Synthesis and Characterization of a Novel Kind of Thermotropic Liquid Crystalline Poly(urea-ester)s Based on Bis(4′-hydroxyphenyl)-tolyene-2,4-diurea

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ABSTRACT: A new diphenol monomer bis(4′-hydroxy-phenyl)-tolyene-2,4-diurea was synthesized by reaction of 2,4-toylene diisocyanate with *p*-aminophenol in *N,N*-dimethylformamide (DMF). The product was characterized by elemental analysis (EA), differential scanning calorimetry (DSC), and ^{1}H-NMR. And a novel kind of liquid crystalline poly(urea-ester)s were obtained by using this monomer. By using a polarizing microscope with hot stage (POM), wide-angle X-ray diffraction (WAXD) and small-angle X-ray diffraction (SAXD) the polymers were proven to be nematic liquid crystal. The result of DSC showed that the effect of the monomer composition on the melting point of poly(urea-ester)s was significant. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 577–583, 2001

Key words: liquid crystalline polymer; poly(urea-ester)s, bis(4′-hydroxy-phenyl)-tolyene-2,4-diurea; nematic

INTRODUCTION

Polyureas were initially developed due to their excellent mechanical properties and outstanding resistance to hydrolysis.[1,2] Recently, polyureas have been reported to be used as piezoelectric and ferroelectric polymers, second-order optical nonlinear polymers, biodegradable polymers, and polymer microcapsules.[3–6] Potentially more useful polyureas are those containing other functional groups.[1] In 1997, Wolinska-Grabczyk and his coworkers prepared liquid crystalline polyurethane-polyureas (PUU) from 4,4′-diaminobiphenyl, 2,4-tolylene diisocyanate, and poly(oxytetramethylene)diols.[7] It is an efficient method to combine the excellent properties of both liquid crystalline polymers and polyureas together. In 1999, authors synthesized two series of liquid crystalline polyureas from 4,4′-diaminobiphenyl or *o*-tolidine, 1,6-hexane diamine, and 2,4-toluene diisocyanate.[8,9] It is the purpose of this study to synthesize a novel kind of liquid crystalline poly(urea-ester)s containing both urea group and other functional groups.[1] Thus, a diphenol monomer, bis(4′-hydroxyphenyl)-tolyene-2,4-diurea, which has urea groups but no mesomorphic group, was synthesized, then it was polymerized with terephthaloyl chloride. The mesogenic units were formed during the polymerization.

EXPERIMENTAL

Materials

N,N-Dimethylformamide (DMF) and *N,N*-dimethylacetamide (DMAc) were azeotropically dis-

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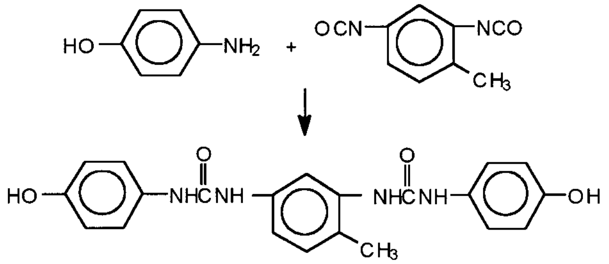
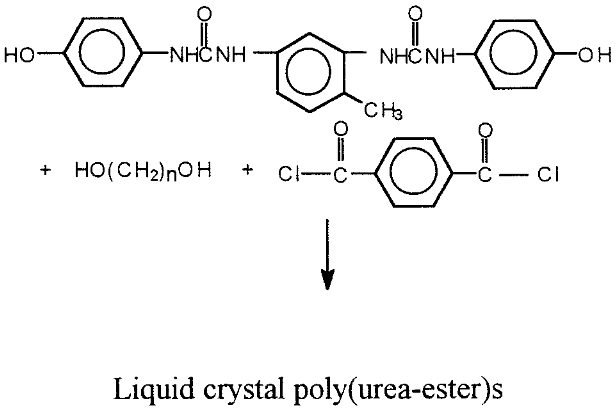


Scheme 1 Synthetic route of Bis(4′-hydroxyphenyl)-tolyene-2,4-diurea.

tilled with benzene for dehydrating and then distilled under vacuum. All other reagents and solvents were used without further purification. The syntheses of bis(4′-hydroxyphenyl)-tolyene-2,4-diurea and poly(urea-ester)s were carried out according to Scheme 1 and 2 as described in detail below.

