

**Physical properties of poly(tetrahydrofuran)-*block*-poly(2-ethyl-2-oxazoline)
triblock copolymer**

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Abstract:

ABA-type triblock copolymers (PEO_{xz}-PTHF-PEO_{xz}) composed of poly(tetrahydrofuran) (PTHF) and poly(2-ethyl-2-oxazoline) (PEO_{xz}), were synthesized by cationic sequential polymerization. Differential scanning calorimetry and wide angle X-ray diffraction analyses revealed that PEO_{xz}-PTHF-PEO_{xz}s afforded micro-phase separation structure, which consisted of a partially crystallized amorphous PTHF phases containing PEO_{xz} chains on both end sides. Tensile testing showed PEO_{xz}-PTHF-PEO_{xz} exhibited tough mechanical property, being different from brittle PTHF homopolymer. Thus, it was suggested that the amorphous PTHF/PEO_{xz} phase played a role of physical cross-linking moieties on entanglement, resulting in cold-drawing and tough mechanical property of PEO_{xz}-PTHF-PEO_{xz}.

Introduction

It is well known that block copolymer sometimes exhibits characteristic properties coming from microphase separation, being quite different from those of random copolymers or polymer blends. Styrene-butadiene rubber (SBR) is a typical block copolymer. The origination of elastic property of SBR is deeply associated with the formation of the microphase-separated structure being comprised of polystyrene domains and a butadiene matrix^{1,2}.

Poly(tetrahydrofuran)s (PTHFs) are commonly used as a soft segment in polyurethanes and polyesters³. Polyurethanes have been widely applied to coating, adhesives, foam, fiber, elastomer and so on. Polyurethane elastomers (PUEs) are generally synthesized from diisocyanate, polymer glycol and a chain extender. The PUEs consist of a hard segment formed from diisocyanate and a chain extender and a soft segment formed from polymer glycol. The hard segment act as a physical cross-linking point of PUEs. The PTHF-based PUEs usually show excellent mechanical property and high resistance for hydrolysis. Yang *et al.* synthesized poly(lactic acid)-PTHF-poly(lactic acid) triblock copolymers and studied effects of hydrophobic PTHF on the enzymatic degradability⁴. They found out that the enzymatic degradation rate decreased with increasing content of PTHF, hydrophobicity of which promoted enzymatic antidegradation of poly(lactic acid). On the other hand, poly(oxazoline) (POxz) has imino acyl groups in the main chain, strong polarity and amorphous property⁵ and utilized to biocompatible materials. Since oxazoline can be polymerized with active halogen atom or cationic active species, well-defined block copolymer POxz-PTHF can be synthesized by sequential polymerization with THF. Block-copolymers of PTHF and POxzs are nontoxic and environmentally compatible and exhibit low glass-transition temperatures and low surface tension. Therefore, the copolymers have been applied to surfactants, lubricants, water repellents, and antifoaming agents. Caeter *et al.* synthesized a ABA-type triblock copolymer⁶, which consisted of 10k-19k number-averaged molecular weight (M_n) of PTHF at the center and 1.5k M_n of poly(2-methyl-2-oxazoline) (PMeOxz) at both ends. They found out shape memory effects, being attributable to phase separation between the two blocks and strong polar interaction between PMeOxz segments.

In this study, we synthesized ABA triblock-copolymers, composed of poly(2-ethyl-2-oxazoline) (PEOxz) blocks and PTHF block by sequential living

ring-opening copolymerization, and investigated the relation between phase structure and mechanical properties the copolymer. We used PTHF of the polymerization degree (DP) 300, which was expected to be enough for crystallization of PTHF block. Then, DP of PEOxz blocks were tuned at 4 and 9 to investigate how end PEOxz blocks affected aggregation structure as well as crystallization of PTHF.

Experimental

Materials. Trifluoromethanesulfonic anhydride (Tf₂O, Sigma-Aldrich Chemicals Japan) was used as received. Acetonitrile (CH₃CN, Sigma-Aldrich Chemicals Japan), 2-ethyl-2-oxazoline (EOxz, Sigma-Aldrich Chemicals Japan), di-*n*-butylamine (WAKO chemicals Co., Ltd.), and tetrahydrofuran (THF, WAKO Chemicals Co., Ltd.) were used after distillation over calcium hydride (WAKO chemicals Co., Ltd.).

