Sedimentation Analysis of Styrene–Butadiene Copolymer Rubber

TERUTAKE HOMMA,* KAZUO KAWAHARA, and HIROSHI FUJITA, *Department of Polymer Science, Osaka University, Osaka, Japan*

Synopsis

Methyl *n*-propyl ketone (MNPK) at 21°C. and methyl isobutyl ketone (MIBK) at 46°C. are found to be theta conditions for a styrene–butadiene copolymer rubber commercially designated as SBR-1500. Data for specific refractive index increment and density indicate that these solvents are appropriate for ultracentrifugation of this polymer by the method of schlieren optics. Sedimentation measurements are made on one whole polymer and six fractions in MNPK at 21°C. It is demonstrated that in this theta solvent the distribution of sedimentation coefficient *s* (at the limit of zero concentration) of a given SBR-1500 can be determined, with a good accuracy, from a single sedimentation run at one nonzero concentration below 0.4 g./dl. A relation between *s* and molecular weight *M* necessary to convert this distribution of *s* to the distribution of *M* is derived by making use of the theory of Flory which correlates *s*, limiting viscosity number, and *M*. It is believed that the theta conditions and the procedure of analysis presented in this paper are readily utilized for heterogeneity studies on this particular type of synthetic rubber SBR-1500.

INTRODUCTION

Methods which permit quick evaluation of mass distributions in given polymer samples are highly desired in many aspects of polymer studies. Unfortunately, none of the methods available at present appear suited for routine work, since they all are time-consuming and often need skill and experience. For example, the sedimentation-transport method is generally complicated by the boundary spreading due to diffusion and the concentration dependence of sedimentation coefficients. For these effects to be eliminated so that the boundary spreading due only to sample's polydispersity in molecular weight may be deduced, it is required that a great number of sedimentation boundary photographs be taken as a function of time and concentration. Thus it does not appear that the ultracentrifugal method may be of use for routine work, at least in circumstances where these two effects are present.

Recent work[1] has demonstrated that the dependence of *s* on concentration in dilute polymer solutions is absent or quite small when the system is under Flory's theta condition. This fact suggests that the sedimentation-

---

* Present address: Research Laboratory, Japan Synthetic Rubber Company, Yokkaichi, Japan.

transport method may be put in routine use for the evaluation of mass distribution if for a given sample there can be obtained a theta solvent in which the concentration dependence of s becomes negligible at concentrations accessible to ultracentrifugal measurements. For, in such circumstances, the desired distribution of s, and hence of molecular weight M, may be calculated if the sedimentation data are determined only at one solute concentration, and thus the experimental and computational labor involved in sedimentation analysis is greatly reduced.

The present paper is concerned with an investigation which purported to find theta solvents useful for quick determination of the molecular weight distribution in a styrene-butadiene copolymer rubber commercially designated as SBR-1500. That we have chosen SBR-1500 for the present study is partly due to our personal interest, but mainly due to the statistical fact that its annual production is the largest among a wide variety of synthetic rubbers now manufactured in the world. However, the research scheme employed below is not restricted to this particular type of rubber but applies to any other linear polymers.

EXPERIMENTAL

Material

The starting sample of SBR-1500 was prepared* at and supplied from the copolymer plant of the Japan Synthetic Rubber Co., Yokkaichi, Japan. We began with removing nonpolymeric impurities from it; the procedure used was as follows.

A 40-g. portion of the material was dissolved in 3.4 l. of benzene with 0.4 g. of phenyl-β-naphthylamine (PBNA), and the mixture was allowed to stand one day. Then it was stirred vigorously for 5 hr., and the resulting solution, which was slightly turbid and showed the presence of a small amount of microgels, was successively filtered through glass wool and a No. 2 sintered glass plate. The polymer was precipitated by dropwise addition of this solution to a large volume of vigorously stirred methanol containing 0.1% PBNA. The precipitate was soaked in methanol and chopped into small pieces, which were then washed three times with methanol, blotted with filter papers, and finally dried in a vacuum oven at room temperature. With 0.359 g. of PBNA the dry pieces were dissolved in benzene to make up a solution of about 6% concentration. The solution was subjected to freeze-drying, and the dry material (35.635 g.) was recovered. This weight corresponds to 88.2% of the starting material. A separate analysis showed that the starting SBR contained 8.05% nonpolymeric impurities; Table I shows the result of this analysis. Thus it is seen that about 4% of the original polymer was lost during the purification process. The purified rubber was stored in a sealed bottle at $-20°$C. in the absence of light. This material is hereafter designated as R–U.

* Polymerized at 5°C. and at a conversion ratio of 60%. Actually, the sample was a portion of the product manufactured industrially under these conditions.

TABLE I
Impurities in Given Sample of SBR-1500

| | | Impurities, wt.-% | |
		Before purification	After purification
Impurities			
Ash		0.76	0.07
Soap		0.04	0.00
Organic acid		6.07	0.00
PBNA (inhibitor)		1.18	0.00
	Totals	8.05	0.07

Fractionation

Sample R–U was separated into eleven fractions by successive precipitation, with benzene as solvent and methanol as nonsolvent. Precipitation was caused either by addition of methanol or by lowering solution temperature, depending on a particular condition. It was interesting to find that the solubility of this polymer in benzene was quite sensitive to temperature. In every case PBNA was added to both solvent and nonsolvent in such a way that its volume concentration amounted to 0.1%.

Figure 1 shows the fractionation scheme followed. Efforts were made to prevent polymer from degradation by light and by oxygen during the proc-
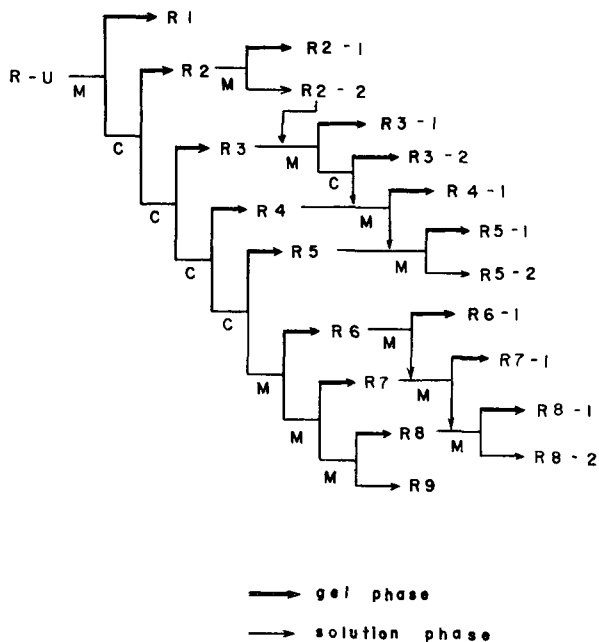

Fig. 1. Fractionation scheme followed: M means addition of methanol and C denotes lowering solution temperature.

