (wt %) = $100(W_w - W_d)/W_d$, where W_w represents the weight of the wet sample after immersing and W_d represents the weight of the sample after drying.

RESULTS AND DISCUSSION

Synthesis of CPUAs

The structure of the prepolymer of PUA-3 prepared above has been confirmed by ^{1}H-NMR. In the ^{1}H-NMR spectrum of the prepolymer of PUA-3 [Figure 1(A)], the chemical shift of protons in the DMSO (solvent) appear at $\delta = 2.50$ ppm. The chemical shift of aromatic protons in the PPP appeared at $\delta = 7.61$ ppm and 7.73 ppm ($-C_6H_4-$ in PPP). The chemical shift of methylene protons in PEG600 were assigned to the peak at $\delta = 3.55$ ppm. Furthermore, the chemical shift of protons in $-NH$ group of urethane are observed at $\delta = 7.1-7.2$ ppm, which confirmed the successful synthesis of the prepolymer. Figure 1(B) shows ^{1}H-NMR spectrum of urethane–methacrylate macromonomer of PUA-3. The peaks appeared at 5.65 ppm and 6.03 ppm were assigned to the protons in terminal groups of vinyl ($CH_2=C-$), which also indicated that the HEMA bonded in the molecular chains of the IPDI and confirmed the
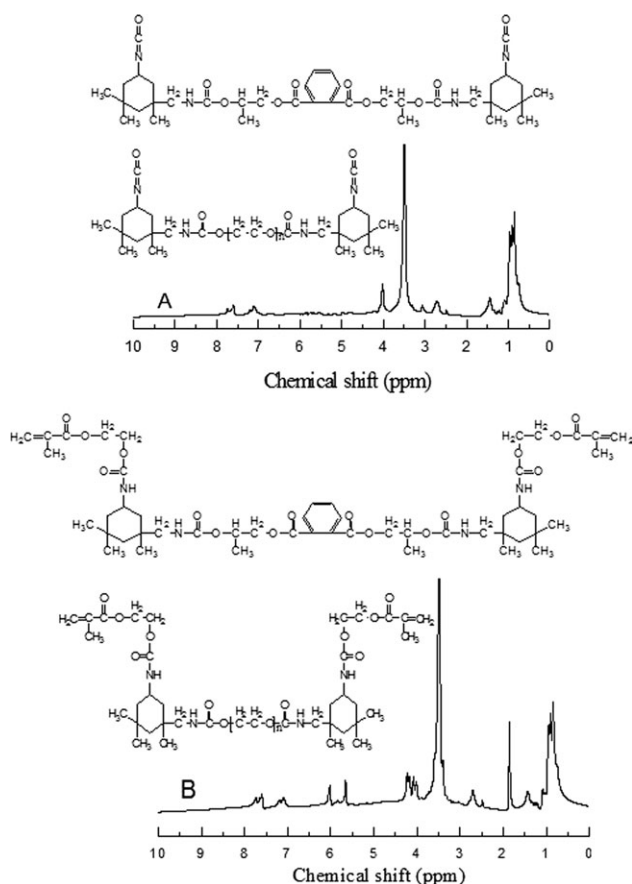
Figure 1. ^{1}H-NMR spectra of (A) the prepolymer of PUA-3 and (B) urethane–methacrylate macromonomer of PUA-3.

structure of the urethane–methacrylate macromonomer was accorded with the design.

Mechanical Properties of the PU

The mechanical properties of the CPUAs with various PPP and PEG600 contents are shown in Figures 2 and 3. The PPP percentage is calculated as the mol % of PPP per total PPP and PEG600 material weight in Figures 2 and 3. The pure PUA-1
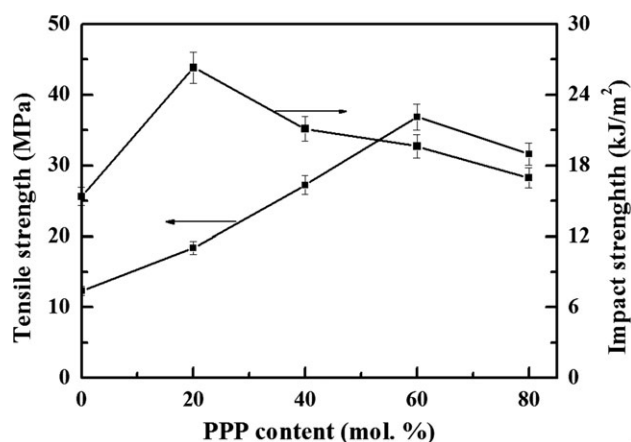

