Anionic Block Copolymerization of Phenylbutadienes with Styrene or Butadiene

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ABSTRACT: Anionic block copolymerizations of 1-phenyl-1,3-butadiene (1PB) or 2-phenyl-1,3-butadiene (2PB) with styrene (St) and with butadiene (Bd) were carried out in tetrahydrofuran (THF) or in toluene. Behavior of these monomers in block copolymerizations was ascertained by gel permeation chromatography. In THF medium, the reactivities of living poly-1PB and poly-2PB ends toward St are low, and a considerable amount of the starting block remained unreacted. However, reactivities of ends of living poly-St toward 1PB or 2PB are high enough to produce A–B-type block copolymer. On the other hand, in toluene medium, for all the cases studied the reactivities of the living ends were high.

We have recently investigated the microstructures of poly(1-phenyl-1,3-butadiene) (poly-1PB) and poly(2-phenyl-1,3-butadiene) (poly-2PB) prepared by use of anionic initiators.[1,2] These two monomers behaved in quite a different way from butadiene (Bd) or isoprene in anionic polymerization.

In the anionic copolymerization of Bd and styrene (St)[3,4] in hydrocarbon media, Bd has a relative reactivity much higher than that of St and forms poly(butadienyllithium) first, which initiates St polymerization. Therefore, such copolymerization gives almost entirely St–Bd block copolymer in the absence of additives.[5,6]

In this study we have investigated the reactivities of living poly-1PB and poly-2PB ends through the anionic block copolymerization of 1PB or 2PB with St and with Bd. The chemistry of these systems was elucidated through the use of gel permeation chromatography.

Experimental Section

Materials. 1PB, 2PB, and BuLi were synthesized by methods described in previous papers.[1,2] THF and toluene were purified by distillation over $LiAlH_4$.

Block Copolymerization. Block copolymerization was carried out in a three-necked flask under an argon atmosphere with *t*-BuLi in THF or *sec*-BuLi in toluene at 0 °C by sequential monomer feed. Monomer A is first reacted with BuLi for 2 h; [monomer A] = 0.23 mol dm^{-3} and [monomer A]/[BuLi] = 15.0. Then an equimolar amount of monomer B was successively added to the living poly-A end and the reaction was carried out for another 2.0 h.[7] Bd was used as a toluene solution (2.42 mol dm^{-3}). When THF was used as the solvent, it was evaporated off and an equal volume of benzene was added. The whole reaction mixture was washed with water and saturated aqueous NaCl and then dried with molecular sieves (3A 1/16).

Gel Permeation Chromatogram. The gel permeation chromatogram (GPC) was recorded on a Waters ALC/GPC 244 equipped with four columns (μ-Styragel; $10^5 + 10^4 + 10^3 + 500$ Å). THF was used as an eluent and the flow rate was set at 1.5 mL/min. The molecular weight of the sample was determined according to the calibration curve obtained with standard polystyrenes.

Results and Discussion

Figure 1 shows the GPC of the product obtained in the block copolymerization of 1PB with St in THF medium. In Figure 1A, 1PB is polymerized to a starting block whose average degree of polymerization ($\overline{DP}$) is 15.[9] The broken line in Figure 1A shows the GPC of poly-1PB prepared under the same condition as for formation of the starting block. The number-average molecular weight ($\bar{M}_n$) of the sample agreed with the theoretical value (2000). The solid line in Figure 1A shows the GPC of the whole product recovered after addition of St to the living poly-1PB end. Ultraviolet (UV, 254 nm) detection was used in recording the upper trace and differential refractometry (RI) was employed in recording the lower one.

