

# Block Copolyesters of Poly(pentamethylene 2,6-Naphthalenedicarboxylate) and Poly(tetramethylene Adipate)

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**ABSTRACT:** Hydroxy-terminated poly(pentamethylene 2,6-naphthalenedicarboxylate) oligomers were prepared by melt polycondensation of dimethyl 2,6-naphthalenedicarboxylate with excess 1,5-pentanediol followed by evacuating out some 1,5-pentanediol. The molecular weight of the poly(pentamethylene 2,6-naphthalenedicarboxylate) oligomers was controlled by the charge molar ratio of 1,5-pentanediol to dimethyl 2,6-naphthalenedicarboxylate and the amount of 1,5-pentanediol removed under vacuum. The <sup>1</sup>H-NMR spectra of the poly(pentamethylene 2,6-naphthalenedicarboxylate) oligomers indicate that the transesterification between dimethyl 2,6-naphthalenedicarboxylate and 1,5-pentanediol was almost complete. Block copolyesters with hard segments of poly(pentamethylene 2,6-naphthalenedicarboxylate) and soft segments of poly(tetramethylene adipate) were prepared by coupling the poly(pentamethylene 2,6-naphthalenedicarboxylate) oligomer and a poly(tetramethylene adipate) glycol with methylene-4,4'-diphenylene diisocyanate in solution. The block copolyesters were charac-

terized by IR, <sup>1</sup>H-NMR, DSC, and X-ray diffraction. The hard segments in the block copolyesters display an amorphous state. However, the thermal transitions of soft segments in the block copolyesters are strongly dependent on the composition. When the content of the hard segments increases, the glass transition temperature of the soft segments increases. Thus, the amorphous parts of the soft segments would be partially miscible with the hard segments. When the content of the hard segments is very low, the soft segments of the block copolyesters exhibit high crystallinity. But, as the content of the hard segments is about 30 wt % or more, the soft segments of the block copolyesters become amorphous. This is described as the effect of the presence of the hard segments which are partially miscible with the soft segments. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3652–3659, 2002

**Key words:** block copolymers; polyesters; oligomers; thermal properties

## INTRODUCTION

The concept of block copolymer can be used to design thermoplastic elastomers. Generally, the soft segments form rubber matrix, and the hard segments become domains that give physical crosslinks.<sup>1,2</sup> A typical commercial type is the block copolyetheresters.<sup>1–8</sup> The 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.<sup>1,2,8–20</sup> The block copolyetheresters are often made by melt polycondensation, and the poly(tetramethylene ether) glycols are ordinarily used. The use of aliphatic polyesters as the soft

segments will be another choice, and it has an advantage in cost reduction because the aliphatic polyester glycols such as poly(tetramethylene adipate) glycols are cheaper than the poly(tetramethylene ether) glycols. The development of block copolyesters has been investigated.<sup>21–26</sup>

One method of preparation of block copolyesters involves controlled transesterification between a high molecular weight aromatic polyester such as poly(ethylene terephthalate) and a high molecular weight aliphatic polyester such as poly(ethylene sebacate) at high temperature.<sup>21,22</sup> However, the transesterification method is suitable only for few systems. For example, we have found the no transesterification reaction occurred between high molecular weight poly(tetramethylene terephthalate) and high molecular weight poly(tetramethylene adipate) at 260°C due to poor miscibility, and we used low molecular weight prepolymers for transesterification, followed by removal of the by-product through vacuum to obtain block copolyesters.<sup>26</sup> However, the extent of transesterification is difficult to control in this method.

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Another method to prepare block copolyesters involves coupling an aromatic polyester glycol and an aliphatic polyester glycol with diisocyanate.<sup>22–25</sup> The coupling reaction can be carried in the melt state. However, if the reaction temperature is too high, there will be some unnecessary by-products such as allophanate formed.<sup>22,27,28</sup> The use of solvent can lower the reaction temperature to decrease the by-products.<sup>27,28</sup> Here we use the coupling reaction in solution to prepare block copolyesters with hard segments of poly(pentamethylene 2,6-naphthalenedicarboxylate) and soft segments of poly(tetramethylene adipate).

In this article, the hydroxy-terminated poly(pentamethylene 2,6-naphthalenedicarboxylate) oligomers were prepared. The block copolyesters were prepared by coupling the poly(pentamethylene 2,6-naphthalenedicarboxylate) oligomer and a poly(tetramethylene adipate) glycol with methylene-4,4'-diphenylene diisocyanate(MDI) in solution, and their thermal transitions were investigated.

## EXPERIMENTAL

Dimethyl 2,6-naphthalenedicarboxylate was supplied by Tedia Chemical Company, Inc. (Japan). 1,5-Pentanediol, tetrabutyl orthotitanate, dimethyl formamide(DMF), methylene-4,4'-diphenylene diisocyanate(MDI), dibutyltindilaurate, *d*-chloroform, and *d*-trifluoroacetic acid were Merck reagent grade. A poly(tetramethylene adipate)glycol, DP-203, with a molecular weight of 2000 was supplied by Dahin Co. Ltd.(Taiwan). Except MDI, all the reagents were used as received.