TABLE II
Fractionation Data for Sample R-U of SBR-1500

Fraction no.		Weight, g.	Weight-%	Cumulative weight-%	$[\eta]$, dl./g.[a]	$\bar{M}_v \times 10^{-4b}$
R9		1.304	4.09	2.05	0.59_3	4.0
R8-2		2.965	9.30	8.74	0.77_5	6.0
R8-1		2.506	7.86	17.32	1.11_4	10.5
R7-1		3.566	11.19	26.85	1.42_2	15.2
R5-2		3.708	11.63	28.26	1.47_6	16.1
R6-1		3.287	10.31	49.23	2.50_0	35.8
R5-1		4.812	15.10	61.93	2.52_9	36.4
R4-1		4.523	14.19	76.58	3.00_0	47.2
R3-2		2.976	9.34	88.34	3.72_0	65.3
R1		0.785	2.46	94.24	4.19_5	79.3
R2-1		1.043	3.27	97.11	4.46_0	86.0
R3-1		0.401	1.26	99.37	4.70_0	93.1
	Total	31.879			$2.23_6{}^c$	
R-U		33.660			2.16_2	28.7
	Recovery	94.7%				

[a] Limiting viscosity number in toluene at 30°C.; values indicated are the average of two independent determinations.

[b] Calculated from $[\eta] = 5.4 \times 10^{-4} M^{0.66}$.

[c] Sum of $[\eta] \times$ weight % divided by 100.

ess of fractionation. The eleven fractions obtained were freeze-dried from benzene solution and were stored at $-20°C$. in the absence of light and oxygen. Table II summarizes the following numerical data of these fractions: weight in grams, weight fraction, cumulative weight fraction calculated by the Schulz procedure, limiting viscosity number $[\eta]$ in toluene at 30°C., and viscosity-average molecular weight $\bar{M}_v$ estimated by the relation of French and Ewart:[2]

$$[\eta] = 5.4 \times 10^{-4} \bar{M}_v{}^{0.66} \tag{1}$$

TABLE III
Bound Styrene Content of SBR-1500
Determined by Refractive Index Method

Sample	$\bar{M}_v \times 10^{-4}$	Refractive index at 25°C.	Bound styrene, wt.-%
R-U	28.7	1.53494	23.9_4
R1	79.3	1.53488	23.8_6
R2-1	86.0	1.53494	23.9_4
R3-2	65.3	1.53474	23.7_0
R4-1	47.2	1.53495	23.9_6
R5-1	36.4	1.53491	23.9_1
R5-2	16.1	1.53491	23.9_1
R6-1	35.8	1.53494	23.9_4
R7-1	15.2	1.53492	23.9_2

The weight fractions and cumulative weight fractions shown in this table are not the values relative to the original sample R–U but those relative to the total weight we were able to recover.   Table III shows the weight per cent bound styrene of sample R–U and its eight fractions, estimated from refractive indices at 25°C. following JIS-K6383 (1961).   It is seen that the bound styrene content is independent of $\bar{M}_v$ and yields an average value close to 23.9 wt.-%.

Theta Solvents

One of the main purposes of the present study was to find pure (i.e., nonmixed) theta solvents suitable for sedimentation analysis of SBR.   To this end, we prepared a sample, designated hereafter as R–S, by removing impurities from the starting industrial product of SBR-1500 and then cutting off its high molecular weight portion (about 5%).   The $\bar{M}_v$ value of this sample estimated by means of eq. (1) was about 2.6×10^5.   With this sample, many solubility tests were made, and eventually it was found that methyl n-propyl ketone (MNPK), methyl isobutyl ketone (MINK), methyl isoamyl ketone (MIAK), and isobutyl ketone (IBK) are likely to have theta temperatures in or near the region of room temperature.   The results of visual determination of the initial clouding temperature, made with 1% solutions of sample R–S in these four solvents, are given in Table IV.

TABLE IV

Solvent	Initial clouding temp., °C.
MNPK	ca. 10
MIBK	ca. 15–20
MIAK	ca. −8
IBK	ca. −9

On the basis of these results, we then proceeded to determine the theta temperatures of MNPK and MIBK for SBR-1500 by the method of critical consolute temperature due originally to Shultz and Flory.[3]   The apparatus and the experimental procedure used are not described here.   However, it would be instructive to remark that the solvent to be used had to be purified thoroughly in order to obtain reproducible data;   the removal of moisture was especially important.   Reagent grade MNPK and MIBK were dried over sodium sulfate and then distilled carefully under reduced pressure (ca. 18 mm. Hg), and their purities were checked by gas chromatography and by infrared analysis.   The solvents for all the physical measurements described below were always purified in this manner.

