Synthesis and Characterization of Block Copolyetheresters with Poly(tetramethylene 2,6-naphthalenedicarboxylate) Segments

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ABSTRACT: The block copolyetheresters with hard segments of poly(tetramethylene 2,6-naphthalenedicarboxylate) and soft segments of poly(tetramethylene oxide) were prepared by melt polycondensation of dimethyl 2,6-naphthalenedicarboxylate, 1,4-butanediol, and poly(tetramethylene ether) glycol (PTMEG) with molecular weights of 650, 1000, and 2000. The block copolymers were characterized by Fourier transform infrared and ^{1}H-NMR spectroscopy, differential scanning calorimetry, thermogravimetric analysis (TGA), and X-ray diffraction. The block copolymer compositions were governed by the charge molar ratio (x) of PTMEG to dimethyl 2,6-naphthalenedicarboxylate. It was found that the thermal transitions were dependent on the compositions. As x increases, T_m and ΔH_m of the polyester segments decrease due to the decrease in the sequence length. The X-ray diffraction data also indicate that the crystallinity of the polyester segments decreased as x increased. The molecular weight of the PTMEG used has a significant influence on the glass transition temperature (T_g) and the crystallizability of the polyether segments. The polyether segments of block copolymers derived from PTMEG 2000 could crystallize after cooling and showed a T_g of about $-67°C$, independent of x. However, the polyether segments of copolymers derived from PTMEG 1000 and PTMEG 650 could not crystallize, and the T_g of the polyether segments decreased as x increased. This is described as the difference in the miscibility between amorphous parts of the polyether segments and those of the polyester segments. The TGA results indicate that the composition had little effect on the nonisothermal thermal degradation under nitrogen. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 1411–1418, 1997

Key words: block copolyetheresters; thermal transitions; crystallinity; poly(tetramethylene 2,6-naphthalenedicarboxylate) segments

INTRODUCTION

The concept of block copolymer can be used to design thermoplastic elastomers.[1,2] A typical commercial type is the block copolyetherester.[1–8] The mechanical properties of the block copolyetheresters are dependent on many factors, including the content, the type and the sequence length of the polyether segments and the polyester segments; the morphology and the miscibility between the polyether and polyester segments; and even the crystallization behavior or thermal history.[1,2,8–16] The majority of studies have been made on the block copolyetheresters based on poly(tetramethylene terephthalate) or poly(tetramethylene isophthalate) hard segments.[1,2,8–16] The lower melting point of poly(tetramethylene terephthyalate) or poly(tetramethylene isophthalate) limits the ultimate heat resistance for these block copolyetheresters. The use of a more rigid aromatic diacid

monomer may improve the heat resistance. There have been some reports about the synthesis and properties of block copolyetheresters with hard segments of poly(alkylene 2,6-naphthalenedicarboxylate) and poly(alkylene 4,4′-bibenzoate), which show higher melting points.[5,7,17,18] In addition to higher melting point for higher heat resistance, crystallization behavior should be considered, which may influence the mechanical properties.[11,12,15,16] Poly(tetramethylene 2,6-naphthalenedicarboxylate) exhibits a rather high melting point of 246°C and can crystallize easily.[19] Thus, here we use poly(tetramethylene 2,6-naphthalenedicarboxylate) to design block copolyetheresters. Wolfe[5,7] has described a series of block copolyetheresters of 50% hard segments, with hard segments of poly(alkylene 2,6-naphthalenedicarboxylate) and soft segments of poly(tetramethylene oxide), and only a composition of poly(tetramethylene 2,6-naphthalenedicarboxylate) has been presented. However, little is known about the effects of the sequence length of poly(tetramethylene ether) and the polymer composition on their properties. In this article, the synthesis and properties of a series of block copolyetheresters with hard segments of poly(tetramethylene 2,6-naphthalenedicarboxylate)(N4) and soft segments of poly(tetramethylene oxide) (PTMO) of various sequence lengths are described. These block copolyetheresters have the following general formula:
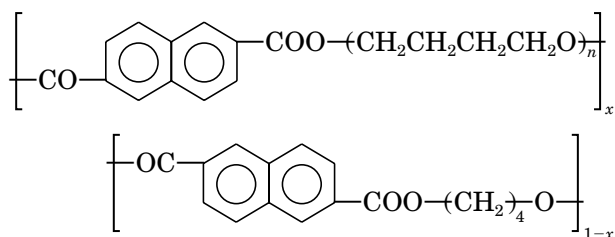
where n is the degree of polymerization of the poly(tetramethylene ether) glycol (PTMEG) used in the synthesis, and x is the molar fraction of the PTMEG in the diol units.

