

One-pot synthesis and characterization of aliphatic poly(oxytetramethylene) ionene

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Dedicated to Professor Imanishi on the occasion of his retirement

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Abstract

One-pot synthesis of poly(oxytetramethylene) ionene (POI) composed of one dimethylammonium group in each repeating unit is described. POI was prepared by using the cationic polymerization of tetrahydrofuran, followed by the chain extension reaction of living poly(oxytetramethylene) (POTM) chain with *N,N*-dimethylaminotrimethylsilane. The weight average molecular weight of the ionene with bromide counter-anion (POI–Br) was 48,000 g/mol and the molecular weight of POTM between the ionic sites was ca. 2100. POI–Br showed polyelectrolyte behavior in polar solvent. The elastomeric film of POI–Br was prepared: its tensile strength at break and elongation at break were ca. 11 MPa and ca. 1900% at 19 °C, respectively. Small-angle X-ray scattering, differential scanning calorimetry and dynamic mechanical analysis suggested the formation of microphase-separated structure for POI–Br film. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Ionenes are defined as polymers consisting of quaternary amines in the main chain. Most ionenes studied so far were prepared by the Menshutkin reaction of aliphatic di-tertiary amines with dihalides. Thus, the variety of starting materials has produced various ionenes [1,2]. On the other hand, the development of living ionic polymerization has enabled us to prepare the uniform-sized polymers with a suitable reactive end group [3]. One of the examples is a living cationic polymerization of tetrahydrofuran (THF), which has been much utilized for the syntheses of tailored polymers such as block and graft polymers, star-shaped polymers and polymer networks, and so on [3–5]. The living poly(oxytetramethylene) (POTM) can be reacted with nucleophiles to give various kinds of macromolecules, because the oxonium group of the living POTM is stable.

One of the authors has employed this technique to synthesize POTM ionenes. Namely dimethylamino-terminated

POTM, which was prepared by a living polymerization of THF and termination reaction using dimethylamine, was reacted with aliphatic or aromatic dihalide to give ionenes [6–8]. The obtained ionenes were elastomeric and showed excellent mechanical properties. POTM viologen ionenes were also prepared by one-pot synthesis using a reaction between living POTM chains and 4,4'-bipyridine [9–14]. The viologen ionenes were high functional elastomers, and displayed thermochromism and photochromism [9,11,12] and/or photomechanical effect [10,11,14]. Recently, we reported the synthesis of POTM ionene with 2,2'-bipyridinium units [15,16] and the results of structural analysis based on the cascade model for physically cross-linked networks [16]. The studies on the viologen ionenes were also carried out in order to investigate the effect of molecular weight between the ionic sites on the properties and higher-order structures [17]. The cascade model was also found to be useful for the small-angle X-ray scattering (SAXS) analysis of the viologen ionenes [18,19].

Generally, unique characteristics of ionene elastomers arise from the ionic aggregation in the flexible polymer matrix. Therefore, the chemical structure of ionic segment

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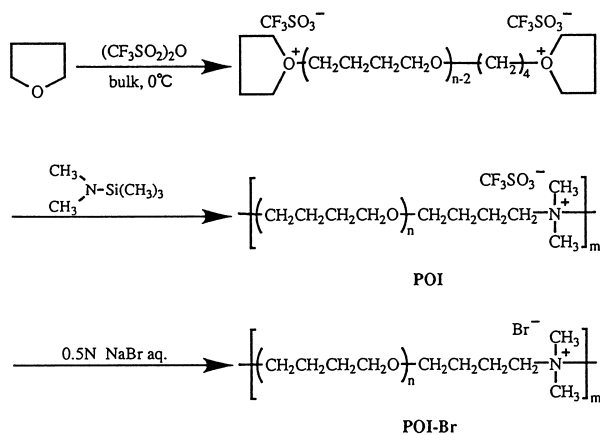


Fig. 1. Synthetic scheme of POI-Br.

including the number of ionic site becomes important for the molecular design of ionene elastomers. The first order structure of ionic segment, such as monocation or dication type ionenes and aliphatic and aromatic ionenes, significantly influences their properties. Until now, many studies on aliphatic or aromatic ionene elastomers were reported, however, most of them were classified as dication type ionenes. Thus, the ionene elastomer alternatively consisting of one dimethylammonium group and a POTM segment in the repeating unit (POI) was newly synthesized in one-pot as shown in Fig. 1 and its characterization was carried out in this study.

