

Further Sedimentation Analysis of Styrene-Butadiene Copolymer Rubber

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Synopsis

Methods are presented by which the limiting viscosity number $[\eta]_\theta$ and the limiting sedimentation coefficient s_0 of a monodisperse linear polymer in its theta solvent as functions of the molecular weight M may be deduced from data taken with a series of polydisperse samples of the polymer. The necessary data are the limiting viscosity numbers and the distribution functions of s_0 of the chosen samples in the theta solvent, plus their number-average molecular weights. The methods are applied to unfractionated and fractionated samples of a styrene-butadiene copolymer rubber (SBR) having 24 wt.-% bound styrene in a theta solvent, methyl *n*-propyl ketone (MNPKE), at 21.0°C. The following relations are deduced for monodisperse unbranched SBR in this theta solvent: $[\eta]_\theta = 1.73 \times 10^{-3} M^{1/2}$ and $s_0 = 0.83 \times 10^{-15} M^{1/2}$, where $[\eta]_\theta$ is expressed in deciliters/gram and s_0 in seconds. Besides these, the viscosity-molecular weight relations for this cold rubber in toluene and in cyclohexane, both at 30°C., are established. The new relation for the toluene system does not accord with the French-Ewart relation for the hot rubber in the same solvent. The integral distribution of molecular weight in an unfractionated SBR is calculated from its distribution function of s_0 in MNPKE at 21.0°C. by using the derived s_0 versus M relationship, and is found to coincide well with the mass distribution obtained from fractionation data if the new viscosity-molecular weight relation is used for the molecular weight of each fraction.

INTRODUCTION

In a recent paper Homma et al.¹ have reported sedimentation analysis of a styrene-butadiene copolymer rubber (SBR) having 24 wt.-% bound styrene in a theta solvent, methyl *n*-propyl ketone (MNPKE), at 21.0°C. Probably the weakest point of this study lies in the fact that no absolute measurement of molecular weight was undertaken and we simply estimated molecular weights of given rubber samples and fractions from their limiting viscosity numbers in toluene at 30°C. by making use of the viscosity-molecular weight relation of French and Ewart² for the hot rubber. Also to deduce the limiting sedimentation coefficient s_0 (the value of the sedimentation coefficient s at infinite dilution) as a function of molecular weight M we had recourse to the Mandelkern-Flory theory³ with the constant $\Phi^{1/3}P^{-1}$ taken to be 2.5×10^6 . The validity of these rather arbitrary procedures, however, has to be checked experimentally before we proceed to utilize the proposed method of sedimentation analysis¹ for routine

evaluation of the mass distribution in a given rubber product. The present paper is concerned with a study of this problem. It is shown that the previously derived relations for the limiting viscosity number and the limiting sedimentation coefficient of the rubber in MNPK as functions of molecular weight have to be revised, that the French-Ewart equation is not valid for the cold SBR, and that use of the newly derived relations leads to a good agreement of the mass distribution functions calculated from sedimentation data and fractionation data.

EXPERIMENTAL

Osmotic Pressure

For eight of the previously separated fractions of SBR osmotic pressure measurements in cyclohexane at 30.00°C. were made in glass osmometers of the Zimm-Myerson type fitted with adequately conditioned gel-cellophane as membrane. In all cases the static method was used. For fraction R7-1 the measurement was also made in toluene at 30.00°C.

Viscosity

Limiting viscosity numbers of seven fractions in cyclohexane at 30.00°C. were again determined. The viscometer used had an efflux time of 295.6 sec. for this solvent.

Sedimentation

Four unfractionated samples of SBR were extracted from industrial products designated as SBR-1502, SBR-1507, SBR-1712, and SBR-1778, and their integral distributions of s_0 in MNPK at 21.0°C. were determined by using the procedure described in the previous paper.¹ The limiting viscosity numbers of these new samples in the same solvent were measured, in anticipation of the analysis to be made.