Figure 2. Tensile and impact strength of CPUAs containing different PPP content.
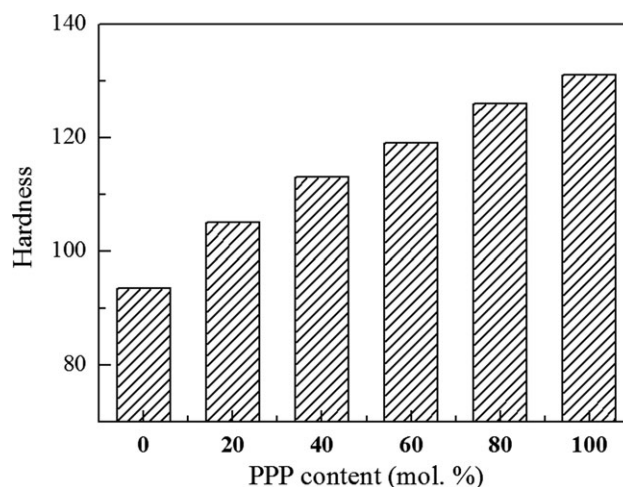

Figure 3. Rockwell hardness of CPUAs with different PPP content.

was rubbery but fairly weak, while the mechanical properties of CPUAs were better than that of the pure PUA-1 samples. As shown in Figure 2, the tensile properties of PUA-1 can be improved dramatically when suitable amounts of PPP were added. The tensile strength of CPUAs increased with increasing content of PPP and then dropped drastically when the PPP content was beyond 60 mol %. The density of crosslinking point was increased when small amount of PPP contents were added, and, the interaction between chains was enhanced. Therefore, the tensile strength of CPUAs was significantly increased. However, the impact strength decreased monotonically with the increasing content of PPP when the content of PPP was beyond 20 mol %. The result attributed to the higher hardness of PPP. The addition of PPP brings on a more notable effect on CPUAs. After adding 60 mol % PPP, the tensile strength of PUA-4 was significantly improved from 12.32 MPa to 36.89 MPa, which is almost three times higher than that of pure PUA-1 prepared by PEG600. Meanwhile, the impact strength of CPUAs is higher than that of the pure PUA-1. This result indicates that more interactions between chains lead to the higher tensile strength. In the case of PUA-5 with 80 mol % PPP, the modified material was more rigid but too brittle. The tensile strength at break and impact strength were 31.61 MPa and 16.97 kJ/m^2, respectively. This phenomenon is probably due to the excess of aromatic contents in polymer chains. Furthermore the rigidity and crosslinking density increase as content of PPP increases. So the tensile strength of PUA-5 slightly decreased, but the impact strength significantly lowed because of poor toughness. Tensile moduli of PUA-1, PUA-2, PUA-3, and PUA-4 are 248.6 MPa, 299.6MPa, 639.5 MPa, 2138.5 MPa, respectively. The tensile moduli increased with the increasing content of PPP due to more rigid groups in CPUAs. As shown in Figure 3, the hardness of the CPUAs increased with the increasing content of PPP, indicating that the interaction between chains was enhanced, as mentioned above.

The Dynamic Mechanical Properties of PU

The storage moduli (E') and loss moduli (E'') of the CPUAs are shown in Figures 4 and 5. The E' and E'' of the CPUAs decreased with the increasing temperature, and the effect of
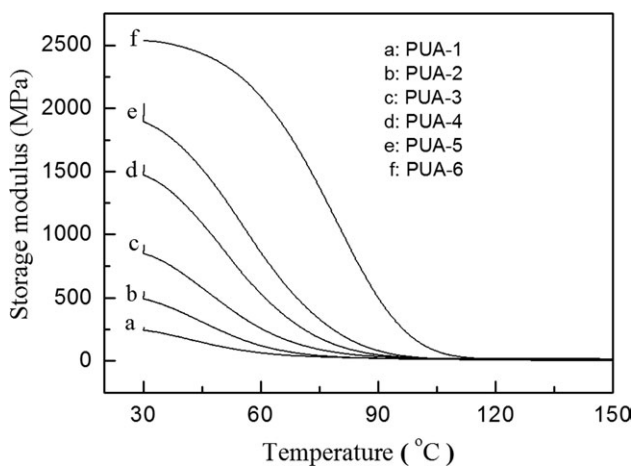
Figure 4. Storage moduli versus temperature of CPUAs, obtained from DMA carried out at a frequency of 1 Hz.

temperature was more significant at the low temperature region. As shown in Figures 4 and 5, the E' and E'' values of CPUAs were higher than those of pure PUA-1, particularly at low temperature, and the increasing extent of E' was higher than that of E''. This phenomenon is more pronounced in the case of PUA-4 and PUA-5. The higher E' and E'' values of the CPUAs at low temperature demonstrated that the crosslinking density increased by the presence of PPP and result in the higher rigidity.