Preparation of Bis(4′-hydroxyphenyl)-tolyene-2,4-diurea (BHPTDU)

p-Aminophenol (22.5 g, 0.205 mol) was dissolved in 100 mL DMF with 0.4 g anhydrous LiCl in a 250-mL four-necked round-bottom flask equipped with a mechanical stirrer, a dropping funnel, a reflux condenser, a nitrogen inlet, and a thermometer. A solution of 2,4-TDI (4.4 g, 0.0253 mol, in 50 mL DMF) was added dropwise into the flask with stirring at room temperature. Then the flask was heated to 50–60°C under nitrogen atmosphere, and the mixture was stirred for 4 h at this temperature, cooled down to room temperature, and poured into water. The solid was collected by filtration and was extracted by alcohol for 24 h (*p*-aminophenol in the extract was recycled), then was recrystallized from a mixed solvent of DMF and water. Yield 8 g (80%): m.p. 272°C.



Scheme 2 Synthetic route of poly(urea-ester)s.

Preparation of Poly(urea-ester)s

The monomer bis(4′-hydroxyphenyl)-tolyene-2,4-diurea and diol were reacted with terephthaloyl chloride (TPC) in *N,N*-dimethylacetamide at 90°C for 10 h, then the reaction mixture was poured into cold water to precipitate the polymer. The polymer was washed with water and subsequently dried under vacuum at 90°C. A series of copolymers were synthesized from BHPTDU, TPC, and a diol, which was one of 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,8-octanediol, and 1,10-decanediol. The copolymers were named PBTB, PBTP, PBTH, PBTO, and PBTD, respectively.

Characterizations

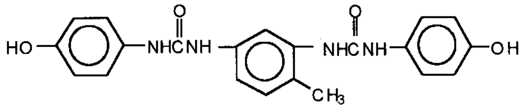
The monomer Bis(4′-hydroxyphenyl)-tolyene-2,4-diurea was characterized by elemental analysis (EA), differential scanning calorimetry (DSC) and ^{1}H-NMR. The polymers were characterized by using a polarizing microscope with hot stage (POM), wide-angle X-ray diffraction (WAXD), small-angle X-ray diffraction (SAXD), and differential scanning calorimeter (DSC).

RESULTS AND DISCUSSION

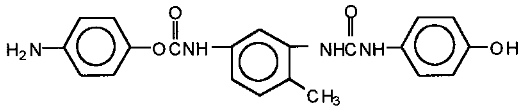
Bis(4′-hydroxyphenyl)-tolyene-2,4-diurea

By reaction of the two agents—,4-TDI and *p*-aminophenol—there were five possible kinds of products:

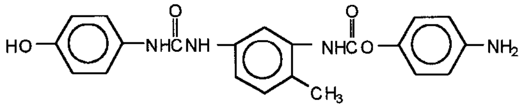
(a)



(b)



(c)



The reason why we obtained our target diphenol monomer was given in the following part of this article. First, *p*-aminophenol was in large excess as described before, and the solution of 2,4-TDI was slowly dropped into the reaction system so there was no possibility to form polymer or oli-

