

Regulation of Molecular Weight Distribution in the Polymerization of Butadiene-Styrene and Butadiene-Nitrile Rubbers*

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Synopsis

Conditions for the preparation of butadiene-styrene and butadiene-nitrile rubbers with desirable molecular weight distributions were developed; regulators of different activities were used in the polymerizations. The character of the dependencies of properties of the butadiene-styrene rubbers on the molecular weight distribution of the polymers was established. Butadiene-styrene and butadiene-nitrile rubbers with the desired distributions and good elastic-plastic and physical-mechanical properties were obtained. These rubbers are now commercially produced on the basis of these findings.

The most important structural parameters of polymers are their molecular weights and molecular weight distributions. Properties of polymers are largely dependent on these parameters.

It is well known that stress resistance and elastic properties arise in polymers only when a minimum molecular weight is reached, and that these properties approach their maximum values at a molecular weight specific for each polymer. Further increase in molecular weight has no practical effect on the physical-mechanical properties, but it does decrease the processibility of the polymer.¹

Since polymers are polydisperse with respect to their molecular weight, an optimum molecular weight distribution exists for each rubber type. Rubbers with the optimum molecular weight distribution give vulcanizates with good physical and mechanical properties and show also good plastic and elastic properties in processing of the rubber mixtures before curing.

Thus the problem of high quality rubbers is directly related to the development of polymerization conditions appropriate for the production of polymer with the necessary molecular weight distribution. Quite obviously, such polymers should not contain large amounts of low molecular fractions since their vulcanizates have very poor stress and elastic characteristics. On the other hand, however, the amount of fractions with very high molecular weights and usually with highly branched macromolecules

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must be kept at a minimum; these fractions form gels easily and significantly diminish the plastoelastic properties of rubbers and the technical properties of the resulting vulcanizates.^{2,3}

It was found possible to control the molecular weight distribution of polymers in the emulsion copolymerization of butadiene with styrene and of butadiene with acrylonitrile. Regulators promoting chain transfer were used. The molecular weight distribution could be controlled, since the activity of the regulators depended on the conditions under which they were introduced into the system.

The action of diisopropylxanthogen disulfide (Diproxid) and of the *tert*-dodecyl mercaptan (Mercaptane) on molecular weight distribution was studied in the copolymerization of butadiene with styrene (70/30 by weight) and of butadiene with acrylonitrile (74/26 and 82/18 by weight) at 5 and 30°C., respectively. These regulators of different activity were studied in the presence of different redox systems and of different emulsifiers.

The conditions for the introduction of the regulators studied into the system were modified on the basis of comparisons of the shape of the molecular weight distribution of the properties of the resulting rubbers and curing mixtures, and of the physical-mechanical parameters of the vulcanizates. The conditions of introduction were so changed as to yield a favorable molecular weight distribution and the necessary complex of corresponding properties.

EXPERIMENTAL

A. Preparation of Polymers

The butadiene-styrene polymers were prepared at 5°C. in the presence of two redox systems: hydroquinone-cumene hydroperoxide-sodium sulfite and ferrous sulfate-cumene hydroperoxide-sodium formaldehyde sulfoxylate. Sodium dibutyl-naphthalene sulfate (Nekal), soaps of synthetic fatty acids and their mixture with the soap of disproportional colophony at a ratio of 1:5 were used. The butadiene-nitrile polymers were prepared at 30°C. in the presence of potassium persulfate and of Nekal.

The compounds used as regulators of the molecular weight and of the molecular weight distribution (Diproxid or Mercaptane) were introduced into the system in their emulsified solutions in styrene or in acrylonitrile. This method of introduction was favorable for the diffusion of the regulators toward the reaction zone at different degrees of conversion of monomers.

The regulators were introduced either before the start of the polymerization or at several points in the polymerization process to yield polymers with different types of molecular weight distribution. The polymerization was stopped at a given degree of conversion by means of sodium dimethyldithiocarbamate in the case of polymerization of butadiene with

styrene; and hydroquinone was used for the case of butadiene polymerization with acrylonitrile.

The effectiveness of the regulators was studied by determination of the intrinsic viscosity and of the molecular weight distribution during the polymerizations; these parameters were investigated in detail in the final rubber samples as well as the properties of standard curing mixtures of the rubbers and the properties of the vulcanizates.

