

Preparation of Amorphous Poly(ethylene terephthalate) from U-Polymer via a Copolymerization Process

SU-HUAI LIU,¹ SHU-FAN ZHANG,¹ ZONG-NENG QI,¹ GUANG-LI ZHANG,² HONG-ZHI ZHANG²

¹ State Key Laboratory of Engineering Plastics, Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

² College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

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ABSTRACT: U-Polymer, a kind of polyarylate, was synthesized by interfacial polycondensation method with terephthaloyl chloride (TPC), isophthaloyl chloride (IPC), and bisphenol A (BPA) as raw materials. The structure of the U-Polymer was characterized by IR and ¹H-NMR spectra. Then, an amorphous poly(ethylene terephthalate) (APET) was prepared with the introduction of the U-Polymer to the PET sequence to improve thermal and mechanical behaviors of PET via the polymerization process. The structure and property of the APET were characterized by DSC and DMA. The results showed that the APET exhibits amorphism, transparency, higher glass-transition temperature (T_g), and higher storage modulus than that of PET. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1653–1657, 2001

Key words: APET; U-polymer; interfacial polycondensation; molten polycondensation

INTRODUCTION

Poly(ethylene terephthalate) (PET) is the most widely used polyester. It is especially used as a packaging material (such as beverage containers) for its excellent mechanical properties and good adaptability for environments.¹ However, the main problems of PET, such as low crystallization rate, low glass-transition temperature (T_g), and low thermal deformation temperature, limit its application. In addition, the crystallinity of PET hinders its application as transparent materials. Although PET can be made as packaging materials with transparency more than 90% through the

bidirectional stretching method, it will distort as the result of cold crystallization when the temperature is higher than its T_g (about 70°C).

Toughening the modification method has been widely adopted to modify PET, such as grafting with elastomer, blending with polycarbonate, and introducing nucleation reagent into PET, to increase the crystallization rate. However, these methods have not acquired satisfactory effects. Another method to modify PET is to avoid its crystallization by copolymerization or blending, which was first reported in Japan.^{2–4} Amorphous poly(ethylene terephthalate) (APET) prepared in this method has excellent impact strength and heat resistance property. In this study, we use U-Polymer as one of the starting materials to prepare APET. U-Polymer is an aromatic polyester-type of engineering plastic, which was developed by Unitika, Ltd. Japan.⁵ U-Polymer is syn-

Correspondence to: Z.-N. Qi.

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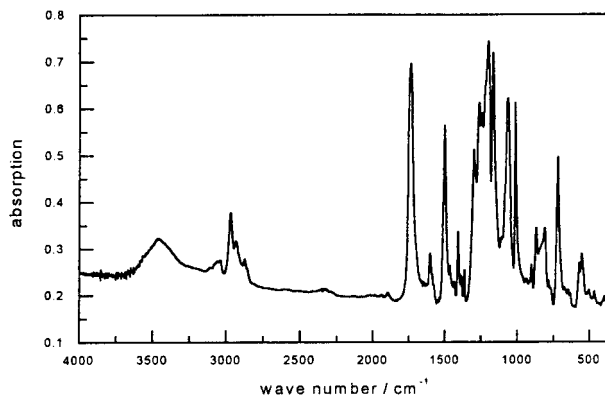


Figure 1 IR diagram of U-Polymer.

thesized from bisphenol A and 50% terephthalic acid/50% isophthalic acid. U-Polymer has excellent mechanical properties and high thermal deformation temperature. However, the processing temperature of U-Polymer is very high (about 330°C), which is close to its decomposition temperature. By introducing U-Polymer into the PET sequence with certain content, not only can we increase PET's heat resistance property but we can also avoid its crystallinity. In this study, we first report the preparation and characterization of APET alloy from U-Polymer and BHET, the oligomer of PET via the copolymerization process.

EXPERIMENTAL

Materials

2,2-Bis(4-hydroxyphenyl)-propane (bisphenol A) was a product of Xinxing Chemical Reagent Factory, Beijing. It was recrystallized twice using 50/50 (v/v) acetic acid–water mixture. The diacid chlorides were prepared from dibasic acids and thionyl chloride.⁶ Highly pure diacid chlorides were obtained first by recrystallization from petroleum ether (60–90°C) and then by fractional distillation under reduced pressure. Sodium lauryl sulfate was a product of Tianjin Sixth Chemical Reagent Factory, Tianjin. It was recrystallized from absolute alcohol. BHET, the oligomer of PET, was obtained from Beijing Yanshan Chemical Factory, Beijing. Antimonous oxide was a product of Chinese Nonferrous Chemical Institute, Beijing.

