

## Modification of Butadiene-Acrylonitrile and Styrene-Acrylonitrile Copolymerizations in Emulsion Systems

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### Synopsis

Modification of acrylonitrile in copolymerizations with butadiene and with styrene in hot and cold emulsion recipes has been studied. Series of primary, secondary, and tertiary mercaptans in addition to several miscellaneous modifiers were tested. Kinetically the rate data for the monomer pairs containing acrylonitrile better fit first-order plots than the curves obtained for an ideal emulsion polymerization. In this study all modifier depletions in nitrile systems were plotted as log mercaptan versus log conversion and the slope of the curve was taken as the transfer constant. Normal mercaptans were inefficient modifiers in nitrile systems as determined in polymerization and depletion experiments. Secondary mercaptans, 2-nonyl, 2-decyl, and mixtures in this molecular weight range, were promising modifiers for low temperature (5°C.) nitrile systems. 2-Nonyl mercaptan gave enhanced modification by incremental addition of the modifier indicating this procedure could be used to advantage in preparing nitrile rubbers. The series of tertiary mercaptans from C<sub>13</sub> to C<sub>7</sub> showed an improvement in modification of low temperature nitrile systems as the molecular weight decreased. A plot of the data on a molar basis shows that the optimum modifier falls in the C<sub>9</sub>-C<sub>8</sub> range. The optimum transfer constant for the most efficient modification of 70/30 and of 80/20 butadiene-acrylonitrile polymerizations at 5°C. terminated at 60% conversion is 2. Depletion data show that the transfer constant for a mercaptan decreases as the nitrile content in mixtures with butadiene increases. The properties of the vulcanizates of the 70/30 and 80/20 butadiene-acrylonitrile polymers prepared in the presence of low molecular weight mercaptans were equivalent to or better than those of the controls. These data show that nitrile polymers could be modified with a lower molecule weight mercaptan with no loss of properties but with a considerable saving in amount of modifier. Mercaptans are essential for the initiation of butadiene-acrylonitrile in the presence of persulfate at 50°C. For the hot nitrile rubber preparations, the series of mercaptan from *t*-C<sub>10</sub> to *t*-C<sub>7</sub> are efficient modifiers. However, the heptyl and octyl mercaptans are retarders, and the *t*-C<sub>9</sub> and *t*-C<sub>10</sub> are the preferred modifiers for efficiency and unretarded polymerization. The modification with a series of mercaptans ranging from *t*-C<sub>13.2</sub> to *t*-C<sub>8</sub> of 75/25 styrene-acrylonitrile at 50°C. in presence of persulfate-bisulfite showed a consistent behavior. The transfer constant decreased in a regular manner as the molecular weight of the mercaptan increased, and for the series of tertiary modifiers the *t*-C<sub>10</sub> mercaptan was the most efficient as judged by a melt flow test.

### INTRODUCTION

Information in the literature on modification of butadiene and of styrene copolymerizations with acrylonitrile in emulsion systems is scant. In a

recent review of nitrile rubbers,<sup>1</sup> the section on modification was largely the same as that presented in older reviews.<sup>2,3</sup> The present study was undertaken to examine more thoroughly the modification of nitrile rubbers and resins with some experimental mercaptans and with some of the newer modifiers that have been recently offered commercially.

In the present study a number of representative modifiers were first tested in standard polymerization systems, and on the basis of these results, several of the promising modifiers were studied more thoroughly. Several polymers were evaluated in compounded stocks.

## POLYMERIZATIONS CONDUCTED AT 5°C.

### Mercaptans

Some of the modifiers that were used repeatedly are tabulated in Table I. Other modifiers used were: *n*-tridecyl mercaptan, *n*-octyl mercaptan, mixture of *n*-nonyl and decyl mercaptans, *n*-dodecyl mercaptan, mixture of *n*-undecyl and tetradecyl mercaptans, cyclododecadienyl mercaptan,

TABLE I  
Modifiers Used

Designation	Mercaptan	Boiling range temp. at interval, °F.			Molecular weight	Mercaptan, wt.-%
		10%	50%	90%		
Sulfole 132 <sup>a</sup>	<i>t</i> -C <sub>13.2</sub>	462	468	552	212	94.5
Sulfole 120 <sup>a</sup>	<i>t</i> -C <sub>12</sub>	451	463	477	199	97
Sulfole 105 <sup>a</sup>	<i>t</i> -C <sub>10.5</sub>	163 <sup>b</sup>	167 <sup>b</sup>	175 <sup>b</sup>	180	98.5
<i>tert</i> -Decyl	<i>t</i> -C <sub>10</sub>	163 <sup>b</sup>	164 <sup>b</sup>	171 <sup>b</sup>	174	98.3
Sulfole 90 <sup>a</sup>	<i>t</i> -C <sub>9</sub>	374	378	383	158	97.6
<i>tert</i> -Octyl	<i>t</i> -C <sub>8</sub>	315	319	323	144	96
<i>tert</i> -Heptyl	<i>t</i> -C <sub>7</sub>	299	303	307	131	98

<sup>a</sup> Trademark; commercial tertiary mercaptans from Phillips Petroleum Co.

<sup>b</sup> At 5 mm. Hg.

4-cyclooctene-1 mercaptan, dipentene dithiol, 1,10-decanedithiol, 3-chloropropyl mercaptan, ethylene glycol 3-mercaptopropionate, Captax, 1,6-hexanedithiol, pentaerythritol mercaptan, 2-dodecyl mercaptan, 4-dodecyl mercaptan, anethole mercaptan, 3-dodecyl mercaptan, 6-dodecyl mercaptan 5-dodecyl mercaptan, mercaptan from tall oil, mercaptan from oleic acid, diisopropyl xanthogendisulfide (Dixie), 2-nonyl mercaptan, mixture of 2-nonyl and decyl mercaptans, and 2-decyl mercaptan.

### Laboratory Procedures

The laboratory bottle technique was used for all the polymerizations, the inherent viscosities of the nitrile rubbers were determined in chloroform at 25°C., and the Mooney viscosities were measured by the standard

ASTM procedure. Mercaptan depletions were determined by the Kolthoff and Harris silver nitrate amperometric procedure.<sup>4</sup>

For comparative purposes, a modification index measurement is sometimes used. The modification index,  $MI_x$ , is the ratio of the amount of a standard modifier required for a 50 ML-polymer to the amount of a test modifier required for the same Mooney viscosity.

### Selection of Recipes and Kinetic Results

A polymerization system that has a rate of about 10% conversion/hr. was desired for conducting mercaptan depletion studies in the laboratory. This rate is not too high for one man to handle a series of polymerizations at one time, and yet the experiment can be completed readily in a 9-hr. interval. The desired rates were obtained in the sulfoxylate-low temperature recipes, but higher rates were the rule in the 50°C. persulfate recipes.