2. Experimental

2.1. Reagents

Commercial THF was distilled twice over lithium aluminum hydride and then over metallic sodium. Trifluoromethanesulfonic acid anhydride ($(\text{CF}_3\text{SO}_2)_2\text{O}$) was prepared from the acid (from Wako Pure Chemical Ind. Ltd) by distilling on P_2O_5 just before use for the polymerization [16,20]. *N,N*-dimethylaminotrimethylsilane (DMATS, 95.7% purity), methanol, ammonium bromide were commercial high-grade origins and were used without purification. Ethanol, chloroform and pyridine were distilled after drying by the conventional methods.

2.2. Synthesis and molecular characterization of POI

The synthetic route of the aliphatic POTM ionene with CF_3SO_3^- counter-anion (POI) is shown in Fig. 1. Cationic living polymerization of THF (50 ml) was carried out by using $(\text{CF}_3\text{SO}_2)_2\text{O}$ (0.23 mol/l) as an initiator at 0°C under dry nitrogen atmosphere for 5 min [6,20]. The chain extension reaction was conducted at 0°C by adding six times amounts of DMATS relative to the concentration of the initiator. The resulted polymer was purified by the reprecipitation from the THF solution of the polymer to water several times. The yield was 39%. The exchange of counter-

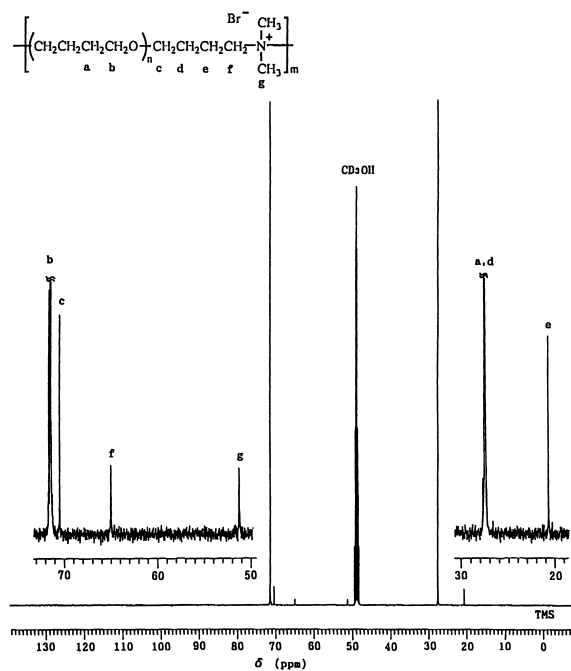
anion of POI from CF_3SO_3^- to Br^- was conducted by pouring the 10 wt% THF solution of the polymer to 0.5N-sodium bromide aqueous solution at room temperature (r.t.), and the procedure was repeated three times. The polymer was purified by the precipitation method from the THF solution to water several times. The obtained aliphatic ionene with bromide counter-anion is abbreviated as POI-Br.

^1H and ^{13}C NMR spectra of POI-Br were recorded on a Fourier-transform high resolution NMR spectrometer JEOL GX-400 (Nippon Denshi Co.) in CD_3OD with tetramethylsilane at 40°C . ^1H NMR; δ : 1.62 ppm (methylene protons of $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$), δ : 3.44 ppm (methylene protons of $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$), δ : 3.09 ppm (methyl protons of $-\text{N}^+(\text{CH}_3)_2-$). The quantitative analysis of molecular weight between the ionic sites of BOI-Br was carried out by using an inversion recovery method in ^1H NMR. ^{13}C NMR; δ : 27.27, 27.47, 27.66, 27.71 ppm (a), δ : 71.23, 71.43, 71.49, 71.62, 71.67 ppm (b), δ : 70.46 ppm (c), δ : 27.38 ppm (d), δ : 20.74 ppm (e), δ : 64.98 ppm (f), δ : 51.27 ppm (g) in Fig. 2.

An elemental analysis of POI-Br was conducted at the Elemental Analysis Center of Kyoto University. Anal. Calcd C 64.25, H 10.81, N 0.71, Br 4.04. Found: C 61.96, H 10.66, N 0.70 Br 4.80.

