

Epoxidation of Styrene-Butadiene Block Polymers. II

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Synopsis

Epoxidation of styrene-butadiene block polymers considerably improves their resistance to hydrocarbon oils. Use of peroxyformic acid generated *in situ* appears to be simple and practical. Although no problems exist when the reactions are carried out in toluene, polymer molecular weight and reactant stoichiometry are important in determining the properties of polymers epoxidized in cyclohexane. In fact, epoxidations in cyclohexane of linear and tapered block polymers of molecular weights in excess of 60,000 with peroxyformic acid invariably lead to gelation. Replacing half or more of formic acid with acetic acid, however, alleviates the problem without adversely affecting the tensile or oil resistance of the resulting polymers. This recipe has also been successfully applied to the epoxidation of divinylbenzene-coupled styrene-butadiene radial block polymers.

INTRODUCTION

Epoxidation of a styrene-butadiene block polymer to obtain improved resistance to hydrocarbon oils and certain chemicals has been described in detail in an earlier publication.¹ The work reported therein was restricted to a linear polymer with a number-average molecular weight of about 60,000 and a styrene content of 40%. Reactions were carried out in toluene and in cyclohexane using peroxyformic acid generated *in situ*. No attempts were made, however, to look into the interrelationship between the polymer composition, its molecular weight, the solvent, and the recipe used for epoxidations. This report describes the work done in such a study.

EXPERIMENTAL

Materials. Hydrogen peroxide (30%), toluene, cyclohexane, formic acid, and isopropyl alcohol were obtained from the same sources as mentioned earlier.¹ Glacial acetic acid, propionic acid, and acetonitrile were received from Malinkrodt Chemicals. Sodium formaldehyde sulfoxylate, dinitrochlorobenzene, and hydroquinone were from Eastman. Ferrous sulfate was obtained from Fisher Scientific and divinylbenzene was procured from Chemsamp Co.

Polymer Preparation. Linear, tapered, and divinylbenzene-coupled radial styrene-butadiene block polymers were prepared following the procedures described elsewhere.¹⁻³ Whereas the linear and radial block polymers were prepared by incremental addition of monomers, the tapered block polymers were prepared by initially forming a polystyrene block and then copolymerizing a mixture of butadiene and styrene onto it. When butadiene and styrene are copolymerized in a hydrocarbon solvent, kinetics favor butadiene to polymerize first with only occasional incorporation of styrene units. As the butadiene content in the system depletes, styrene units get incorporated more and more to eventually form styrene block at the end.^{4,5} This results in a polymer with tapered composition and hence the name.

Epoxidation. Polymers were epoxidized in various solvents by the procedure described earlier.¹ Two recipes, marked as "100" and "125" (Table I) were employed in this study. Recipe 100 contains 0.5 mole each of formic acid and hydrogen peroxide, whereas recipe 125 contains 25% excess of each of the two reagents to compensate for the generally lower oxygen contents obtained in cyclohexane with recipe 100.¹

Analysis of Products. The oxirane and oxygen contents of the epoxidized polymers were determined by the methods referred to earlier.¹ Molecular weights and molecular weight distributions were obtained with a Waters gel permeation chromatograph Model 200, equipped with four Styragel columns ranging in pore sizes from 10^4 to 10^7 Å. Polymer solutions of 0.05% (w/v) concentration in tetrahydrofuran were used for this purpose.

Inherent viscosities of the polymer were determined in toluene at 25°C. Gel fractions reported are the insolubles recovered from the toluene solutions used for inherent viscosity measurements. The compositions and the molecular weights of polymers before and after epoxidation are given in the ensuing tables.

RESULTS AND DISCUSSION

In order to study the interrelationship between the polymer composition, its molecular weight, the epoxidation solvent, and the recipe, styrene-butadiene linear and tapered block polymers ranging in molecular weights from 45,000 to about 160,000 were epoxidized in various solvents using recipes 100 and 125. Polymers so generated varied from those completely soluble in toluene to some containing high gel contents, as can be seen from the details below.