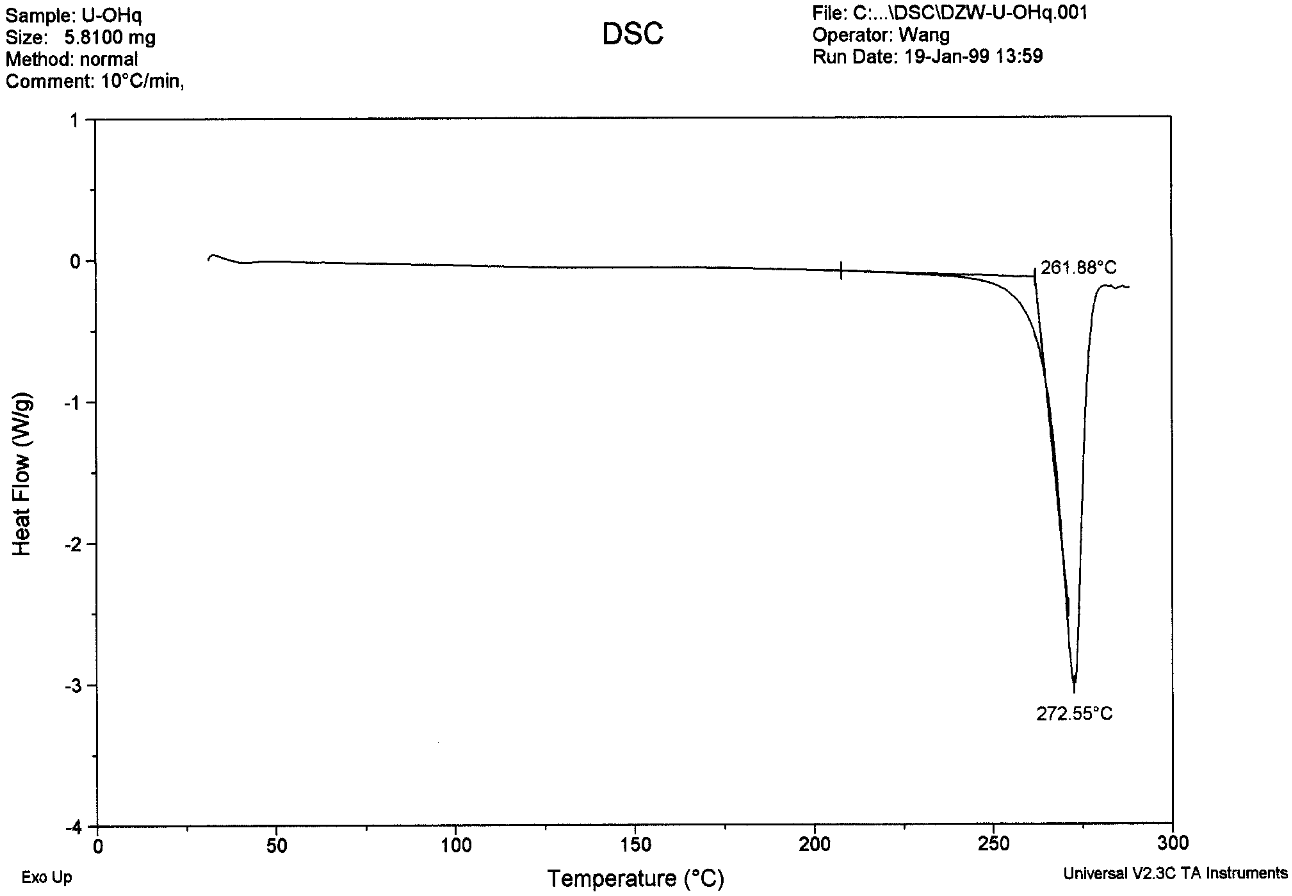


Figure 1 DSC curve for bis(4′-hydroxyphenyl)-tolyene-2,4-diurea.

gomer. Second, although both —OH and —NH_2 in the reaction system could react with the —NCO group, the product must be (a) because the reactivities of the amino group and the hydroxy group of *p*-aminophenol were not to be equal. In general, the sequence of relative reactivities of the compounds containing active hydrogen with isocyanate is shown as the following:[10] aliphatic amine $>$ aromatic amine $>$ primary alcohol $>$ H_2O $>$ secondary alcohol $>$ tertiary alcohol $>$ phenol.