Synthesis of PTHF. Polymerization of 44.5 g (617.50 mmol) THF was carried out by stirring at 25 °C for 45 min in bulk with 0.25 g (0.87 mmol) Tf₂O as a bifunctional initiator. The oxonium-ended PTHF prepolymer was terminated with 0.59 g (4.59 mmol) di-*n*-butylamine. Precipitation with hexane and filtration gave 43.7 g PTHF.

Synthesis of PEOxz-PTHF-PEOxz. To the active PTHF, prepared from 9.88 g (136.8 mmol) THF and 0.03 g (0.12 mmol) Tf₂O as described above, was added 0.02 g (0.24 mmol) EOxz. After evaporation of residual THF under vacuum, 20 mL CH₃CN and 0.23 g (2.32 mmol) EOxz were added to the mixture, followed by stirred at 60 °C for 20 hours. The initial ratio of EOxz to Tf₂O was changed to prepare block copolymer with various PEOxz block lengths. Termination of polymerization by addition of 0.19 g (1.46 mmol) di-*n*-butylamine, and precipitation from chloroform solution with hexane gave 9.62 g block copolymer, PEOxz4-PTHF300-PEOxz4. Here, the copolymer was presented by abbreviation as PEOxz9-PTHF300-PEOxz9, in which number was designative to polymerization degree. It was impossible to synthesis copolymers with PEOxz block higher than that of DP 9.

Characterization. Chemical structures, polymerization degree of the each block and number average of molecular weight (M_n) of PTHF300 and PEOxz-PTHF-PEOxz were characterized by ¹H-NMR spectroscopy (JNM-GX400, JEOL Co. Ltd., Japan) with tetramethylsilane (TMS) as an internal standard. The number average and weight average molecular weights (M_n and M_w ,

respectively) and polydispersity index (M_w/M_n) were estimated by a gel permeation chromatography (GPC) on a polystyrene gel column (shimazu shim-pack GPC-802) using a Shimazu HPLC 20AD pump system equipped with a refractive index detector with eluent of THF at 1.0 mL/m, calibrated by a polystyrene standard. Molecular arrangement of the polymers was evaluated using wide angle X-ray diffraction (WAXD). WAXD profiles were obtained with a 2θ scan mode with a RINT2200 (Rigaku, Co., Ltd. Japan). Voltage and current of a $\text{CuK}\alpha$ X-ray source were set to 30 kV and 16 mA, respectively.

Thermal and mechanical properties. Differential scanning calorimetry (DSC) curves were obtained on a DSC (DSC 8230, Rigaku Denki Co., Ltd., Japan) from -100 to 100 °C at a heating rate of 10 °C min^{-1} under nitrogen atmosphere. The dynamic viscoelastic properties were measured with a DMS 6100 (Seiko Instruments, Co., Ltd., Japan) from -150 to 50 °C at a heating rate of 2 °C min^{-1} under nitrogen atmosphere. The size of samples used is 10 mm x 5 mm x 0.25 mm. Imposed dynamic strain and frequency were 0.2% and 10 Hz, respectively. Tensile testing was performed with an Instron type tensile tester (Shimadzu Autograph; AGS-100A, Japan) at 20 °C. An initial length, distance between chucks and elongation rate were set to 30 mm, 50 mm and 10 mm min^{-1} , respectively.

Results and discussion

Figure 1 shows $^1\text{H-NMR}$ spectra of (a) PTHF300, (b) $\text{PEO}_{xz}4\text{-PTHF300-PEO}_{xz}4$ and (c) $\text{PEO}_{xz}9\text{-PTHF300-PEO}_{xz}9$ in CDCl_3 . Signals a and c at 3.4 ppm, b at 1.6 ppm, f at 0.95 ppm, g at 1.45 ppm, and h at 2.89 ppm on spectra were assigned to $-\text{CH}_2\text{-O-CH}_2-$ of PTHF and $-\text{CH}_2\text{-N(C=O-Et)-CH}_2-$ of PEO_{xz} , $-\text{CH}_2\text{-CH}_2-$ of PTHF, CH_3 of butyl groups, $\beta\text{-CH}_2$ of dibutyl amino group, $\alpha\text{-CH}_2$ of dibutyl amino groups, respectively. Signals d at 2.2-2.6 ppm and e at 1.23 ppm on spectra (b) and (c) were assignable to CH_2 and CH_3 of side chain of PEO_{xz} , respectively. The DP and M_n of these polymers were estimated from peak areas of signals, a, d and f.

