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Novel copolyester-based ionomer for a shape-memory biodegradable material

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Abstract

A series of biodegradable poly(oxyethylene-*b*-butylene adipate) ionomers (POBAis) were synthesized by bulk polymerization of adipic acid and mixed monomers of bis(poly(oxyethylene)) sulfonated dimethyl fumarate and 1,4-butanediol. The POBAis exhibited notable recovery rate ranging from 81% to 95% at near body temperature, depending on the content of ionic group. From the dynamic mechanical analysis it was found that storage modulus above rubbery plateau region significantly increased as ionic monomer was introduced up to 2.5 mol%, indicating a good dimensional stability above glass transition region. Wide angle X-ray analysis was carried out to investigate the structural variation over shape deformation and/or recovery. WAXD pattern of POBAi-2.5 revealed that α–β transition of crystal occurred during recovery process. These results may provide crucial information of the crystallizable ionomers as a potential shape-memory polymer (SMP).

Keywords: Biodegradable; Shape-memory polymer; Ionomer

1. Introduction

Recently, a number of thermal-responsive shape-memory polymers (SMPs) have been investigated as a potential family of special biological or medical devices, such as sutures and microactuators for endovascular treatment [1–6]. Many of the studies of these applications have focused on the predominant shape-memory effect at a low response temperature. In fact, SMPs that exhibit excellent shape-memory behavior at body temperature will have the potential to be used in an extensive number of applications. However, SMPs with such behavior remain to be developed.

Typically, the structure of SMPs involves two phases: a thermally reversible phase for maintaining a transient shape and a fixed phase for recovering the original shape. Appropriate control of the two phases is a critical factor in determining the shape-memory behavior. Advances in this structural approach are being developed actively using methods like copolymerization, blending, and the introduction of a cross-linking agent or chain extender. Lee et al. found that polyurethane can be blended with poly(tetramethylene glycol) effectively and suggested that the hard segments that constitute the cross-linking points lead to high shape recovery at above T_g [5]. Recently, Mather et al. synthesized cross-linked polycyclooctene and attributed its thermally induced shape-memory behavior to the underlying cross-linked structure [7].

Despite the extensive research in SMP area, little is actually known about shape-memory behavior of polyester-based polymer, therefore there is no investigation about that of polyester-based ionomers. An ionomer is defined as an ion-containing polymer with some (usually 10–15 mol%) ionic groups along the backbone chains or as pendant groups. A previous study examined polyester-based ionomers synthesized by melt polycondensation and verified that such polyester-based ionomers

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have lower crystallinity than the parent polyester, with no significant change in melting point [8]. A subsequent study of the crystallization behavior of polyester-based ionomers showed that the presence of ionic aggregates effectively restricts chain folding into crystalline lamellae [9,10]. Based on these findings, we expected that introduction of ionic groups into the main chain might not only act as a fixing point memorizing shape during deformation but also findings about structural characteristics of the ionomer will aid in future designs of aliphatic polyester-based ionomers having shape-memory properties [11–13]. The present study deals with synthesis, characterization and shape-memory behaviors of poly(oxyethylene-*b*-butylene adipate) ionomers (POBAis) prepared by employing bis(poly(oxyethylene)) sulfonated dimethyl fumarate as the synthesized novel monomer.

2. Experimental

2.1. Materials and polymerization of POBA and POBAis

ACS grade chemicals were used without further purification. Ionomer groups, bis(poly(oxyethylene)) sulfonated dimethyl fumarate (SPEO), were prepared by using dimethyl fumarate, $NaHSO_4$ and poly(ethylene oxide) (PEO, M_n 600) according to a reported procedure [14]. POBAis were prepared via two-step polycondensation. First, the calculated amounts of adipic acid, SPEO, and 1,4-butanediol were introduced into a four-neck flask equipped with an overhead stirrer and a temperature-control device. The monomer mixture was melted and stirred at 190 °C for 2 h, evolving water condensates. Then, the reaction temperature was raised to 230 °C over 30 min with a gradual reduction in pressure to remove low-molecular-weight condensates. POBA-2.5 was also prepared by above method using adipic acid, 1,4-butanediol, and non-SPEO that was synthesized by using succinic acid and PEO. The poly-(oxyethylene-*block*-butylene adipate) ionomers (POBAis) are denoted by the mole fractions of the ionic groups determined using ^{1}H NMR spectroscopy: e.g., POBAi-2.5 represents poly-(oxyethylene-*block*-adipate) ionomer containing 2.5 mol% SPEO.

