

Incremental Modification of Styrene-Butadiene Rubber with *tert*-Dodecyl Mercaptan

C. BOOTH, L. R. BEASON, and J. T. BAILEY

Shell Chemical Company, a Division of Shell Oil Company, Synthetic Rubber Division, Torrance, California

INTRODUCTION

The molecular weights and molecular weight distributions of styrene-butadiene rubbers, and hence the physical properties of the rubbers, are controlled principally by the addition of a suitable modifier to the polymerization recipe. *n*-Dodecyl mercaptan is usually included in recipes for "hot" rubbers (50°C. polymerization temperature), and *tert*-dodecyl mercaptan in recipes for "cold" rubbers (5°C. polymerization temperature).

Incremental or continuous addition of modifier to the polymerizing system (as opposed to conventional modification in which all the modifier is added initially) has been advanced^{1,2} as a simple method of improving the molecular weight distribution of the rubber. Suitable incremental modification (and for practical purposes this has been taken to mean modification which results in the production of a polymer of constant intrinsic viscosity throughout the reaction) should lower the proportions of very high and very low molecular weight polymer in the rubber, and the resulting product should show improved performance.

Lawrence, Hobson, and Borders² have characterized continuously modified "hot" rubber produced to a constant intrinsic viscosity throughout the reaction and have reported surprisingly little difference in molecular weight distribution in comparison with a conventionally modified control. We have recently taken the opportunity to examine the effect of incremental modification upon the cold polymerization of styrene-butadiene copolymer with the use of *tert*-dodecyl mercaptan modifier. Working with "cold" rubber precludes direct comparison with the work of Lawrence, Hobson, and Borders; however, the "cold" rubber offers considerable advantages in the matter of interpretation of experimental data, in that such rubber has a narrower molecular weight distribution and contains little highly branched polymer.

BACKGROUND OF THE EXPERIMENT

The "cold" emulsion polymerization system has been shown³ to conform to case II of the Smith-Ewart theory,^{4,5} in which the initiation of polymerization is the consequence of the diffusion of a single radical into a particle, while termination takes place almost immediately upon the diffusion of a second radical into the particle. In the presence of a suitable chain transfer agent (modifier), the rate of entry of radicals into the particles is very much lower than the rate of chain transfer. Consequently, the initiation and termination reactions can be neglected when the molecular weight distribution is under consideration. The kinetic scheme generally applied to this polymerization involves, therefore, an initiation-termination reaction (chain-transfer reaction) which simultaneously terminates a growing chain and produces a single initiating radical, and a propagation reaction which is assumed to be free from branching and crosslinking (we shall see later that this assumption is quite reasonable).

It has been shown⁶ that the weight distribution $w(x)$ of degree of polymerization (x) of the polymers produced under these conditions can be represented by the summation of a series of distributions of the form

$$w(x) = x(1 - p)^2 p^{x-1} \quad (1)$$

Each distribution is characterized by a certain value of p calculated for an increment of conversion over which the concentration of reactants (monomer and modifier) can be taken as constant. The distribution described by eq. (1) has been called⁶ the "most probable," and its ratio of weight-average molecular weight \bar{M}_w to number-average molecular weight \bar{M}_n is equal to two.

The quantity p is given by the equation

$$(1 - p) \simeq C_s[S]/[M] \quad (2)$$

where C_s is the transfer constant (i.e., the ratio of the specific rate constant for transfer to that for propagation) and $[S]$ and $[M]$ are the concentrations of modifier and monomer in the monomer-polymer particles (i.e., at the locus of the polymerization).

In a conventionally modified reaction the ratio $[S]/[M]$ normally varies throughout the reaction, thus varying p and so producing a polymer with molecular weight distribution of ratio \bar{M}_w/\bar{M}_n greater than two. However, if the ratio $[S]/[M]$ is constant throughout the reaction, then p is constant and polymer of the narrowest molecular weight distribution obtainable from this reaction is produced. Such a reaction with constant p is the aim of an incremental modification.

In designing the polymerization experiment there would appear at first glance to be some advantage to continuous addition of modifier throughout the reaction. However, a simple calculation based upon eqs. (1) and (2) and reasonable values of C_s reveals that there is very little to be gained, in terms of narrowing the distribution, by preferring continuous addition over incremental addition at 10% conversion intervals.