The mercaptans were tested in the three recipes developed for low temperature nitrile rubber given in Table II.

TABLE II  
Recipes for the Polymerization of Butadiene-Acrylonitrile at 5°C.

	Parts		
	A	B	C
Butadiene	70	80	90
Acrylonitrile	30	20	10
Water	180	180	180
KFA soap <sup>a</sup>	4.6	4.6	4.6
KOH	0.03	0.03	0.03
KCl	0.30	0.30	0.30
Daxad 15	0.20	0.20	0.20
EDTA Na <sub>4</sub> , in soap solution	0.010	0.010	0.010
in activator	0.010	0.022	0.0116
FeSO <sub>4</sub> ·7H <sub>2</sub> O	0.0050	0.0110	0.0058
NaSO <sub>2</sub> CH <sub>2</sub> OH·2H <sub>2</sub> O (SFS)	0.0250	0.0550	0.0290
Cumene hydroperoxide	0.0268	0.061	—
<i>p</i> -Menthane hydroperoxide	—	—	0.0372
Modifier	Variable	Variable	Variable
Shortstop: dinitrochlorobenzene	0.20	0.22	0.20
Antioxidant: Polygard	1.5	1.8	1.5

<sup>a</sup> Rosin soap used in several comparisons.

The rate curves for the polymerization with the three recipes in Table I differ considerably from that of an SBR system obeying the kinetics predictable by the Harkins-Smith-Ewart theory.<sup>5,6</sup> The butadiene-acrylonitrile rate curves represent monotonically decreasing rates and are similar to first-order rate curves. Typical results obtained by plotting monomers remaining versus time on semilog paper are straight lines that usually extrapolate slightly below the expected origin (Fig. 1). Sets of curves similar to that for the 80/20 mixture in Figure 1 were obtained for

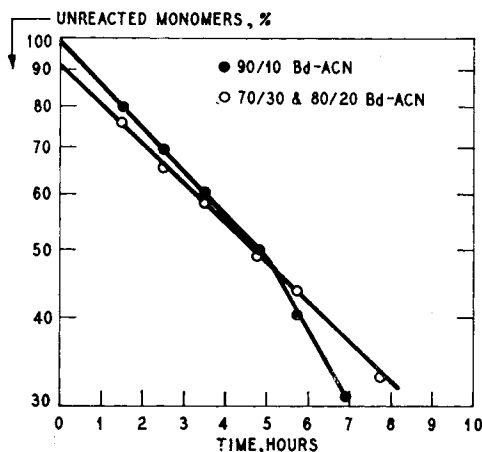


Fig. 1. Rate curves for 70/30, 80/20, and 90/10 butadiene-acrylonitrile mixtures in recipes A, B, and C of Table II.

polymerization of the 80/20 mixture in recipe B at four different initiator levels, and a similar set was also obtained with recipe A modified with the retarding *tert*-heptyl mercaptan at variable initiator levels.

Although the rate data do show a deviation from first-order kinetics, the treatment of monomer polymerization in this manner proves useful in the mercaptan depletion measurements. This will become more apparent when the latter studies are presented in various parts of this report.

### Modification of 70/30 Butadiene-Acrylonitrile Polymerization

The general approach to studying modification of the monomer ratio was first to test modifiers, then to examine some of the interesting modifiers more extensively, and finally to evaluate samples in compounded stocks.

A criterion used in this report to rate an efficient modifier was an inherent viscosity  $<3$  for the polymer made at a modifier level of 0.25 phm.

**Primary and Secondary Mercaptans.** In three series of polymerizations, a variety of primary and secondary mercaptans and miscellaneous compounds were tested as modifiers for the 70/30 butadiene-acrylonitrile mixture in recipe A of Table II. Modifiers that were considered inefficient by the criterion previously stated are given in Table III. The poor modifiers were the *n*-mercaptans, both simple and complex, several cyclic mercaptans, and Captax. Although some of these compounds listed in Table III are inefficient, the polymers formed in their presence were gel-free, whereas others did not prevent gel formation.

In the same three sets of polymerizations, some of the modifiers tested were promising (Table IV). Dixie, a modifier used in commercial production of nitrile rubber, is a serious retarder in this sulfoxylate recipe. The secondary mercaptans were much more efficient than the primary com-

TABLE III  
Experimental Results with Inefficient Modifiers  
for 70/30 Butadiene-Acrylonitrile Polymerization

Modifier no. <sup>a</sup>	Range or amount used, phm	Range of Mooney viscosity, ML-4	Range of inherent viscosity, dl./g.	Range of gel, %
1, 2, 3, 4, 5	0.4-0.5	111-168	3.2-6.2	0
6, 7, 8, 9	0.5	25-146	2.1-3.9	0
10, 11, 12, 13, 14	0.5	128-152	—	64-89

<sup>a</sup> In each row the modifiers are arranged in order of increasing inherent viscosity of polymer or increasing Mooney viscosity for gelled polymers. Modifiers are: (1) *n*-tridecyl mercaptan, (2) *n*-octyl mercaptan; (3) mixture of *n*-nonyl and *n*-decyl mercaptans, (4) *n*-dodecyl mercaptan, (5) mixture of *n*-undecyl and tetradecyl mercaptans, (6) cyclo-dodecyldienyl mercaptan, (7) cyclooctene-1 mercaptan, (8) dipentene dithiol, (9) 1,10-decanethiol, (10) 3-chloropropyl mercaptan, (11) ethylene glycol 3-mercaptopropionate, (12) Captax, (13) 1,6-hexanedithiol, (14) pentaerythritol mercaptan.

pounds as modifiers for 70/30 butadiene-acrylonitrile polymerizations at 5°C., and the modification index shows that the *sec*-C<sub>9</sub>-C<sub>10</sub> mixture was the most efficient of the secondary mercaptans. For comparative purpose, the modification data for the linear secondary mercaptans are plotted in Figure 2.

**Tertiary Mercaptans.** The tertiary mercaptans were also efficient modifiers for the 70/30 butadiene-acrylonitrile mixture and the *t*-C<sub>10</sub>-C<sub>11</sub> and

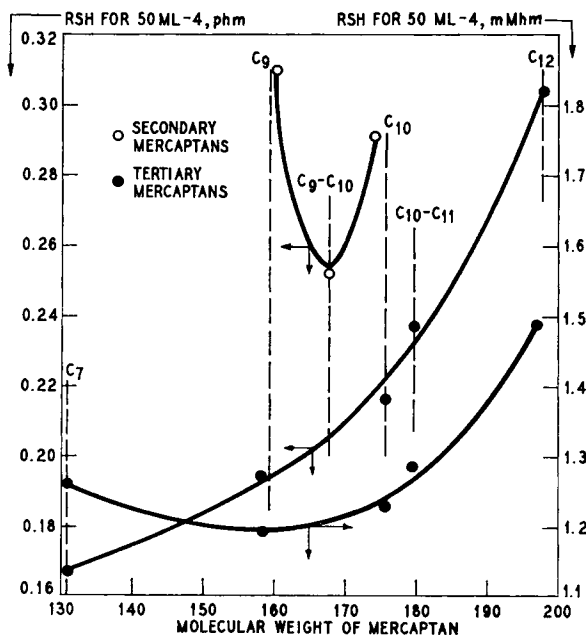


Fig. 2. Mercaptan requirement for 50 Mooney vs. molecular weight.