The bimodal GPC trace obtained consists of a peak in the lower molecular weight region corresponding to the poly-1PB starting block ($\bar{M}_n$ = 2000) and a peak in the higher molecular weight region ($\bar{M}_n$ = 13 000) for a block copolymer formed by addition of St to the living poly-1PB end. The $\bar{M}_n$ of the peak (13 000) in the higher molecular weight region is too high for the block copolymer ($\bar{M}_n$ = 3600) formed by addition of St to the living poly-1PB end. Furthermore, the peak intensity ratio of the upper trace (UV detection)[10] to the lower one (RI detection) in the higher molecular weight region is 0.8, which is 3.5 times larger than that of poly-St homopolymer. These results indicate that only a small amount of the living poly-1PB end could initiate the polymerization of St and most of the living poly-1PB end remains unreacted without any added St. As for the higher molecular weight part, the short poly-1PB block (15 units) is attached to the long poly-St block (106 units).

On the other hand, when the monomer addition sequence is reversed, the GPC of the whole reaction mixture shows interesting differences, as shown in Figure 1B. St is polymerized to a starting block whose $\overline{DP}$ is 15. The broken line in Figure 1B shows the GPC of the starting poly-St block. The $\bar{M}_n$ of the sample is the theoretical value (1600), showing the absence of unconverted monomer. The solid line in Figure 1B shows the GPC of the whole product formed by adding an equimolar amount of 1PB to the living poly-St end. Different from Figure 1A, the GPC is unimodal, indicating that all of the living poly-St ends initiate the polymerization of 1PB uniformly to give A–B-type block copolymer. The $\bar{M}_n$ of this copolymer is consistent with the theoretical value (3600).

Figure 2 shows the results of the block copolymerization of 2PB with St. 2PB is polymerized to the starting block whose $\overline{DP}$ is 15. The broken line in Figure 2A shows the GPC of the poly-2PB starting block. The $\bar{M}_n$ of this sample agreed with the theoretical value (2000) and unconverted 2PB could not be detected. The solid line in Figure 2A shows the GPC of the whole product formed by adding equimolar amounts of St to the living poly-2PB end. The GPC is bimodal and similar to Figure 1A, and the peak in the lower molecular weight region corresponds to the poly-2PB starting block without St unit, which was shown by the broken line above. $\bar{M}_n$ of the peak in the higher molecular weight region (29 000) is too high for the block copolymer (3600) formed by uniform addition of St to the living poly-2PB end. The peak intensity ratio of

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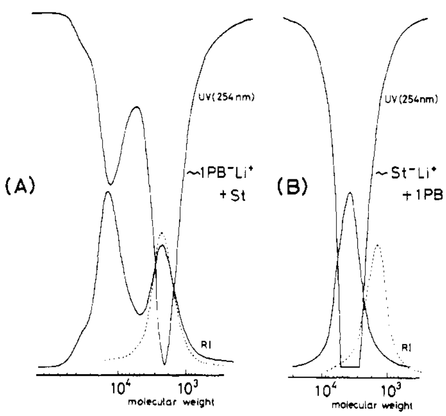


Figure 1. Gel permeation chromatograms of (A) sample 1 and (B) sample 5 prepared in THF.

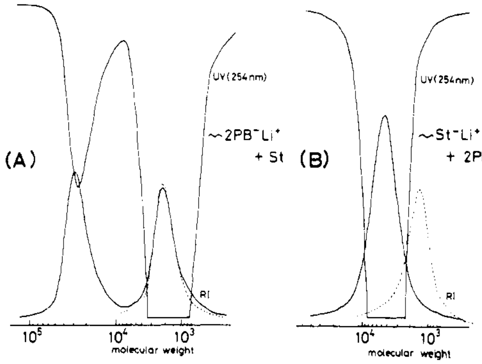


Figure 2. Gel permeation chromatograms of (A) sample 3 and (B) sample 6 prepared in THF.

Table I
List of Block Efficiencies

sample	medium[a]	monomer[b] A	B	block efficiency,[c] %
1	THF	1PB	St	14
2	THF	1PB	Bd	35
3	THF	2PB	St	6
4	THF	2PB	Bd	16
5	THF	St	1PB	~100
6	THF	St	2PB	~100
7	THF	Bd	1PB	~100
8	THF	Bd	2PB	~100

[a] When the block copolymerizations are carried out in *toluene*, the block efficiencies of all the cases listed in this table are almost 100%. [b] See Experimental Section. [c] Estimated with eq 1.