MDI has a tendency to dimerize at room temperature, and hot sintering is required to eliminate any MDI dimer or other impurities insoluble in molten MDI.<sup>29</sup> After hot sintering and filtering, MDI was cooled rapidly, and stored in a refrigerator at  $-30^{\circ}\text{C}$ .

The poly(pentamethylene 2,6-naphthalenedicarboxylate) oligomers were prepared by melt polycondensation of dimethyl 2,6-naphthalenedicarboxylate with excess 1,5-pentanediol, followed by eliminating some amount of 1,5-pentanediol through a vacuum stage. A typical example is as follows. 244.0 g (1.0 mol) of dimethyl 2,6-naphthalenedicarboxylate, 187.2 g (1.8 mol) of 1,5-pentanediol, and 0.5 g of tetrabutyl orthotitanate were added into a 2-L stainless steel reactor equipped with a mechanical stirrer, nitrogen inlet tube, and a distillation head connected to a condenser. The reactants were heated to 170–200°C under nitrogen at a stirring speed of 50 rpm and held for 2 h. Most methanol was distilled off at this stage. Then, the reaction mixture was heated to 240°C and vacuum (about 5 mmHg) was applied. 1,5-Pentanediol was evaporated and collected in a flask. After about 41.6 g (0.4 mol) of 1,5-pentanediol was collected, the reaction was stopped and the product was discharged. The molar ratio of 1,5-pentanediol to dimethyl 2,6-naph-

thalenedicarboxylate in this oligomer would be around 1.4, and thus, this oligomer is denoted as N5(1.4).

Block copolyesters were prepared by coupling the poly(pentamethylene 2,6-naphthalenedicarboxylate) oligomer and the poly(tetramethylene adipate)glycol(DP-203) with MDI in the presence of dibutyltindilaurate in DMF. Typical procedures are as follows. 15.0 g of N5(1.4) and 15.0 g of DP-203 were dissolved in 150 g of DMF in a 1-L four-necked flask at 80°C under stirring. Then, under the purge of nitrogen gas, the mixture was heated to 100°C at a stirring speed of 100 rpm, and 6.86 g of MDI and four drops of dibutyltindilaurate were added gradually in 4 h. During the reaction, the viscosity of the reaction mixture increased significantly after the added amount of MDI was close to the stoichiometric value as indicated by the increasing torque value of the stirrer, and the addition of MDI should be slowed down. As the viscosity of the reaction mixture became high enough and it was difficult to stir the system, the reaction was stopped.

The inherent viscosity ( $\eta_{\text{inh}}$ ) of the block copolyesters in DMF at a concentration of 0.5 g/dL was determined with an Ubbelohde viscometer at 70°C.

The IR spectra were measured by a Perkin-Elmer 1600 series FTIR. The <sup>1</sup>H-NMR spectra of the poly(pentamethylene 2,6-naphthalenedicarboxylate) oligomers in *d*-chloroform and those of the block copolyesters in *d*-trifluoroacetic acid were determined by a Bruker AM 400 NMR.

The thermal properties from 100 to 260°C were determined by a Du Pont 910 DSC at a heating rate of 20°C/min under nitrogen. The X-ray diffraction patterns were recorded on a Shimadzu XD-5 X-Ray Diffractometer using Cu K<sub>α</sub> radiation.

## RESULTS AND DISCUSSION

### Oligomers

The method using only transesterification of dimethyl 2,6-naphthalenedicarboxylate in the presence of tetrabutyl orthotitanate at 260°C for 6 h similar to a method described in the literature<sup>22,25,26</sup> was tried to prepare an oligomer. However, it was found by its <sup>1</sup>H-NMR spectrum that more than 10 mol % of methyl ester group remained untreated in this oligomer. Thus, this oligomer cannot be considered to be a well-defined hydroxy-terminated oligomer.

To obtain hydroxy-terminated oligomers, a vacuum stage was applied latterly to force the transesterification reaction between dimethyl 2,6-naphthalenedicarboxylate and 1,5-pentanediol to be complete. By varying the charge molar ratio 1,5-pentanediol to dimethyl 2,6-naphthalenedicarboxylate and the amount of 1,5-pentanediol evacuated out at the vacuum stage, four

TABLE I  
 $n$ ,  $R'$  and  $M_n$  of Poly(pentamethylene 2,6-Naphthalenedicarboxylate) Oligomers

N5(R)	$n$	$R'$	$M_n$
N5(1.8)	1.47	1.68	521
N5(1.4)	2.80	1.36	899
N5(1.2)	4.32	1.23	1331
N5(1.1)	7.78	1.13	2313

$R$  is the estimated molar ratio 1,5-pentanediol to dimethyl 2,6-Naphthalenedicarboxylate.

$$n = A_{H2}/A_{H4}$$

$$R' = (n + 1)/n$$

$$M_n = 284n + 105$$

poly(pentamethylene 2,6-naphthalenedicarboxylate) oligomers were prepared. Their estimated molar ratio 1,5-pentanediol to dimethyl 2,6-naphthalenedicarboxylate,  $R$ , and the notation, N5( $R$ ), are described in Table I. A typical  $^1\text{H-NMR}$  spectrum of N5(1.2) is shown in Figure 1. The assignments are also shown in the figure. It can be seen that little amount of methyl ester group (H3) has been detected. The content of methyl ester group remained unreacted are less than 1 mol % for these four oligomers. Thus, almost well-defined polyester oligomers have obtained by our method.