EXPERIMENTAL

Styrene-Butadiene Rubbers

The incrementally modified rubber 2M26 and its control, conventionally modified rubber 2M11, were prepared by M. Feldon and R. F. York of the Shell Chemical Company, Torrance, California. Both were prepared according to the 1502 recipe⁷ (sulfoxylate activator and mixed soaps of rosin and fatty acids). Also used for comparison with 2M26 were two samples of commercial 1500-type rubber⁷ (pyrophosphate activator and rosin acid soap). These rubbers are NBS-1500, the National Bureau of Standards standard bale No. 386, and S-1500. (S polymers are the styrene-butadiene copolymers manufactured by Shell Chemical Company. The differences between the recipes for the 1502 and 1500 rubbers are slight and do not qualify our conclusions.

The calculation of a program of incremental addition of the modifier requires a knowledge of C_s , eq. (2). The effective transfer constant C_s' (here we distinguish between the experimentally determined transfer constant C_s' and the transfer constant defined by kinetics) has been measured⁸ for our system in the usual way,¹ i.e., by determining the residual modifier at various conversions

in a conventionally modified reaction and by use of the relation

$$C_s' = d \ln[S']/d \ln[M'] \quad (3)$$

where $[S']$ and $[M']$ are the modifier and monomer concentrations in the system. A value of $C_s' = 4.1$ was found,⁸ and this value was used in computing the program of modifier addition for 2M26, shown in Table I. The relevant preparative details for the other rubbers are also given in Table I. The variation of the inherent viscosity (~ 0.25 g. rubber in 100 cc. toluene at 30°C.) of 2M26 and 2M11 is given in Table II.

TABLE I
Details of Preparation of the Styrene-Butadiene Rubbers

Rubber	Basic recipe	Conversion, %	Modifier, ^a phm ^b	Program of addition
2M26	1502	60	0.0258	Initially
			0.0515 ^c	At 5% conversion
			0.1025 ^c	In equal increments at 10, 20, 30, 40, and 50% conversion
2M11	1502	63	0.18	Initially
S-1500	1500	~ 60	0.18	Initially
NBS-1500	1500	~ 60	0.20	Initially

^a Sulphole B-8: 96 wt.-% *tert*-dodecyl mercaptan.

^b Parts per hundred monomer.

^c Added as a 4 wt.-% solution in styrene.

TABLE II
Inherent Viscosity During the Polymerization of 2M26 and 2M11

Rubber	Inherent viscosity at various conversions					
	10%	20%	30%	40%	50%	60%
2M26	2.1	2.1	2.1	2.1	2.1	2.0
2M11	1.0	1.1	1.2	1.4	1.6	1.8

Characterization of the Rubbers

2M26 and NBS-1500 have been fractionated. Number- and viscosity-average molecular weights have been determined for all the rubbers.

All the experimental techniques used in this work have been fully described in an earlier paper.⁹ Any departure from these procedures is noted below or in the tables of results. A brief description of each technique follows.

Fractionation. Fractions were obtained by successive precipitation fractionation, i.e., by the incremental addition of methanol to a dilute solu-

tion of the polymer in toluene. The fractions were characterized by dry weight, osmometry, and dilute solution viscometry.

Osmometry. Number-average molecular weights were obtained with the use of Stabin-Immergut¹⁰ osmometers with gel cellophane (type 450) membranes conditioned to toluene via methyl ethyl ketone.⁹ The number-average molecular weights so obtained are peculiar to the membrane used and are denoted by $\bar{M}_n(450)$.

Viscometry. Intrinsic viscosities $[\eta]$ were determined with modified Ubbelohde viscometers. Kinetic energy corrections were applied. Viscosity-average molecular weights (\bar{M}_v) were calculated from the equation of French and Ewart.¹¹

$$[\eta] = 5.4 \times 10^{-4} \bar{M}_v^{0.66} \quad (4)$$

The use of eq. (4) for "cold" rubbers has been discussed in the earlier paper.⁹

Fractionation Data. The fractionation data were analyzed by the statistical method with the generalized exponential distribution.⁹ This method of analysis has been shown^{9,12} to give a satisfactory representation of polymer molecular weight distributions. The fractionation data for 2M26 are given in Table III; the data for NBS-1500 have been reported earlier.⁹

TABLE III
Fractionation of 2M26^a

Fraction	Weight, g.	$\bar{M}_n(450)$	$[\eta]$	\bar{M}_v	k
1	1.776	428,000	4.06	746,000	0.50
2	1.532	295,000	2.63	387,000	0.41
3	1.734	173,000	1.77	205,000	~0.52
4	1.457	121,000	1.34	139,000	0.46
5	1.043	68,000	0.97	85,000	0.44
6	1.070	51,000	0.77	60,000	0.39
7	0.449	(18,000)	0.36	19,000	0.41
Original (methanol- extracted)	—	99,000	2.02	261,000	0.41

^a Sample weight 10.05 g.; last fraction taken from 40/60 methanol/toluene (v/v).

