

Molecular Weight Distribution of Polystyrene and of Butadiene-Styrene Copolymers Prepared in Emulsion Systems

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Synopsis

Polystyrene and butadiene-styrene copolymers (SBR) were prepared in emulsion systems with a homologous series of commercial mercaptan modifiers. The molecular weight distribution (MWD) of the sets of polymers changed in a consistent manner when the regulating index of the mercaptan was relatively low. However the shape of the MWD curves appeared distorted in comparison to theoretical curves when the modifier depleted rapidly and when divinylbenzene was present in the system. The divergence from the theoretical curve is attributed to a higher degree of branching in the high molecular weight fractions. Differences in MWD of SBR made with *n*- and *tert*-dodecyl mercaptans was marked. Notable differences were also found for SBR 1500 samples from the industry at random, but only slight differences were seen in a set of SBR 1503 samples. This study shows how the MWD of polymers prepared in emulsions can be varied simply by use of modifiers with different regulating indexes.

INTRODUCTION

In previous reports the problems of selecting an optimum modifier¹ and of incremental addition of modifiers^{1,2} for emulsion polymerization systems were considered theoretically and tested experimentally. In those publications the molecular weight distribution (MWD) was examined briefly and in another report the fractionation of some emulsion polymers by the Baker-Williams technique was reported more extensively.³ Since the previous work was completed, the Waters' gel permeation chromatograph has made the study of MWD of polymers feasible. Some of the polymers prepared in the previous studies^{1,2} have been examined by means of the Waters' apparatus.

The present report covers the MWD of polystyrene and of butadiene-styrene copolymers (SBR) prepared in an emulsion system with a homologous series of commercial modifiers as well as with several experimental modifiers. For comparison of experimental results with theory, simulated curves were obtained by calculations with known equations.

EXPERIMENTAL

Modifiers

The homologous series of Sulfole mercaptans (Phillips), ranging from 160 to 90 (the numbers represent the average number of carbons in the alkyl chains times ten), used in the previous studies have been characterized already.¹ Two of the experimental modifiers, cyclododecadienyl and *tert*-octyl mercaptan, were also included in the same report.

Polymerization Procedure

In the laboratory the sulfoxylate⁴ and persulfate⁵ recipes were used in bottle batch polymerizations⁵ to prepare polymers at 5° and 50°C. Attempts were made to compare polymers at either the same inherent viscosity or Mooney viscosity (ML-4, 100°C, ASTM D 927-57T).

Commercial SBR Elastomers

SBR 1500, 1502, 1503, and 1712 samples were obtained from the industry at random.

Gel Permeation Fractionation

Fractionations were conducted in a Water's apparatus provided with 10⁷, 10⁶, 10⁴, and 10³ Å columns, and the determinations were run at the ambient temperature of an air-conditioned room. The solvent was tetrahydrofuran pumped at a rate of 1 ml/min. Calibration curves were based on commercially available, standard polystyrenes and on narrow distribution polybutadiene and random butadiene-styrene copolymers prepared in solution and standardized in these laboratories. The calibration equations obtained with the standards and used in the Tung⁶ procedure of correction for dispersion were, for polystyrene:

$$v = 47.1 - 4.2 \log (M) \quad (1)$$

for butadiene-styrene random copolymer:

$$v = 47.93 - 4.485 \log (M) \quad (2)$$

where v is the eluant volume and M is the weight-average molecular weight. The polybutadiene calibration curve, which was not linear, was also used in calculating molecular weight by applying a factor of 1.9 for polystyrene and 1.2 for the copolymer. Thus for each fractionation, three sets of molecular weight values are given: one based on the nonlinear calibration curve, assumed to be parallel to the standard polybutadiene curve, a second based on the calibration with standard polymers of the same type and an assumed infinite resolution, and the third based on the Tung correction or dispersion by the polynomial expansion method.

TABLE I
 MWD Data for NBS Polystyrenes 705 and 706

Poly- styrene	Nonlinear calibration			Linear calibration					
	\bar{M}_w^a	\bar{M}_n	HI^a	Infinite resolution			Tung correction		
				\bar{M}_w	\bar{M}_n	HI	\bar{M}_w	\bar{M}_n	HI
705	174	143	1.22	183	147	1.25	178	151	1.18
706	302	109	2.76	315	122	2.58	307	126	2.44

^a \bar{M}_w , \bar{M}_n , and HI for NBS 705: 179.3×10^3 , 170.9×10^3 , and 1.07, respectively; for 706: 257.8×10^3 , 136.5×10^3 , and 2.1; all \bar{M} 's are $\times 10^{-3}$; $HI = \bar{M}_w/\bar{M}_n$.

The apparatus and procedure used gave the characteristics shown in Table I for National Bureau of Standards (NBS) polystyrenes 705 and 706. The same columns and calibrations were used throughout this study.