2.2. Polymer characterization

The synthesis of the copolymers was confirmed using Bruker 300 MHz ^{1}H NMR in d-chloroform polymer solutions containing tetramethylsilane (TMS) as an internal standard. The molecular weight and molecular distribution of POBA-2.5 and POBAis were measured using gel permeation chromatography (GPC, Shimaz) equipped with an HPLC pump, a refractive index detector using PMMA standards, and a Styragel HR series (eluent: dichloroacetic acid, 35 °C, flow rate: 0.3 ml/min).

In order to provide identical samples and to ensure consistency in various measurements (DSC, DMA, tensile test), the synthesized polymers were compression-molded using a Carver Press at 100 °C and 10 MPa. The molded films were quenched and dried in a vacuum oven at 40 °C for 48 h. The melting behavior of the samples was studied using a differential scanning calorimeter (DSC 2900, TA Instrument) with a heating and cooling rate of 5 °C/min. Dynamic mechanical analysis (DMA 2980, TA Instrument) was performed using dual cantilever tensile mode at a frequency of approximately 1 Hz with a heating rate of 3 °C/min under a nitrogen atmosphere. The samples were cooled to −60 °C and then heated gradually to 30 °C at a rate of 3 °C/min.

The microstructural changes were investigated using wide angle X-ray diffraction (WAXD). Spectra were taken at room

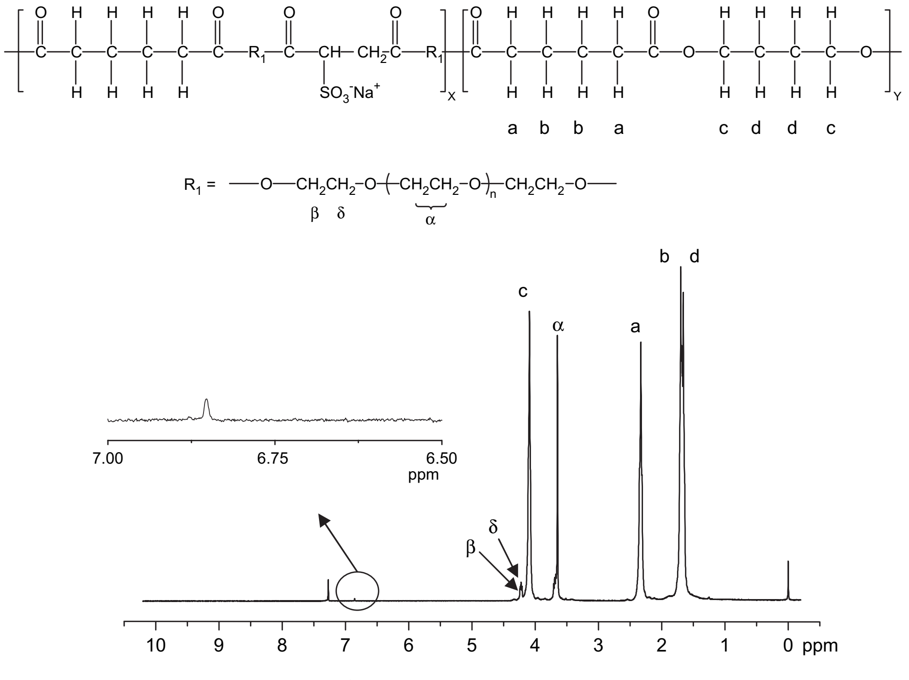

Fig. 1. ^{1}H NMR spectra of POBAi-2.5.

temperature at a scan speed of 10°/min over the range of 5°–40° using an X-ray diffractometer equipped with nickel-filtered Cu Kα radiation (40 kV, 100 mA) (Rigaku Denki, Model DMAX 2000). Cyclic tensile tests at room temperature were carried out on an Instron 4465 tensile tester (Instron Corp.). The samples were elongated to 200% strain at room temperature and then were held for at least 10 min. The samples for recovery test were subsequently heated to around T_{m1}. Cycles were repeated three times each.

