

# Phase structure and properties of some thermoplastic polyesteramide elastomers

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(Received 31 July 1996; revised 30 January 1997)

Thermoplastic polyesteramide elastomers with aromatic moieties were prepared and their structure–property relations were studied. The elastomers were synthesized by the polycondensation of 4,4'-methylenediphenyl diisocyanate, carboxylic acid-terminated poly(butylene adipate) oligomers and three different aliphatic dicarboxylic acids. Mixing between the hard and soft phases, examined by thermal and i.r. spectroscopic measurements, depended on the contents and the molecular weights of the poly(butylene adipate) oligomers and also on the types of the aliphatic dicarboxylic acids used. The dissolution of the hard polyamide segment into soft polyester domains increased with decreasing molecular weights of the constituent segments. The mixing was more effective when adipic acid, 1,10-decanedicarboxylic acid and azelaic acid (in increasing order of effectiveness) were used. A higher degree of phase mixing appeared to enhance the moduli of the elastomers but impair the tensile properties at high deformation. © 1997 Elsevier Science Ltd.

(Keywords: polyesteramide elastomers; phase structure; tensile properties)

## INTRODUCTION

Many thermoplastic elastomers are linear multiblock copolymers which have a characteristic microphase-separated structure due to incompatibility between the hard and soft segments<sup>1–7</sup>. Polymers with low glass transition temperatures ( $T_g$ ), such as aliphatic polyesters and polyethers, are used as soft segments, which endow the elastomers with the necessary flexibility and extensibility. The glassy or semicrystalline hard segment phase, on the other hand, acts as a thermally reversible physical crosslinkage as well as reinforcing filler for the soft phase. Besides the nature of the hard and soft segments, the extent of mixing between the two phases is a very important factor determining the physical properties of the resulting elastomer. The mixing depends in turn on the chemical structure, molecular weight, crystallinity and composition of the hard and soft segments.

Polyamides with aromatic moieties can be used as the hard segment of thermoplastic elastomers, although systematic studies on the structure and properties of such materials are rare<sup>8</sup>. By virtue of their high melting temperature and rigidity, polyamides with aromatic moieties are thought to augment the physical properties without impairing the intrinsic extensibility of elastomers<sup>9</sup>. They can be synthesized by polycondensation of aromatic diisocyanates and dicarboxylic acids<sup>10,11</sup>. In the present study, thermoplastic polyesteramide (PEA) elastomers were prepared by polycondensation of 4,4'-methylenediphenyl diisocyanate (MDI), carboxylic acid-terminated poly(butylene adipate) (PBA) oligomers and various types of aliphatic dicarboxylic acid. The relations among their chemical structure, phase structure and tensile properties were examined.

## EXPERIMENTAL

### Materials

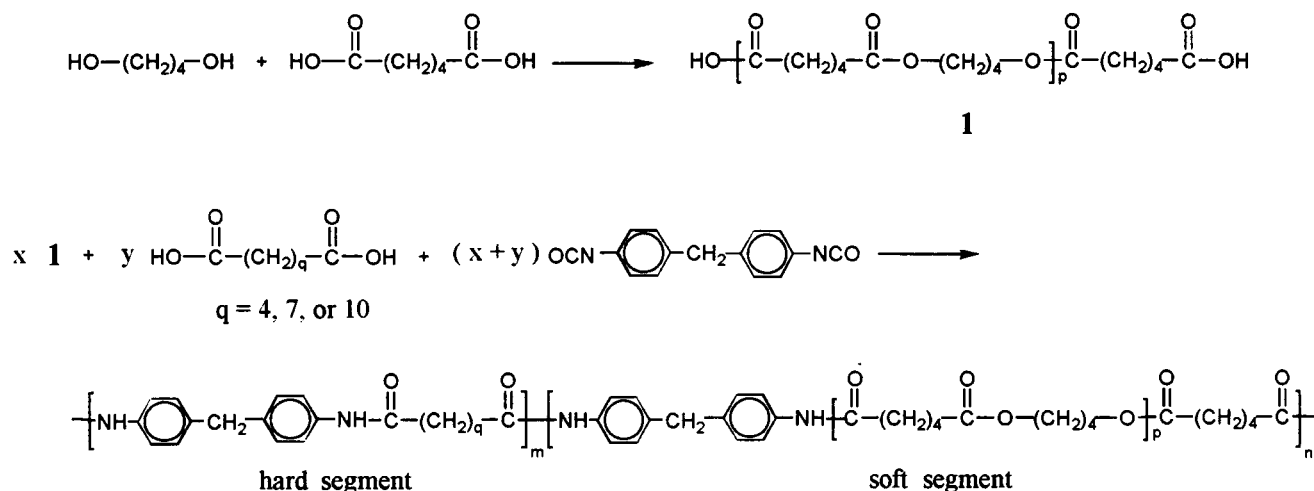
MDI (Tokyo Kasei) was melted at 50°C and a white precipitate of dimers in the melt was removed before use. Adipic acid (Showa), azelaic acid (Aldrich), 1,10-decanedicarboxylic acid (Aldrich) and PbO (Aldrich) were used as received. Sulfolane (Aldrich) and 1,4-butanediol (Junsei) were dried over 4A molecular sieve before use. 3-Methyl-1-phenyl-2-phospholene-1-oxide was synthesized by a known method<sup>12</sup>.

