

Synthesis and Properties of Poly(ethylene-1,4-cyclohexanedimethylene naphthalate)

YIH-MIN SUN,¹ KUO-RUN HSU,¹ CHUN-SHAN WANG²

¹ Department of Industrial Safety and Hygiene, China Junior College of Medical Technology, Tainan, Taiwan, 701, Republic of China

² Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan, Republic of China

Received 19 April 1997; accepted 22 June 1997

ABSTRACT: Copolyesters were synthesized from bis(hydroxyethyl) naphthalate/bis-(hydroxymethylcyclohexane)naphthalate (BHEN/BHCN) with various compositions. Copolyesters having intrinsic viscosities of 0.58–0.65 dL/g were obtained by melt polycondensation in the presence of metallic catalysts. The optimum condition for polyethylene-1,4-cyclohexanedimethylene naphthalate (PECN) copolyester manufacturing is the transesterification under a nitrogen atmosphere for 4 h at a temperature of 245 ± 5°C followed by polymerization under 2 mmHg for 50 min at a temperature of 290–320°C. Most copolyesters have better thermal stability than has poly(ethylene naphthalate) (PEN) and the effect of the cyclohexane–dimethylene structure on the thermal and crystalline properties of the resulting copolyesters was investigated using differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). Glass transition temperatures of the copolyesters were in the range of 115.2–138.4°C, and 10% weight losses in nitrogen were all above 453°C. The solubility, crystallinity, and moisture absorption of the copolyesters were also investigated. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 67: 2245–2252, 1998

Key words: poly(cyclohexanedimethylene naphthalate); poly(ethylene naphthalate); copolyesters; melt polycondensation; physical properties

INTRODUCTION

Engineering plastics have found wide applications in automobile, precision instruments, electronics, other electrical uses, and communications.^{1–4} However, the requirements of superior performance in heat and chemical resistance, flame retardance, and electrical, optical, and mechanical properties are getting very strict. In the past, the study of high-performance engineering

plastics was centered on the benzene ring structure. The newly developed high-performance poly(alkylene naphthalates) (PAN) with their superior physical, mechanical properties, and processability have caught the world's attention. The most important feature of PAN polymers is the increased stiffness of the polymer chains due to the presence of the naphthalene ring instead of the benzene ring in poly(alkylene terephthalate) (PAT).

Of the PANs studied, polyethylene-2,6-naphthalate (PEN) and polybutylene-2,6-naphthalate (PBN) have exhibited superior thermal, mechanical, barrier, and chemical resistance properties relative to, for example, polyethylene-1,4-terephthalate (PET) and polybutylene-1,4-terephthalate (PBT).⁵ For this reason, much research is

Correspondence to: C.-S. Wang.

Contract grant sponsor: National Science Council of the Republic of China; contract grant number: NSC84-2622-E006-007.

Journal of Applied Polymer Science, Vol. 67, 2245–2252 (1998)
© 1998 John Wiley & Sons, Inc. CCC 0021-8995/98/132245-08

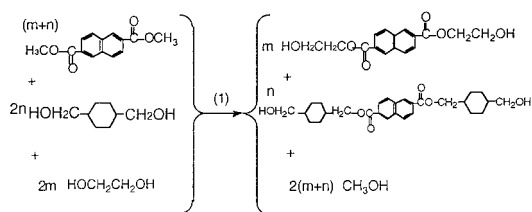
currently underway to develop commercial applications for these new high-performance polyesters.

Although PEN and PBN have superior physical and mechanical properties to those of PET and PBT, their high price still remains to be overcome; otherwise, they will be limited to specialty applications. We have already reported on the preparation and characterization of copolyesters derived from bis(hydroxyalkyl)naphthalate and bis[4-(2-hydroxyethoxy)]aryl compounds.⁶ The physical properties of PAN were successfully modified by the introduction of the aryl ether linkage and the bulky pendant group, while the raw material cost was reduced by choosing an inexpensive comonomer, such as bisphenol A.

