Novel Copolyesters Containing Naphthalene Structure III. Copolyesters Prepared from 2,6-Dimethyl Naphthalate, Ethylene Glycol, and 2,2-Dialkyl-1,3-Propanediols

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ABSTRACT: Poly(ethylene naphthalate) (PEN) copolymers were prepared by melt polycondensation of dimethyl naphthalate and excess ethylene glycol with 5–40 mol % (in feed) of 1,3-propanediol or 2,2-dialkyl-1,3-propanediols, where the dialkyl groups are dimethyl, diethyl, and butyl-ethyl. No significant depression of reduced specific viscosity was observed. The comonomer contents in the copolymers are considerably higher than those in the feed. The effects of the copolymer composition on the structures of the films were investigated using thermal analyses, density measurements, X-ray diffraction methods, and other physical tests. The crystallinities and densities of heat-treated films decreased with increasing content of comonomer and length of alkyl side chain in the comonomer. The glass transition temperature (T_g) and melting temperature (T_m) were decreased by the copolymerization, while an increase in the length of the alkyl side chain hardly affected T_ms of the heat-treated films. Alkali resistance, moisture resistance, dye ability, and thermal shrinkage were increased by the incorporation of comonomer having an alkyl side chain. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 2754–2763, 2001

Key words: PEN copolymer; dialkyl propanediols; characterization

INTRODUCTION

Engineering plastics have found wide applications in automobiles, precision instruments, electronics, electrical applications, and communications.[1–4] However, the requirements of superior performance in heat and chemical resistance, flame retardancy, electrical, optical, and mechanical properties are becoming severe. Poly(ethylene 2,6-naphthalate)(PEN)[5–9] is one engineering plastic produced worldwide on a large industrial scale. The most important feature of PEN polymer is the increased stiffness of the polymer chains due to the presence of the naphthalene ring instead of the benzene ring in the poly(ethylene terephthalate)(PET). For this reason, much research is underway to develop commercial applications for the high-performance polyesters.[10–13]

Chemical modification of poly(ethylene naphthalate) (PEN) by incorporating various glycol or acid comonomers has been intensively investigated in the past with the aim of extending the use of PEN in new application fields. We have already reported on the preparation and characterization of copolyesters derived from bis(hydroxyalkyl)naphthalate and bis[4-(2-hydroxyethoxy)]aryl compounds[14] or bis(hydroxyethyl)-arylate and ethylene.[15] The physical properties of PEN were successfully modified, while choosing an inexpensive comonomer reduced the raw material cost.

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Gordon and Mera[16] reported on PET copolymers with 2,3-dialkyl-1,4-butanediols, where the dialkyl groups are longer than butyl, and studied the effect of varying length and amount of long alkyl side chains on copolymer composition, inherent viscosity, and thermal behavior (glass transition, melting, and side-chain crystallization). So, we report on the preparation and characterization of PEN copolymers with 2,2-dialkyl-1,3-propanediols, where the dialkyl groups are shorter than dibutyl. The thermal, physicochemical, and mechanical properties of the copolymers are studied to elucidate the effect of the short alkyl side chains on the structure and properties. We hope to improve the solubility and processability of PEN, without sacrificing its thermal properties.

EXPERIMENTAL

Monomers

Scheme 1 shows the structural formulae and codes of the comonomers. 2,2-Diethyl-1,3-propanediol (C_2C_2) and 2-butyl-2-ethyl-1,3-propanediol (C_2C_4), donated by Acros Corp., were used without further purification. 1,3-Propanediol (HH), 2,2-dimethyl-1,3-propanediol (CC), and dimethyl naphthalate (DMN) were used as received. Ethylene glycol was distilled under reduced pressure.

Preparation of Copolymers

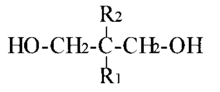
Copolymers were prepared by a melt polycondensation method. A mixture of dimethyl naphthalate (1 mol) and glycols (2.1 mol) with a small amount of zinc acetate (20×10^{-5} mol/mol DMN) and antimony trioxide (20×10^{-5} mol/mol DMN) as a catalyst were introduced into a 250-mL four-neck flask fitted with a reflux condenser, a thermometer, a gas inlet, a gas outlet, and a mechanical stirrer. The reaction mixture was heated at 190–195°C for 3 h in a stream of nitrogen gas, and further maintained for 1 h at 210°C, then increased to 245–250°C and heated for 1 h. 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 285–290°C. The polymerization was carried out isothermally at this temperature for 1.5 h. Finally, the pressure was returned to normal atmospheric pressure using nitrogen to prevent degradation by oxidation. Amber-colored copolymers were obtained.

Table I Intrinsic Viscosities[a] of Copolymers

Code	η (dL/g^{-1})	Code	η (dL/g^{-1})
PEN	0.54		
HH-5	0.4504	C_2C_2-5	0.6659
HH-10	0.4543	C_2C_2-10	0.5732
HH-20	0.5898	C_2C_2-20	0.7812
HH-40	0.7104	C_2C_2-40	0.4378
CC-5	0.5144	C_2C_4-5	0.6634
CC-10	0.4752	C_2C_4-10	0.4932
CC-20	0.6447	C_2C_4-20	0.5268
CC-40	0.4676	C_2C_4-40	0.4404

Numbers in the polymer code represent the comonomer content (mol %) in the feed.

[a] 0.06 g/25 mL in phenol/tetrachloroethane (60/40 wt %) at 25°C.



$$HO\text{-}CH_2\text{-}\underset{R_1}{\overset{R_2}{C}}\text{-}CH_2\text{-}OH$$

R_1	R_2	Code
H	H	HH
CH_3	CH_3	CC
C_2H_5	C_2H_5	C_2C_2
C_2H_5	C_4H_9	C_2C_4

Scheme 1

Film Preparation

Film was melt pressed (230–260°C, 2.5–3 h) between aluminum plates with an aluminum spacing plate of 200 μm thickness and then quenched into iced water. After dissolving off the aluminum plates in 10% hydrochloric acid, the film was washed with water and dried overnight at 70–80°C in vacuum.