RESULTS AND DISCUSSION

Molecular Weight Data

Figure 1 shows plots for π/c versus c for the eight fractions studied osmotically; here π is the osmotic pressure and c is the polymer concentration in grams per deciliter of solution. It is seen that the plots for each fraction follow a straight line and permit reliable determination of π/c at infinite dilution. The values of the number-average molecular weight \bar{M}_n and the osmotic second virial coefficient A_2 derived from the intercept and slope of each line drawn are recorded in Table I. In no case did permeation of the polymer solute through the membrane occur.

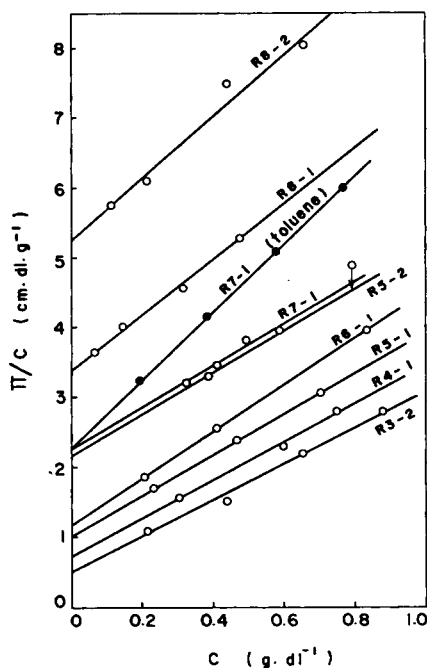


Fig. 1. Osmotic pressure measurements on SBR fractions in cyclohexane at 30.00°C.

TABLE I
Results from Osmotic Pressure Measurements

| Fraction no. | $\bar{M}_n \times 10^{-4}$ | $A_2 \times 10^{-4}(\text{c.g.s.})^a$ |
|--------------|----------------------------|---------------------------------------|
| R8-2 | 4.9 | 1.7 |
| R8-1 | 7.6 | 1.5 ₆ |
| R7-1 | 11.4 | 1.3 |
| R5-2 | 11.9 | 1.2 |
| R6-1 | 22.5 | 1.3 |
| R5-1 | 25.2 | 1.1 ₆ |
| R4-1 | 35.2 | 1.0 ₆ |
| R3-2 | 51.4 | 1.0 |

^a Osmotic second virial coefficient in cyclohexane at 30.00°C.

Relation between Limiting Sedimentation Coefficient s_0 and Molecular Weight M

In our previous study,¹ this relation had to be derived indirectly on the basis of the familiar Mandelkern-Flory equation,³ because no measurement of the absolute molecular weight was undertaken. With the \bar{M}_n data now available, the desired relation between s_0 and M for SBR can be established more directly.

To this end, we start with the relation:

$$s_0 = kM^{1/2} \quad (1)$$

which is now universally accepted to be valid for any monodisperse, nonbranched polymer molecule under theta conditions. In the manner similar to that described by McCormick⁴ and also by Homma et al.,⁵ it is

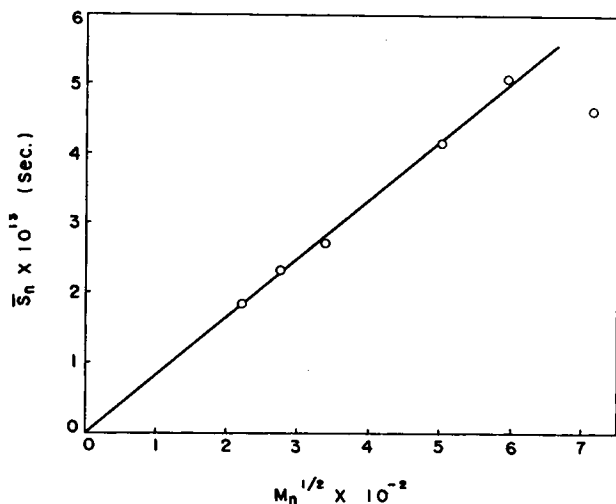


Fig. 2. Linear relation between \bar{s}_n and $M_n^{1/2}$ for SBR in methyl *n*-propyl ketone at 21.0°C. (θ solvent).