B. Methods for the Investigation of the Molecular Weight Distribution of Polymers

Sedimentation experiments were carried out in an ultracentrifuge with pneumatic drive at a rotation speed of 50,000 rpm, corresponding to a centrifugal field of 180,000*g*.

The sedimentation was observed by means of Philpot-Svensson optics; differential curves of the changes in the concentration gradients of the solution in the cell in the direction of the centrifugal field, i.e., $dc/dx = f(x)$ were directly registered on the photoplates. The investigation was carried out on thermodynamically ideal, i.e., theta solutions; the butadiene-styrene polymers were studied in octane and the butadiene-nitrile polymers in a mixture of acetone with isopropanol (61/39). From the $dc/dx = f(S)$ curves the usual molecular weight distribution curves $dc/dM = f(M)$ were calculated for the investigated polymers. For these calculations the dependence of the sedimentation constants S_0 on molecular weights of the polymers was determined and applied. The molecular weights of the fractions were calculated from the equation of Svedberg. The necessary values of the diffusion coefficients were measured with a polarization diffractometer.⁴ The dependence resulting from the analysis of the experimental data, was for the above theta solutions:

$$S_0 = 1.90 \times 10^{-2} M^{0.46}$$

for the butadiene-styrene polymers, and

$$S_0 = 9.33 \times 10^{-3} M^{0.54}$$

for the butadiene-nitrile polymers.

DEPENDENCE OF THE MOLECULAR WEIGHT DISTRIBUTION OF EMULSION RUBBERS ON CONDITIONS OF THE INTRODUCTION OF REGULATORS

Samples obtained at different extents of conversion in polymerization without regulator were investigated in order to determine the conditions of polymerization yielding polymers free from gel. The presence of gel was detected from the shape of the sedimentations curves. Figure 1 represents a typical molecular weight distribution curve of a butadiene-styrene copolymer sample obtained in the presence of Nekal at a degree of polymerization of 23%. A continuous curve without additional peaks

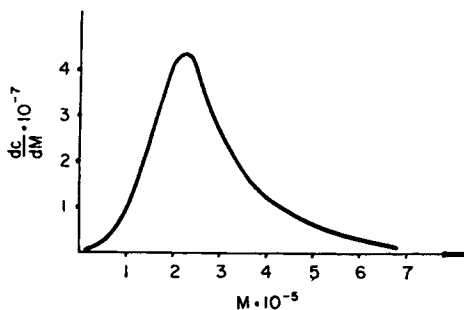


Fig. 1. Molecular weight distribution of the butadiene-styrene polymer at 23% conversion without regulator.

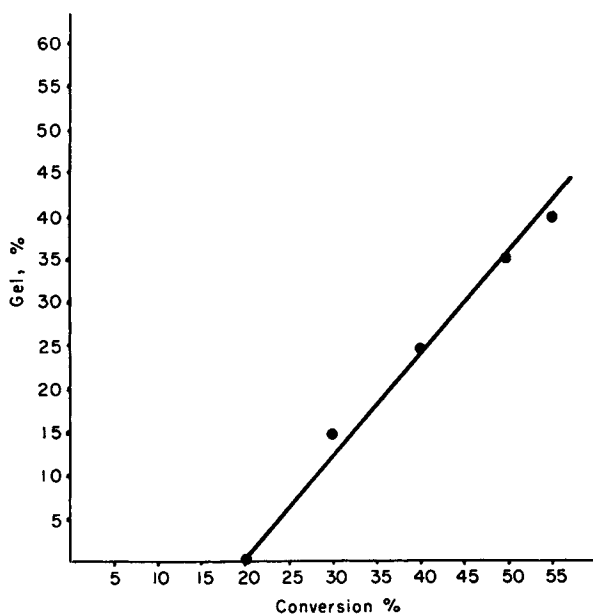


Fig. 2. Dependence of gel formation on the conversion of monomers in absence of regulator.

