

Modification of Emulsion Polymerization by Multiple Addition of Modifier

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Synopsis

Model equations were used to determine approximately the optimum condition needed to obtain the lowest molecular weight, \bar{P}_v , with a fixed molar amount of modifier by the addition in three portions of modifiers with different regulating indexes. Simulated calculations were also conducted to determine the effect two- and three-portion additions of a modifier had on the \bar{P}_v/\bar{P}_n ratio. The simulated calculations served as guides for two-, three-, and manifold incremental modifier addition experiments. The calculations and experiments establish the need for matching the portioning of the modifier to the regulating index in order to obtain efficient use of the modifier.

INTRODUCTION

Some theoretical and experimental results for modification in emulsion systems arising from the addition of modifier in two portions have been reported.^{1,2} In one report,² the three-portion addition of modifier was treated briefly. In the present report, the three-portion procedure will be considered more extensively, and results for a manifold addition of modifier are also presented. These experiments should help to determine whether multiple addition of modifier is justified.

EXPERIMENTAL

Modifiers. The commercial mercaptans Sulfole 120, 105, and 90 have been characterized previously.^{2,3} The *t*-decyl and *n*-octyl mercaptans are development products available in limited amounts from Phillips Petroleum Company.

Polymerization Procedures. The sulfoxylate⁴ and persulfate⁵ recipes were used in bottle polymerizations⁵ to prepare polymers at 5° and 50°C.

Gel Permeation Fractionation. The procedure used was described in detail in a preceding publication.⁶

Multiple Addition Procedure. In all the multiple addition experiments the modifier is divided into two or more portions, and one portion is always added initially. The remaining modifier consisting of equal-sized portions is added during the course of polymerization. Polymerizations are stopped at a specified conversion, and properties of the final polymer are measured.

MODEL EQUATIONS

The basic equation used in the theoretical consideration is the viscosity-average degree of polymerization:

$$\bar{P}_v = K(M_0/S_0) \{ [\exp(arX) - 1] / [aXr^{(1+a)}] \}^{1/a*} \quad (1)$$

where M_0 is the initial monomer, S_0 is the initial modifier concentration, r is the regulating index, a is the Mark-Houwink exponent, and X is the fractional conversion. A $\bar{P}_v - r$ plot gives a concave curve, and eq. (1) is differentiable and solvable²:

$$\exp(arX)[arX - (1 + a)] = -(1 + a). \quad (2)$$

The value of the optimum r for polymerizations stopped at different conversions can be determined by means of eq. (2), Table I.

The implications of the data in Table I for multiincremental addition of modifier are apparent. If the polymerization were terminated at 10% conversion, the modifier should have an r of about 17. If increments were

TABLE I
Optimum Regulating Index and Modifier Remaining for
Polymerizations Terminated at Different Conversions

| Terminal conversion X | Optimum regulating index r^a | Modifier remaining at X , ^b % |
|-------------------------|--------------------------------|--|
| 0.6 | 2.82 | 16.9 |
| 0.5 | 3.38 | 16.9 |
| 0.4 | 4.23 | 16.9 |
| 0.3 | 5.64 | 16.9 |
| 0.2 | 8.46 | 16.9 |
| 0.1 | 16.9 | 16.9 |
| 0.05 | 33.8 | 16.9 |

^a For calculations with eq. (2), a was taken as 0.66.

^b Calculated from the depletion equation, $S = S_0 \exp(-rX)$.

to be added every 10% conversion, a modifier with a similar r value should be used for the most efficient utilization of modifier. Experimental evidence supporting this induction is presented in a following section.

The number-average degree of polymerization for the three-increment modifier addition was derived by the procedure outlined previously.² The integral form for this case is

$$\bar{P}_n = \frac{\int_{X_0}^{X_1} M_0 dX + \int_{X_1}^{X_2} M_0 dX + \int_{X_2}^{X_3} M_0 dX}{\int_{X_0}^{X_1} rS dX + \int_{X_1}^{X_2} rS_1 dX + \int_{X_2}^{X_3} rS_2 dX} \quad (3)$$

where X_1 and X_2 are conversions for the first and second increments, respectively, X_3 is the final conversion, and S , S_1 , and S_2 are generalized ex-

* Equation (8) of reference 2 contains a misprint. The equation in this report is correct.

