Preparation and properties of poly(ethylene terephthalate) copolymers with 2,2-dialkyl-1,3-propanediols

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Poly(ethylene terephthalate) (PET) copolymers were prepared by melt polycondensation of dimethyl terephthalate and excess ethylene glycol with 5–30 mol% (in feed) of 1,3-propanediol and 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 smaller than those in the feed. 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 the T_m depression of heat-treated films. Alkali resistance, dyeability and thermal shrinkage were remarkably increased by the incorporation of comonomer having an alkyl side chain.

(Keywords: PET copolymer; dialkyl propanediols; characterization)

INTRODUCTION

Chemical modification of poly(ethylene terephthalate) (PET) by incorporating various glycol or acid comonomers has been intensively investigated in the past with the aim of extending the use of PET in new application fields[1]. Recently, Gordon and Mera[2] reported 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 behaviour (glass transition, melting and side-chain crystallization).

Here, we report on the preparation and characterization of PET 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.

EXPERIMENTAL

Monomer

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 Chisso Corp., were used without further purification. 1,3-Propanediol (HH), 2,2-dimethyl-1,3-propanediol (CC) and dimethyl terephthalate were used as received. Ethylene glycol was distilled under reduced pressure.

Preparation of copolymers

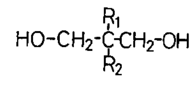
Copolymers were prepared by a melt polycondensation method. A mixture of dimethyl terephthalate and comonomer with a small amount of zinc acetate and antimony trioxide as a catalyst was heated at 200–205°C for 1 h in a stream of nitrogen gas, and further maintained for 2 h while adding excess ethylene glycol, then increased to 270–275°C and heated for 1 h followed by heating at 280–285°C for 3 h in a vacuum of 0.3–1.0 Torr.

Film preparation

Film was melt-pressed between aluminium plates with an aluminium spacing plate of 100 μm thickness and then quenched into iced water. After dissolving off aluminium plates in 10% hydrochloric acid, the film was washed with water and dried overnight at 40–50°C *in vacuo*.

Characterization

Reduced specific viscosity (η_{sp}/c) was determined at 30°C in phenol/tetrachloroethane (60/40 by weight). The



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

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

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concentration of polymer solution was 1.0 g dl^{-1}. ^{1}H nuclear magnetic resonance (n.m.r.) was performed in CF_3COOD at 50°C. Wide-angle X-ray scattering (WAXS) was performed with nickel-filtered Cu K_α radiation. Density was measured in a heptane–tetrachloromethane density gradient column at 30°C. Differential thermal analysis (d.t.a.) was performed at a heating rate of 10°C min^{-1} in a nitrogen atmosphere. Thermogravimetry (t.g.) was performed at a heating rate of 10°C min^{-1} in a nitrogen atmosphere. Solubility of 5 mg of polymer was examined in 0.5 ml of solvent. Alkali hydrolysis was carried out in a 10% NaOH aqueous solution at 70°C for 4 h. 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. Tensile test was performed with strain rate of 100% min^{-1} under the condition of 20°C and 65% r.h. Thermal shrinkage was carried out in boiling water for 15 min.

RESULTS AND DISCUSSION

Table 1 shows reduced specific viscosities of copolymers prepared. The copolymerization does not provide significant depression of η_{sp}/c, which suggests that the 2,2-substituted short alkyl side group in propanediol hardly affects the reactivity of polymerization. On the contrary, 2,3-disubstituted long alkyl side groups in butanediols remarkably decreased the inherent viscosities of copolymers[2].

The comonomer contents in copolymers measured by ^{1}H n.m.r. are plotted against the comonomer contents in the feed in *Figure 1*. The comonomer contents in the copolymers are considerably smaller than those in the feeds. It was reported that the alkyl disubstituted butanediol cyclizes during the polyesterification due to steric strain of the substituents by forcing them apart, and so the PET copolymers are enriched in ethylene glycol[2]. Thus, the largest decrease in the comonomer content in copolymer CC could be ascribed to the cyclization due to the methyl disubstituents in addition to the increase of volatility of comonomer CC with smaller molecular weight.