The variation of the loss factor (tan δ) with temperature for the CPUAs samples is shown in Figure 6. T_g of the crosslinked materials are detected as the α-relaxation peak of the loss factor. It can be observed that the maximum loss factor shift to higher temperature with the introduction of PPP. The effect of PPP contents on the loss factor is associated with the glass transition. T_g of PUA-1 and PUA-6 are 56.4°C and 111.3°C, respectively. The T_g values of PUA-2, PUA-3, PUA-4, and PUA-5 are 71.6°C, 78.3°C, 89.5°C, and 100.9°C, respectively, which are between those of PUA-1 and PUA-6. The T_g values of CPUAs
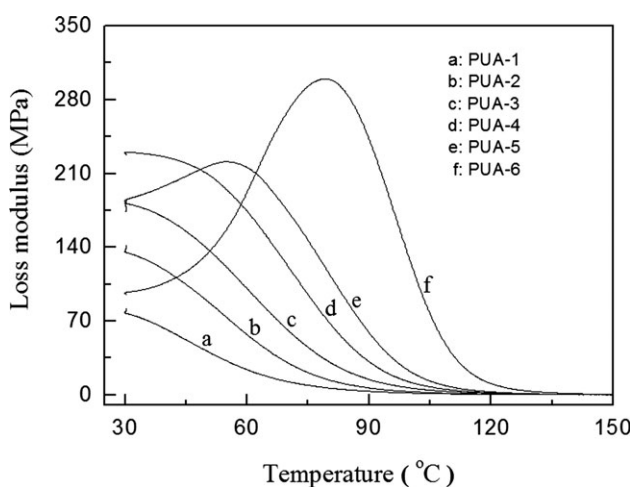
increased with increasing content of PPP, which implies that the addition of PPP enhanced the rigid behavior of the CPUAs and the rigidity increased with the increasing content of PPP, but flexibility of the polymer chains was reduced. Therefore, the CPUAs need higher temperatures from glass state to the rubbery state. Furthermore, the loss factor peaks of CPUAs become narrower with the increasing content of PPP, which indicates that the distribution of crosslinking density became narrower.

Thermal Properties of PU

TGA curves of the CPUAs with different PPP contents are shown in Figure 7. The samples were heated from ambient temperature to 650°C at a heating rate of 10°C/min. The decomposition started at 230°C and ended at 450°C, and the shapes of the weight loss curves were similar in the whole temperature range for all of the samples. Two main degradation processes are revealed. The samples lost 20% weight in the first step and then lost 70–80% weight in the next step. The first weight loss is related to the decomposition of the urethane bonds, which takes place through the dissociation to isocyanate and alcohol,

Figure 6. Variation of loss factor (tan δ) of CPUAs as a function of temperature.

Figure 5. Changes in the loss moduli (E'') of PU with temperature, obtained from DMA carried out at frequency of 1 Hz.
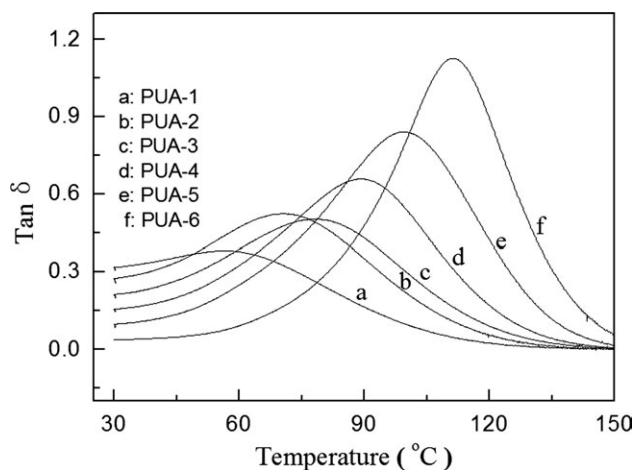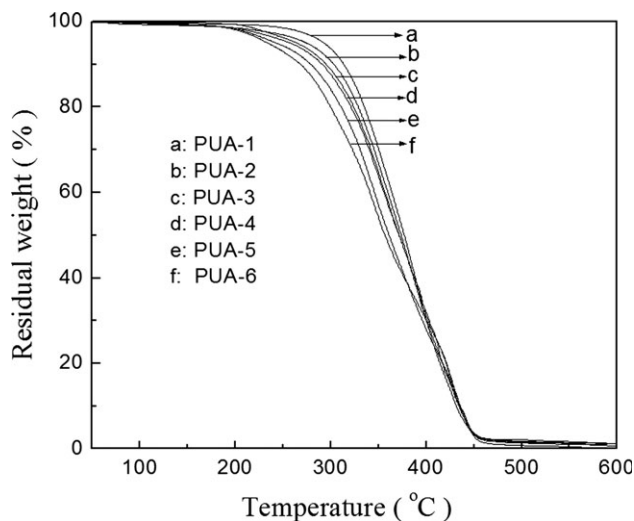

Figure 7. TGA curves of the CPUAs plastic sheets at 10°C/min heating rate.