EXPERIMENTAL

Materials

Dimethyl 2,6-naphthalenedicarboxylate (DMN) was supplied by Tedia Chemical Company, Inc. Poly(tetramethylene ether)glycols (PTMEG) with molecular weights of 650, 1000, and 2000

were supplied by Du Pont. All other chemicals were Merck reagent grade and used as received.

Preparation

The block copolyetheresters were prepared by melt polycondensation of dimethyl 2,6-naphthalenedicarboxylate (DMN), 1,4-butanediol (BDO), and a poly(tetramethylene ether) glycol (PTMEG) in the presence of 0.1% of tetrabutyl orthotitanate and 0.1% of lead acetate as the catalysts. A typical example is as follows. Into a 2 L stainless steel reactor were added 135.0 g (0.50 mol) of DMN, 100.0 g (0.05 mol) of PTMEG2000, 82.6 g (0.70 mol) of BDO, 0.3 g of lead acetate, and 0.3 g of tetrabutyl orthotitanate. The reactants heated with outer temperature set to be 170°C under nitrogen at a stirring speed of 50 rpm and held for 2 h. Then, the outer temperature of the reactor was raised to 220°C and held for 1 h. Most methanol, the by-product of the transesterification between DMN and glycols, was distilled off during this period. Afterwards, low vacuum was slowly applied from 760 to 5 torr. Some of the excess BDO was distilled off at this stage. Then, the outer temperature was raised to 260°C, and a high vacuum (0.5 torr) was applied for an additional 2 hrs.

Characterizations

The infrared (IR) spectra were measured by a Perkin Elmer 1600 series Fourier transform infrared (FTIR) spectrometer. The characteristic peaks of the block copolyetheresters are at 3068, 2943, 2857, and 2797 cm^{-1} (C—H stretching); 1715 cm^{-1} (C=O stretching of the ester groups); 1603 and 1503 cm^{-1} (aromatic absorptions); and 1107 cm^{-1} (ether groups). The ^{1}H-NMR spectra of the block copolyetheresters in d-chloroform (or trifluoroacetic acid if not dissolved in chloroform) were determined by nuclear magnetic resonance (NMR) on a Bruker AM 400.

The inherent viscosity (η_{inh}) of the block copolyetheresters in phenol–1,1,2,2-tetrachloroethane (60 : 40 wt : wt) mixture at a concentration of 0.5 g dL was determined with an Ubbelohde viscometer at 30°C. The thermal properties were determined by differential scanning calorimetry (DSC) on a Du Pont 910 DSC calorimeter at a heating rate of 20°C min under nitrogen. The X-ray diffraction (XRD) patterns were recorded on a Shimadzu XD-5 X-ray diffractometer using Cu K$_\alpha$ radiation. The thermogravimetric curves were de-

Table I Charge Composition, Measured Polymer Composition, and η_{inh} of the Block Copolyetheresters

Sample	M_n of PTMEG	Charge Composition[a]	Polymer Composition[a]	η_{inh} (dL/g)
N4	—	1.0 : 1.8 : 0.0	1.00 : 1.01 : 0.00	0.56
N4E1(0.1)	650	1.0 : 1.8 : 0.1	1.00 : 0.90 : 0.11	0.76
N4E1(0.2)	650	1.0 : 1.8 : 0.2	1.00 : 0.80 : 0.21	0.92
N4E1(0.3)	650	1.0 : 1.8 : 0.3	1.00 : 0.71 : 0.29	1.17
N4E2(0.1)	1000	1.0 : 1.8 : 0.1	1.00 : 0.89 : 0.12	0.63
N4E2(0.2)	1000	1.0 : 1.8 : 0.2	1.00 : 0.80 : 0.21	0.88
N4E2(0.3)	1000	1.0 : 1.8 : 0.3	1.00 : 0.72 : 0.30	1.04
N4E3(0.1)	2000	1.0 : 1.8 : 0.1	1.00 : 0.91 : 0.12	0.87
N4E3(0.2)	2000	1.0 : 1.8 : 0.2	1.00 : 0.81 : 0.21	1.04
N4E3(0.3)	2000	1.0 : 1.8 : 0.3	1.00 : 0.72 : 0.31	1.16

[a] DMN : BDO : PTMEG.

termined by thermogravimetric analysis on a Du Pont 9191 TGA analyzer at a heating rate of 10°C min under nitrogen.