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 2* shows the WAXS curves of HH and C_2C_4 films heat-treated at 170°C for 2 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. It is found that the crystallinity of heat-treated films decreases with increasing content of comonomer and length of the alkyl

Table 1 Reduced specific viscosity[a] of copolymers. Numbers in the polymer code represent the comonomer content (mol%) in the feed

Code	η_{sp}/c (dl g^{-1})	Code	η_{sp}/c (dl g^{-1})
PET	0.78		
HH-5	0.67	C_2C_2-5	0.72
-10	0.71	-10	0.66
-20	0.58	-20	0.63
-30	0.48	-30	0.73
CC-5	0.75	C_2C_4-5	0.54
-10	0.90	-10	0.61
-20	0.74	-20	0.76
-30	0.75	-30	0.71

[a] 0.1 g/10 ml in phenol/tetrachloroethane (60/40 wt%) at 30°C

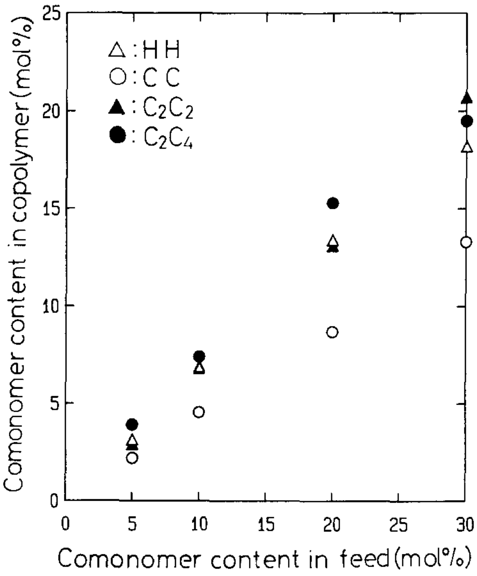

Figure 1 Change of copolymer composition by polymerization

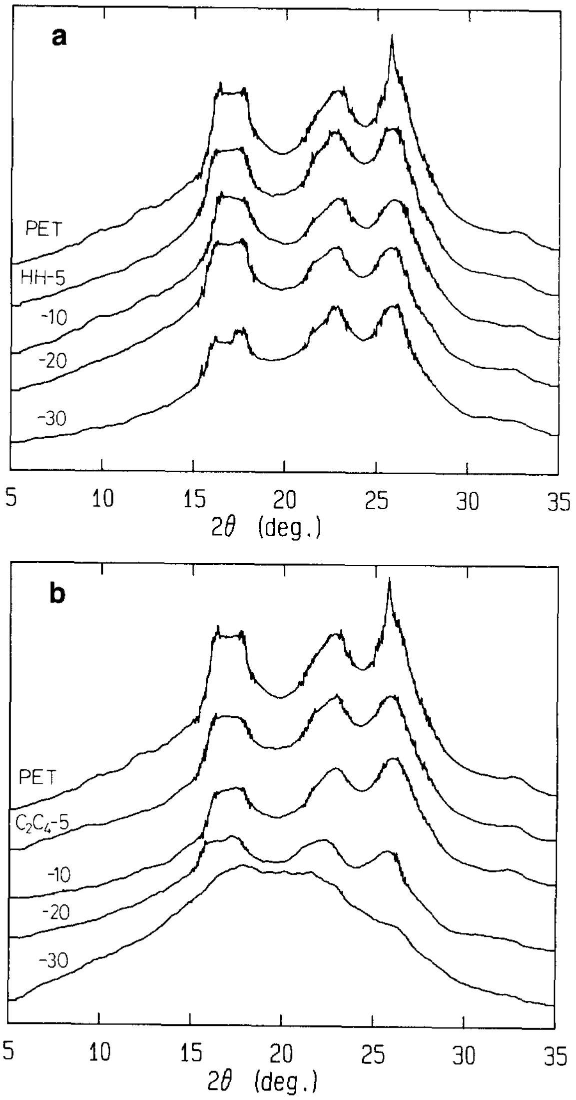

Figure 2 WAXS curves for (a) HH and (b) C_2C_4 films heat-treated at 170°C for 2 h

side chain in the comonomer; thus C_2C_2-30 and C_2C_4-30 films are hardly crystallized by the heat treatment.

The comonomer contents in the copolymers are plotted against the densities of melt-pressed and heat-treated films in *Figure 3*. 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 HH) have densities smaller than the amorphous density of 1.335 g cm^{-3} for PET homopolymer[3]. Heat treatment causes the increase of density, and thus the degree of crystallinities calculated from densities are 9 and 50% for the melt-pressed and heat-treated PET homopolymer films, respectively. The heat treatment hardly increases the densities of C_2C_2-30 and C_2C_4-30 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 suppresses the crystallization of PET chains.