Figure 2 shows GPC profiles of PTHF300 and block copolymers. In Figure 2, elution peaks of PTHF and PTHF- PEO_{xz} exhibited unimodal profiles and M_n of PTHF- PEO_{xz} were obviously higher than for PTHF300. Furthermore, the peak of $\text{PEO}_{xz}\text{-PTHF-PEO}_{xz}$ was shifted to short elution time without changing peak width. These results suggested that the block copolymers had block structure consisting of PTHF and PEO_{xz} segments. In Table 1, DP, M_n , M_w and M_w/M_n

were summarized.

Figure 3 shows WAXD profiles of homopolymer and block copolymers. Two intense diffraction peaks were observed at 20.2 and 24.7° on spectra of homopolymer and block copolymers. These peaks were assignable to (020) and (110) planes of monoclinic unit cell of PTHF⁷. Peak widths of block copolymers were clearly broader than those of PTHF300 and PTHF showed amorphous halo as well as diffraction peaks from a crystallized PTHF phase. Moreover, the scattering intensity of amorphous halo of block copolymers increased with increasing length of PEOxz blocks. These results clearly show that PEOxz block makes degree of crystallinity in the PTHF block decreased. The decrease is probably due to crystallization of PTHF block retarded by incorporation of the PEOxz blocks on chain ends. In other word, this implies that the extent of microphase separation becomes lower with increasing length of PEOxz blocks.

Figure 4 shows DSC thermograms of PTHF300 and block copolymers in the temperature range (a) from -100 to 100 °C and (b) from -100 to -40 °C. In Table 2, glass transition temperature (T_g) and melting temperature (T_m) of PTHF homo- and block co- polymers and fusion heat of crystallized PTHF block were summarized. A base line shift and endothermic peaks were observed at -80 and 48 °C in thermograms of PTHF300 and block copolymers. Values of T_g and T_m of PEOxz4-PTHF300-PEOxz4 were observed to be mostly same as those of PTHF300. The endothermic peaks, corresponding to fusion heat of crystallized PTHF, shifted to lower temperature with increasing PEOxz moiety. Furthermore, the heat of PTHF block decreased with increasing PEOxz block moiety. These results indicate that crystallization of the PTHF block is suppressed by incorporation of PEOxz block. The discussion is well supported by the result of WAXD analysis. On the other hand, T_g of PEOxz block was not observed, while it was reported that T_g of PEOxz was 59 °C⁸. It was probably due to overlapping on endothermic peak corresponding to melting of crystallized PTHF block.

In order to investigate thermal and mechanical properties, we conducted dynamic viscoelastic analyses. Figure 5 shows the temperature dependence of dynamic storage modulus (E'), loss modulus (E'') and loss tangent ($\tan\delta$) of PTHF300 and block copolymers. In these cases, values of E' showed remarkable decrease and $\tan\delta$ curve gave the peak around -80 °C. Since the T_g of PTHF chains was -85 °C, these significant changes can be attributed to

α -relaxation associated with glass transition of the amorphous PTHF chains. In the temperature range from 20 to 40 °C, the values of E' for all three samples decreased, while $\tan \delta$ increased. These phenomena are probably related with terminal flow due to melting of crystallized PTHF chains. In cases of PEO_{xz}4-PTHF300-PEO_{xz}4 and PEO_{xz}9-PTHF300-PEO_{xz}9, another $\tan \delta$ peaks appeared at -20 and 25 °C, respectively. On increasing the length of PEO_{xz} block from 4 to 9, the peak clearly shifted to high temperature side. As shown in DSC and WAXD results, it is suggested that an increase of the PEO_{xz} block induces retardation of crystallization of the PTHF block due to mixing PEO_{xz} blocks with non-crystallized PTHF blocks. These peaks observed at -20 and 25 °C in $\tan \delta$ curves (Figure 5) are probably attributable α -relaxation of amorphous PTHF chains in the mixing phase. Therefore, PEO_{xz}-PTHF300-PEO_{xz} copolymer presumably forms phase-separation phase composed of crystallized PTHF domain surrounded by amorphous PTHF/PEO_{xz} mixing domain.

