Synthesis and Properties of Segmented Block Poly(oxyethylene-*block*-esteramide)

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ABSTRACT: A series of poly(oxyethylene-*block*-esteramide)s (PASHs) containing *p*-aminobenzoic acid units were prepared by bulk polymerization of N, N'-bis(*p*-ethoxycarbonylphenyl) sebacamide and mixed diols of 1,6-hexanediol and poly(ethylene glycol) (PEG, MW 600, up to 34 mol%). The poly(oxyethylene-*block*-esteramide)s exhibited the inherent viscosity ranging from 0.61 to 0.87 dL g^{-1} while the parent poly(ester-amide) yielded an inherent viscosity of 0.41 dL g^{-1}, which is attributable to chain extension and homogeneity of reaction mixture in the presence of PEG. The parent poly(ester-amide) showed relatively fast crystallization and high T_g for its alternating arrangement of ester-amide sequence, resulting in extremely brittle characteristics. However, the glass transition temperatures, T_g, of the poly(oxyethylene-*block*-esteramide)s containing 13–16 mol% of PEG were found in the range 31–45 °C and demonstrated greatly improved mechanical properties. The storage modulus in ambient temperature was *ca*. 1300–1400 MPa, and the tensile strength was measured 40–85 MPa. From the dynamic mechanical analysis it was also found that storage modulus at rubbery plateau region increased as PEG was introduced up to 16 mol%, indicating a good dimensional stability above T_g.

KEY WORDS Poly(ester-amide) / Poly(oxyethylene-*block*-esteramide)s / Hard Segment / Soft Segment / Dimensional Stability / Dynamic Mechanical Properties /

There has been growing interest in aromatic poly(ester-amide)s as a new series of thermoplastic materials.[1,2] Among many structural features of poly(ester-amide)s, the distribution of amide and ester segments is one of the most critical factors determining the physical properties.[3–5] Recently, alternating poly(ester-amide)s have been synthesized to implement structural regularity to the random poly(ester-amide)s.[6,7] Van Benekom *et al.* reported that alternating poly(ester-amide)s derived from bisesteramide (1,4-buthylene terephthalamide dimethyl ester (T4T-dimethyl)) demonstrated rapid crystallization rate and high dimensional stability.[8] However, these alternating poly(ester-amide)s are very brittle for practical use. To overcome these shortcomings, new type of aromatic poly(ester-amide)s was developed by introducing flexible spacers comprising aliphatic polyesters or polyethers. Conventionally, it was well recognized that the molecular weight, crystallinity and mechanical property of these copolymers depends on compatibility and composition between the hard phase and the soft phase. Niesten synthesized poly(ester-amide)s from 1,4-phenylene terephthalamide dimethyl ester (TΦT-dimethyl) and poly(tetramethylene oxide) (PTMO) as a soft phase.[10] A major disadvantage of TΦT-PTMO copolymers system was that the polymerization was conducted in the presence of NMP, since TΦT-dimethyl is poorly soluble in the reaction mixture at the polymerization temperature.

In this present study, we prepared the segmented poly(oxyethylene-*block*-esteramide)s employing N, N'-bis(*p*-ethoxycarbonylphenyl) sebacamide and PEG *via* bulk polymerization route. The solvent-free melt polymerization is preferred since no post-treatment is necessary after the reaction. It was anticipated that N, N'-bis(*p*-ethoxycarbonylphenyl) sebacamide inherently provides alternating arrangement of amide and ester groups, while PEG segments serve as a reaction medium as well as a flexible spacer. The compatibility of N, N'-bis(*p*-ethoxycarbonylphenyl) sebacamide and PEG should favorably affect the synthesis. The effects of PEG content on the thermal and physicochemical properties of resulting copolymers were investigated.