Model Equations and Simulated Calculations

Heterogeneity Index. The number-average and weight-average degree of polymerization equations have been derived and used by others previously⁷⁻⁹

$$\bar{P}_n = (M_0X)/S_0[1 - \exp(-rX)] \quad (3)$$

$$\bar{P}_w = 2(M_0/S_0) \{ [\exp(rX) - 1]/r^2X \} \quad (4)$$

$$\bar{P}_w/\bar{P}_n = 2 [\exp(rX) - 2 + \exp(-rX)]/(rX)^2 \quad (5)$$

where M_0 and S_0 are initial monomer and modifier concentrations, X is fractional conversion, and r is the regulating index, defined as $r = -d(\ln S)/dX$. The value of r is obtained by plotting $\ln S$ versus X , and the slope gives the value of r . Calculations with eq. (5) were used to show the effect of conversion on the heterogeneity index, HI , for modifiers with different regulating indexes (Fig. 1). A plot of the calculations with eq. (4) shows how \bar{P}_w varies with conversion of styrene polymerized with modifiers of different r values (Fig. 2). For these calculations M_0/S_0 was 1943, which is the value for the polymerization of 100 g of styrene in the presence of 0.1 g of *tert*-dodecyl mercaptan. Both sets of curves show only small changes in the dependent variables with conversion when r is small, but pronounced changes when r is 6 or greater.

Molecular Weight Distribution. Bardwell and Winkler⁷ derived an expression for the weight fraction of the most probable distribution of molecular weights for polymers terminated solely by chain transfer with a modifier:

$$W_{yx} = 1/rX \{ P_1^Y [1 - [Y/(1+Y)]P_1] - P_0^Y [1 - [Y/(1+Y)]P_0] \} \quad (6)$$

where W_{yx} is the accumulated weight fraction of polymer with a degree of polymerization of Y at conversion X , and P_1 and P_0 are the probabilities that the growing molecule adds an additional monomer unit at conversions

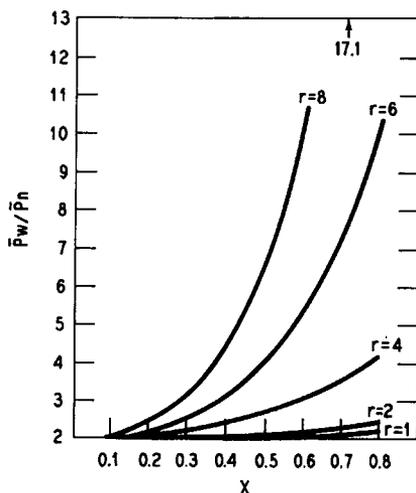


Fig. 1. Theoretical variation of \bar{P}_w/\bar{P}_n with conversion X for modifiers with $r = 1, 2, 4, 6,$ and 8 .

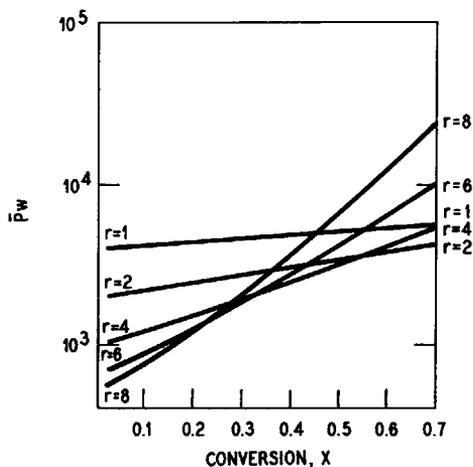


Fig. 2. Theoretical variation of \bar{P}_w with conversion X for modifiers with $r = 1, 2, 4, 6,$ and 8 .

X_1 and X_0 . $P_1 = 1 - rR_0 \exp(-rX)$ and $P_0 = 1 - rR_0$ where R_0 is S_0/M_0 .

The cumulative distributions were converted into log functions in order to correspond with the function given in the Tung procedure.⁸ Only one set of concentrations was used to calculate the simulated curves with eq. (6). This represents the case for polymerizing 100 g of styrene with 0.1 g of a C_{12} -mercaptan which gives an R_0 value of 0.00052. The distribution curves for which the regulating index was varied from 1 to 10 are plotted in Figure 3. The theoretical distribution curves show the following three trends as the regulating index varies: a broadening of the distribution, a

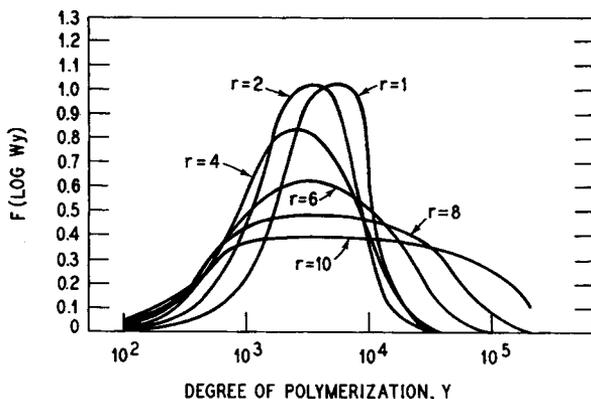


Fig. 3. Theoretical variations of distributions of weight fractions, W_y , of polystyrene for modifiers with $r = 1, 2, 4, 6, 8,$ and 10 .