From the ratio of integrated intensity of H2 to that of H4, the degree of polymerization,  $n$ , of N5( $R$ )s can be determined. The calculated  $n$  values are listed in Table I. The molar ratio of 1,5-pentanediol to dimethyl 2,6-

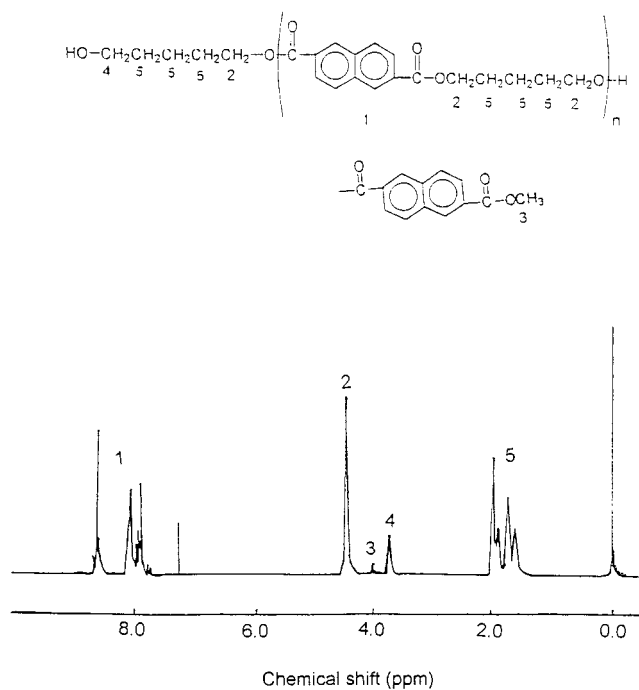


Figure 1  $^1\text{H-NMR}$  spectrum of N5(1.2).

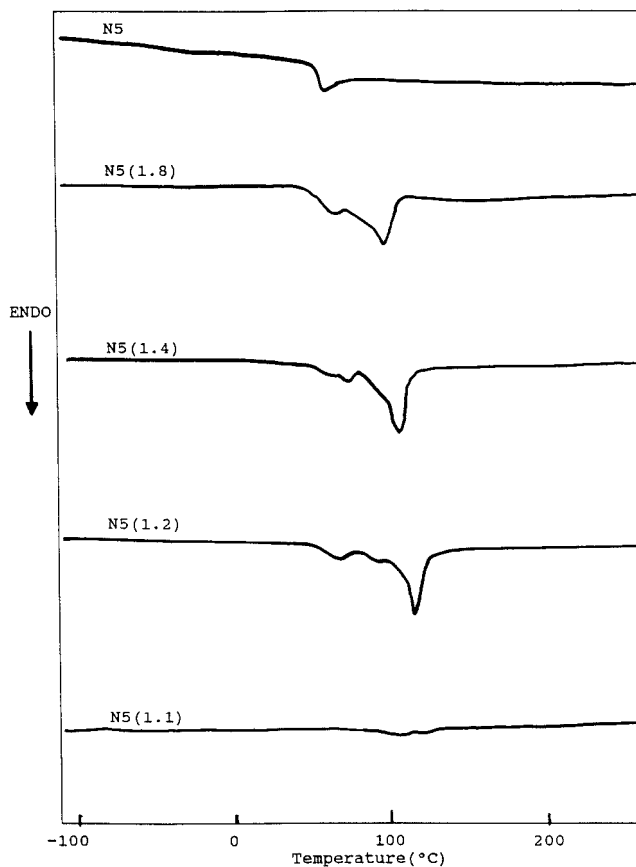


Figure 2 The DSC heating curves of N5, and N5( $R$ )s.

naphthalenedicarboxylate in these oligomers,  $R'$ , is calculated by  $R' = (n + 1)/n$ . The number average molecular weight,  $M_n$ , can be determined by  $M_n = 284n + 104$ . The  $R'$  and  $M_n$  values are listed in Table I.

A high molecular weight poly(pentamethylene 2,6-naphthalenedicarboxylate), N5, with an inherent viscosity of 0.60 dL/g is used here to compare the thermal transitions of N5( $R$ )s. The DSC heating curves of N5 and N5( $R$ )s are shown in Figure 2. The DSC heating curve of N5 exhibits a step inflection, but no melting endotherm. Thus, N5 is amorphous. The DSC heating curves of N5( $R$ )s exhibit a step inflection, and a melting endotherm. The midpoint of the step inflection is taken as the glass transition temperature ( $T_g$ ) and the peak temperature of the endotherm is taken as the melting temperature ( $T_m$ ). The transition temperatures ( $T_g$  and  $T_m$ ), and the melt transition heats ( $\Delta H_m$ ) of N5 and N5( $R$ )s are summarized in Table II.