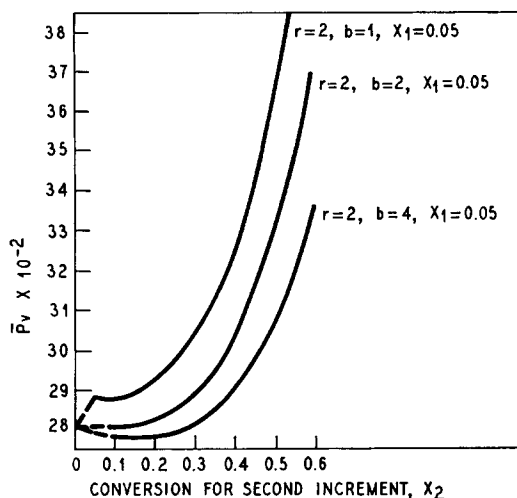


Fig. 1. Favorable and unfavorable ways of dividing modifier for incremental addition when regulating index is low, $r = 2$.

pressions for the modifier increments. A useful expedient is to let S_{0i} be the increment added initially and the other two increments be of equal size, so that $S_{0i}/S_i = b$; then $S = S_{0i} \exp(-rX)$, $S_1 = \{[b + \exp(rX_1)]/b\} \exp(-rX)$, and $S_2 = \{[b + \exp(rX_1) + \exp(rX_2)]/b\} \exp(-rX)$. Substituting these expressions into eq. (3) and integrating gives the equation for the number-average degree of polymerization:

$$\bar{P}_n = (M_0 X_3) / S_{0i} \{ 1 - \exp(-rX_1) + K_1 [\exp(-rX_1) - \exp(-rX_2)] + K_2 [\exp(-rX_2) - \exp(-rX_3)] \} \quad (4)$$

where $K_1 = [b + \exp(rX_1)]/b$ and $K_2 = [b + \exp(rX_1) + \exp(rX_2)]/b$.

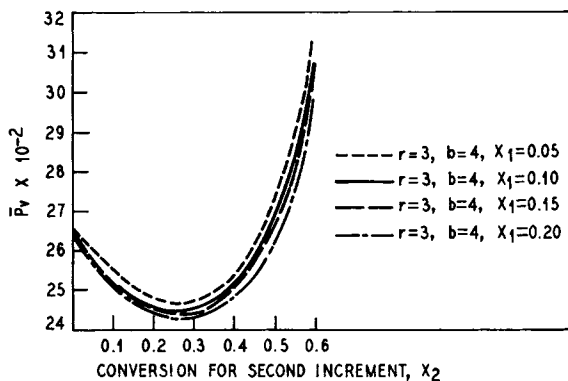


Fig. 2. Addition of increments is not critical when modifier is divided favorably for a low regulating index, $r = 3$.

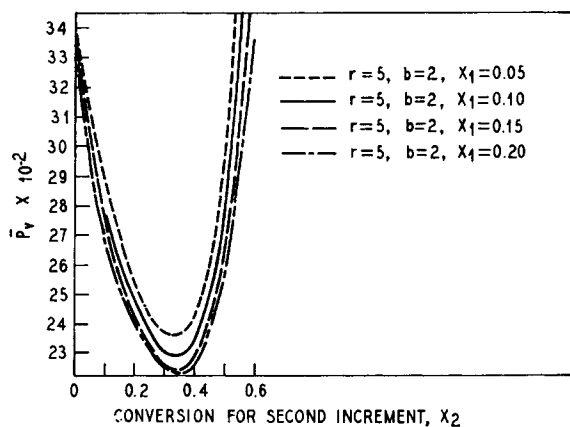


Fig. 3. The effectiveness of incremental additions for modifier is notable at a regulating index of 5.