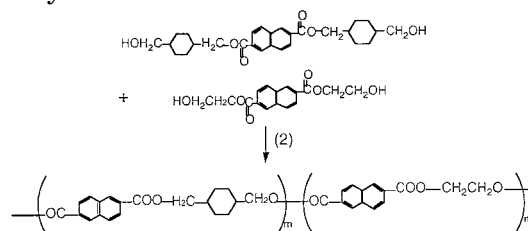
However, these polyester resins are noncrystalline or exhibit such a low crystallization rate as not to attain complete crystallization in injection-molding applications even if they are crystalline, that is, they gradually crystallize in service under high-temperature conditions to lower physical properties. This results in poor dimensional stability which is unsuitable for injection molding. We are attempting to develop a material which has excellent heat resistance and such a high crystallization rate as to be free from postprocessing changes. In the present study, a novel heat-resistant polyester resin which has excellent heat resistance, high crystallinity, and a high crystallization rate was prepared by copolymerizing 1,4-cyclohexanedimethanol and ethylene glycol with 2,6-dimethylnaphthalate.

Transesterification is generally the preferred synthesis for PECN.⁷⁻⁹ There are two steps in the preparation of PECN: The first is the formation of 2,6-bis(hydroxyethyl)naphthalate (BHEN) and bis(hydroxymethylcyclohexane)naphthalate (BHCN), respectively, from the transesterification of 2,6-dimethylnaphthalate (DMN) with ethylene glycol (EG) or cyclohexanedimethanol (CHDM); the second is PECN formation from the polycondensation of the BHEN and BHCN mixture at elevated temperature and reduced pressure. The reaction schemes are shown below:

1. Ester interchange or transesterification:



2. Polycondensation:



EXPERIMENTAL

Raw Materials

2,6-Dimethylnaphthalate (DMN; Amoco) is a commercial product and was used without further purification. 1,4-Cyclohexanedimethanol (CHDM; Janssen, *trans/cis* ratio: 7/3), and ethylene glycol (EG; Ferak) were reagent grade and used without further purification. Solvents used for the determination of solubility, tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), and pyridine, were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. $\text{Ti}(\text{O}i\text{Bu})_4$ and Sb_2O_3 were commercial products (guaranteed reagent grade) and were used without further purification. Phenol (Ferak) and tetrachloroethane (Merck), employed for the determination of solubility and intrinsic viscosity measurements of the polymers, were also used without purification.

Instrumentation

Elemental analyses were performed with a Heraeus CHN-O-Rapid elemental analyzer. FTIR spectra were recorded with a Nicolet 5DX-B spectrophotometer. Mass spectra were recorded with a VG 70-250s GC/MS. Intrinsic viscosities were obtained using an Ubbelohde capillary viscometer (Schott-AVS310). Melting points of BHEN and BHCN were determined with a polarizing microscope (Laboratory Devices MEL-TEMP II). The thermal behavior of each polymer was studied on a DuPont 910 DSC and 951 TGA. ¹H-nuclear magnetic resonance (NMR) was performed in CF_3COOD at 50°C. The wide-angle X-ray measurements were performed at room temperature with powdered specimens with Rigaku Geiger Flex D-Max/IIIa X-ray diffractograms, using Ni-filtered $\text{CuK}\alpha$ radiation (40 kV, 15 mA); the scanning rate was 2° min⁻¹. The degree of crystallinity for the powder polymer was estimated from the

ratio of the crystalline and amorphous area in the X-ray diffractograms.

Syntheses of BHEN and BHCN Compounds

BHCN was prepared from DMN and CHDM by the modified method (modification in catalyst and reaction condition) of Lin and Baliga.¹⁰ BHEN was synthesized from DMN and EG following the method described in the previous report.⁸ The purified BHCN and BHEN monomers were analyzed by elemental analyses, mass spectra, IR spectra, and melting points.

BHEN: mp 129–131°C (ref. 10: 128–130°C). BHCN: mp. 187–188°C; IR (KBr) cm^{-1} : 3450 (OH), 3045 (aromatic C—H), 2900 (alkyl C—H), 1700 (C=O), 1600 (aromatic C—C), 1150 (C—OH); mass spectrum EI *m/e* intensity (%): 468 (20, M^+). ANAL. Calc for $\text{C}_{28}\text{H}_{36}\text{O}_6$: C, 71.80%; H, 7.67%; O, 20.53%. Found C, 71.90%; H, 7.67%; O, 20.43%.