Epoxidation in Toluene

Linear and tapered block polymers epoxidized in toluene are described in Tables II and III, respectively. Those of molecular weights as high as 160,000 can be epoxidized without encountering any gelation problems although there was some evidence to the formation of small amounts of higher molecular weight fractions, as can be seen, for example, in Figure 1. The above epoxidized polymers were all soluble in toluene. The higher molecular weight parent polymers do not have any melt flow at 180°C (5 kg) and as such are not very useful. They were epoxidized to find out if any gelation problem exists at that molecular weight level. Results proved to the contrary.

TABLE I
Epoxidation Recipes

	Parts	
	"100"	"125"
Polymer	100	100
Cyclohexane (Toluene)	780(860)	780(860)
Formic Acid, 88%	26	32.5
Hydrogen peroxide, 30%	56	70
Temperature, °C	70	70
Time, hr	2	2

TABLE II
Epoxidation of Styrene-Butadiene-Styrene (20-60-20) Linear Block Polymers in Toluene

Recipe	\bar{M}_w	\bar{M}_n	Inh. viscosity	Gel, %
—	85,000	74,000	0.79	0
100	109,000	94,000	0.75	0
125	123,000	99,000	0.80	0
—	102,000	90,000	0.90	0
100	146,000	120,000	0.85	0
125	222,000	162,000	0.81	0
—	163,000	143,000 ^a	1.20	0
100	242,000	189,000 ^a	1.11	0
—	189,000	164,000 ^a	1.11	0
100	256,000	198,000 ^a	1.20	0

^a Melt flow at 180°C, 5 kg, is zero.

TABLE III
Epoxidation of Styrene-Butadiene (49/51) Tapered (S-B/S-S) Block Polymers in Toluene

Recipe	\bar{M}_w	\bar{M}_n	Inh. viscosity	Gel, %
—	58,000	51,000	0.53	0
100	63,000	53,000	0.58	0
125	83,000	69,000	0.48	0
—	71,000	60,000	0.63	0
100	93,000	77,000	0.57	0
125	116,000	89,000	0.56	0
—	136,000	118,000 ^a	1.00	0
100	202,000	161,000 ^a	0.91	0
—	195,000	166,000 ^a	1.16	0
100	436,000	284,000 ^a	1.20	0

^a Melt flow at 180°C, 5 kg, is zero.

Epoxidation in Cyclohexane

Attempts were then made to repeat the above epoxidations in cyclohexane. The results, however, were quite different. The polymer molecular weight and the epoxidation recipe had a considerable effect on the properties of the resulting polymers. Such effects were more pronounced in the case of tapered block polymers than linear polymers, as can be seen from Tables IV and V.

Whereas a linear block polymer of \bar{M}_n 61,000 can be epoxidized in cyclohexane with recipe 100 to a product exhibiting monomodal distribution in GPC analysis, recipe 125 generates a rubber that exhibits a bimodal distribution. When \bar{M}_n is increased to 76,000, the recipe 100 causes the molecular weight to double and the recipe 125 leads to a polymer with 90% gel content. Increasing the parent molecular weight to 90,000 produces more gelation problems. (Table IV).

In the epoxidation of tapered block polymers (Table V), however, gelation seems to appear at lower molecular weights compared to linear triblocks. Whereas a tapered block polymer of \bar{M}_n 45,000 can be epoxidized with either recipe to polymers with monomodal distribution, one of \bar{M}_n 51,000 can be epoxidized to such a product only with recipe 100. Use of recipe 125 leads to a bimodal distribution (Fig. 2). Increasing the parent molecular weight to 60,000 leads to bimodal distribution with recipe 100 and a 89% gel content with recipe 125 (Fig. 3).

