

$$\ln P_g = \frac{\sum X_i \Delta(V_i \alpha_i) \ln P_{gi}}{\sum X_i \Delta(V_i \alpha_i)} \quad (6)$$

The theories for the compositional variation of P_g and T_g are evidently parallel in form. Consequently, the entire analysis for the isobaric transition¹⁻⁷ can be appropriated for the isothermal transition, with the ΔC_{p_i} and T_{g_i} exchanged for in turn the ΔC_{T_i} and P_{g_i} .

For binary blends an alternative version of eq 2 can be derived from the partial differential equality $(dT/dP)_{X_2} = (-dX_2/dP)_T/(dX_2/dT)_P$ and eq 5 and 6. This, which can be written as

$$\frac{d \ln T}{d \ln P} = - \left[\frac{X_1 \Delta(V_1 \alpha_1) + X_2 \Delta(V_2 \alpha_2)}{X_1 \Delta C_{p_1} + X_2 \Delta C_{p_2}} \right]^2 \times \left[\frac{\Delta C_{p_1} \Delta C_{p_2} \ln(T_{g_2}/T_{g_1})}{\Delta(V_1 \alpha_1) \Delta(V_2 \alpha_2) \ln(P_{g_2}/P_{g_1})} \right] \quad (7)$$

when compared with eq 2 gives as a consistency condition

$$P = - \left[\frac{X_1 \Delta(V_1 \alpha_1) + X_2 \Delta(V_2 \alpha_2)}{X_1 \Delta C_{p_1} + X_2 \Delta C_{p_2}} \right] \times \left[\frac{\Delta C_{p_1} \Delta C_{p_2} \ln(T_{g_2}/T_{g_1})}{\Delta(V_1 \alpha_1) \Delta(V_2 \alpha_2) \ln(P_{g_2}/P_{g_1})} \right] \quad (8)$$

Comment

On the basis of the success of eq 3 (typically in the form of eq 5), the new principal relations (eq 1, 2, and 6—the

last of these modified if necessary for pressure-dependent ΔC_T) should give acceptable predictive descriptions of their particular aspects of the solution glass-transition boundary for miscible blends (including plasticized polymers), molecular weight effects, copolymerization effects, and cross-linking effects.

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- (16) For miscible blends of polystyrene with poly(α -methylstyrene), for example, it may be necessary to include the temperature dependence of the ΔC_{p_i} to obtain good agreement between predictions of the thermodynamic theory and the experimental data¹³ (cf., however, ref 8, where T_g data for these blends are accounted for by eq 5).

Sequence Distribution of Styrene-Butadiene Copolymer Initiated by *n*-Butyllithium

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ABSTRACT: The sequence distribution of styrene-butadiene copolymer initiated with *n*-butyllithium in toluene was investigated by GPC measurements of ozonolysis products in relation to the time-conversion and time-copolymer composition relationships. Rapid increase of conversion and styrene content in the copolymer was observed from about 75% conversion after the consumption of almost all of the butadiene. GPC analysis of the ozonolysis products showed three peaks corresponding to 1-3 styrene sequences flanked by 1,4-butadiene units for the copolymers obtained below 75% conversion. A broad peak due to long styrene sequences was observed in addition to the peaks due to 1-4 styrene sequences for the copolymers obtained above 75% conversion. The average number of styrene units in the long styrene sequence increased from 43 to 65 with increase of conversion from 89% to 100%. The sequence distribution of styrene units determined from the ozonolysis-GPC measurement was in good agreement with that calculated by monomer reactivity ratios.

Introduction

Styrene-butadiene rubber (SBR) is commercially produced by emulsion polymerization or anionic polymerization initiated with alkylolithium. The latter is characterized by the variety of the sequence distribution of styrene units, ranging from almost random copolymers to S-B-S-type triblock copolymers. The sequence distribution can be controlled by the modification of the polymerization conditions, e.g., addition of a polar compound as a randomizing agent, control of the conversion, the controlled charge

of styrene and butadiene, or use of a polymer-Li as an initiator to make the block sequence. The approximate distribution of styrene and butadiene units can be predicted from the copolymerization parameters. In practice, however, it seems very difficult to determine the sequence distribution in the case of a partial block copolymer. The occurrence of 1,2 addition of butadiene units may further complicate the situation.