The relative reaction rates of primary, secondary, and tertiary alcohol with isocyanate are 1.0, 0.3, and 0.05. Amino group is more active than the other kinds of active hydrogen. The acidity of phenol makes the reaction of phenol with isocyanate so slow that without catalyst the reaction could hardly go on.[11] Thus, the product cannot be (b) or (c). Furthermore, the results of elementary analysis, DSC (Fig. 1) and ^{1}H-NMR (Fig. 2) demonstrated the correct molecular formula and high purity of the product: EA: C 63.78(caled. 64.28), H 5.31(5.10), N 14.30(14.29).

^{1}H-NMR(Me_2SO-d_6): δ9.00(s, 2H, —OH), 8.74(s, 1H, —NH—), 8.48(s, 1H, —NH—), 8.17(s, 1H, —NH—), 7.88(s, 1H, —NH—), 7.74(s, 1H, 3-toluene-2,4-diurethane), 6.65–7.26(m, 10H, 5,6-toluene-2,4-diurea and *o,m*-phenoxy).

Poly(urea-ester)s

By copolymerization of bis(4′-hydroxyphenyl)-tolyene-2,4-diurea and diols [OH—$(CH_2)_n$—OH, n = 4,6,8,10] with terephthaloyl chloride, four series of poly(urea-ester)s (PUE)s were synthesized. These polymers were characterized by a polarizing microscope with hot stage (POM), a differential scanning calorimeter (DSC), wide-angle X-ray diffraction (WAXD), and small-angle X-ray diffraction (SAXD). Typical nematic textures were observed through the polarizing microscope with hot stage when the polymers were heated to a certain temperature range. Figure 3 showed the polarizing optical micrographs of PUEs from BHPTDU, TPC, and 1,6-hexanediol. On the other