TABLE IV  
Modification of 70/30 Butadiene-Acrylonitrile Mixture with Some Efficient Modifiers

Modifier		Polymeri- zation time, hr.	Conver- sion, %	Mooney viscosity ML-4	Inherent viscosity, dl./g.	Gel, %	Requirement for 50 ML-4, phm	MI <sub>z</sub> <sup>a</sup>
Type	phm							
Dixie	0.5	11.8	53	20	1.44	0	—	—
2-C <sub>8</sub> SH	0.324	6.1	61.3	50	2.28	0	0.310	95.8
2-C <sub>9</sub> -C <sub>10</sub> SH	0.252	5.3	60	53	2.21	0	0.253	126
2-C <sub>10</sub> SH	0.280	5.8	62	54	2.31	0	0.291	105
sec-C <sub>10</sub> SH	0.50	5.8	61	14	1.54	0	—	—

<sup>a</sup> Modification index, MI<sub>z</sub> = 100 (phm *t*-C<sub>12</sub>SH for 50 ML-4)/(phm test RSH for 50 ML-4).

TABLE V  
Modification of 70/30 Butadiene-Acrylonitrile Polymerization with Tertiary Mercaptans

Mercaptan		Polymeri- zation time, hr.	Conver- sion, %	Mooney viscosity, ML-4	$\eta$ , dl./g.	Gel, %	Requirement for 50 ML-4, phm	MI <sub>z</sub>
Type	phm							
<i>t</i> -C <sub>7</sub>	0.160	6.3 <sup>a</sup>	60	53.5	2.15	0	0.167	183
Sulfole 90	0.192	5.6	59	51.5	2.19	0	0.194	165
<i>t</i> -C <sub>10</sub>	0.220	5.8	61	48.5	2.05	0	0.217	141
Sulfole 105	0.222	5.3	59	56	2.25	0	0.237	135
Sulfole 120	0.298	6.1	61	52	2.20	0	0.304	100

<sup>a</sup> *p*-Methane hydroperoxide used in place of cumene hydroperoxide.

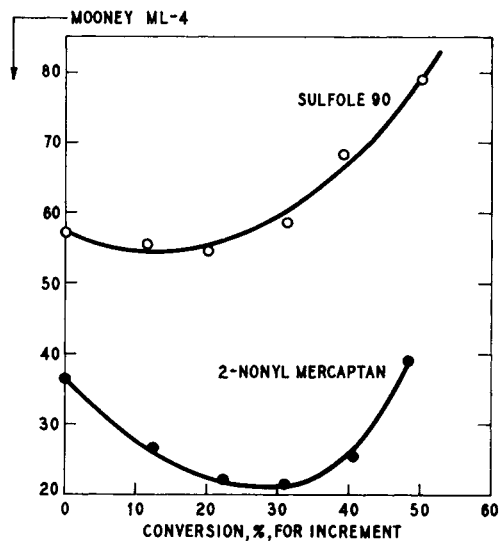


Fig. 3. Effect of incremental addition of Sulfole 90 or 2-nonyl mercaptans on modification of 70/30 butadiene-acrylonitrile.

lower molecular weight modifiers were more efficient than any of the secondary mercaptans screened. In general, as the molecular weight of the tertiary mercaptans increased, modification efficiency decreased (Table V, Fig. 2). In order to obtain the rate of polymerization shown in Table V for the system modified with *t*-C<sub>7</sub> mercaptan, *p*-menthane hydroperoxide had to be substituted for cumene hydroperoxide and the initiator level was also increased. The heptyl mercaptan is a serious retarder, and Sulfole 90 is the preferred modifier in this system since it is the most efficient mercaptan that did not retard polymerization.

**Incremental Addition.** Two of the interesting modifiers tested, 2-nonyl and Sulfole 90 mercaptans, were used in incremental addition tests. In these experiments two-thirds of the modifier was added initially and one-third was injected at a later conversion.<sup>7,8</sup> The data plotted in Figure 3 show that a greater enhancement of modification was obtained with 2-nonyl than with Sulfole 90 mercaptan. The enhancement obtained by the incremental addition of 2-nonyl mercaptan amounted to a 41% lowering of the Mooney viscosity compared to the control.

**Mercaptan Depletions.** Depletion curves of some of the mercaptans that are considered inefficient for modification of the 70/30 butadiene-acrylonitrile polymerization are shown in Figure 4. The top three curves for *n*-, *sec*-, and *tert*-C<sub>12</sub> mercaptans are examples of modifiers that deplete too slowly to be considered efficient modifiers.

The curve for the *n*-C<sub>11</sub>-C<sub>14</sub> mercaptan is an example of a difficulty encountered with the use of all normal mercaptans. Under average laboratory charging conditions, the monomers and mercaptan may be together at a temperature between 5°C. and room temperature for as long

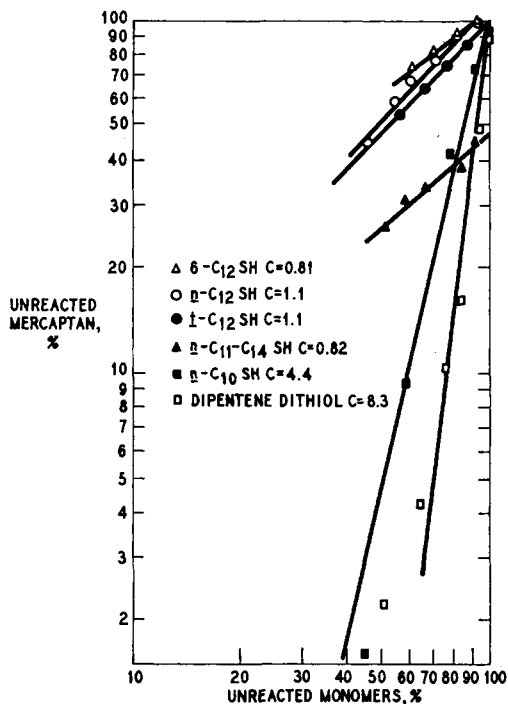


Fig. 4. Disappearance of inefficient mercaptans in 70/30 butadiene-acrylonitrile polymerization.

as  $\frac{1}{2}$  hr. Under these conditions a rapid disappearance of normal mercaptans, even in the absence of activator, is found. This premature disappearance is indicated by the large deviation from 100% mercaptan the extrapolated curve has at zero conversion. To overcome this premature disappearance of mercaptans, the modifier should be charged just before the activator. The latter charging procedure gave curves that went through the origin as is shown by the data for  $n$ - $C_{10}$  mercaptan in Figure 4.

