Novel Synthesis of a Block Copolymer consisting of Styrene and Ethylene by Means of Active Site Modification

Kiyoshi Endo and Takayuki Otsu*

Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558, Japan

A block copolymer consisting of styrene and ethylene with a narrow molecular weight distribution has been synthesized by means of active site modification performed by the addition of tertiary diamines to living poly(styrene).

It is well known that alkyl-lithium catalysts can cause anionic polymerizations of many unsaturated monomers including isoprene (IP) and styrene (St) to give living polymers bearing terminal carbon–lithium bonds.[1,2] When effective modifiers such as *N,N,N',N'*-tetramethylethylenediamine (TMEDA) are added to the living polymers, the nature of the active site changes markedly, and then polymerization of ethylene (E) is induced subsequently to give block copolymers. We propose to term this modification process 'active site modification,' and briefly reported that block copolymers consisting of IP and E could be synthesized with this approach.[3] The corresponding block copolymer can be also prepared with the active site transformation being achieved by the addition of $TiCl_4$ to the living polymers.[4,5]

However, this transformation is not an effective method for synthesizing block copolymers consisting of St and E segments owing to chain breaking by β-hydrogen abstraction from the styryl chain.[5] We have been attempting to synthesize such a block copolymer by means of active site modification, and now report our preliminary results.

A 300 ml glass reactor equipped with a magnetic stirrer and connected to a vacuum system was used for the polymerizations. The polymerization of St was carried out under high vacuum, whereas in the polymerization of E, the pressure was kept at 2 atm.

The results of the polymerization of St and E with s-butyl-lithium as catalyst are summarized in Table 1. Although St gave a living polymer in the absence of TMEDA, the polymerization of E proceeded only in the presence of TMEDA.[6] These results suggested that the required block copolymer could be synthesized by means of active site modification. We therefore carried out the block copolymerization with E by using the living polymer of St.

When TMEDA was added to the living poly(St), the cherry red solution turned wine red, indicating that active site modification had been performed. The polymerization of E was then induced and a polymer insoluble in cyclohexane was produced as the polymerization of E proceeded. However, in the absence of TMEDA the copolymerization with E did not take place, and only a homopolymer of St was recovered. The effect of other amines as a modifier was examined. Sparteine and 1,2-dipiperidinoethane were also effective modifiers for this copolymerization.

The copolymers thus obtained were analyzed by GPC, NMR, and other methods to prove that they were block copolymers. A GPC plot of the polymers is depicted in Figure 1. The elution curve of the polymer obtained from the block copolymerization of St and E was unimodal and shoulders based on homopolymers of St and E were not observed. The whole curve was also shifted towards the higher molecular weight side than that of the original living poly(St) and an increase of molecular weight was also observed as shown in Table 1. In addition, it is noteworthy that the resulting copolymers have a narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n = 1.16$), *i.e.* the polymerization of E is also likely to proceed through a living mechanism.

The ^{13}C NMR spectrum of the resulting copolymer is depicted in Figure 2. The chemical shifts for each carbon resonance were calculated on the basis of the polymer being a

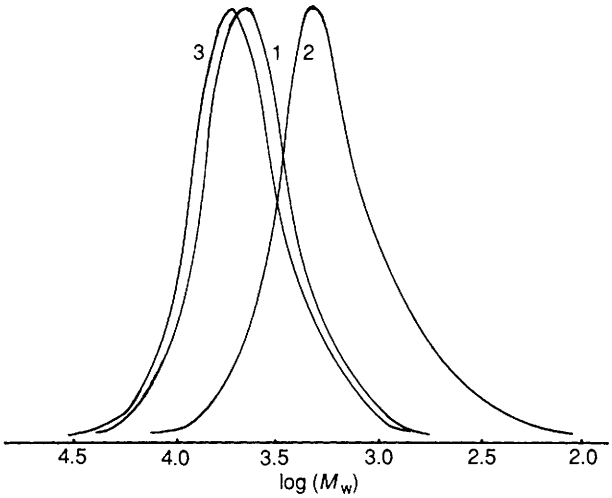

Figure 1. GPC elution curves of (1) Poly(St), (2) Poly(E), and (3) Poly(St)-block-poly(E), measured at 130 °C using trichlorobenzene as an eluent.