possible to show that eq. holds under theta conditions, irrespective of the polydispersity of the given linear polymer sample:

$$\bar{s}_n = k\bar{M}_n^{1/2} \quad (2)$$

Here \bar{s}_n is an average sedimentation coefficient defined by

$$\bar{s}_n = \left[\int_0^\infty (1/s_0^2)g(s_0)ds_0 \right]^{-1/2} \quad (3)$$

and $g(s_0)$ is the differential distribution of s_0 of the given sample in the given theta solvent. Thus plots for \bar{s}_n versus $\bar{M}_n^{1/2}$ should yield a straight line passing through the coordinate origin. The desired value for the constant k can be obtained from its slope. A test of this prediction on SBR is shown in Figure 2, where the values of \bar{s}_n for the plotted points have been calculated from the $G(s_0)$ curves shown in Figure 9 of the preceding paper.¹ It is seen that, except for the point corresponding to the highest molecular weight fraction, the plots fall on a straight line passing through the coordinate origin, in agreement with the theoretical prediction. The slope of the line is $0.83_0 \times 10^{-15}$. Thus the relation between s_0 and \bar{M} for monodisperse linear SBR having 24 wt.-% bound styrene in methyl *n*-propyl ketone at 21°C. would be

$$s_0 = 0.83_0 \times 10^{-15} \bar{M}^{1/2} \text{ (in sec.)} \quad (4)$$

The coefficient $0.83_0 \times 10^{-15}$ is about 20% smaller than the value 1.04×10^{-15} previously derived from sedimentation and viscosity data with the aid of the Mandelkern-Flory relation.

Relation between Limiting Viscosity Number $[\eta]$ and Molecular Weight M

Table II summarizes our previous viscosity data on toluene solutions and MNPK solutions and the new data on cyclohexane solutions. The usual log-log plots for $[\eta]$ versus \bar{M}_n constructed from these data are shown in Figure 3, wherein the results of French and Ewart² for the hot SBR in toluene at 30°C. are indicated for comparison. The straight lines drawn in the figure are represented by eqs. (5-7).

In toluene at 30°C.:

$$[\eta] = 3.7_9 \times 10^{-4} \bar{M}_n^{0.71} \quad (5)$$

In cyclohexane at 30°C.:

$$[\eta] = 3.1_6 \times 10^{-4} \bar{M}_n^{0.70} \quad (6)$$

In MNPK at 21°C.:

$$[\eta] = 1.8_8 \times 10^{-3} \bar{M}_n^{0.50} \quad (7)$$

We may notice that the French-Ewart data on hot SBR come close to our cyclohexane data on the cold SBR. It is seen that both the toluene and MNPK data for samples of \bar{M}_n above 3×10^6 deviate downward from the straight lines. This behavior may be taken as indicative of the molecular branching of these relatively high molecular weight samples. If this is the case, the cyclohexane data also should exhibit a similar downward deviation

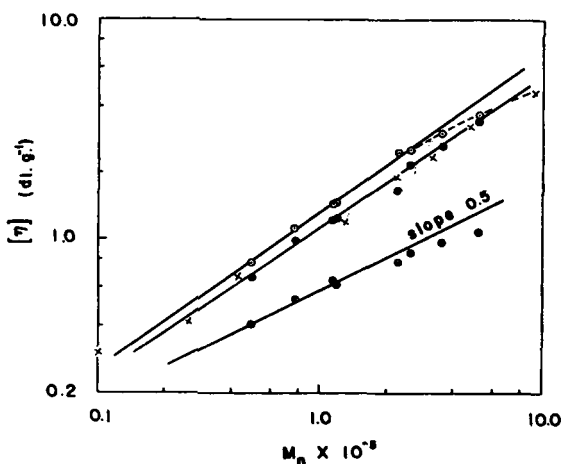


Fig. 3. Mark-Houwink-Sakurada plots for SBR in various solvents: (○) cold SBR in toluene at 30°C., (●) cold SBR in cyclohexane at 30°C., (⊙) cold SBR in methyl *n*-propyl ketone at 21°C. (θ solvent), (×) hot SBR in toluene at 30°C. (data of French and Ewart²).