Figure 6 shows stress-strain curves of PTHF300 and block copolymers. In Table 3, Young's modulus, tensile strength and fracture strain obtained from Figure 6 were listed. Homopolymer of PTHF300 was brittle, and fracture strength was 9.0 MPa at 0.1 strain. Interestingly, block copolymers exhibited quite different stress-strain curves from that of PTHF300. Young's modulus of block copolymers slightly decreased with increasing PEO_{xz} chain length. Further, in cases of PEO_{xz}4-PTHF300-PEO_{xz}4 and PEO_{xz}9-PTHF300-PEO_{xz}9, cold-drawing and strain due to crystallization were observed. Resultant tensile strengths and strains of these copolymers at break were much higher than that of PTHF300. Tensile strength and elongation of PEO_{xz}4-PTHF300-PEO_{xz}4 and PEO_{xz}9-PTHF300-PEO_{xz}9 at break were 15.0 MPa and 5.0, and 12.1 MPa and 4.5, respectively. According to above results, in Figure 7 schematic representations of the phase structure of PTHF300 and PEO_{xz}9-PTHF300-PEO_{xz}9 were illustrated. PEO_{xz}9-PTHF300-PEO_{xz}9 is probably comprised of partially crystallized PTHF domain and amorphous PTHF phase including PEO_{xz} chains. Thus, entanglement of PTHF chains might occur in the amorphous PTHF/PEO_{xz} phase to make physical cross-linking, and then resulted in cold-drawing and strain-induced crystallization for PEO_{xz}-PTHF-PEO_{xz}. In the case of PTHF, since there is no physical cross-linking, mechanical strength is quite low.

Conclusions

PEO_{xz}-PTHF-PEO_{xz} was prepared by sequential cationic ring opening polymerization of THF and EOXz. The properties of block copolymers were dependent on length of PEO_{xz} moiety. As length of the PEO_{xz} moiety increased, crystallinity of the PTHF chains decreased. Block copolymers are comprised of partially crystallized PTHF phase and amorphous phase composed of PTHF and PEO_{xz} chains. Existence of the PTHF/PEO_{xz}s phase exhibited improved tough mechanical properties.

Reference

1. Hamley, I. W. *Developments in Block copolymer Science and Technology* 159 (John Wiley & Sons, Ltd., New York, 2004).
2. Leibler, L. Theory of Microphase Separation in Block Copolymers. *Macromolecules*, **13**, 1602-1617 (1980).
3. Nierzwicki, W., Wysocka, E. Microphase separation and properties of urethane elastomers. *J. Appl. Polym. Sci.*, **25**, 739-746 (1980).
4. Yang, J.-H., Lee, Y.-D., Tsai, R.-S., Tsai, H.-B. Enzymatic Degradation of Poly(L-lactide)/Poly(tetramethylene glycol)triblock Copolymer Electrospun Fiber. *Mater. Chem. and Phys.*, **133**, 1127-1136 (2012).
5. Kobayashi, S., Uyama, H., Ihara, E., Saegusa, T. Block Copolymerization of Tetrahydrofuran with Cyclic Imino Ether: Synthesis of New Nonionic Polymer Surfactant. *Macromolecules* **23**, 1586-1589 (1990).
6. Caeter, P. V., Goethals, E. J., Gancheva, V., Velichkova, R. Synthesis and Bulk Properties of Poly(tetrahydrofuran)-Poly(2-methyl-2-oxazoline) ABA Triblock Copolymer. *Polym. Bull.* **39**, 589-596 (1997).
7. Imada, K., Miyakawa, T., Chatani, Y., Tadokoro, H., Murahashi, S. Structural Studies of polyethers, $[-(\text{CH}_2)_m\text{-O-}]_n$. III. Molecular and Crystal Structure of Polytetrahydrofuran. *Makromol. Chem.* **83**, 113-128 (1965).
8. Kempe, K., Jacobs, S., Lambermont-Thijs, H. M. L., Fijten, M. M. W. M., Hoogenboon, R. & Schubert, U. S. Rational Design of Amorphous Poly(2-oxazoline) with a Low Glass-Transition Temperature: Monomer Synthesis, Copolymerization, and Properties. *Macromolecules* **43**, 4098-4104 (2010).