Figure 2 shows T_p, the temperature at which the given solution began turbid, as a function of polymer concentration c for the system SBR 1500–
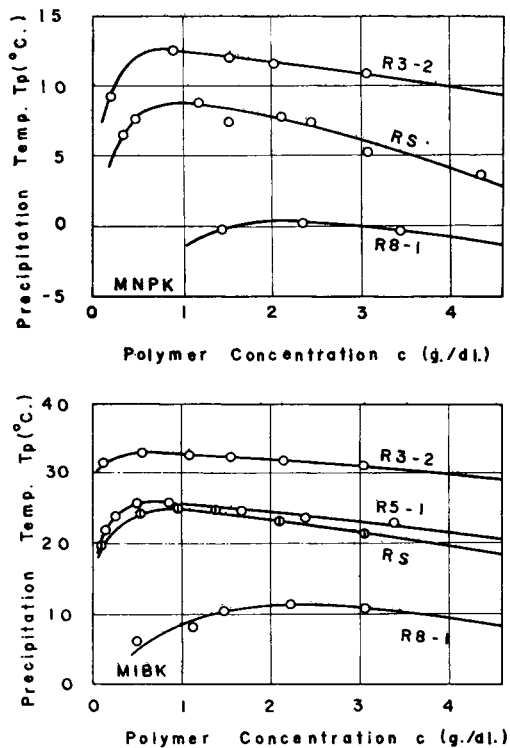
Fig. 2. Plots of T_p (precipitation temperature) vs. polymer concentration: (top) SBR-1500 in MNPK; (bottom) SBR-1500 in MIBK.
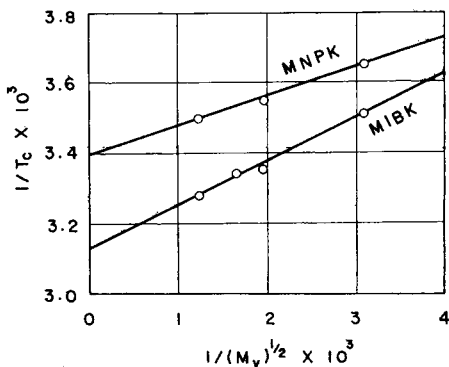

Fig. 3. Plots for $1/T_c$ vs. $1/(M_v)^{1/2}$ for solutions of SBR-1500 in MNPK and in MIBK.

MNPK and the system SBR 1500–MIBK.   The critical consolute temperatures T_c (in °K.) estimated for respective samples from the smooth curves in Figure 2 are plotted as $1/T_c$ versus $1/(\bar{M}_v)^{1/2}$ in Figure 3.   It is seen that, in agreement with the theory of Flory,[4] each set of data follows well a straight line and its intercept on the ordinate axis yields 21.0°C. as the

theta temperature θ for the MNPK system and 46.0°C. as θ for the MIBK system. These values of θ are uncertain to within ±1.0°C., depending on how we draw a straight line through plotted points. It is gratifying that these theta temperatures lie in the temperature region convenient for ultracentrifugal measurements.

Specific Refractive Index Increment and Density

For the theta solvents thus found to be useful for ultracentrifugation of SBR-1500 it is required that the specific refractive index increments dn/dc of this polymer in these solvents are fairly large and also the product $\rho_0 \bar{v}$ for each system is not very close to unity. Here ρ_0 is the density of the solvent and $\bar{v}$ is the partial specific volume of the polymer in the same solvent, both at the same temperature.

The measurement of dn/dc was made with the aid of a photoelectric differential refractometer of the Debye type (Shimazu Seisakusho Co., Kyoto), calibrated with aqueous solutions of a pure sucrose obtained from the National Bureau of Standards, Washington, D. C. The results are recorded in Table V. It is seen that these dn/dc values are large enough to warrant the use of schlieren optics for sedimentation boundary measurements on SBR 1500 in both MNPK and MIBK at the respective theta temperatures.

TABLE V
Specific Refractive Index Increment of SBR-1500
in Theta Solvent

Solvent	Temp., °C.	Specific refractive index increment, ml./g.	
		$\lambda = 436$ mμ	$\lambda = 546$ mμ
MNPK	21.0	0.172	0.164
MIBK	46.0	0.176	0.168

Pycnometric measurements were made on several solutions of sample R–S in MNPK and in MIBK, at two temperatures slightly above and below the respective theta temperature. The values of ρ_0 and $\bar{v}$ at 21.0 and 46.0°C. were then obtained by linear interpolation of the data from these measurements. The results were as follows: at 21.0°C., ρ_0 of MNPK = 0.805$_8$ g./ml., $\bar{v}$ of SBR 1500 in MNPK = 1.03 ml./g.; at 46.0°C., ρ_0 of MIBK = 0.776$_4$ g./ml., $\bar{v}$ of SBR 1500 in MIBK = 1.04 ml./g. Thus, $1 - \rho_0\bar{v} = 0.17$ for MNPK at 21.0°C.; $1 - \rho_0\bar{v} = 0.19$ for MIBK at 46.0°C. These values for the buoyancy factor are moderately large, so that as regards this point, too, both MNPK and MIBK are suitable for the ultracentrifugal study of SBR-1500.

Viscosity

Besides the measurements in toluene at 30°C. for the evaluation of viscosity-average molecular weights of individual samples, we performed

careful viscosity measurements for ten fractions in MNPK at 21.0°C. to determine whether the limiting viscosity number varies with molecular weight following the relation predicted under theta conditions.[4] In all of these measurements use was made of a capillary viscometer of the Ubbelohde type having a flow time of 160.2 sec. for toluene containing 0.1% PBNA at 30°C. The desired limiting viscosity number was determined by linear extrapolation of plots for $(\ln \eta_r)/c$ to zero concentration, where η_r is the relative viscosity of a given solution.

Ultracentrifugation

A Spinco Model E ultracentrifuge equipped with a temperature-controlling unit was used with schlieren optics and a phase plate. Use was made of a single-sector cell and a double-sector cell, both with 12 mm. optical path, depending on the particular condition of each solution. Data were taken only in MNPK at 21.0°C., all at a rotor speed of 59780 rpm. The samples examined were one unfractionated SBR-1500 (R-U) and six fractions (R3-2, R4-1, R5-1, R7-1, R8-1, R8-2) separated therefrom. Sedimentation patterns were read on a Universal Contour Projector (Nihon Kogaku Co., Tokyo) to an accuracy of 0.005 mm.

Preliminary experiments demonstrated that the apparent sedimentation coefficient of this synthetic rubber in MNPK at 21.0°C., determined from the rate of movement of the maximum refractive index gradient, is practically independent of polymer concentration at concentrations below about 0.4 g./dl. This behavior is just what we hoped to obtain at the beginning of this study, and is in line with recent data[1] on typical polymer-theta solvent systems and also with the theoretical calculation by Yamakawa.[5] However, it must be remarked that more recent studies[6] do not always support the absence of concentration dependence of the sedimentation coefficient under theta conditions.