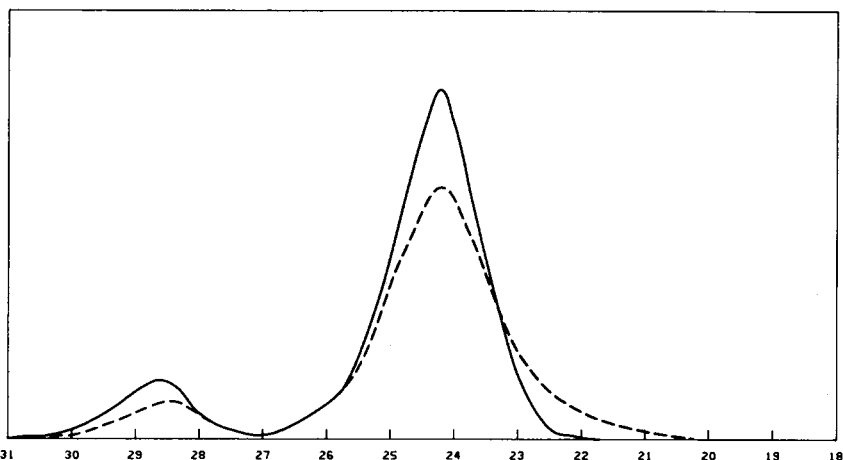


Fig. 1. Gel permeation chromatograms of styrene-butadiene (49-51) tapered block polymer (\bar{M}_w/\bar{M}_n 195,000/166,000) before (—) and after (---) epoxidation with recipe "100" in toluene.

TABLE IV
Epoxidation of Styrene-Butadiene-Styrene (20-60-20) Linear Block Polymers in Cyclohexane

Recipe	\bar{M}_w	\bar{M}_n	Inh. viscosity	Gel, %
—	71,000	61,000	0.79	0
100	84,000	65,000	0.92	0
125	Bimodal	—	1.05	0
—	85,000	74,000	0.79	0
100	238,000	148,000	1.00	0
125	—	—	—	90
—	102,000	90,000	0.90	0
100	—	—	—	26
125	—	—	—	95

TABLE V
Epoxidation of Styrene-Butadiene (49-51) Tapered (S-B/S-S) Block Polymers in Cyclohexane

Recipe	\bar{M}_w	\bar{M}_n	Inh. viscosity	Gel, %
—	52,000	45,000	0.71	0
125	73,000	61,000	0.58	0
—	58,000	51,000	0.53	0
100	70,000	58,000	0.56	0
125	Bimodal	—	0.82	0
—	71,000	60,000	0.63	0
100	Bimodal	—	0.94	0
125	—	—	—	89

Epoxidation in Mixtures of Toluene and Cyclohexane

In view of the contrasting features seen above in toluene and cyclohexane, it was decided to look into mixtures of toluene and cyclohexane as epoxidation solvent. Tapered block polymer of \bar{M}_n 60,000 was epoxidized with recipe 125 in 2:1 and 1:2 mixtures of toluene and cyclohexane and the gel permeation chromatograms of the two polymers are shown in Figure 4. The polymer