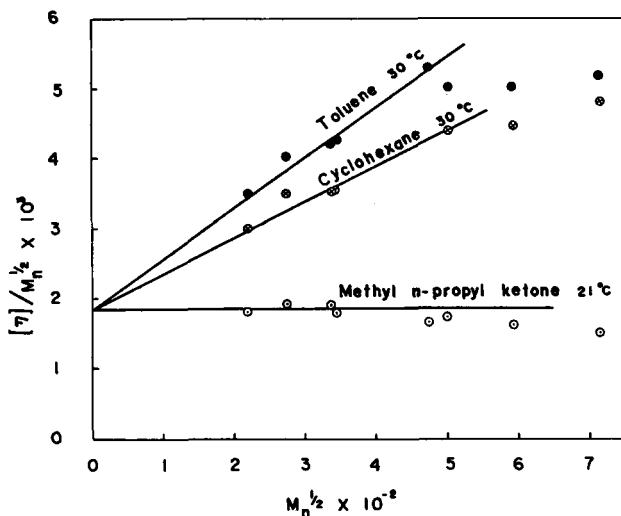


Fig. 4. Stockmayer-Fixman-Kurata plots for SBR in various solvents.

from the straight line at \bar{M}_n above 3×10^5 . That it is not apparent in the cyclohexane data is probably due to our errors in the measurement of $[\eta]$, but the real reason is not clear yet.

The data of Table II may be treated in terms of a recent theory of Stockmayer and Fixman⁶ and also of Kurata.⁷ According to these authors, plots for $[\eta]/M^{1/2}$ versus $M^{1/2}$ of a linear polymer in different solvents should be linear in the region of low molecular weight and should yield ordinate intercepts which are, to a first approximation, independent of the kind of solvent and also of temperature. Figure 4 demonstrates that these predictions are approximately valid for SBR. The downward deviation of the MNPK data at high molecular weights from the horizontal line again may be attributed to the branching of the samples.

None of the viscosity-molecular weight relations given in eqs. (5-7) can be taken as being valid for perfectly monodisperse linear SBR in the solvents indicated. For the MNPK system at 21.0°C., however, the relation valid for monodisperse linear SBR can be deduced by using the procedure worked out by Homma et al.⁵ We denote by $[\eta]_0^m$ and $[\eta]_0$ the limiting viscosity numbers of a monodisperse sample and any polydisperse sample of a given linear polymer in its theta solvent. Then according to the current theory of dilute polymer solutions, we may write

$$[\eta]_0^m = KM^{1/2} \quad (8)$$

where M is the molecular weight of the monodisperse sample and K is a constant. Next we define an average sedimentation coefficient \bar{s}_v by the equation:

$$\bar{s}_v = \int_0^\infty s_0 g(s_0) ds_0 \quad (9)$$

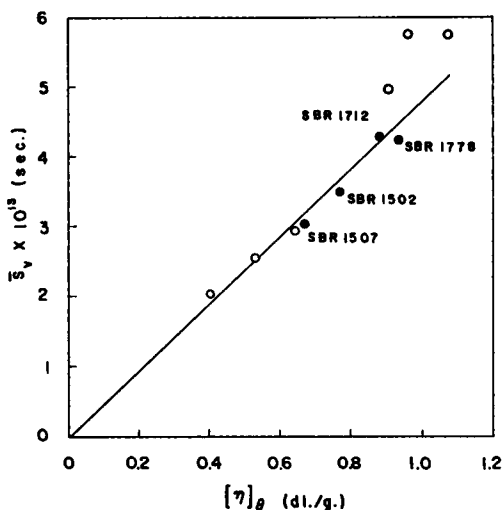


Fig. 5. Linear relation between $(\bar{s}_v)_\theta$ and $[\eta]_\theta$ for SBR in methyl *n*-propyl ketone at 21.0°C. (θ solvent): (O) from previous measurements on fractions; (●) from new measurements on unfractionated samples.