### Synthesis and characterization of carboxylic acid-terminated PBA oligomers

The overall synthesis scheme is shown in *Scheme 1*. The synthesis of PBA oligomers was carried out in two steps. For the oligomer with a number-average molecular weight ( $M_n$ ) of 1200, 1,4-butanediol (118.06 g, 1.31 mol), adipic acid (219.21 g, 1.50 mol), and PbO (0.28 g, 0.08 wt% of monomers) in xylene (70 mL) were heated to 180°C and stirred for 9 h in the first step. Conversion at this stage, estimated from the amount of water removed in a Dean–Stark apparatus, was ~90%. In the second step, the reaction was continued to completion under reduced pressure at 200°C for 10 h. The mixture was then poured into chloroform and the solid was filtered off. A white solid product was obtained after evaporation of chloroform under reduced pressure. PBA oligomers with different molecular weights were prepared by controlling the molar ratio of 1,4-butanediol to adipic acid. For example, the oligomer with  $M_n = 2400$  was prepared from 1.49 mol (134.28 g) of 1,4-butanediol and 1.50 mol (219.21 g) of adipic acid.

The completion of the reaction and the formation of dicarboxylic terminal groups were confirmed by the disappearance of the methylene proton peak of terminal alcohol at 3.4 ppm and the appearance of terminal carboxylic acid peak at 2.2 ppm in the n.m.r. spectrum.  $M_n$

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Scheme 1

Table 1 Characteristics of PBA oligomers synthesized

Oligomer	$M_n$		$T_{g,s}$ (°C)	$T_{m,s}$ (°C)	$\Delta H$ at $T_{m,s}$ (J g <sup>-1</sup> )
	N.m.r.	Titration			
PBA1200	1200	1200	-52	52	101.3
PBA2400	2400	2500	-57	59	74.6

of the oligomers was determined by n.m.r. and titration measurements. In the n.m.r. method the peak intensity of methylene protons in non-terminal dicarboxylic acid units at 2.3 ppm was compared with that in terminal dicarboxylic acid at 2.2 ppm. In a typical titration procedure, 1.2 g of PBA oligomer was dissolved in 100 mL of 1,4-dioxane and the carboxyl content was titrated with 0.125N aqueous NaOH. Phenolphthalein was used as an indicator.  $M_n$  thus determined appeared to be lower than expected from the Carothers equation, which was attributed to the loss of 1,4-butanediol from transesterification in the second step<sup>13,14</sup>. PBA oligomers with  $M_n$  of 1200 and 2400, Table 1, were used for the synthesis of PEA elastomers.

#### Synthesis of PEA elastomers

A total of 18 elastomers, listed in Table 2, were prepared. The synthesis procedure was the same for all the elastomers; that for P4-1-5 is described here. Adipic acid (2.13 g, 14.6 mmol), PBA1200 (7.48 g, 6.8 mmol), and 3-methyl-1-phenyl-2-phospholene-1-oxide (11.5 mg, 0.06 mmol) in 70 mL of sulfolane were heated to 200°C with stirring under nitrogen atmosphere. To the solution, 5.36 g (21.4 mmol) of MDI in 15 mL of sulfolane was added dropwise over a period of 5 min and the mixture was stirred at 200°C for another 3 h under nitrogen. As the viscosity of the reaction mixture increased, additional sulfolane was added, to a final solid content of ~12% (w/v). The reaction mixture was then poured into 3000 mL of methanol and the precipitate was dried under vacuum at 80°C. Yields were in the range of 80–90 wt%.

Each sample designation code for the elastomers in Table 2 indicates the number of methylene groups in the aliphatic dicarboxylic acid, the molecular weight of PBA oligomer and the content of hard segment (MDI + aliphatic dicarboxylic acid) in the feed. For example, P7-1-5 denotes that the PEA elastomer was synthesized with azelaic acid (by the number 7) and PBA1200 (by the number 1), and that

the content of hard segment in feed was 50 wt% (by the number 5).  $M_n$  of the hard segment was estimated from the molar ratio of MDI to aliphatic dicarboxylic acid in the feed, assuming that the probability of incorporation of dicarboxylic acid and PBA oligomer into an elastomer chain is the same.