3. Results and discussion

Fig. 1 shows the representative ^{1}H NMR spectrum of POBAi-2.5. The integration ratio of the peaks at 6.80 ppm ($-OC-CHSO_3^-Na^+-CH_2COO-$) and 2.35 ppm ($-OCOCH_2CH_2CH_2CH_2OCO-$) was used to determine ionic content in the polymer. The gel permeation chromatography (GPC) results are summarized in Table 1. The molecular weights of POBAis and POBA-2.5 were in the range of 30,000–39,000. POBAis had higher polydispersity index (PDI) values than POBA-2.5. The presence of ionic groups on the ionomers may retard ester interchange due to the inter- or intra-chain interactions between the polymer chains and ionic groups. Previous studies have shown similar trends for a polyester-based ionomer [10].

As shown in Fig. 2(a) and (b), exotherm and endotherm curves of POBAi-5 shifted to lower temperatures with a relatively lower intensity compared to that of POBAi-2.5. This result, together with the fact that POBAi-5 had a relatively higher degree of supercooling ($T_{m1}-T_c$) for crystallization (Table 2), indicates that 5 mol% of ionic groups effectively reduced the regularity of the polymer chains. In Fig. 2(b) all samples were shown double melting peaks due to the melting and recrystallization [15].

Fig. 3 plots the storage modulus of POBA-2.5 and POBAis against temperature. POBAi-2.5 had the highest storage modulus above the rubbery plateau region, which might have been attributable to the strong physical cross-linkage between polymer chains. Previous studies have verified that the introduction of a 2.5 mol% ionic monomer into polyester chains can induce strong physical cross-linkage via electrostatic attractive forces between ionic groups, while the introduction of a 5 mol% ionic monomer can lead to the reverse effect of physical cross-linkage resulting from preferential intramolecular ion-pair associations [8,9,16].

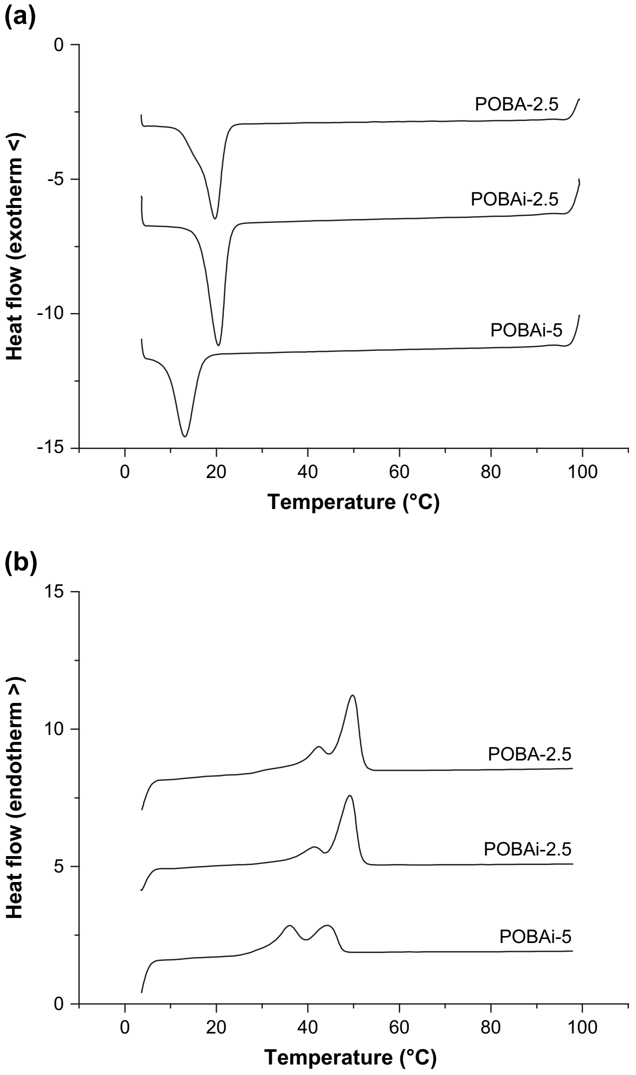

Fig. 2. Differential scanning calorimetry (DSC) traces of POBA-2.5 and POBAis in the cooling (a) and the second heating (b) at 5 °C/min.