shift in the molecular weight of the most abundant fraction, and an elongated curve still possessing one maximum for the broader MWD. The broadening is consistent with predictions that could be made on the basis of curves in Figure 1. However, the trend in the peak molecular weights was not anticipated. Equation (6) is differentiable with respect to Y ,

TABLE II
Variation of Peak Molecular Weights at Different
Conversions with Regulating Index

Terminal conversion, %	Approximate peak molecular weight for r of						
	1	2	4	6	8	10	14
50	5000	3000	2250	2000	2000	2000	3200
60	5000	3500	2500	2500	2250	2500	—
70	5000	3500	3000	2700	2700	4000	—

but the solution is too complicated for easy programming. An approximation to the trend of the peak molecular weights with regulating index can be obtained by calculation with eq. (6) over sufficiently narrow Y intervals in the critical molecular weight regions. Data in Table II show that for each terminal conversion the molecular weight of the most abundant fraction goes through a minimum as the regulating index increases.

RESULTS

The experiments with styrene were included to aid in the interpretation of the MWD of the styrene-butadiene copolymers. Styrene was selected as a control monomer which is not as subject to branching and crosslinking as are dienes.

Characterization and Fractionation of Polystyrene

Styrene was polymerized in an SBR 1500-type recipe at 5°C with variable amounts of the homologous series of tertiary mercaptans ranging from *tert*-C_{18.2}SH to *tert*-C₉SH. After isolation, the polystyrene from each set with an inherent viscosity closest to 1 was selected for fractionation. The polymerization and characterization data are shown in Table III and the normalized MWD curves are plotted in Figure 4. Although the inherent viscosities of the polymers in Table III are not as close to 1 as might be made, other experimental data will show that these differences do not invalidate the trends shown by these fractionation data.

TABLE III
Characterization and MWD Data for Polystyrene
Polymerized with Different Mercaptans

Sulfole mercaptan	Amount, phm ^a	Conversion, %	Time, hr	η_{inh}	Regulating index <i>r</i>
132	0.151	65	8.2	0.87	2.9
120	0.100	58	9.3	0.92	3.8
105	0.120	61	8.6	0.96	5.6
90	0.102	57	9.1	1.10	6.1

Linear calibration									
Nonlinear calibration			Infinite resolution			Tung correction			
\bar{M}_w^a	\bar{M}_n	HI	\bar{M}_w	\bar{M}_n	HI	\bar{M}_w	\bar{M}_n	HI	
132	271	121	2.24	283	130	2.18	276	133	2.08
120	301	112	2.69	313	124	2.52	305	127	2.40
105	347	87	4.01	348	100	3.48	342	103	3.20
90	418	88	4.74	410	103	3.98	405	106	3.82

^a Parts per one hundred parts monomer; all \bar{M} 's are $\times 10^{-3}$.

The experimental curves (Fig. 4) show the following trends: a spread in MWD of the polystyrenes as the regulating index of the modifier increases, a shift in the molecular weight of the most abundant fraction, and a noticeable hump in the curves for the polymers made with the mercaptans having the higher regulating indexes.

Characterization and Fractionation of Butadiene-Styrene Copolymers

The SBR 1500 recipe was also used to prepare several series of polymers for the fractionation studies. In each series, except one, the same rates of polymerization, the same conversion, and the same Mooney viscosity were strived for. In the one series the conversion and Mooney viscosity were varied.

Variation of MWD with a Homologous Series of Mercaptans. The series of Sulfole mercaptans from *tert*-C₁₆SH to *tert*-C₉SH were used in one set of polymerizations to prepare the copolymers. Two polymers were

TABLE IV
 Characterization and MWD Data for Butadiene-Styrene Copolymers Prepared in an SBR 1500 Recipe

Sulfolo mercaptan	Amount, phm	Conversion, %	Time, hr	$\eta_{inh}/ML-4$	Regulating index, r
160	2.00	59	7.5	1.77/37	0.6
132	0.276	58	6.5	1.99/47	1.8
120	0.186	59	6.4	1.99/46	3.0
105	0.175	59	6.6	2.05/47	5.5
100	0.176	60	6.6	2.22/50	5.7
90	0.211	59	7.5	2.22/46	7.1
cyclo-C ₁₂ ^a	1.398	61	9.0	3.10 ^c /62	12.7
120 ^b	0.275	58	5.7	1.78/48	3.0