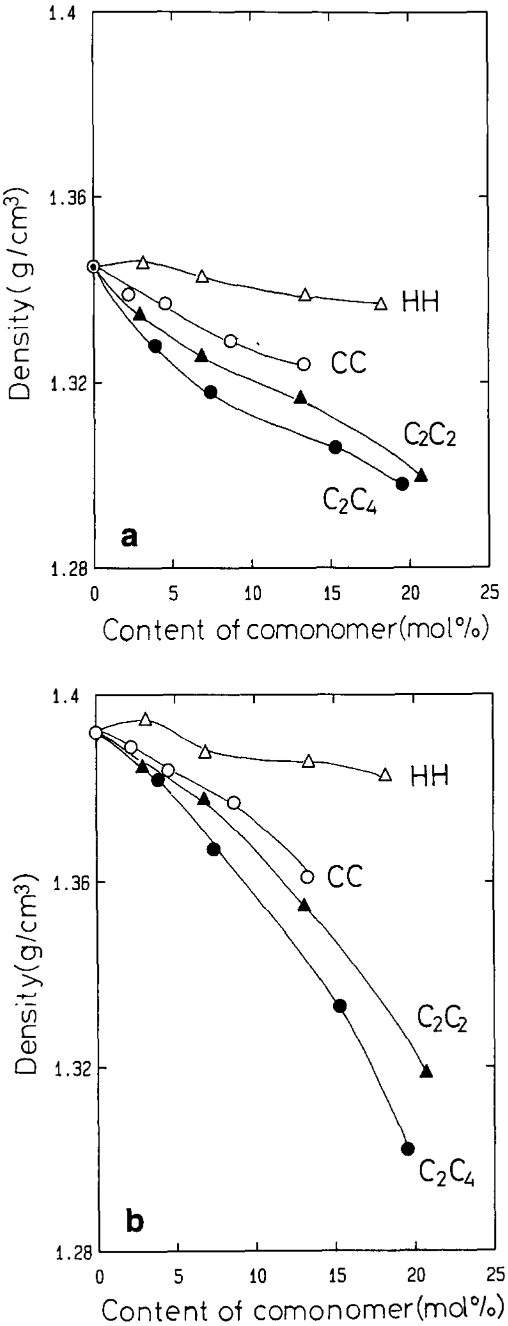

Figure 3 Change of density with copolymer composition for (a) melt-pressed films and (b) heat-treated films at 170°C for 2 h