RESULTS AND DISCUSSION

Preparation

The charge compositions and η_{inh} values of the block copolyetheresters are listed in Table I. In the preparation of the block copolyetheresters, the charge molar ratio of BDO to DMN was held at 1.8 : 1.0, and that of PTMEG to DMN was x : 1.0. It should be noted that the PTMEG would not be distilled off during synthesis significantly due to its high boiling point. The excess BDO would be

Figure 1 ^{1}H-NMR spectrum of N4E1(0.3).

distilled off. Thus, the composition of the block copolyetheresters would be dependent mainly on the charge molar ratio of PTMEG to DMN. This can be verified by ^{1}H-NMR. Figure 1 shows a typical ^{1}H-NMR spectrum of N4E1(0.3). The assignments are also shown in the figure. The polymer composition can be calculated by the ratio of integrated intensities of the resonance peaks. Consider N4E1(0.3): the charge molar ratio of PTMEG 650 to DMN was 0.3 : 1.0, and that of BDO to DMN was 1.8 : 1.0. The calculated molar ratio of DMN : BDO : PTMEG650 in polymer is 1.0 : 0.71 : 0.29. It indicates that PTMEG650 was not distilled off significantly, but most of the excess BDO was distilled off during synthesis. Clearly, the charge molar ratio of PTMEG to DMN determined the composition. The measured polymer compositions are also tabulated in Table I. The block copolymers are denoted as N4En(x), where N4 means the poly(tetramethylene 2,6-naphthalenedicarboxylate) hard segment; E1, E2, and E3 indicate that the molecular weights of PTMEG used are 650, 1000, and 2000, respectively; and x is the charge molar ratio of the PTMEG to DMN.

Thermal Properties

The DSC heating curve of a poly(tetramethylene 2,6-naphthalenedicarboxylate), N4, is shown in Figure 2. N4 exhibited a T_m of 244°C and a ΔH_m of 32.1 J/g. In addition, when N4 melt was poured into cool water, it became opaque, indicating that it would be easy to crystallize. And this quenched N4 exhibited similar T_m and ΔH_m as the slow-cooled one. Thus,
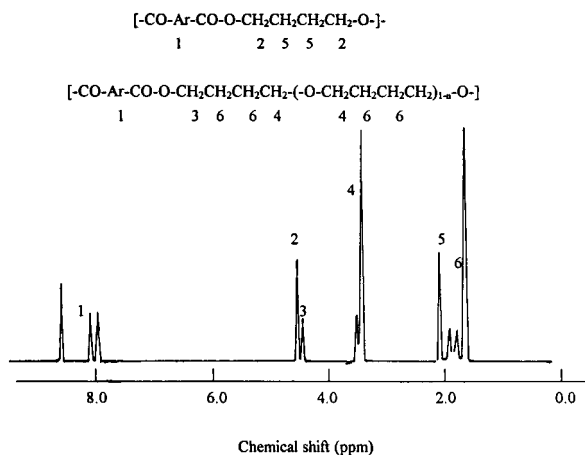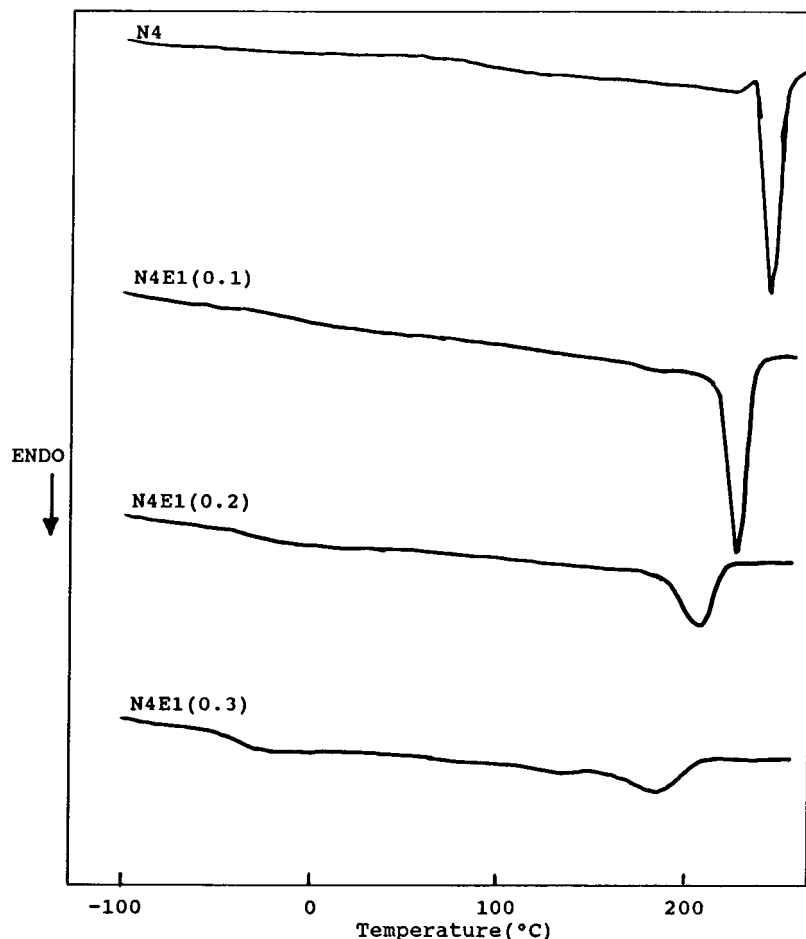
Figure 2   DSC heating curves of N4 and N4E1(x)s.