The curve for dipentene dithiol (Fig. 4) shows this modifier depleted too rapidly for efficient modification, and apparently the normal mercaptans below  $C_9$  proved inefficient (Table III) for the same reason.

Other examples of mercaptan depletion for the 70/30 butadiene-acrylonitrile mixture are given in the section on modification of 80/20 monomer mixture.

**Physical Evaluation.** Four 270-g. samples of 70/30 butadiene-acrylonitrile polymer were prepared according to recipe A of Table II. The control was modified with 0.320 phm Sulfole 120 mercaptan. Experimental polymers were modified with 2- $C_9$ - $C_{10}$  mercaptan and with initial or incremental addition of Sulfole 90 mercaptan. The data indicated a 35% saving of mercaptan when Sulfole 90 was used in place of Sulfole 120 and a 14% saving when 2- $C_9$ - $C_{10}$  mercaptan was the substitute. There was no



enhancement obtained with the incremental addition of Sulfole 90 mercaptan over initial addition.

The polymers were submitted for physical evaluation in a gasket formulation. Comparisons were made with Paracril C, a "hot" rubber, which was the only polymer available with the same acrylonitrile content. The processing data showed that the three polymers prepared with the nonyl mercaptans were essentially the same as the Sulfole 120 mercaptan control and were apparently easier to process than Paracril C. The stress-strain values of the Sulfole 90 mercaptan vulcanizates were equal to or higher than the Sulfole 120 and those of the 2-nonyl mercaptan-modified polymers, and the hardnesses for the four vulcanizates were the same. The effect the different modifiers had on the physical properties was essentially the same for the 70/30 and 80/30 butadiene-acrylonitrile pairs. For this reason only one set of physical evaluation data is presented; that for the 80/20 monomer mixture (Table X).

### Modification of 80/20 Butadiene-Acrylonitrile Polymerization

The initiator level was increased for this monomer combination to obtain 60% conversion in approximately 6 hr. (Table II, recipe B). Since the primary mercaptans showed up poorly as modifiers for the 70/30 monomer ratio, they were not tested for the 80/20 ratio.

TABLE VI  
Experimental Results with Inefficient Modifiers  
for 80/20 Butadiene-Acrylonitrile Polymerizations

Modifier no. <sup>a</sup>	Range or amount used, phm	Range of inherent viscosity, dl./g.	Gel, %
15, 16, 17, 18, 19, 20, 21	0.5-0.6	2.3-3.5	0
26, 22, 15, 16, 19	0.25-0.29	3.5-4.8	0

<sup>a</sup> In each row the modifiers are arranged in order of increasing inherent viscosity of polymer formed. Modifiers: (15) 2-dodecyl mercaptan, (16) 4-dodecyl mercaptan, (17) anethole mercaptan, (18) 3-dodecyl mercaptan, (19) 6-dodecyl mercaptan, (20) 5-dodecyl mercaptan, (21) mercaptan from tall oil, (22) mercaptan from oleic acid, (26) 2-decyl mercaptan.

In another three series of polymerizations, a variety of secondary and tertiary mercaptans and miscellaneous compounds were tested at approximately the 0.25 or 0.5 phm levels. The modifiers rated as inefficient are given in Table VI. None of the isomeric series of secondary dodecyl mercaptans with the thiol groups in positions 2- to 6- along the chain rated as efficient modifiers. Furthermore, the modification effectiveness showed no correlation with the position of the —SH group. The long-chain fatty acids, anethole, and the cyclic C<sub>12</sub> mercaptans were also rated as inefficient in these tests. However, all the polymers prepared with these modifiers were free of gel.

Dixie, two low molecular weight secondary mercaptans, and a homologous series of tertiary mercaptans were rated as efficient for modification of the 80/20 butadiene-acrylonitrile mixture (Table VII). The nonyl and decyl secondary mercaptans were notably more effective than any of the dodecyl isomers. For the homologous series of tertiary mercaptans, the viscosity data show that the modification efficiency of the mercaptan increases as the molecular weight decreases. Modification efficiency increased markedly going from Sulfole 120 to 105 mercaptan and continued to improve to a smaller extent for *t*-C<sub>10</sub> to Sulfole 90 mercaptan. No retardation was apparent with Sulfole 90 although the rosin soap slowed the polymerization rate in comparison to the system with fatty acid soap as emulsifier (Table VII).

TABLE VII  
Modification of the 80/20 Butadiene-Acrylonitrile  
Mixture with Some Efficient Modifiers

Modifier		Polymeri- zation time, hr.	Conver- sion, %	Mooney viscosity, ML-4	Inherent viscosity, dl./g.	Gel, %
Type	phm					
Dixie	0.25	8.3	60	—	2.53	0
2-C <sub>9</sub> -C <sub>10</sub>	0.51	5.8	59	—	1.39	0
2-C <sub>10</sub>	0.5	6.2	60	—	1.29	0
Sulfole 120	0.2	8.6 <sup>a</sup>	55	62	2.47	0
Sulfole 105	0.2	8.9 <sup>a</sup>	60	49	2.13	0
<i>t</i> -C <sub>10</sub>	0.2	8.9 <sup>a</sup>	59	44	2.03	0
Sulfole 90	0.2	8.7 <sup>a</sup>	57	39	1.91	0

<sup>a</sup> Rosin soap substituted for fatty acid soap as emulsifier.

Modifier requirements for 50-Mooney, ML-4, 80/20 butadiene-acrylonitrile were determined for Sulfole 120, 90, and *t*-C<sub>10</sub> mercaptans in recipe B for both emulsifier systems, rosin and fatty acid soaps. The modification indexes for Sulfole 90 and *t*-C<sub>10</sub> mercaptans were calculated based on Sulfole 120 at 100 (Table VIII). Tertiary mercaptans were more efficient in the 80/20 butadiene-acrylonitrile than in the 70/30 system. However, with Sulfole 120 as the reference mercaptan, the modification

TABLE VIII  
Modifier Requirements for Mooney 50 ML-4, for  
80/20 Butadiene-Acrylonitrile Copolymer

Soap	Mercaptan		Modification index, MI <sub>z</sub>
	Type	phm for 50 ML-4	
KFA	Sulfole 120	0.275	100
KFA	<i>t</i> -C <sub>10</sub>	0.178	154
KFA	Sulfole 90	0.165	167
Rosin	Sulfole 120	0.216	100
Rosin	Sulfole 90	0.161	134