#### Characterization

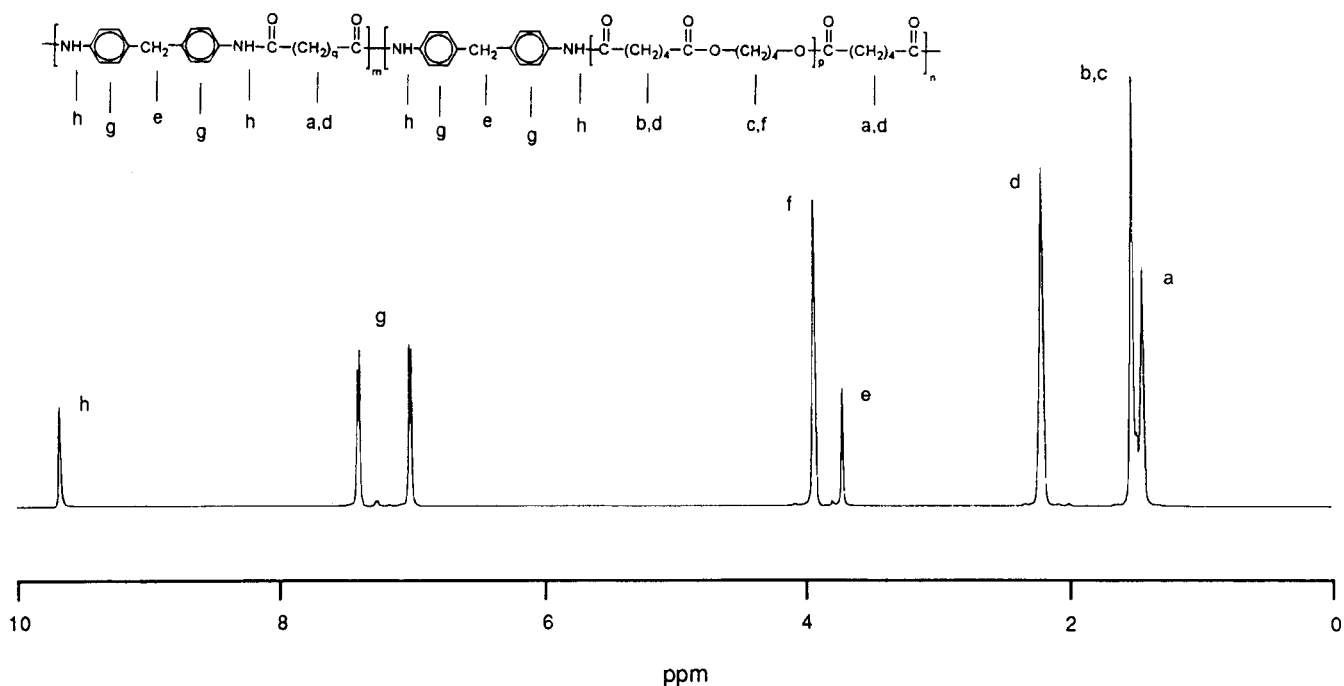
Intrinsic viscosities of PEA elastomers were measured with an Ubbelohde viscometer at 25°C in *m*-cresol. <sup>1</sup>H n.m.r. spectra were obtained in dimethyl sulfoxide-*d*<sub>6</sub> on a Bruker AMX-500 spectrometer. FTi.r. spectra were taken with a Bomem MB-100 spectrometer. PEA elastomers cast on KBr discs were dried under vacuum at 80°C for 35 h before measurement. Scanning resolution was 2 cm<sup>-1</sup> and 32 scans were averaged to obtain each spectrum.

Differential scanning calorimetry (d.s.c.) was carried out with a Mettler TA-3000 calorimeter at a heating or cooling rate of 20°C min<sup>-1</sup>. All runs were carried out with a sample of ~10 mg under nitrogen atmosphere. Samples were quenched in liquid nitrogen after annealing at temperatures 10°C above the melting temperature ( $T_m$ ) of the hard phase for 1.5 min. For each sample  $T_g$ ,  $T_m$  and heat of fusion ( $\Delta H_m$ ) were measured during the subsequent heating. Crystallization temperature on cooling ( $T_{mc}$ ) and heat of crystallization at  $T_{mc}$  ( $\Delta H_{mc}$ ) were measured during the next cooling cycle.

Uniaxial tensile tests were performed according to ASTM method D882 at a strain rate of 200 mm min<sup>-1</sup> using a universal testing machine (Instron, Model 1123). Tensile specimens were prepared by the following procedure. Cast films were obtained by pouring 18% (w/v) of PEA solution in *m*-cresol on to a glass plate, followed by drying at 70°C for 24 h. All samples were dried under vacuum at 70°C for another 24 h and rectangular specimens were cut from selected cast films. Typical specimens were 90 mm long, 10 mm wide and 0.17 mm thick. Recovery experiments