Captions

Figure 1. $^1\text{H-NMR}$ spectra of (a) PTHF300, (b) PEO_{xz}4-PTHF300-PEO_{xz}4 and (c) PEO_{xz}9-PTHF300-PEO_{xz}9.

Figure 2. GPC profiles of PTHF300, and block copolymers.

Figure 3. WAXD profiles of PTHF300 and PEO_{xz}-PTHF-PEO_{xz}.

Figure 4. DSC thermograms of PTHF and block copolymers (a) from -100 to 100 °C and (b) from -100 to -40 °C.

Figure 5. Temperature dependence of E' , E'' and $\tan \delta$ of PTHF and block copolymers.

Figure 6. Stress-strain curves of PTHF and block copolymers.

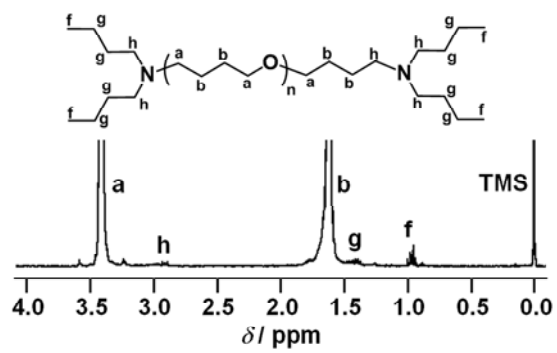
Figure 7. Schematic illustration of phase structure of (a) PTHF300 and (b) PEO_{xz}9-PTHF300-PEO_{xz}9.

Table 1 Degree of polymerization, M_n , M_w and M_w/M_n of PTHF and block copolymers.

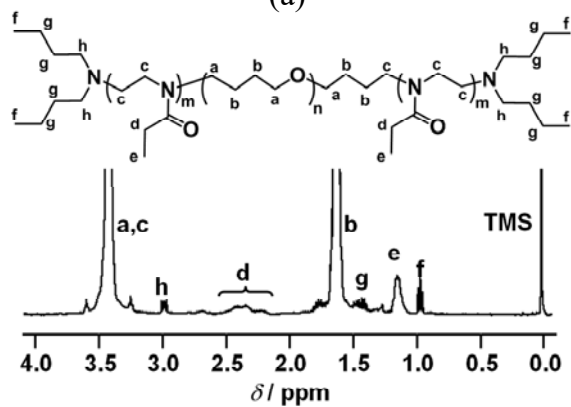
Table 2 Thermal properties of PTHF and block copolymers.

Table 3 Young's modulus, tensile strength and strain at break for PTHF and block copolymers.

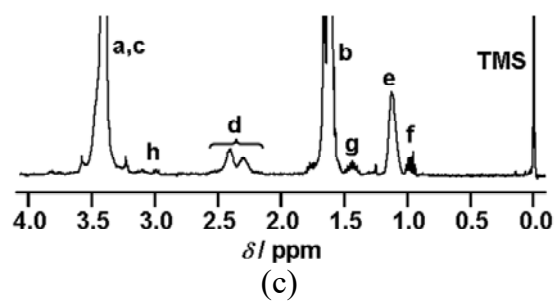
Figure 1



(a)



(b)



(c)