The melt transition of the poly(pentamethylene 2,6-naphthalenedicarboxylate) oligomers is affected by the molecular weight significantly. The three lower molecular weight oligomers, N5(1.8), N5(1.4), and N5(1.2), show rather high crystallinity as indicated by the high  $\Delta H_m$  values, and as the molecular weight decreases, their  $T_m$  increases as expected. However,

TABLE II  
The Thermal Transitions of N5 and N5(R)s Determined by DSC

N5(R)	$T_g$ (°C)	$T_m$ (°C)	$\Delta H_m$ (J/g)
N5(1.8)	56	97	35.2
N5(1.4)	52	107	38.9
N5(1.2)	55	115	37.9
N5(1.1)	56	109	4.9
N5	55	—	—

N5(1.1) shows very low crystallinity, its  $\Delta H_m$  is as low as 4.9 J/g. It should be due to the kinetic effect. As the molecular weight is high enough, for example,  $M_n > 2300$ , the molecular chains become difficult to pack into the crystalline lattice possibly due to their poor mobility. It is not unexpected that N5, which has a high molecular weight, is amorphous.

The X-ray diffraction patterns of N5, N5(1.1), and N5(1.4) are shown in Figure 3. N5(1.8), N5(1.4), and N5(1.2) exhibit similar X-ray diffraction patterns with five to six sharp diffraction peaks, indicating high crystallinity of these three low molecular weight oligomers. The X-ray diffraction patterns of N5, and

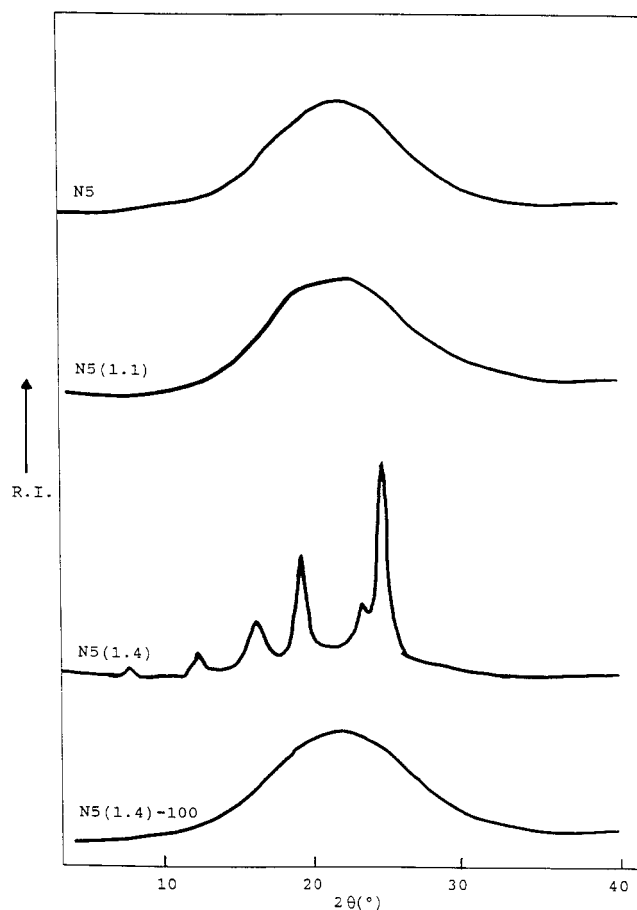


Figure 3 The X-ray diffraction patterns of N5, N5(1.1), N5(1.4), and N4(1.4)-100.

TABLE III  
The Composition, and  $\eta_{inh}$  of the Block Copolyesters

Sample	N5(R) (g)	DP-203 (g)	MDI (g)	$\eta_{inh}$ (dL/g)
DP203-P	0.0	90.0	11.84	0.41
N5(1.8)-10	3.0	27.0	5.69	0.42
N5(1.8)-30	10.0	23.0	8.83	0.36
N5(1.8)-50	15.0	15.0	10.41	0.42
N5(1.8)-100	15.0	0.0	7.94	0.44
N5(1.4)-10	3.0	27.0	5.30	0.52
N5(1.4)-30	10.0	23.0	7.24	0.47
N5(1.4)-50	15.0	15.0	7.80	0.42
N5(1.4)-100	15.0	0.0	5.17	0.41
N5(1.2)-10	3.0	27.0	4.92	0.39
N5(1.2)-30	10.0	25.0	6.20	0.38
N5(1.2)-50	10.0	10.0	4.00	0.42
N5(1.2)-100	15.0	0.0	3.58	0.43
N5(1.1)-10	3.0	27.0	4.59	0.44
N5(1.1)-30	10.0	23.0	5.03	0.41
N5(1.1)-50	16.0	16.0	4.77	0.42
N5(1.1)-100	15.0	0.0	2.09	0.32

N5(1.1) show a broad peak, indicating that their crystallinity is very low. The X-ray diffraction data are consistent with the results observed by the DSC.