**Table 2** Characteristics of PEA elastomers synthesized

Polymer	Aliphatic dicarboxylic acid	$M_n$ of PBA	Content of hard segment		$M_n$ of hard segment	$[\eta]$ (dL g <sup>-1</sup> )	Yield (wt%)
			Feed	Found <sup>a</sup>			
P4-1-7	adipic acid	1200	70	69	3400	0.82	81.2
P4-1-5	adipic acid	1200	50	51	1500	0.97	82.9
P4-1-3	adipic acid	1200	30	27	600	—	85.4
P7-1-7	azelaic acid	1200	70	63	3700	0.75	82.0
P7-1-5	azelaic acid	1200	50	46	1600	0.91	81.3
P7-1-3	azelaic acid	1200	30	24	600	—	73.9
P10-1-7	1,10-DDA <sup>b</sup>	1200	70	66	3900	1.00	83.6
P10-1-5	1,10-DDA	1200	50	39	1600	1.00	84.3
P10-1-3	1,10-DDA	1200	30	23	700	1.44	84.8
P4-2-7	adipic acid	2400	70	66	7400	0.86	86.0
P4-2-5	adipic acid	2400	50	44	3100	0.98	85.7
P4-2-3	adipic acid	2400	30	27	1300	1.71	87.4
P7-2-7	azelic acid	2400	70	62	7700	0.83	82.9
P7-2-5	azelic acid	2400	50	42	3300	0.99	85.6
P7-2-3	azelic acid	2400	30	25	1400	1.34	86.8
P10-2-7	1,10-DDA	2400	70	60	8000	1.10	85.8
P10-2-5	1,10-DDA	2400	50	38	3400	1.17	86.2
P10-2-3	1,10-DDA	2400	30	20	1500	—	87.5

<sup>a</sup> Content in polymer determined by n.m.r.<sup>b</sup> 1,10-decanedicarboxylic acid**Figure 1** N.m.r. spectrum of PEA elastomer P4-1-5

were performed at room temperature by stretching the tensile specimen to 300% of its original length with a cross-head speed of 200 mm min<sup>-1</sup> and releasing it. Tensile set was determined by measuring the length of the specimen 5 min after the removal of stress. The results of tensile and recovery experiments were averaged over at least five specimens.

## RESULTS AND DISCUSSION

### Structure of PEA elastomers

A typical <sup>1</sup>H n.m.r. spectrum of the PEA elastomer is presented in *Figure 1* for P4-1-5. Amine protons (h) at 9.7 ppm, aromatic protons (g) at 7.0–7.4 ppm, methylene protons of the butanediol unit in PBA (f) at 4.0 ppm,

methylene protons of MDI (e) at 3.8 ppm, and other methylene protons (a–d) at 1.4–2.2 ppm were observed. The content of hard segments in the elastomers could be determined by comparing the intensity of peak f with that of peak e, g or h. The results are summarized in Table 2. The content of hard segments were lower than expected from the feed ratio. This is thought to be related to the fact that the reactivities of PBA oligomers are lower than those of aliphatic dicarboxylic acids.

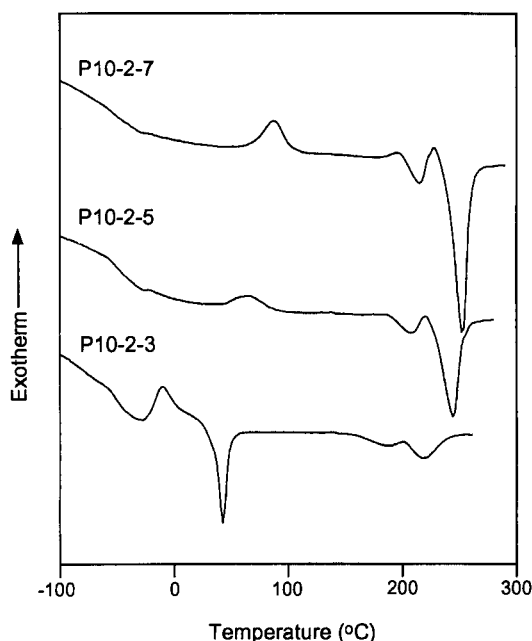


Figure 2 Typical d.s.c. thermograms of the elastomers obtained on heating

### Thermal properties

Typical d.s.c. thermograms obtained on heating are shown in Figure 2. The thermograms of both P10-2-7 and P10-2-5 exhibit glass transitions of the soft phase, exothermic crystallization peaks and multiple endothermic melting peaks of the hard phase. The thermogram of P10-2-3, which has a higher content of soft segments, shows additional exothermic crystallization and endothermic melting peaks of the soft phase. The results of the thermal analyses are summarized in Table 3.

The glass transition temperatures of the soft phase ( $T_{g,s}$ ) are higher than those of the respective PBA oligomers in Table 1. This indicates that some amount of hard segment is dissolved in soft segment domains, which is frequently observed in polyurethane elastomers<sup>15,16</sup>. For each series of elastomers with the same aliphatic dicarboxylic acid and PBA oligomer,  $T_{g,s}$  increases as the content of hard segment decreases. This seems to be due to the decreasing molecular weight of the hard segment with decreasing content, as shown in Table 2. PEA elastomers with PBA1200 have a higher  $T_{g,s}$  than those with PBA2400 when the aliphatic dicarboxylic acid and the content of hard segment are the same. This suggests that the dissolution of hard segment into soft segment domains increases as  $M_n$  of the soft segment decreases, probably due to the accompanying decrease in the length of hard segment<sup>15,16</sup>.