In view of this finding from preliminary experiments, sedimentation runs for each sample were carried out only at two concentrations of about 0.15 and 0.3 g./dl. It will be seen below that these concentrations were dilute enough to permit the distribution of sedimentation coefficient at the limit of zero concentration to be determined without extrapolation to infinite dilution. In other words, as far as the system SBR-1500–MNPK at 21.0°C. is concerned, the true distribution of the sedimentation coefficient for a given sample can be derived from boundary patterns taken at one polymer concentration below about 0.4 g./dl. The actual procedure used for this derivation is described in the Results and Discussion section.

RESULTS AND DISCUSSION

Limiting Viscosity Number

The values of the limiting viscosity number in MNPK at 21.0°C. are plotted against $\bar{M}_v$, the viscosity-average molecular weight estimated from the limiting viscosity number in toluene at 30°C. by the use of eq. (1), on a
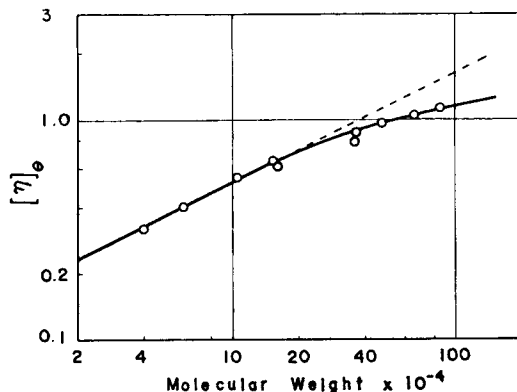
Fig. 4. Logarithmic plots of $[\eta]_\theta$ vs. $\bar{M}_v$ for SBR-1500 in MNPK at 21.0°C. (theta temperature). The dashed line has a slope of $^1/_2$.

log-log graph in Figure 4. If the samples used were nonbranched and the temperature of 21.0°C. were the correct theta temperature for the system SBR-1500–MNPK, these plots would fall on a straight line of slope 1/2 over the entire range of $\bar{M}_v$, as required by the recent theory[4] of dilute polymer solutions. The present data, however, follow this relation only in the region of $\bar{M}_v$ below about 3×10^5 (as seen from the dashed line drawn in the figure), and beyond this limit they systematically deviate downward from the expected slope. One might attribute this deviation to an increasing branching of our rubber samples with increasing molecular weight. Cragg and Fern[7] concluded, from a careful viscometric study on SBR having 28 wt.-% bound styrene in benzene, that no molecular branching was detectable when the rubber was polymerized at 15°C. If this is generally true, our SBR-1500, which had been polymerized at 5°C., should contain no branching, since the lower the polymerization temperature, the less branched polymer is obtained in general. However, since our starting material was an industrial product which had been prepared at as high a conversion ratio as 60%, it is quite likely that it contained branched molecules in its high molecular fractions. A partial support to this view is given by Figure 5, where the Huggins slope parameter k' in toluene at 30°C. is plotted against the limiting viscosity number in the same solvent at the same temperature. According to Cragg and Fern,[7] this increasing trend of k' with $[\eta]$ is an indicative of the fact that higher molecular weight fractions are more molecularly branched. If this is the case, the validity of $\bar{M}_v$ values of our rubber fractions, especially those of high molecular weight fractions, depends largely on what samples French and Ewart[2] used in deducing their viscosity–molecular weight relation (1). If they happened to use linear fractions only, our $\bar{M}_v$ values could not be correct. However, they believed that their high molecular weight fractions were also branched. It is, therefore, not unreasonable to infer that the $\bar{M}_v$ values for our high molecular weight fractions are not very incorrect. In any event, in order
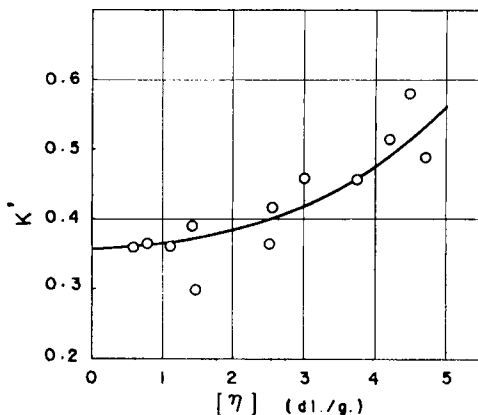
Fig. 5. Huggins slope parameter k' vs. limiting viscosity number $[\eta]$ in toluene solution of SBR-1500 at 30° C.

to resolve these ambiguities it is necessary that direct molecular weight determination, as for instance by light scattering, be made for all the samples.

Distributions of Sedimentation Coefficient and Molecular Weight

Method of Analysis.   Various methods of analysis, all essentially similar in nature, have been proposed for the determination of the distribution of sedimentation coefficient s (more rigorously, the limiting sedimentation coefficient s_0) from sedimentation boundary patterns.   These all are exact only under the condition that the dependence of s on solute concentration is absent and the boundary spreading due to diffusion is negligible.   When at least one of these effects is present, the methods remain semiempirical, and the results thereby obtained are checked only by comparison with other independent data, for instance from precise fractionation experiment. For the details of existing methods for sedimentation analysis one may consult reviews by Williams, et al.,[8] Baldwin and Van Holde,[9] and Elias,[10] or a monograph by Fujita.[11]

In any of these methods, the process of analysis consists of the following four steps: calculation of a function of s and time t, called the apparent distribution of s, from a series of sedimentation boundary patterns taken for a given initial concentration c_0; extrapolation of a series of apparent distributions of s thus obtained as a function of t to infinite time (this operation purports to eliminate boundary spreading due to diffusion); determination of such diffusion-corrected distributions of s at other values of c_0; and elimination of the effect of concentration dependence of s from these diffusion-corrected distribution functions by suitable extrapolation to infinite dilution.   Empirically, the distribution function of s so obtained at zero concentration is taken as representing the desired distribution of limiting sedimentation coefficient s_0 of the given sample in the given sol-

vent.   In such special circumstances when the study can be made with a specific solvent in which the dependence of s on concentration vanishes, at least in the region of low concentration accessible to sedimentation measurements by the current ultracentrifuge, the third and fourth steps in the above process may be omitted, and the amount of work needed to obtain the desired distribution is greatly reduced.   As has been mentioned above, our preliminary measurements demonstrated that the sedimentation coefficient of dilute MNPK solutions of SBR-1500 at 21.0°C. is practically independent of concentration.   Thus the problem is now reduced to simplifying the first and second steps in the above process without great loss of accuracy.   The method we used for this purpose is as follows.