We have proposed a new method for the characterization of the sequence distribution of styrene and 1,2-butadiene

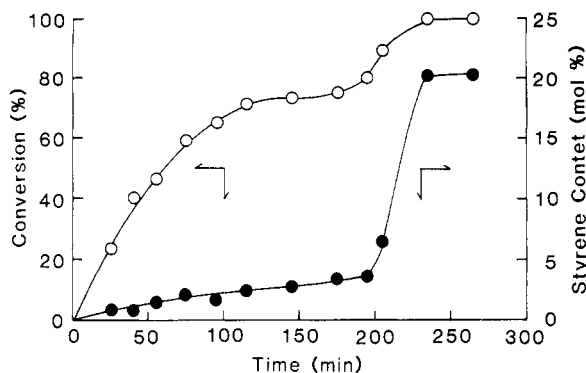


Figure 1. Conversion and copolymer composition curves.

units by ozonolysis-gel permeation chromatography.¹ This method was proved to be of greater advantage than the usual ¹H NMR, ¹³C NMR, or pyrolysis-gas chromatography methods, because it provides direct information about the distribution of the long and short sequences of the styrene and 1,2 units. In this work, the ozonolysis-GPC method was applied to the characterization of the sequence distribution of styrene and butadiene units in copolymers initiated with *n*-butyllithium.

Experimental Section

Polymerization. Commercially available styrene and butadiene were purified in the usual way. Polymerization was conducted in a 500-mL vessel equipped with a dry ice condenser, stirrer, and a solution outlet with a stopcock at the bottom. Styrene (0.162 mol) and butadiene (0.665 mol) in toluene (400 mL) were polymerized with *n*-butyllithium (3 mmol) at 40 °C for 265 min. During the polymerization, 20-mL samples were taken at 15–30-min intervals. As a typical random copolymer, styrene and butadiene were polymerized with benzoyl peroxide as an initiator in toluene at 60 °C and terminated at 4.3% conversion. The copolymers were purified by precipitation from benzene solution into methanol followed by vacuum drying at room temperature and were analyzed for their conversion and styrene content.

Ozonolysis. Ozone was prepared by submitting oxygen to an electric discharge. Ozonated oxygen (1.5%) was introduced through a glass filter inlet into a copolymer solution in methylene chloride (200 mg/100 mL) at –30 °C until the uptake of ozone ceased, which was detected by a color change of a potassium iodide aqueous solution attached to the outlet of the reaction vessel. The ozonide was decomposed to alcohols by dropping lithium aluminum hydride in ethyl ether into the reaction mixture at 0 °C and refluxing for 30 min followed by the addition of a small amount of water.

Measurements. GPC measurements were made with a Jasco Trirotar-II high-pressure pump and a Jasco Uvidex 254-II detector. The GPC measurements were conducted by using analytical columns (7.5-mm i.d. × 60 cm × 2) having exclusion limits of 30 000 and 3000. The high-resolution GPC was obtained by using preparative columns (21.2-mm i.d. × 60 cm × 3) packed with a styrene-divinylbenzene gel having an exclusion limit of 3000 and 29 000 theoretical plates for each column.² Chloroform was used as an eluent at a flow rate of 1 and 2.4 mL/min for analytical and high-resolution measurements, respectively. The molar fraction of the styrene unit in the copolymers was analyzed by 200-MHz ¹H NMR measurements using a JEOL FX-200 spectrometer.

Results and Discussion

Variation of Sequence Distribution with Conversion. The conversion and content of the styrene unit in the copolymer increased gradually up to about 200 min, where almost all of the butadiene was consumed, and afterward both increased rapidly as shown in Figure 1. After the consumption of butadiene, the residual styrene is expected to be incorporated into the copolymer chains to make long block sequences. This was also confirmed by

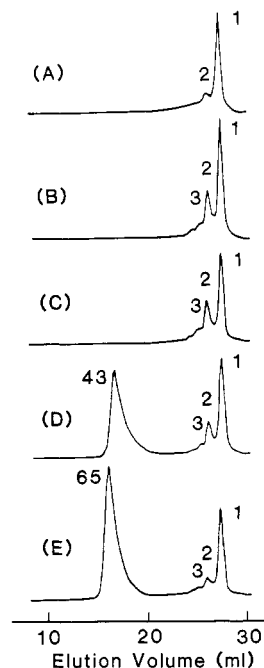
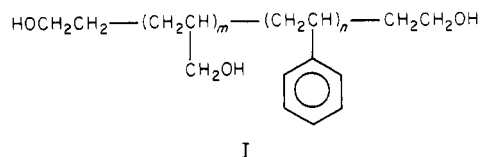