where $g(s_0)$ is the differential distribution of s_0 of the polydisperse sample in the given theta solvent. According to Homma et al.,^{1,5} \bar{s}_v and $[\eta]_\theta$ thus defined are related by the equation:

$$\bar{s}_v = (k/K)[\eta]_\theta \quad (10)$$

where k is the coefficient that appeared in eq. (1). This equation predicts that plots for \bar{s}_v versus $[\eta]_\theta$ should form a straight line passing through the coordinate origin. The slope of this line, being equal to k/K , allows the constant K to be determined if the value of k is known separately. Thus the desired relation (8) for a given polymer–theta solvent system can be established even with the use of polydisperse samples, provided that data for $g(s_0)$ and $[\eta]_\theta$ of the samples are obtained experimentally and, in addition, k is evaluated separately, for example, by making use of eq. (2). The applicability of eq. (10) to SBR in MNPK at 21.0°C. is demonstrated in Figure 5, wherein the open circles refer to our previous measurements on SBR fractions and the closed circles to the new measurements on unfractionated samples extracted from the commercial products mentioned above. Except for the data on three high molecular weight fractions, all other data appear to follow eq. (10). The slope of the line indicated is $4.8_0 \times 10^{-13}$. As deduced above, the k value for this system is $0.83_0 \times 10^{-15}$, and so the desired K value is found to be $1.7_3 \times 10^{-2}$. Thus the viscosity–molecular weight relation for monodisperse nonbranched SBR with 24 wt.-% bound styrene in methyl *n*-propyl ketone at 21°C. is

$$[\eta]_\theta^m = 1.7_3 \times 10^{-3} M^{1/2} \text{ (in dl./g.)} \quad (11)$$

TABLE II
Limiting Viscosity Numbers of SBR Fractions in Three Solvents

| Fraction no. | $\bar{M}_n \times 10^{-4}$ | Limiting viscosity number $[\eta]$, dl./g. | | |
|--------------|----------------------------|---|--------------------|---------------------------------|
| | | Toluene, 30°C. | Cyclohexane, 30°C. | MNPK, 21°C. (θ solvent) |
| R8-2 | 4.9 | 0.775 | 0.660 | 0.401 |
| R8-1 | 7.6 | 1.11 | 0.975 | 0.530 |
| R7-1 | 11.4 | 1.42 | 1.20 | 0.644 |
| R5-2 | 11.9 | 1.48 | 1.21 | 0.614 |
| R6-1 | 22.5 | 2.50 | — | 0.781 |
| R5-1 | 25.2 | 2.53 | 2.20 | 0.875 |
| R4-1 | 35.2 | 3.00 | 2.63 | 0.962 |
| R3-2 | 51.4 | 3.72 | 3.43 | 1.09 |

This coefficient, $1.7_3 \times 10^{-3}$, is about 25% lower than the value derived in our previous study¹ by assuming the Mandelkern-Flory relation with a value of 2.5×10^6 for the constant $\Phi^{1/2}P^{-1}$. It is even smaller than the value $1.8_5 \times 10^{-3}$ appearing in eq. (7). Certainly, this new value should be more correct, and it is recommended for the routine evaluation of the viscosity-average molecular weight of a given SBR sample. The deviation of the three points from the straight line in Figure 5 may be attributed to molecular branching and, in part, to errors in the determination of $g(s_0)$. A detailed investigation of these effects, however, will be left for future work.