EXPERIMENTAL

Materials

Ethyl 4-aminobenzoate (Aldrich Chem. Co), 1,6-hexanediol (Aldrich Chem. Co), and poly(ethylene gly-

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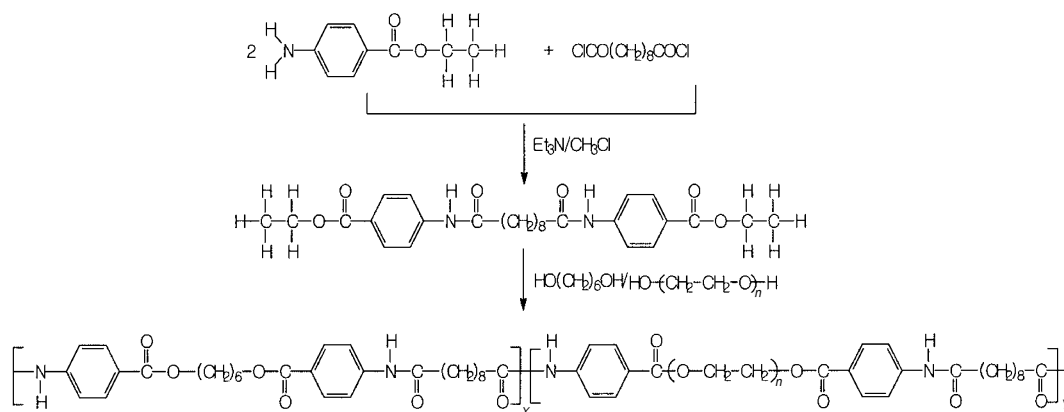
Scheme 1. Synthesis of poly(oxyethylene-*block*-esteramide)s by melt condensation.

col) (M_w 600) (Yakuri Pure Chem. Co) were without further purification. Triethylamine (Aldrich Chem. Co) was distilled over calcium hydride under a nitrogen atmosphere. Sebacoyl chloride (Aldrich Chem. Co) was used after vacuum distillation.
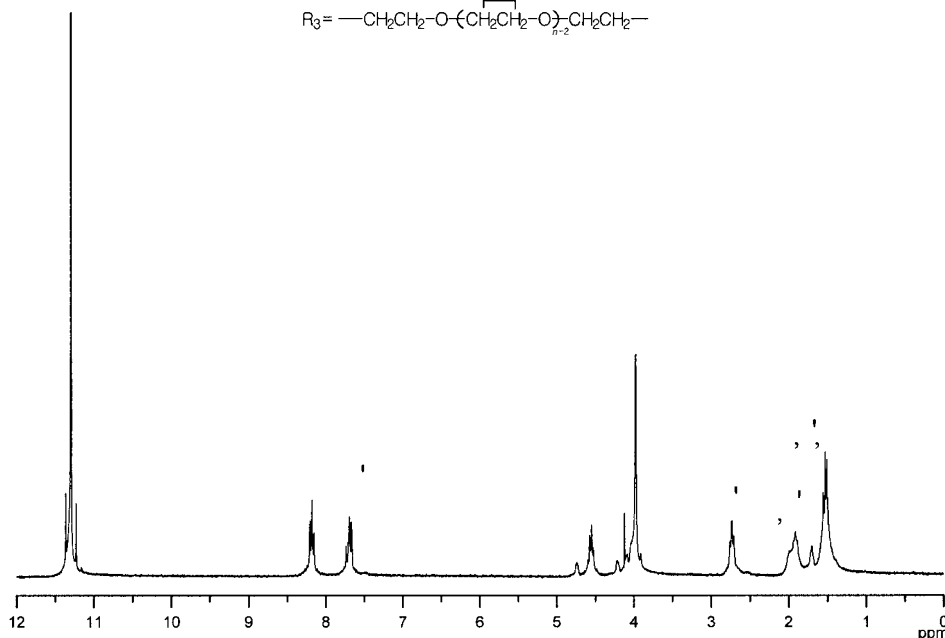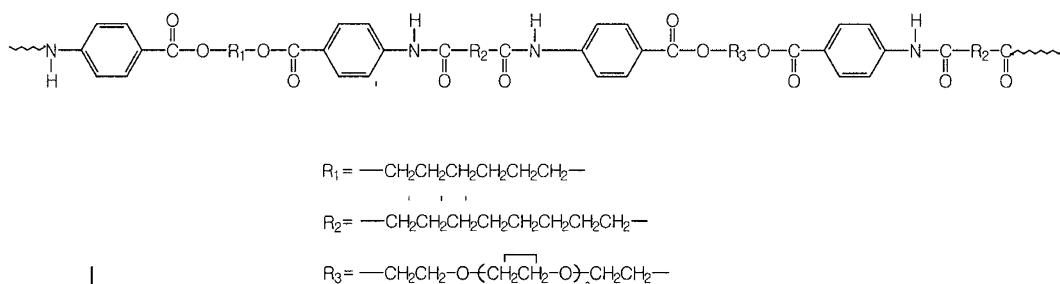
Polymerization