Table 1
Polymerization data and GPC results for POBA-2.5 and POBAis

Polymer code	Composition		GPC results	
	Feed composition[a]	Content of secondary monomer (non-SPEO or SPEO)[b] (mol%)	$M_n \times 10^{-4}$	M_w/M_n
POBA-2.5	1/1.17/0.03	2.5	3.1	1.5
POBAi-2.5	1/1.17/0.03	2.5	3.0	3.0
POBAi-5	1/1.14/0.06	5	3.9	2.0

[a] Feed molar ratio of the monomer; (adipic acid/1,4-butanediol/bis(poly(oxyethylene)) dimethyl succinate (non-SPEO) or bis(poly(oxyethylene)) sulfonated dimethyl fumarate) (SPEO).

[b] Real composition of non-SPEO or SPEO determined using ^{1}H NMR.

In Fig. 4(a), WAXD patterns of POBAi-2.5 at initial state showed distinct crystalline peaks at 21.2° (β_I), 22.3° (α_{II}), and 24.3° (β_{II}), indicating coexistence of the α- and β-form crystals arising form PBA segments. Typically, the monoclinic α-form crystal is more stable than the orthorhombic β-form crystal [15,17]. After deformation widths of all peaks are broadened and α_{II} peak is disappeared. Especially, β_I and β_{II} peaks are also shifted to higher and lower degree. After recovery, it is found that the values of 2 theta of all peaks are changed to close to α-form and the intensity of α_{II} peak is

Table 2
The thermal properties of POBA-2.5 and POBAis

Polymer code	T_g[a] (°C)	T_c (°C)	T_{m1} (°C)	T_{m2} (°C)	$T_{m1}-T_c$ (°C)	ΔH_f (J/g)
POBA-2.5	−49.1	19.7	42.4	49.2	22.7	37.8
POBAi-2.5	−48.8	20.4	41.4	49.7	21.0	35.6
POBAi-5	−47.7	13.1	36.1	44.6	23.0	27.9

[a] T_g was measured using DMA.

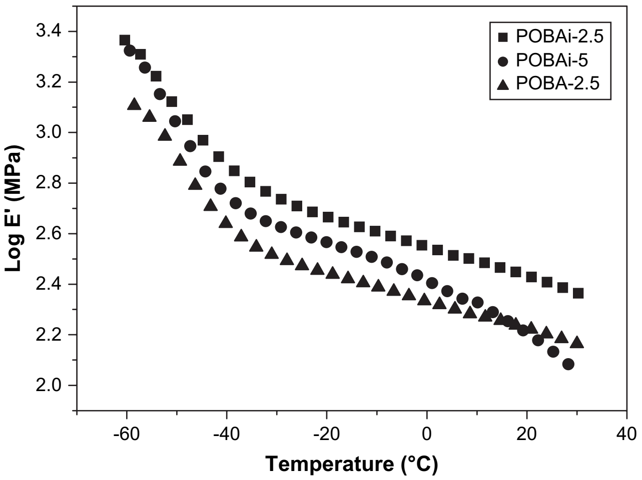

Fig. 3. Storage modulus of the samples as a function of temperature. POBA-2.5 (▲), POBAi-2.5 (■), POBAi-5 (●).