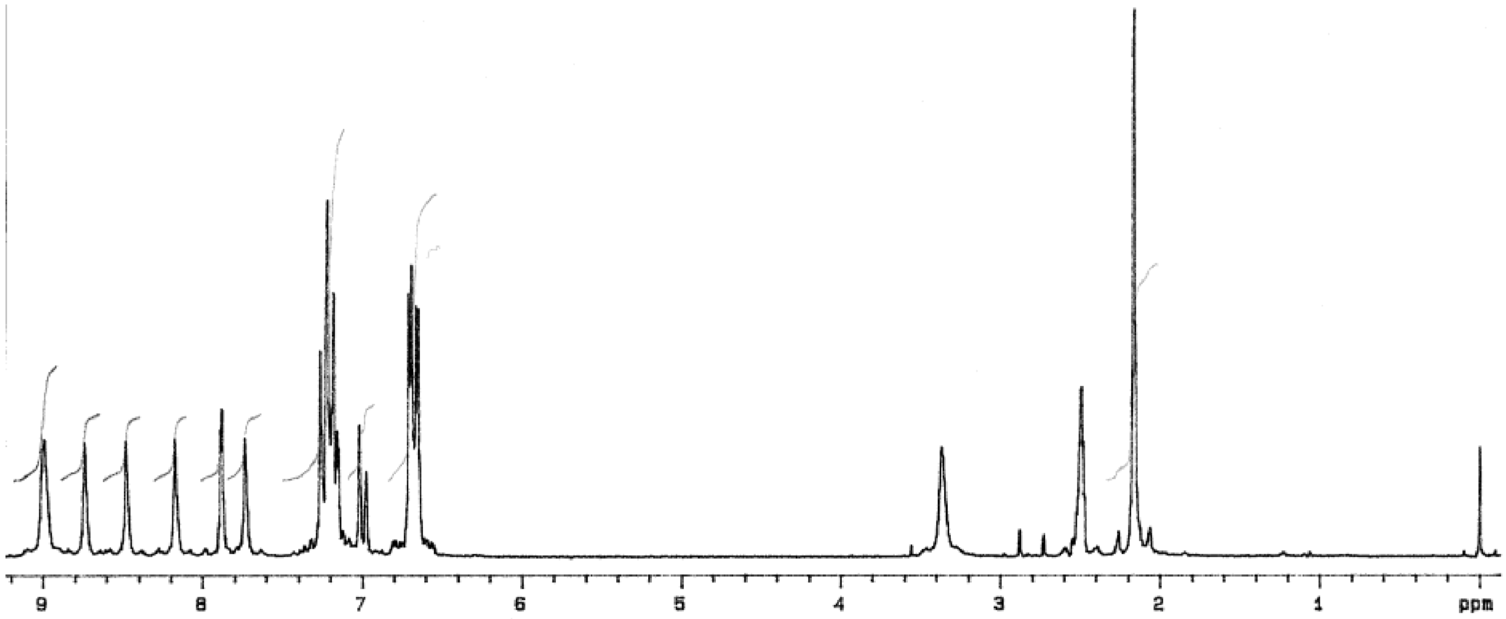


Figure 2 ^{1}H-NMR spectra of bis(4′-hydroxyphenyl)-tolyene-2,4-diurea.