Figure 2. Ozonolysis-GPC curves of copolymer samples at various conversions: (A) conversion 23.6% (styrene, 1.7 mol %); (B) conversion 65.6% (styrene, 4.9 mol %); (C) conversion 75.6% (styrene, 6.9 mol %); (D) conversion 89.3% (styrene, 13.0 mol %); (E) conversion 100% (styrene, 20.6 mol %).

a color change of the solution from slightly yellow to orange at about 200 min due to the absorption of the styryl anion. The same composition-conversion relationship was observed for the copolymerization of styrene and butadiene with alkylolithium in nonpolar solvents.³⁻⁵

The sequence distribution of the samples collected at different conversions was determined by using the ozonolysis-GPC method.¹ Figure 2 shows the ozonolysis-GPC curves of these samples. Each peak was assigned with a calibration curve of standard styrene oligomers and also by ¹H NMR measurements of the collected fractions. The ozonolysis products are represented by the general formula



The peak at 27.3 mL in Figure 2A-E was identified as 3-phenyl-1,6-hexanediol ($m = 0$ and $n = 1$ in I) derived from the 1,4-St-1,4 sequence. Similarly, the peaks at 25.7 and 25.0 mL were assigned to the 1,4-(St)₂-1,4 ($m = 0$ and $n = 2$ in I) and 1,4-(St)₃-1,4 ($m = 0$ and $n = 3$ in I) sequences, respectively. A broad peak observed at 15–20 mL in Figures 2D,E was assigned to the long styrene sequence; the average sequence length was estimated to be 43 for Figure 2D and 65 for Figure 2E. The molecular weight distribution of the long sequence peak expressed by M_w/M_n was found to be 1.6–1.7 for each. In these chromatograms, the products from the sequences of the 1,2 and 1,4 units ($m = 1, 2, 3$, etc. and $n = 0$ in I) were not detected due to their low absorptivity for the UV detector observed at 254 nm.

These findings clearly show that at the initial stage of polymerization, the styrene units predominantly exist as isolated sequences. The dyad and triad sequences of the styrene unit increased with increasing conversion up to 75%. At the final stage of polymerization, long styrene block sequences were formed in addition to the styrene 1–3

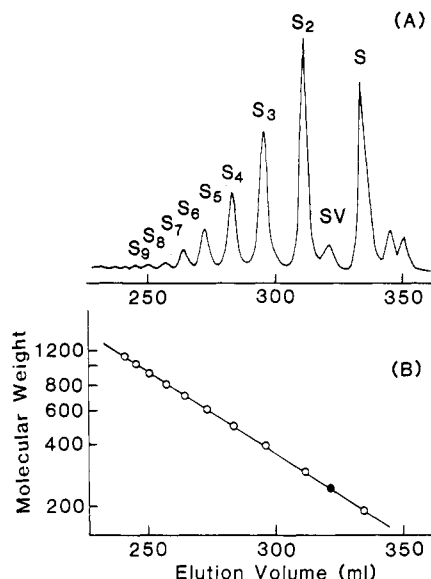


Figure 3. High-resolution ozonolysis-GPC curve for SBR initiated with benzoyl peroxide (A) and GPC calibration (B); solid circle corresponds to the SV sequence.

sequences. The number-average sequence length of the block styrene sequences increased from 43 to 65 with increasing conversion from 89.3% to 100%, whereas the distribution of short styrene sequences remained unaltered. This demonstrates that partial block copolymers are synthesized after the consumption of butadiene as expected from the composition-conversion relationship. The number-average length of the observed block styrene sequences was about 1.6 times that expected from the ratio of initial butyllithium and residual styrene. This can be attributed to the termination reaction due to small amounts of impurities such as water or oxygen and the transmetalation to toluene.

Determination of Sequence Distribution. As a model copolymer, SBR prepared with benzoyl peroxide as an initiator was analyzed by the ozonolysis-GPC method using high-resolution GPC columns as shown in Figure 3. By ¹H NMR and ¹³C NMR measurements of the collected fractions, the peaks at 333, 320, 310, and 295 mL were assigned to the products derived from the 1,4-St-1,4, 1,4-1,2-St-1,4, 1,4-(St)₂-1,4, and 1,4-(St)₃-1,4 sequences, respectively, which are represented by S, SV, S₂, and S₃. SV was observed as an isolated peak in this high-resolution measurement. A plot of log MW vs. elution volume gave a straight line for S to S₁₀. It is remarkable that SV lies on the same line as that determined from the products of the styrene sequences. This indicates that the alcohol side chain derived from the 1,2-butadiene unit has a molecular weight corresponding to its molecular weight.