Preparation of Copolyesters

The monomers synthesized above were mixed in various mol ratios for copolymerization reactions. Besides the esterification between BHEN and BHCN, the polycondensation of BHEN (or BHCN) itself could occur at the same time to give a random copolymer [eq. (2)]. A mixture of BHEN/BHCN (0.4 mol) and the catalyst (8×10^{-5} mol) were introduced into a 250 mL four-neck flask fitted with a reflux condenser, a thermometer, a gas inlet, a gas outlet, and a mechanical stirrer. The reaction mixture was heated to $245 \pm 5^\circ\text{C}$ and maintained at that temperature for 90 min under dry nitrogen. The temperature was increased to 265°C and stirring was continued for 30 min. The pressure of the reaction system was gradually reduced first to 180–200 mmHg over the course of 20 min. Over the course of another 10 min, the pressure was further reduced to 1–3 mmHg and the reaction was increased to the final temperature of $290\text{--}320^\circ\text{C}$. The polymerization was carried out isothermally at this temperature for the required period of time with simultaneous removal of EG and other volatiles by distillation. Finally, the pressure was returned to normal atmospheric pressure using nitrogen to prevent degradation by oxidation. Light amber-colored copolymers were obtained.

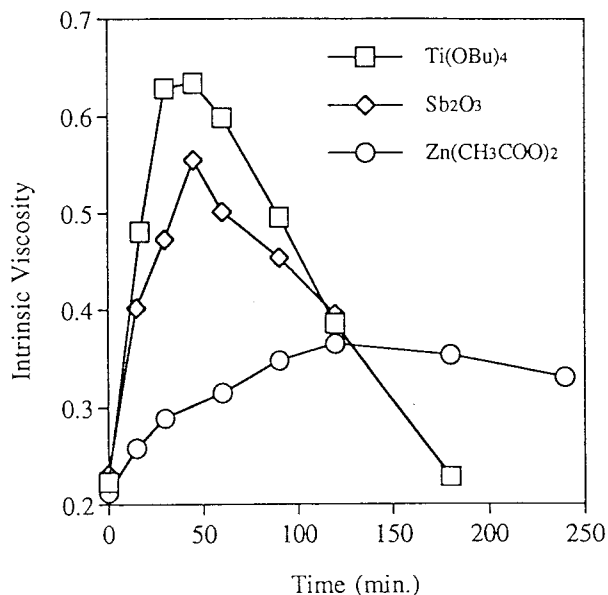


Figure 1 Time-intrinsic viscosity curve for the polycondensation of BHEN-BHCN (50 : 50).

Solubility Test

The solubilities of these polymers were determined by adding polymer (1–2% by weight) to the desired solvent in a test tube. The tube was left standing for 24 h to observe whether the polymer dissolved. When the polymer did not completely dissolve at room temperature, the test tube was heated and cooled. The polymer was defined to be soluble when no polymer precipitated after the tube was cooled.

Intrinsic Viscosity Determination

Intrinsic viscosities of the polymers were measured using an Ubbelohde viscometer. A polymer sample (0.06 g) was accurately weighed (± 0.001 g) and dissolved in 25 mL of a symmetric tetrachloroethane-phenol mixture (2 : 3 w/w). The solution was maintained at 120°C for 20–25 min to achieve complete solution of the polymer in the solvent. The solution was then cooled to room temperature and filtered through a $0.45\text{-}\mu\text{m}$ disposable membrane filter (cellulose acetate). Using the viscometer at 30°C , the intrinsic viscosity was calculated from the relative viscosity.¹¹

Thermal Analysis

To compare the rate of crystallization, the sample (10 mg) was heated at a rate of $320^\circ\text{C min}^{-1}$ to the

desired temperature (330°C) to ensure complete melting, then slowly cooled (5°C min⁻¹) to the room temperature. The temperature at which crystallization began (T_c) was monitored with a DuPont 910 DSC apparatus under nitrogen.

In addition, the crystallization half-time ($t_{1/2}$, the time required at 240°C to evolve one-half of the heat of crystallization) was measured as follows: About 10-mg quantities of the copolymer samples were heated at a rate of 320°C min⁻¹ to 330°C. The samples were held at that temperature for about 10 min to melt all crystalline nuclei before cooling very rapidly to room temperature, then reheated at a rate of 320°C min⁻¹ to 240°C and held at that temperature for the remainder of the test.

Determination of the Moisture Absorption of Copolyesters

Disk samples [3 mm (T) × 20 mm (D)] were dried under a vacuum at 120°C until the moisture had been expelled. The samples were put inside a dry box for cooling. After being weighed, the samples

were placed in boiling water (100°C) for 72 h and then weighed again. The moisture absorption was calculated as percent weight gain = $[(W/W_0) - 1] \times 100\%$, where W is the weight of the copolymer sample after standing at 100°C water for 72 h and W_0 is the weight of the copolymer sample after drying under a vacuum at 120°C.