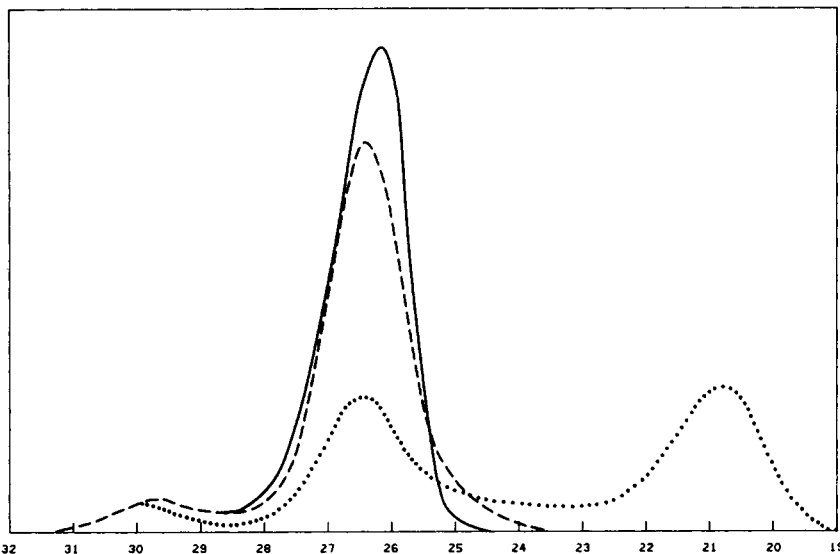


Fig. 2. Gel permeation chromatograms of styrene-butadiene (49/51) tapered block polymer ($\bar{M}_w/\bar{M}_n = 58,000/51,000$) before (—) and after epoxidation with recipe "100" (---) and recipe "125" (....) in cyclohexane.

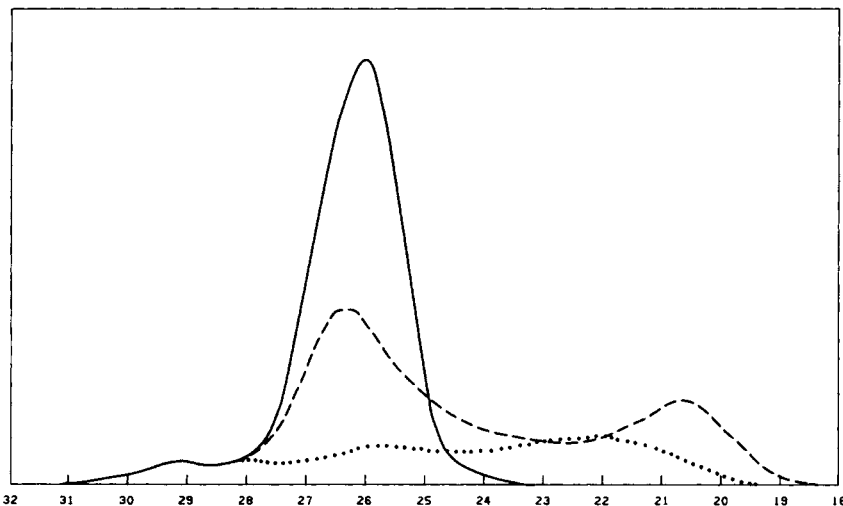


Fig. 3. Gel permeation chromatograms of styrene-butadiene (49-51) tapered block polymer ($\bar{M}_w/\bar{M}_n = 71,000/60,000$) before (—) and after epoxidation with recipe "100" (---) and recipe "125" (....) in cyclohexane.

epoxidized in 2:1 mixture of toluene/cyclohexane exhibits a monomodal distribution and resembles that epoxidized in toluene alone. On the other hand, the polymer epoxidized in 1:2 mixture of toluene/cyclohexane has a bimodal distribution such as is observed in cyclohexane alone.

Epoxidation in Mixtures of Cyclohexane and Acetonitrile

In order to study the effect of a polar solvent in admixture with cyclohexane on the properties of the resulting polymer, a tapered block polymer of \bar{M}_n 60,000 was epoxidized in a 5:2 mixture of cyclohexane/acetonitrile using recipe 100.