When  $M_n$  and the content of soft segment are the same,  $T_{g,s}$  increases in the order P4 < P10 ≤ P7. PEA elastomer whose hard segment has the fewest methylene groups (P4) should have the highest crystallinity due to the higher concentration of amide groups that could form hydrogen bonds. The extent of mixing between the phases should therefore be smaller. However, the reason why the phase mixing in P7 elastomers is as high as in P10 is not clear. One possible explanation is that the odd methylene sequence in P7 does not provide optimum packing, due to

Table 3 Thermal properties of PEA elastomers

Polymer	$T_{g,s}$ (°C)	$T_{m,s}$ (°C)	$\Delta H$ at $T_{m,s}$ (J g <sub>soft</sub> <sup>-1</sup> )	$T_{m,h}^a$ (°C)	$T_{mc}$ (°C)	$T_{m,h} - T_{mc}$ (°C)	$\Delta H_{mc}$ (J g <sub>hard</sub> <sup>-1</sup> )
P4-1-7	-41	—	—	315	296	19	63.4
P4-1-5	-36	—	—	290	281	9	52.0
P4-1-3	-35	—	—	—	—	—	—
P7-1-7	-38	—	—	275	222	53	48.3
P7-1-5	-31	—	—	252	203	49	2.6
P7-1-3	-28	—	—	181	—	—	—
P10-1-7	-38	—	—	256	204	52	46.0
P10-1-5	-34	—	—	238	188	50	43.4
P10-1-3	-28	—	—	157	132	25	17.3
P4-2-7	-56	52	9.2	326	299	27	59.1
P4-2-5	-51	49	11.6	315	292	23	58.4
P4-2-3	-47	44	19.1	—	—	—	—
P7-2-7	-49	—	—	278	220	58	47.0
P7-2-5	-47	—	—	270	223	47	46.2
P7-2-3	-44	—	—	260	181	79	38.0
P10-2-7	-51	—	—	261	205	56	39.3
P10-2-5	-47	—	—	252	197	55	45.0
P10-2-3	-46	55	19.6	207	170	37	29.7

<sup>a</sup>Highest peak temperature of multiple endothermic melting peaks

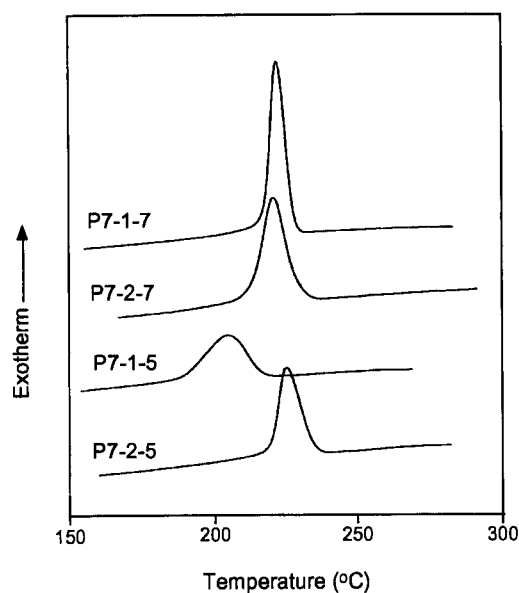


Figure 3 D.s.c. thermograms of the elastomers obtained on cooling

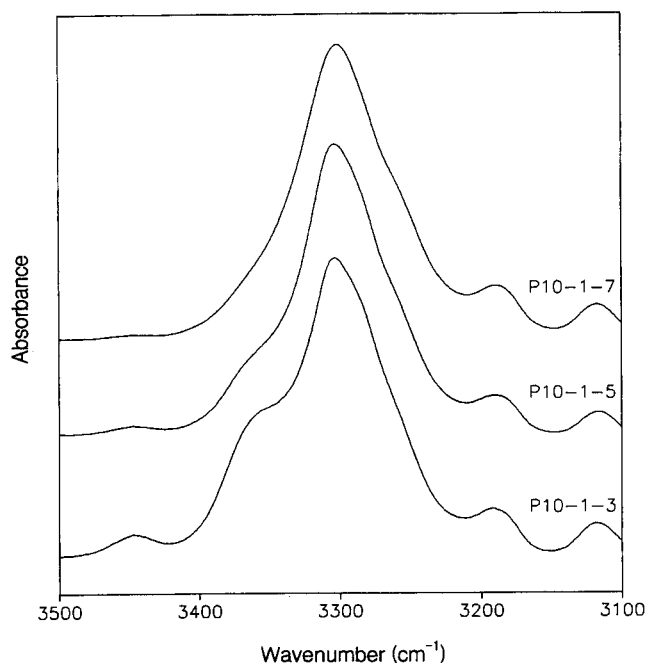


Figure 4 FTi.r. spectra of P10-1 series elastomers, showing N-H stretching region

conformational limitations, resulting in low crystallinity and high degree of dissolution of hard segment into soft segment domains. This so-called even-odd effect is commonly observed in aliphatic polyamides and liquid-crystalline polyesters<sup>17,18</sup>.