We define an apparent integral distribution of s, $G^*(s,t)$, by the equation:

$$G^*(s,t) \ = \ \frac{\int_0^s r^3 (\partial n_c / \partial r)_{r \ = \ r_m} \ \exp(\omega^2 st) ds}{\int_0^\infty r^3 (\partial n_c / \partial r)_{r \ = \ r_m} \ \exp(\omega^2 st) ds} \tag{2}$$

where r is the radial distance from the axis of the rotor to any point in the cell, r_m is the value of r at the meniscus of the solution in the cell, ω is the angular speed of the rotor, and $\partial n_c / \partial r$ is the excess refractive index gradient of the solution being centrifuged.   The value of $G^*(s,t)$ as a function of s can be calculated from each schlieren boundary diagram photographed. However, since this calculation is rather tedious and time-consuming, it is desirable for routine work that eq. (2) be replaced by a form which allows quicker computation but which retains a similar accuracy.   This is done by observing the fact that in actual ultracentrifuge cells, $r - r_m$ is sufficiently small in comparison with r_m.   Without great loss of accuracy, we may then replace the factor r^3 in eq. (2) by $r_m{}^3$, and also the relation $r = r_m \exp(\omega^2 st)$ by $r = r_m (1 + \omega^2 st)$.   With these approximations eq. (2) reduces to the form:

$$G^*(s,t) \ = \ \int_0^{sr_m \omega^2 t} (\partial n_c / \partial x) dx / \int_0^\infty (\partial n_c / \partial x) dx \tag{3}$$

with x defined by

$$x \ = \ r \ - \ r_m \tag{4}$$

The calculation of $G^*(s,t)$ in terms of eq. (3) is simple and straightforward. The actual process may be as follows.

(1) Trace the given schlieren pattern on a transparent millimeter graph paper after the photograph has been magnified by a suitable factor, say 20. Arbitrary scales may be used for both the ordinate and abscissa axes, but the image of the meniscus must be placed exactly on the ordinate axis. Denote the abscissa and ordinate values by X and Y, as illustrated in Figure 6.

(2) Evaluate the quantity $\int_0^X Y \, dX$ as a function of X until it becomes independent of X, and divide successive values of this integral by its final, convergent value.   The resulting values are denoted by Z.
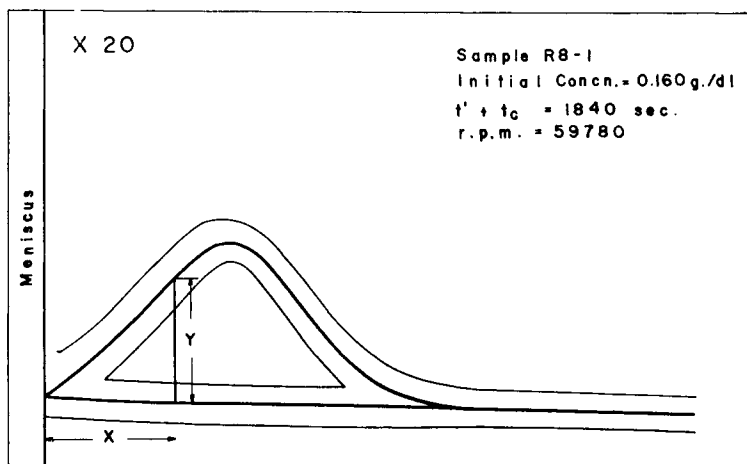
Fig. 6. An example of magnified schlieren boundary photograph. The thick line running through the middle of the upper and lower traces (thin lines) of the photograph is taken as the real refractive index gradient curve.

(3) Find the proportionality factor k between X and the corresponding real distance x, and also measure r_m, in the manner described in a standard technical manual on ultracentrifugation.

(4) Plot Z against $X/kr_m\omega^2 t$. The resulting graph represents the desired curve for $G^*(s,t)$ against s. In this plotting, the time t may be taken, to a first approximation, as the sum of t' and t_c, where t_c is one-third of the time in which the rotor attains the speed ω from rest, and t' is the time elapsed after the rotor has reached ω.

Several recent studies, including ours on anionically polymerized polystyrene samples,[6,12] have demonstrated that the following empirical procedure works well for extrapolating $G^*(s,t)$ to infinite time. This is to plot s for fixed values of $G^*(s,t)$ (say, 0.05, 0.1, 0.2, ..., 0.9, 0.95) against $1/t$ and extrapolate graphically the resulting curves to infinite time. The chosen values of G^* are then plotted against the corresponding s values obtained in this manner at infinite time. The resulting curve is denoted by $G^*(s,\infty)$. When there is no concentration dependence of s, as is the case with the system SBR-1500–MNPK at 21.0°C., this $G^*(s,\infty)$ curve is in turn regarded as equal to the integral distribution of limiting sedimentation coefficient s_0, i.e., $G(s_0)$, for the given system, provided that the data are taken at a low concentration for the dependence of s on concentration to be negligible. The desired differential distribution of s_0, $g(s_0)$, is readily obtained by numerical or graphical differentiation of $G(s_0)$.