Similar substitutions into the integral equation for the viscosity-average molecular weight results in the following expression:

$$\bar{P}_v = K_3 \{ \exp(arX_1) - 1 + K_4 [\exp(arX_2) - \exp(arX_1)] + K_5 [\exp(arX_3) - \exp(arX_2)] \}^{1/a} \quad (5)$$

where $K_3 = KM_0/S_{0i} [1/aX_3 r^{(1+a)}]^{1/a}$, $K_4 = \{b/[b + \exp(rX_1)]\}^a$, and $K_5 = \{b/[b + \exp(rX_1) + \exp(rX_2)]\}^a$.

TABLE II
Approximate Optimum Conversions for Addition of Increments of Mercaptans for Minimum Molecular Weight

| Regulating index r | Modifier ratio b | Optimum conversion for addition of increments | | Minimum degree of polymerization \bar{P}_v |
|----------------------|--------------------|---|-------|--|
| | | X_1 | X_2 | |
| 2 | 1 | 0.00 | 0.00 | 2809 |
| 2 | 2 | 0.05 | 0.10 | 2805 |
| 2 | 4 | 0.05 | 0.15 | 2778 |
| 3 | 1 | 0.05 | 0.20 | 2473 |
| 3 | 2 | 0.10 | 0.25 | 2434 |
| 3 | 4 | 0.15 | 0.30 | 2432 |
| 5 | 1 | 0.10 | 0.30 | 2260 |
| 5 | 2 | 0.20 | 0.30 | 2250 |
| 5 | 4 | 0.20 | 0.30 | 2332 |
| 6 | 1 | 0.15 | 0.30 | 2273 |
| 6 | 2 | 0.15 | 0.40 | 2292 |
| 6 | 4 | 0.20 | 0.40 | 2394 |
| 8 | 1 | 0.20 | 0.40 | 2328 |
| 8 | 2 | 0.20 | 0.40 | 2333 |
| 8 | 4 | 0.20 | 0.40 | 2638 |
| 12 | 1 | 0.20 | 0.40 | 2706 |
| 12 | 2 | 0.20 | 0.40 | 2842 |
| 12 | 4 | 0.20 | 0.40 | 3448 |

TABLE III
Comparison of the Minimum Molecular Weights Obtained for
the Control and the Two- and Three-Portion Addition Procedure

| Regulating index r | Degree of polymerization \bar{P}_n for division of modifier into portions | | |
|-------------------------|---|------|------|
| | 1 | 2 | 3 |
| 2 | 2809 | 2781 | 2778 |
| 3 | 2654 | 2452 | 2432 |
| 5 | 3377 | 2360 | 2250 |
| 6 | 4202 | 2431 | 2273 |
| 8 | 7350 | 2753 | 2328 |
| 12 | 30782 | 4146 | 2706 |

A large number of simulated calculations were conducted with eq. (5), but only selected data will be presented here to show the trends and extremes for specific r , b , and X_1 values as X_2 was varied. For these calculations, $M_0 = 100$ g butadiene = 1.849 moles, $S_0 = 0.18$ g $C_6SH = 0.001123$ mole, $a = 0.66$; X_3 , the terminal conversion, was 0.6; r ranged from 2 to 12; b was 1, 2, or 4; X_1 was 0, 0.05, 0.10, 0.15, or 0.20; and X_2 was variable. For $b = 1$, the modifier is divided $1/3, 1/3, 1/3$; for $b = 2$, the division is $1/2, 1/4, 1/4$; for $b = 4$, the division is $2/3, 1/6, 1/6$. When the regulating index is low, calculations with eq. (5) show that b is critical (Fig. 1). When r is close to the optimum value for the control, i.e., all modifier added