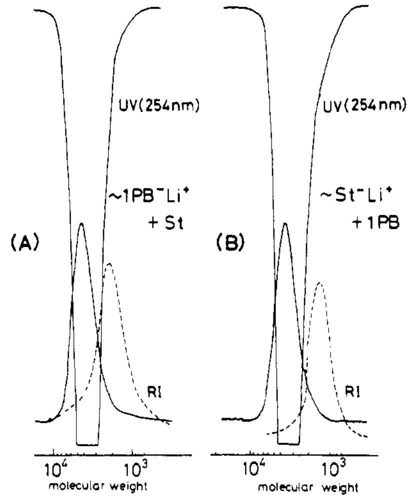
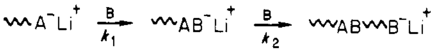


Figure 3. Gel permeation chromatograms of samples prepared in toluene under conditions similar to those for (A) sample 1 and (B) sample 5.

Scheme I



$$\sim\!\sim A^-Li^+ \xrightarrow[k_1]{B} \sim\!\sim AB^-Li^+ \xrightarrow[k_2]{B} \sim\!\sim AB\sim\!\sim B^-Li^+$$

the upper trace (UV detection) to the lower one (RI detection) in the higher molecular weight region is 1.2, which is 5.3 times larger than that of poly-St homopolymer. These results indicate that only a small amount of the living poly-2PB end could initiate the polymerization of St and most of the living poly-2PB end remains unreacted, similar to the case of Figure 1A. The higher molecular weight part can be explained as a poly-2PB block (15 units) to which is attached a longer poly-St block (260 units).

On the other hand, when the monomer addition sequence is reversed, that is, when St is polymerized first and then 2PB is added to the living poly-St end, the GPC of the whole product is unimodal in the same manner as Figure 1B. All the living poly-St ends initiate the polymerization of 2PB uniformly to give A–B-type block copolymer. The $\bar{M}_n$ of this copolymer is consistent with the theoretical value (3500).

These results show that the reactivities of the living poly-1PB and poly-2PB ends toward St are low. In those cases most of the starting blocks remain unreacted. Reactivities of the living poly-St ends toward 1PB or 2PB are high enough to produce A–B-type block copolymer in THF medium. Although the GPC's of some samples are bimodal, the two peaks are separated well enough for positive identification of the fraction and the molecular weight distribution of each peak is rather narrow. Therefore, the block efficiency can be defined and calculated with the molecular weight of the each peak by eq 1. M is the $\bar{M}_n$

$$\text{block efficiency} = \frac{15M_B}{M - (15M_A + 57)} \times 100 \qquad (1)$$

of the block copolymer ($\bar{M}_n$ of the higher molecular weight peak when the GPC is bimodal). M_A and M_B are the molecular weights of monomers A and B, 57 is the molecular weight of the Bu group, and 15 indicates the molar ratio of the monomer A or B to the BuLi. Table I shows the block efficiencies in the copolymerization thus defined. The results of the block copolymerizations of Bd with 1PB or 2PB are also listed in Table I. High block efficiency means $k_1 \geq k_2$ and low block efficiency means $k_1 \ll k_2$ in Scheme I. The absolute values of k_1 for St and other several monomer pairs were determined by Szwarc et al.[11] However, in this way the relative reactivity of living chain end can be estimated by means of gel permeation chromatography.

Different results are obtained when block copolymerizations are carried out in toluene. In all the cases that appear in Table I the block efficiencies are ~100%, regardless of the monomer pairs and the monomer addition sequence. One example of the GPC in those cases is shown in Figure 3 for the block copolymerization of 1PB with St. In other cases almost the same GPC's are obtained. The molecular weight distributions are rather narrow and the $\bar{M}_n$'s of the block copolymer are theoretical values.