IR measurement of POI-Br was carried out on an infrared spectrometer IR-810 (Shimadzu Co.). IR (thin film): $\nu(\text{CH}_2)$ 2850, 2930 cm^{-1} , $\nu(\text{C}-\text{O}-\text{C})$ 1100 cm^{-1} , $\delta(\text{CH})$ 1365 cm^{-1} .

The reduced viscosity (η_{sp}/c) of POI-Br was measured with an Ubbelohde viscometer at 30°C in a thermostatic bath. The ionenes were dissolved in ethanol, chloroform

Fig. 2. ^{13}C -NMR spectrum of POI-Br in 9% CD_3OD solution at 40°C .

and 0.1N methanol solution of ammonium bromide. η_{sp}/c was plotted as a function of concentration (c). Here, $\eta_{sp} = (\eta - \eta_0)/\eta_0$, where η and η_0 represent the viscosity of the solution and solvent, respectively.

Light scattering experiment was carried out with an ALV SP86 goniometer in combination with an ALV 3000 correlator at 20 °C [21,22]. A krypton-ion laser (Spectra Physics, Model BeamLok 2065-11) operating at 647.1 nm wavelength was used as a light source at an output power of 500 mW. POI-Br was dissolved in 0.1N methanol solution of ammonium bromide. The dust-free solution was prepared by filtering through a Millex GS 0.2 μm pore size filter. The reduced scattering intensities were derived according to the standard procedures, using toluene as a reference with the absolute scattering intensity ($R_l = 1.27 \times 10^{-5} \text{ cm}^{-1}$ at 20 °C) at 647.1 nm wavelength. The specific refractive index increment (dn/dc) of the methanol solution of POI-Br containing 0.1N ammonium bromide was measured at 20 °C by using a compact scanning Michelson interferometer equipped with two identical flow cells which was developed by Becker et al. [23]. A diode laser (650 nm wavelength) was served as a light source.

As a reference for POI-Br, a telechelic POTM oligomer with pyridinium units in the ends was synthesized by polymerization of THF and following to react living POTM chains with pyridine under the same reaction conditions with POI. The yield of the telechelic oligomer was 32%. The chemical structure of telechelic oligomer was identified by NMR, IR and elemental analysis. The molecular weight between the ionic sites was determined to be 1900 by ^1H NMR.

2.3. Film preparation and its characterization

The POI-Br film was prepared from its 10% THF solution by casting onto Teflon^R mold at r.t. and was dried under a reduced pressure. The thickness of the film was 0.5 mm.

Tensile measurement was carried out with an extension speed of 10 mm/min on a Tensile Tester TOM 200D (Shinko Thushin Kogyo Co.) on ring-shaped samples at 19 °C.

Differential scanning calorimetry (DSC) measurement was carried out on a Rigaku Thermoflex DSC-8230 under nitrogen in the temperature range from -120 to 195 °C. The sweep rate of temperature was 10 °C/min, and the sample loaded was 10 mg.

SAXS measurement was performed at r.t. with SAXES having the focusing optics, installed at the BL10C of the Photon Factory, Tsukuba, Japan [24]. The wavelength of X-ray used was 1.488 Å. The specimen-to-detector distance was calibrated using the diffraction peaks from collagen fiber. The acquisition of scattering data from the position sensitive proportional counter was made by the CAMAC system controlled by NEC 8901 RX.

The temperature dispersions of dynamic modulus (E') and loss tangent ($\tan \delta$) of polymer films were measured

on a dynamic mechanical analyzer (DVE-V4 FT Rheospectra of Rheology Co., Japan). The sample dimension was 15 mm \times 5 mm \times 0.5 mm. The strain mode was used and the heating rate was 2 °C/min. The frequency was 10 Hz.