Points of interest in the experiments are as follows.

(1) *Soluble Material.* Some 8.2 wt.-% of the 2M26 was soluble in the 40/60 methanol-toluene mixture. When the 7 wt.-% of nonpolymeric materials (organic acids, soaps, antioxidants, etc.) present in the rubber is subtracted, some 1.2 wt.-% of very low molecular weight polymer is left, which is excluded from Table III and hence from

the molecular weight distribution. This amount is comparable with the 0.7 wt.-% of the NBS-1500 discounted in the corresponding experiment;⁹ the difference between the two values is due in large part to the differing methanol-toluene mixtures used to obtain the last fractions in the two fractionations.

(2) *Material Balance and Intrinsic Viscosity Balance.* The recovery in the experiments was 99.3% (2M26) and 96.3% (NBS-1500). The weight averages of the intrinsic viscosities of the fractions were 2.02 (2M26) and 1.89 (NBS-1500); the intrinsic viscosities of the original polymers were 2.02 and 1.95, respectively. The deficit in both material and intrinsic viscosity for NBS-1500 is consistent with the loss of a small amount of high molecular weight polymer.

(3) *Number-average Molecular Weights.* In each fractionation experiment the molecular weight of the last fraction was low enough to render the osmometric method of determination of molecular weights useless because of membrane permeation. The number-average molecular weight $\bar{M}_n(450)$ for these fractions was therefore estimated by equating the number-average molecular weight

$$\frac{\sum w_i}{\sum w_i / (\bar{M}_n)_i}$$

obtained by summing the fractions with the number-average molecular weight determined for the original polymer. The values so obtained are quoted in parentheses in Table III and in Table VI of Reference 9. The approximations implicit in this procedure have been discussed in the previous paper.⁹

(4) *Branching.* The values obtained for the Huggins constant (k) are given in Table III and in Table VI of Reference 9. Following Cragg and co-workers¹³ we interpret these values as indicating the absence of serious branching and crosslinking in these rubbers, which supports the assumptions used in deriving eq. (1).

The Molecular Weight Distributions

The integral weight distributions of the degrees of polymerization of 2M26 and NBS-1500, as calculated by the statistical method, are shown in Figure 1.

Direct comparison of these distributions is not strictly meaningful, since the total modifier levels used in the polymerization differ for the two polymers (see Table I). However, it is known⁹