#### Preparation and spectroscopic analyses of the block copolyesters

Block copolyesters with soft segments of poly(tetramethylene adipate) and hard segments of poly(pentamethylene 2,6-naphthalenedicarboxylate), and some polyesters were prepared by coupling the poly(pentamethylene 2,6-naphthalenedicarboxylate) oligomer and DP-203 of different weight ratio with MDI. The composition and  $\eta_{inh}$  of the block copolyesters are shown in Table III. The block copolyesters are denoted as N5(R)- $w$ , where  $w$  is the weight percentage of the poly(pentamethylene 2,6-naphthalenedicarboxylate) oligomer in diols.

The block copolyesters show similar IR spectra. A typical IR spectrum of N5(1.8)-50 is shown in Figure 4. The characteristic peaks of the block copolyesters are at  $3343\text{ cm}^{-1}$  (NH),  $2952\text{ cm}^{-1}$  (C—H),  $1733\text{ cm}^{-1}$  (C=O),  $1654$  and  $1527\text{ cm}^{-1}$  (aromatic absorptions). The absorption peak corresponding to isocyanate group at about  $2270\text{ cm}^{-1}$  was not found, thus the isocyanate group was consumed in the coupling reaction.

The  $^1\text{H-NMR}$  spectrum of N5(1.1)-50 is shown in Figure 5. The assignments are also shown in the figure. The peak at about 3.8 ppm corresponding to the  $\alpha$ -methylene protons of the hydroxyalkyl-terminated group almost disappeared after the coupling reaction. Thus, the reaction between hydroxy groups and isocyanate groups would be almost complete.

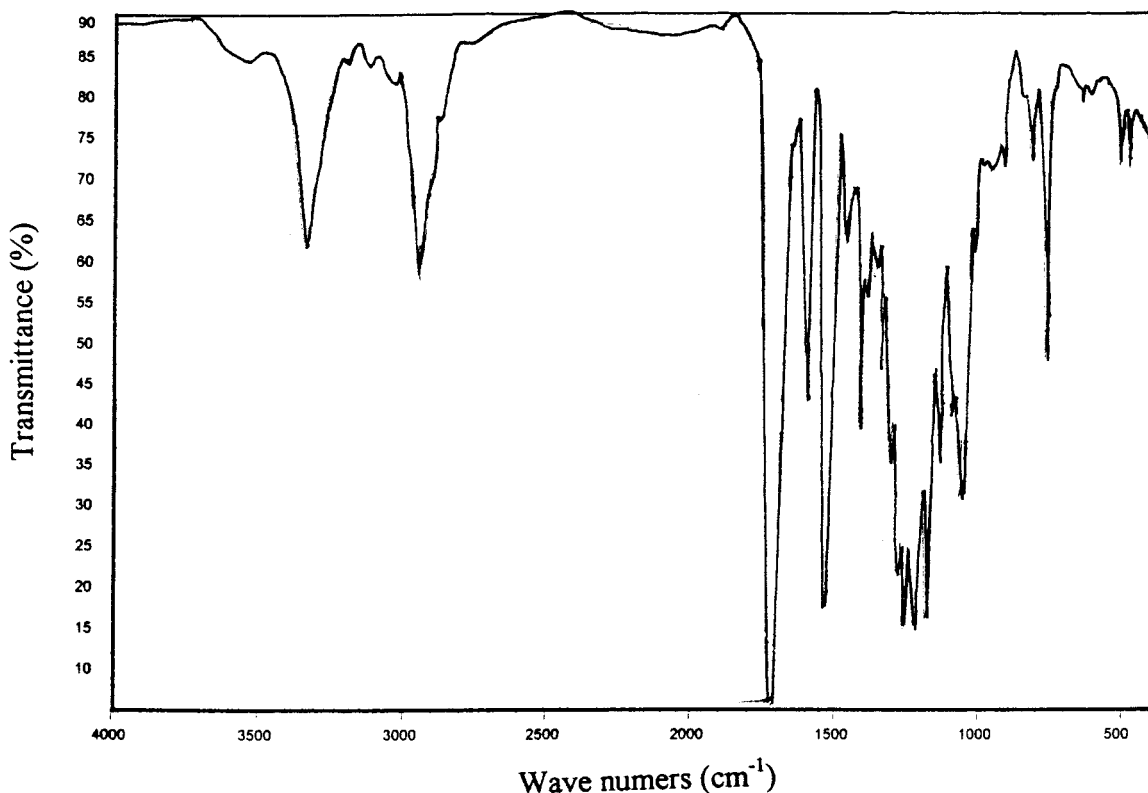


Figure 4 IR spectrum of N5(1.8)-50.