RESULTS AND DISCUSSION

Characterization of BHCN and BHEN

Both monomers were synthesized under the most preferred conditions, with the results summarized in the Experimental section. A polarizing microscope was used to determine the melting points of BHCN and BHEN. The sharp melting points indicated that the monomers were pure.

The results of elemental analyses of these monomers agreed well with the assigned structures. Electron impact-induced fragmentation patterns at 30 eV were obtained. Prominent peaks

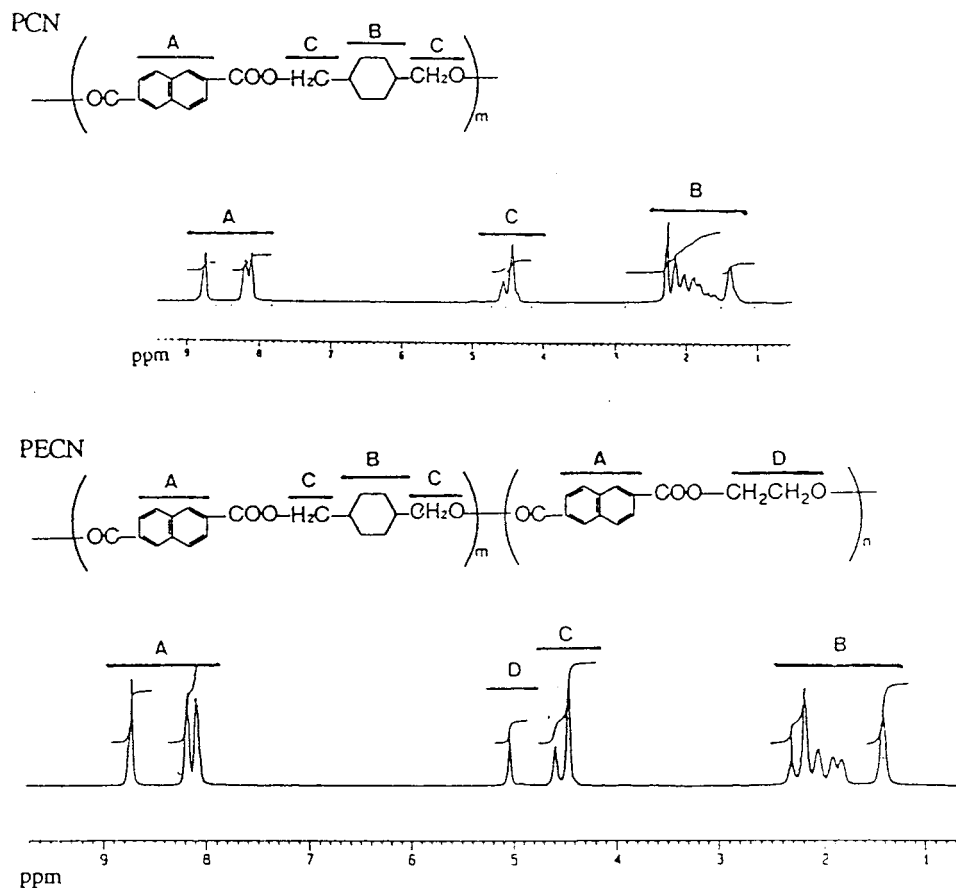


Figure 2 ¹H-NMR spectra of the homopolymer PCN and 1 : 1 copolymer.

observed in the mass spectra and the infrared spectra are included in the Experimental part which confirms the assigned structures.

Syntheses of Copolyesters

In search of the optimum reaction time required for polycondensation, a 50/50 mol ratio of BHEN/BHCN and final reaction temperatures of 300°C were chosen. Because of the low solubility of these polymers in common solvents for molecular weight determination, an assumption was made that the copolymers all have the same hydrodynamic volume, and intrinsic viscosity was used as the criteria in comparing growth of the molecular weight.

The results are plotted in Figure 1 and indicate that Sb_2O_3 and $\text{Ti}(\text{OBU})_4$ were more active catalysts than was $\text{Zn}(\text{CH}_3\text{COO})_2$. The optimum reaction times were all about 50 min. In comparison of the color of the polymers obtained with Sb_2O_3 or $\text{Ti}(\text{OBU})_4$ as the catalyst, the $\text{Ti}(\text{OBU})_4$ gave an undesirable yellow color and Sb_2O_3 was chosen as the catalyst for PECN synthesis.