Linear calibrations								
Nonlinear calibration			Infinite resolution			Tung correction		
\bar{M}_w^d	\bar{M}_n	HI	\bar{M}_w	\bar{M}_n	HI	\bar{M}_w	\bar{M}_n	HI
325	85	3.84	299	102	2.93	296	104	2.85
328	90	3.64	322	113	2.85	319	116	2.75
353	90	3.93	341	113	3.02	336	116	2.90
339	78	4.34	331	101	3.28	328	104	3.14
404	71	5.70	374	96	3.90	371	99	3.75
401	62	6.47	370	85	4.36	371	88	4.22
882	17	52.0	624	37	17.0	608	36	16.9
411	66	6.24	369	90	4.12	370	92	4.0

^a Cyclododecadienyl mercaptan.

^b 0.06 phm DVB present during polymerization.

^c In a previous study the same modifier gave a copolymer with η_{inh} of 2.64 at an ML-4 of 52.

^d All \bar{M} 's $\times 10^{-3}$.

added to the study after the set of chromatographs was obtained: one polymer was prepared with cyclododecadienyl mercaptan as a modifier and the second polymer was branched with divinylbenzene (DVB) in the presence of sufficient *tert*-C₁₂SH to give a product that was free of gel at 50 Mooney viscosity. The characterization and fractionation data are presented in Table IV.

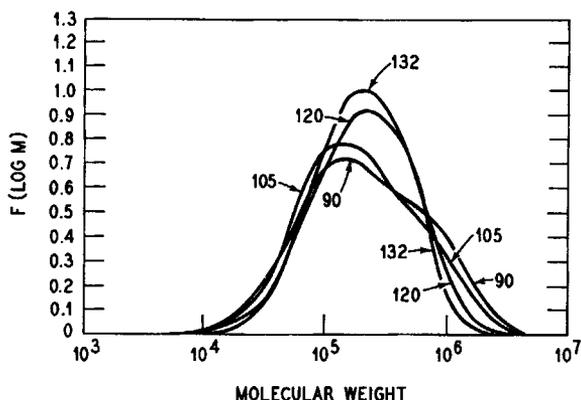


Fig. 4. MWD of polystyrene prepared with tertiary mercaptans possessing different regulating indices. The numbers refer to Sulfole mercaptans.

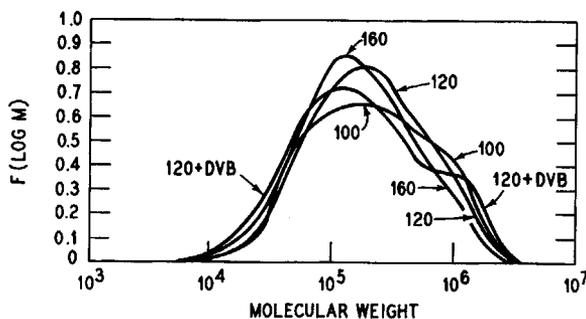


Fig. 5. MWD of butadiene-styrene copolymers prepared with tertiary mercaptans possessing different regulating indices. Numbers refer to Sulfole mercaptans.

The MWD for the polymers characterized in Table IV are plotted in two sets in order to avoid overcluttering (Figs. 5 and 6). The curves for the butadiene-styrene copolymers prepared to the same Mooney viscosity do show some of the trends observed previously: a broadening of MWD with increasing regulating index of modifier, a shift in the molecular weight of the most abundant fraction, and a marked hump in the curve for the polymer made with the modifier possessing the higher regulating index. The polymers made with the cyclic C₁₂-mercaptan, which has the highest regulating index, and that made in the presence of divinylbenzene show the presence of bimodal distributions.

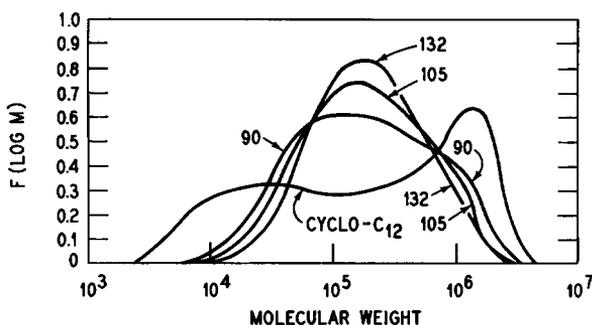


Fig. 6. MWD of butadiene-styrene copolymers prepared with tertiary mercaptans possessing different regulating indices. Numbers refer to Sulfone mercaptans.

Variation of MWD with Conversion. Another series of polymerizations was done to test the effect conversion has on MWD. Two sets of conditions were selected. In one set at a constant modifier level, polymerizations were terminated at 50%, 60%, and 70% conversions; and in the second set the modifier level was adjusted to give a 50 ML-4 polymer at 50% and 70% conversions. Characterization and fractionation data are presented in Table V.