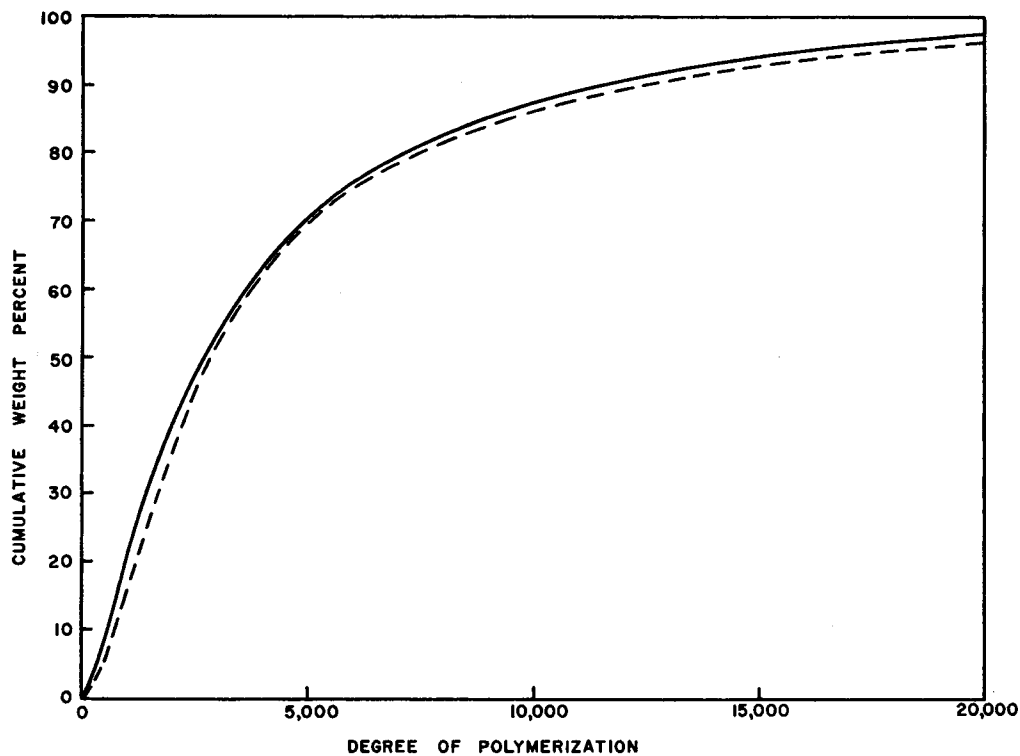


Fig. 1. The integral weight distributions of 2M26 (--) and NBS-1500 (—).

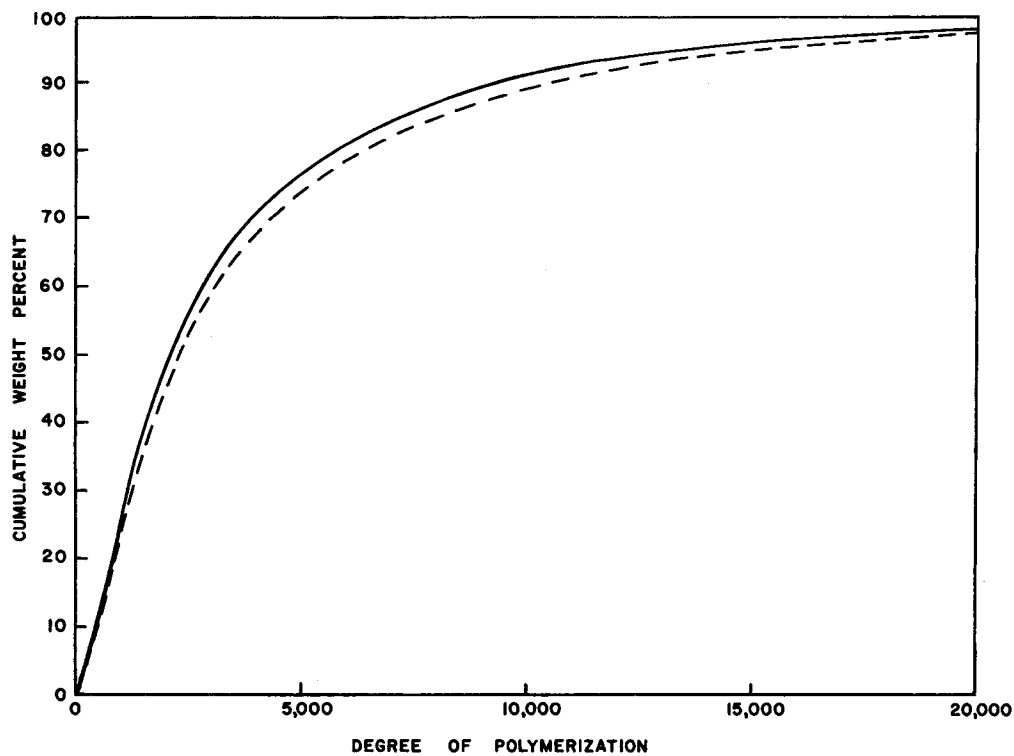


Fig. 2. The integral weight distributions of conventionally modified styrene-butadiene rubber calculated for initial modifier levels of 0.18 phm (--) and 0.20 phm (—) with $C_s = 4.1$.

