Anionic Polymerization of Isoprene. II. Synthesis and Characterization of A—B—A-Type Block Copolymers by Oligomeric Dilithium Initiator

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ABSTRACT: We prepared oligodilanions of styrene (St) and isoprene (Ip) which are capable of growing at both ends and are completely soluble in nonpolar solvents, in the presence of a lithium-containing catalyst. Using initiators of this new type, we investigated the synthesis of block copolymers.

Block copolymers of the three segment A—B—A-type were prepared in a two-step reaction. Polyisoprene (PIp) with 90% or more of the *cis*-1,4 structure was chosen as segment B and polystyrene (PSt), poly(methyl methacrylate) (PMMA), and polyacrylonitrile (PAN) as segment A. With PMMA and PAN in segment A, the copolymers formed became partly insoluble in solvent. It was possible to make transparent film from the copolymers containing PMMA, but the properties were not as desirable as expected. With PAN in segment A, the copolymers possessed poor properties and were colored yellow. In the case of PSt, however, the formation of copolymers with excellent properties similar to the styrene—butadiene—styrene (S—B—S) block copolymers reported previously was confirmed by the gel-permeation chromatography (GPC), measurement of dynamic viscoelasticity, plotting of stress—strain curves, and electron microscopic study of the morphology of block copolymers.

KEY WORDS Anionic Block Copolymerization / Isoprene / Styrene / Methyl Methacrylate / Acrylonitrile / Oligomeric Dilithium / Microstructure / Molecular Weight Distribution / Morphology / A—B—A-Type Block Copolymer /

When Ip is polymerized in a hydrocarbon solvent in the presence of a lithium-containing initiator, 90% or more of the monomer is known to polymerize *via* the *cis*-1,4 addition. With alkylolithium as an initiator,¹⁻⁶ the polymerization is homogeneous and monoanionic polymer is formed which will grow at one end. It is necessary to carry out the reaction in three steps to synthesize the A—B—A-type copolymers with the use of an initiator of this type.⁷⁻⁸ Polymethylene-dilithium⁹⁻¹² or phenylenedilithium¹³ yields dianions which grow at both ends; however, the polymerization in nonpolar solvent becomes heterogeneous and the A—B—A-type block copolymers synthesized in this initiator system show relatively broad molecular weight distribution and are often mixed with homo-

polymers. Fetters, *et al.*,¹⁴ prepared α MS—I μ — α MS block copolymers with 1,4-dilithio-1,1,4,4-tetraphenylbutane as an initiator. This initiator is soluble in nonpolar solvents, capable of growing at both ends, and favorable for the synthesis of block copolymers. However, the content of *cis*-1,4 structure is fairly low at a level of 65–70%. A number of studies have been published on the structure and properties of block copolymers of St and butadiene (Bd).¹⁵⁻²³ However, any preparation of styrene—*isoprene*—styrene (S—I—S) block copolymers with 90% or more of Ip in this *cis*-1,4 structure in a two-step reaction with an initiator which is soluble in nonpolar solvents and capable of growing at both ends, has not been published to our knowledge. In Part I²⁴, we prepared oligodi-

anions of St or Ip using a lithium-containing catalyst and showed that these dianions are soluble in nonpolar solvents and capable of growing at both ends. In the present study, we attempted to synthesize S—I—S block copolymers in which 90% or more of Ip is present in the *cis*-1,4 structure. In addition, we tried to prepare block copolymers having PMMA or PAN at both ends. The block copolymers thus prepared were proved to be such by GPC, measurement of dynamic viscoelasticity, plotting of stress-strain curves, and electron microscopic study of the morphology of copolymers.

EXPERIMENTAL

Materials

Naphthalene, Lithium, Isoprene, Styrene, Diethylether, and Benzene. The principal reagents were purified in the manner described in Part I.²⁴

Tetrahydrofuran. Tetrahydrofuran (THF) was dried over NaOH for more than 12 hr and fractionated under a nitrogen atmosphere immediately before use.

Methylmethacrylate. Commercial MMA of the reagent first grade was placed in a separatory funnel, washed three times with one tenth of its volume of a saturated aqueous solution of sodium sulfite, then three times with one tenth of its volume of 5-% aq NaOH, finally three times with one tenth of its volume of 20-% aq sodium chloride, and then dried over CaCl₂ for

more than 12 hr. After filtration, the filtrate was distilled under reduced pressure in N₂ gas with the addition of a small amount of sublimed sulfur.