we use N4 segments to design block copolyetheresters as thermoplastic elastomers.

Typical second-run DSC heating curves from -100 to $260°C$ of the block copolyetheresters are shown in Figures 2 and 3. It can be seen that the thermal properties of the block copolyetheresters were dependent on the composition. In the temperature range of -100 to $50°C$, the DSC heating curves of N4E1(x)s and N4E2(x)s exhibit a step inflection, and those of N4E3(x)s exhibit a step inflection and an endotherm. Since N4 showed no thermal transition below $50°C$, the observed transition(s) by DSC would be attributed to polyether segments. The midpoint of the step inflection is taken as the glass transition temperature of the polyether soft segment, T_gS; and the peak temperature of the endotherm is taken at the melting temperature of the polyether soft segments, T_mS. The values of T_gS, T_mS, and ΔH_mS are listed in Table II. In the temperature range of 50 to $260°C$, the

second-run DSC heating curves of all block copolyetheresters show an endothermic peak due to the melting of the polyester hard segments. The peak temperature is taken as T_mH. Some block copolyetheresters seemed to exhibit a T_gH, but this was not obvious partially due to the high crystallinity of the polyester segments. The T_gH, T_mH, and ΔH_m data are also tabulated in Table II.

It can be seen from Table II that the effect of x on T_mH followed a similar trend for the three different series of block copolyetheresters. As x increases, the sequence length and the content of the polyester segments decreased, and T_mH and ΔH_m decreased accordingly. The effect of composition on T_gH was not as simple as expected; further investigations by dynamic mechanical properties (DMA) and thermally stimulated current (TSC) will be made to describe this phenomenon.