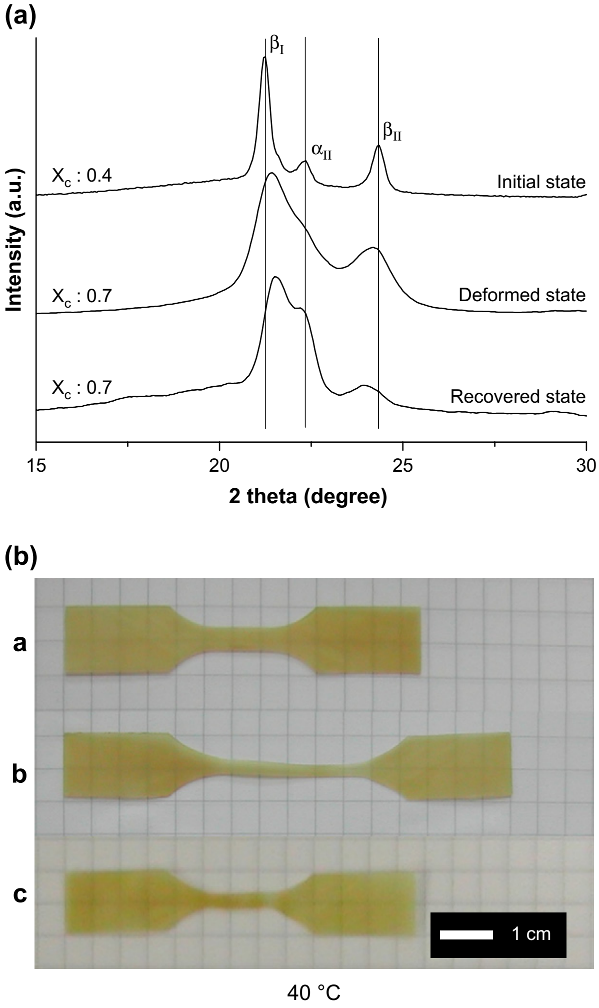

Fig. 4. WAXD patterns of the melt-crystallized POBAi-2.5 films at room temperature (a). The crystallinity was calculated by deconvoluting the WAXD patterns using an XPS peak fitting program (version 4.1). Image of POBAi-2.5 in the shape-recovery state at 40 °C obtained during the third shape-recovery test (b); a: initial state, b: deformed state, c: shape-recovered state.

Table 3
The corresponding *d* spacing values and reflection planes of WAXD diffraction peak at each state

State	2 Theta[a] (°)	*d* (obs)[a] (nm)	*d* (calc)[b] (nm)	*hkl*[b]	Crystal form[b]
Initial	21.20	0.419	0.417	110	β_I
	22.33	0.397	0.400	020	α_{II}
	24.34	0.365	0.368	020	β_{II}
Deformation	21.39	0.415			
	24.17	0.368			
Recovery	21.49	0.413	0.409	110	α_I
	22.27	0.399	0.400	020	α_{II}
	23.97	0.371	0.372	021	α_{III}

[a] Data from this work.

[b] Data from Refs. [23,24].

increased compared to those in initial state (Table 3). This result indicates that the β-form crystal of PBA portion at initial state is changed to the structurally more stable α-form crystal with increasing the cycle times of deformation and recovery. Even though the stress-induced phase transition of crystal form is reversible for poly(tetramethylene naphthalate) and poly(tetramethylene succinate), most of phase transitions are irreversible [18−24]. It is found that the polymer here is also irreversible and α-form crystal formed during recovery process does not turn back to the ones of initial state. Moreover, the recovery rate and crystallinity of POBAis increased with the times of cyclic tensile test (Table 4). Especially, POBAi-2.5 had a lower recovery rate than POBAi-5 in the first recovery test, but had a higher value in subsequent recovery test compared to that of POBAi-5. In our previous paper, Han et al. reported that the presence of ion aggregates affects the extent of diffusion of chains toward crystallization when the chains constrained in an amorphous region are recrystallized [25]. Nevertheless, these results were thought to indicate that deformation/recovery process makes the chains' easy crystallization despite cross-linking by ionic groups. Polylactide-*co*-poly(glycolid-*co*-caprolactone) multiblock copolymer obviously had shown that shape-recovery rate increased with increasing the cycle times of deformation and recovery [22]. In this paper, there is no mention of the cause of the increase of shape-recovery rate with increasing cycle times. Kim et al. [13] have investigated shape-memory effect of polyurethane ionomer based on polycaprolactone diols. According to Kim et al., phase separation by ionomer leads to different morphologies, which affect shape-memory properties. We thought that the above-mentioned structural stability

Table 4
The recovery rate of POBAis at 40 °C in the thermocycle shape-recovery test

Sample code	R_r (%)		
	First test	Second test	Third test
POBAi-2.5	81	92	95
POBAi-5	88	91	94

The strain recovery rate was calculated using the following equation:

$$\text{Strain recovery rate } (R_r) = \frac{\varepsilon_e - \varepsilon_r}{\varepsilon_e - \varepsilon_0} \times 100$$

where ε_0 is the length of initial stage; ε_e is the sample length after extension; and ε_r is the sample length after recovery.

and phase separation between soft segment and hard segment during deformation and recovery have an effect on shape-recovery rate. The verification of this postulate will be discussed hereafter.

4. Conclusions

Consequently, POBAis were successfully synthesized by two-step polycondensation. The WAXD data and shape-recovery test for deformed and recovered specimens verified that POBAis show strong recovery ability with respect to its crystalline structure, depending on the ionic content. The relatively higher storage modulus around 30 °C and shape-recovery rate exceeding 90% of POBAi-2.5 show its potential as a shape-memory plastic for use in a body-temperature environment.

Acknowledgement

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