Characterization

Intrinsic viscosity of the copolymer was measured using an Ubbelohde viscometer and was calculated from the relative viscosity by the Ram Mohan Rao equation.[17] ^{1}H-nuclear magnetic resonance (NMR) was performed in CF_3COOD at 50°C. Wide-angle X-ray scattering (WAXS) was performed at room temperature with Rigaku Geiger Flex D-Max/IIIa X-ray diffractograms, using Ni-filtered CuKα radiation (40 kV, 15 mA); the scanning rate was 2° min^{-1}. Density was mea-

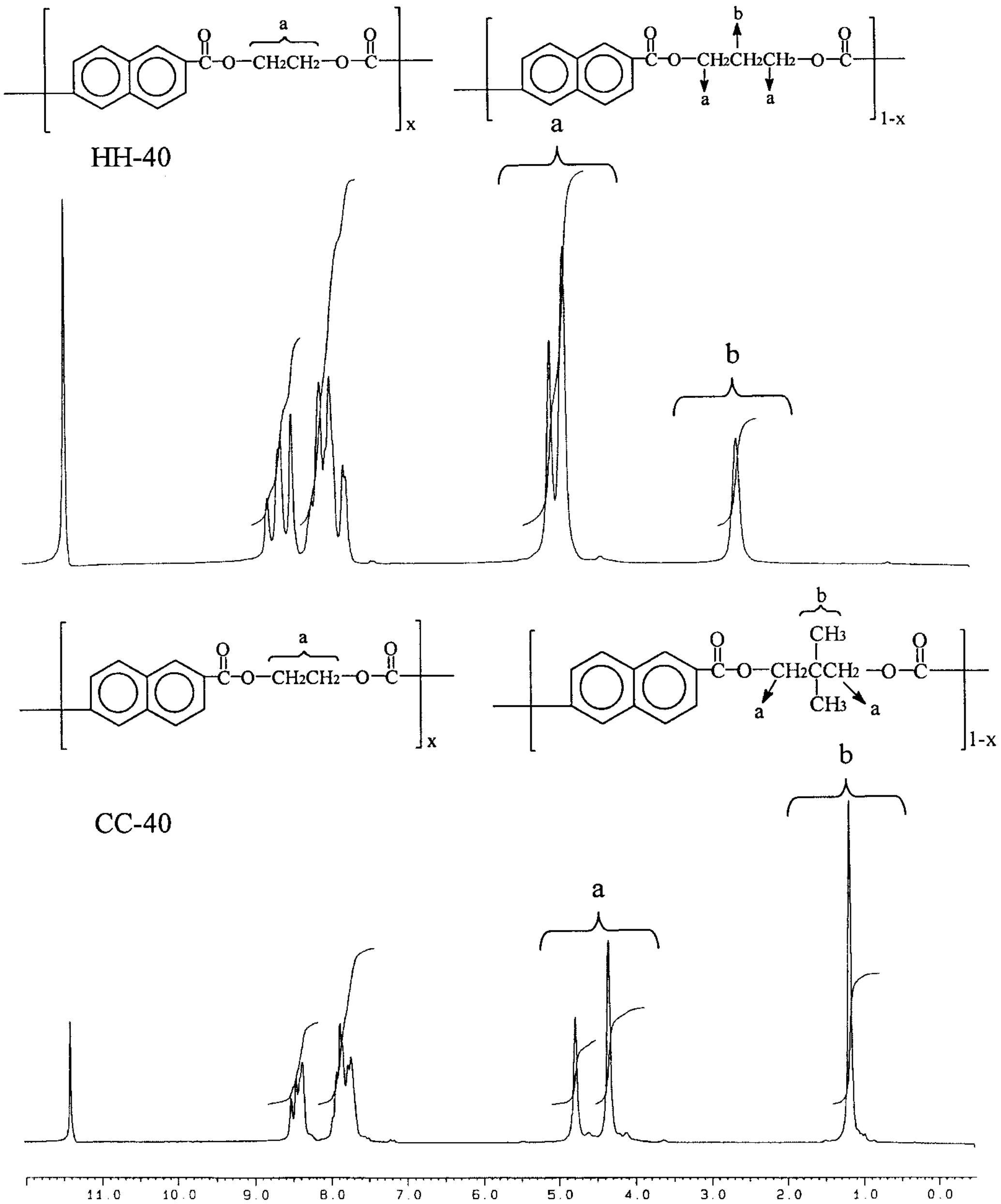


Figure 1 (a) ^{1}H-NMR spectra of copolyesters.

sured in a benzene–carbon tetrachloride density gradient column at 30°C. The thermal behavior of each copolymer was studied on a Perkin-Elmer DSC7 and TGA7. The solubilities of these copolymers were determined by adding polymer (1–2% by weight) to the desired solvent in a test tube. The tube was left to stand 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 has precipitated after the tube was cooled. Alkaline hydrolysis was carried out in a 10% NaOH aqueous solution at 70°C for 4 h. The moisture absorption was calculated as: percent weight gain = $[(W/W_0) - 1] \times 100\%$, where W is the weight of copolymer sample after standing at 100°C water for 24 h, and W_0 is the weight of copolymer sample after being dried under vacuum at 120°C. Dyeing was carried out in a dye bath of 1 g 1,4-diaminoanthraquinone (disperse dye) in 300 mL water at 80°C for 24 h. Thermal shrinkage was carried out in boiling water for 15 min.