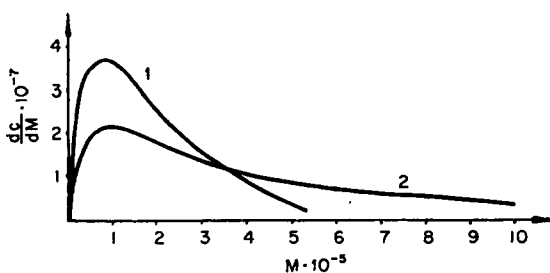


Fig. 3. Molecular weight distribution of butadiene-styrene polymers obtained at (1) 40% conversion and (2) 60% conversion with Diproxid introduced before the start of polymerization.

TABLE I

Dependence of the Changes in the Molecular Weights of Polymers on the Extent of Polymerization of Butadiene with Styrene in the Presence of Diproxid (0.15 Parts Added before the Start of Polymerization)

Conversion of monomer, %	Weight-average molecular weight $M_w \times 10^{-3}$
10	20
25	40
40	100
60	340

shows the absence of high molecular gel components. At the same time at a relatively narrow molecular weight distribution and relatively low extent of conversion in polymerization, the polymer is as well free from the low molecular weight component, and therefore it has a high weight-average molecular weight ($\bar{M}_w = 250,000$). It was found that the point of gel formation depended to some extent on the composition of the polymerizing system, particularly on the nature of the emulsifier. In the case of butadiene-styrene copolymerization, gel formation was observed at 30% conversion in the presence of Nekal and at 15% in the presence of colophonic or fatty acid soaps. As polymerization proceeded, the amount of gel increased, and finally an insoluble polymer was formed. The quantitative data are shown in Figure 2 for the copolymerization of butadiene with styrene in the presence of Nekal.

Introduction of Diproxid into the same system before the start of polymerization resulted in comparatively low molecular weight polymer at up to 30-40% conversion and of a high molecular weight polymer at higher conversions (Table I and Fig. 3).

These observations are consistent with the curve for Diproxid consumption; it can be seen from the curve that at 40% conversion Diproxid is practically absent in the polymerizing system (Fig. 4).

The molecular weight distribution curves obtained on introduction of Diproxid in several portions at increasing monomer conversions during the course of the polymerization show that butadiene-styrene polymers in which molecular weight distributions are practically independent of the extent of polymerization may be prepared up to 80% conversion (Fig. 5). Comparison of these curves with the curves obtained with introduction of a single portion of Diproxid before the start of polymerization discloses that the addition of the regulator at higher conversions (50, 60, and 70%) not only eliminates gel formation but also appreciably decreases the amount of the highest fractions.

Addition of the Diproxid in equal parts at 0, 20, 40, and 50% conversions yielded a butadiene-styrene rubber with a molecular weight distribution similar to that of Europrene-1500.

When Mercaptane was used as the regulator in similar polymerizing systems, no dependence of molecular weight distribution on the introduc-

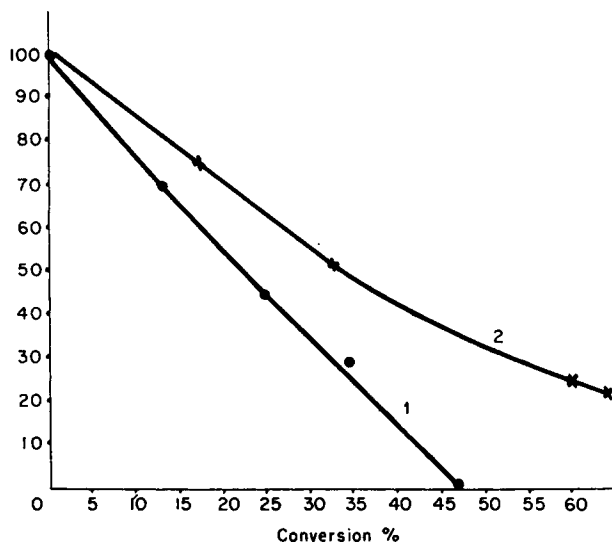


Fig. 4. Consumption of regulators in the course of polymerization: (1) Diproxid; (2) Mercaptane.