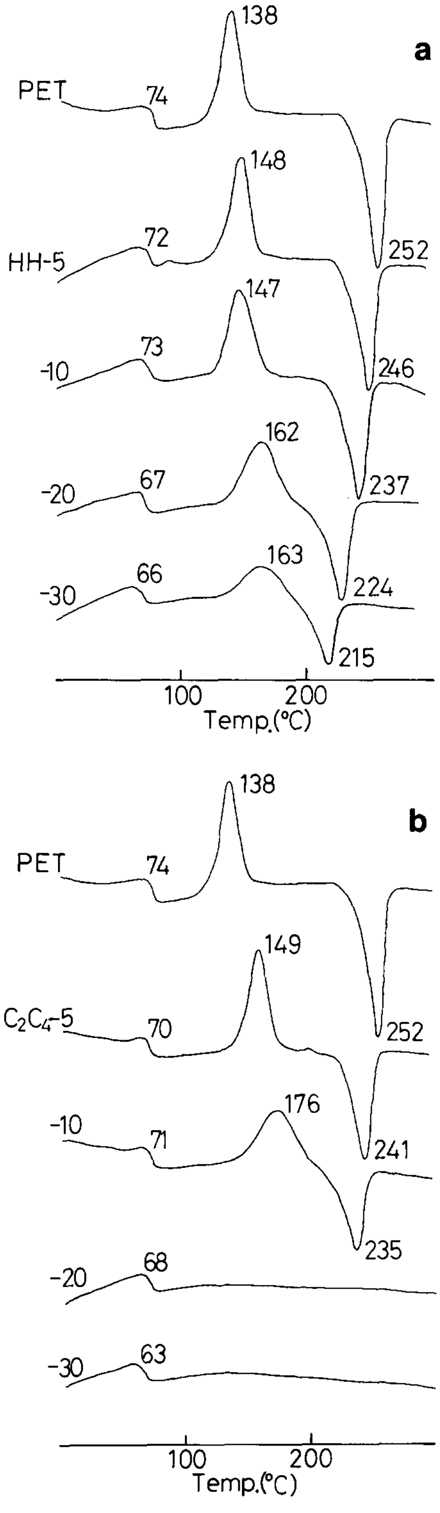

Figure 4 D.t.a. curves for melt-quenched (a) HH and (b) C_2C_4 samples

Figure 4 shows d.t.a. curves of melt-quenched samples for HH and C_2C_4 copolymers. The d.t.a. curves of melt-quenched samples for CC and C_2C_2 copolymers were similar to those for HH and C_2C_4 copolymers, respectively, with small variations. Glass transition temperature (T_g) decreases, cold crystallization temperature (T_{cc}) increases and melting temperature (T_m) decreases with increasing content of comonomer and length of alkyl side chain. The T_{cc} and T_m peaks disappear at a comonomer content in the feed above 20 mol% for C_2C_2

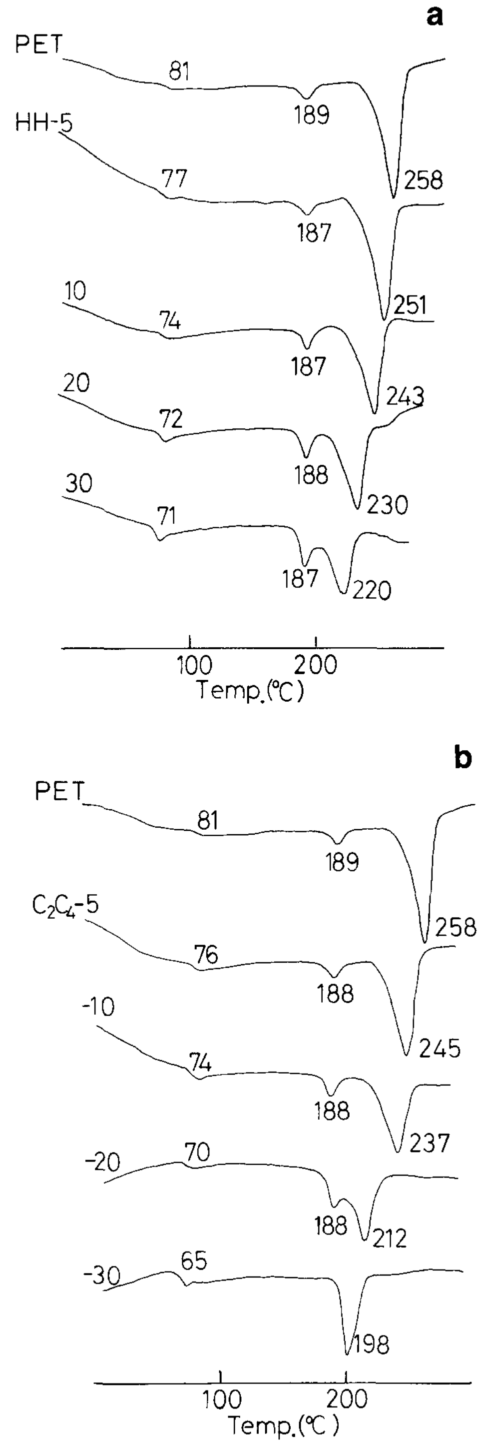

Figure 5 D.t.a. curves for (a) HH and (b) C_2C_4 films heat-treated at 170°C for 2 h

and C_2C_4 copolymers, suggesting that these copolymers do not crystallize during the heating run on the d.t.a.

Figure 5 shows the d.t.a. curves of heat-treated films for HH and C_2C_4 copolymers. The d.t.a. curves for heat-treated CC and C_2C_2 films were similar to those for HH and C_2C_4 films, respectively, with small variations. T_g decreases and T_m increases with increasing content of comonomer and length of alkyl side chain. The higher melting peak temperatures in the d.t.a. curves are plotted against the comonomer contents in the copolymers in *Figure 6*. The T_m depression of HH is intermediate between those calculated from Flory's equation[4] using the highest reported value[5] of $\Delta H_u = 3980\ \mathrm{cal\ mol^{-1}}$ and the lowest[6] $\Delta H_u = 2200\ \mathrm{cal\ mol^{-1}}$, while those of CC, C_2C_2 and C_2C_4 are larger than Flory's curve with $\Delta H_u = 2200\ \mathrm{cal\ mol^{-1}}$. 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, but the increase of the length of the alkyl side chain hardly affects the T_m depression of the copolymers.