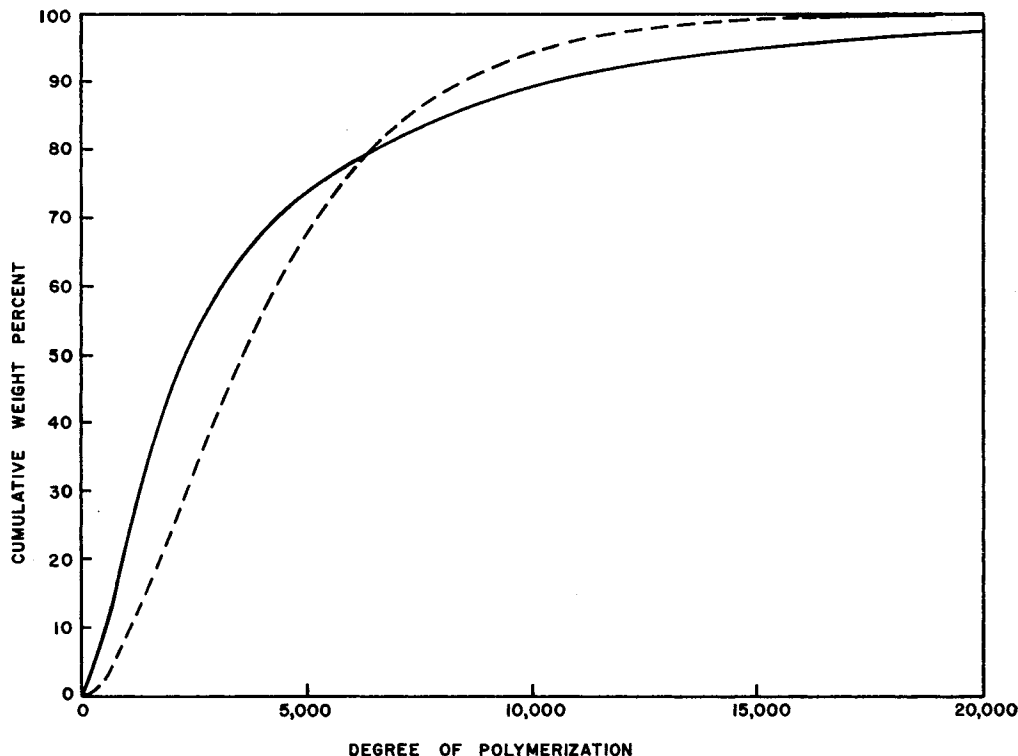


Fig. 3. The integral weight distributions of a conventionally modified rubber (—) and an ideally incrementally modified rubber (- -) of the same weight-average molecular weight.

that the distribution of a conventionally modified rubber is approximated fairly well by the distribution one can obtain from the kinetic treatment given earlier in this paper, i.e., eqs. (1) and (2). The differences which exist between the molecular weight distributions of two polymers prepared in the conventional manner at differing modifier levels can therefore be predicted with some confidence.

Figure 2 shows the comparison of the calculated distributions of conventionally modified polymers having modifier levels of 0.20 phm and 0.18 phm; C_s was assumed to be 4.1. It can be seen that the differences between the molecular weight distributions of 2M26 and NBS-1500 are quite similar to the differences one would expect between two rubbers conventionally modified at these modifier levels.

We conclude that incremental modification in this system produced very slight changes in the molecular weight distribution as compared to the predicted effect. The predicted effect is illustrated in Figure 3 where molecular weight distributions calculated for a conventionally modified rubber and for an ideally incrementally modified rubber

are compared. Comparison of Figures 1, 2, and 3 clearly illustrates the absence of the desired effect.

The Molecular Weight Ratios

It is well known that the ratio of the viscosity-average molecular weight to the number-average molecular weight, \bar{M}_v/\bar{M}_n , is a measure of the width of the number distribution of molecular weights. In Table IV are given the ratios $\bar{M}_v/\bar{M}_n(450)$ for methanol-extracted samples of the four rubbers considered in this work. Both 2M11 and S-1500 were prepared with a modifier level of 0.18 phm and are directly comparable with 2M26.

As anticipated, the $\bar{M}_v/\bar{M}_n(450)$ ratio is higher for NBS-1500 than for the other rubbers. However, the $\bar{M}_v/\bar{M}_n(450)$ ratios for the two con-

TABLE IV
 $\bar{M}_v/\bar{M}_n(450)$

Rubber	$\bar{M}_n(450)$	\bar{M}_v	$\bar{M}_v/\bar{M}_n(450)$
2M11	99,000	261,000	2.6
2M26	96,000	246,000	2.6
S-1500	95,000	246,000	2.6
NBS-1500	80,000	246,000	3.1

ventionally modified rubbers of 0.18 phm modifier level are identical with that for 2M26. This finding is in complete agreement with our fractionation experiments.