Preparation of U-Polymer and APET

First, the U-Polymer was synthesized using the interfacial polycondensation method.⁷ A solution

of 4.57 g (0.02 mL) bisphenol A and 1.6 g (0.04 mL) NaOH in 120 mL water was prepared in a 250-mL three-neck flask. To this slowly stirred solution, 12 mL 10% sodium lauryl sulfate was added. With vigorous stirring, a second solution, 2.03 g (0.01 mL) terephthaloyl chloride and 2.03 g (0.01 mL) isophthaloyl chloride in 60 mL toluene, was added to the first solution. After 20 min, the reaction mixture was poured into excess acetone to precipitate the U-Polymer and washed with water and 1% aqueous HCl.

The APET was prepared using the molten polycondensation method. A mixture of 7 g U-Polymer and 28 g BHET was placed in a 250-mL three-neck flask. Nitrogen was passed over the mixture when the flask was inserted in a salt bath at 280°C. With slow mechanical stirring, the U-Polymer totally dissolved in BHET after 1.5 h. The system was a transparent, amber homogeneous melt. Then, 15 mg Sb₂O₃ was added into the melt and a vacuum of 0.2 mm was applied. After 7 h under vacuum, the product was taken out under nitrogen atmosphere.

Characterization

The Fourier transform infrared (FTIR) spectrum of U-Polymer was acquired in a Perkin–Elmer FT-IR 2000 spectrometer (Perkin Elmer Cetus, Norwalk, CT). The sample was collected using the KBr pellet method. The ¹H–NMR spectrum of U-Polymer was collected on a Bruker DMX-300 ¹H–NMR spectrometer (Bruker Instruments, Billerica, MA), using tetramethylsilane as the internal standard and deuterated chloroform as a solvent. The thermal properties of APET were measured with a Perkin–Elmer DSC DELTA-7 differential scanning calorimeter at a heating

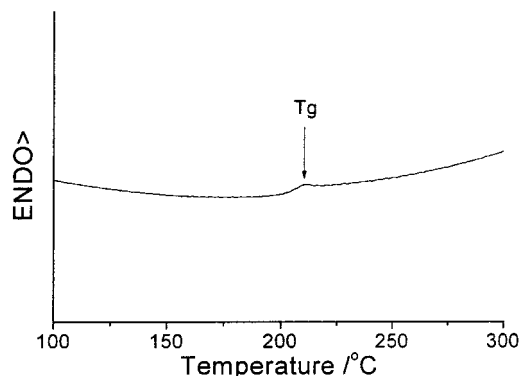


Figure 2 DSC curve of U-Polymer.

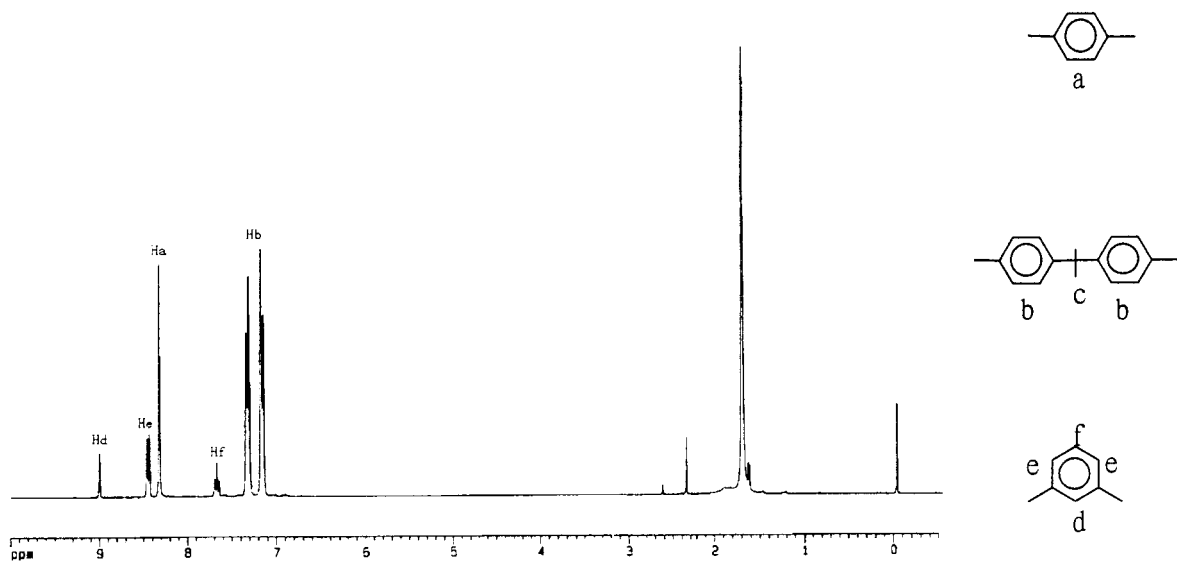


Figure 3 ^1H -NMR diagram of U-Polymer.

rate of $20^\circ\text{C}/\text{min}$ under nitrogen atmosphere. Dynamic mechanical analysis of APET was carried out using a Perkin-Elmer DMA-7 analyzer at a heating rate of $5^\circ\text{C}/\text{min}$. Inherent viscosities were obtained for solutions of 0.125 g in 25 mL of 4 : 6 (w/w) tetrachloroethane-phenol at 30°C .