Properties of Copolyesters

Structures of the copolymers were analyzed by FTIR spectra. Two strong aromatic absorptions appeared at 1600 and 1500 cm^{-1} due to the naphthalene and benzene rings along with prominent absorptions due to ester carbonyls (1680–1700 cm^{-1}) and methylene groups (2950 cm^{-1}). A strong hydroxy (—OH) absorption at 3450 cm^{-1} for the starting monomers (BHEN and BHCN) decreased as the reaction proceeded. The nearly complete overlap of the peaks for aromatic PCN/PEN systems in the FTIR spectra disqualified the use of this analytical tool for compositional analysis.

Figure 2 shows the $^1\text{H-NMR}$ spectra of the homopolymer PCN and copolymer PECN (BHEN : BHCN = 50 : 50). The comonomer contents (EG/CHDM) in the copolymers were determined by $^1\text{H-NMR}$ and are plotted against the comonomer contents in the feed in Figure 3. The EG comonomer contents in the copolymers were considerably smaller than those in the feeds. The reason may be that EG is more volatile than is CHDM during the condensation step.

The TGA curves of all polymers exhibited a 10% weight loss (T_d) at 453–461°C and a residual weight (RW) at 530°C of 25–39% in nitrogen. Their thermal stability increased with increase in CHDM content as shown in the TGA data of Table I.

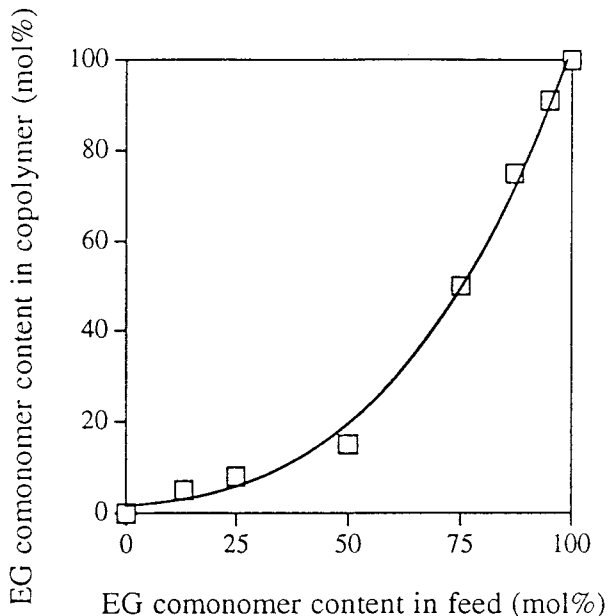


Figure 3 Change of copolymer composition with polymerization.

The T_g of the polymers evaluated by DSC are also tabulated in Table I. The T_g of PCN is 138.3°C, which is 23.1°C higher than that of PEN (115.2°C). All copolymers showed single T_g values between those of the two homopolymers, which increased monotonically with increase in the CHDM content. The higher T_g 's and better thermal stability of the copolyesters over PEN should be ascribed to the existence of bulky and thermally more stable cyclohexylene groups in the main chain. Figure 4 is a plot of the T_g and T_m of the copolymers against the CHDM content in the copolymer. The copolyesters have melting points when the content of CHDM is larger than 85 mol%. However, between EG/CHDM = 75/25 and 50/50, the copolymers were amorphous with single T_g 's and no T_m 's.

Figure 5 shows the DSC thermograms of the crystallization temperature (T_c) of the PECN copolymers from the melt state. The sample was heated rapidly to the desired temperature to ensure complete melting and then slowly cooled to room temperature. For all compositions except EG/CHDM = 75/25 and 50/50, it was observed that a single cold crystallization temperature (T_c) occurred at 220–280°C depending upon the EG and CHDM contents. T_c increased with the CHDM content in the copolymer from EG/CHDM = 50/50 ($T_c = 0$) to the homopolymer PCN ($T_c = 280^\circ$). The relationship should be attributed to