DISCUSSION

Incremental modification in this recipe has produced little or no improvement of the molecular weight distribution over conventional modification.

Any hypothesis advanced to account for this finding must explain, in addition, the almost constant intrinsic viscosity ($\pm 5\%$) observed during the reaction. In the following paragraphs it is shown that a consistent explanation is provided by the limiting effect of diffusion upon the mass transfer of modifier in the system.

We will make no attempt to explain why the molecular weight distributions of the two polymers discussed in this work are essentially identical. We do not, in fact, regard this identity as significant. We assume that it is merely an interesting coincidence.

The Effect of Mass Transfer of Modifier

In order to equate C_s' with C_s it would be necessary to assume that the ratio of the concentrations of modifier and monomer in the monomer-polymer particles is equal to their ratio in the system, i.e.,

$$[S']/[M'] = [S]/[M] \quad (5)$$

In other words, it would be assumed that any effects due to diffusion can be neglected. (We are ignoring here any loss of mercaptan in reactions other than the chain-transfer reaction. In a "cold" polymerization such losses will be quite small and will not affect our subsequent argument.)

The effective transfer constant (C_s') for these systems (butadiene-styrene at 5°C. with *tert*-dodecyl mercaptan modifier and a reaction time of 6-8 hr.) has been determined in reactors of varying size and varying agitation. Under the conditions of preparation of 2M26 and 2M11, i.e., 9- or 20-gal. reactors with Brumagim stirring, $C_s' = 4.1$ was obtained.⁸ For 1/2- or 1-gal. reactors and anchor, marine, and Brumagim stirrers, values of C_s' from 2.7 to 3.5 have been found.¹⁴ Furthermore, the value of C_s' one would obtain by extrapolating to 5°C. values obtained¹ at higher temperatures (where diffusion effects are demonstrably smaller) is about 4.7. It is clear, then, that diffusion has a considerable effect upon the value of C_s' in this system and hence upon the course of reaction (see also Reference 16).

Since, of necessity,

$$C_s' [S']/[M'] = C_s [S]/[M] \quad (6)$$

then, by eq. (2),

$$(1 - p) \simeq C_s' [S']/[M'] \quad (7)$$

However, if C_s' is a function of the experimental conditions (rate of stirring, time of reaction, concentration of reactants, etc.), a value of C_s' determined under one set of conditions cannot be expected to hold under another. Thus, in the system under study, i.e., the incremental modification of 2M26 with the use of *tert*-dodecyl mercaptan, it is apparent that the value of C_s' determined for the conventional reaction, 4.1, will not hold since the conditions of concentration of the modifier are greatly different (see Table I). (This implies that the transfer constant measured in a conventional polymerization should vary with the modifier level whenever diffusion effects are important. Pertinent data available¹⁵ do not contradict this, but variations of reaction time and stirring rate between experiments do not allow unequivocal conclusions to be drawn.) It is possible, however, to state with some confidence that the additions of modifier programmed for $C_s' = 4.1$ should not give the desired modification, i.e., a constant value of p . Moreover, it is clear that even if addition of modifier were programmed so that the ratio of monomer to mercaptan in the system, $[S']/[M']$, were constant throughout the reaction, the desired modification would still not be produced since the rate of mass transfer, and hence C_s' (it is the product $C_s' [S']/[M']$ which determines p), would still vary: the rate of mass transfer must be dependent upon the concentration of modifier in the monomer phase, and the monomer phase will diminish more rapidly than the concentration of monomers in the system.

One can speculate further concerning the effect of diffusion upon the course of the reaction. It has been shown¹⁶ that the rate-determining step in the transfer of mercaptan from the monomer phase to the monomer-polymer particles is mass transfer through the oil/water interface (i.e., the monomer phase/water interface), diffusion through the water phase being of secondary importance. If we assume that the coefficient governing the transfer of modifier through the interface (the mass transfer coefficient) does not depend upon concentration, and if we assume also that the modifier is distributed evenly throughout the whole monomer phase, then the effective transfer constant

(C_s) for the incrementally modified polymerization will vary from a low value (<4.1) initially, when the concentration of modifier in the monomer phase is low and the surface-to-volume ratio of the phase is low, to a high value (>4.1) at high conversions when the monomer phase is but a small fraction of the total monomer in the system and the modifier concentration and the surface-to-volume ratio are greater. If the coefficient controlling transfer across the oil/water interface does vary with concentration the above conclusions remain broadly true, since the most probable effect of an increase in concentration would be to raise its value.