TABLE IV
Approximate Optimum Conversions for Addition
of Increments of Modifier for Lowest \bar{P}_v/\bar{P}_n Values

| Regulating index r | Modifier ratio b | Optimum conversions for addition of increment | | Minimum \bar{P}_v/\bar{P}_n |
|-------------------------|-----------------------|--|-------|----------------------------------|
| | | X_1 | X_2 | |
| 2 | 1 | 0.05 | 0.3 | 1.87 |
| 2 | 2 | 0.15 | 0.4 | 1.83 |
| 2 | 4 | 0.20 | 0.4 | 1.83 |
| 3 | 1 | 0.15 | 0.3 | 1.89 |
| 3 | 2 | 0.20 | 0.4 | 1.85 |
| 3 | 4 | 0.20 | 0.4 | 1.88 |
| 5 | 1 | 0.15 | 0.4 | 1.98 |
| 5 | 2 | 0.20 | 0.4 | 1.94 |
| 5 | 4 | 0.20 | 0.4 | 2.09 |
| 6 | 1 | 0.15 | 0.4 | 2.02 |
| 6 | 2 | 0.20 | 0.4 | 2.01 |
| 6 | 4 | 0.20 | 0.4 | 2.22 |
| 8 | 1 | 0.20 | 0.4 | 2.16 |
| 8 | 2 | 0.20 | 0.4 | 2.21 |
| 8 | 4 | 0.20 | 0.4 | 2.55 |
| 12 | 1 | 0.20 | 0.4 | 2.65 |
| 12 | 2 | 0.20 | 0.4 | 2.81 |
| 12 | 4 | 0.20 | 0.4 | 3.43 |

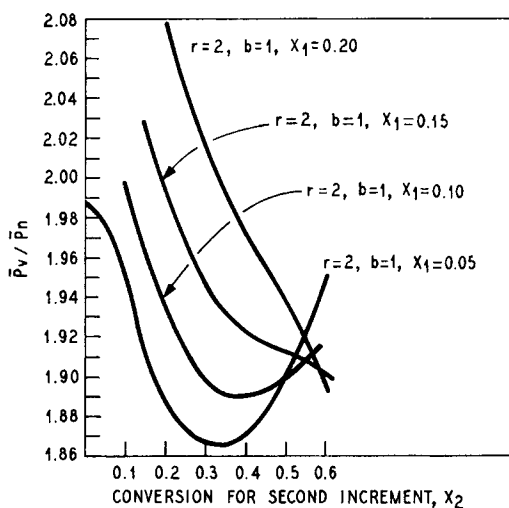


Fig. 4. Influence of an unfavorable division of a slow-reacting modifier on MWD.

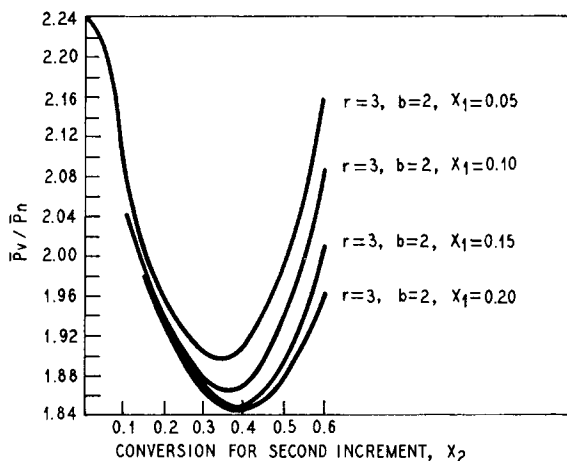


Fig. 5. Effect of incremental addition of modifier with a regulating index of 3 on P_v/P_n .

initially and terminal conversion is 0.6, the conversions for adding the increments are not critical when the modifier is divided favorably (Fig. 2). When r becomes larger, as when $r = 5$, the effectiveness of the incremental procedure becomes pronounced (Fig. 3).

Another way of showing the relationship of r , b , X_1 , and X_2 is to tabulate the X_1 and X_2 values which give minimum molecular weights for each r at the three b values, Table II. The data show the need to add the increments early when r is low and later when r is high.

A further comparison of interest is the lowest molecular weight attainable by the three procedures being considered—the control and two and three increments, Table III.