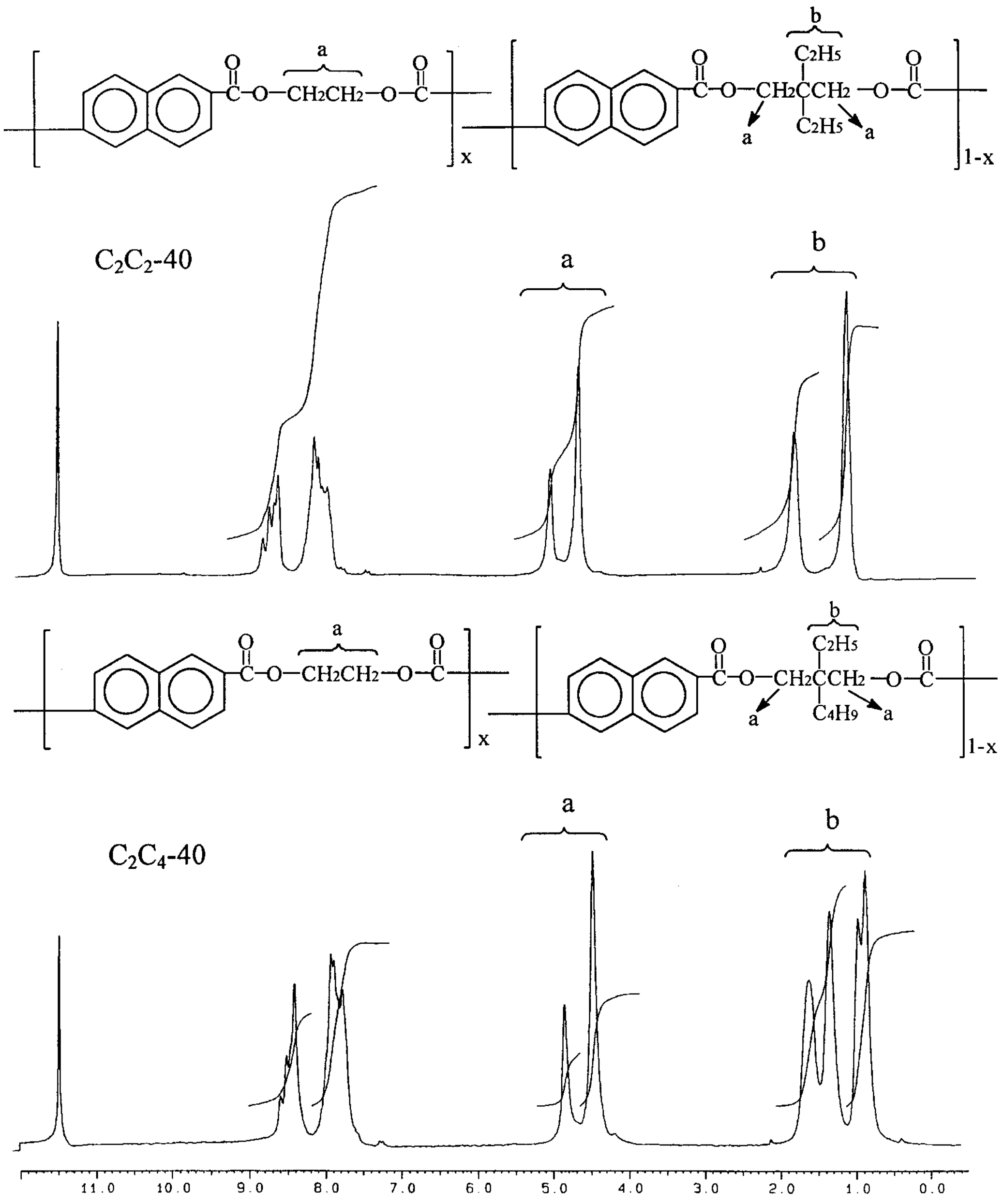


Figure 1 (b) ^{1}H-NMR spectra of copolyesters.

RESULTS AND DISCUSSION

Table I shows intrinsic viscosities $[\eta]$ of the copolymers prepared. The copolymerization does not provide significant depression of $[\eta]$, which suggests that the 2,2-substituted short alkyl side groups in propanediol hardly affect the reactivity of polymerization. On the contrary, 2,3-disubstituted long alkyl side groups in butanediol remarkably decreased the intrinsic viscosity of the copolymer.[16]

Figure 1(a) and (b) show the ^{1}H-NMR spectrum of copolyesters (HH40, CC40, $C_2C_2$40, and $C_2C_4$40). The comonomer contents in copolymers measured by ^{1}H-NMR are plotted against the comonomer contents in the feed in Figure 2. The comonomer contents in the copolymers are higher than those in the feeds. This may be explained as follows: the boiling point of ethylene glycol (196°C) is lower than 2,2-dialkyl-1,3-propanediol (above 200°C) and near reaction temperature (190–195°C), so ethylene glycol is more easily