Acrylonitrile. AN of the reagent first grade was fractionated under N₂ gas and dried over CaH₂ immediately before use.

Preparation of Initiator

The preparation of the initiators were carried out in accordance with the methods described in Part I.²⁴

Polymerization

Since the polar solvent remaining in the initiator oligodanion greatly affects the *cis*-1,4 content of PIp, the polar solvent was removed almost completely before Ip was polymerized.

Block Copolymerization

The synthesis of A—B—A-type block copolymers was undertaken in a vacuum system such as shown in Figure 1. A reaction tube has an ampoule F containing a benzene solution of PIp and an ampoule D containing THF and a given amount of purified St in side tubes. A given amount of THF is placed in the reaction tube E through A—B—C and the upper part is sealed off. Then a seal between E and the reaction tube is broken by a magnet and the PIp solution is mixed with THF to reduce the viscosity of PIp. Next, a seal between D and E is broken to introduce St monomer. The reaction is completed in 2 to 3 hr at 25°C. In the same manner, block

Figure 1. Experimental apparatus of block copolymer.

copolymers of MMA and Ip and those of AN and Ip were prepared. The polymers thus formed were treated as in the synthesis of PIP;²⁴ the polymers were obtained as white precipitates by pouring the polymer solution into 10 times its volume of MeOH containing a small amount of acetic acid. The precipitates were washed three times with MeOH; an antioxidant BHT (2,6-di-*tert*-butyl-*p*-cresol) was added in an amount of 1% based on the polymers, and dried in vacuum at 40°C for 72 hr.

Measurement

Characterization. Measurements of the molecular weight, the molecular weight distribution, and the microstructure of PIP were made according to the methods given in Part I.²⁴ The samples for measurements of properties were prepared by casting a 4% cyclohexane solution of the block copolymers into a thin film with the thickness of 0.2–0.5 mm. The St content in block copolymers was calculated either from the relationship between the feed and the yield or from eq 1 after measurement of the refractive index by means of an Abbe refractometer.²⁵

$$n_D^{20}(\text{S—I—S}) = n_D^{20}(\text{PIp}) + \left\{ n_D^{20}(\text{PSt}) - n_D^{20}(\text{PIp}) \right\} \frac{\text{Mst}}{100} \quad (1)$$

$n_D^{20}(\text{S—I—S})$, refractive index of S—I—S block

copolymer

$n_D^{20}(\text{PIp})$, refractive index of polyisoprene

$n_D^{20}(\text{PSt})$, refractive index of polystyrene

Mst, styrene content (wt%).

Physical properties. Tensile properties were measured at 20°C, at a test rate of 500 mm/min and at the elongation ratio of 6 using Tensilon, a testing apparatus from the Toyo Sokki Company. Hardness was measured at 20°C by a rubber durometer from the Hokushin Kagaku Kogyo Company. Dynamic viscoelasticity was measured at a frequency of 1 Hz by using a viscoelasticity spectrometer from the Iwamoto Seisakusho Company. Electron micrographs were taken with an electron microscope Type JE M-7A of the Japan Electron Optics Laboratory Co. Ltd., after the PIP phase of the sample was dyed with osmic acid,^{26–27} buried in epoxy resin, and cut into ultrathin sections in the range of 50 to 150 mμ by an ultramicrotome.

RESULTS AND DISCUSSION

The results of the synthesis of block copolymers are shown in Table I. Expt nos 93–128 and 136–139 are block copolymers and the copolymers obtained could be made into films from their cyclohexane solutions. The polymerization proceeded almost quantitatively and the yield was close to 100%. As for the poly-

