Structure–Physical Property Relationships in Peroxide-Cured Butadiene–Styrene Copolymers

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Synopsis

Structure–physical property relationships in high-vinyl butadiene–styrene copolymers have been determined for samples cured with dicumyl peroxide under the same conditions. Three different structures, butadiene–styrene–butadiene (B–S–B) triblocks, butadiene–styrene (B–S) diblocks, and random butadiene–styrene copolymers, have been examined. Flexural modulus increases with increasing styrene content owing to the inherent stiffness of a polystyrene backbone. Swelling increases whereas hardness and heat distortion temperature decrease with increasing styrene content. This behavior is explained by the decrease in crosslink density with increasing styrene content in all structures. Heat distortion temperatures of the B–S–B and B–S networks are superior to the heat distortion properties of the random structures. The B–S–B structure is the most solvent resistant, followed by the random copolymers, with the B–S structures swelling to the greatest extent. Swelling differences between the B–S–B and random networks decrease with increasing styrene content, while swelling differences between the B–S–B and B–S networks increase with increasing styrene content. These results are explained by the nature of the crosslinking reaction and the number of loose ends present in each network.

INTRODUCTION

Much work has been done on structure–physical property relationships of anionically prepared butadiene–styrene copolymers.[1–3] The majority of this work deals with block polymers in which about 90% of the butadiene repeat units have a 1,4-microstructure. The S–B–S triblocks, where S represents a polystyrene block and B represents a polybutadiene block, show behavior similar to that of crosslinked rubbers, even though they themselves are uncured.[4]

Some studies have been done on highly cured styrene–butadiene copolymers in which 50% or more of the butadiene repeat units have a 1,2-microstructure.[5–7] These materials are crosslinked with peroxide catalyst to obtain hard thermosetting resins. The crosslinking reaction is of very high efficiency, presumably because it occurs via a chain polymerization type mechanism in which several double bonds are consumed by each peroxide molecule.[8]

The present study is concerned with various structures of butadiene–styrene copolymers in which the butadiene portion has a high proportion

($\geq 85\%$) of 1,2-units. Specifically, B–S–B triblock, B–S diblock, and random butadiene–styrene copolymers were synthesized. These copolymers were then cured under the same conditions with dicumyl peroxide to obtain highly crosslinked network structures. Physical property measurements, including swelling, were made on the cured resins. The effects of polymer structure and composition on the physical properties of the resins were then investigated.

EXPERIMENTAL

Reagents

Styrene was purified by successive washings with 10% sodium hydroxide and water. After being dried (sodium sulfate), it was fractionally distilled under nitrogen in the presence of calcium hydride. Butadiene was treated with a sodium–fluorene mixture (molar ratio 0.022 sodium, 0.066 fluorene, and 6.5 butadiene) in 28-oz bottles and was flash distilled as needed.

Tetrahydrofuran (THF) and benzene were purified by distillation in the presence of sodium metal. Biphenyl was purified by recrystallization from methanol. Dicumyl peroxide (98% active) was obtained from Hercules Incorporated and was used without further purification.

A mixture of lithium (3.12 g, 0.45 mole) and biphenyl (75 g, 0.49 mole) was stirred in 500 ml purified THF under nitrogen at 5°C overnight. The resulting initiator complex was stored at -30°C and used as needed. Solutions of butyllithium and *tert*-butyllithium in hexane were obtained from Lithium Corporation of America and used without further purification. Analysis of all initiators was accomplished using the Gilman[9,10] double titration procedure.

Polymerization

All polymerizations were run at -25°C in THF (100 parts monomer/600 cc THF). B–S–B triblock polymers were prepared by polymerizing styrene with the desired amount of lithium biphenyl followed by addition of butadiene to the polystyryl dianion. B–S diblock polymers were prepared by polymerizing butadiene with *tert*-butyllithium followed by addition of styrene to the polybutadienyl monoanion. Random butadiene–styrene copolymers were prepared by adding the desired amount of butyllithium to a solution of styrene and butadiene in THF. Polymers were recovered by precipitation with methanol and were dried in a vacuum oven at 25°C overnight.