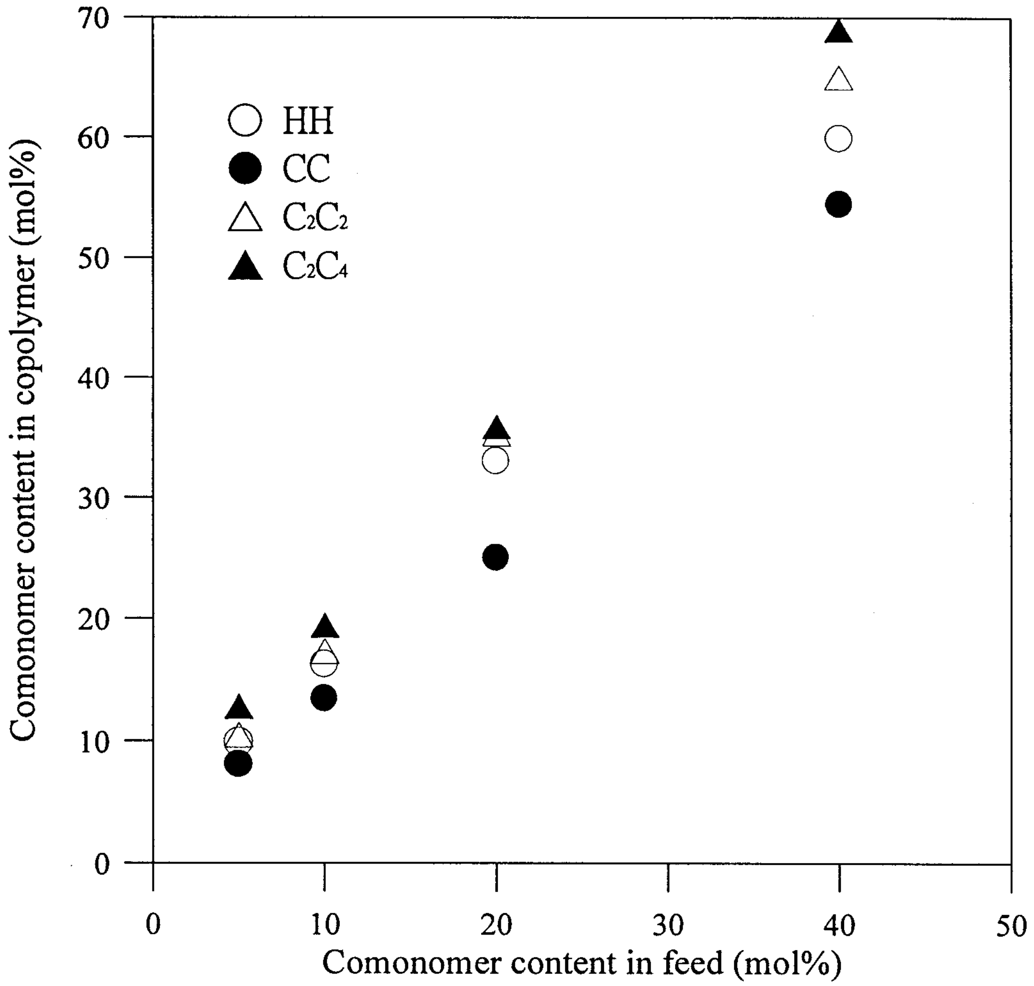


Figure 2 Change of copolymer composition by polymerization.

carried out by nitrogen gas than 2,2-dialkyl-1,3-propanediol, and so the PEN copolymers are enriched in 2,2-dialkyl-1,3-propanediol. Another interesting phenomenon is observed: the largest decrease in the comonomer content in copolymer CC could be ascribed to cyclization due to the methyl disubstituents[16] in addition to the increase of volatility of comonomer CC with smaller molecular weight. The sequence of distribution of copolyesters will be discussed in the future.

WAXS curves of all melt-pressed copolymer films gave rise to broad amorphous patterns, showing that all copolymers did not crystallize during the film preparation process. Figure 3 shows the WAXS curves of HH and C_2C_4 films heat treated at 190°C for 4 h. The WAXS patterns of CC films were similar to those of HH films but showed a small decrease in intensity, and those of C_2C_2 films were similar to those of C_2C_4 films but showed a small increase in intensity. In addition, copolymer film exhibited an extra crystalline peak at $2\theta = 17°$ owing to the presence of propandiol. It is found that the crystallinity of the heat-treated films decreases with increasing content of comonomer and length of the alkyl side chain in the comonomer; thus C_2C_2 and C_2C_4 20–40 films are hardly crystallized by the heat treatment.

The comonomer contents in copolymers are plotted against the densities of melt-pressed and heat-treated films in Figure 4. The density of melt-pressed films decreases with increasing length of alkyl side chain and content of comonomer. Almost all the melt-pressed films (except for HH5 and HH10) have densities smaller than the amorphous density of 1.325 g cm^{-3} for the PEN homopolymer.[18] Heat treatment causes the increase of density and thus the degree of crystallinities (X_c) [calculated by the eq. (1)] are 8 and 46% for the melt-pressed and heat-treated PEN homopolymer films, respectively