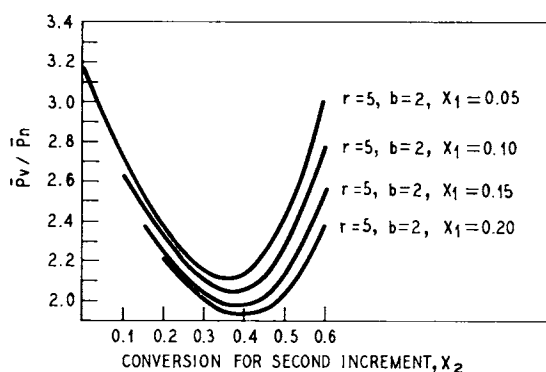


Fig. 6. Effect of incremental addition of modifier with a regulating index of 5 on \bar{P}_v/\bar{P}_n .

The molecular weight distribution (MWD) is an important parameter of any commercial polymer, and methods of controlling MWD are of interest. The \bar{P}_v/\bar{P}_n ratios for the modifier with a low regulating index, $r = 2$, and an unfavorable division of modifier, $b = 1$, are seen in Figure 4. In these instances, a delay in the addition of the first increment, $X_1 = 0.20$, for instance, is unfavorable for obtaining low \bar{P}_v/\bar{P}_n values. For $r = 3$, $r = 5$, and higher, appreciable decreases for \bar{P}_v/\bar{P}_n were found for all combinations of adding the modifier (Figs. 5 and 6).

The best X_1 and X_2 values for obtaining the lowest \bar{P}_v/\bar{P}_n ratio for the different r and b combinations are summarized in Table IV. These data show a notable shift in the X_1 value as r increases in order to obtain the minimum distribution value; but in all but two cases, the best X_2 value for the minimum \bar{P}_v/\bar{P}_n was 0.4.

A comparison of the three procedures for adding modifier to obtain the lowest \bar{P}_v/\bar{P}_n value is shown by the data in Table V. Again the greatest decrease in the parameter being studied is found for the highest r value.

The theoretical results were used as guides to prepare polymers by the incremental addition procedure.

TABLE V
Comparison of \bar{P}_v/\bar{P}_n for the Control and the
Two- and Three-Portion Addition Procedures

| Regulating index r | \bar{P}_v/\bar{P}_n for division of modifier into portions | | |
|-------------------------|--|------|------|
| | 1 | 2 | 3 |
| 2 | 1.99 | 1.86 | 1.83 |
| 3 | 2.24 | 1.91 | 1.85 |
| 5 | 3.25 | 2.12 | 1.94 |
| 6 | 4.14 | 2.25 | 2.01 |
| 8 | 7.38 | 2.65 | 2.16 |
| 12 | 31.14 | 4.14 | 2.65 |

RESULTS

Modification was accomplished by incremental addition of t -C₁₀SH and Sulfole 90 mercaptans to a 70/30 butadiene-styrene mixture polymerized in an SBR 1500 recipe. The decyl mercaptan was divided only into two portions, and the nonyl isomer was added in two and in three portions. The amounts were adjusted to give a polymer of approximately 50 ML-4 Mooney viscosity, and the coagulated rubbers were fractionated in the gel permeation chromatograph. Polymerization and characterization data for the low-temperature experiments are given in Table VI, and the fractionation data are given in the corresponding five lines of Table VII. Plots of the distributions for the control and two-portion addition of t -C₁₀ mercaptan are presented in Figure 7, and the distribution data for the three experiments with Sulfole 90 mercaptan are plotted in Figure 8. The curves in Figures 7 and 8 show an obvious narrowing of the distribution for the polymers modified by incremental addition, and these curves also show a marked decrease in the humps which are on the control curves.