Compounding and Molding

All copolymers were dissolved in benzene containing two parts of dicumyl peroxide per hundred parts of copolymer. Benzene was removed under vacuum, and the dried resins were molded at 145°C for 4 hr (13 half-lives for dicumyl peroxide).[11]

Physical Property Measurements

Flexural modulus and strength were measured according to ASTM method D-790. Impact resistance was measured by the ASTM Izod notch method D-256 (method A) and Rockwell hardness according to ASTM method D-785 (procedure A). Heat distortion temperatures were determined by ASTM method D-648 at 264 psi stress loading.

Discs measuring $1^1/_4$ in. in diameter and $^1/_{64}$ in. thick were used for all swelling measurements. The discs were immersed in toluene treated with phenyl-beta-naphthylamine (PBNA) (2 g/1000 ml) and were swollen overnight (16 hr) at 75°C. After weighing, the discs were placed in an oven and dried at 120°C and 0.1 mm Hg.

In order to ensure swelling equilibrium, many samples were swollen for several days at 75°C. These, however, were swollen to the same extent as corresponding samples that were allowed to swell for only 16 hr.

Polymer Characterization

NMR spectra were measured at 60 MHz for all copolymers in CCl_4 at room temperature to investigate copolymer composition and microstructure of the butadiene segments. Peak areas of signals for aromatic protons as well as for terminal and nonterminal olefinic protons were determined and analyzed according to the method of Senn.[12]

GPC measurements were made with a Waters Model 200 GPC unit. Intrinsic viscosities were measured in toluene at 25°C.

RESULTS AND DISCUSSION

Polymer Characterization

The compositions, microstructures, and molecular weights of the copolymers examined are presented in Tables I, II, and III. The values reported for found block styrene were obtained by NMR measurements according to the method of Mochel and Johnson.[13] This method considers block styrene as average sequence lengths of ≥ 4. All the styrene in the B–S–B

TABLE I
Characterization of B–S–B Block Polymers[a]

Sample no.	Styrene in copolymer, wt-%	Block styrene, wt-% found	1,2-Content of butadiene segments, wt-%	$[\eta]$, dl/g	$\bar{M}$, (g/mole) $\times$ 10^{-4}
1	25.3	25.3	92	0.286	2.86
2	30.1	30.1	93	0.376	3.48
3	50.2	48.4	88	0.215	2.38
4	52.1	52.1	93	0.262	2.86
5	75.8	75.8	94	0.240	2.86

[a] $[\eta]$ = Intrinsic viscosity. Molecular weight ($\bar{M}$) determined by GPC.

TABLE II
Characterization of B–S Block Polymers

Sample no.	Styrene in copolymer, wt-%	Block styrene, wt-% found	1,2-Content of butadiene segments, wt-%	$[\eta]$, dl/g	$\bar{M}$, (g/mole) $\times$ 10^{-4}
6	25.2	25.1	86	0.343	2.86
7	30.3	26.8	86	0.418	3.90
8	49.6	44.6	96	0.340	3.26
9	50.0	49.7	85	0.641	5.65
10	67.1	67.1	90	0.408	4.70
11	75.6	72.6	90	0.308	3.48

TABLE III
Characterization of Random Butadiene–Styrene Copolymers

Sample no.	Styrene in copolymer, wt-%	Block styrene, wt-% Calcd	Block styrene, wt-% Found	1,2-Content of butadiene segments, wt-%	$[\eta]$, dl/g	$\bar{M}$, (g/mole) $\times$ 10^{-4}
12	27.3	0	0	92	0.418	3.26
13	30.6	0	0	85	0.488	4.15
14	48.2	6	24.1	97	0.334	3.26
15	52.1	6	27.9	83	0.322	2.69
16	71.1	27	48.8	91	0.390	3.65
17	74.2	36	54.0	93	0.293	2.69

triblock and in the B–S diblock polymers is essentially in block form. The values reported for calculated block styrene for the random structures in Table III are values representative of a "perfectly random copolymer."[14] Wall[15] has defined a "perfectly random copolymer" as one whose monomer reactivity ratios are $r_1 = r_2 = 1$. The experimental values for block styrene of these copolymers are somewhat higher than those calculated for "perfectly random copolymers," particularly at moderate to high styrene levels. A comparison of the total styrene content with the block styrene values, however, indicates that our random structures have considerably less block styrene than corresponding block polymers.