The melting temperatures of the soft phase ( $T_{m,s}$ ) also support the above explanations. The crystallization of soft phase is expected to be hindered more as the amount of dissolved hard segment increases. PEA elastomers synthesized with PBA1200 or with azelaic acid do not show a  $T_{m,s}$ , which indicates that the dissolution of hard segment into soft segment domains is severe enough to hinder the crystallization of the soft phase. For the elastomers synthesized with PBA2400 and adipic acid, on the other hand, the dissolution of hard segment into soft segment

domains appears not to be great enough to hinder the crystallization: the thermograms show a  $T_{m,s}$ .

The melting temperature of the hard phase ( $T_{m,h}$ ) is higher for the elastomers prepared with aliphatic dicarboxylic acids with fewer methylene groups, resulting from the higher aromaticity and amide concentration in the hard segment. It is also observed that  $T_{m,h}$  decreases as  $M_n$  of the soft segment decreases or the content of soft segment increases. The decrease in  $M_n$  of the hard segment seems to be the cause of these findings<sup>1,19-21</sup>.

There are two possible ways in which the soft phase can affect the crystallization of the hard phase. One is the plasticization effect, by which the crystallization is enhanced with improved chain mobility. The other is the dilution effect, by which the crystallization is retarded. The crystallization peaks of hard phase obtained on cooling from the melt are shown in Figure 3. It is seen that the crystallization peak of P7-1-7 is sharper than that of P7-2-7. This result, together with the facts that P7-1-7 has a higher value of  $\Delta H_{mc}$  and a lower degree of supercooling for crystallization ( $T_{m,h} - T_{mc}$ ) shows that intimately mixed shorter soft segments enhance the crystallization of hard phase more effectively by plasticizing the chains. Comparisons of P4-1-7 with P4-2-7 and of P10-1-7 with P10-2-7 reveal the same trends as shown in Table 3. However, P7-1-5 has a broader crystallization peak than P7-2-5 (Figure 3). Furthermore, the changes in  $T_{m,h} - T_{mc}$  and  $\Delta H_{mc}$  are not consistent with those observed in other elastomers. This is considered to be due to the dilution effect, which is greater at a higher content of soft segment.

#### FTi.r. spectra

The phase structure of the elastomers was studied by investigating the probable hydrogen bonds between the phases, using i.r. spectroscopy. The N-H stretching region of the spectra for the P10-1 series are shown in Figure 4. It is observed that the intensity of the band at  $3444\text{ cm}^{-1}$  and that of the shoulder at  $\sim 3360\text{ cm}^{-1}$  increase as the amount of soft segment increases. The band at  $3444\text{ cm}^{-1}$  can be assigned to the free N-H stretching mode, while hydrogen-bonded N-H stretching is located between  $3230$  and  $3400\text{ cm}^{-1}$  as a broad band reflecting the distributions of hydrogen bonds at different distances and geometries<sup>21,22</sup>. The shoulder at  $\sim 3360\text{ cm}^{-1}$  should correspond to the relatively weakly hydrogen-bonded N-H groups, since the frequency of hydrogen-bonded N-H stretching has been found to increase as the average strength of the hydrogen bond decreases<sup>22,23</sup>. The results of Figure 4 therefore indicate that the concentrations of the free and the weakly hydrogen-bonded N-H groups increase as the amount of intimately mixed soft segment increases. This trend was observed for the other series of elastomers and is consistent with the results of thermal analysis. Spectra for the elastomers with different aliphatic dicarboxylic acids and different  $M_n$  of soft segment are compared in Figure 5. The intensities of the bands at  $\sim 3360\text{ cm}^{-1}$  relative to those at  $\sim 3305\text{ cm}^{-1}$  are in the order P4-1-5 < P10-1-5 < P7-1-5 and P7-2-5 < P7-2-5 < P7-1-5. These orders are also consistent with the orders of mixing between the hard and soft phases observed by thermal analysis.