Two multiple addition experiments were conducted with the SBR 1000 recipe. Both Sulfole 105 and n -C₈ mercaptans were divided into seven equal portions. One was added initially, and the six remaining were added

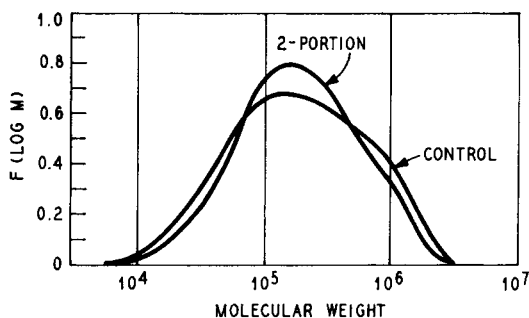


Fig. 7. MWD for the control and two-portion addition of t -C₁₀SH for modification of an SBR 1500 system.

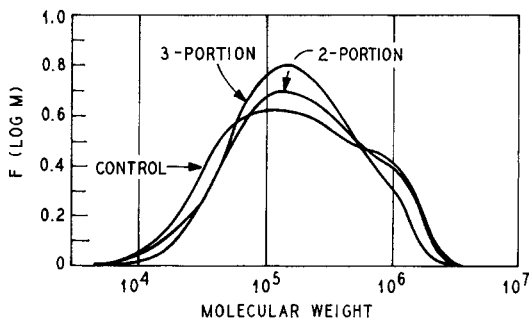


Fig. 8. MWD for the control, two-, and three-portion additions of t -C₉SH for modification of an SBR 1500 system.

TABLE VI
 Characterization Data for Copolymers Prepared by the Incremental Modifier Addition Procedure

| Recipe SBR | Type | Total amount, phm | Division of RSH, phm | Conversion for addn., % | Conv., % | Time, hr | Viscosity η_{inh}/M^{-4} | Regulating index r |
|------------|-----------------------------|-------------------|----------------------|-------------------------|----------|----------|-------------------------------|----------------------|
| 1500 | <i>t</i> -C ₁₀ | 0.176 | 0.175 | 0 | 60 | 6.6 | 2.22/50 | 5.7 |
| 1500 | <i>t</i> -C ₁₀ | 0.150 | 0.1, 0.05 | 0, 25 | 60 | 7.3 | 1.99/48 | |
| 1500 | <i>t</i> -C ₉ | 0.211 | 0.211 | 0 | 59 | 7.5 | 2.22/46 | 7.1 |
| 1500 | <i>t</i> -C ₉ | 0.150 | 0.1, 0.05 | 0, 20 | 59 | 7.9 | 2.10/47 | |
| 1500 | <i>t</i> -C ₉ | 0.150 | 0.1, .025, .025 | 0, 16, 31 | 59 | 7.8 | 1.87/46 | |
| 1000 | <i>t</i> -C ₁₂ | 0.293 | 0.293 | 0 | 68 | 9.2 | 1.89/44 | 3.8 |
| 1000 | <i>t</i> -C ₁₀₋₅ | 0.280 | 0.28/7 | Each 10% | 70 | 10.6 | 2.82/58 | 4.9 |
| 1000 | <i>n</i> -C ₈ | 0.250 | 0.25/7 | Each 10% | 70 | 10.3 | 2.51/44 | 19.1 |

TABLE VII
 MWD Data for Copolymers Prepared by the Incremental Modifier Addition Procedure^a