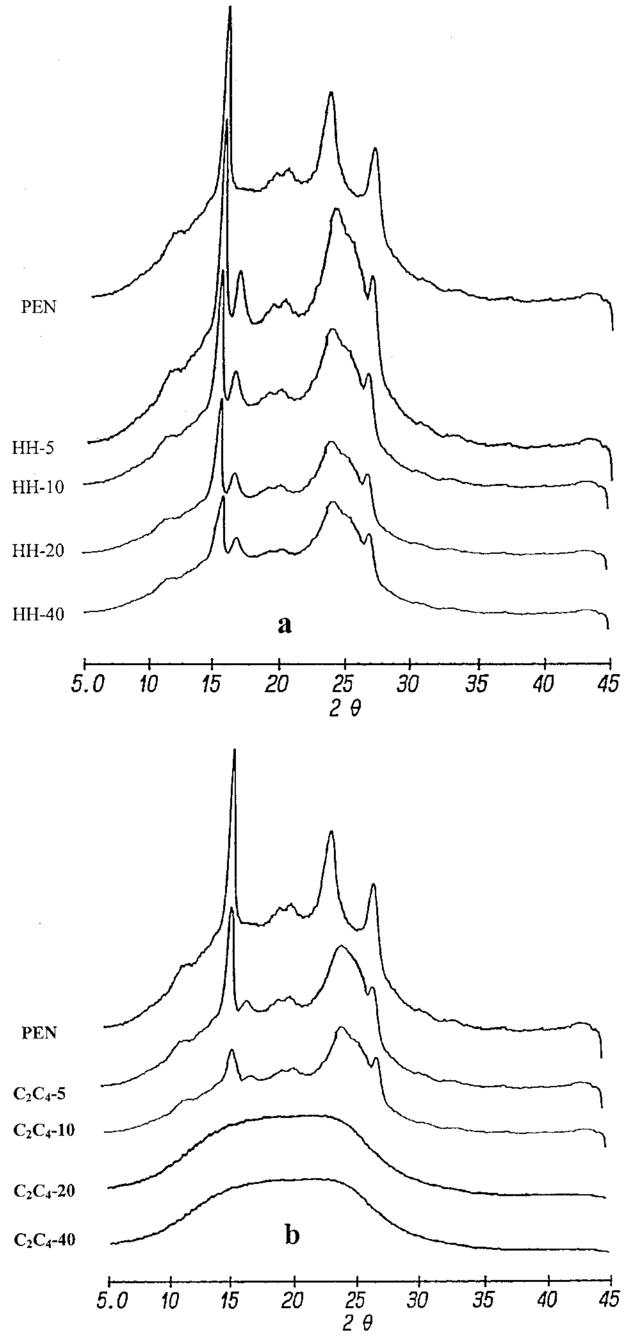


Figure 3 WAXS curves for (a) HH and (b) C_2C_4 films heat treated at 190°C for 4 h.

$$1/d = X_c/d_c + (1 - X_c)/d_a \quad (1)$$

where d_c is the crystal density (1.407 g cm^{-3})[19] and d_a is the amorphous density (1.325 g cm^{-3}).[18] The heat treatment hardly increases the densities of C_2C_2 and C_2C_4 20–40 films, which corresponds well to the results of WAXS. This result suggests that the increase of steric hindrance due to the longer alkyl side chains considerably suppress the crystallization of PEN chains.

Figures 5 and 6 show the DSC curves of melt-quenched samples for HH and C_2C_4 copolymers. The DSC curves of melt-quenched samples for CC and C_2C_2 copolymers are similar to those for HH and C_2C_4 copolymers, respectively, with small variations. Glass transition temperature (T_g) decreases, crystallization temperature (T_c) increases, and melting temperature (T_m) decreases with increasing content of comonomer and length of alkyl side chain. The T_c and T_m peaks disappear at a comonomer content in the

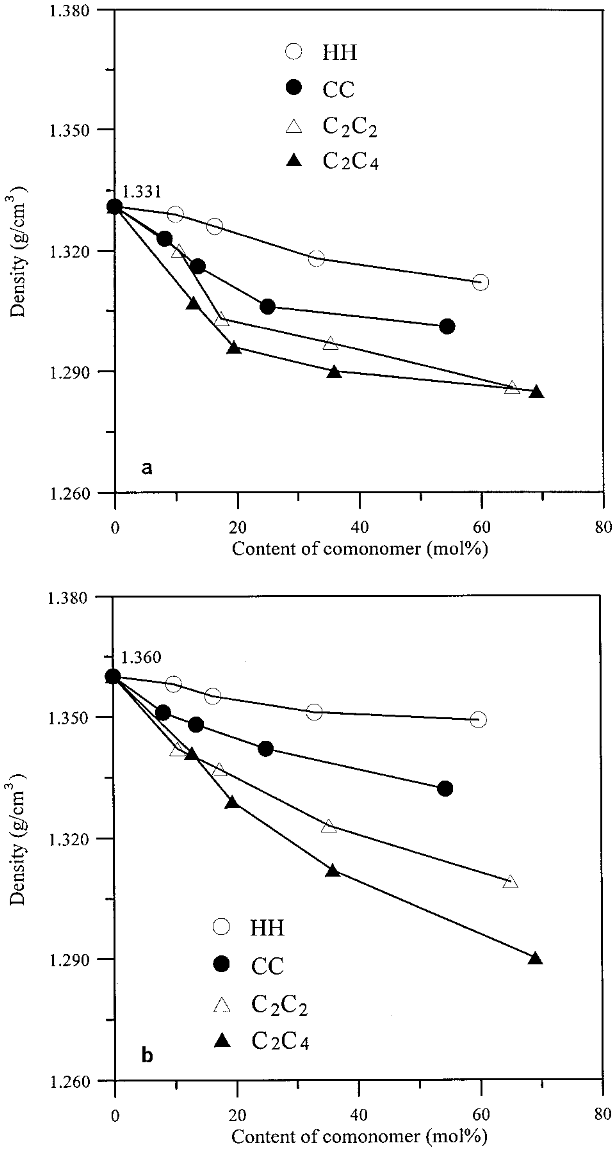


Figure 4 Change of density with copolymer composition for (a) melt-press films and (b) heat-treated films at 190°C for 4 h.

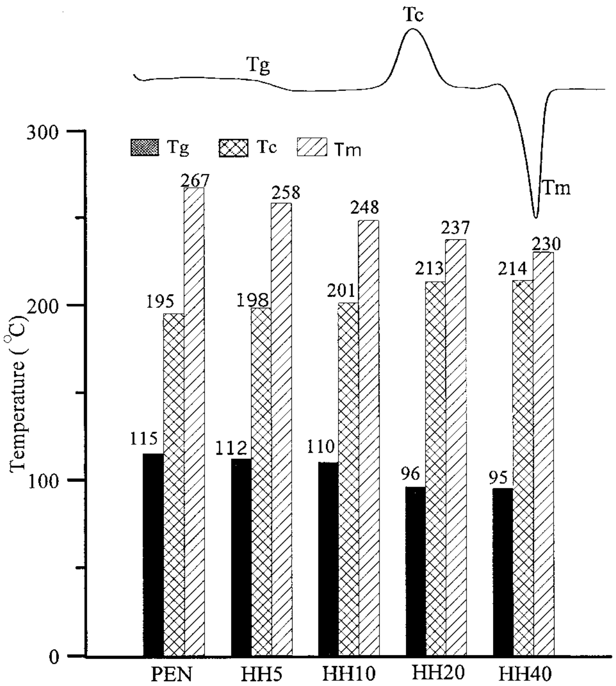


Figure 5 Phase transition temperature (T_g, T_c, and T_m) of melt-quenched samples for the HH copolymer.