Table I Thermal Properties of PECN

Polymer Code	Feed Ratio BHEN : BHCN	Composition of Polymer EG : CHDM	T_m (°C)	T_g (°C)	T_d^a (°C)	RW (%) ^b	$[\eta]$ (dL/g)
PEN	100 : 0	100 : 0	267.1	115.2	453.3	33	0.578
	95 : 5	91 : 9	261.5	117.3	453.9	29	0.581
	87 : 13	75 : 25	— ^c	122.4	455.4	27	0.573
	75 : 25	50 : 50	—	124.3	458.6	25	0.617
PECN	50 : 50	15 : 85	301.9	130.8	460.6	27	0.621
	25 : 75	8 : 92	311.2	134.1	461.6	35	0.633
	13 : 87	5 : 95	315.8	135.2	463.6	33	0.654
PCN	0 : 100	0 : 100	320.2	138.4	465.1	39	0.584

^a A 10% weight-loss temperature observed by TGA at a 20°C/min heating rate in nitrogen.

^b Residual weight at 530°C in nitrogen.

^c —, Amorphous, no T_m .

the existence of the easily crystallizable CHDM unit. The slight decrease in T_c for EG/CHDM = 91/9 is ascribed to the eutectic phenomenon as reported in ref. 12. The degree of crystallinity and the half-time of crystallization for various composition copolymers are tabulated in Table II. CHDM had a significant effect on the PECN crystallization rate and crystallinity.

X-ray diffraction is a good tool to define the behavior of the crystallization of copolyesters. The melting temperature for variant-composition copolyesters in Table I can therefore be explained by X-ray diffractograms. The WAXS curves of the PECN copolymers are given in Figure 6. Figure 6 shows the WAXS curves of the PECN copolymers heat-treated at 240°C for 90 min. The crystallinity

of the copolymers increased with increase in CHDM content of the polymers except for copolymers with EG/CHDM between 75/25 and 50/50.

The solubilities of the copolymers were determined using powdery specimens in various solvents at ambient temperature, and the results are summarized in Table III. The homopolyesters (PEN, PCN) had the poorest solubility as they dissolved only partially in 1,1,2,2-tetrachloroeth-

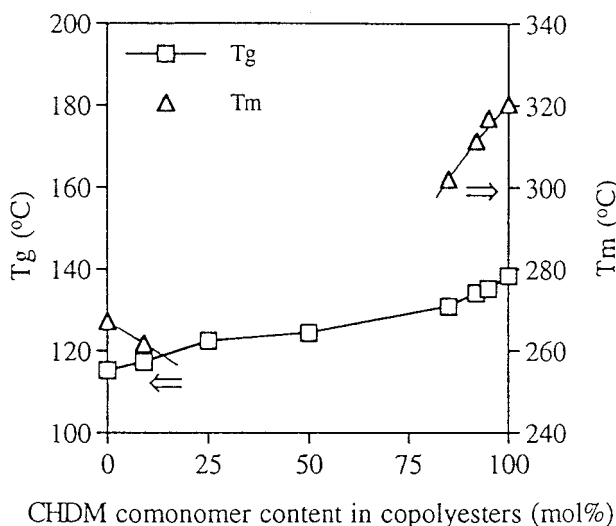


Figure 4 Glass transition temperature (T_g) and crystalline melt point (T_m) versus CHDM content in reactants.

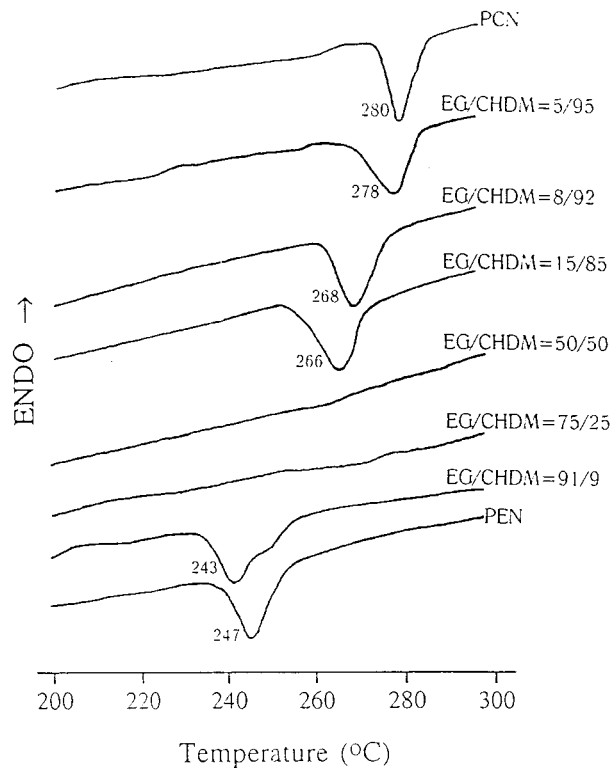


Figure 5 DSC traces indicating T_c of PECN copolymers.