| Recipe SBR | Mercaptan | Nonlinear calibration | | | Infinite resolution | | | Linear calibration | | |
|------------|-----------------------------|-----------------------|-------------|-------|---------------------|-------------|------|--------------------|-------------|------|
| | | \bar{M}_w | \bar{M}_n | HI | \bar{M}_w | \bar{M}_n | HI | \bar{M}_w | \bar{M}_n | HI |
| | | Tung correction | | | Tung correction | | | Tung correction | | |
| 1500 | <i>t</i> -C ₁₀ | 404 | 71 | 5.7 | 374 | 96 | 3.90 | 371 | 99 | 3.76 |
| 1500 | <i>t</i> -C ₁₀ | 333 | 72 | 4.6 | 323 | 98 | 3.23 | 321 | 101 | 3.19 |
| 1500 | <i>t</i> -C ₉ | 401 | 62 | 6.4 | 370 | 85 | 4.35 | 371 | 88 | 4.23 |
| 1500 | <i>t</i> -C ₉ | 416 | 67 | 6.2 | 358 | 90 | 3.99 | 356 | 92 | 3.86 |
| 1500 | <i>t</i> -C ₉ | 344 | 86 | 3.99 | 315 | 103 | 3.06 | 311 | 105 | 2.95 |
| 1000 | <i>t</i> -C ₁₂ | 361 | 60 | 6.07 | 315 | 79 | 3.97 | 311 | 81 | 3.84 |
| 1000 | <i>t</i> -C ₁₀₋₅ | 593 | 52 | 11.39 | 450 | 73 | 6.19 | 439 | 75 | 5.89 |
| 1000 | <i>n</i> -C ₈ | 262 | 42 | 6.25 | 249 | 60 | 4.18 | 243 | 61 | 4.01 |

^a All M values shown are data obtained $\times 10^{-3}$.

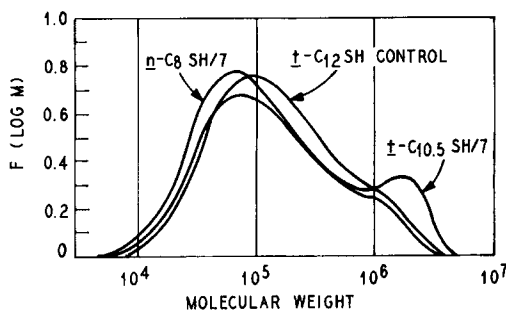


Fig. 9. MWD for modification of an SBR 1000 system with t -C₁₂SH as control and seven-portion additions of n -C₈SH and t -C_{10.5}SH.

at approximately 10% conversion intervals. These polymerizations were terminated at 70% conversion, and again Mooney viscosities of 50 ML-4 were strived for. A Sulfole 120 mercaptan-modified polymer was taken as a control. The polymerization and characterization data are in Table VI, and the fractionation data are in Table VII. Plots of these three "hot" copolymers are drawn in Figure 9. A saving of 15 wt-% of mercaptan was obtained by the seven portion addition of n -C₈SH in comparison to the t -C₁₂SH control, which is the modifier usually used in the commercial production of SBR 1000. However, on a molar basis, the t -C₁₂SH is still more efficient than the n -C₈SH.

Both the characterization and fractionation data indicate that the portion-wise addition of Sulfole 105 mercaptan gave a MWD different from that of the others, as is evident from the bimodal shape of the curve.

DISCUSSION

Model Equations and Simulated Calculations

These mathematical results are useful guides for selecting conditions and establishing limits for the incremental addition experiments. Equations (1) and (2) can be used to show that modifiers with high regulating indexes are needed for efficient modification of polymerizations terminated at low conversions. If a manifold incremental modifier experiment is viewed as a sum of a consecutive series of short conversion intervals, than in manifold addition modifiers with much higher regulating indexes are needed for efficient modification in comparison to the single addition control taken to the same final conversion.

Calculations with eq. (5) show that little benefit in modification is obtained by the multiple addition of a modifier with low r values; and in cases of improper addition, the results are poorer than that obtained for the control (Fig. 1). The data in Table II show that the lowest molecular weight was calculated for a regulating index of 5. A plot of the last column of this data, r versus molecular weight, indicates a minimum falls at about $r = 5.5$. This r value checks well with the polymerization terminated at

30% conversion (Table I). Another interesting observation from the data in Tables II and III is that a lower molecular weight could be obtained with incremental addition of modifiers with r greater than 2 than for any of the conditions used for the calculations for $r = 2$.