Figure 6 shows the FTi.r. spectra in the C=O stretching region. The band of ester C=O groups in the soft segment at  $1733\text{ cm}^{-1}$  does not show a noticeable shift in peak position, which suggests little change in hydrogen bonding of ester groups in the soft segment. The amide I band in the range  $1640\text{--}1700\text{ cm}^{-1}$  shows some changes. The amide I

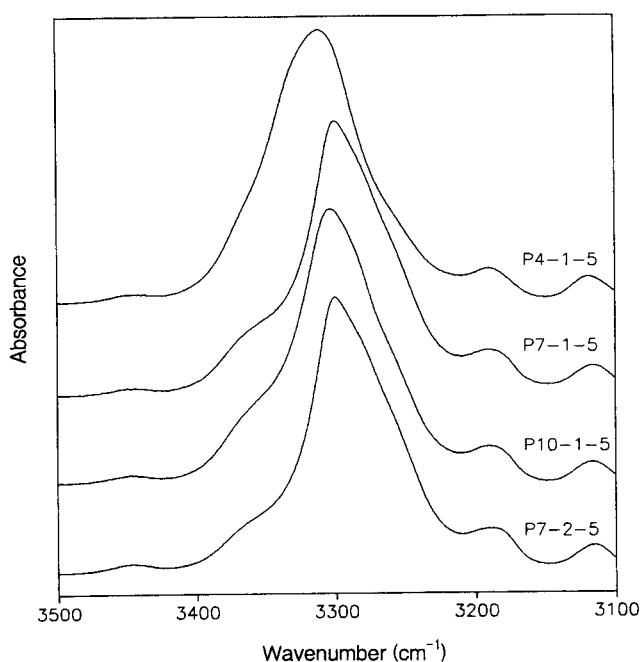


Figure 5 FTIR spectra of Px-y-5 elastomers, showing N-H stretching region

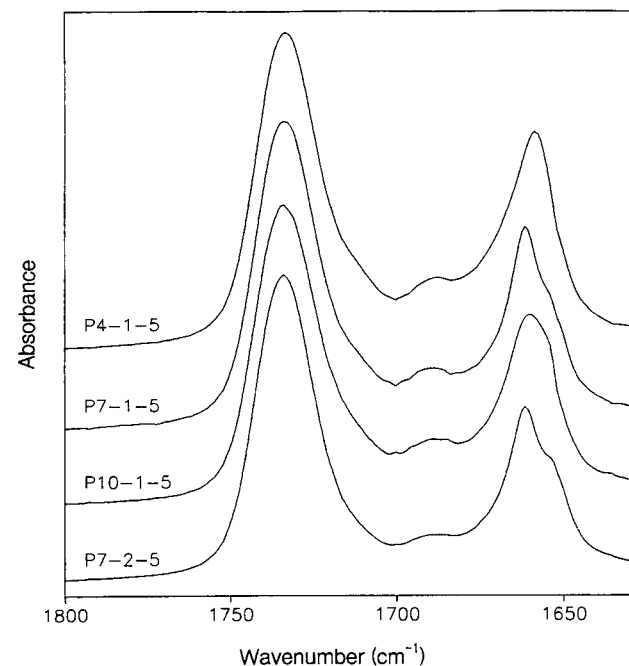


Figure 6 FTIR spectra of Px-y-5 elastomers, showing C=O stretching region

band of semicrystalline polyamides is known to be composed of three bands: one for free carbonyl stretching and the other two for the stretching of hydrogen-bonded carbonyl groups in amorphous and crystalline regions. In the case of polyamide 11 they are observed at 1684, 1654 and 1641  $\text{cm}^{-1}$  respectively<sup>23</sup>. For PEA elastomers the intensities of the amorphous band at  $\sim 1660 \text{ cm}^{-1}$  relative to the crystalline band (right shoulder) are in the order P4-1-5 < P10-1-5 < P7-1-5 and P7-2-5 < P7-1-5. The results are consistent with those from Figure 5 and thermal analysis.