It can be seen that both the molecular weight of PTMEG used and x had significant influence
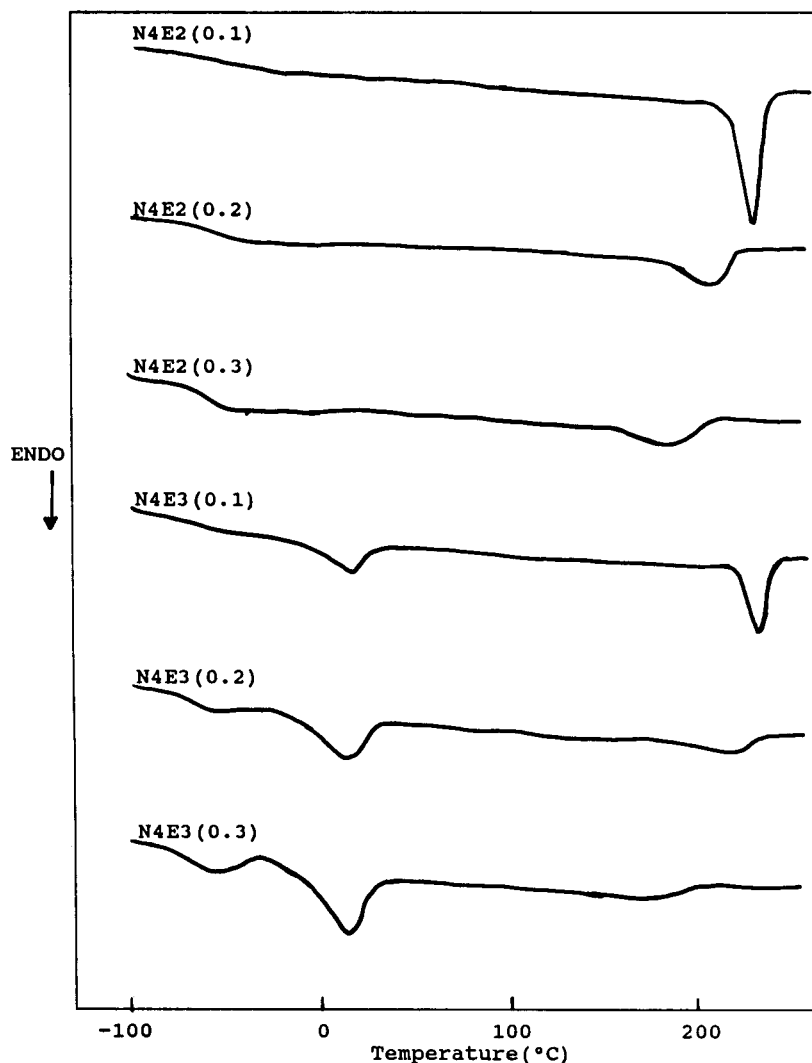
Figure 3 DSC heating curves of N4E2(x)s and N4E3(x)s.

on the thermal transitions of the polyether segments (T_gS, T_mS, and ΔH_mS). The molecular weight of PTMEG had a significant effect on the crystallizability of the polyether segments. With the restriction of the polyester segments, the sequence length of polyether segments of N4E1(x) and N4E2(x) series may be too short for them to crystallize after cooling, and no T_mS was observed. The sequence length of the polyether segments of N4E3(x) series would be long enough for them to crystallize after cooling. However, the T_mS and ΔH_mS of N4E3(x) block copolyetheresters are lower than those of the PTMEG 2000 ($T_m = 31°C$ and $\Delta H_m = 89.2$ J/g). Thus, the crystallizability of the polyether soft segments of the block copolyetheresters was af-

fected by the presence of the polyester hard segments significantly.

The T_gS of N4E1(x) series was from -8 to $-37°C$ and decreased as x increased. The T_gS of N4E2(x) series also decreased as x increased, but the T_gS values (-46 to $-57°C$) were lower than those of N4E1(x) series. N4E3(x) series exhibited a T_gS of about $-68°C$, which was independent of x. This is considerably different from the case of some commercial block copolyetheresters, such as the block copolyetheresters with soft segments of poly(tetramethylene oxide) and hard segments of poly(butylene terephthalate), of which the T_gS was from -70 to $20°C$ and decreased significantly as the polyether content increased.[8] That is attributed to the fact that

Table II Thermal Transitions of the Block Copolyetheresters Determined by DSC

Sample	T_gS (°C)	T_mS (°C)	ΔH_mS (J/g)	T_gH (°C)	T_mH (°C)	ΔH_mH (J/g)
N4	—	—	—	—	244	32.1
N4E1(0.1)	−8	—	—	—	230	36.4
N4E1(0.2)	−32	—	—	57	209	19.9
N4E1(0.3)	−37	—	—	—	187	4.45
N4E2(0.1)	−46	—	—	—	229	26.5
N4E2(0.2)	−53	—	—	—	206	12.3
N4E2(0.3)	−57	—	—	62	186	10.5
N4E3(0.1)	−67	16	9.85	—	234	13.3
N4E3(0.2)	−67	13	17.6	—	220	8.12
N4E3(0.3)	−68	14	21.3	—	169	7.74