Table I. Synthesis and characterization of block copolymers^a

Expt no.	Block type	Initiator	Conversion, %	Vinyl content, %	<i>cis</i> -1,4 Content, %	$\bar{M}_n$	Gel	Film
93	St—Ip—St	Ip oligomer	99.5	22.0	89.0	1.0×10^6	No	Trans-parent
97	"	St oligomer	99.8	37.5	90.0	2.7×10^5	"	"
125	"	Ip oligomer	97.5	21.0	"	3.6×10^5	"	"
126	"	"	100.0	30.0	"	5.1×10^5	"	"
127	"	"	97.5	44.0	"	5.0×10^5	"	"
128	"	"	80.0	79.0	"	—	"	"
136	"	St oligomer	97.2	28.8	91.5	4.5×10^4	"	"
137	"	"	100.0	37.5	"	5.0×10^4	"	"
139	"	"	100.0	53.5	"	2.4×10^4	"	"
129	MMA—Ip—MMA	Ip oligomer	90.2	14.0	90.0	—	Yes	"
130	"	"	84.0	19.3	"	—	"	"
131	AN—Ip—AN	"	88.0	8.8	"	—	"	Yellow
132	"	"	78.5	11.7	"	—	"	"

^a Solvent, benzene or benzene+THF; polymerization temp, 15, 25, and –78°C.

Table II. Physical properties of block copolymers

Expt no.	Block type	Film	Tensile strength, kg/cm ²	Elongation, %	300-% Modulus, kg/cm ²	Hardness, shore A
93	St—I _p —St	Transparent	18.0	1300	8.2	35
97	"	"	105.0	1400	8.5	45
125	"	"	15.0 up	1400 up ^a	5.8	35
126	"	"	133.0 up	1400 up ^a	7.4	40
127	"	"	100.0 up	1400 up ^a	14.5	50
128	"	"	—	—	—	—
136	"	"	16.3	700	6.4	—
137	"	"	23.5	520	16.8	—
139	"	"	18.0	500	16.0	—

^a Did not break.

merization of Ip, the proportion of the *cis*-1,4 addition exceeded 90%. In particular, when St oligomer was used as an initiator, the proportion of the *cis*-1,4 addition was larger by 1–2% than when Ip oligomer was used. This is probably because the initiator oligomer is more than 75% in the 3,4 structure and the rest is essentially in the *trans*-1,4 structure; such a low *cis*-1,4 content consequently reduces the *cis*-1,4 content in Ip as a whole. Samples varying in the St wt% and molecular weight were prepared, and the polymerization proceeded almost quantitatively in each case.

MMA—I_p—MMA block copolymers were prepared in expt nos 129–130 and AN—I_p—AN block copolymers in no. 131–132. The polymerization temperature was kept at –78°C to keep side reactions to a minimum. The yields were 80–90%, somewhat lower than in the case of St, and the formation of gels insoluble in THF was observed. Since the AN—I_p—AN block copolymers are colored yellow, it appears likely that side reactions besides propagation at terminal carbanions took place during block copolymerization and the polymers formed are not linear A—B—A block copolymers. In copolymerization reactions of these monomers, other special synthetic conditions should be taken into consideration.

Properties of the block copolymers obtained are shown in Table II. The polymers in expt no. 93–128 were synthesized at different St wt% while the molecular weight was kept in the order of 10⁵. Those in expt no. 136–139

were prepared at different St wt% while molecular weight was kept in the order of 10⁴. The tensile strength increased with increasing St content and reached a maximum at 35–38 wt-% St. The polymers with a molecular weight in the order of 10⁵ showed higher tensile strength than those with the molecular weight in the order of 10⁴. The elongation at the break increased with increasing molecular weight and was not affected so much by the St content although it was less for higher St content. Both the 300-% modulus and the hardness increased with increasing St content.

The polymers synthesized in the present study were expected to show good monodispersion, and this was investigated by means of GPC. The GPC curves of the initiator, PIp, S—I—S block copolymer, and the standard PSt are shown in Figure 2. The horizontal axis shows the elution volume or count number and a lower count number means higher molecular weight. The pattern of the initiator roughly resembles that of the standard PSt and it is seen that the molecular weight distribution is fairly narrow. PIp prepared with the use of this initiator shows a slightly broader pattern with only one peak. The pattern of S—I—S block copolymer prepared by reacting the above PIp with St has approximately the same stretch and one peak on the higher molecular weight side than the PIp. This proves that homopolymers are not formed. Both PIp and S—I—S block copolymers show a narrow molecular weight distribution and seem to be well mono