Figure 2

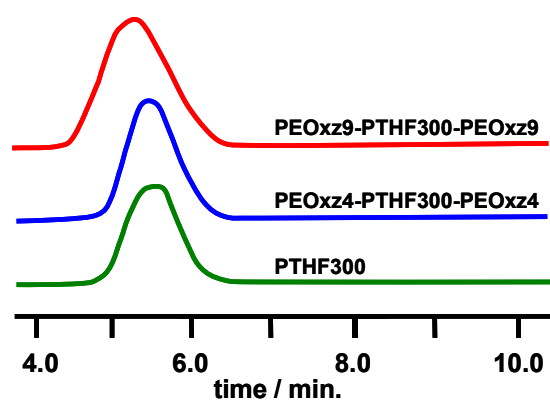


Figure 3

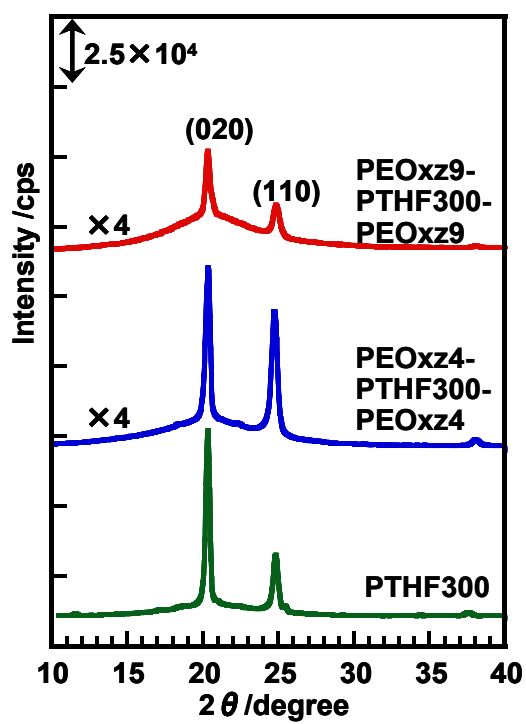
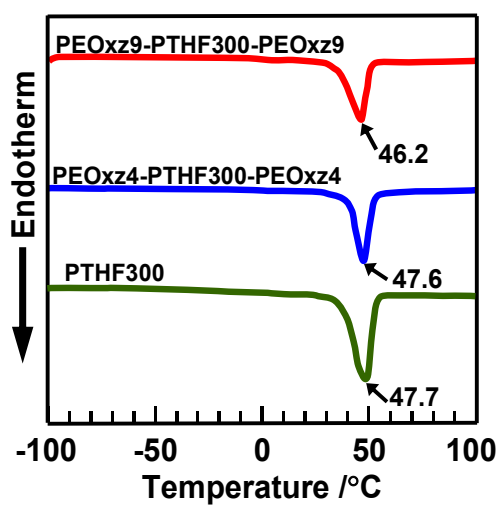
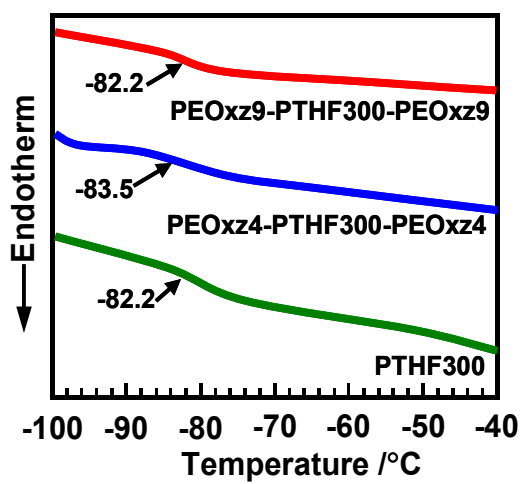


Figure 4



(a)



(b)