### Thermal transitions of the block copolyesters

The DSC heating curves of N5(R)-100s, and the block copolyesters are shown in Figures 6 and 7. The transition temperatures and the melt transition heat of the

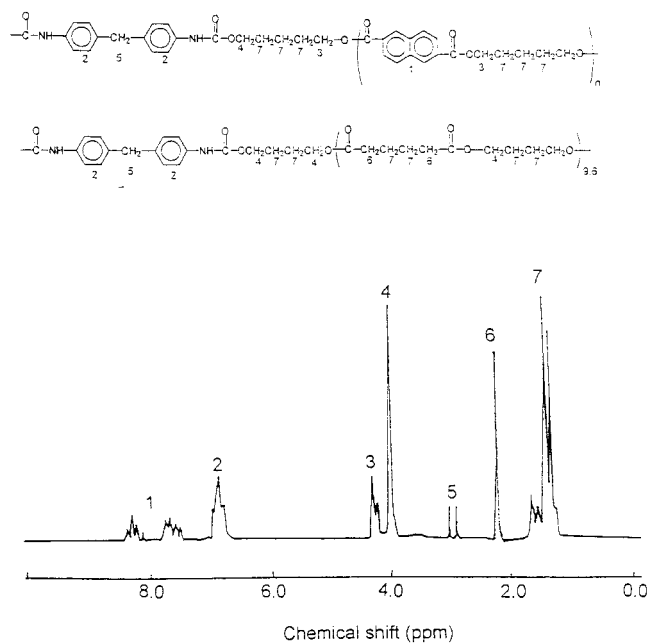


Figure 5  $^1\text{H-NMR}$  spectrum of N5(1.1)-50.

soft segments,  $\Delta H_m S$ , determined by the DSC are summarized in Table IV.

N5(R)-100s were obtained by coupling the poly(pentamethylene 2,6-naphthalenedicarboxylate) oligomers with MDI; thus, they contain no poly(tetramethylene adipate) soft segment. The DSC heating curves of N5(R)-100s exhibits only a step inflection, but no melting endotherm. Thus, all N5(R)-100s are amorphous. The X-ray diffraction patterns, typically shown in Figure 3, also indicate the amorphous nature of the N5(R)-100s. Although some N5(R)-s show rather high crystallinity, they become amorphous after coupling with MDI. One possible reason is the kinetic effect due to the increase in molecular weight as described earlier, another one may be due to the effect of the presence of the urethane groups.

The poly(pentamethylene 2,6-naphthalenedicarboxylate) hard segments of the block copolyesters exhibit an amorphous state as that of N5(R)-100s possibly due to the effect of the presence of the urethane groups.

The MDI coupled poly(tetramethylene adipate) glycol, DP203-P, exhibits a  $T_g$  at  $-43^\circ\text{C}$ , and a  $T_m$  with a  $\Delta H_m S$  of  $54.4 \text{ J/g}$  at  $48^\circ\text{C}$  as shown in Table IV. Thus, DP203-P shows high crystallinity.

The thermal transitions of the poly(tetramethylene adipate) soft segments of the block copolyesters are influenced by the presence of the hard segments sig-

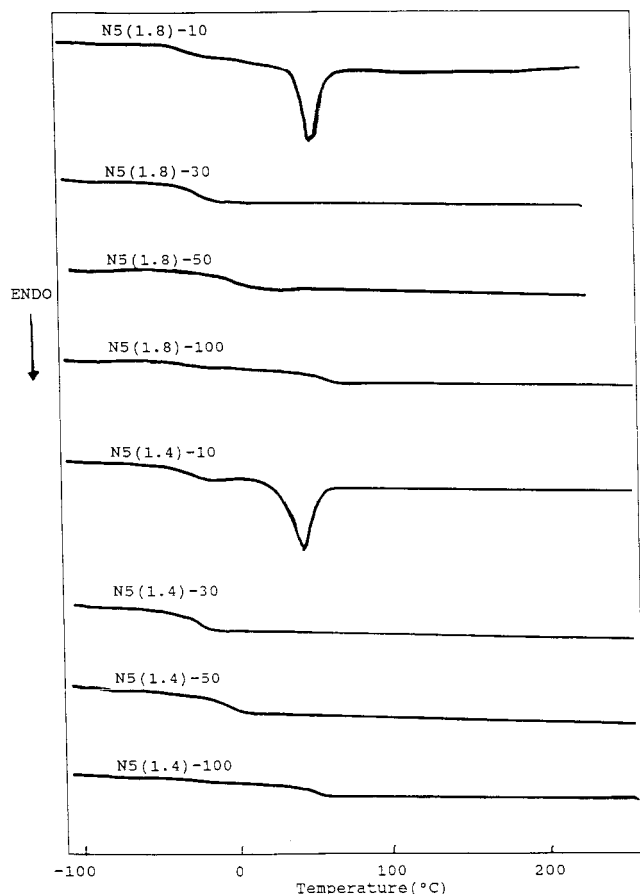


Figure 6 The DSC heating curves of N5(1.8)-ws, and N5(1.4)-ws.