Table 2 shows that the copolymers have higher weight-loss temperatures than those of PET homopolymer, suggesting that the copolymerization slightly increases the thermal stability.

Table 3 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 the lower crystallinity of copolymers.

Figure 7 shows the weight losses of melt-pressed films in alkali solution against the comonomer contents in the copolymers. The weight loss decreases with increasing content of comonomer and length of alkyl side chain, suggesting that alkali 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 8 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, whereas the dye uptake for films copolymerized with comonomer having alkyl side

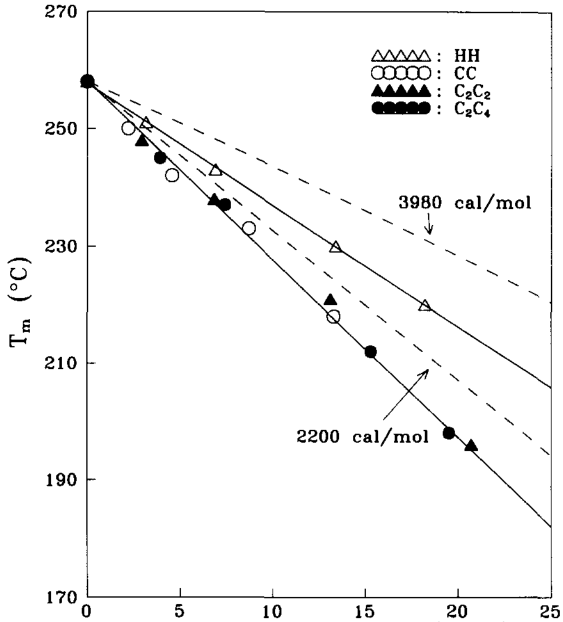

Figure 6 Melting-temperature depression curves of copolymers

Table 2 Weight-loss temperatures of copolymers

Code	Weight-loss temperature (°C)	
	5%	50%
PET	364	400
HH-30	386	436
CC-30	388	409
C_2C_2-30	371	412
C_2C_4-30	370	413

Table 3 Solubility (cold/hot)[a] of copolymers in 1,3-dimethyl-2-imidazolidinone (A), *N,N*-dimethylformamide (B), dimethylsulfoxide (C), pyridine (D) and *N*-methyl-2-pyrrolidone (E)

	Solvent				
Polymer code	A	B	C	D	E
PET	×/△	×/×	×/×	×/×	×/●
HH-5	×/●	×/×	×/×	×/×	×/●
-10	×/●	×/×	×/●	×/×	×/●
-20	×/●	×/×	×/●	×/×	×/●
-30	×/●	×/●	×/●	×/×	×/●
CC-5	×/●	×/●	×/×	×/×	×/●
-10	×/●	×/●	×/●	×/×	×/●
-20	×/●	×/●	×/●	×/×	×/●
-30	×/●	×/●	×/●	×/×	×/●
C_2C_5-5	×/●	×/●	×/●	×/×	×/●
-10	×/●	×/●	×/●	×/×	×/●
-20	△/●	△/●	×/●	×/△	×/●
-30	△/●	△/●	×/●	×/●	×/●
C_2C_4-5	×/●	×/△	×/△	×/×	×/●
-10	△/●	×/△	×/●	×/×	×/●
-20	△/●	△/●	×/●	×/△	△/●
-30	△/●	△/●	×/●	×/●	△/●

[a] ● = soluble, △ = partially soluble, × = insoluble

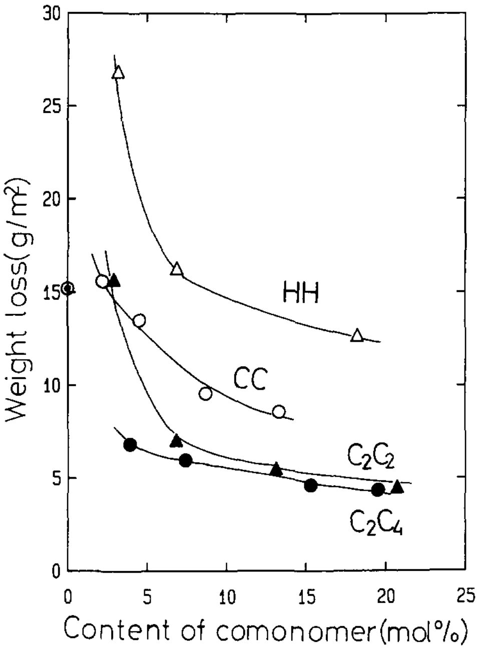

Figure 7 Alkali resistance of melt-pressed films in NaOH aqueous solution at 70°C for 4 h