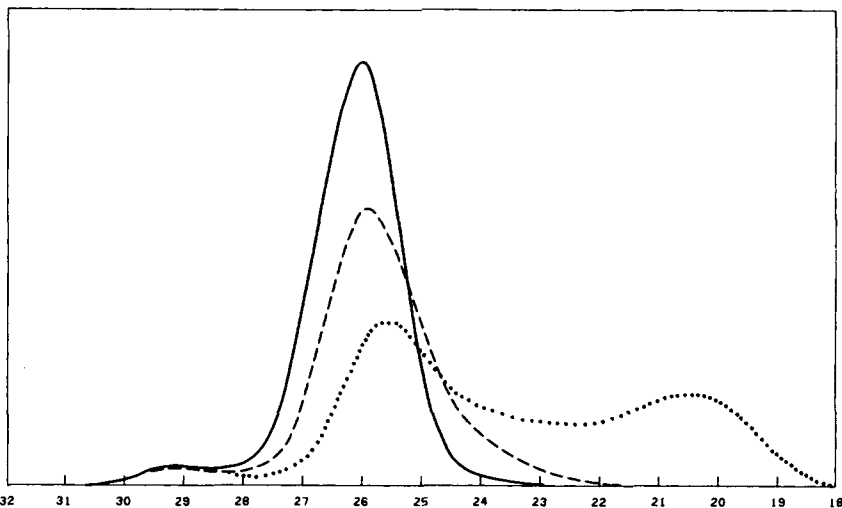


Fig. 4. Gel permeation chromatograms of styrene-butadiene (49-51) tapered block polymer ($\overline{M}_w/\overline{M}_n = 71,000/60,000$) before (—) and after epoxidation with recipe "125" in 2:1 toluene-cyclohexane (---) and 1:2 toluene-cyclohexane (.....).

Whereas the control was insoluble in toluene, the polymer epoxidized in the presence of acetonitrile was soluble. However, the total oxygen content incorporated in the polymer (3.2%) had been adversely affected. When the molecular weight of the parent was lowered to 55,000, it was possible to reduce the acetonitrile content (5:1) and yet obtain a toluene-soluble polymer. The polymer so epoxidized was very similar to the parent polymer (Fig. 5) in GPC analysis but, as in the previous instance, had a low total oxygen content (2.5%) compared to the control with 8.5%. Although the addition of acetonitrile to cyclohexane

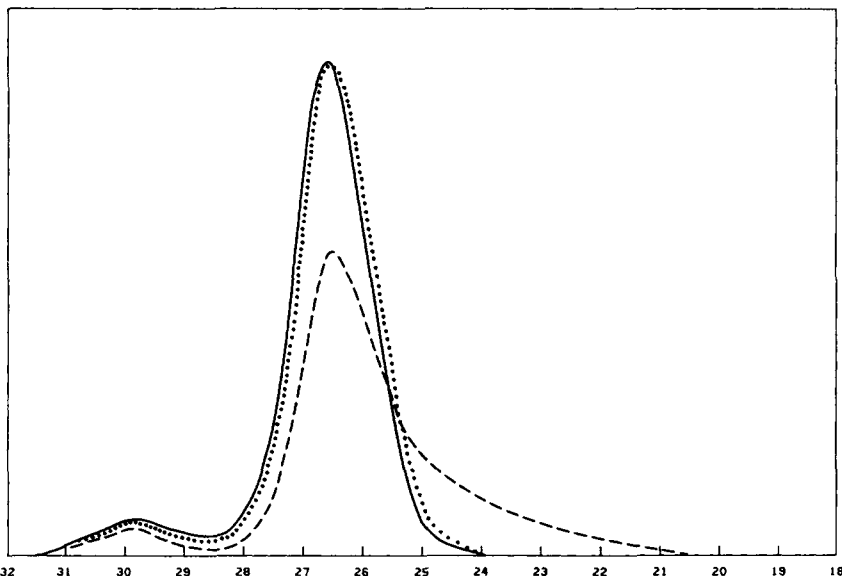


Fig. 5. Gel permeation chromatograms of styrene-butadiene (49-51) tapered block polymer ($\overline{M}_w/\overline{M}_n = 62,000/55,000$) before (—) and after epoxidation with recipe "100" in cyclohexane (---) and in 5:1 cyclohexane-acetonitrile (.....).