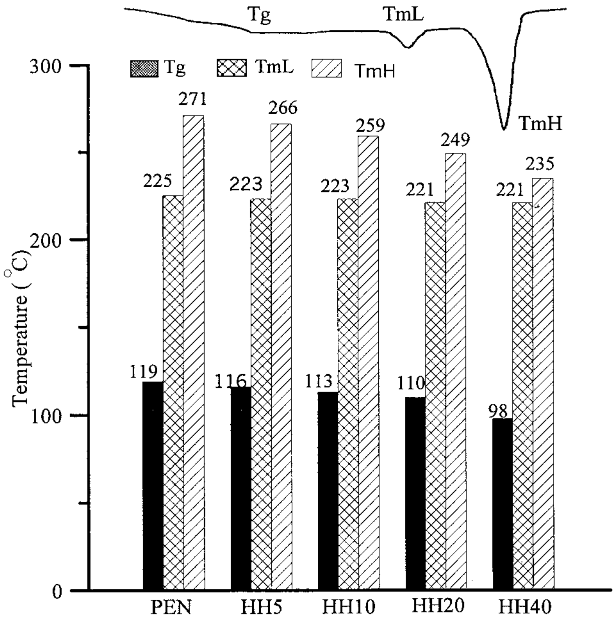


Figure 7 Phase transition temperature (T_g, T_{mL}, and T_{mH}) of heat-treated samples for the HH copolymer.

feed above 20 mol % for C_2C_2 and C_2C_4 copolymers, suggesting that these copolymers do not crystallize during the heating run on the DSC.

Figures 7 and 8 show the DSC curves of heat-treated samples for HH and C_2C_4 copolymers. The DSC curves of heat-treated samples for CC and C_2C_2 copolymers are similar to those for HH and C_2C_4 copolymers, respectively, with small variations. Glass transition temperature (T_g) decreases with increasing the content of the comonomer and length of the alkyl side chain. Similar multiple melting peak behavior has been

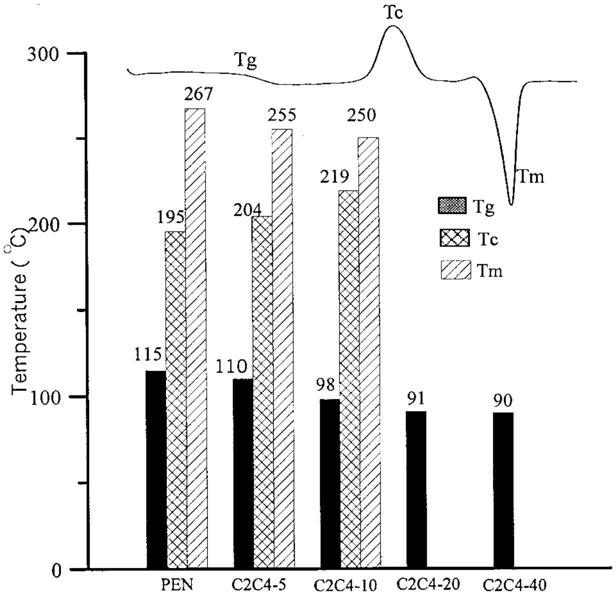


Figure 6 Phase transition temperature (T_g, T_c, and T_m) of melt-quenched samples for the C_2C_4 copolymer.

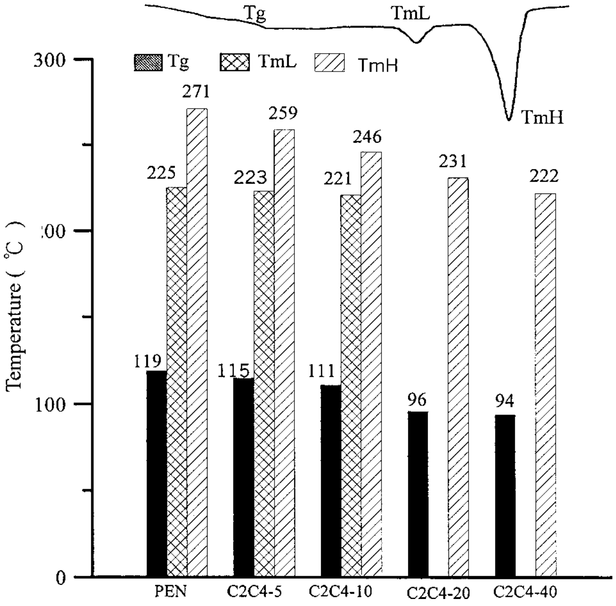


Figure 8 Phase transition temperature (T_g, T_{mL}, and T_{mH}) of heat-treated samples for the C_2C_4 copolymer.

observed by others[20–22] and interpreted on the basis of distributions of crystallite sizes or perfection induced by thermal treatments. As can be seen, the temperature difference occurring between the higher melting peak (T_{mH}) and lower melting peak (T_{mL}) decreases with increasing content of the comonomer and length of the alkyl side chain.

The higher melting peak temperatures in the DSC curves are plotted against the comonomer contents in the copolymers in Figure 9. The variations of T_m depression of CC, C_2C_2, and C_2C_4 are alike and larger than HH. It is confirmed from these results that the incorporation of a comonomer having an alkyl side chain suppresses the crystal growth of the polymer chain more than in the case without an alkyl side chain. Nevertheless, the increase in the length of the alkyl side chain seemed to hardly affect the T_m depression of the copolymers.