Figure 4 shows the high-resolution GPC curves of the ozonolysis products of SBR at conversions of 75.6% and 89.3%. The peaks were tentatively assigned by using the relationship shown in Figure 3. In Figure 4B it is remarkable that the peaks due to the short styrene sequences overlap with that of the block styrene sequences. This is to say, a small amount of residual butadiene copolymerizes into the styrene block chains to make styrene sequences of $n = 4-9$ and above at this stage of polymerization. After the complete consumption of butadiene, it is expected to form the block styrene sequences at the terminal. This was confirmed by the fact that the peak due to the long styrene sequences reduced the extent of overlap with the short styrene sequences with increasing conversion from 89.3% to 100%. The rather wide molecular weight distribution in the long styrene sequence peak (see Figures

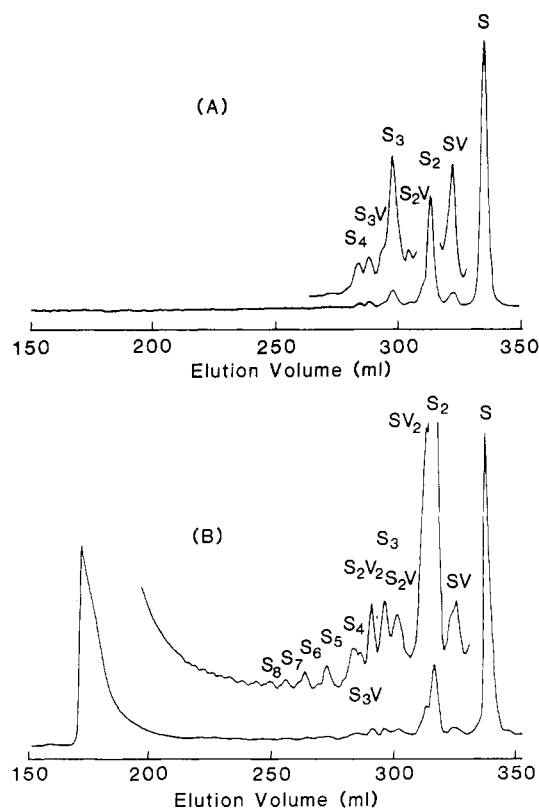


Figure 4. High-resolution ozonolysis-GPC curves for the copolymer sample at 75.6% conversion (styrene, 6.9%; 1,2, 10.8%; 1,4, 82.3%) (A) and the copolymer sample at 89.3% conversion (styrene, 13.0%; 1,2, 11.2%; 1,4, 75.8%) (B).

2D,E) can also be interpreted by the presence of small amounts of isolated 1,4 unit distributed along the chain.

In Figure 4B it is also noteworthy that each of the peaks derived from styrene sequences of $n = 4-9$ and above is accompanied by a small shoulder peak, which corresponds to the elution volume of S₄V to S₉V and above. On the other hand, in Figure 3A only the SV peak is observed as the sequence containing the 1,2 unit. This may be due to the fact that the content of the 1,2 unit in this copolymer initiated with benzoyl peroxide is only 1/4 that of the styrene unit, whereas for the sample in Figure 4B the 1,2/styrene ratio is close to unity. These facts imply that the formation of the 1,2-styrene linkage is appreciably lower than the value expected from a Bernoullian or random propagation process. Here, SV is expected to be composed of the isomers SV and VS, i.e., HO(CH₂)₃CH(Ph)CH₂CH(CH₂OH)(CH₂)₂OH and HO(CH₂)₃CH(CH₂OH)CH₂CH(Ph)(CH₂)₂OH, derived from the sequences formed by the addition of the 1,2 unit to living styryl anion and addition of the styrene unit to living 1,2-butadiene anion, respectively. The probability of the addition of the styrene, 1,4, and 1,2 units can be determined by the analysis of these styrene-1,2 sequences. The separation of SV and VS and the quantitative treatment of the addition of the 1,2 units will be presented in a subsequent paper.

In order to carry out a quantitative analysis, the extinction coefficients at 254 nm were determined for styrene oligomer models as shown in Table I. The extinction coefficient per styrene unit showed practically the same value for the models corresponding to S to S₆. This finding indicates the integrated intensity of the GPC peaks can be used to analyze the sequence distribution of styrene units.