Poly(oxyethylene-*block*-esteramide)s (PASH) were synthesized *via* melt polycondensation and esterification steps as given in Scheme 1. N, N'-Bis(p-ethoxycarbonylphenyl) sebacamide was synthesized from ethyl 4-aminobenzoate and sebacoyl chloride according to the procedure previously reported.[11] Polymerization was performed using antimony(III) oxide as a catalyst *via* two step reaction. A mixture of 10 mmol (5 g) of N, N'-bis(p-ethoxycarbonylphenyl) sebacamide and 12 mmol (1.4 g) of 1,6-hexanediol with PEG (M_w 600, 0–3 mmol) were placed in a four-necked 50 mL flask equipped with a nitrogen inlet, condenser, and an overhead stirrer. Excess diols was used to control stoichiometry at 260 °C under vacuum, as well as to form ester linkage by esterification reaction with N, N'-bis(p-ethoxycarbonylphenyl) sebacamide. Bath temperature was allowed to increase to 100 °C and maintained at the temperature for 20 min. Antimony(III) oxide was introduced when all the reaction mixture was melted. The reaction mixture was heated to 200 °C for 20 h under a nitrogen atmosphere. Ethanol was distilled off in the process. Then, nitrogen supply was disconnected and the reactor was connected to a vacuum pump with a pressure gage. The reactor temperature was gradually increased to 260 °C and maintained for 5–6 h in a vacuum of < 0.1 torr. The synthesized polymer was dissolved in hot N, N'-dimethyl acetamide, then precipitated from water. The product was collected by filtration and dried under reduced pressure at 40 °C to give a yellow powdery material.

Copolymers are coded with the initials of starting materials. The numbers at the end of these codes denote the contents of poly(ethylene glycol). For instance, a poly(oxyethylene-*block*-esteramide) derived from the components of ethyl 4-aminobenzoate, sebacoyl chloride, 1, 6-hexanediol, and PEG (7 mol% of mixed diol) is denoted as PASH-7.

Polymer Characterization

The copolymer composition was confirmed using 400 MHz ^{1}H NMR (Bruker) after the samples were dissolved in deuterated trifluoroacetic acid without an internal standard or deuterated dimethyl sulfoxide containing TMS. Inherent viscosity was determined by measurement using a Cannon-Ubbelhode microviscometer at the concentration of 0.3 g dL^{-1} in N, N'-dimethyl acetamide at 25 °C ± 0.1 °C. Samples for the analysis (DSC, DMA, WAXD, tensile test) were prepared on the compress mould machine. The temperature setting was 30–50 °C above T_m. After melting, samples were quenched to ice water. Before use, all polymers were dried in a vacuum oven at 40 °C for 48 h. The melting behaviors of PASH series were studied using a Perkin–Elmer DSC-7, which was precalibrated with Indium and Zinc standards. Upon melting, the samples were heated to 250 °C at a rate of 10 °C min^{-1}. The peak point of the melting peak was taken as the melting temperature. The micro-structural changes were investigated by wide angle X-Ray diffraction (WAXD). Spectra were taken at room temperature by a scan speed of 10 ° min^{-1} over the range of 5° to 40° using an X-Ray diffractometer equipped with a Nickel filtered Cu-$K\alpha$ radiation. (40 kV, 30 mA) (Rigaku Denki, Model DMAX 2000). Morphology of spherullites was observed under a polarizing optical microscope (Nikon HFX-11A). The storage and loss moduli were measured as a function of temperature by dynamic mechanical analysis (TA-DMA 2980) at a frequency of 1 Hz

Figure 1. The ^{1}H NMR spectra of PASH–26, poly(oxyethylene-*block*-esteramide).