nificantly as shown in Table IV. N5(R)-10s exhibit a  $T_m$ s with a  $\Delta H_m$ s of about 30 J/g, thus displaying rather high crystallinity, but as  $w$  is 30 or over, the soft segments of the block copolyesters become amorphous. The influence of the hard segments on the crystallinity of the soft segments of the block copolyesters can be also seen from their X-ray diffraction data. The X-ray diffraction patterns of the block copolyesters are shown in Figures 8 and 9. All N5(R)-100s show a broad peak similar to the diffraction pattern of N5(1.4)-100 or N5 as shown in Figure 3. Thus, the sharp diffraction peaks of the block copolyesters shown in Figures 8 and 9 are attributed to the soft segments. DP203-P exhibits two obvious and sharp diffraction peaks at  $2\theta = 21.5^\circ$ , and  $24.4^\circ$ . Thus, DP203-P exhibits high crystallinity. As  $w = 10$ , the block copolyesters exhibit an obvious diffraction peaks at  $2\theta = 21.5^\circ$ , indicating that they display rather high crystallinity. When  $w = 30$  or 50, only a broad amorphous scattering peak has been observed. This trend is consistent with the DSC data. The  $\Delta H_m$ s and X-ray diffraction data indicate that as the content of the hard segments,  $w$ , increases, the crystallinity of the soft segments decreases considerably. This may be

due to the effect of the presence of the urethane groups, but the presence of the hard segments seems to play an important role.

The  $T_g$ s of block copolyesters increases significantly as the content of the hard segments,  $w$ , increases as shown in Table IV. This indicates that the amorphous parts of the soft segments are partially miscible with the hard segments. The partial miscibility between the soft and hard segments may also affect the crystallization of the soft segments. Thus, the crystallinity of the soft segments decreases considerably as the content of the hard segments increases.

## CONCLUSION

Hydroxy-terminated poly(pentamethylene 2,6-naphthalenedicarboxylate) oligomers, N5(R), have been prepared by melt polycondensation of dimethyl 2,6-naphthalenedicarboxylate with excess 1,5-pentanediol followed by elimination of some 1,5-pentanediol. Block copolyesters with hard segments of poly(pentamethylene 2,6-naphthalenedicarboxylate) and soft segments of poly(tetramethylene adipate) were pre-

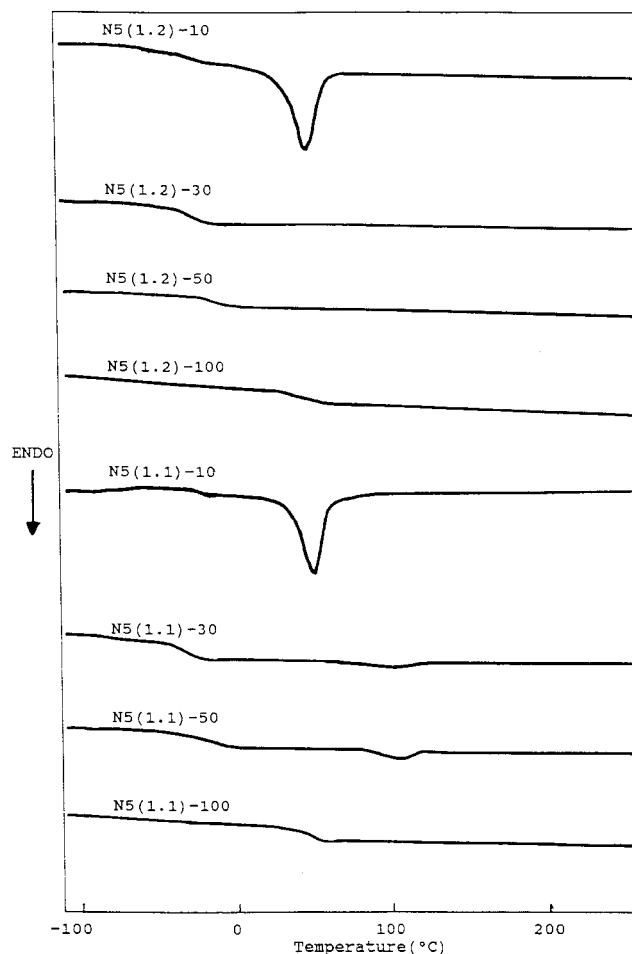


Figure 7 The DSC heating curves of N5(1.2)-ws, and N5(1.1)-ws.

TABLE IV  
The Thermal Transitions of the Block Copolyesters Determined by DSC

Sample	$T_g^S$ (°C)	$T_m^S$ (°C)	$\Delta H_m^S$ (J/g)	$T_g^H$ (°C)	$T_m^H$ (°C)	$\Delta H_m^H$ (J/g)
DP203-P	-43	48	54.4	—	—	—
N5(1.8)-10	-28	51	27.6	—	—	—
N5(1.8)-30	-20	—	—	—	—	—
N5(1.8)-50	2	—	—	—	—	—
N5(1.8)-100	—	—	—	59	—	—
N5(1.4)-10	-31	44	30.4	—	—	—
N5(1.4)-30	-27	—	—	—	—	—
N5(1.4)-50	-6	—	—	—	—	—
N5(1.4)-100	—	—	—	52	—	—
N5(1.2)-10	-27	46	35.2	—	—	—
N5(1.2)-30	-39	—	—	—	—	—
N5(1.2)-50	-41	—	—	—	—	—
N5(1.2)-100	—	—	—	49	—	—
N5(1.1)-10	-31	49	31.3	—	—	—
N5(1.1)-30	-32	—	—	—	—	—
N5(1.1)-50	-11	—	—	—	—	—
N5(1.1)-100	—	—	—	48	—	—

pared by coupling N5(R) and a poly(tetramethylene adipate)glycol with MDI in DMF.