3. Results and discussion

3.1. Molecular characterization of POI-Br

POI-Br was light yellow, clear and rubbery at r.t. This ionene was not soluble in water, but was soluble in both polar and non-polar solvents like *N,N*-dimethylformamide, methanol, acetone, chloroform, THF, benzene and toluene, because of its amphiphilic nature. The chemical structure of POI-Br was confirmed by ^1H and ^{13}C NMR measurements with IR. ^{13}C NMR spectrum of POI-Br is shown in Fig. 2 with the peak assignment of each carbon. In the ^1H NMR spectrum of POI-Br, the dimethyl protons adjacent to the ammonium group were clearly detected at 3.09 ppm. The molecular weight of POTM between the ionic sites was 2100, which was quantitatively evaluated by ^1H NMR. The found values of elemental analysis for POI-Br were in relatively good agreement with those of calculated assuming $n = 25$ in POI-Br shown in Fig. 1. The molecular weight between the ionic sites calculated by using the results of elemental analysis was ca. 2000, which was similar with that determined by ^1H -NMR. The weight average molecular weight (M_w) of POI-Br was 48,000 g/mol, which was measured by a light scattering technique. From the Zimm plot of the methanol solution of POI-Br added with NH_4Br , the M_w was calculated using the dn/dc value ($0.152 \text{ cm}^3/\text{g}$) of this solution.

(a) in Fig. 3 shows a reduced viscosity (η_{sp}/c) of POI-Br in ethanol as a function of polymer concentration. POI-Br

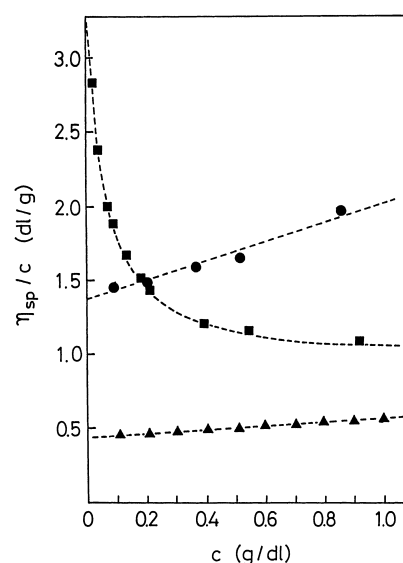


Fig. 3. Concentration dependence of the reduced viscosity of POI-Br at 30 °C in (a) ethanol (■), (b) chloroform (●) and (c) 0.1N methanol solution of NH_4Br (▲).

shows a typical characteristics behavior of polyelectrolyte: the η_{sp}/c remarkably increased with decreasing of polymer concentration in ethanol. The similar viscosity behavior has been reported for salt-free ionene elastomers [16,25,26] and random ionomers [27,28] in polar solvents, as well as many salt-free polyelectrolytes in water. On the contrary, POI-Br behaves as a non-polyelectrolyte in chloroform (b) and 0.1N methanol solution of NH_4Br (c), as shown in Fig. 3. The reduced viscosity of POI-Br increases linearly with increasing of the polymer concentration in both cases, which was expressed by the Huggins equation [29]. The intrinsic viscosity and the Huggins constant of POI-Br were 1.36 dl/g and 0.36 in chloroform, and 0.44 dl/g and 0.49 in the methanol solution with the salt, respectively.

3.2. Synthesis of POI-Br

The ring-opening polymerization of THF by $(\text{CF}_3\text{SO}_2)_2\text{O}$ has been utilized to prepare telechelic POTM oligomers with reactive end groups. In many cases, the obtained telechelic oligomers were subjected to further reaction to synthesize high molecular weight polymers or polymer networks. In this study, however, the one-pot synthesis of high molecular weight ionene was conducted, namely, the chain-extension reaction was carried out together with the termination reaction of living polymerization of THF to produce POI as shown in Fig. 1. In this termination reaction, trialkyloxonium ions of living POTM are speculated to react with DMATS to produce dimethylamino-terminated oligomers. The generated dimethylamino groups in the ends of POTM chain were further reacted with living POTM chains to give an aliphatic ionene. The chain-extension reaction seemed to occur during the termination reaction to yield the polymer whose M_w was 48,000 g/mol under the experimental conditions of this study.