Such a variation in transfer constant C_s' can only result in the formation of more high molecular weight material initially and more low molecular weight material later in the reaction than would be formed in an ideally incrementally modified reaction. The molecular weight distribution of the polymer so formed would be wider than the "most probable."

The possibility of uneven distribution of the modifier in the monomer phase due to its mode of addition as a 4 wt.-% solution in styrene must be considered. It is just conceivable that this circumstance, coupled with an extreme dependence of the mass transfer coefficient upon concentration, could lead to a cycling of C_s' with the period of the addition of increments of modifier. This again would lead to a distribution wider than the "most probable." However, this possibility is not thought to be worthwhile pursuing in further discussion: no evidence of cycling can be found in intrinsic viscosity data; the linearity of the plots of $d \ln [S']/d \ln [M']$ in the conventional determination of C_s' suggests the absence of an extreme dependence of the mass transfer coefficient upon concentration; finally, the instability of the unstirred monomer emulsion (a monomer layer is known to form rapidly when stirring is stopped) argues against a lengthy persistence of any large variation of modifier concentration in the monomer phase droplets in the stirred system.

The Intrinsic Viscosity-Conversion Curve

We have shown that the effect of mass transfer dependence would be a broadening of the molecular weight distribution. We have yet to show that the distribution found experimentally, \bar{M}_v/\bar{M}_n (450) $\simeq 2.6$, is consistent with the small variation in intrinsic viscosity ($\pm 5\%$) recorded for the polymerization (Table II).

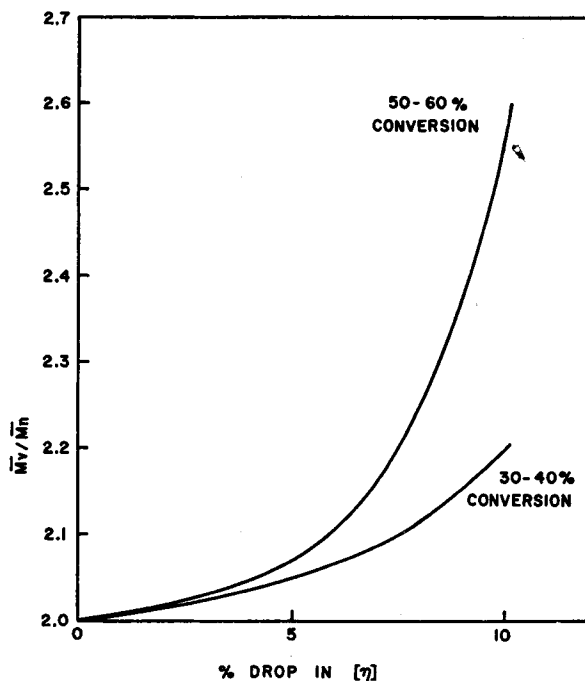


Fig. 4. The variation of the ratio \bar{M}_v/\bar{M}_n with intrinsic viscosity.

This is easily shown provided that it is accepted, following the earlier argument, that in an incrementally modified polymerization the low molecular weight material will be formed toward the end of the reaction. For example, let us assume that at 50% conversion the reaction has been rather well modified and the ratio \bar{M}_v/\bar{M}_n is 2.0 with $[\eta] = 2.0$ (i.e., $\bar{M}_v = 255,000$). If the value of $[\eta]$ drops 10% (the maximum permissible within the limits of error of the experiment) then the polymer made between 50% and 60% conversion would be of $[\eta] = 0.80$, or $\bar{M}_v = 64,000$. Assuming that this polymer was of the same distribution as the polymer produced previously, i.e., $\bar{M}_v/\bar{M}_n = 2$, then the number-average molecular weight of the polymer would be 32,000 and so the viscosity- to number-average ratio at 60% conversion would be 2.56.

Actually, it is inconceivable that $\bar{M}_v/\bar{M}_n = 2.0$ for the polymer produced in the 50-60% conversion interval, in view of the large drop in molecular weight of the polymer. It seems possible that \bar{M}_v/\bar{M}_n values for this polymer might be 3 or 4. The calculation will give the minimum possible change in \bar{M}_v/\bar{M}_n of the whole polymer; the actual changes could be several times larger.

Figure 4 indicates the changes in \bar{M}_v/\bar{M}_n which may be calculated in this way for a given percentage drop in intrinsic viscosity in two conversion ranges.