Table II Degree of Crystallinity and Crystallization Half-time for PECN Copolymers

Polymer Code	Composition of Polymer EG : CHDM	DC ^a (%)	$t_{1/2}$ (s)
PEN	100 : 0	45.6	44
	91 : 9	42.5	63
	75 : 25	— ^b	—
PECN	50 : 50	—	—
	15 : 85	52.2	35
	8 : 92	56.9	29
PCN	5 : 95	59.4	27
	0 : 100	65.1	24

^a Degree of crystallinity estimated from X-ray diffractograms.

^b —, Amorphous.

ane on heating. The solubilities of the copolyesters improved dramatically for those amorphous copolymers in solvents such as *m*-cresol, pyridine, and tetrachloroethane. Another interesting phe-

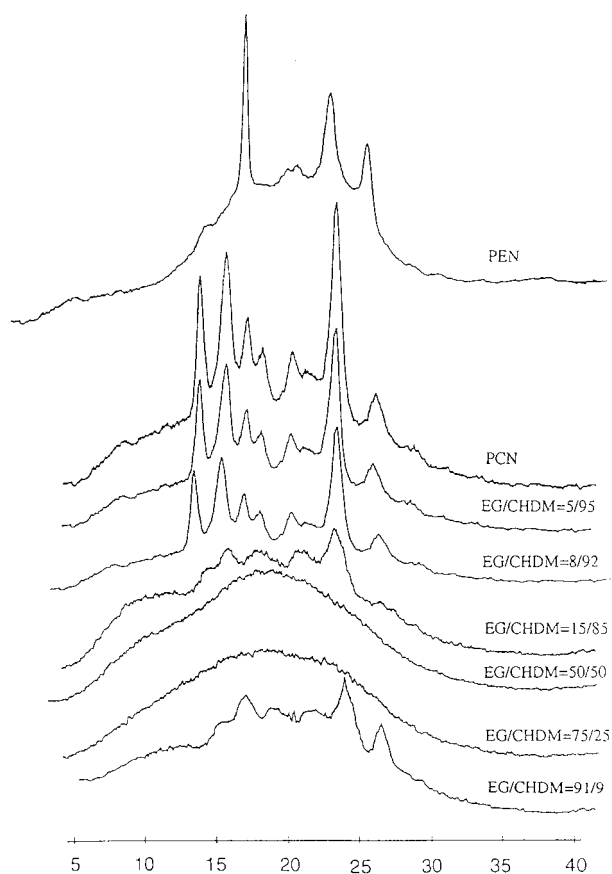


Figure 6 WAXS diffraction intensity profiles of copolyesters with different copolymer compositions (heat-treated at 240°C for 1.5 h).

Table III Solubilities of PECN

Solvent ^a	PEN	PECN	PECN	PECN	PECN	PECN	PECN	PECN	PECN	PECN
	EG : CHDM 100 : 0	EG : CHDM 91 : 9	EG : CHDM 75 : 25	EG : CHDM 50 : 50	EG : CHDM 15 : 85	EG : CHDM 8 : 92	EG : CHDM 5 : 95	EG : CHDM 0 : 100	EG : CHDM 0 : 100	EG : CHDM 0 : 100
DMAC	—	—	—h	—	—	—	—	—	—	—h
DMF	—	—	—h	—	—	—	—	—	—	—
DMSO	—	—	—	—	—	—	—	—	—	—
THF	—	—	—	—	—	—	—	—	—	—
<i>m</i> -Cresol	—	—	++	++	—h	—h	—	—	—	—
Pyridine	—	—h	—h	—h	—h	—	—	—	—	—
CHCl ₃	—	—	++	++	—	—	—	—	—	—
C ₂ H ₂ Cl ₄	—h	—h	++	++	—h	—h	—h	—h	—h	—h

(++) Soluble at room temperature; (+h) soluble on heating; (—h) partially soluble on heating; (—) insoluble.

^a DMAC: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran.