The Constant $\Phi^{1/2}P^{-1}$ for SBR

The Mandelkern-Flory relation yields, when applied to theta conditions,

$$\Phi^{1/2}P^{-1} = [N_A \eta_0 / (1 - \rho_0 \bar{v})] k(K)^{1/2} \quad (12)$$

Here N_A is Avogadro's number, η_0 is the viscosity coefficient of the theta solvent considered, ρ_0 is its density, \bar{v} is the partial specific volume of the given polymer in that theta solvent, and k and K are the coefficients which appear in eqs. (1) and (8), respectively. Substituting the numerical values obtained previously¹ for η_0 and $1 - \rho_0 \bar{v}$ and the new values for k and K into eq. (12), we find

$$\Phi^{1/2}P^{-1} = 1.7_0 \times 10^6$$

This value is about 30% lower than the value 2.5×10^6 taken as the basis of our previous analysis.¹ If P is taken to be 5.1 as generally suggested,⁸ the above value for $\Phi^{1/2}P^{-1}$ leads to $\Phi = 0.65 \times 10^{21}$. This is only about 30% of the value 2.1×10^{21} considered as a best average for Φ on the basis of experimental results for a great variety of polymer-solvent systems.⁸ The reason for the discrepancy is not clear, and may deserve further investigation. In this connection, we wish to remark that a similar low value of Φ has been encountered by Kurata et al.⁹ in their recent light-scattering study on 1,4-*trans*-polybutadiene solutions.

Molecular Weight Distribution of Sample R-U

With the aid of eq. (4) we are now able to convert the $G(s_0)$ curves of Figure 9 of the previous study¹ to the integral distributions of molecular weight $F(M)$. The solid line in Figure 6 shows the $F(M)$ curve so obtained for the unfractionated sample R-U. This curve may be compared with a $F(M)$ curve which we may derive, by the usual Schulz procedure, from the fractionation data given in Table II of the previous study.¹ Before this is done, however, the \bar{M}_n value of each fraction has to be recalculated in terms of eq. (5), since the previously employed relation of French and Ewart has been found to be inappropriate for cold SBR. The $F(M)$ curve of sample R-U so obtained from fractionation data is indicated by the dashed line in Figure 6. The two distribution curves are seen to agree

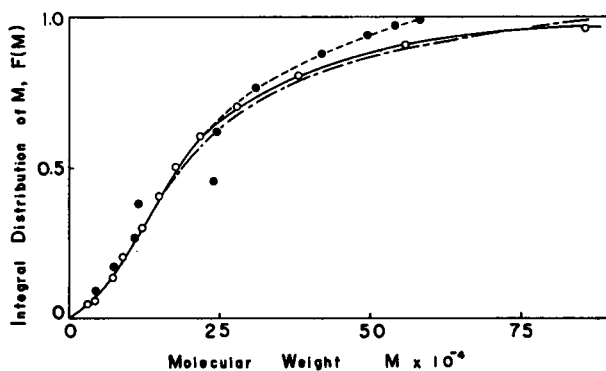


Fig. 6. Integral distributions of unfractionated sample R-U: (—○—) from sedimentation measurement in methyl *n*-propyl ketone at 21.0°C. (θ solvent): (---●---) from fractionation data, with molecular weights calculated in terms of eq. (5) for the toluene system; (—) from fractionation data, with molecular weights corrected as described in the text.

fairly well except at molecular weights higher than 3×10^5 . This discrepancy mainly stems from the fact that, as seen from Figure 3, the actual data of $[\eta]$ versus \bar{M}_n for the toluene system does not follow eq. (5) in this high molecular weight region. In fact, if the \bar{M}_n values of the fractions in this region are estimated in terms of a dashed line drawn in Figure 3, then the curve indicated by the chain line in Figure 6 is obtained. Agreement of the corrected $F(M)$ with the result from sedimentation analysis now appears to be quite satisfactory.

This result is encouraging, but not sufficient to warrant the validity of the procedure of sedimentation analysis developed in this and previous study. Before it is put in practical use, similar comparisons between sedimentation and fractionation data must be made for as many SBR samples as possible. Such work will elucidate the scope and limitations of the proposed method and also indicate what improvement has to be made on its present form. Finally, we wish to mention that it takes only two

days for this sedimentation analysis to be carried through for the evaluation of $F(M)$ of one rubber sample.