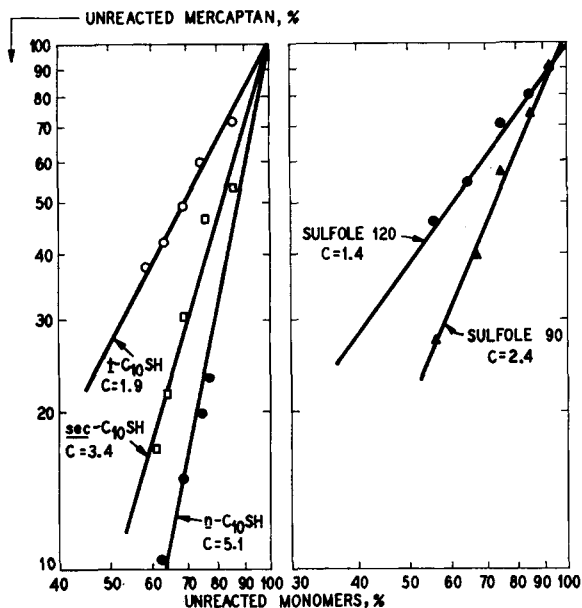


Fig. 5. Comparison of rate of depletion of three isomeric decyl mercaptans and of Sulfole 120 and 90 in 80/20 butadiene-acrylonitrile polymerizations at 50°C. (Sulfoles 120 and 90 in rosin soap recipe.)

indexes for a series of mercaptans for the two monomer ratios were similar, (compare with Table V).

Sulfole 120 mercaptan was more efficient in all-rosin system than in the all-fatty acid soap recipe (Table VIII). However, Sulfole 90 mercaptan was not much more efficient in the rosin soap than in the fatty acid soap system.

**Mercaptan Depletions.** Two types of mercaptan depletion comparisons were made in this part of the investigation. First, certain of the mercaptans were compared in the 80/20 butadiene-acrylonitrile polymerizations, and second, mercaptan disappearances of the same mercaptan in the presence of different monomer ratios were followed.

In the comparative tests, secondary C<sub>12</sub> mercaptans were inefficient modifiers (Table VI). Modifier depletion measurements for 2- and 6-dodecathiol in the 80/20 butadiene-acrylonitrile polymerizations support these viscosity results, since at 50% conversion, more than 60% of the mercaptan still remained. The secondary C<sub>12</sub> mercaptans react too slowly for efficient modification.

A comparison of the rate of depletion of *n*-, *sec*-, and *tert*-decyl mercaptans and of Sulfole 120 and 90 mercaptans in 80/20 butadiene-acrylonitrile polymerizations are shown in Figure 5. For the three mercaptans, Sulfole 120, 90, and *t*-C<sub>10</sub>, the modification indexes follow directly the transfer constants (Table VIII).

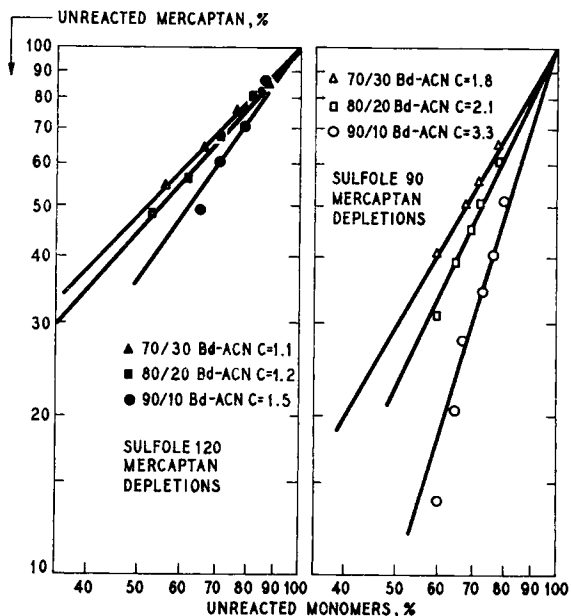


Fig. 6. Depletion of Sulfole 120 and of Sulfole 90 mercaptans at three butadiene-acrylonitrile ratios.

Depletions of Sulfole 120 and 90 mercaptans for 70/30, 80/20, and 90/10 butadiene-acrylonitrile polymerizations are presented in Figure 6. For the two mercaptans the depletion curves show an interesting trend; rate of modifier depletion decreases with increasing acrylonitrile content.

The  $n$ -C<sub>11</sub>-C<sub>14</sub> mercaptan mixture in contact with the 80/20 butadiene-acrylonitrile mixture disappears prematurely as was found for the 70/30 monomer ratio. However, the depletion curve extrapolated to zero conversion showed less mercaptan was lost prematurely in presence of the lower quantity of acrylonitrile.

**Physical Evaluation.** Three 270-g. samples of 80/20 butadiene-acrylonitrile copolymers were prepared according to recipe B, Table II. The control was modified with 0.267 phm Sulfole 120 mercaptan. Two other polymers were modified with 0.150 and 0.160 phm Sulfole 90 mercaptan; added incrementally in one and initially in the other (Table IX). A saving of about 45 wt.-% was realized in using Sulfole 90 rather than Sulfole 120 mercaptan in this recipe. No significant enhancement in modification by incremental addition of the Sulfole 90 mercaptan was found.

Paracril AJ was used as the formulation control in the physical evaluation of the experimental stocks. A standard mechanical rubber compounding formulation was used and the results of the evaluation are given in Table X. The polymers prepared with Sulfole 90 mercaptan were easy to process, and no apparent differences can be attributed to the modification; and the stress-strain properties were as good as or better than the Sulfole 120

TABLE IX  
Polymerization Data for Preparation of Polymers for Evaluation

	Sulfole 120	Sulfole 90	Sulfole 90
Initial mercaptan, phm	0.267	0.160	0.100
Increment, phm <sup>a</sup>	—	—	0.050 <sup>a</sup>
Polymerization time, hr.	5.1	5.6	5.8
Conversion, %	60	59	59
Bound acrylonitrile, %	26.9	26.5	26.5
Mooney, ML-4	56	48.5	56
$\eta$ , dl./g.	2.64	2.22	2.43
Gel, %	0	0	0

<sup>a</sup> At 19% conversion.

TABLE X  
Physical Properties of 80/20 Butadiene-Acrylonitrile Copolymer  
Modified with Sulfole 120 or 90 Mercaptan

	80/20 Butadiene-acrylonitrile polymer			
	Sulfole 120 initial	Sulfole 90 initial	Sulfole 90 incremental	Paracril AJ
<b>Processing data</b>				
Compd. ML-4 at 212°F.	76	71	78	57
Scorch at 280°F., 5 pt. rise, min.	11.3	12.0	10.6	6.2
Min. Mooney, ML-4	43	38	43	39
Extrusion, g./min.	132.5	127	127	107.5
Rating, Garvey	11	11	10	10
Swell at 7 days at R.T., %				
ASTM Oil #3	8.5	9.2	9.0	13.0
<b>Physical properties (30 min. at 307°F.)</b>				
Compression set, %	7.2	7.6	7.4	11
300% Modulus, psi	2050	1980	2090	2260
Tensile, psi	2950	2970	3190	2650
Elongation, %	395	410	420	335
Shore A hardness	71	71	71	67
Crescent tear, lb./in.	300	260	290	240

mercaptan control. These results indicate that this monomer combination could be modified with the lower molecular weight mercaptan with no loss of properties but with a considerable saving in amount of modifier.