TABLE V
Characterization and MWD Data for Butadiene-Styrene Copolymers

Expt. no.	Sulfone mercaptan	Amount, phm	Conversion, %	Time, hr	$\eta_{inh}/ML-4$
1	120	0.185	50	5.75	1.78/44
2		0.185	61	7.0	1.90/53
3		0.185	70	8.0	2.12/64
4		0.175	52	5.75	1.92/54
5		0.202	70	8.1	1.90/53

Nonlinear calibration			Infinite resolution			Tung correction			
\bar{M}_w^*	\bar{M}_n	HI	\bar{M}_w	\bar{M}_n	HI	\bar{M}_w	\bar{M}_n	HI	
1	340	79	4.30	324	104	3.11	320	107	2.98
2	358	87	4.12	342	112	3.06	339	114	2.95
3	397	93	4.27	375	118	3.18	372	121	3.08
4	326	77	4.23	322	104	3.10	319	107	2.98
5	348	88	3.96	337	111	3.04	334	114	2.94

* All \bar{M} 's $\times 10^{-3}$.

Only the MWD data for the 50% and 70% conversions polymers, nos. 1 and 3 of Table V, were plotted (Fig. 7). The MWD's for all the polymers prepared in this series are so similar that showing the differences by curves is difficult. The data indicate that small differences in conversions and in inherent viscosity will not be detected by the instrument and procedures

used in this investigation when the regulating index of the modifier is small.

Comparison of *n*- and *tert*-Dodecyl Mercaptans as Modifiers in the SBR 1000 Recipe. A 70/30 butadiene-styrene mixture was polymerized in an SBR 1000 system with *n*- and *tert*-dodecyl mercaptans as modifiers. The characterization and MWD are given in Table VI and the fractionation data are plotted in Figure 8. Since these experimental results dif-

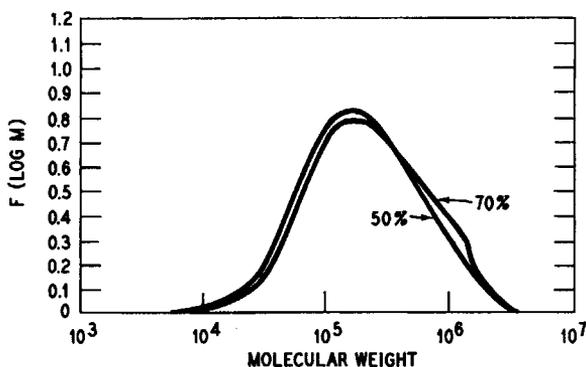


Fig. 7. MWD of butadiene-styrene copolymers prepared with the same modifier to different conversions.

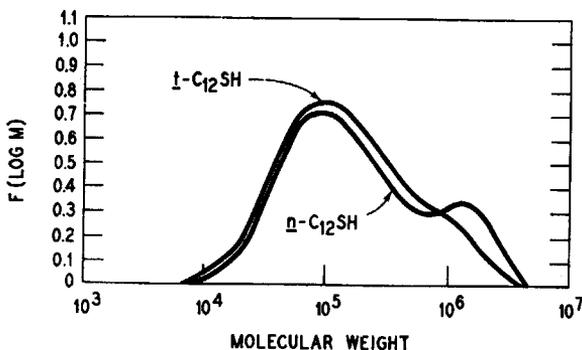


Fig. 8. MWD for butadiene-styrene copolymers prepared in SBR 1000 with *n*- and *tert*-dodecyl mercaptans.

ferred from those presented previously,³ the complete experiment was repeated and the results were essentially identical to those reported here.

Fractionation of Commercial SBR's. Samples of commercial SBR's were obtained from the industry at random. These polymers were fractionated and the data were then plotted in sets which showed some interesting features. One set of curves for the same type of polymer, SBR 1500, from three suppliers showed appreciable differences in MWD (Fig. 9); a second set of three curves for SBR 1503 showed only small differences

TABLE VI
 Characterization and MWD Data for Butadiene-Styrene Copolymers Prepared in an SBR 1000-Type Recipe with *n*- and *tert*-Dodecyl Mercaptans as Modifiers

Mer-captan modifier	Amount, phm	Conversion, %	Time, hr	$\eta_{inh}/ML-4$	Regulating index, r	Linear calibration								
						Nonlinear calibration			Infinite resolution			Tung correction		
						\bar{M}_w^a	\bar{M}_n	HI	\bar{M}_w	\bar{M}_n	HI	\bar{M}_w	\bar{M}_n	HI
<i>tert</i> -C ₁₂	0.293	68	9.2	1.89/44	3.7									
<i>n</i> -C ₁₂	0.302	70	9.0	2.02/47	2.6									
<i>tert</i> -C ₁₂						361	60	6.07	315	79	3.97	311	81	3.84
<i>n</i> -C ₁₂						616	62	9.89	462	86	5.40	454	87	5.19

^a All \bar{M} 's $\times 10^{-3}$.

in distribution (Fig. 10); and the third set of curves showed differences in distribution for different types of SBR (Fig. 11). A summary of the fractionation data is presented in Table VII.