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Résumé

On présente des méthodes au moyen desquelles on a déduit l'indice viscosimétrique $[\eta]_{\theta}$ et le coefficient limite de sédimentation s_0 d'un polymère linéaire monodispersé dans son solvant thêta en fonction du poids moléculaire M , à partir des résultats expérimentaux obtenus avec une série d'échantillons polydispersés du polymère. Les données nécessaires sont les indices viscosimétriques, et les fonctions de distribution de s_0 des échantillons choisis dans le solvant thêta, plus leur poids moléculaire moyen en nombre. On a appliqué ces méthodes aux échantillons non-fractionnés et fractionnés d'un polymère caoutchouteux de styrène-butadiène (SBR), possédant 24% en poids de styrène incorporé, dans un solvant thêta méthyl *n*-propylcétone (MNPK) à 21.0°C. Les relations suivantes ont été déduites pour le (SBR) monodispersé non-ramifié dans ce solvant thêta: $[\eta]_{\theta} = 1.7_3 \times 10^{-3} M^{1/2}$ et $s_0 = 0.83 \times 10^{-15} M^{1/2}$, où $[\eta]_{\theta}$ est exprimé en dl/g et s_0 en sec. En outre, les relations viscosité-poids moléculaire pour ce caoutchouc obtenu à froid, ont été établies dans le toluène et le cyclohexane comme solvants à 30°C. La nouvelle relation pour le système dans le toluène ne s'accorde pas avec la relation de French-Ewart pour le caoutchouc obtenu à chaud dans le même solvant. La distribution intégrale des poids moléculaires du SBR non-fractionné est calculée à partir de la fonction de distribution de s_0 dans MNPK à 21.0°C, en employant la relation dérivée s_0 en fonction de M , et on a trouvé que cela coïncide bien avec la distribution de masse obtenue à partir des résultats de fractionnement si la relation viscosité-poids moléculaire est employée pour le poids moléculaire de chaque fraction.

Zusammenfassung

Es werden Methoden angegeben, nach welchen die Grenzviskositätszahl $[\eta]_{\theta}$ und der Grenzviskositätskoeffizient s_0 eines monodispersen linearen Polymeren in seinem Theta-Lösungsmittel als Funktion des Molekulargewichts M aus Messergebnissen an einer Reihe polydispenser Proben des Polymeren bestimmt werden können. Die dazu notwendigen Daten sind die Grenzviskositätszahl und die Verteilungsfunktion für s_0 der verwendeten Proben im Theta-Lösungsmittel sowie ihr Molekulargewichtszahlenmittelwert. Die Methoden werden auf unfraktionierte und fraktionierte Proben eines Styrol-Butadien-Kopolymerkautschuks (SBR) mit 24 Gewichtsprozent gebundenem Styrol in Methyl-*n*-Propylketon (MNPK) bei 21,0°C als Theta-Lösungsmittel angewendet.

Folgende Beziehungen werden für monodisperses, unverzweigtes SBR im diesem Theta-Lösungsmittel abgeleitet: $[\eta]_{\theta} = 1,7_3 \times 10^{-3} M^{1/2}$ und $s_0 = 0,83 \times 10^{-15} M^{1/2}$, mit $[\eta]_{\theta}$ in dl/g und s_0 in sec. Ausserdem werden Viskosität-Molekulargewichtsbeziehungen für diesen Tieftemperaturkautschuk in Toluol und Zyklohexan bei 30°C aufgestellt. Die neue Beziehung für das Toluolsystem stimmt nicht mit der French-Ewart-Beziehung für Hochtemperaturkautschuk im gleichen Lösungsmittel überein. Die integrale Molekulargewichtsverteilung in einem unfraktionierten SBR wird aus seiner s_0 -Verteilungsfunktion in MNPK bei 21,0°C unter Benützung der für s_0 gegen M abgeleiteten Beziehung berechnet und stimmt bei Verwendung der neuen Viskositäts-Molekulargewichtsbeziehung für das Molekulargewicht jeder Fraktion gut mit der aus Fraktionierungsergebnissen erhaltenen Massenverteilung überein.

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