Figure 2. GPC elution patterns of standard polymer and sample polymers: $\circ$, polystyrene, $\overline{M}_n=2.3 \times 10^3$; $\bullet$, polyisoprene, $\overline{M}_n=3.1 \times 10^4$; $\triangle$, S—I—S block copolymer, $\overline{M}_n=5.0 \times 10^4$; $\times$, standard polystyrene, $\overline{M}_n=1.0 \times 10^4$; $\overline{M}_w/\overline{M}_n=1.06$ (by Pressure Chemical Co. Ltd.).

dispersed. The initiator used is soluble in non-polar solvents, gives a homogeneous polymerization system, and is oligolithium growing at both ends. Moreover, since this initiator is a monodispersed oligomer with an extremely sharp molecular weight distribution, polymerization of Ip and the ensuing block copolymerization with St proceed only by propagation without any initiation or termination, and this seems to have produced PIP and S—I—S block copolymer with a narrow molecular weight distribution. The fact that the polymers produced in the steps from the initiator to PIP and from PIP to S—I—S block copolymer all show only one peak in their GPC patterns indicates that a single monodispersed polymer is formed in each case. Therefore, the S—I—S block copolymer is considered to be a single monodispersed polymer.

With application of a proper method of preparing samples, block copolymers are known to show a sea-island structure.^{16,18,23} In Figures 3–6 are shown electron micrographs of films of S—I—S block copolymers with St contents of 21, 30, 44, and 79% by weight prepared from their cyclohexane solutions. Dark portions are PIP dyed with osmic acid and white portions PSt. With the PSt contents of 21 and 30% by weight, PSt is dispersed in the PIP matrix as separate phases. With the PSt content of 44% by weight, however, partial formation of a

continuous phase of PSt is observed. The particle diameters of PSt for different PSt contents are as follows: about 0.04μ for 21% by weight, about 0.06μ for 30% by weight, and 0.08 – 0.1μ for 44% by weight. Thus the particle diameter increases with increasing PSt content, but the particles are spherical, or nearly so, in all cases. The finding that the particle diameter is relatively uniformly dispersed on the average in this manner seems to be a phenomenon characteristic of the A—B—A-type block copolymers. With the PSt content of 79% by weight, PIP is dispersed in the matrix of PSt and the PIP phases

Figure 3. The inner structure of S—I—S block copolymer film prepared from cyclohexane solution; St, 21 wt%.

Figure 4. The inner structure of S—I—S block copolymer film prepared from cyclohexane solution; St, 30 wt%.

Figure 6. The inner structure of S—I—S block copolymer film prepared from cyclohexane solution; St, 79 wt%.

Figure 5. The inner structure of S—I—S block copolymer film prepared from cyclohexane solution; St, 44 wt%.

are spherical or irregular probably because cyclohexane used for making the film is a good solvent for PIP but a poor one for PSt, and tends to become spherical whereas PIP is irregular.

Dynamic viscoelasticity of the sample films of S—I—S block copolymers prepared from cyclohexane solution was studied. The temperature dispersion of relaxation modulus is shown in Figure 7. Curves are nearly the same for 21 and 30% by weight of PSt with a point of inflection somewhere between 10^7 and 10^8 and falling gradually over the temperature range

Figure 7. Temperature dependence of dynamic modulus (E') for S—I—S block copolymers: measured frequency, 1 Hz; ●, St, 21 wt%; ○, St, 30 wt%; △, St, 44 wt%.

from -50 to 100°C . This type of curve is considered to be characteristic of the sea-island structure of the A—B—A-type block copolymers. With the PSt content of 44% by weight, the point of inflection is between 10^8 and 10^9 and the curve falls gradually over the temperature range from -50 to 100°C ; this is probably because a continuous phase begins to form in part of the PSt island in the sea-island structure. It is known that a simple polymer blend of PSt and PIP shows not a curve falling gently over the temperature range from -50 to 100°C but a curve running roughly parallel to the horizontal axis.²⁸ Thus the formation of S—I—S block copolymers is also expected from the results given above.

Figure 8. Temperature dependence of dynamic loss factor ($\tan \delta$) for S—I—S block copolymers: measured frequency, 1 Hz; ●, St, 21 wt%; ○, St, 30 wt%; △, St, 44 wt%.

In Figure 8 is shown the temperature dispersion of $\tan \delta$. The peak near -50°C appears to be due to the transition of PIP and that near 120°C to the transition of PSt. Both transition temperatures are higher than those of homopolymers reported thus far,²⁹ and this difference is probably caused by monodispersion of poly-

mers. An extremely small peak for the PSt content of 44% by weight seems to have arisen from restriction of the PIP phase by the continuous PSt phase.