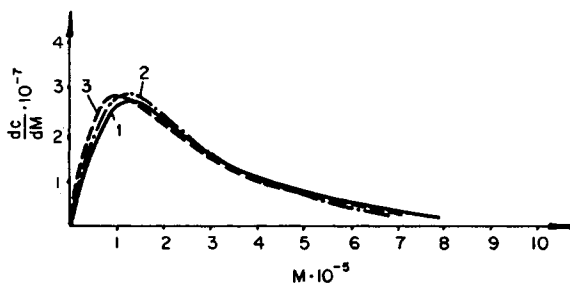


Fig. 5. Dependence of molecular weight distribution of polymers on the introduction of Diproxid: (1) 60% conversion, Diproxid introduced at 0, 20, and 40% conversion; (2) 70% conversion, Diproxid introduced at 10, 20, 30, 40, and 50% conversion; (3) 80% conversion, Diproxid introduced at 15, 30, 45, 60, and 70% conversion.

tion of the regulator was observed (Fig. 6). These findings may be obviously explained by the lower activity of Mercaptane in chain transfer, as can be seen from the kinetics of Mercaptane uptake (Fig. 4).

A good correlation was observed between the time at which the optimum molecular weight distribution of polymers, i.e., the distribution corresponding to high physical-mechanical properties and good plastic-elastic properties, was attained and the character of the dependence of intrinsic viscosity on the extent of polymerization.

In the case of butadiene-styrene and butadiene-nitrile rubbers the optimum molecular weight distribution corresponded to the change in the intrinsic viscosity of the polymers in benzene solutions during the polymerization from 0.6–0.8 at 10% conversion to 1.8–2.3 at 60% conversion.

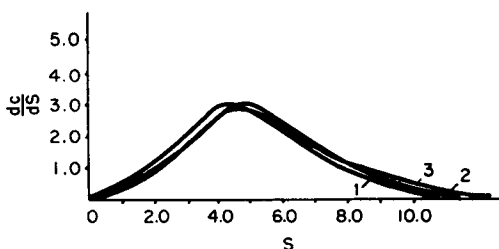


Fig. 6. Dependence of the sedimentation diagrams of the butadiene-styrene polymers on the conditions of introduction of the *tert*-dodecyl mercaptan: (1) all before the start of polymerization; (2) $\frac{2}{3}$ before the start and $\frac{1}{3}$ at 30% conversion; (3) unequal portions in course of the process.

Such changes in the intrinsic viscosity and the preparation of the resulting polymers with the necessary molecular weight distribution are easily realizable by means of the appropriate dosage of Diproxid or of a single introduction of Mercaptane. Introduction of Diproxid in four equal portions with butadiene-styrene copolymers, and in portions of 40, 25, and 10% at 0, 20, 40, and 50% conversions in the case of butadiene-nitrile copolymers, may be recommended.

DEPENDENCE OF THE PROPERTIES OF RUBBERS ON THE METHOD OF REGULATION AND OF THE SHAPE OF THE MOLECULAR WEIGHT DISTRIBUTION

The plastic-elastic properties of rubber as well as the physical-mechanical properties of the vulcanizates were studied. The uncured stocks were prepared according to a standard recipe with 50 parts (by weight) of channel black on the laboratory rolls at 30–40°C. during 40 min.; the weight of the sample of rubber was 600 g.

The method of introduction of Diproxid influences both the molecular weight distribution and the plastic-elastic properties of the rubber and of the curing mixtures as well as the physical-mechanical properties of the resulting vulcanizates. Butadiene-styrene rubbers, for instance, with practically equal average molecular weights but different molecular weight distributions displayed different plastic-elastic properties, as can be seen from the values of the elastic component by the Defo test and results of measurements of the elastic recovery by plasticity. The best plastic-elastic properties (Table II) were obtained by introduction of $\frac{2}{3}$ of the Diproxid before the start of polymerization and $\frac{1}{3}$ at 40% conversion or by its introduction in four equal parts.