the amorphous parts of the poly(tetramethylene ether) segments are miscible with the amorphous parts of the poly(butylene terephthalate) segments. However, our trend was similar to, but somewhat different from, that of the block copolyetheresters with soft segment of poly(tetramethylene oxide) and hard segments of poly(pentamethylene p,p'-bibenzoate) segments.[20] The T_g of N4E3(x) series was almost independent of their composition and rather close to that of the corresponding PTMEG (−74°C). This indicates that the amorphous parts of the poly(tetramethylene ether) segments in this series of block copolyetheresters would be immiscible with the amorphous parts of the polyester segments. The T_gS of N4E2(x) and N4E1(x) series was significantly higher than that of N4E3(x) series and PTMEGs. Thus, the amorphous parts of the polyether segments in these two series might be partially miscible with the amorphous parts of the polyester segments. Of course, the compatibility between polyether segments and polyester segments in N4E1(x) series would be better than in N4E2(x) series. This difference in miscibility may be due to the difference in the sequence length of the polyether segments. The sequence length of the polyether segments in N4E1(x) series is shorter than those of the other two series. The shorter polyether segments attached to the 2,6-naphthalenedicarboxylate unit may render them more or less similar to the polyester segments; thus, the polyether segment was more compatible with the polyester segments in N4E1(x) series. Comparing the effect of composition on T_gS, the compatibility between polyether segments and polyester segments for N4-based block copolyetheresters would be better than in poly(pentameth-ylene p,p'-bibenzoate)-based block copolyetheresters,[20] but poorer than that in poly(butylene terephthalate)-based block copolyetheresters.[8] This would be due to the difference in the rigidity of the polyester segments, which is in the order of poly(pentamethylene p,p'-bibenzoate) > poly(tetramethylene 2,6-naphthalenedicarboxylate) > poly(butylene terephthalate).

X-ray Diffraction

The XRD patterns of N4 and typical block copolyetheresters are shown in Figure 4. N4 showed two sharp diffraction peaks at 2θ = 15.3 and 24.1° (d = 5.8 and 3.7 nm), and two smaller diffraction peaks at 2θ = 19.8 and 28.6° (d = 4.5 and 3.1 nm.) Since the polyether segments are amorphous at room temperature, the diffraction peaks of the block copolyetheresters are attributed to the polyester segments. It can be seen from Figure 4 that the diffraction patterns of the block copolyetheresters are similar to N4 but dependent on the compositions. N4E1(0.1) exhibited three diffraction peaks at 2θ = 15.4, 24.2, and 28.5° (d = 5.7, 3.7 and 3.1 nm); but the peak at 2θ = 19.8° (d = 4.5 nm) seemed to disappear. N4E1(0.2) exhibited a broader peak at 2θ = 15.2° (d = 5.8 nm) and a sharp peak at 2θ = 24.1° (d = 3.7 nm); the original peaks at 2θ = 19.8 and 28.6° (d = 4.5 and 3.1 nm) for N4 disappear. There is only a smaller and broader diffraction peak at 2θ = 24.1° (d = 3.7 nm) for N4E1(0.3). This results indicate that the crystallinity of the polyester segments decreases as x increases due to the decrease in the sequence length of the polyester segments. The trend of N4E2(x) and N4E3(x) series is the same as N4E1(x) series and consistent with DSC data (Table II).
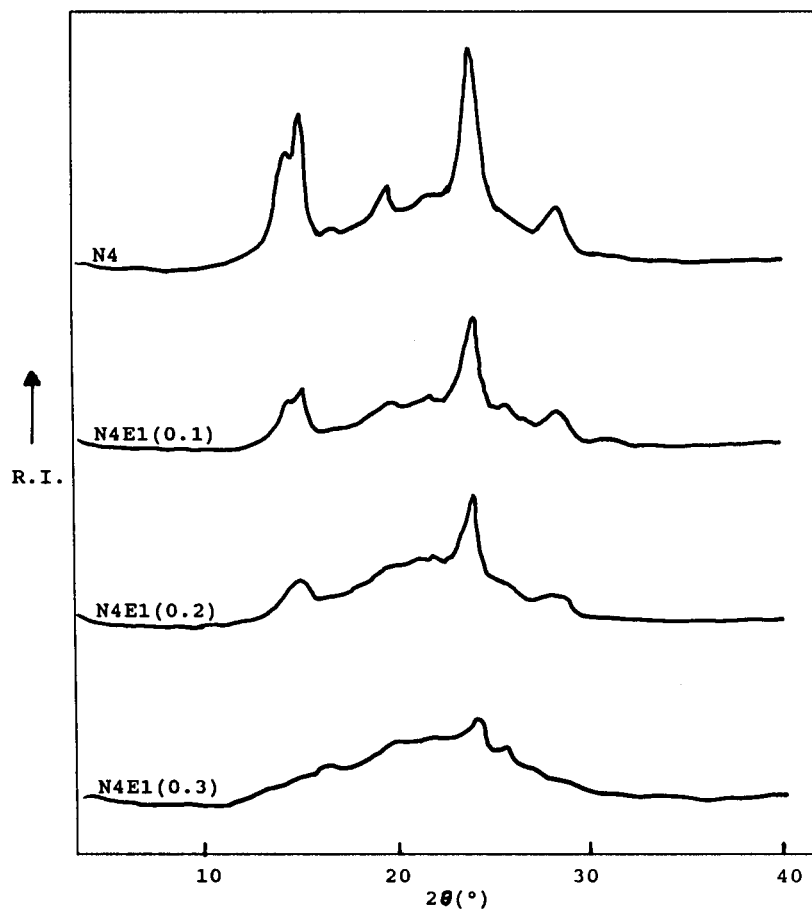
Figure 4 XRD patterns of N4 and N4E1(x)s.