### POLYMERIZATIONS CONDUCTED AT 50°C.

Typical recipes for nitrile rubber and styrene-acrylonitrile resin preparations are given in Table XI. For nitrile rubber rate studies, variation in amount of persulfate was examined in addition to the effect of modifiers on modification. For the styrene-acrylonitrile polymerization, only the modification study was conducted.

TABLE XI  
Recipes for the Polymerization at 50°C.

	Parts	
	A	B
Butadiene	70-90	—
Styrene	—	75
Acrylonitrile	30-10	25
Water	180	180
SF flakes	5.0	5.0
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.05-0.30	0.30
NaHSO <sub>3</sub>	—	0-0.06
Mercaptan	Variable	Variable
Shortstop: DTBHQ	0.20	0.20

### Rate Data for Butadiene-Acrylonitrile Polymerization

The polymerization of butadiene-acrylonitrile mixtures with persulfate initiator show the following characteristics. First, the rate of polymerization is not greatly affected by appreciable variations of persulfate concentration. This is shown by the small changes in rate with variation in persulfate concentration for the 70/30, 80/20, and 90/10 butadiene-acrylonitrile mixtures (Fig. 7). Second, initiation of the butadiene-acrylonitrile by persulfate is dependent on the presence of a mercaptan. This is shown by the rate curves for the polymerization of a 70/30 mixture in the presence of a standard modifier, in the presence of a rapidly depleted modifier, and in the absence of a modifier (Fig. 8.) Other investigators<sup>9</sup> found similar kinetics for persulfate-initiated butadiene-styrene copolymerization which deviated from the Smith-Ewart theory for ideal emulsion polymerization systems.

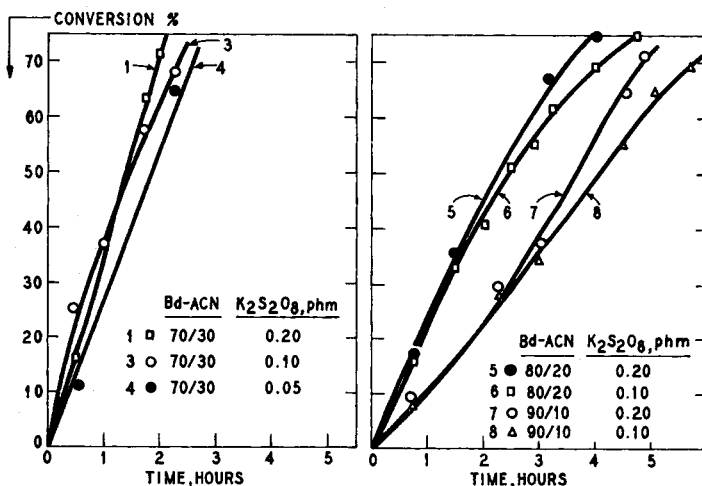


Fig. 7. Effect of persulfate concentration on rate of polymerization of 70/30, 80/20, and 90/10 butadiene-acrylonitrile mixtures.

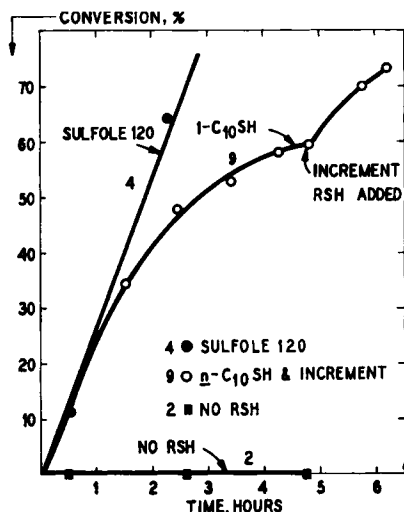


Fig. 8. Effect of mercaptan on initiation of 70/30 butadiene-acrylonitrile with persulfate.

In the persulfate-initiated system, the monomer rate data are also treated as first-order kinetics in the mercaptan depletion studies. This is an arbitrary choice but is justified as a consistent way of handling the modifier depletion data.

### Modification of 70/30 and 80/20 Butadiene-Acrylonitrile Polymerization

The polymerization systems used to obtain the rate curves in Figures 7 and 8 were sampled at approximately 70% conversion and the inherent viscosity of the samples determined (Table XII). For these polymerizations, 0.3 phm Sulfole 120 mercaptan was employed as the modifier.

TABLE XII  
Effect of Variable Monomer Ratio and Variable Persulfate on Modification of Butadiene-Acrylonitrile (Bd-ACN) Mixtures in Presence of 0.3 phm Sulfole 120 Mercaptan

Expt. no. <sup>a</sup>	Bd ACN	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> , phm	Time to 70% conversion, hr.	Inherent viscosity, dl./g.
1	70/30	0.2	2	3.94
3	70/30	0.1	2.3	3.94
4	70/30	0.05	2.6	3.94
5	80/20	0.2	3.5	3.90
6	80/20	0.1	4.1	3.68
7	90/10	0.2	4.9	3.15
8	90/10	0.1	5.75	3.7

<sup>a</sup> Numbers correspond to numbered curves in Figs. 7 and 8.

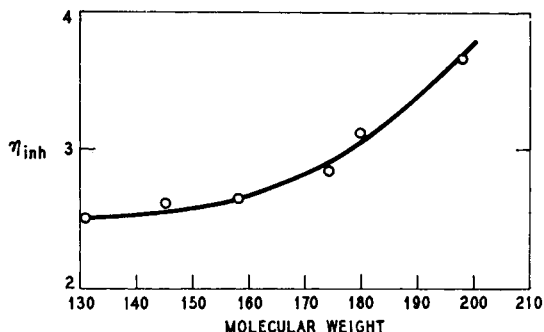


Fig. 9. Effect of molecular weight of tertiary mercaptan on inherent viscosity of 80/20 butadiene-acrylonitrile polymerized at 50°C.

In one series for polymerization of the 80/20 butadiene-acrylonitrile mixture, the homologous series of tertiary mercaptans and three normal mercaptans were tested at the 0.3 phm level (Table XIII). At this level only the polymers modified with tertiary mercaptans were free of gel at 70% conversion. Only the gel-free polymers were used in the plot of inherent viscosity at 70% conversion versus molecular weight of mercaptan (Fig. 9). The shape of this curve resembles that of a similar plot obtained with the same mercaptans in an NBR 1503 recipe (Fig. 2). In both systems initiator changes were made to give rates comparable for the whole series. The data in Table XIII show that the primary mercaptans were much less efficient than the tertiary mercaptans of the same molecular weight.