RESULTS AND DISCUSSION

Characterization of U-Polymer

The U-Polymer has high molecular weight, with inherent viscosity of 0.94 dL/g. The FTIR spectrum of U-Polymer is shown in Figure 1. In the spectrum, a strong carbonyl stretching absorption band at 1739 cm^{-1} together with several bands between 1050 and 1300 cm^{-1} characteristic of C—O—C stretching indicate the presence of ester bond. A characteristic absorption band at 1201

cm^{-1} is attributed to the gem dimethyl of bisphenol A. The glass-transition temperature of U-Polymer determined from the DSC curve is 205.5°C , as shown in Figure 2, which is in agreement with the result reported by others.⁸

Figure 3 is the ^1H -NMR spectrum of U-Polymer. As illustrated, the peaks at $\delta 8.9$ (s), $\delta 8.4$ (d), $\delta 7.7$ (t) are assigned to H_d , H_e , and H_f , respectively, on the benzene ring of isophthaloyl. The peak at $\delta 8.3$ (s) is assigned to H_a on the benzene ring of terephthaloyl. The peaks at $\delta 7.3$ (dd) are assigned to H_b on the benzene ring of bisphenol A. By calculating the peak area we can conclude that the ratio of terephthaloyl and isophthaloyl in U-Polymer is 1 : 1.

Table I Effect of U-Polymer Content on the Intrinsic Viscosity $[\eta]$ of the APET

Sample	U-Polymer Content (wt %)	Reaction Time (h)	Appearance of APET	$[\eta]$
PAr1	10	7	Opaque	0.53
PAr2	15	7	Semitransparent	0.49
PAr3	20	7	Transparent	0.45
PAr4	25	7	Transparent	0.42

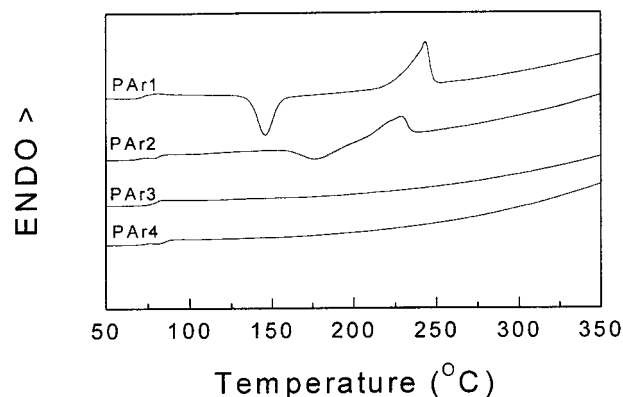


Figure 4 DSC curves of APET. U-Polymer contents (wt %): PAr1, 10%; PAr2, 15%; PAr3, 20%; PAr4, 25%.

Table II Effect of U-Polymer Content on Thermal Properties of the APET

Sample	U-Polymer Content (wt %)	T_g ($^{\circ}\text{C}$)	T_{cc} ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)
PAr1	10	72.2	146.1	243.3
PAr2	15	82.6	177.4	228.5
PAr3	20	82.8	—	—
PAr4	25	84.4	—	—

Characterization of APET

The preparation conditions of APET are shown in Table I. PAr1–PAr4 represent the products with different U-Polymer content. When the content of U-Polymer reaches 20 wt %, the product shows transparency, which indicates that PAr3 is an amorphous PET (APET). With the increase of U-Polymer content, it is more difficult for U-Polymer to dissolve in BHET and the reaction proceeds with more difficulty, which can be reflected by the decreasing molecular weight of APET as the content of U-Polymer increases, as shown in Table I.

Figure 4 shows DSC curves of APET. The T_g and T_m obtained from the DSC spectra are shown in Table II. With the increase of U-Polymer con-

tent in APET, the rigid component content increases in the polyester, resulting in the increase of T_g and T_{cc} , and the decrease of T_m . When the content of U-Polymer reaches 20 wt %, the T_m and T_{cc} disappear from the DSC spectrum. This suggests that the product was an amorphous PET. The transesterification reaction between U-Polymer and BHET hinders the formation of the crystalline component of PET.