Table II shows that the copolymers have higher weight-loss temperatures than those of PET homopolymer and nearing those of PEN homopolymer, suggesting that copolymerization does not sacrifice the thermal stability of these polymers.

The solubilities of copolymers were determined by using powdery specimens in various solvents at ambient temperature, and the results are summarized in Table III. Table III shows that the increase in the content of comonomer and the length of the alkyl side chain increases the solubility of copolymers in several organic solvents. This result may be due to lower crystallinity of the copolymers.

Figure 10 shows the weight losses of melt-pressed films in alkaline solution against the comonomer contents in the copolymers. The weight gain from the moisture absorption tests is shown in Figure 11. The weight loss and moisture absorption decrease with increasing the content

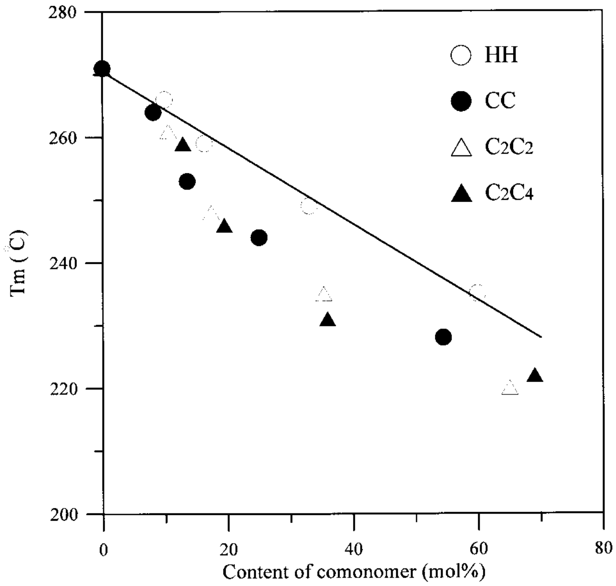


Figure 9 Melting temperature depression curves of the copolymers.

Table II Weight-Loss Temperature of Copolymers

Polymer Code		Weight-Loss Temperature[a] (°C)			
		5	10	20	40
PEN	421				
HH		435	431	430	430
CC		429	429	428	429
C_2C_2		422	420	417	415
C_2C_4		419	415	405	401
PET	390				

[a] A 5% weight-loss temperature observed by TGA at a 20°C/min heating rate in nitrogen.

Table III Solubility of Copolymers[a]

Polymer Code	Solvent[b]					
	DMAC	DMF	DMSO	NMP	*m*-Cresol	Pyridine
PEN	—	—	—	—	—	—
HH-5	—	—	—	−h	—	—
HH-10	—	—	—	−h	−h	—
HH-20	—	−h	−h	+h	+h	—
HH-40	−h	+h	+h	+h	+h	—
CC-5	—	—	−h	−h	−h	—
CC-10	—	−h	−h	+h	+h	—
CC-20	−h	−h	−h	++	+h	—
CC-40	−h	+h	+h	++	++	—
C_2C_2-5	—	−h	−h	+h	+h	—
C_2C_2-10	—	−h	−h	+h	+h	—
C_2C_2-20	−h	+h	−h	++	+h	—
C_2C_2-40	−h	+h	+h	++	++	−h
C_2C_4-5	—	−h	−h	+h	+h	—
C_2C_4-10	—	−h	−h	+h	+h	—
C_2C_4-20	−h	+h	−h	++	+h	—
C_2C_4-40	−h	+h	+h	++	++	−h
PET	—	—	—	+h	—	—

[a] (++) Soluble at room temperature; (+h) Soluble on heating; (−h) Partially soluble on heating; (—) Insoluble.

[b] DMAC: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; NMP: *N*-methyl-2-pyrolidone.

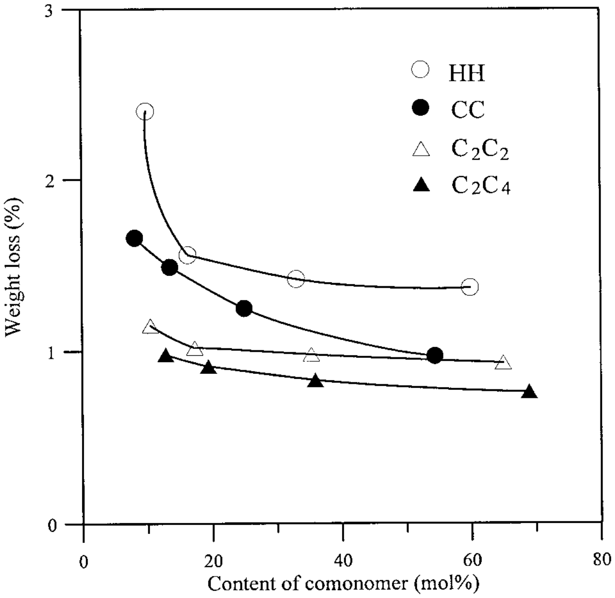


Figure 10 Alkaline resistance of melt-pressed film in aqueous NaOH solution at 70°C for 4 h.