Distribution of Sedimentation Coefficient. The extrapolation of s for fixed values of $G^*(s,t)$ to infinite time is illustrated in Figures 7a and 7b. It has been our experience that the smoothness of this type of plot, and hence the ease and correctness with which s at fixed G^* may be extrapolated to infinite time, depends primarily on how we draw a smooth line through
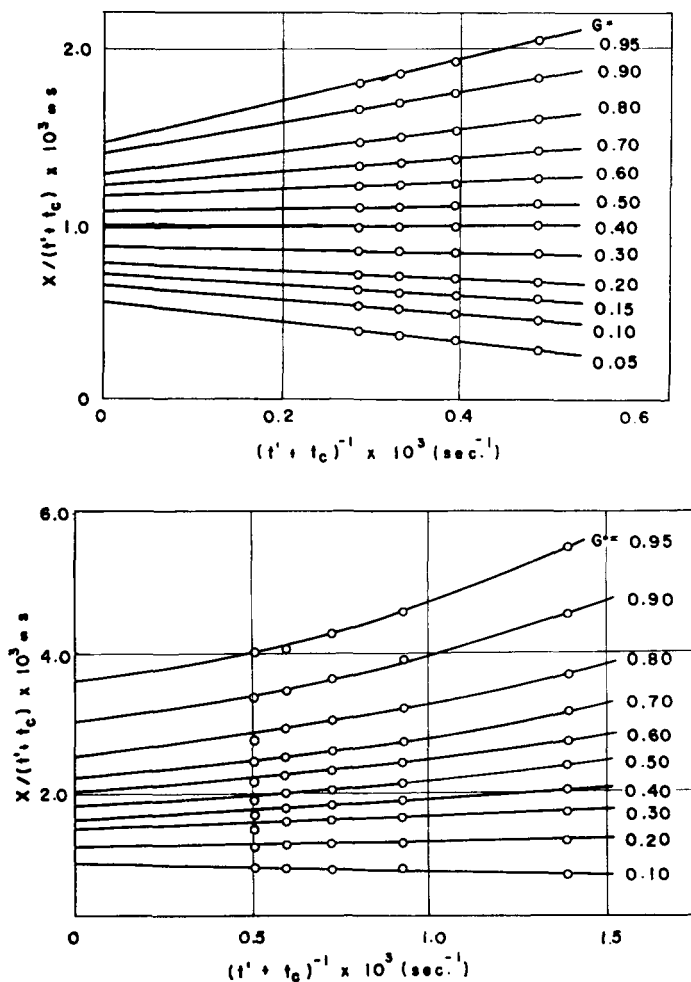
Fig. 7. Examples of the graphical extrapolation of s for various fixed values of $G^*(s,t)$ to infinite time: (a) for sample R8-2 in MNPK at 21.0°C. at an initial concentration of 0.170 g./dl.; (b) for sample R-U in the same solvent at an initial concentration of 0.160 g./dl.

midpoints of the somewhat blurred image of the base line in a magnified schlieren boundary photograph. This problem is particularly important in determining the upper and lower edges of $G^*(s, \infty)$; in other words, the values of s corresponding to $G^*(s,t)$ near zero and unity are very sensitive to the location of the base line to be drawn to each schlieren diagram. This implies that the ultracentrifuge method, in its present form, is less dependable for precise determination of the tails of a mass distribution curve. Figure 8 illustrates that under the theta condition treated here the $G^*(s, \infty)$ curves at different low concentrations are independent of concentration to a good approximation. Similar results were obtained for
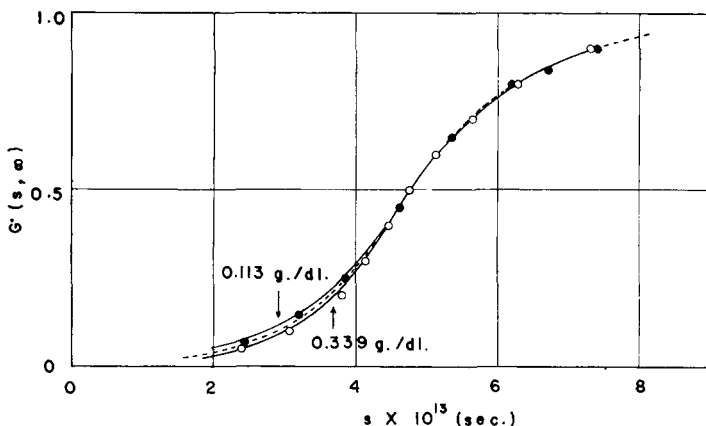
Fig. 8. Curves of $G^*(s, \infty)$ for sample R5-1 in MNPK at 21°C. at different initial concentrations. The dashed line shows the average of the two solid lines.
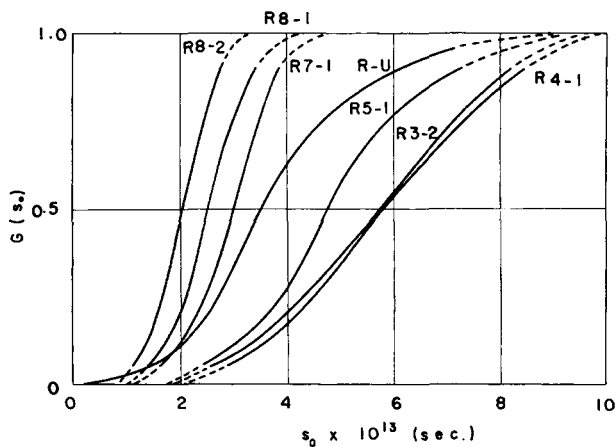

Fig. 9. $G(s_0)$ curves of six samples of SBR-1500 in MNPK at 21°C. R-U designates the unfractionated sample and others are fractions separated from it.

all other samples studied. Thus, as far as the system SBR-1500–MNPK at 21.0°C. is concerned, the mass distribution of a given sample may be deduced from sedimentation data taken at only one initial concentration below about 0.4 g./dl. The dashed line in Figure 8 represents the average of the two solid lines indicated, and is taken as the desired $G(s_0)$ for this sample in MNPK at 21.0°C. The $G(s_0)$ curves thus obtained for seven SBR samples in this theta solvent are shown graphically in Figure 9.

Relation between Limiting Sedimentation Coefficient s_0 and Molecular Weight M. In order to convert these $G(s_0)$ curves to the integral distributions of molecular weight, $F(M)$, of the respective samples, it is necessary to find the relation between s_0 and M valid for the monodisperse SBR-1500 molecule in MNPK at 21.0°C. The method recently proposed and used by
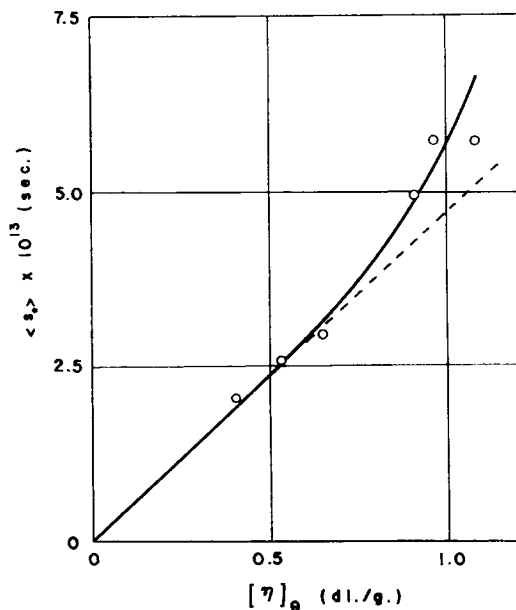
Fig. 10. Relation between $<ms_0>$ and $[\eta]_\theta$ for SBR 1500 in MNPK at 21°C. The dashed line indicates a relation which would be obtained if the sample were nonbranched.