The values in the last column ($\bar{M}$) in Tables I, II, and III represent square roots of the $\bar{M}_w \cdot \bar{M}_n$ products, i.e. $\bar{M} = \sqrt{\bar{M}_n \cdot \bar{M}_w}$. $\bar{M}_n$ and $\bar{M}_w$ are in turn determined from standard GPC calibration curves relating molecular weights to elution volume (counts).

GPC measurements were used to determine not only polymer molecular weight but also blocking efficiency in the block polymers. Figures 1 and 2 are typical GPC traces of the B–S–B triblock and B–S diblock polymers. There was no evidence of even small amounts of unblocked homopolymer in either case.
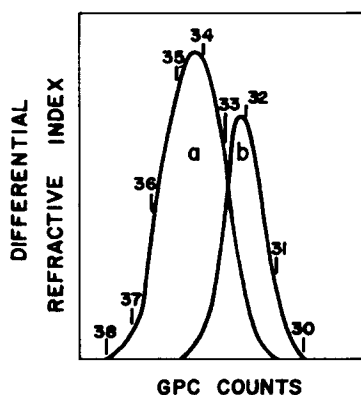
Fig. 1. Gel permeation chromatographs of (a) polystyrene center block and (b) B–S–B triblock polymer by two-stage lithium biphenyl polymerization.
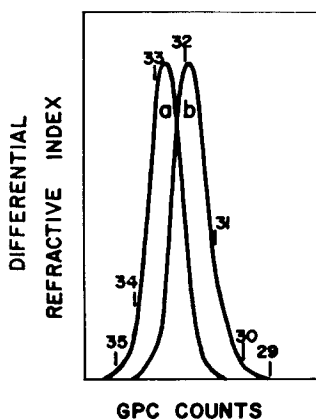

Fig. 2. Gel permeation chromatographs of (a) polybutadiene block and (b) B–S diblock polymer by two-stage alkyllithium polymerization.

Polymer Evaluation

Physical properties of the copolymers described in Tables I, II, and III are listed in Tables IV, V, and VI. These were obtained from samples cured with dicumyl peroxide for 4 hr at 145°C. The values reported as equilibrium swelling Q are equal to the weight of solvent at swelling equilibrium divided by the weight of dried polymer.

Certain general physical property behavior patterns have been followed by these cured copolymers, regardless of polymer structure. Flexural modulus increases with increasing styrene content due to the inherent stiffness of a polystyrene backbone. Swelling increases whereas hardness and heat distortion temperature decrease with increasing styrene content. This is best explained by the decrease in crosslink density of the cured samples with increasing styrene content.

TABLE IV

Physical Properties of Cured B–S–B Block Polymers

Sample no.	Flexural modulus, psi $\times 10^{-5}$	Rockwell hardness, E scale	Heat distortion temp. at 264 psi, °C	Equilibrium swelling Q
1	3.69	84	210	0.185
2	3.52	79	185	0.193
3	4.05	57	92	0.275
4	4.17	60	93	0.327
5	4.24	37	87	0.638

TABLE V

Physical Properties of Cured B–S Block Polymers

Sample no.	Flexural modulus, psi $\times 10^{-5}$	Rockwell hardness, E scale	Heat distortion temp. at 264 psi, °C	Equilibrium swelling Q
6	3.26	91	230	0.207
7	3.40	80	—	0.208
8	3.93	57	80	0.620
9	4.14	60	94	0.590
10	3.44	40	91	1.490
11	4.18	37	87	3.275