TABLE XIII  
Modification of 80/20 Butadiene-Acrylonitrile Mixtures with  
Primary and Tertiary Mercaptans

Expt. no.	$K_2S_2O_8$ , phm	Mercaptan		$\eta$ (at 70% conversion), dl./g.	Gel (at 70% conversion), %
		Type	phm		
1	0.05	<i>n</i> -C <sub>11</sub> -C <sub>14</sub>	0.300	1.95	82
2	0.05	<i>n</i> -C <sub>12</sub>	0.302	3.25	80
3	0.05	<i>n</i> -C <sub>10</sub>	0.300 <sup>a</sup>	—	50
4	0.05	Sulfole 120	0.304	3.66	0
5	0.05	Sulfole 105	0.302	3.10	0
6	0.05	<i>t</i> -C <sub>10</sub>	0.298	2.87	0
7	0.05	Sulfole 90	0.300	2.65	0
8	0.05	<i>t</i> -C <sub>8</sub>	0.300	2.60	0
9	0.10	<i>t</i> -C <sub>7</sub>	0.304	2.50	0

<sup>a</sup> Increment of 0.16 phm added at 4.8 hr. in addition to the initial 0.300 phm.

### MODIFICATION OF 75/25 STYRENE-ACRYLONITRILE POLYMERIZATION

In a series of experiments with the 75/25 styrene-acrylonitrile ratio at a Sulfole 120 mercaptan level of 0.25 phm, the variation in potassium per-



TABLE XIV  
Effect of Variable Persulfate and of Variable Bisulfite on Melt Flow

Expt. no.	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> , phm	NaHSO <sub>3</sub> , phm	Sulfole 120, phm	Polymerization time, hr.	Conversion, %	$\eta$ , dl./g.	Gel, %	Melt flow, g./10 min. <sup>a</sup>
1	0.10	—	0.250	4.0	92	1.13	0	1.87
2	0.20	—	0.250	4.0	93	1.11	0	1.88
3	0.30	—	0.250	4.0	94	1.12	0	1.71
4	0.40	—	0.250	4.0	94	1.10	0	1.44
5	0.30	0.015	0.250	4.0	94	1.15	0	1.79
6	0.30	0.030	0.250	4.0	95	1.12	0	1.57
7	0.30	0.060	0.250	4.0	95	1.17	0	2.08

<sup>a</sup> 5 kg. at 200°C.

sulfate from 0.1 to 0.4 phm at zero bisulfite content showed the melt flow tended to decrease with increased persulfate, while at constant persulfate, the melt flow increased with increased bisulfite (Table XIV).

In another series of modification experiments of styrene-acrylonitrile polymerizations, a series of six tertiary mercaptans, Dixie, and Captax were tested in the 50°C. persulfate recipe at 0.30 phm persulfate with bisulfite absent (Table XV). Inherent viscosity did not differentiate well between the various modifiers. However, the melt flow showed that the *t*-C<sub>10</sub> mercaptan was the most efficient modifier in the series (Fig. 10). Dixie showed modifier activity equivalent to Sulfole 132 mercaptan and Captax showed negligible activity.

Another set of experiments was run with the series of tertiary mercaptans at the 0.5 phm level and melt flows for these polymers were also increased.

TABLE XV  
Modification of 75/25 Styrene-Acrylonitrile Polymerization at 50°C.

Expt. no.	Modifier		Polymerization time, hr.	Conversion, %	$\eta$ , dl./g.	Gel, %	Melt flow, g./10 min.
	Type	phm					
1	Sulfole 132	0.251	4.8	94	1.40	0	0.52
2	Sulfole 120	0.250	4.8	95	1.10	0	1.67
3	Sulfole 105	0.251	4.8	94	1.08	0	2.57
4	<i>t</i> -C <sub>10</sub>	0.250	4.8	94	0.92	0	3.68
5	Sulfole 90	0.250	4.8	95	0.93	0	2.88
6	<i>t</i> -C <sub>8</sub>	0.250	4.8	95	0.98	0	0.80
7	Dixie	0.253	5.7	95	1.55	0	0.45
8	Captax	0.252	5.7	95	2.01	0	0.06
9	None	—	4.8	95	7.63	0	No flow
Dow Tyril 767	—	—	—	—	1.07	0	1.30

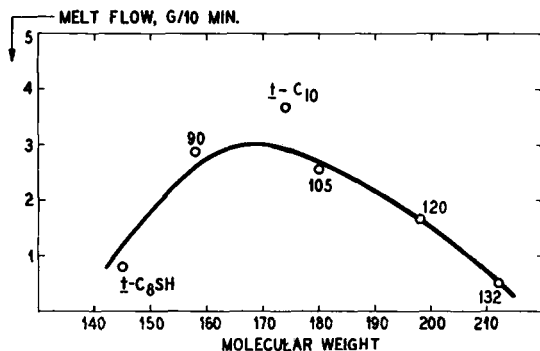


Fig. 10. Effect of molecular weight of mercaptan on melt flow of 75/25 styrene-acrylonitrile resins. Numbers refer to Sulfole mercaptans.

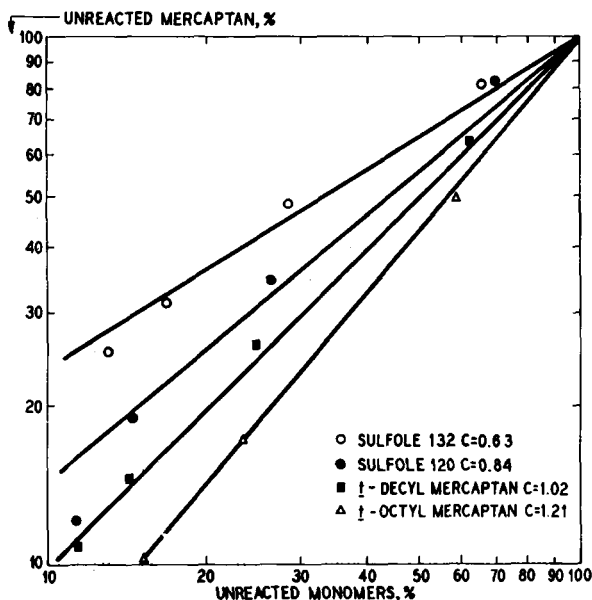


Fig. 11. Depletion rates for four tertiary mercaptans in a 75/25 styrene-acrylonitrile polymerization.

These values ranged from 18 to 38 g./10 min., and a melt flow-molecular weight curve was similar to that shown in Figure 10.