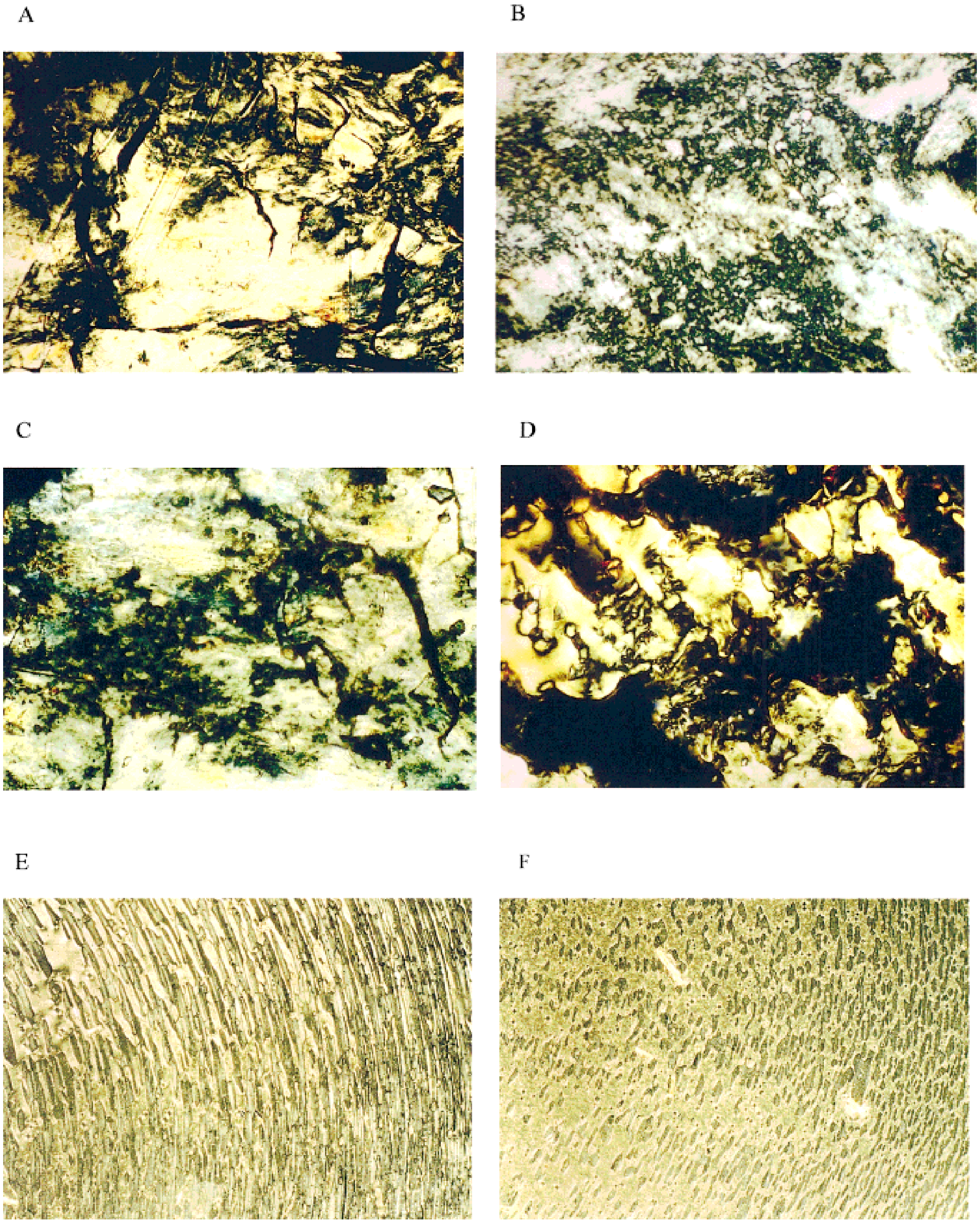


Figure 3 Polarizing optical micrograph of PBTHs, BHPTDU/hexanediol (A) = 90/10, ×400, (B) = 70/30, ×200, (C) = 50/50, ×400, (D) = 40/60, ×200, (E) = 20/80, ×400, (F) = 10/90, ×400.

hand, a diffused diffraction peak was observed when the diffraction angle 2θ was around 20°. This illustrated that there was short-ranged order of about 0.4 nm mean intermolecular distance. And there was no diffraction peak observed when the diffraction angle 2θ was between 1.3–5°. This proved that the polymer had no long-range order. Figure 4 showed the X-ray diffraction spectra.

From the results of DSC analysis, the melting temperature of PUEs showed dependence on monomer composition. The effect of monomer ra-

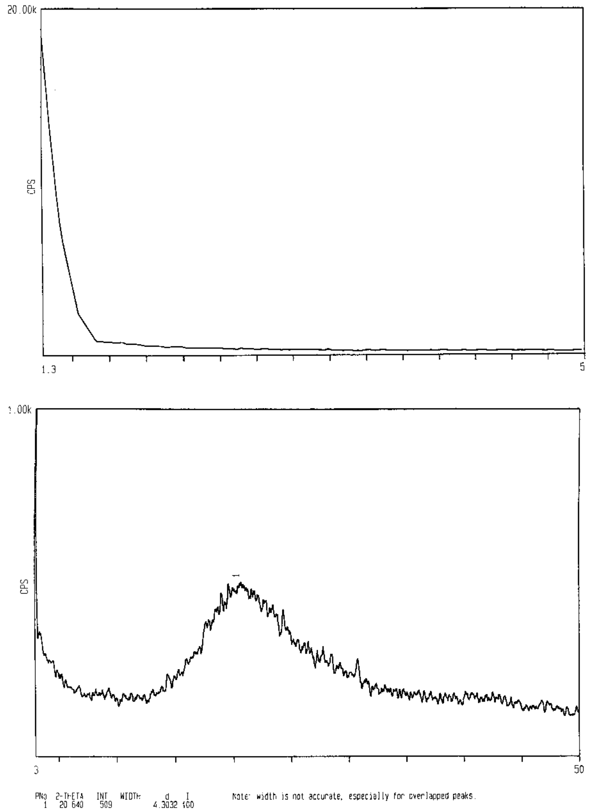


Figure 4 X-ray diffraction spectra of PUE, BHPTDU /1,4-butanediol = 50/50 (A) SAXD, (B) WAXD.