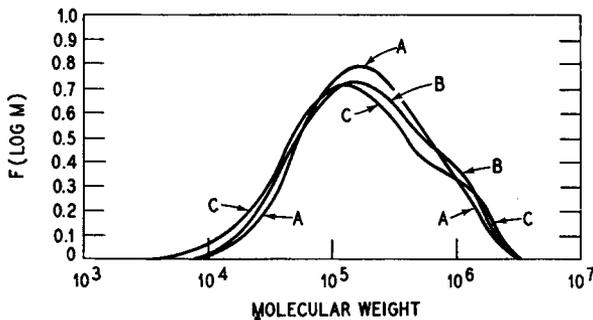


Fig. 9. MWD for SBR 1500 selected at random from industry. See Table VII for data.

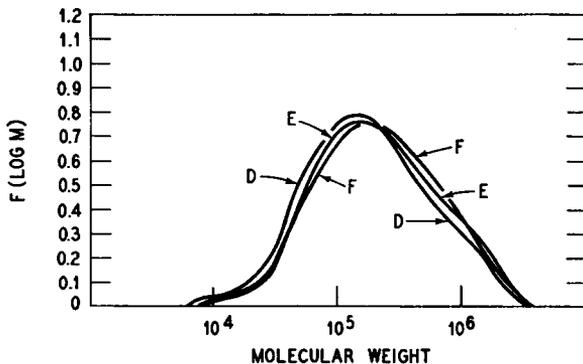


Fig. 10. MWD for SBR 1503 selected at random from industry. See Table VII for data.

TABLE VII
MWD Data for Some Commercial SBR's

Expt. no.	SBR type	η_{inh}	Nonlinear calibration			Infinite resolution			Linear calibration		
			\bar{M}_w^a	\bar{M}_n	HI	\bar{M}_w	\bar{M}_n	HI	\bar{M}_w	\bar{M}_n	HI
A	1500	—	348	84	4.14	331	106	3.12	327	109	3.00
B	1500	—	385	75	5.14	359	100	3.59	357	102	3.50
C	1500	—	358	56	6.01	330	76	4.34	327	79	4.14
D	1503	2.04	418	93	4.50	382	118	3.24	379	121	3.14
E	1503	2.10 ^b	361	70	5.14	329	90	3.66	325	93	3.49
F	1503	2.03	406	89	4.56	376	109	3.45	373	112	3.33
G	1712	—	449	112	4.00	448	136	3.30	448	140	3.19
H	1502	—	368	97	3.80	350	118	2.96	346	121	2.86

^a All \bar{M} 's $\times 10^{-3}$.

^b This polymer contained about 10% gel. The other samples were gel free.

The MWD's for the SBR 1500 show notable differences in shape of curves and in the heterogeneity indexes. These are as marked as was found in the laboratory for the preparation of polymers with part of the homologous series of mercaptans (Figs. 4 and 5). The SBR 1503 polymers were quite

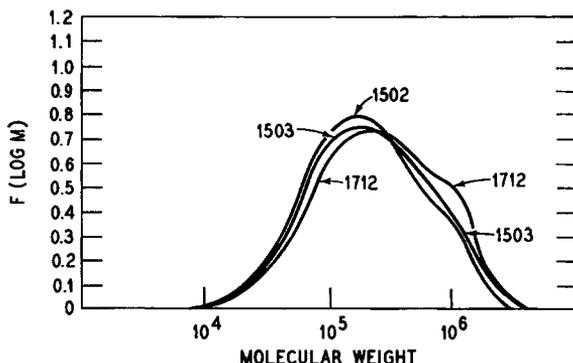


Fig. 11. MWD data for different types of SBR's. See Table VII for data.

similar in both shape of curves and in heterogeneity values. The differences between the SBR 1712 and the lower Mooney rubbers are not unexpected.

DISCUSSION

MWD Determined by Gel Permeation Chromatography

Recent reviews discuss the limitations and potentials of the gel permeation for fractionation of polymers.^{10,11} In the present study attempts were made to use procedures recommended for the most efficient fractionation. The data for polystyrenes NBS 705 and 706 furnish a comparison for the procedure used. Meyerhoff¹² recently presented a tabulation of fractionation data obtained by various investigators for NBS 706. The uncorrected heterogeneity indexes for solvent flow rates of 1 ml/min ranged from 2.6 to 1.4. The higher value corresponds with the result obtained in this study, but the Tung correction did not bring the index to a value of 2, which is the average of the indexes given for the NBS standard. Similarly the values for the NBS 705 in this study are higher than those given for the standard and for at least one gel permeation fraction of the same sample.¹³ The procedure used in this study gave higher heterogeneity indexes than those recognized as standard, and this trend corresponds with that of Alliet¹⁴ who made a comparative study of the fractionation of polystyrene by permeation and standard procedures.