Table I. Polymerization data and thermal properties of PASHs

| Polymer Code | Composition | | Yield | η_{inh}^{c} | T_m | ΔH_f | T_c^{d} | $T_m - T_c^{d}$ |
	Monomer mol ratio[a]	H·D:PEG mol%[b]	%	dL g^{-1}	°C	J g^{-1}	°C	°C
PASH-0	1/1.2/0	100 : 0	85	0.47	221.3	50.6	203.3	18.0
PASH-7	1/1.2/0.05	92 : 7	92	0.64	214.1	39.3	190.5	23.6
PASH-13	1/1.2/0.10	87 : 13	87	0.63	208.9	38.7	180.7	28.2
PASH-16	1/1.2/0.16	84 : 16	80	0.61	207.1	37.7	179.9	27.2
PASH-26	1/1.2/0.21	74 : 26	85	0.66	166.0	11.6	127.4	38.6
PASH-34	1/1.2/0.30	66 : 34	78	0.87	165.0/176.0	23.2	152.2	23.8

[a]Feed molar ratio of monomers; (*N,N'*-bis(*p*-ethoxycarbonyl/phenyl)sebacamide/1,6-hexanediol/poly(ethylene glycol)). [b]Calculated molar ratios of H·D (1,6-hexanediol) : PEG (poly(ethylene glycol)) determined by ^{1}H NMR. [c]Inherent viscosity in *N, N*-dimethyl acetamide at 25 °C ± 0.1°C, 0.3 g dL^{-1}. [d]Obtained as crystallization temperature on cooling scan at 10 °C min^{-1} after melting.

under nitrogen atmosphere. Samples were quenched to −40 °C and then gradually heated to 180 °C at a rate of 2 °C min^{-1}. The peak position of loss modulus is taken as a glass transition temperature. The films were prepared by compressing the polymer melt between Teflon® sheet and subsequent quenching in water. Mechanical properties were measured on a TA 4465 instruments with 1 kN load cell at the cross head speed of 10 mm min^{-1}. The polymer films were prepared on the film with a dimension of 5 mm width, 15 mm gauge length, and 0.1–0.2 mm thickness.
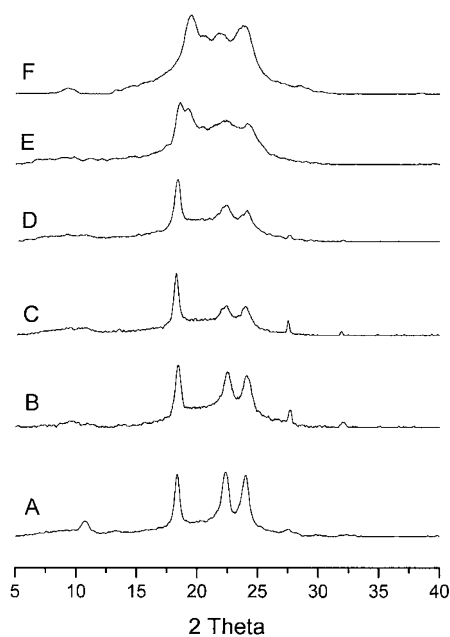
RESULTS AND DISCUSSION