Table I Melting Point of PUEs with Diffirent Monomer Composition

Molar Ratio of Diols (%)	T_m (°C)		T_i (°C)	
	PBTP	PBTH	PBTP	PBTH
10	243	240	—	—
20	235	234	—	—
30	224	222	260	249
40	232	226	260	245
50	235	231	263	257
60	235	230	260	255
70	229	227	260	250
80	221	221	258	244
90	209	206	245	246

— Decomposed before T_i.

tio of BHPTDU and diols on the melting point of PUEs was significant. And PUEs of different monomers showed different melting temperature when they had equal molar monomer ratio of BHPTDU and diols. By varying the monomer ratio of bis(4′-hydroxyphenyl)-tolyene-2,4-diurea and diol, poly(urea-ester)s with different melting temperature were obtained. Table I showed the relationship between melting and isotropization temperature and the monomer composition. It can be seen that when the diols ratio was lower than 30%, the melting temperature decreased with the diols ratio. This was because of the increase of the flexible segment composition in the macromolecule chain, which caused segmental motion easier. After that, the melting temperature increased with the hexanediol ratio. This can be explained by the hydrogen bond, which made the PUEs difficult to melt. It is true that the incremental flexible segment made the poly(urea-ester)s easier to melt. But segmental motion was in favor of forming regular folding structure, which made it possible to form more hydrogen bonds, which increased the melting energy. Thus, the melting temperature reached the extremum when the diols ratio was between 50–60%. When the hexanediol continued increasing, the melting temperature dropped because the hard segment content was too low to form regular folding structure. Figure 5 shows the DSC thermograms of PBTPs. When the molar ratio of pentanediol was below 20%, PBTPs were decomposed before isotropization temperature. PBTP with a composition of 60% pentanediol had Ti at 265°C. Other PBTPs behaved similarly.

Different poly(urea-ester)s showed different melting temperature when they have equal molar monomer ratio of bis(4′-hydroxyphenyl)-tolyene-2,4-diurea and diols. Figure 6 showed that the melting point of the poly(urea-ester)s (molar ratio of diols was 50%) decreased with the number of —(CH_2)—.

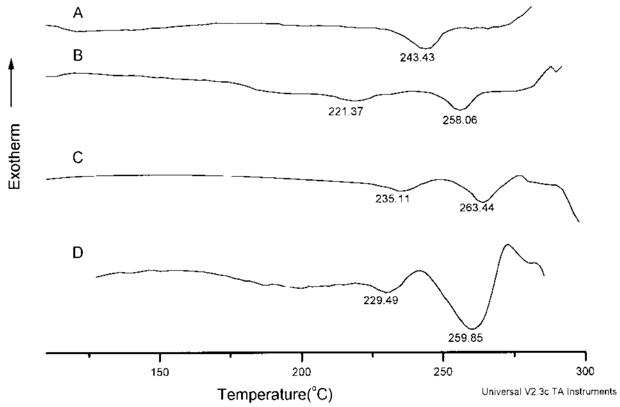


Figure 5 DSC curves of PBTPs, BHPTDU/pentanediol (A) = 90/10, (B) = 20/80, = 50/50, (D) = 30/70.

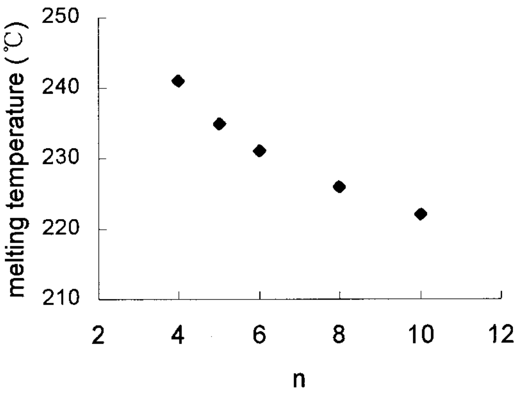


Figure 6 Relationship between the melting point and *n* (molar ratio of diols is 50%).

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