Generally, the equimolecular amount of bi-functional nucleophile such as 4,4'-bipyridine against $(\text{CF}_3\text{SO}_2)_2\text{O}$ was used for the termination and chain-extension reactions of living POTM in the one-pot synthesis of ionene. In this study, however, six times amounts of DMATS against the initiator was necessary to produce the POTM ionene whose molecular weight between the ionic sites was ca. 2100. This result suggests that the reaction between DMATS and oxonium ion of living POTM chain was slow and that between the dimethylamino group of POTM and oxonium ion of living POTM chain was fast. The former phenomenon may be ascribed to the steric hindrance of DMATS. The polymerization result of telechelic POTM oligomer with pyridinium end groups supports this consideration: The molecular weight between the ionic sites of the oligomer was 1900 and smaller than that of POI-Br, which implies that the reaction between DMATS and oxonium ion of living POTM chain was slower than that between pyridine and oxonium ion of living POTM chain. The study on characteristics of this one-pot synthesis of aliphatic ionene is in progress. For example, the molecular weights between the

ionic sites of POIs were found to be ca. 6000 and 3000, when the equimolecular and twice amounts of DMATS against $(\text{CF}_3\text{SO}_2)_2\text{O}$ were used for the synthesis of POIs, respectively. These observations also support the consideration described earlier. Since DMATS is liable to be decomposed to dimethylamine [30], the synthesis of POI may be influenced by dimethylamine, but the effect is considered to be low at this moment. The detailed experimental results on the synthesis will be reported in the near future.

3.3. Properties and structure of POI-Br film

The clear film of POI-Br was obtained by casting its THF solution at r.t. The stress-strain curve of POI-Br film is shown in Fig. 4. Although the POI-Br film is a non-crosslinked elastomer, the tensile strength at break was up to 10.8 MPa and the elongation at break (E_B) was 1890% at 19 °C. The aggregates of ionic groups in POTM matrix of POI-Br seemed to work as cross-linking sites and/or reinforcing fillers resulting in a large strength for an elastomer. The stress at the lower elongation than 500% was very small like a non-crosslinked rubber, but the stress gradually increased with elongation, which was ascribed by the strain induced crystallization of POTM segments at the high elongation.

Comparing the tensile properties of POI-Br film with those of the reported POTM ionenes, the stress and E_B of the POI-Br film were observed to be smaller and larger, respectively, [6,8,25,31,32]. The reported ones contained two quaternary dimethylamino cations, because they were chain-extended by dihalide. POI-Br possesses one ammonium cation in each repeating unit and this characteristic brought about the difference in the tensile properties among the ionenes. In order to make this point clear, the morphological study on the POI-Br film was conducted next.

The SAXS measurement gave an observation that the microphase-separated structure was formed in the POI-Br film. The SAXS profile of POI-Br film showed a maximum

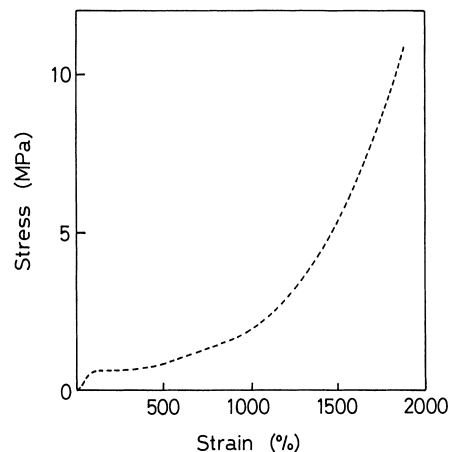


Fig. 4. Stress-strain curve of POI-Br film at 19 °C.

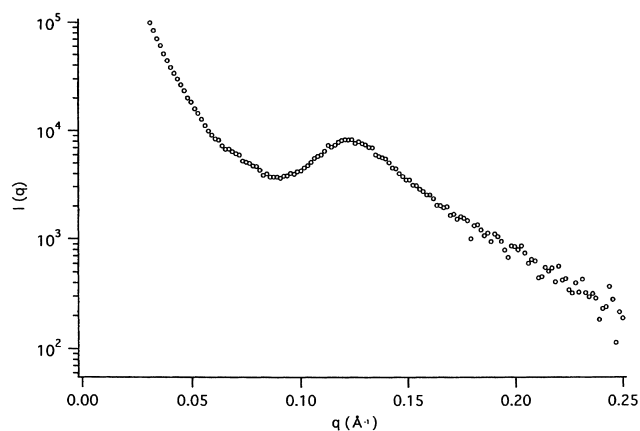


Fig. 5. SAXS profiles of POI-Br film at r.t.

as shown in Fig. 5, which was an evidence for the microphase separation. The Bragg spacing (d) of the POI-Br film was calculated to be 53 Å using $2d \sin \theta = n\lambda$, which corresponds to the mean distance between the ionic aggregates. The scattering vector (q) is defined by $q = 4\pi \sin \theta / \lambda$, where θ is the Bragg angle, n is the order of reflection, and λ is the wavelength of X-ray.