Mercaptan depletion measurements were made for Sulfole 132, 120,  $t$ -C<sub>10</sub>, and  $t$ -C<sub>8</sub> mercaptans in the styrene-acrylonitrile system. The depletion curves (Fig. 11) show the rate of disappearance was inversely related to the molecular weight of the mercaptan.

## DISCUSSION

### Kinetics of Polymerization

Kinetics of the low-temperature emulsion copolymerization of butadiene-acrylonitrile differ from that of butadiene-styrene. The rate curves of the

70/30 and 80/20 mixtures of monomers decreased monotonically with time and do not exhibit the S shape associated with "ideal" emulsion polymerization of a system that obeys Harkins-Smith-Ewart kinetics.<sup>5,6</sup> The rate curves for the butadiene–nitrile polymerizations resembled those for first-order kinetics much better than those of "ideal" emulsion polymerizations (Fig. 1). Furthermore, plotting mercaptan depletions versus monomer disappearance on log–log paper gave more linear curves and closer extrapolation through the origin that did plotting the same data on semilog paper as is done for SBR systems.

### Modification of Butadiene–Acrylonitrile Emulsion Polymerization

**Low-Temperature Polymerization.** The screening tests showed that a few of the primary and miscellaneous modifiers, several of the secondary mercaptans, and a series of the tertiary mercaptans could be satisfactory modifiers in the emulsion polymerization of the 70/30 and 80/20 butadiene–acrylonitrile mixtures. In the first group belong Dixie and possibly *n*-decylthiol; 2-nonyl, 2-decylthiol and mixtures were the secondary modifiers; and the series of tertiary mercaptans from C<sub>12</sub> to C<sub>8</sub> all showed promise as modifiers under the conditions studied.

The performance of the mercaptan can be correlated with the depletion curve. Mercaptans deplete slower in the presence of acrylonitrile than in the presence of butadiene or styrene or their mixtures. This is shown by the decrease in transfer constant as the nitrile content is increased and by the amount of modifier remaining at a specific conversion. A comparison of transfer constants for the nitrile systems and of the regulating indexes for the butadiene and/or styrene systems is shown in Table XVI.

TABLE XVI  
Regulating Indexes and Transfer Constants for Butadiene,  
Styrene, and Butadiene–Acrylonitrile Systems

System	Regulating index <i>R</i> <sup>a</sup>		Transfer constant <i>C</i>	
	Sulfole 90	Sulfole 120	Sulfole 90	Sulfole 120
Styrene	5.0	1.9		
70/30 Butadiene–styrene	5.7	2.1		
Butadiene	5.7	1.8		
70/30 Butadiene–acrylonitrile			1.8	1.1
80/20 Butadiene–acrylonitrile			2.1	1.2
90/10 Butadiene–acrylonitrile			3.3	1.5

<sup>a</sup> Unreported data from Phillips Petroleum Co. and data taken from Uraneck and Burleigh.<sup>7,8</sup>

The screening and modification index results (Table IV and Fig. 2) show that secondary mercaptans are efficient over a rather narrow molecular weight range. However, even the most efficient secondary mercaptans are not as good as the C<sub>7</sub>–C<sub>11</sub> series of the tertiary mercaptans (Fig. 2.) The 2-nonyl mercaptan exhibited enhanced modification in

incremental addition tests. This result was comparable to those obtained with *t*-C<sub>9</sub> mercaptan in the SBR system.<sup>7</sup>

The tertiary series of mercaptans from *t*-C<sub>7</sub> to *t*-C<sub>11</sub> were the most efficient group of modifiers tested. A plot of the moles of mercaptan required for 50 ML-4 Mooney viscosity against molecular weight gives the curve in Figure 2. The minimum of this curve is shifted to a lower molecular weight mercaptan than was the case for a similar series of experiments in the SBR system.<sup>8</sup> Also, efficient modification can be obtained with a broader range of tertiary mercaptans in the nitrile system than in SBR preparations. The tertiary mercaptans below C<sub>12</sub> are more efficient than the other mercaptans tested both on a weight and a molar basis (Fig. 2). Modification of the 70/30 butadiene-acrylonitrile polymerizations with the homologous series of tertiary mercaptans showed that the nonyl mercaptan was the most efficient on a molar basis (Fig. 2). Depletion measurements for this modifier for both the 70/30 and 80/20 monomer mixtures gave transfer constants of approximately two for this modifier (Fig. 5 and 6). These results and also those for *t*-C<sub>10</sub> mercaptan support a value of two as an optimum transfer constant.

The depletion data also show that some of the mercaptans would not be economical because they deplete too fast. This is seen for *n*-decyl mercaptan and the dipentene dithiol (Figs. 4 and 5).

The evaluation data (Table X) show that the polymers made with the lower molecular weight mercaptan process as well and possess as good a balance of physical properties, as do the nitrile rubbers prepared with the standard mercaptan. In case of incremental addition of mercaptan, the polymer made with the light mercaptan had a better balance of properties than the control.

**"Hot" Nitrile Rubber Preparation.** The preliminary experiments for modification of the 70/30 and 80/20 monomer polymerizations at 50°C.

TABLE XVII  
Viscosity of Polymers Prepared at Equal Modifier Levels  
in the SBR and in the Nitrile Systems

System	Modifier		$\eta$ , dl./g.
	Type	phm	
70/30 Butadiene-styrene	Sulfole 120	3.04	2.59
70/30 Butadiene-styrene	Sulfole 105	3.02	2.66
80/20 Butadiene-acrylonitrile	Sulfole 120	3.04	3.66
80/20 Butadiene-acrylonitrile	Sulfole 105	3.02	3.10

also showed that tertiary mercaptans were more efficient than the other modifiers in these systems (Tables XII and XIII). The difference in reactivity of mercaptans in butadiene-styrene and butadiene-nitrile polymerization is seen in the viscosities of the polymers at equal mercaptan levels for Sulfole 120 and 90 mercaptans in the two systems (Table XVII).

### Modification of Styrene-Acrylonitrile Polymerization

The depletion data for the series of tertiary mercaptans in the styrene-acrylonitrile polymerization also show a consistent set of curves when plotted on log-log paper. The experimental points falling on a straight line up to 80 and 90% conversion support the application of first-order kinetics to the monomer rate data (Fig. 11). However, in this instance, as noted in a preceding section, this might be an apparent first-order reaction.

For this monomer pair, the optimum modifier, as judged by melt flow measurements, is the *t*-C<sub>10</sub> isomer. The transfer constant for this mercaptan was 1.02. This means the modifier was reacting at almost the same rate as the monomer. The shift of the optimum to a higher molecular weight modifier for this system, in comparison to the butadiene-nitrile system, arises from the higher conversion at which the resin preparation was terminated. In the SBR system, as the terminal conversion increased, the optimum regulating index decreased for the most efficient modification.<sup>8</sup> This same trend applies to the styrene-nitrile resin preparation, and the optimum transfer constant is lower whenever the terminal conversion is higher.

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