Figure 5 and Figure 6 show the temperature dependence of the dynamic storage modulus E' and mechanical loss $\tan \delta$, respectively. The results indicate that the storage modulus shows a tendency to increase as the U-Polymer content was increased. This can be explained by the introduction of the rigid component, bisphenol A, into PET. Note that the storage modulus of PAr3 is lower than that of PAr2. This is because PAr1 and PAr2 are both crystalline polymers but PAr3 is noncrystalline. Although the rigid component content in PAr3 is higher than that in PAr2, the disappearance of crystallinity of PAr3, which causes the decrease of storage modulus, has a greater effect on PAr3's storage modulus. The T_g measured by $\tan \delta$ peak temperature is in agreement with that measured by DSC; that is, T_g increases with the increase of U-Polymer content.

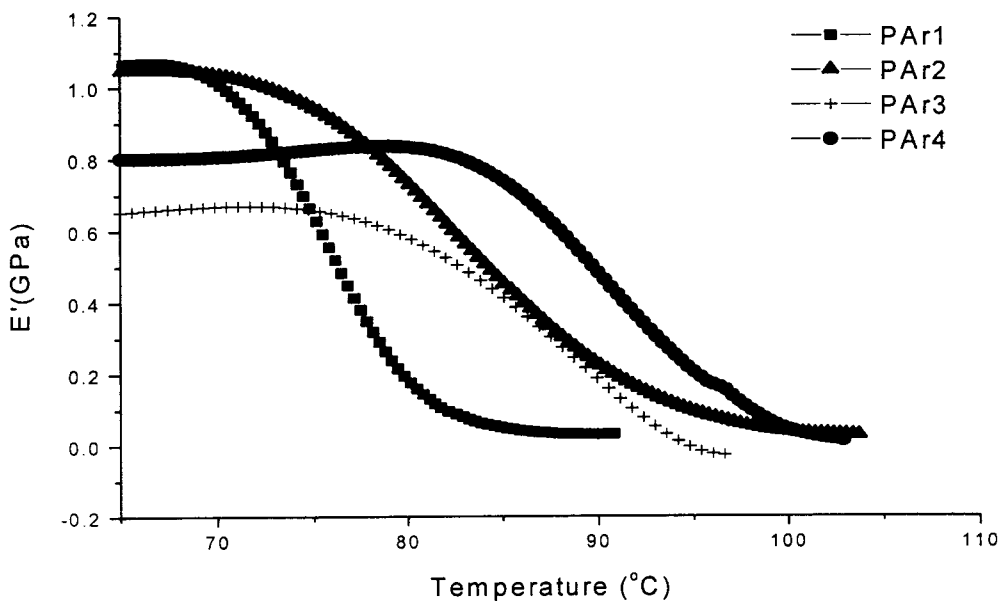


Figure 5 Dynamic storage modulus (E') of APET as a function of temperature. Symbols as in Figure 4.

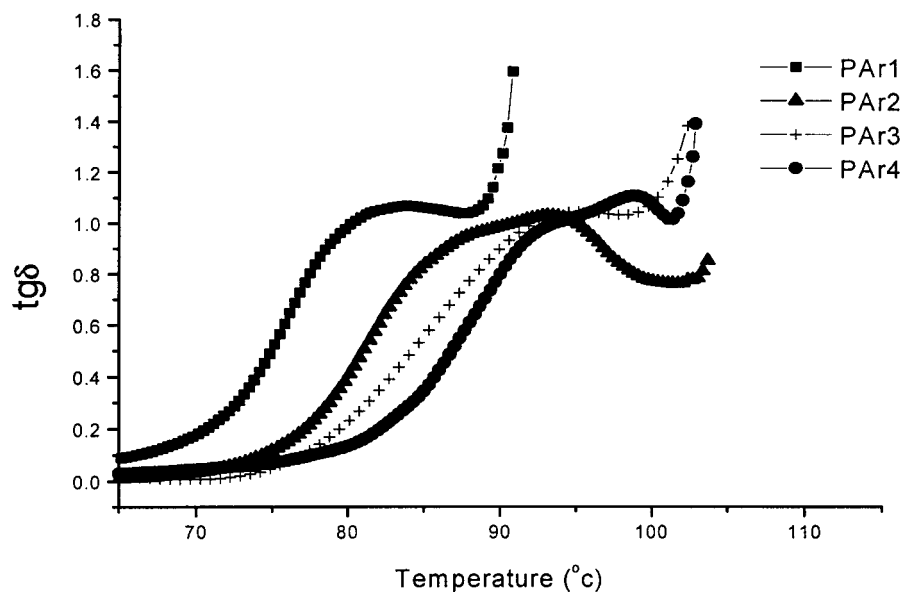


Figure 6 Temperature dependence of dynamic loss $\tan \delta$ of APET. Symbols as in Figure 4.

CONCLUSIONS

APET was successfully prepared with the introduction of U-Polymer into the PET sequence via the copolymerization process. The introduction of U-Polymer hinders the crystallization of PET. When the content of U-Polymer reaches 20 wt %, the resulting product is an amorphous PET (APET). APET exhibits transparency, higher glass-transition temperature (T_g), and higher storage modulus than that of PET.

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