The three low molecular weight oligomers, N5(1.8), N5(1.4), and N5(1.2), show rather high crystallinity,

but N5(1.1), which has higher molecular weight ( $M_n = 2313$ ), exhibits very low crystallinity as indicated by the DSC and X-ray diffraction data. However, all the MDI coupled oligomers, N5(R)-100s, are amorphous.

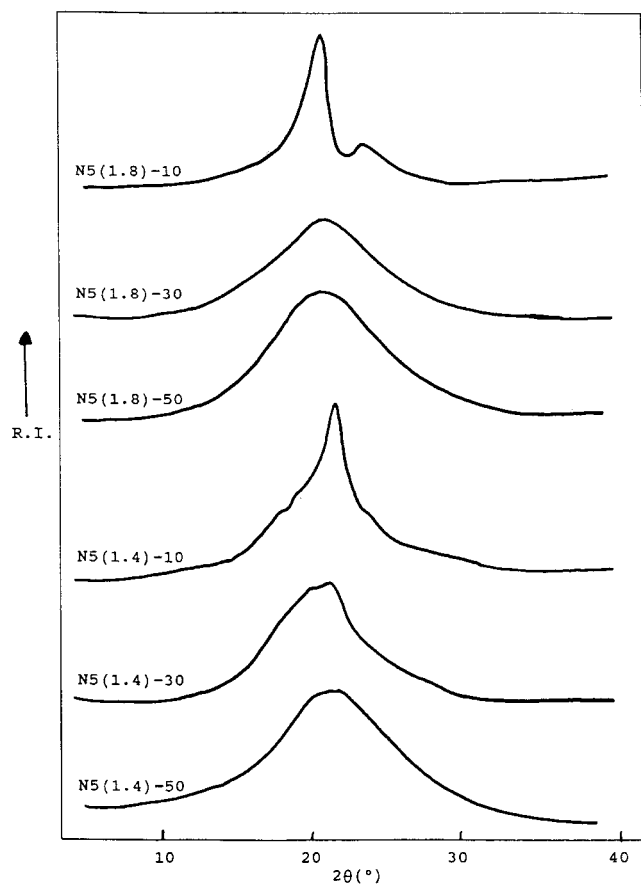


Figure 8 The X-ray diffraction patterns of N5(1.8)-ws, and N5(1.4)-ws.

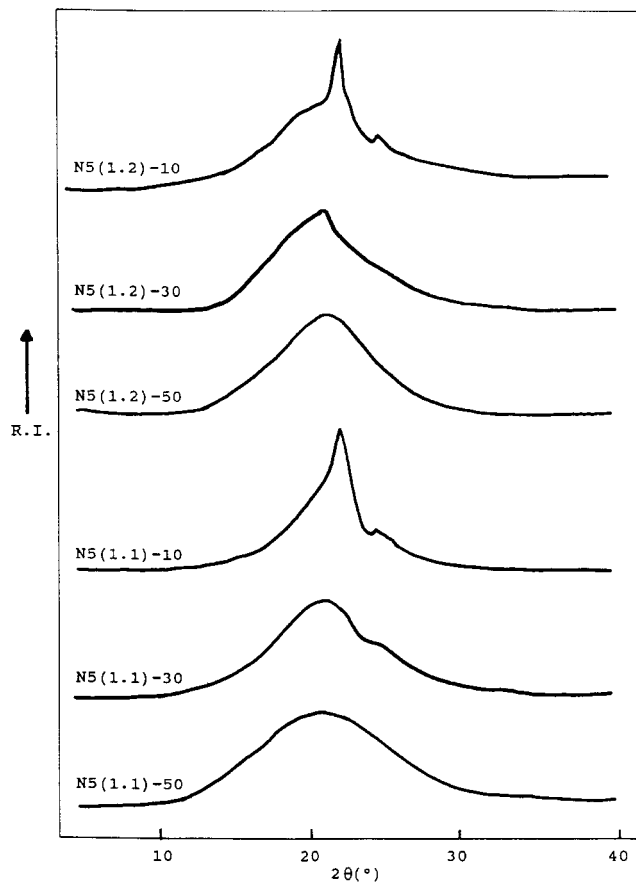


Figure 9 The X-ray diffraction patterns of N5(1.2)-ws, and N5(1.1)-ws.

The DSC and X-ray diffraction data show that the hard segments of the block copolyesters are amorphous possibly due to the effect of the presence of the urethane groups.

The thermal transitions of soft segments in the block copolyesters are strongly dependent on the composition. When the content of the hard segments increases, the  $T_g$  of the block copolyesters increases. Thus, the amorphous parts of the soft segments would be partially miscible with the hard segments. The soft segments of the N5(R)-10s show rather high crystallinity. But, as the content of the hard segments is about 30 wt % or more, N5(R)-30s and N5(R)-50s, the soft segments of the block copolyesters become amorphous. This is described as the effect of the presence of the hard segments that are partially miscible with the soft segments.

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