From the conversion and copolymer composition relationship, the monomer reactivity ratios were calculated for

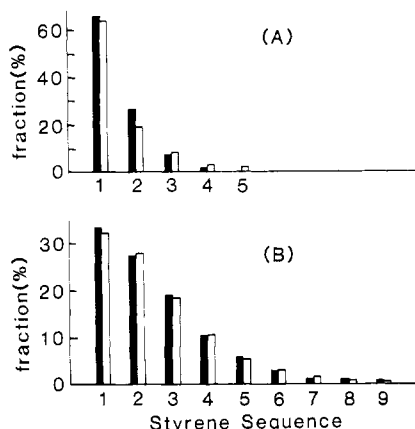
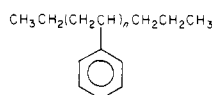


Figure 5. Sequence distribution of styrene units in the copolymer sample at 75.6% conversion (A) and the copolymer initiated with benzoyl peroxide (styrene, 42.6%; 1,2, 11.2%; 1,4, 46.2%) (B).

Table I
Extinction Coefficients for Styrene Oligomers

<i>n</i>	<i>E</i> ₂₅₄ ^a (mol/L)/cm	<i>E</i> / <i>n</i>
1	242	242
2	570	285
3	811	270
4	975	244
5	1391	278
6	1471	245
av		261

^a Extinction coefficient at 254 nm for styrene oligomers:



copolymers initiated with *n*-butyllithium using the integrated equation of Mayo and Lewis.⁶ The values of $r_{\text{St}} = 0.16$ and $r_{\text{Bd}} = 13$ are consistent with those of Spirin et al.⁵ showing $r_{\text{St}} = 0.1$ and $r_{\text{Bd}} = 12.5$ for the copolymerization

in toluene with ethyllithium. Monomer reactivity ratios of $r_{\text{St}} = 0.94$ and $r_{\text{Bd}} = 1.2$ were determined for the copolymers initiated with benzoyl peroxide using the Fineman-Ross equation. The sequence distribution of the styrene unit calculated from the copolymerization parameters was compared with that determined by the ozonolysis-GPC measurement as shown in Figure 5. Here, both 1,4-(St)_{*n*}-1,4 and 1,4-1,2-(St)_{*n*}-1,4 sequences are counted as the (St)_{*n*} sequence. The observed sequence distribution for the radical copolymer at low conversion showed fairly good agreement with that calculated from monomer reactivity ratios. On the other hand, a small difference was observed between the observed and calculated distributions for the copolymer initiated with *n*-butyllithium and terminated at 75.6% conversion. This may be due to the error inherent in the determination of monomer reactivity ratios by the integrated equation; good agreement is obtained by the assumption of $r_{\text{Bd}} = 13$ and $r_{\text{St}} = 0.18$. These facts demonstrate the validity of our ozonolysis-GPC method to characterize the sequence distribution of styrene units in SBR.

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Registry No. Butadiene-styrene copolymer, 9003-55-8.

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Some Remarks on the Transport Theory for Wormlike Cylinder Models

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ABSTRACT: It is pointed out that whenever the Yamakawa-Fujii transport theory for wormlike cylinders fails to consistently explain experimental data, the diameter of the cylinder estimated from the intrinsic viscosity is definitely smaller than that from the sedimentation coefficient. Examination of various possible sources of this disagreement leads to the conclusion that the most probable one is the replacement of a rough surface of a real macromolecular chain by the smooth cylinder surface. Then the breakdown of the stick boundary condition that may occur on the rough surface has no significant effect on the result.

Introduction

During the past decade, there have been a number of experimental investigations of steady-state transport coefficients of stiff-chain macromolecules in dilute solution. Most of them have aimed to determine the model parameters by the use of the theoretical expressions that we derived by an application of the Oseen-Burgers (OB) procedure of classical hydrodynamics to wormlike (or helical wormlike) cylinder models.¹⁻⁴ On the whole, it appears that there is rather good agreement between

theory and experiment, considering the approximations used in the theoretical derivation. However, disagreement beyond experimental uncertainty has been observed for several cases.⁵⁻⁷ Then, in the language of experimentalists, the diameter of the cylinder estimated from, for instance, the sedimentation coefficient is inconsistent with that from the intrinsic viscosity; the diameter estimated from crystallographic data agrees with the former for some cases and with the latter for others. As a result of reexamination of these results, we have found that the diameter from the