The most important conclusion derived from the MWD data in Tables IV and V is that this parameter is controlled principally by the regulating index. The lowest heterogeneity index was obtained for the modifier with the lowest r value. It appears doubtful that a b value could be found for addition of the most efficient modifier in this study, $r = 5$, that would give a heterogeneity index lower than that calculated for $r = 2$. This means the most efficient modifier does not give the narrowest molecular weight distribution. The plot of the \bar{P}_w/\bar{P}_n versus X_2 data for $r = 2$ in Figure 4 shows that the distribution can be changed unfavorably by the improper incremental addition of the modifier. However, impressive lowering of \bar{P}_w/\bar{P}_n is obtained by incremental addition of modifier even if the regulating index is still relatively low (Figs. 5 and 6). And in the case where $r = 12$, a 12-fold decrease in the ratio was calculated for the most favorable conditions used for this modifier. Significantly, a narrower distribution is calculated for the most efficient modifier studied, $r = 5$, by the three-portion addition than is shown for the control addition for the modifier with $r = 2$.

Experimental Results

All the incremental addition experiments in this study show an enhanced modification in comparison to the control. Previous reports^{1,2,7} show, however, that not all modifiers respond to incremental addition. Only those modifiers that distribute rapidly between phases show beneficial responses. Furthermore, the simulated calculations assume that all the increments are distributed instantly between phases. Since the latter condition is impossible to attain under the most favorable conditions,¹ some divergence between theory and experiment can be expected. Another assumption made in the derivation of the model eq. (3) was that for the copolymerization of butadiene and styrene a constant average monomer concentration could be used over the conversion interval of interest. This assumption has been found satisfactory in previous studies, but this simplification will contribute some divergence from experimental reality also.⁸ An additional complication in diene polymerizations is the occurrence of branching and crosslinking during the course of the reaction.^{6,9,10} These factors contribute to the divergence between theoretical and experimental molecular weights. For this reason, qualitative comparison and trends will be relied on in most of the comparisons with theory.

Both incremental addition modifications at 5°C showed a marked change in the MWD curve in comparison to the control. The experimental curves were narrower, more symmetrical, and had lost the hump on the curve for the higher molecular weight fraction (Figs. 7 and 8). The decrease in heterogeneity for the C₁₀SH-incremental polymer was 17%, whereas that for the three-increment C₉SH modification was 30%. Although the latter

reduction is about one half that estimated from the theoretical values in Table V, the value for the index of 3.0 is about as low as has been obtained by the standard procedure for the homologous series of mercaptans ranging from *t*-C₁₆ to *t*-C₉ mercaptans in a previous study.⁶ The possibility exists that even a lower heterogeneity index might be obtained if a better set of conditions for adding the modifier were selected.

The multiple addition of *n*-octyl mercaptan was tried to test the idea that satisfactory modification could be obtained with this modifier when addition is carried out properly. Excellent results were obtained for the seven-portion addition of the *n*-octyl mercaptan ($r = 19.1$), but much poorer results were obtained with the *t*-C_{10.5} mercaptan ($r = 4.9$), Table VII. The former polymer had a \bar{P}_w/\bar{P}_n value approaching that of the Sulfole 120 mercaptan control,⁶ whereas the latter polymer had a much higher ratio as well as a bimodal distribution. Although the octyl modifier was more efficient than the dodecyl control on a weight basis, the control was more efficient on a molar basis. Nevertheless, the experimental \bar{M}_w/\bar{M}_n ratio for the polymer made with the octyl modifier is much lower, Table VII, than would be expected from the theoretical calculation for a polymer made with *n*-octyl mercaptan added all originally, Table V. The differences of weight and molar efficiencies are adequately discussed in the previous publication.²

The experimental results support the contention that for a manyfold addition of modifier, the regulating index should be high. If the interval between additions of increments is 10%, the regulating index of the modifier preferably should be close to the one that would give efficient modification if polymerization were terminated at 10% conversion. The theoretical r values for optimum modifiers for polymerizations stopped at different conversions are listed in Table III.

The authors are indebted to H. L. Shreffler of the Research Division and to Lee Boyer of the Computer Department of Phillips Petroleum Company.

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Received August 3, 1970

Revised October 29, 1970; December 24, 1970