Table 4 Tensile properties for (3 ×) C_2C_4 films

Code	η_{sp}/c (dl g^{-1})	Tensile strength (kg mm^{-2})	Elongation (%)	Young's modulus (kg mm^{-2})
PET	0.61	6.5	39	259
C_2C_4-5	0.48	11.5	90	254
-10	0.55	8.2	61	218
-20	0.69	10.8	82	220
-30	0.64	10.0	60	189

chain increases with increasing content of comonomer and increases a little with increasing length of alkyl side chain. The increase of dye uptake for disperse dye may be attributed to the decrease of crystallinity and the increase of hydrophobicity due to the alkyl side chain.

Table 4 shows the results of tensile tests for drawn (3 ×) C_2C_4 films. The tensile strength and elongation are increased and the Young's modulus is decreased by the copolymerization. The alkyl side chain may disturb the interaction and cohesion of the polymer chain, which leads to the increase of extensibility of the polymer chain, and thus increases the tensile strength and elongation and decreases the Young's modulus.

Figure 9 shows the shrinkage of drawn (4 ×) films in boiling water. The shrinkage increases with increasing content of comonomer and length of alkyl side chain. It is noted that the shrinkage of C_2C_2-30, C_2C_4-20 and C_2C_4-30 films is 100%. The alkyl side chain may disturb the cohesion of the polymer chain and the crystallization

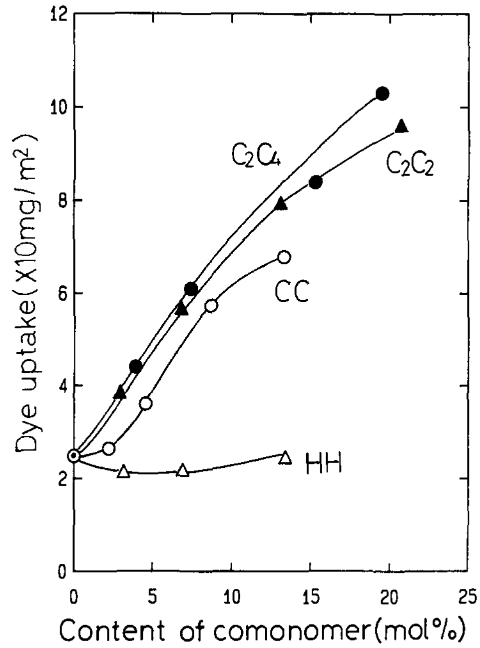

Figure 8 Dyeability of melt-pressed films for disperse dye at 80°C for 24 h

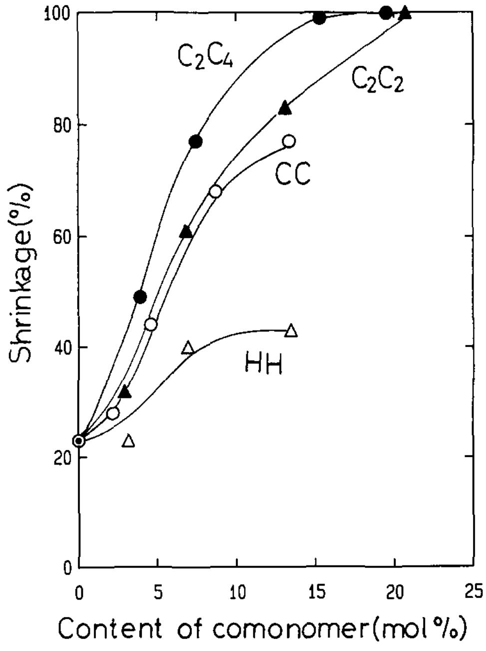

Figure 9 Shrinkage of drawn (4 ×) films after treating in boiling water for 15 min

on the drawing process (oriented crystallization), and thus increases the thermal recovery. The high thermal shrinkage of these copolymer films is promising for their use as heat-shrinkable film or wrap.

ACKNOWLEDGEMENTS

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