The DSC curve of POI-Br film is shown in Fig. 6. The POI-Br film showed a distinct glass transition temperature of POTM segment ($T_{g,s}$) at ca. -76°C and a phase transition temperature attributable to ionic aggregates (T_i) at around 56, 109 and 170°C , respectively. Melting temperature of POTM segments ($T_{m,s}$) was also detected at ca. 15°C . These observations also suggest the formation of the microphase-separated structure in the POI-Br film, i.e. the ionic aggregated domains were present in the POTM amorphous matrix at r.t. The temperature and heat of fusion (ΔH) of T_i are interpreted to reflect the degree of aggregation of the ionic sites. The smaller the aggregate of ionic segments was, the lower the temperature and the smaller the ΔH of T_i became. Therefore, Fig. 6 suggests that several kinds of ionic aggregates like a multiplet and a cluster are presented in the POI-Br film. Here, a multiplet is a group of a few ion pairs aggregated and a cluster is defined as a group of several multiplets that form a domain in the matrix [33]. The present ratio of the cluster in the POI-Br film was found to be high.

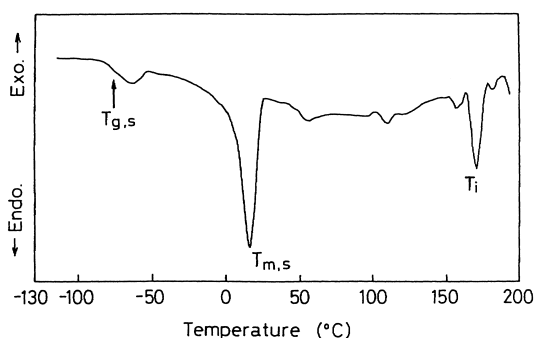
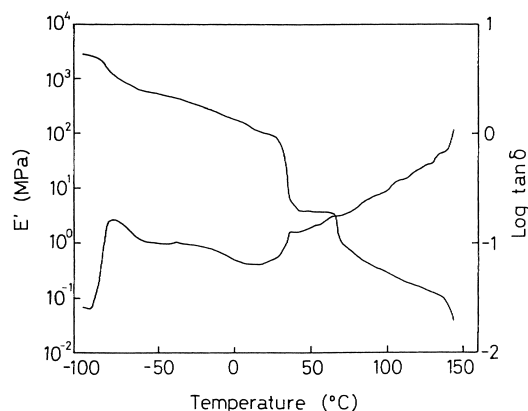


Fig. 6. DSC curve of POI-Br film.

Fig. 7. Temperature dispersions of E' and $\tan \delta$ of POI-Br film.

The temperature dispersions of E' and $\tan \delta$ of POI-Br film are shown in Fig. 7. The drops of E' corresponding to the $T_{g,s}$, $T_{m,s}$ and T_i were observed. As expected from the results of DSC, the rubbery plateau region after the melting of the POTM crystalline did not expand so much because of the presence of the weakly aggregated ionic segments. The flowing point of POI-Br film was ca. 130°C but it was not so clear comparing with those of the POTM ionenes composed of dications in each repeating unit [16,31,32]. Generally, the morphology of ionenes is significantly influenced by the molecular weight between the ionic sites, the counter-anion and the casting condition, so on. Therefore, the more detailed experiment on the morphology for this aliphatic ionene elastomer is necessary.

4. Conclusions

The aliphatic ionene alternatively composed of one dimethylammonium unit and POTM segment was newly synthesized by polymerization of THF and termination reaction using *N,N*-dimethylaminotrimethylsilane in one-pot. The casting film of this aliphatic ionene with bromide counter-anion (POI-Br) was an elastomer, where the microphase-separated structure was formed. As POI-Br possessed only one ammonium cation in each repeating unit, the ionic sites did not tightly aggregate and the presence of weakly aggregated ionic segments were detected by DSC and dynamic mechanical analysis. The synthetic method reported here is very simple and useful for the preparation of aliphatic ionene elastomer. The characteristics of synthesis and morphology on this ionene elastomer will be investigated systematically.