McCormick[13] cannot be applied here, since the weight-average molecular weight $\bar{M}_w$ of each sample was not measured in this study.   We therefore devised another method which resorts to the theory of Flory.[14,4]   According to this theory, it can be shown (see Appendix) that an average limiting sedimentation coefficient $\langle s_0 \rangle$ of a polydisperse sample of a linear polymer in a theta solvent is related to the limiting viscosity number $[\eta]_\theta$ of the same sample in the solvent by the equation:

$$\langle s_0 \rangle = (A/K^{4/3}) [\eta]_\theta \tag{5}$$

As regards the definitions of $\langle s_0 \rangle$, A, and K the reader should refer to Appendix.   Both $\langle s_0 \rangle$ and $[\eta]_\theta$, and also the constant A are obtainable experimentally.   Hence eq. (5) allows determination of the value of K from experiment.   As shown in the Appendix, the relation between s_0 and M for a monodisperse, linear polymer in a theta solvent is represented by

$$s_0 = (A/K^{1/3}) M^{1/2} \tag{6}$$

Therefore, once A and K are known, the relation between s_0 and M for the given polymer–theta solvent system is established.   With the value of K known, the relation between limiting viscosity number and M for the same system is also determined (see Appendix).

Plots for $\langle s_0 \rangle$ and $[\eta]_\theta$, derived from the $G(s_0)$ curves shown in Figure 9 and the viscosity data plotted in Figure 4, are given in Figure 10.   The plots fall on a straight line passing through the coordinate origin in the
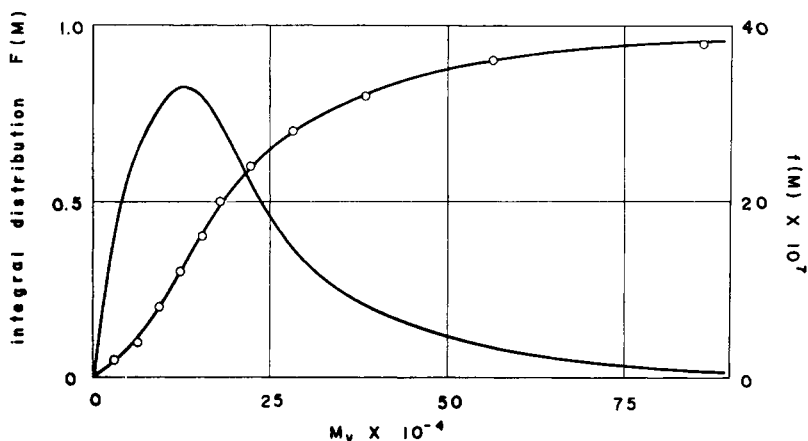
Fig. 11. Integral and differential distributions of molecular weight in original unfrac-
tionated SBR-1500, derived from this sedimentation analysis.

region of relatively small $[\eta]_\theta$, where the samples are believed to be non-
branched.   This behavior agrees with eq. (5).   The plots upswing at higher
$[\eta]_\theta$, but this is not unexpected, provided that, as has been inferred above
from viscosity data, our rubber fractions are more or less branched at
higher molecular weights.   In any event, the dashed line in Figure 10
represents the relation which would be obtained if the sample were per-
fectly linear.   From the slope of this line and the A value for SBR-1500 in
MNPK at 21.0°C. (see Appendix) the value of K is found to be $2.2_3 \times 10^{-3}$.
Thus we find

$$s_0 = 1.0_4 \times 10^{-15}M^{1/2} \text{ (in sec.)} \qquad (7)$$

for the limiting sedimentation coefficient s_0 of a perfectly monodispersed
nonbranched sample of SBR-1500 in MNPK at 21.0°C. as a function of its
molecular weight M.   The corresponding relation between limiting vis-
cosity number $[\eta]_\theta{}^m$ (superscript m designates "monodisperse") and M
reads

$$[\eta]_\theta{}^m = 2.2_3 \times 10^{-3}M^{1/2} \text{ (in dl./g.).} \qquad (8)$$

This coefficient $2.2_3 \times 10^{-3}$ should, according to current theory of dilute
polymer solution,[4] be characteristic of (linear) SBR-1500 to a first approxi-
mation, i.e., independent of solvent and temperature.   The value of this
coefficient for polystyrene is known[4] to be about 8.0×10^{-4}, while our re-
cent studies on 1,4 cis-polybutadiene[15] and 1,4 trans-polybutadiene[16] have
yielded values of about 1.3×10^{-3} and 1.5×10^{-3}, respectively, when
$[\eta]_\theta$ was plotted against the square root of $\bar{M}_w$.   These values are much
lower than the value $2.2_3 \times 10^{-3}$ appearing in eq. (8), and hence it is ex-
pected that when the proportionality factor between $[\eta]_\theta{}^m$ and $M^{1/2}$ for
linear styrene–butadiene copolymer is plotted against the styrene composi-
tion, there should appear at least one maximum in the resulting graph.

In this connection, mention may be made that Utiyama, et al.,[17] have recently observed a similar behavior with random copolymers of styrene and methyl methacrylate.