Table 1. Polymerization of St and E with Bu^sLi in cyclohexane at 50 °C.[a]

Monomer 1st	Monomer 2nd	TMEDA /Bu^sLi	Yield/g	$10^3 \bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[b]
E	—	—	0.0	—	—
E	—	1.5	4.8	1320	1.45
St	—	—	23.2	3390	1.07
St	—	1.5	23.2	1850[d]	2.65[d]
St	E	—	23.4	—	—
St	E	1.5[c]	28.8	4530	1.16

[a] Polymerizations were carried out for 5.0 h for each monomer: [St] = 1.1 mol dm^{-3}, E = 2 atm, [Bu^sLi] = 2.3×10^{-2} mol dm^{-3}. [b] Determined by GPC at 130 °C. [c] TMEDA was added after the first polymerization. [d] Measured at 38 °C; elution curve was not unimodal.

$$^{1}CH_3—^{2}CH_2—^{3}CH(^{4}CH_3)—^{5}CH_2—^{6}CHPh—(^{7}CH_2—^{8}CHPh)_m—^{9}CH_2—^{10}CH_2—(^{11}CH_2—^{12}CH_2)_n—^{13}CH_2—^{14}CH_2—^{15}CH_2—^{16}CH_3$$

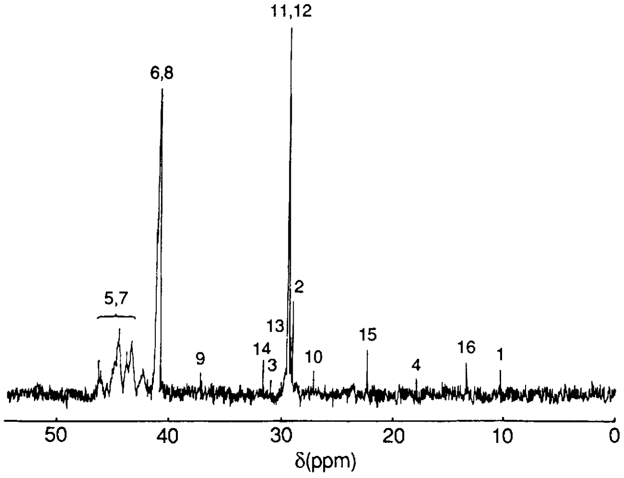

Figure 2. ^{13}C NMR spectrum of the polymer obtained from block copolymerization of E by using living poly(St).

block copolymer having St and E segments.[7] From comparison with the calculated values, the observed chemical shifts could be assigned as indicated in Figure 2, *i.e.* the supposed structure is accurate.

In contrast with the solubility of poly(St) in acetone, the copolymer is almost insoluble, and the small amount of the soluble fraction consists of the E segment. Moreover, the copolymer is completely soluble in hot tetrahydrofuran (THF), but the poly(E) synthesized in this work is insoluble. On the basis of these results, we conclude that the polymer is a block copolymer consisting of St and E segments.

In order to elucidate the composition and the nature of each segment, we further analysed the resulting block copolymer. The content of St segment in the block copolymer was estimated to be 46 mol% from the ^{1}H NMR spectra, a value in agreement with that calculated from the polymer yield. From DSC data, a glass transition resulting from the atactic structure of St sequences appeared at 94 °C, and the melting point due to crystallinity of the E segment was observed at 111 °C.

Received, 9th April 1990; Com. 0/01588A

References

1 M. Morton, 'Anionic Polymerization: Principles and Practice,' Academic Press, New York, 1983.
2 M. Szwarc, *Adv. Polym. Sci.,* 1982, **45**, 1.
3 K. Endo and T. Otsu, *Polym. Prepr. Jpn. Engl. Ed.,* 1988, **37**, E17.
4 G. Riess and G. Hurtrez, 'Encyclopedia of Polymer Science and Engineering 2nd ed. Vol.2,' Wiley–Interscience, New York, 1985, p. 324; D. R. Richards, *Br. Polym. J*, 1980, **12**, 89; A. Siove and M. Fontanille, *Makromol. Chem.*, 1980, **181**, 1815.
5 A. Siove and M. Fontanille, *Eur. Polym. J.*, 1981, **17**, 1175; *J. Polym. Sci., Polym. Chem. Ed.*, 1984, **22**, 3877; A. Soum, A. Siove, and M. Fontanille, *J. Appl. Polym. Sci.*, 1983, **28**, 961; M. A. Drezewinski and R. H. Cohen, *J. Polym. Sci., Polym. Chem. Ed.*, 1982, **23**, 1523. K. Endo and J. E. McGrath, *Polym. Prepr. Jpn.*, 1986, **36**, 211.
6 G. G. Eberhardt and W. A. Butte, *J. Org. Chem.*, 1964, **29**, 2928; G. G. Eberhardt and W. R. Davis, *J. Polym. Sci., Part A*, 1965, **3**, 3753; A. W. Langer, *Am. Chem. Soc., Polym. Div., Polym. Prepr.*, 1966, **7**, 132; J. N. Hay, J. F. McCabe, and J. C. Robb, *J. Chem. Soc., Faraday Trans 1*, 1972, **68**, 127; J. N. Hay, D. S. Harris, and M. Wiles, *Polymer*, 1976, **17**, 613; M. S. Delaney, W. B. Marshall, and J. L. Brewbaker, U. S. Pat. 4,668,746, 1987.
7 E. Breitmaier and W. Voelter, '^{13}C-NMR Spectroscopy,' Verlag Chemie, Weinheim, 1978, p. 208.