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References

- [1] Meyer WH, Dominguez L. In: MacCallum JR, Vincent CA, editors. *Polymer electrolyte reviews*–2. London: Elsevier Applied Science, 1989. p. 191.
- [2] Schulz RC, Hochberg G, Walter F. *Angew Makromol Chem* 1995;223:177.
- [3] Goethals EJ, editor. *Telechelic polymers: synthesis and applications*. Boca Raton, FL: CRC Press, 1989.
- [4] Goethals EJ, Caeter PV, Geeraert JM, Du Prez FE. *Angew Makromol Chem* 1994(223):1.
- [5] Tezuka Y, Shida T, Shiomi T, Imai K. *Macromolecules* 1993;26:575.
- [6] Kohjiya S, Ohtuki T, Yamashita S. *Makromol Chem Rapid Commun* 1981;2:417.
- [7] Kohjiya S, Ohtuki T, Yamashita S. *Makromol Chem* 1990;191:397.
- [8] Kohjiya S, Ohtuki T, Yamashita S, Taniguchi M, Hashimoto T. *Bull Chem Soc Jpn* 1990;63:2089.
- [9] Kohjiya S, Hashimoto T, Yamashita S, Irie M. *Chem Lett* 1985:1497.
- [10] Kohjiya S, Hashimoto T, Yamashita S. *Makromol Chem Rapid Commun* 1989;10:9.
- [11] Kohjiya S, Ikeda Y, Moriya N, Hashimoto T, Yamashita S, Shibata Y. *MRS Int Mtg Adv Mats* 1989;12:255.
- [12] Hashimoto T, Kohjiya S, Yamashita S, Irie M. *J Polym Sci, Part A: Polym Chem Ed* 1991;29:651.
- [13] Kohjiya S, Hashimoto T, Yamashita S. *J Appl Polym Sci* 1992;44:555.
- [14] Hashimoto T, Sakurai S, Morimoto M, Nomura S, Kohjiya S, Kodaira T. *Polymer* 1994;35:2672.
- [15] Murakami T, Ikeda Y. *Koubunshi Ronbunshu* 1998;55:637.
- [16] Ikeda Y, Murakami T, Yuguchi Y, Kajiwara K. *Macromolecules* 1998;31:1246.
- [17] Murakami T, Ikeda Y, Urakawa H, Kajiwara K, Kohjiya S. *Rubber Chem Technol* 2000;73:864.
- [18] Ikeda Y, Murakami T, Kajiwara K. *J Macromol Sci, Phys* 2001;B40:171.
- [19] Ikeda Y, Yuguchi Y, Kajiwara K, Murakami T, Kohjiya S. *German Rubber Conference 2000. Abstract, Nurnberg; 2000*. p. 199.
- [20] Smith S, Hubin AJ. *J Macromol Sci Chem* 1973;A7:1399.
- [21] Forster S, Schmidt M, Antonietti M. *J Phys Chem* 1992;96:4008.
- [22] Ikeda Y, Beer M, Schmidt M, Huber K. *Macromolecules* 1998;31:728.
- [23] Becker A, Kohler W, Muller B. *Ber Bunsenges Phys Chem* 1995;99:600.
- [24] Ueki T, Hiragi Y, Izumi Y, Tagawa H, Kataoka M, Muroga M, Matsushita T, Amemiya Y. *Photon Fact Rep* 1983;IV:70.
- [25] Kohjiya S, Yamashita S. *Kautschuk Gummi Kunst* 1991;44:1128.
- [26] Wu J-L, Wang Y-M, Hara M, Granville M, Jerome R. *Macromolecules* 1994;27:1195.
- [27] Otocka EP. *J Macromol Sci Rev Macromol Chem* 1971;C5(2):275.
- [28] Fitzgerald JJ, Weiss RAJ. *Macromol Sci Rev Macromol Chem Phys* 1988;C28(1):99.
- [29] Huggins ML. *J Am Chem Soc* 1942;64:2716.
- [30] Pratt JR, Massey WD, Pinkerton FH, Thanos SF. *J Org Chem* 1975;40:1090.
- [31] Feng D, Wilkes GL, Lee B, McGrath JE. *Polymer* 1992;33:526.
- [32] Venkatheswaran LN, Leir CE, Wilkes GL. *J Appl Polym Sci* 1991;43:951.
- [33] Yarusso DJ, Cooper SL. *Macromolecules* 1983;16:1871.