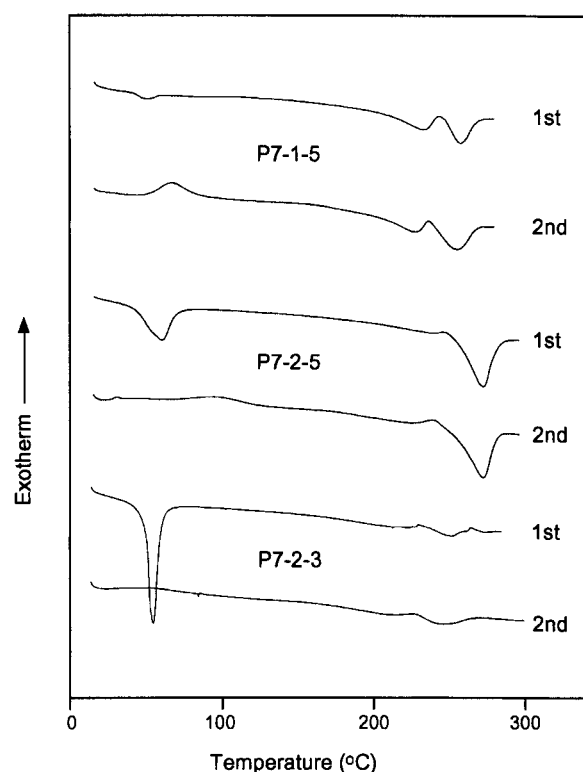


Figure 7 D.s.c. thermograms of P7 series elastomers after tensile tests

#### Tensile properties

Tensile properties of some of the PEA elastomers are given in Table 4. The elastomers with 50 wt% of hard segment have higher secant moduli, higher tensile strengths and lower elongations at break than those with 30 wt% of hard segment. Comparing the elastomers with 50 wt% of hard segment, PEA prepared with PBA2400 generally (with one exception) have lower secant moduli and higher tensile strengths and elongations at break than those prepared with PBA1200 and the same aliphatic dicarboxylic acid. These results suggest that when the content of hard segment is 50 wt%, intimate mixing between the hard and soft phases enhances the rigidity at low deformation but impairs the high-deformation tensile properties.

When the content (50 wt%) and  $M_n$  of soft segment are the same, the tensile properties at high deformation increase in the order P7 < P10 < P4, which is the order of decreased mixing. From the results, mixing of hard and soft phases is an important factor determining the tensile properties at high deformation. However, the modulus increases in the order P10 < P4 < P7, which is not the order of increased mixing. This is probably due to the higher aromaticity of the hard segment of the P4-series elastomers, which outweighs the effect of phase mixing.

Elastic recovery of the elastomers was determined by measuring the lengths at 300% extension and after free recovery. Tensile set, a measure of recovery, is defined by<sup>24</sup>:

$$\text{Tensile set (\%)} = 100 \times (L_2 - L_0)/(L_1 - L_0) \quad (1)$$

where  $L_0$  is the original gauge length,  $L_1$  the length at full extension (300% strain) and  $L_2$  the final length after recovery. That is, the higher the set, the lower the recovery. The tensile set values of PEA elastomers in Table 4 appear to be generally higher than those of polyurethane elastomers based on MDI and poly(tetramethylene glycol),

**Table 4** Tensile properties of PEA elastomers<sup>a</sup>

Polymer	3% secant modulus (MPa)	100% secant modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Tensile set (%)
P4-1-5	134 (14.2)	18.4 (1.1)	48.1 (4.0)	721 (121)	67.8 (3.4)
P7-1-5	175 (32.9)	18.2 (0.5)	26.7 (0.8)	425 (22)	—
P10-1-5	118 (10.1)	17.2 (1.5)	31.8 (2.7)	628 (43)	—
P10-1-3	26 (2.3)	5.5 (0.3)	26.4 (2.7)	807 (59)	—
P4-2-5	113 (13.4)	13.6 (0.9)	40.0 (2.5)	757 (106)	50.8 (0.4)
P4-2-3	21 (4.9)	6.0 (0.3)	27.3 (8.2)	801 (155)	73.5 (2.6)
P7-2-5	117 (16.0)	16.7 (1.2)	32.0 (1.5)	593 (74)	—
P7-2-3	45 (2.5)	8.4 (0.3)	19.8 (10.5)	840 (278)	70.1 (1.5)
P10-2-5	96 (16.5)	13.4 (0.7)	34.1 (7.6)	734 (149)	—
P10-2-3	57 (11.6)	8.1 (0.3)	27.4 (1.2)	979 (104)	80.5 (2.6)

<sup>a</sup> Figures in parentheses are standard deviations

which are < 25%<sup>25</sup>. This could be attributed to more phase-separated morphology in those polyether-based polyurethane elastomers than in PEA elastomers. The lower the degree of mixing of hard segment into soft domain, the greater the elastic recovery. For the PEA elastomers of the P4 series, tensile set decreased as  $M_n$  of the soft segment or the content of hard segment increased. Although this could also be explained by the degree of mixing, the crystallization of the soft phase at high elongation appeared to contribute, as is revealed below.

Thermal properties of some specimens after tensile testing were examined by d.s.c. As shown in *Figure 7*, the melting peaks of the soft phase observed in the first scan disappeared in the subsequent second heating, whereas those of the hard phase were almost invariant. This implies that the soft phase had been under considerable stress during tensile testing, which appeared to induce crystallization of that phase. This stress-induced crystalline phase was corrupted during annealing, which resulted in the disappearance of melting peaks in the second heating. The melting peak of the soft phase is more explicit in the order P7-1-5 < P7-2-5 < P7-2-3, which is in accordance with increasing elongation at break. The same was found in the P4-series elastomers, and this is thought to affect the recovery behaviour of these elastomers.

## CONCLUSIONS

Mixing of the hard and soft phases in the PEA elastomers prepared increased as the molecular weight of constituent segment decreased and in the order adipic acid < 1,10-decanedicarboxylic acid < azelaic acid in the hard segment. Tensile measurements revealed that the phase mixing enhanced the low-deformation property (modulus) but impaired the properties at high deformation (tensile strength and elongation at break) and elastic recovery.

## ACKNOWLEDGEMENTS

This work was financially supported by a research grant

(94-0502-08-03-3) from the Korea Science and Engineering Foundation.

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