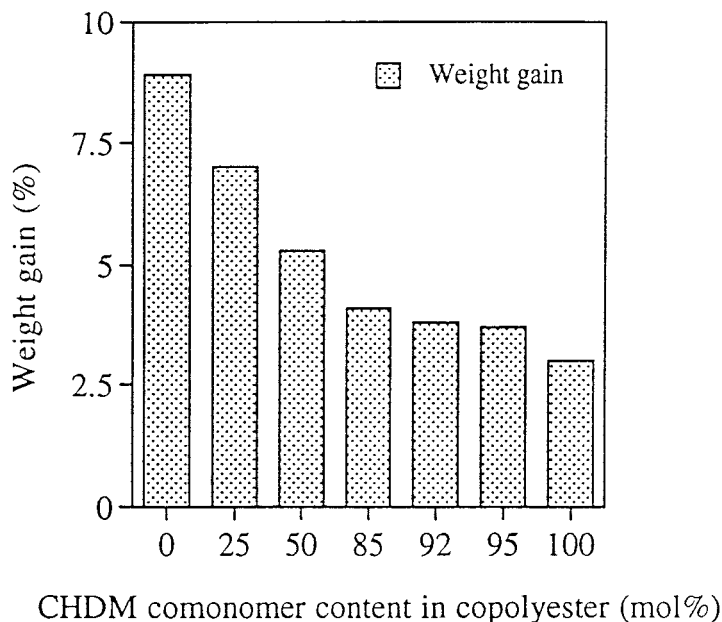


Figure 7 Moisture absorption for various compositions (100°C, 72 h in water).

nomenon observed from Table III is that the enhanced solubility depended greatly on their random composition, which makes it more difficult to form crystalline domains.

Disk-shaped samples [3 mm (T) \times 20 mm (D)] were fabricated from copolyesters and placed into 100°C boiling water for 72 h. The weight gains from this moisture absorption test are shown in Figure 7. Moisture absorption decreased monotonically with increase in the CHDM content.

CONCLUSIONS

A series of PECN copolyesters were synthesized through melt polycondensation of BHEN and BHCN. Generally, Sb_2O_3 was the best catalyst for the synthesis with the reaction at 4 h and $240 \pm 5^\circ C$ for the transesterification, followed by 2 mmHg for 50 min at 290–320°C for the polycondensation to yield a good copolymer.

The copolymers generally showed higher solubility, less moisture absorption, and greater thermal stability than did PEN, while the crystallinity increased with increasing CHDM content (>85%). These copolymers would be expected to have commercial applications and be suitable for injection molding.

Financial support of this work by the National Science

Council of Republic of China is gratefully appreciated (NSC84-2622-E006-007).

REFERENCES

1. I. N. Duling, U.S. Pat. 3,436,376 (1969); A. A. Browne and I. E. McIntyre, 3,842,040 (1974); K. Y. Lee, B. H. Cho, and Y. W. Kim, 5,294,695 (1994).
2. K. Yuki, Ed., *Saturated Polyester Resin Handbook*, Nikan Industrial, Tokyo, Japan.
3. T. Tahoda, A. Hamano, and K. Kuze, Jpn. Kokay 91-224,722 (1991) (to Toyobo Co. Ltd.); *Chem. Abstr.*, **116**, 61164s (1991).
4. M. K. Maintal, W. S. Rodenback, and U. T. Bruch Koebel, U.S. Pats. 5,198,530 (1993); C. C. Yau, 5,340,907 (1994).
5. C. S. Wang and Y. M. Sun, in *Polymeric Materials Encyclopedia*, J. C. Salamone, Ed. CRC Press, Boca Raton, FL, 1996.
6. Y. M. Sun and C. S. Wang, *J. Appl. Polym. Sci.*, **58**, 1189 (1995).
7. C. S. Wang and Y. M. Sun, *J. Polym. Sci. Part A Polym. Chem.*, **32**, 1305 (1994).
8. C. S. Wang and Y. M. Sun, *J. Polym. Sci. Part A Polym. Chem.*, **32**, 1295 (1994).
9. R. Benavente and J. M. Perena, *Macromol. Chem.*, **189**, 1207 (1988).
10. C. C. Lin and S. Baliga, *J. Appl. Polym. Sci.*, **31**, 2483 (1986).
11. M. V. Ram Mohan Rao and M. Yaseen, *J. Appl. Polym. Sci.*, **31**, 2501 (1986).
12. S. L. Sakellarides, *Plast. Eng.*, **Dec.**, 33 (1996).