The introduction of Diproxid at high monomer conversions (50%) corresponding to lower hardness and higher plasticity, has a considerable effect on the properties. By single-portion introduction of Diproxid these properties deteriorate due to the high molecular weight fractions and to the gel in spite of the presence of noticeable amounts of low molecular weight fractions. Comparison of the physical-mechanical properties of

TABLE II
 Dependence of Plastic-Elastic Properties of Butadiene-Styrene Rubber and Its Curing Mixtures on Conditions of Addition of Molecular Weight Distribution Regulator (Diproxid, Total Addition 0.15 Parts by Weight per 100 Parts Monomer Mixture)

Sample no.	Conversion at addition of regulator, %	Amt. regulator added, parts	Rubber			Curing mixtures		
			Hardness and elasticity (Defo test), g./0.1 mm.	Plasticity	Elastic recovery ($h_2 - h_1$), mm.	Hardness and elasticity (Defo test), g./0.1 mm.	Plasticity	Elastic recovery ($h_2 - h_1$), mm.
1	—	0	900/27	0.34	2.3	1100/20	0.40	0.8
2	0	0.1	960/28	0.32	2.3	900/18	0.43	0.6
	40	0.02						
	50	0.03	940/31	0.28	2.6	1400/32	0.33	1.5
3	0	0.05						
	40	0.10	960/31	0.28	2.7	1080/21	0.39	1.1
4	0	0.05						
	20	0.03	950/29	0.27	2.8	1100/25	0.39	0.98
	40	0.05						
	50	0.05	800/28	0.32	2.3	850/19	0.43	0.80
6	0	0.0375						
	20	0.0375	0.32	2.3	850/19	0.43	0.80	
	40	0.0375						
	50	0.0375						

TABLE III
Physical-Mechanical Parameters of Standard Cured Butadiene-Styrene Rubbers

Sample no.	Diperoxid introduction	Optimum curing time at 143°C., min.	Modulus at 300% elongation, kg./cm. ²	Tensile strength, kg./cm. ²	Elongation, %	Residual elongation, %	Rebound elasticity, %		
							20°C.	70°C. 100°C.	
1	Before start of polymerization	80	81	275	640	24	25	35	38
2	0.1, 0.2, and 0.3 parts at 0, 40, and 50% conversion respectively	80	70	276	630	22	28	40	45
3	Equal parts at 0, 40, and 50% conversion	80	82	294	640	24	32	41	44
4	Equal parts at 0, 20, 40, and 50% conversion	80	67	302	685	28	33	40	45

vulcanizates (Table III) shows that the best results are obtained when Diproxide is introduced in four equal portions. Note the tensile strength and elasticity, which are lower with single-portion introduction of Diproxid.)

Similar data were obtained for other types of emulsion rubbers. Thus, rational methods of polymerization regulation make possible the preparation of polymers with the desirable molecular weight distributions and corresponding high physical-mechanical and plastic-elastic properties.

Application of regulators with high values of the transfer constant results, however, in the necessity of a rather complicated introduction scheme in course of the polymerization in order to obtain the optimum molecular weight distribution. The use of regulators with relatively low transfer constants is therefore desirable; simpler technological schemes and higher polymerization rates are possible then. For the butadiene-styrene rubbers the *tert*-dodecyl mercaptan may be such a regulator.

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Résumé

On a mis au point les conditions nécessaires pour préparer des caoutchoucs butadiène-styrène et butadiène-nitrile possédant une distribution du poids moléculaire désirable. Des régulateurs d'activité différente ont été employés pour les polymérisations. On a établi la dépendance des propriétés des caoutchoucs butadiène-styrène vis-à-vis de la distribution du poids moléculaire. On a obtenu des caoutchoucs butadiène-styrène et butadiène-nitrile possédant la distribution du poids moléculaire nécessaire ainsi que de bonnes propriétés élastico-plastiques et physico-mécaniques. Les caoutchoucs sont actuellement commercialisés d'après ces découvertes.

Zusammenfassung

Günstige Versuchsbedingungen für die Darstellung von Butadien-Styrol- und Butadien-Nitrilkautschuken mit wünschenswerter MWD wurden entwickelt; bei der Polymerisation wurden Regulatoren mit verschiedener Aktivität verwendet. Der Charakter der Abhängigkeit der Eigenschaften des Butadien-Styrolkautschuks von der MWD der Polymeren wurde bestimmt. Butadien-Styrol- und Butadien-Nitrilkautschuk mit der notwendigen MWD sowie guten elastisch-plastischen und physikalisch-mechanischen Eigenschaften wurden erhalten. Diese Kautschuke werden jetzt, entsprechend den hier erhaltenen Befunden, kommerziell erzeugt.

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