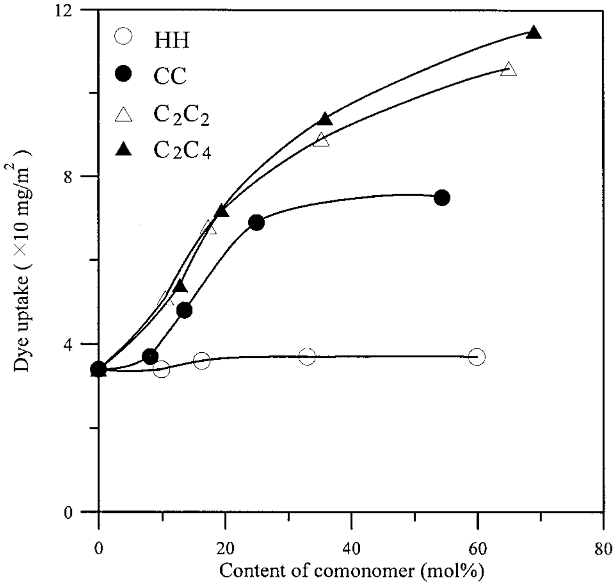


Figure 12 Dyeability of melt-pressed films for dispersed dye at 80°C for 24 h.

of the comonomer and length of alkyl side chain, suggesting that alkaline resistance is increased by copolymerization. This result may be ascribed to the decrease of ester linkage concentration and the steric hindrance of an alkyl side chain adjacent to the ester linkage.

Figure 12 shows the dye uptake of melt-pressed films against the comonomer content in the copolymers. The dye uptake for HH films is hardly changed by copolymerization, where the dye uptake for films copolymerized with comonomer having alkyl side chain increases with increasing the content of the comonomer and increases a little with increasing the length of the alkyl side chain. The increase of dye uptake for the disperse dye may be attributed to the decrease of crystallinity and the increase of hydrophobicity due to the alkyl side chain.

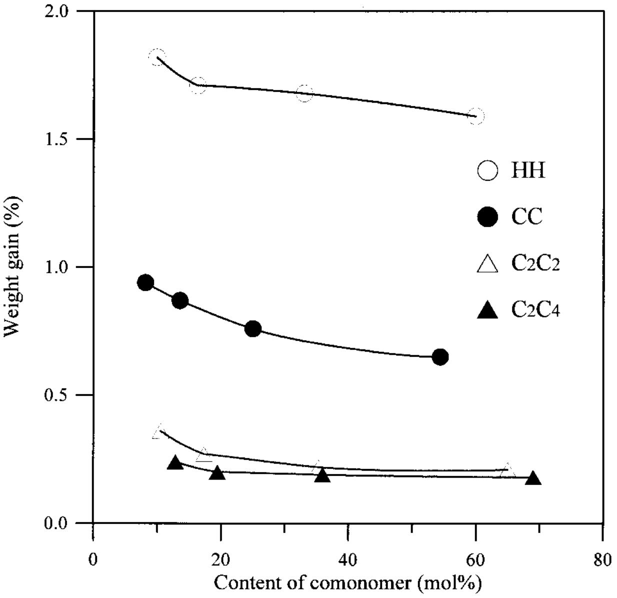


Figure 11 Moisture absorption for various compositions (100°C, 24 h in water).

The test pieces [300 mm (L) ×15 mm (W)] were fabricated from copolyesters and placed into 100°C boiling water for 15 min. The heat-shrinkage ratio was calculated from the following formula:

$$\text{Heat-shrinkage ratio} = \left[\frac{\text{length before the heat treatment} - \text{length after the heat treatment}}{\text{length before the heat treatment}}\right] \times 100\%$$

Figure 13 shows the shrinkage ratio of test pieces in boiling water. The shrinkage ratio increases with increasing the content of the comonomer and length of the alkyl side chain. The alkyl side chain may disturb the cohesion of the polymer chain and the crystallization during the drawing process (oriented crystallization), and thus increases the heat-shrinkage ratio. Nev-

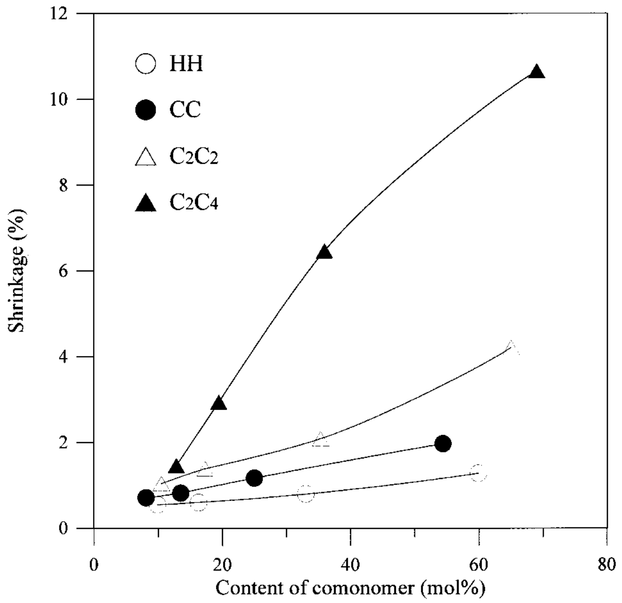


Figure 13 The shrinkage ratio of test pieces after boiling in water for 15 min.

ertheless, the heat-shrinkage ratios of the polymers studied are not all greater than 2%. If the heat-shrinkage ratio is more than 2%, the film shrinka excessively when forming a recording tape, thereby deteriorating the flatness.[23] To reduce the heat-shrinkage ratio, the stretched film is generally subjected to heat treatment at high temperature. A stretched polyethylene terephthalate film is difficult to subject to heat treatment at a high temperature because the haze is increased and the film is likely to be torn if the film is subjected to heatset treatment at too high a temperature. So, it may be advantageous to subject some low heat-shrinkage copolymer films to a heatset treatment at a higher temperature for use as recording tape.

CONCLUSION

1. The crystallinities and densities of heat-treated films decreased with increasing content of comonomer and length of alkyl side chain in the comonomer.
2. Alkaline resistance, less moisture absorption, and dye ability were considerably increased by the incorporation of comonomer having an alkyl side chain.
3. The copolymers have higher solubility, higher T_gs, and better thermal stability than PET. Thus, these copolymers would be expected to find various commercial applications.
4. Some of these low heat-shrinkage copolymer films are promising for use as recording tape or wrap at high temperature.

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