Thermogravimetric Analysis

Figure 5 shows a typical thermogravimetric (TG) curve of N4E1(0.1). The temperatures at weight losses of 5, 10, and 20%, denoted as T_5, T_{10}, and T_{20}, respectively, are tabulated in Table III. Under nitrogen, N4 and the block copolyetheresters showed similar TG curves. It can be
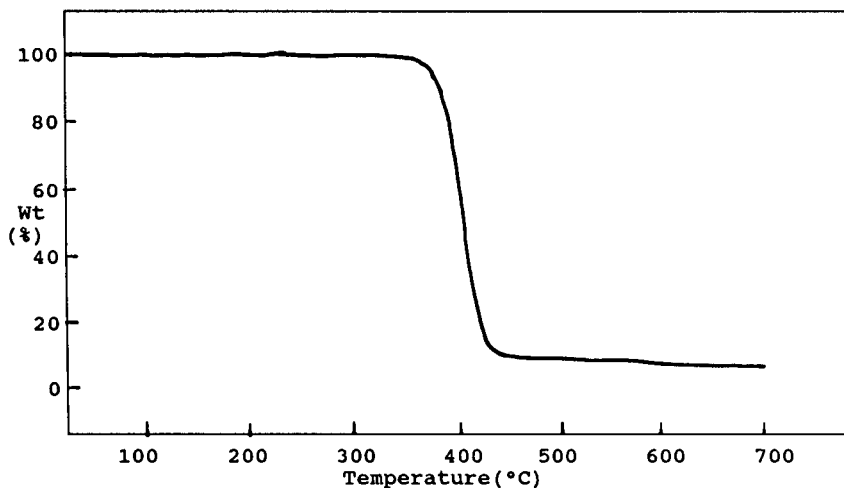

Figure 5 TG curves of N4E1(0.1).

Table III T_5, T_{10}, and T_{20} of the Block Copolyetheresters Measured by TGA

Sample	T_5 (°C)	T_{10} (°C)	T_{20} (°C)
N4	377	384	392
N4E1(0.1)	378	384	392
N4E1(0.2)	375	384	393
N4E1(0.3)	378	385	394
N4E2(0.1)	375	381	390
N4E2(0.2)	374	383	393
N4E2(0.3)	374	383	392
N4E3(0.1)	373	382	391
N4E3(0.2)	375	384	394
N4E3(0.3)	373	382	392

seen that there was no significant variation in T_5, T_{10}, and T_{20}. Thus, the block copolyetheresters exhibited similar thermal degradation under nitrogen.

CONCLUSION

The thermal transitions of the block copolyetheresters were dependent on the composition and the molecular weight of the PTMEG used. The T_mH of the polyester segments were greatly dependent on x and decreased as x increased. The ΔH_mH and XRD data indicate that the crystallinity of the polyester segments decreased as x increased. The thermal transitions of the polyether segments depend both on the molecular weight of the PTMEG used and x. Only the polyether segments of the block copolyetheresters derived from PTMEG2000 could crystallize after cooling. The results of T_g indicate that the amorphous parts of the polyether segments would be immiscible with the amorphous parts of the polyester segments for the block copolyetheresters derived from PTMEG 2000 but became partially miscible for the block copolyetheresters derived from PTMEG 1000 and PTMEG 650. Comparing the effect of composition on T_gS, the compatibility between polyether segments, and polyester segments, the block copolyetheresters would be dependent on the type of polyester segments and in the order of poly(butyl- ene terephthalate) > poly(tetramethylene 2,6- naphthalenedicarboxylate) > poly(pentamethylene p,p'-bibenzoate).

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