TABLE VI

Physical Properties of Cured Random Butadiene–Styrene Copolymers

Sample no.	Flexural modulus, psi $\times 10^{-5}$	Rockwell hardness, E scale	Heat distortion temp. at 264 psi, °C	Equilibrium swelling Q
12	3.16	73	98	0.245
13	3.77	65	90	0.258
14	3.89	54	74	0.340
15	4.19	44	76	0.389
16	4.12	27	66	0.650
17	4.82	21	69	0.737

Flexural modulus does not seem to vary much with polymer structure. Hardness remains constant when changing from the B–S–B to B–S structure, but hardness values for the random copolymers cured under the same conditions are lower than for corresponding B–S or B–S–B structures. This behavior can be explained by considering the nature of the crosslinking reaction in the butadiene portion of these copolymers. It has been shown that the crosslinking reaction of high-vinyl polybutadiene with dicumyl peroxide is a free-radical chain polymerization reaction through the vinyl double bonds.[8,16] It was further shown that by lowering the 1,2-content of polybutadiene, the rate of cure is reduced.[16] Although this reduction in rate of cure with decreasing 1,2-content is partially due to the difference in reactivities of vinyl and internal double bonds, the primary

reason for this rate reduction was attributed to the increase in number of allylic protons available for transfer.[16]

Since benzylic and allylic radicals have about the same stability, it is necessary that we consider benzylic hydrogen sites as possible cure retardants in our copolymers. In the B–S and B–S–B block polymers, the styrene blocks are well segregated from the butadiene segments owing to their incompatibility. This means that the crosslinking reaction in the polybutadiene phase can occur without much interference from transfer reactions to polystyrene benzylic hydrogens. On the other hand, the styrene units are well dispersed throughout the polymer chains in the random copolymers. This means that the crosslinking reaction will probably be interrupted more frequently by transfer reactions to benzylic hydrogens than in either the B–S or B–S–B cases. Support to this reasoning is given by Hergenrother[16] who was able to double the termination rate of the curing reaction of high-vinyl polybutadiene with dicumyl peroxide by adding one part of xylene to 100 parts resin. Those polybutadienes containing xylene were found to have a lower crosslink density than corresponding xylene-free polybutadienes cured under the same conditions. In view of this, one would expect a network of lower crosslink density from the random copolymer structure than from either the B–S or B–S–B structures if all are cured under the same conditions. Hardness values show this to be the case.

Heat distortion values follow the same pattern as hardness and can also be interpreted in terms of crosslink density. Both B–S–B triblock and B–S diblock polymers have high heat distortion temperatures at low styrene levels ($\leq 30\%$), but heat distortion temperatures fall rapidly at moderate to high styrene levels. The random structure has low heat distortion temperatures at all styrene levels. This, too, reveals a lower crosslink density for the random copolymers than for corresponding B–S or B–S–B structures cured under the same conditions.

Although impact resistance and flexural strength were also measured on the cured samples, very little variation of these properties with polymer structure was noted within the precision of these measurements.

Swelling Behavior vs. Polymer Structure

Figure 3 illustrates the swelling behavior of all three copolymer structures. The B–S–B triblock polymers swell less than the random structures, which in turn swell less than the B–S diblock structures.

Two factors having major influences on the swelling behavior of these materials are network crosslink density and the number of loose ends present in the final network. There are two ways in which a loose or dangling end affects the degree of swelling. First, it has a more favorable entropy condition associated with it than a chain tied down at both ends. This allows the loose end to interact with solvent to a greater degree than is possible for a chain bound at both ends. The result is a greater contribution to the degree of swelling of a network from a loose end than from a
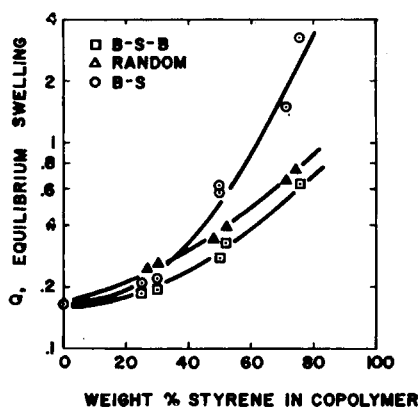
Fig. 3. Equilibrium swelling vs. styrene content in copolymers: (□) B–S–B; (△)random; (○) B–S.

bound chain. A second consideration is the chain length of the loose end. If we visualize the loose end as forming a random coil when interacting with solvent, the amount of swelling that occurs will be proportional to the coil size. Therefore, one would not really expect much of a contribution to the swelling of a network from a loose end made up of only a few mono-mer units. Thus, both the favorable entropy factor as well as the length of the loose chain end are important when considering the amount of addi-tional swelling obtained from a loose end compared with a chain bound into the network at both ends.