The tensile properties of A—B—A-type block copolymers were investigated. Stress—strain

Figure 9. Stress—first strain relationships for S—I—S block copolymers: ●, St, 21 wt%; ○, St, 30 wt%; △, St, 44 wt%.

Figure 10. Stress—second strain relationships for S—I—S block copolymers: ●, St, 21 wt%; ○, St, 30 wt%; △, St, 44 wt%.

curves of S—I—S block copolymers for the PSt contents of 21, 30, and 44% by weight in application of the first tension are shown in Figure 9 and stress—strain curves of the same materials in application of the second tension are shown in Figure 10. The block copolymers with the PSt contents 21 and 30% by weight showed stress—strain curves similar to those of vulcanized rubber, but a rise in the initial stress and the necking phenomenon were observed in the block copolymers with 44% by weight of PSt. It is suggested in this respect that condensed PSt blocks are entwined to form a continuous phase and show plastic behavior. However, this continuous phase is readily destroyed by elongation, yielding dispersed particles, and is not restored immediately after removal of the stress. Consequently, in application of the second tension, the rising phenomenon characteristic of plastic behavior was not observed any more, as shown in Figure 10.

Stress—strain curves of the S—I—S block copolymers with 30% by weight of PSt and molecular weight in the order of 10^4 and 10^5 , and with 37.5% by weight of PSt and molecular weight in the order of 10^4 and 10^5 are shown in Figures 11 and 12 respectively. It is apparent that the block copolymers with a PSt

Figure 11. Stress—first strain relationships for S—I—S block copolymers: $\circ$, $\bar{M}_n$, 5.1×10^5 , St, 30.0 wt%; $\times$, $\bar{M}_n$, 2.7×10^5 , St, 37.5 wt%; $\square$, $\bar{M}_n$, 4.5×10^4 , St, 30.0 wt%; $\blacksquare$, $\bar{M}_n$, 5.0×10^4 , St, 37.5 wt%.

Figure 12. Stress—second strain relationships for S—I—S block copolymers: $\circ$, $\bar{M}_n$, 5.1×10^5 , St, 30.0 wt%; $\times$, $\bar{M}_n$, 2.7×10^5 , St, 37.5 wt%; $\square$, $\bar{M}_n$, 4.5×10^4 , St, 30.0 wt%; $\blacksquare$, $\bar{M}_n$, 5.0×10^4 , St, 37.5 wt%.

content of less than 37.5% by weight behave like vulcanized rubber. The tensile modulus increases with diminishing molecular weight probably for the reason that the pseudo cross-linking density increases because of the short chain length of PIP.

The permanent elongation is large compared with that of vulcanized rubber, as is seen in Figures 9–12, and this phenomenon may be explained as follows. Slipping takes place between PSt phases in the condensed PSt blocks, such phases serving as pseudo cross-linking points, upon application of tension. This slipping does not return to the original state when the stress is removed, resulting in larger permanent elongation.

The relationship between the PSt content and the formation of a continuous PSt phase was examined from diagrams of tensile properties. The relationship between the PSt content and the 300-% modulus is shown in Figure 13. The 300-% modulus is seen to increase sharply at the PSt content of 35–38% by weight and this

Figure 13. Dependence of 300-% tensile modulus on styrene ratio in S—I—S block copolymers.

suggests that a continuous PSt phase begins to form near the PSt content of 30% by weight, then increases with increasing PSt content, and shows plastic behavior resulting in a larger 300-% modulus.

It was made clear above that, with the use of oligodanion which is soluble in nonpolar solvents and capable of growing at both ends, the A—B—A-type block copolymers containing as segment B PIP with more than 90% of the *cis*-1,4 structure were synthesized in a two-step reaction. With this method, it became possible to use as segment A a component more polar than segment B—such as MMA or AN. As for the S—I—S-type block copolymers, the polymers with molecular weight in the order of 10^5 show good mechanical properties; the particle size of St condensates increases with increasing St content; a continuous PSt phase begins to form at the St content of 30–38% by weight and a transition from vulcanized rubber-like properties to plastics-like properties takes place gradually.

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