Figure 1 shows a representative ^{1}H NMR spectrum of PASH-26. The integration ratios between the peaks at 4.55 ppm (–CH$_2$–OCO–) and 3.98 ppm (–O–(CH$_2$CH$_2$O–)$_{n-2}$) were used to determine the compositions of 1, 6-hexanediol and of PEG in the copolymer. The feed and observed compositions of respective monomer are presented in Table I. ^{1}H NMR study indicates that the copolymers contain less amounts of
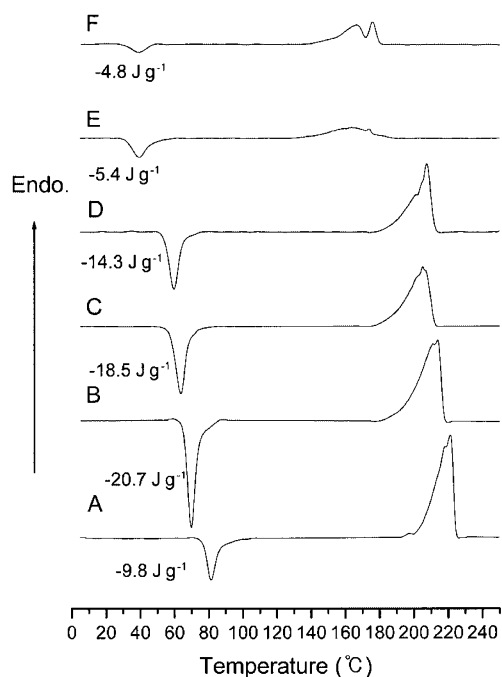
Figure 2. DSC traces for PASHs in first heating run at $10\,^{\circ}\mathrm{C\,min^{-1}}$; A, PASH-0; B, PASH-7; C, PASH-13; D, PASH-16; E, PASH-26; F, PASH-34.

Figure 3. WAXD patterns of PASH films crystallized at ambient temperature; A, PASH-0; B, PASH-7; C, PASH-13; D, PASH-16; E, PASH-26; F, PASH-34.

hexane diol than the corresponding feed compositions due to the higher volatility than PEG. The inherent viscosity, η_{inh}, of PASHs containing PEG measured in the range of 0.61 to 0.87 dL g^{-1}. The η_{inh} value consistently increased with the incorporation of PEG segments.

Figure 2 shows the DSC thermograms of PASH series. The melting endotherms of these poly(oxyethylene-*block*-esteramide)s shifted to lower temperatures as the PEG content increases. The PASH-0 without PEG has an exotherm peak with relatively lower intensity. This result may be due to the relatively dominant crystallization rate of alternating poly(esteramide), PASH-0. The crystallization peak of PASH-7 obtained on heating scan or cooling scan has a sharper crystallization peak than the other PASHs containing PEG. This result, together with the facts that PASH-7 has a lower degree of supercooling (T_m–T_c) for crystallization, indicates that 7% of soft segments enhance the crystallization of hard segments more effectively by plasticizing the chains. On the other hand, when the PEG content was 26% or higher, the melting temperature shifted below 170 °C, displaying the dual melting peaks. The shape of melting endotherms became broader and the crystallinity decreased drastically because of loss of structural order as well as retardation of crystallization by the dilution effect.[12] Interestingly, PASH-34 showed slightly higher heat of fusion than PASH-26. From the combination of DSC, X-Ray diffraction studies and spherulite morphology, it seems that the crystallization of isolated hard segment is fa-

vorably affected in the presence of high content of PEG. Sorta *et al.* investigated the thermal properties of aromatic poly(ester-amide)s with polyether block and proposed that two melting peaks are due to the melting of isolated segments, which can join in the neighboring hard segments or crystallize in the form of clusters.[13]

X-Ray diffraction patterns for the films crystallized at ambient temperature are depicted as in Figure 3. WAXD pattern of PASH-0 exhibits distinct crystalline peaks at 18°, 22°, and 24°. As PEG content in the segmented block copolymers increased, WAXD curves become only broader without any significant changes. He and Olley previously reported that the aromatic poly(ester-amide) with flexible spacers showed only minor variations with different crystallization temperature, suggesting that it resulted in the minor modification within one phase.[14] In this study, in spite of insignificant variations in the WAXD pattern, several features are worth to be noted. WAXD curves of PASH-26 revealed two peaks with an additional peak at 19°. In case of PASH-34, the two peaks are distinctly associated at 19°, indicating that different crystallite could be formed by the introduction of excess PEG.