The swelling behavior exhibited by the cured structures examined in this study is not unexpected on the basis of the considerations presented above. The B–S–B block polymers have no loose ends. In addition, the bound styrene is 100% blocked in these materials. Thus, chain transfer
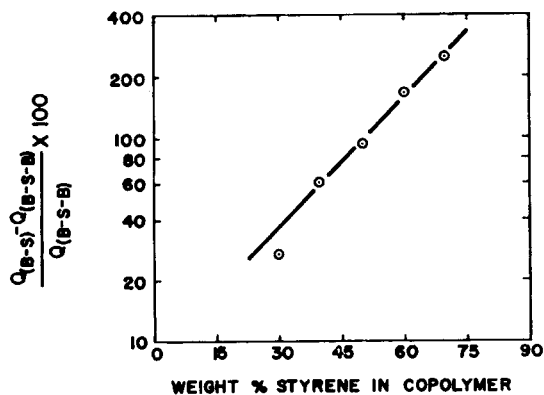

Fig. 4. Equilibrium swelling differences between B–S and B–S–B block polymers vs. styrene content in copolymers.

reactions to the benzylic hydrogens of the polystyrene segments during cure would be at a minimum. Both of these conditions lead to low swelling. This has been observed. The random copolymers, on the other hand, have lower crosslink densities than corresponding B–S–B structures when cured under the same conditions because of reasons discussed earlier. They therefore swell to greater extents than the B–S–B structures. The B–S diblock polymers contain styrene segments unbound at one end. This, of course, is a condition leading to high swelling. Figure 4 shows that although at low styrene levels the B–S copolymers do not swell much more than the B–S–B structures, there are dramatic differences among the swelling characteristics of the samples having moderate to high styrene contents. This is simply a function of the length of the styrene segments in these B–S structures. At low styrene levels, the polystyrene blocks are relatively short. This explains the low degree of swelling at these styrene
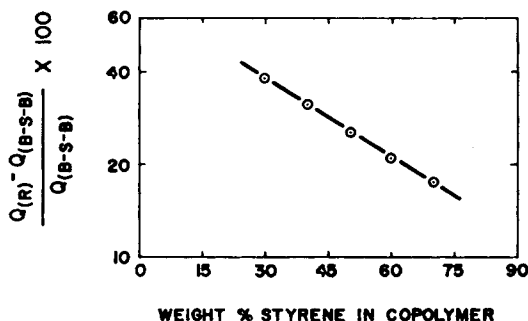

Fig. 5. Equilibrium swelling differences between random and B–S–B copolymers vs. styrene content in copolymers.

levels in spite of the fact that many loose ends are present in the polymer network. At moderate to high styrene levels, the length of these styrene blocks increases. A marked increase in swelling is then noted.

Finally, Figure 5 illustrates the swelling differences between the random and the B–S–B structures. These differences are seen to decrease with increasing styrene content. As styrene content increases, the amount of block styrene contained in these random structures also increases (Table 1). However, the randomized styrene (≤ 3 monomer units) in these structures is seen to remain reasonably constant with increasing styrene content. Thus, the retardation of cure which occurs because of benzylic hydrogen placements is more dependent on completely randomized styrene units (≤ 3 monomer units) than on block styrene units (≥ 4 monomer units). It would be interesting to compare the swelling behavior of cured random butadiene–styrene copolymers and cured B–S–B triblock polymers having the same crosslink densities. From the data illustrated in Figure 5, one would predict a higher degree of swelling for the B–S–B network than for corresponding random copolymer networks, at least at moderate to high styrene levels.

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