TABLE VI
Epoxidation of Styrene-Butadiene (49/51) Tapered (S-B/S-S) Block Polymer in Cyclohexane
with HCOOH/CH₃COOH

HCOOH/ CH ₃ COOH	\bar{M}_w	\bar{M}_n	Inh. viscosity	Gel, %	Percent	
					Epoxy	Oxygen
—	71,000	60,000	0.63	0	—	—
2:1	bimodal		1.07	0	4.6	10.4
1:2	67,000	43,000	0.63	0	3.8	7.5
1:1	90,000	65,000	0.66	0	4.5	8.7

prevents the formation of higher molecular weight fractions during epoxidation, the total oxygen incorporated in the polymers was too low to warrant any further work. The lower oxygen contents are however consistent with observations made earlier with epoxidation in other hydrogen bonding solvents.⁶

It is apparent from the above that the solvent indeed plays a critical role in determining the properties of epoxidized polymers. The problem seems to aggravate in cyclohexane as the molecular weights and the styrene contents of the polymers get higher. It is likely that the limited solubility of the epoxidized polymer in cyclohexane, particularly in the presence of water from hydrogen peroxide, causes the polymer molecules to aggregate and thereby favor undesirable intermolecular reactions such as crosslinking. Presence of acetonitrile seems to reduce such a tendency and prevent formation of higher molecular weight fractions. Assuming that the increase in molecular weight as being due to free radical crosslinking, attempts were made to run a few epoxidation experiments in the presence of inhibitors. If the assumption is correct, the same should alleviate the problem. Use of such inhibitors as dinitrochlorobenzene, hydroquinone, or sodium formaldehyde sulfoxalate/ferrous sulfate combination separately and in various proportions did not help. The resulting products contained gel fractions as before. Although these results rule out crosslinking through free radicals, the actual mechanism of gel formation is not yet fully understood. It is possible that the epoxide groups may be participating in an acid-catalyzed intermolecular coupling reaction similar to that in the formation of glycol ethers from alkylene oxides, to form higher molecular weight fractions.

TABLE VII
Epoxidation Recipe 125 Using Formic and Acetic Acids

	Parts
Polymer	100
Cyclohexane	780
88% Formic acid	16.3
Glacial acetic acid	18.8
30% Hydrogen peroxide	70
Temperature, °C	70
Time, hr	2

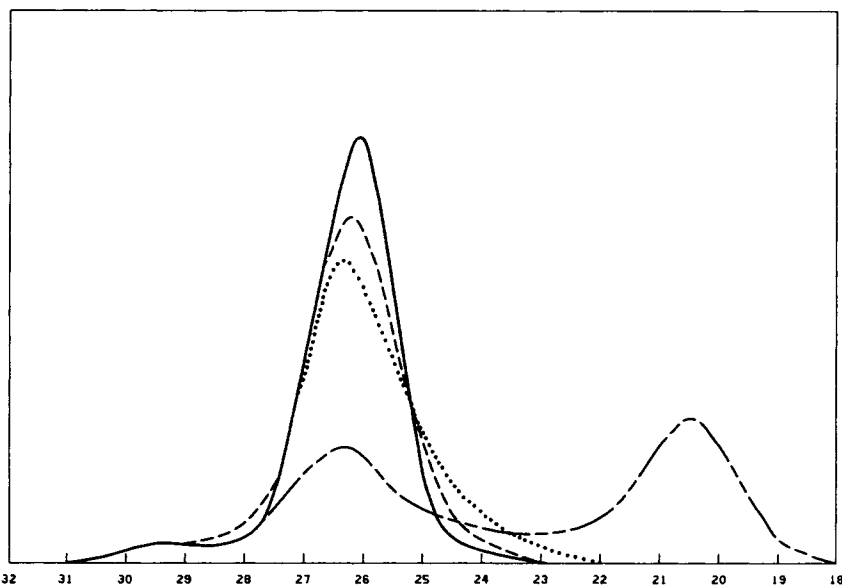


Fig. 6. Gel permeation chromatograms of styrene-butadiene (49-51) tapered block polymer ($\bar{M}_w/\bar{M}_n = 71,000/60,000$) before (—) and after epoxidation in cyclohexane with recipe "125" using 2:1 (----), 1:2 (-----), and 1:1 (....) ratios of formic and acetic acids.