Figures 4a–4c show the polarizing micrographs of PASHs crystallized for 2 h at 25 °C below their melting points. Different kinds of spherulites were observed from the crystallization of PASHs with various compositions. In polyamides, the positive spherulites are usually observed due to the preferred alignment of the hydrogen-bonding direction along the spherullite radii.[15] PASH-0 showed impinging large spherulites as

(a)

(b)

(c)
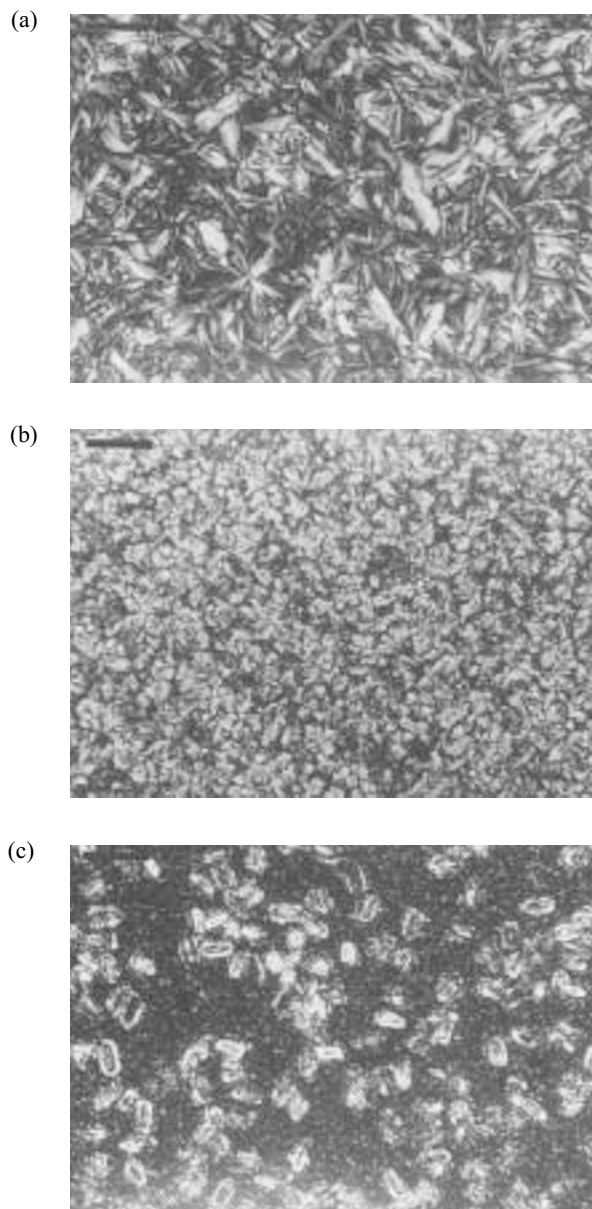
Figure 4. The polarizing optical micrographs of spherulites grown from melts; (a) PASH-0, isothermal crystallization at 200 °C; (b) PASH-16, isothermal crystallization at 180 °C; (c) PASH-34, isothermal crystallization at 140 °C (scale bar : 50 μm).
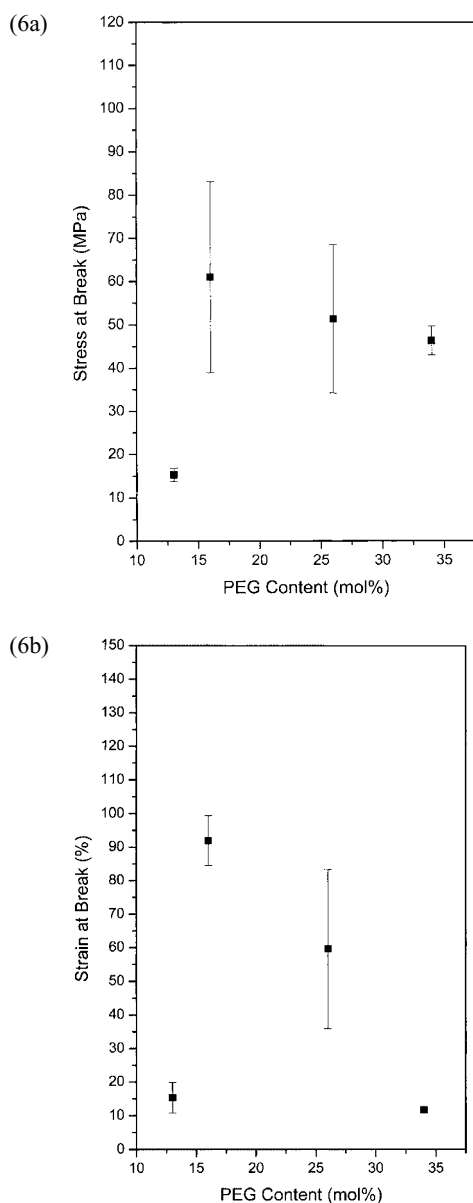
shown in Figure 5a. It is considered to be a characteristic of the lamellar containing rigid *p*-aminobenzoic acid unit, which is likely to orient regularly along radii of spherulite. The spherulites of PASH-16 are smaller than those in the PASH-0. The spherulitic morphology of PASH-34 was observed as an occasional appearance of oval textures with small concentric ring as shown in Figure 4c.