The quantitative values for molecular weight obtained by gel permeation can be no better than the calibration standards. Originally one calibration curve and an appropriate Q (molecular weight per angstrom of equivalent

straight chain length) value were recommended for different polymers. This technique is perhaps suitable for rough approximations as can be seen by the different calibration curves, eqs. (1) and (2), and the data in the tables. Molecular weights based on the nonlinear calibration curve agree fairly well with the values based on the identical type of polymer used in calibration when a narrow MWD polymer was fractionated. When heterogeneity index increased, the differences between the fractionation data based on the different calibration curves became appreciable. However, in no case did the relative position of polymers in a particular series change because of the calibration curve employed or because of correction for dispersion.

Theoretical Calculations

The simulated \bar{P}_w - X curves (Fig. 2) obtained by calculation with eq. (4) show an apparent irregularity at the higher conversions. This arises from the existence of an optimum regulating index for each terminal conversion. The existence of these optimum modifiers was established previously,¹ and this trend can also be seen in the modifier requirements for polymers prepared to the same Mooney as shown in Table IV. Although \bar{P}_v - r as well as \bar{P}_w - r curves¹ exhibit minima, the HI - X curves (Fig. 1) do not. These calculations mean that the most efficient modifier does not give the narrowest MWD. This same trend was not found by Tobolsky and associates¹⁵ for calculations based on kinetics applicable to the solution polymerization system. Theoretical calculations for the latter system show a minimum in the HI - C curve, where C is the transfer constant of the modifier.

Two more points of note shown by the theoretical curves are that heterogeneity index changes only slightly with conversion when the regulating index is low and that with all the modifiers both heterogeneity index and \bar{P}_w increase with conversion. These trends are the consequence of the assumption made in deriving the equations, i.e., the monomer concentration remains constant during the course of polymerization but the modifier concentration is decreasing with conversion. Another relationship of interest shown by \bar{P}_w/\bar{P}_n ratio is that the value is independent of the amount of monomer and modifier since these expressions cancel in the division. The heterogeneity index depends on the regulating index and the conversions.

The MWD does depend on the monomer and modifier concentrations as well as on the regulating index and conversion, eq. (6). Only one set of conditions was used to calculate the simulated curves in Figure 3, and that was for styrene modified with a C_{12} -mercaptan for which r was assumed to range from 1 to 10. In this study the relative position and shapes of the theoretical curves as the regulating index of the modifier changes will be used for comparison with the experimental curves.

MWD of Polystyrene Modified with a Homologous Series of Mercaptans

The experimental MWD curves (Fig. 4) show regular trends as the regulating index was increased. The curves broaden, the amount and position of the most abundant fraction shift, and the shape of the curve becomes distorted with the appearance of an obvious hump for the polymer made with the *tert*-C₉ modifier. The heterogeneity index of the polystyrene made with the *tert*-C_{13.2} mercaptan is close to the theoretical value for modifiers with low regulating indexes, and similar correspondences are also found for the shape of the MWD curve and the calculated molecular weights. Montgomery and Winkler⁸ found a correspondence between theory and experiment of polystyrene polymerized in an emulsion system modified with *tert*-C₁₂ mercaptan.

As the regulating index increases, a hump on the experimental curve appears which is not seen on the theoretical curve. This hump is attributed to branching and it is more evident in the butadiene-styrene copolymers. Another trend of the theoretical values not seen in the experimental results is a minimum in molecular weight as the regulating index increases. However this conclusion must be qualified because the viscosity of all the polystyrenes was not the same. This point will be discussed again for the butadiene-styrene copolymers.

MWD of Butadiene-Styrene Copolymers Modified with a Homologous Series of Mercaptans

The theoretical equations used for homopolymerizations in emulsions can be used for a copolymerization by assuming an average constant monomer concentration over the conversion interval of interest. Previous experimental results have shown that this simplifying assumption holds well for the copolymerization of butadiene and styrene.¹ Again the experimental MWD curve for the copolymer resembles that of the theoretical curve when the regulating index of the modifier is low (Fig. 5 and 6). Vaclavek¹⁶ found good checks for calculated and theoretical viscosity values for butadiene-styrene copolymers prepared in emulsion systems with *tert*-C₁₂, *tert*-C₁₄, and *tert*-C₁₆ mercaptans.