Figure 5

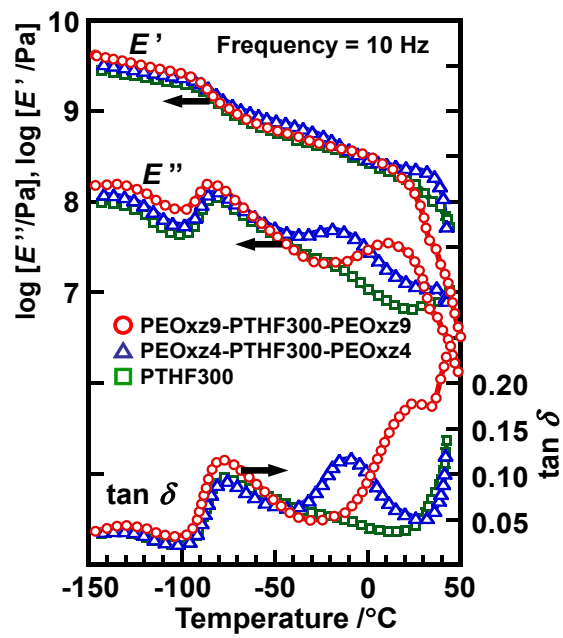


Figure 6

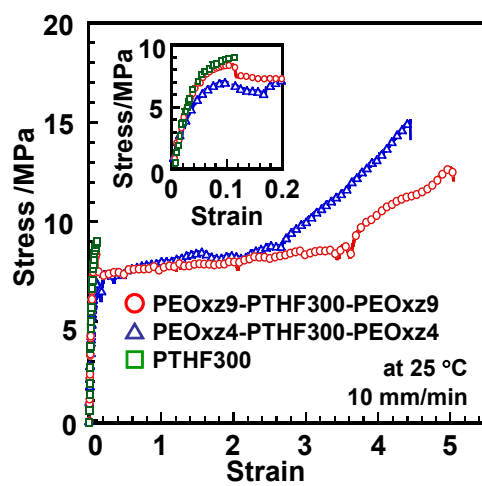


Figure 7.

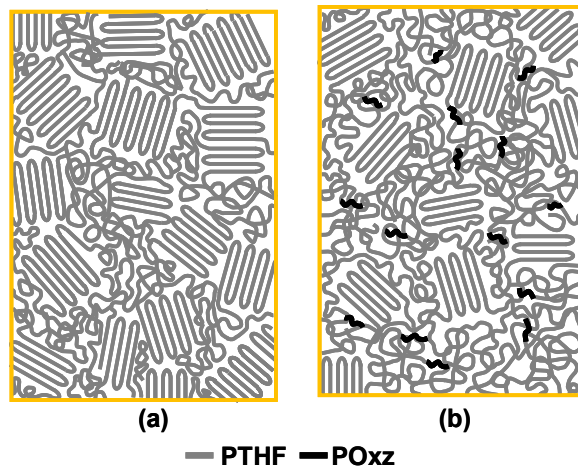


Table 1

Sample	DP ¹⁾		$M_n^{1)}$	$M_n^{2)}$	$M_w^{2)}$	$M_n/M_n^{1)}$
	PTHF	PEO _{xz}				
PTHF300	300	-	21,900	26,700	40,600	1.52
PEO _{xz} 4-PTHF300-PEO _{xz} 4	300	8	22,700	29,800	48,900	1.64
PEO _{xz} 9-PTHF300-PEO _{xz} 9	300	18	23,700	29,900	50,200	1.68

1) Determined by ¹H-NMR, 2) Estimated by GPC

Table 2

Sample	T _g (°C)	T _m (°C)	Heat of fusion (J/g)
PTHF300	-82.2	47.7	134.0
PEO _{xz} 4-PTHF300-PEO _{xz} 4	-83.5	47.6	79.3
PEO _{xz} 9-PTHF300-PEO _{xz} 9	-82.2	46.2	73.8

Table 3

Sample	Young's modulus (MPa)	Tensile Strength (MPa)	Strain at break
PTHF300	59.4	9.0	0.1
PEO _{xz} 4-PTHF300-PEO _{xz} 4	48.5	15.0	4.5
PEO _{xz} 9-PTHF300-PEO _{xz} 9	41.5	12.1	5.0

Graphical abstract

Physical Properties of Polymers

Physical properties of poly(tetrahydrofuran)-*block*-poly(2-ethyl-2-oxazoline) triblock copolymer

Suguru Motokucho, Mutsuhisa Furukawa, Masahiro Kawashima, Ken Kojio, Kohji Yoshinaga

Linear ABA-type triblock copolymer with poly(tetrahydrofuran) (PTHF) and poly(2-ethyl-2-oxazoline) (PEOxz) was synthesized by a one-pot sequential copolymerization, utilizing the living cationic polymerization of both monomers. Films of the ABA-type copolymer configure PTHF pure phase and mixing phase of PTHF and PEOxz, which was attributed by DSC thermograms and WAXD profiles.