Storage modulus and loss modulus were measured using dynamic mechanical analysis (DMA). For the poly(oxyethylene-*block*-esteramide) containing less than 13 mol% of PEG, the modulus could not be measured because compress molded film was extremely brittle. The PASHs containing 26 mol% and

(a)

(b)
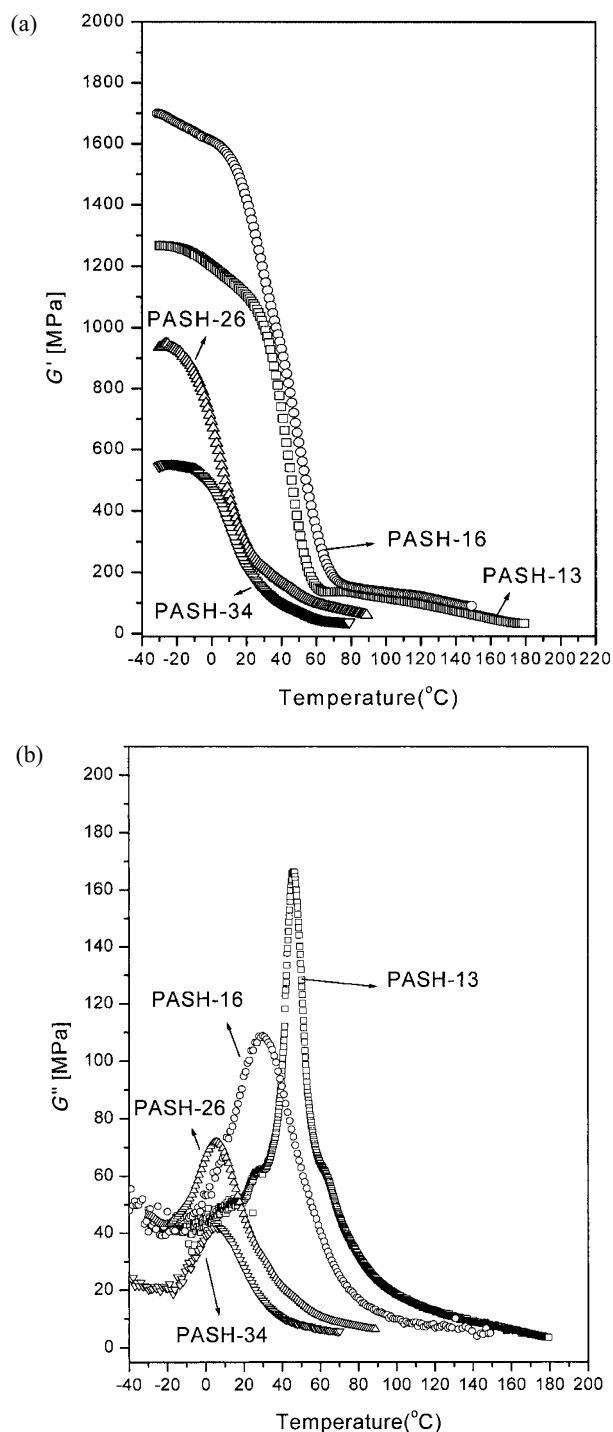
Figure 5. Storage modulus (a) and Loss modulus (b) of PASHs versus the temperature.