The characterizations of the living anion chain ends of oligomeric 1PB and 2PB have been carried out by means of ^{13}C and ^1H NMR spectroscopy, showing that the negative charge distribution of the living chain end of oligomeric 1PB is a π-benzyl type[12] and that of oligomeric 2PB is a π-allylphenyl type.[13]

In THF the negative charge was delocalized to a larger extent on the living chain end of 1PB[12] and 2PB[13] than on that of St and Bd. The low block efficiencies observed in THF medium may be the result of the delocalization of charge on the chain end. Furthermore, comparing 1PB with 2PB, 2PB has a more delocalized living chain end and consequently may have a lower block efficiency than 1PB. On the other hand, in toluene for all cases studied the block efficiencies are high and almost 100%. We cannot explain this drastic change with changes in negative charge delocalization, since we have concluded by means of NMR spectroscopy that the living chain ends of 1PB and 2PB have similar charge distributions in THF and hydrocarbon media. In THF a solvent-separated ion pair is predominant, whereas in toluene the chain end is visualized as a contact ion pair. Such different types of ion pairs may be responsible for the drastic change in the block efficiency observed in this study.

References and Notes

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(9) The chromatograph and its four μ-Styragel columns provide insufficient resolution for high molecular weight samples. Therefore, we carried out the block copolymerizations for a low molecular weight range.
(10) The molar absorptivity for each homopolymer, which depends on the microstructure, decreases as follows: poly-2PB > poly-1PB > poly-St.
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Domain-Boundary Structure of Styrene–Isoprene Block Copolymer Films Cast from Solutions. 6. Effect of Temperature on Spherical Microdomain Structure

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ABSTRACT: The effect of heating on the spherical microdomain structure was investigated for a particular diblock polymer of polystyrene and polyisoprene. The radius of the sphere and interdomain distance are observed to increase slightly with increasing temperature from room temperature to 180 °C. The observation is interpreted as follows. The original domain structure is in a nonequilibrium state in that the number of block polymer molecules per domain in the real system (and therefore the size of the spherical domain and interdomain distance) is far less than that in the equilibrium state. As the system is heated, it tends to approach equilibrium, resulting in an increased number of block polymer molecules per domain and therefore in increased interdomain distance and size of the domain. The thickness of the interfacial region in which the unlike segments intermix tends to increase with increasing temperature by an amount which can be predicted from the temperature dependence of the Flory–Huggins interaction parameter χ.

I. Introduction

It is well-known that the repulsive interaction between polystyrene and polyisoprene block sequences in the block polymer causes microphase separation, resulting in a microdomain structure with a size determined primarily by the molecular dimensions of the respective sequences.[1-8] The low compressibility of polymeric solid demands uniform filling of the domain space by the respective segments,[4,5] which further specifies the most stable shape of the domain; e.g., a spherical microdomain is most stable when the molecular volume of one of the block sequences is very large compared with the others.

In a previous paper[6] in this series we clarified equilibrium and nonequilibrium aspects of the spherical domains observed in solvent-cast films. The spherical domain is not in a state of equilibrium in that the number of block polymer molecules per domain, N, in real systems is far less than the value in the equilibrium state, resulting in the size of the domain (e.g., the radius of the A domain) and interdomain distance D being much less than the equilibrium values:

$$(4\pi/3)R_A^3 = N\bar{v}_A \tag{1}$$

$$\epsilon D^3 = N(\bar{v}_A + \bar{v}_B) \tag{2}$$

where $\bar{v}_K$ is the molecular volume of the K-block chain[19] and ϵ is the packing constant of the spherical domains (ϵ being $1/\sqrt{2}$ in the case of hexagonal close packing). However, conformations of the respective chain molecules within the domain space are close to those in the equilibrium state, giving rise to a $^2/_3$ power law[6,7] in the mo-

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