When the regulating index is large, the experimental curve becomes distorted (Fig. 6). The curves display humps and with cyclododecadienyl mercaptan, regulating index 12.7, a bimodal distribution is found. The latter is attributed to nonuniform branching occurring in the later stage of polymerization in a peripheral region of the monomer-polymer particle. Brodnyan¹⁷ has previously postulated that most of the polymerization occurs in an outer region of a monomer-polymer particle where the monomer concentration is relatively high. The same argument applied to a diene emulsion polymerization in the presence of a rapidly depleting modifier leads to the conclusion that the high molecular weight polymers increase the viscosity of the outer region but reduce the mobility of all species,

thereby subjecting the molecules produced last to more attack by the free radicals than those in the inner sphere of the particle produced earlier, when the viscosity was low. In a recent report on branching in polymers,¹⁸ the results indicated that for the low-temperature SBR, only the four fractions of highest molecular weight contained crosslinked molecules. Further evidence that branching or crosslinking causes a distorted gel permeation curve is seen in the curve for the polymer prepared with divinylbenzene (Fig. 5).

Some heterogeneity indexes reported for emulsion copolymers prepared at 10°C in standard systems ranged from 2.3 to 14.6, depending on the method of measurement.¹⁹ The lower values were based on the summation of viscosity measurements and the higher values were the ratio of light scattering and osmometric molecular weights. The high weight-average molecular weights obtained by light scattering were apparently due to microgel which on removal gives much lower values.²⁰ These few results show that wide variations in molecular weight characterizations can result from the analytical method and polymer treatment used.

The numerical values of molecular weights increased for the SBR polymers made to the same Mooney viscosity with the series of modifiers with increasing regulating indexes (Table IV). This differs from the theoretical calculations which show that the molecular weights should go through a minimum as the regulating index increases (Fig. 2). Again, as in case of the polystyrene samples, the conclusion must be qualified because the copolymers were probably not prepared to the proper constant property, such as constant intrinsic viscosity instead of constant Mooney. One trend of interest in this series of SBR polymers is the increase in inherent viscosity with regulating index for the polymers made to the same Mooney viscosity. This trend is attributed to the plasticization by the low molecular weight fraction in bulk viscosity measurement and the absence of a similar action of the same fraction in solution viscosity measurements.

Variation of MWD with Conversion and Modifier Concentration. The theoretical \bar{P}_w/\bar{P}_n ratio is independent of the modifier concentration but is dependent on the conversion. The data in Table VI do show that heterogeneity index is independent of modifier level for the 50% conversion polymers, nos. 1 and 4, but the same correspondence of values is not shown by the 60% conversion polymers, nos. 3 and 5. Although the indexes for the polymers prepared to different conversions do not show a consistent trend (nos. 1, 2, and 3), the actual \bar{M}_w and \bar{M}_n values do increase with conversion. However, the precision of the procedure might not be good enough to detect the small differences and similarities predicted by the model equations. The same experiments should be run with a modifier having a higher regulating index.

MWD of High-Temperature Polymers. The fractionation curves show a marked difference for the polymers made with the *n*- and *tert*-dodecyl mercaptans (Fig. 8). These results are consistent with some of the known characteristics of the two polymers. The one made with the normal mer-

captan is easier to process and has a broader MWD. The fractionation data shows this polymer also has a bimodal distribution. The latter might arise from the greater degree of branching found for polymers made with the normal in comparison to the tertiary dodecyl modifier.²¹ The better balance of vulcanizate properties of the copolymer made with the tertiary mercaptan also reflects a narrower MWD in comparison to the polymer made with the normal isomer. The value of tertiary mercaptans for the preparation of "hot" SBR is recognized in industry by the gradual replacement of the normal with the tertiary isomer.

MWD of Commercial Copolymers. A random selection of polymers from the industry show that for one type of polymer, SBR 1500, measurable differences in MWD were found (Fig. 9, Table VII). These differences were as great as those shown for the same polymerization system modified with a series of mercaptans in the laboratory. However, the actual differences shown by the commercial polymers cannot at this time be put on the use of different modifiers because the actual conditions used in the preparation of the polymers is unknown. Some ranges in plant operation specifications are permissible and the effects these have on MWD have not been established.

Fractionation results for the SBR 1503 polymers (Fig. 10) did not show as great a difference as did the preceding type. For the SBR 1500 polymers the differences between the high and low heterogeneity indexes is over 30%, whereas the difference for the SBR 1503 is only 10%.

The shape of the SBR 1712 curve with the prominent hump (Fig. 11) differs from that of the 1503 and 1502 curves and one of the 1500 curves. However, the heterogeneity values for the same set of polymers show only a 10% spread between the highest and lowest value (Table VII). This is consistent with the model eq. (5) which show the heterogeneity index to be independent of modifier concentration.

The MWD examination of the commercial SBR's shows the existence of differences between polymers of the same type. The significance of these differences to polymer physical properties remains to be established.

The authors are indebted to the following people of Phillips Petroleum Company for their contributions: H. L. Shreffler for most of the polymerization data; O. F. McKinney for fractionation data; G. Kraus, L. E. Boyer, and B. D. Hendrickson for discussions and Tung computations.

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Received October 1, 1969