Table II. Characterization of CPUAs

Sample code	Hardness	Water uptake (%)	Transparency (%)	T_g (°C)[a]	TGA (°C)	
					$T_{5\%}^{\text{loss}}$[b]	$T_{10\%}^{\text{loss}}$[c]
PUA-1	94	26.65	90.5	56.4	293.1	313.7
PUA-2	105	17.51	90.3	71.6	274.7	303.2
PUA-3	113	8.85	91.3	78.3	264.2	295.3
PUA-4	119	6.88	91.0	89.5	257.6	291.0
PUA-5	126	4.95	90.7	100.9	243.2	278.9
PUA-6	131	0.33	91.5	111.3	240.0	268.4

[a]T_g was determined by the loss tangent experiment (see Figure 6).
[b]Temperature of 5% weight loss(see Figure 7).
[c]Temperature of 10% weight loss (see Figure 7).

the formation of primary amines and olefins, or the formation of secondary amines.[20] The main decomposition process is attributed to the polyester or polyether polyol chain scission.

This weight loss increases and occurs at lower temperatures as the content of PPP increases. The decomposition data listed in the Table II also suggest that the thermal stability of the CPUAs decreased with the increasing content of PPP. The results are in accordance with the existence of a higher amount of weaker urethane bonds.

Water Absorption

Water absorption was measured to determine the bulk hydrophilicity of polyurethane. The water uptake in 24 h for all of the samples is shown in Table II. Water uptake of the polyurethane obtained from PUA-1, PUA-2, PUA-3, PUA-4, PUA-5, and PUA-6 was measured for comparison. The content of PPP is the main factor that controls the amount of absorbed water. The water uptake of PUA-1 and PUA-6 are 26.65% and 0.33%, respectively. The water values of PUA-2, PUA-3, PUA-4, and PUA-5 are 17.51%, 8.85%, 6.88%, and 4.95%, respectively, which are between those of PUA-1 and PUA-6. The water

uptake is decreased with the increasing content of PPP due to fewer ether bonds in CPUAs.

Transparency of CPUAs

The optical properties of CPUAs are presented in Table II. The transmittance values of CPUAs films with a thickness of 3 mm in the visible light range were measured to be above 90%, which indicated that the normalized transparency of all CPUAs films was excellent and similar to that of polymethyl methacrylate. Figure 8 shows the WXRD patterns of CPUAs. The appearance of a broad diffraction peaks indicated that the CPUAs were amorphous. This result accords with the analysis of transmittance.

CONCLUSIONS

A series of novel crosslinked CPUAs were synthesized from HEMA, IPDI and different content of PPP and PEG600. The results showed that the glass transition temperature, tensile strength, and hardness of obtained materials increased with increasing content of PPP in the CPUAs. Moreover, the result of TGA revealed that the CPUAs present a good thermal stability, but the degradation temperature declined with the increasing PPP contents in the CPUAs. WAXD results indicate that obtained CPUAs are amorphous. These results indicate that the CPUAs can be a potential candidate used in a wide range of excellent optical applications.
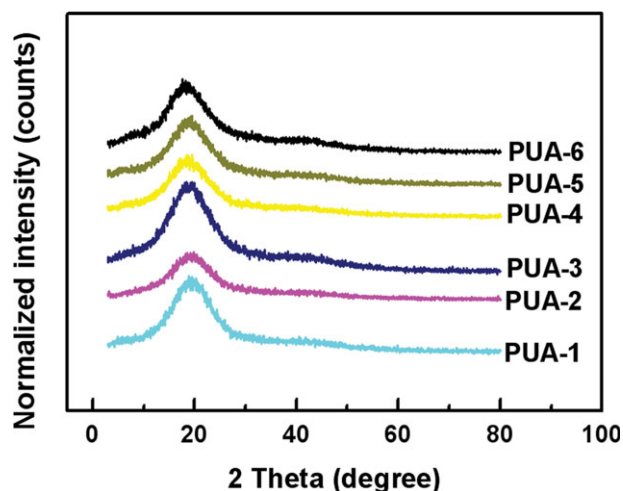
Figure 8. WAXD patterns of CPUAs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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