34 mol% of PEG were obtained as rubber-like materials with low values (100–200 MPa) of G' at ambient temperature. Figure 5a shows the storage modulus of PASHs plotted against the temperature for various PEG contents. PASH-16 has a higher storage modulus compared with PASH-13. A plausible explanation may be that the introduction of 16 mol% PEG is able to increase the chain mobility, which lead to the increase of crystallinity by the plasticization effect during heating process. The level of the modulus above T_g is im-

(6a)

Table II. DMA results for PASHs and other thermoplastics

Polymer Code	$T_g(°C)$	$\dfrac{G' \text{ at } 150°C}{MPa}$	$\Delta G'$	$T_g(K)/T_m(K)$
PASH-13	45	61	2.1	0.66
PASH-16	31	90	1.9	0.63
4NT6[7]	94	174	2.5	0.65
PBT[17]	50	79	5.6	0.65

PBT, indicating that the dimensional stability above T_g is similar to PBT. Comparing with poly(alkylene terephthalate) such as PBT, PASH-13 and PASH-16 have a lower T_g, which is ascribed to the longer flexible chains being present in the amorphous phase. In addition, PASH-13 and PASH-16 have 0.66 and 0.63 of the T_g/T_m, respectively. These values are nearly consistent with the T_g/T_m ratio (2/3) for most semi-crystalline homopolymers.[18, 19]

PASHs containing PEG ranging from 0 to 13 mol% possess an extremely low strain since they are in the glassy state at ambient temperature. The tensile strength depends largely on the molecular weight of the polymer. Moreover, the ultimate tensile strength at application temperature can be considerably influenced by the position of glass transition temperature. The PASH-16 exhibits greatly improved the tensile strength among the PASHs series, comparable to the commercial thermoplastics. The stress at break of PASH-16 is approximately 60 MPa. PASHs containing 26 mol% or more PEG were obtained as rubber-like materials at ambient temperature and have low stress and strain at break. These results imply that the control of T_g determine the mechanical properties and the intramolecular hydrogen bondings can be restricted by excess PEG.

(6b)

Figure 6. Stress at break (a) and strain at break (b) of PASHs.

portant for high temperature applications. As shown in Figure 5b, the T_g was taken as maximum of the curve of the loss modulus. G' in the rubbery plateau region above T_g is usually measured at $T_g + 40\,°C$.[16] The decrease of the modulus above T_g is expressed as following eq 1.[6]

$$\Delta G' = \frac{G'_{(T_g+40)}}{G'_{(T_{fl}-40)}} \qquad (1)$$

The values of $\Delta G'$ and T_g/T_m are given in Table II. High values of $\Delta G'$ indicate strong decrease of the modulus. In eq 1 T_{fl} is the temperature of flow ($G' < 5$ MPa) due to a loss of crystallinity. Table II also shows $\Delta G'$ values and T_g/T_m of a commercial engineering plastic such as PBT and 4NT6 for comparison purposes.[17] It is clear that PBT and 4NT6 have a good dimensional stability above T_g. PASH-16 has a higher value of $\Delta G'$ than

CONCLUSIONS

Poly(oxyethylene-*block*-esteramide)s were synthesized with varying PEG content by bulk polymerization. N,N'-Bis(p-ethoxycarbonylphenyl) sebacamide inherently provided alternating arrangement of amide and ester groups, while PEG segments served as a chain extender and a reaction medium. The improved solubility of N,N'-bis(p-ethoxycarbonylphenyl) sebacamide in the reaction mixture comprising PEG resulted in the increase of molecular weights. While the parent poly(ester-amide) was too brittle to give any measurable mechanical strength the poly(oxyethylene-*block*-esteramide) containing 16 mol% of PEG formed flexible film with significant tensile strength. The DMA tests showed that poly(oxyethylene-*block*-esteramide)s containing ~16 mol% had high storage modulus at ambient temperature. The T_g appeared to decrease with increasing PEG, implying that the intramolecular hydro-

gen bondings in amorphous phase might be restricted by excess PEG. From the spherulitic morphology and their WAXD curves, different kinds of spherulites and new crystalline peaks were observed with excess PEG (> 26 mol%), suggesting the amount of PEG accompanying with insignificant variations. PASH-16 presents a high $\Delta G'$ similar to commercial engineering plastic, indicating that it has good dimensional stability above T_g.

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