The effect is sufficiently large to explain the distribution widths found in this work.

CONCLUSIONS

Incremental modification with the use of a modifier (such as *tert*-dodecyl mercaptan at 5°C.) which results in the modification reaction being mass transfer-controlled will be effective only when the programming of the modifier additions is such that mass transfer effects are properly taken into account. Putting this another way, the modifier program must ensure that the intrinsic viscosity of the product is constant to $\pm 1\%$, especially in the later stages of the reaction. These requirements are quite severe and we conclude, therefore, that incremental modification should not be attempted with modifiers which are mass transfer-controlled (see also Reference 1).

These conclusions are probably quite general. *n*-Dodecyl mercaptan, the modifier, used by Lawrence, Hobson, and Borders in their work² at 50°C. is, in fact, mass transfer sensitive.

We wish to thank Mr. A. R. Calloway and Mr. F. S. Harryman for much of the experimental work. In addition, we are greatly indebted to Mr. M. Feldon and Mr. R. F. York, who prepared the experimental rubbers discussed in this paper.

References

1. Kolthoff, I. M., and W. E. Harris, *J. Polymer Sci.*, **2**, 49 (1947).
2. See C. F. Fryling, in *Synthetic Rubber*, G. S. Whitby, Ed., Wiley, New York, 1954, p. 253.
3. Morton, M., P. P. Salatiello, and H. Landfield, *J. Polymer Sci.*, **8**, 215 (1952).
4. Smith, W. V., and R. H. Ewart, *J. Chem. Phys.*, **16**, 592 (1948).
5. Bovey, F. A., I. M. Kolthoff, A. I. Medalia, and E. J. Meehan, *Emulsion Polymerization*, Interscience, New York, 1955, p. 180.
6. See for example P. J. Flory, *Principles of Polymer Chemistry*, Cornell Univ. Press, 1953, p. 335.
7. See, for example, ASTM Standards, Vol. 9, Am. Soc. Testing Materials, Philadelphia, 1958, p. 1812.

8. Feldon, M., H. L. Vincent, and R. F. York, private communication.

9. Booth, C., and L. R. Beason, *J. Polymer Sci.*, **42**, 81, 93 (1960).

10. Stabin, J. V., and E. H. Immergut, *J. Polymer Sci.*, **14**, 209 (1954).

11. French, D. M., and R. H. Ewart, *Anal. Chem.*, **19**, 165 (1947).

12. Booth, C., *J. Polymer Sci.*, **45**, 443 (1960).

13. See, for example, L. H. Cragg and G. R. H. Fern, *J. Polymer Sci.*, **10**, 185 (1953).

14. Ehrig, R. J., A. O. Rockswold, and R. F. York, private communication; J. S. Buehler and A. O. Rockswold, private communication.

15. Reich, M. H., Office of Rubber Reserve Development Report CD-1985, November 1, 1949.

16. Meehan, E. J., I. M. Kolthoff, and P. R. Sinha, *J. Polymer Sci.*, **16**, 471 (1955).

Synopsis

The molecular weights and molecular weight distribution of a styrene-butadiene rubber produced at 5°C. according to an incrementally modified recipe with *tert*-dodecyl mercaptan modifier, do not differ significantly from those of similar conventionally modified rubbers. The limiting effect of diffusion upon the mass transfer of mercaptan in the system provides a consistent explanation of this finding.

Résumé

Les poids moléculaires et la distribution de poids moléculaire de caoutchoucs styrène-butadiène préparés à 5°C en employant un procédé à variations progressives et utilisant le *tert*-dodécyl mercaptan comme agent modificateur, ne diffèrent pas de façon significative de ceux de caoutchoucs semblables, modifiés suivant la méthode habituelle. L'effet limite de la diffusion sur le transfert du mercaptan dans ce système explique cette constatation.

Zusammenfassung

Die Molekulargewichte und die Molekulargewichtsverteilung eines bei 5°C nach einem durch Zusatz von *tert*-Dodecylmercaptan in steigendem Masse modifizierten Rezept erzeugten Styrol-Butadienkautschuks weichen nicht wesentlich von denen ähnlicher, auf übliche Weise modifizierter Kautschuke ab. Der begrenzende Einfluss der Diffusion auf den Massentransfer des Mercaptans im System macht diesen Befund verständlich.

Received July 12, 1960