TABLE VIII
Evaluation of Epoxidized Divinylbenzene-Coupled Styrene-Butadiene Block Polymers

	1	2	3	4
Styrene, %	40	40	30	30
\bar{M}_w	165,000	179,000	158,000	176,000
\bar{M}_n	118,000	127,000	116,000	127,000
Oxygen, %	—	7.8	—	8.1
Melt flow (180°C, 5 kg)	0.20	0.09	0.16	0.39
	Original			
300% Modulus, MPa	4.5	4.2	3.0	2.0
Tensile strength, MPa	26.5	31.5	25.4	25.8
Elongation, %	690	670	780	790
Shore A hardness	89	86	73	63
	Aged 7 Days in ASTM Oil #3 at Room Temperature			
Tensile strength, MPa	dissolved	18.9	Dissolved	0.5
Elongation, %	—	760	—	1150
	% Swell After 7 Days at Room Temperature			
ASTM Oil #1	11.6	1.5	26.2	3.0
#2	19.3	4.4	42.9	8.7
#3	184.2	21.6	223.6	39.7
Reference fuel A	235.8	29.0	312.1	35.4
fuel B	dissolved			

Partial Substitution of Formic Acid with Acetic Acid

Attempts were then made to substitute a part of formic acid, in recipe 125, with the relatively weaker acetic acid. Results are shown in Table VI. The oxirane and oxygen contents incorporated in the polymer are not in any way adversely affected. It is also noted (Fig. 6) that when $\frac{1}{2}$ or $\frac{2}{3}$ of formic acid is replaced by acetic acid, the epoxidized polymer exhibits a monomodal distribution with some

tailing at the high molecular weight end, but a bimodal distribution results when a third of formic acid is replaced with acetic acid. However, all three polymers were soluble in toluene. Propionic acid used with formic acid in a corresponding manner produced similar results.

In order to study the effect of molecular weight, linear and tapered block polymers in the molecular weight range of 80,000 to 115,000 were epoxidized with the recipe shown in Table VII. All the polymers were soluble in toluene and exhibited monomodal distributions (with some tailing at the high molecular weight end) in GPC analysis.

Efforts were then made to extend the recipe in Table VII to radial block polymers. Divinylbenzene coupled styrene-butadiene (40/60 and 30/70) block polymers so epoxidized were soluble in toluene and resembled the parent polymers in GPC analysis (Fig. 7). They were evaluated for their tensiles and resistance to ASTM oils. Results (Table VIII) indicate that use of acetic acid along with formic acid does not adversely affect the tensile. The resistance to ASTM oils is considerably improved over the parent polymers.

Compounding studies on epoxidized tapered block polymers show that only about 10 parts oil (Flexon 766) can be incorporated. Although incorporation of oil lowers the tensile strength from 34.2 MPa to 26.2 MPa (Table IX), there is no noticeable change in the improved oil resistance. It retains about 90% of its original tensile after swelling in ASTM oil #3 for 7 days at room temperature. Incorporation of Atomite Whiting or Whitex Clay (40 phr, Table X) gave similar results and the sample swollen in ASTM oil #3 retained about 60% of their original tensile strength.

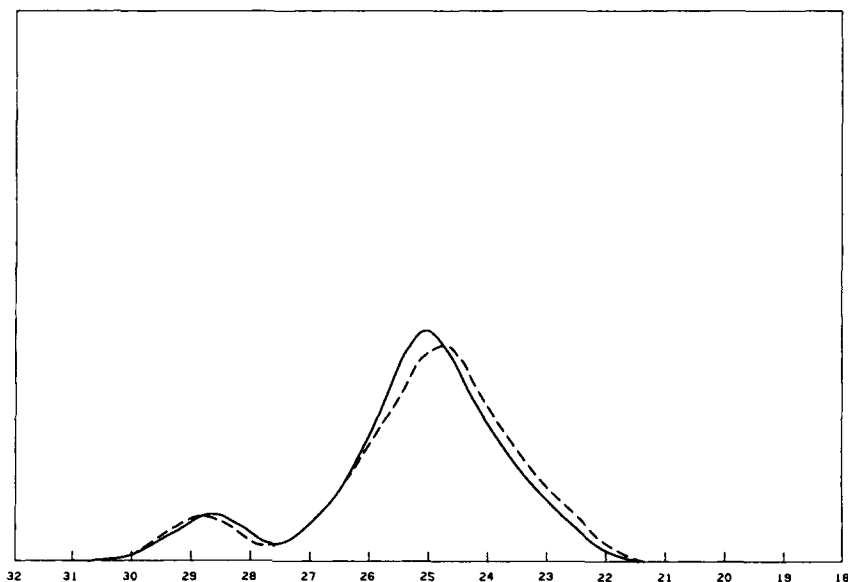


Fig. 7. Gel permeation chromatograms of divinylbenzene-coupled styrene-butadiene (40-60) radial block polymer before (—) and after (---) epoxidation in cyclohexane with recipe shown in Table VII.

TABLE IX
Evaluation of Oil Extended Epoxidized Styrene-Butadiene Tapered Block Polymer

	1	2	3	4
				Control
Epoxidized polymer ^a	100	100	—	—
Parent polymer ^b	—	—	100	100
Flexon 766	10	—	10	—
				Original
Melt flow (180°C, 5 kg)	1.7	0.66	3.1	1.6
300% Modulus, MPa	4.1	5.7	4.0	4.8
Tensile strength, MPa	26.2	34.2	27.0	28.0
Elongation, %	680	680	890	790
				Aged 7 Days in ASTM Oil #3 at Room Temperature
Tensile strength, MPa	23.5	35.0	dissolved	dissolved
Elongation, %	710	710	dissolved	dissolved
				% Swell After 7 Days at Room Temperature
ASTM Oil #1	0.2	0.4	4.7	6.9
#2	1.1	1.3	13.8	12.3
#3	8.0	7.3	185.5	163.0
Reference fuel A	22.9	10.0	92.8	110.5
fuel B	dissolved	→		
			Inh. viscosity	% Oxygen
^a Epoxidized polymer:	\bar{M}_w 150,000	\bar{M}_n 118,000	0.86	8.2
^b Parent polymer:	102,000	91,000	0.84	-

TABLE X
Evaluation of Compounded Epoxidized Styrene-Butadiene Tapered Block Polymer

	A	B	C	D
				Control
Epoxidized polymer ^a	100	100	—	—
Parent polymer ^a	—	—	100	100
Atomite whiting	40	—	40	—
Whitex clay	—	40	—	40
				Original
Melt flow (180°C, 5 kg)	0.18	0.04	0.35	0.40
300% Modulus, MPa	7.1	15.8	5.6	7.8
Tensile strength, MPa	28.1	24.8	25.6	23.8
Elongation, %	620	590	670	670
				Aged 7 days in ASTM Oil #3 at Room Temperature
Tensile strength, MPa	16.8	15.6	dissolved	dissolved
Elongation, %	650	615	dissolved	dissolved
				% Swell After 7 Days at Room Temperature
ASTM Oil #1	1.7	1.3	8.2	8.4
#2	2.8	2.4	15.9	15.3
#3	10.7	10.0	214.8	205.1
Reference fuel A	15.1	15.1	109.4	108.9
fuel B	dissolved	→		

^a Same as those in Table IX.

CONCLUSIONS

Gelation problems experienced in the epoxidation of higher molecular weight styrene-butadiene block polymers in cyclohexane with *in situ* peroxyformic acid can be alleviated by replacing half or more of the formic acid with acetic acid.

This does not adversely affect the tensile properties or oil resistance of the resulting polymers. The new recipe can also be used to epoxidize divinylbenzene coupled radial block polymers.

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