Distribution of Molecular Weight in Sample R-U. Figure 11 shows the integral and differential distributions of M calculated from the $G(s_0)$ curve for sample R-U by using the s_0 versus M relation derived above in eq. (7). However, these curves, specifically their high molecular weight tails, have to be accepted with reservation, since eq. (7) should be valid only for linear SBR-1500, whereas, as has been inferred above, sample R-U probably contains branched molecules in its high molecular weight portion. If, for the moment, we ignore this ambiguity, it is concluded that the distribution of molecular weight in unfractionated SBR-1500 is of the type of a single peak and not much different from those of ordinary vinyl polymers prepared by radical polymerization. It is of interest to compare these results from ultracentrifugation with data from fractionation experiment. For the comparison to be made with confidence, however, we have to examine the following two problems. (1) Whether the rather old viscosity–molecular weight relationship, eq. (1), which was originally derived with the hot rubber, is also applicable to the cold rubber studied? (2) Is eq. (7) for the relation between s_0 and M correct? This is equivalent to questioning if the value of 2.5×10^6 taken for the constant $\Phi^{1/3}P^{-1}$ is appropriate also for SBR-1500. Studies of these problems require the absolute determination of molecular weights of the samples treated, and are now in progress at the Research Laboratories, Japan Synthetic Rubber Co., Yokkaichi. The results, along with the comparison of the ultracentrifuge and fractionation data, will be reported soon in this journal.

APPENDIX

According to Flory,[14] the following relation holds for a monodisperse, linear polymer of molecular weight M in a solvent:

$$s_0([\eta]^m)^{1/3}M^{-2/3} = \Phi^{1/3}P^{-1}(1 - \rho_0\bar{v})/(N_A\eta_0). \tag{1'}$$

Here s_0 is the limiting sedimentation coefficient (i.e., the value of s at zero concentration), $[\eta]^m$ is the limiting viscosity number, ρ_0 and η_0 are the density and the viscosity coefficient of the solvent, $\bar{v}$ is the partial specific volume of the polymer in the given solvent, N_A is Avogadro's number, and $\Phi^{1/3}P^{-1}$ is a universal constant, the best value of which, according to Flory,[4,14] is 2.5×10^6. Applying eq. (1') to the theta condition and noticing that $[\eta]^m$ at the theta temperature, denoted here by $[\eta]_\theta^m$, is known to be related to M by the equation:[4]

$$[\eta]_\theta^m = KM^{1/2} \tag{2'}$$

we obtain

$$s_0 = (A/K^{1/3})[\eta]_\theta^m \tag{3'}$$

or

$$s_0 = (A/K^{1/3})M^{1/2} \qquad (4')$$

with A defined by

$$A = \Phi^{1/3}P^{-1}(1 - \rho_0\bar{v})/(N_A\eta_0) \qquad (5')$$

Both theoretically and experimentally it is known[4] that the factor K is, to a first approximation, independent of temperature and solvent, and thus characteristic of the given polymer species.

The differential distribution of M, $f(M)$, of a given polydisperse sample is related to the differential distribution of s_0, $g(s_0)$, of the same sample in any given solvent by the equation:

$$f(M)dM = g(s_0)ds_0 \qquad (6')$$

provided that s_0 varies only with M. Combining eqs. (3') and (6'), it follows that for any polydisperse sample in its theta solvent there holds

$$\langle s_0 \rangle = (A/K^{1/3})[\eta]_\theta \qquad (7')$$

where $\langle s_0 \rangle$ is an average sedimentation coefficient defined by

$$\langle s_0 \rangle = \int_0^\infty s_0 g(s_0)ds_0 \qquad (8')$$

and $[\eta]_\theta$ is the limiting viscosity number of the given sample in the given theta solvent. It should be noted that $g(s_0)$ in eq. (8') also refers to the same sample in the same solvent, and that eq. (7') is valid only for non-branched polymers. The value of $\langle s_0 \rangle$ can be calculated when $g(s_0)$ is determined from sedimentation measurements in the manner as described in the test, while $[\eta]_\theta$ can be directly measured.

The value of A for SBR-1500 in MNPK at 21.0°C. is found to be 1.37 $\times$ 10^{-16} if we substitute 2.5 $\times$ 10^6 for $\Phi^{1/3}P^{-1}$ and the experimental data $1 - \rho_0\bar{v} = 0.17$ and $\eta_0 = 4.97 \times 10^{-3}$ poise.

References

1. Cantow, H.-J., *Makromol. Chem.*, **30**, 169 (1959); A. Haug and G. Meyerhoff, *ibid.*, **53**, 91 (1962); D. McIntyre, A. Wims, L. C. Williams, and L. Mandelkern, *J. Phys. Chem.*, **66**, 1932 (1962); I. H. Billick, *ibid.*, **66**, 1941 (1962).

2. French, D. M., and R. H. Ewart, *Ind. Eng. Chem., Anal. Ed.*, **19**, 165 (1947).

3. Schultz, A. R., and P. J. Flory, *J. Am. Chem. Soc.*, **74**, 4760 (1952).

4. Flory, P. J., *Principles of Polymer Chemistry*, Cornell Univ. Press., Ithaca, N. Y., 1953.

5. Yamakawa, H., *J. Chem. Phys.*, **36**, 2995 (1962).

6. Papers by McIntyre et al. and by Billick cited above in ref. 1; and also T. Homma, K. Kawahara, H. Fujita, and M. Ueda, *Makromol. Chem.*, **67**, 132 (1963).

7. Cragg, L. H., and G. R. H. Fern, *J. Polymer Sci.*, **10**, 185 (1953).

8. Williams, J. W., K. E. Van Holde, R. L. Baldwin, and H. Fujita, *Chem. Revs.*, **58**, 715 (1958).

9. Baldwin, R. L., and K. E. Van Holde, *Fortschr. Hochpolymer. Forsch.*, **1**, 451 (1960).

10. Elias, H.-G., *Ultrazentrifugen-Methoden*, Beckman Instruments GmbH, München, 1962.

11. Fujita, H., *Mathematical Theory of Sedimentation Analysis*, Academic Press, New York, 1962.

12. Kawahara, K., *Makromol. Chem.*, **73**, 1 (1964).

13. McCormick, H. W., *J. Polymer Sci.*, **36**, 341 (1959).

14. Mandelkern, L., W. R. Krigbaum, H. A. Scheraga, and P. J. Flory, *J. Chem. Phys.*, **20**, 1392 (1952).

15. Fujita, H., K. Kawahara, N. Takeguchi, M. Abe, M. Kurata, H. Utiyama, and K. Kajitani, unpublished data.

16. Kurata, M., H. Utiyama, and K. Kajitani, unpublished data.

17. Utiyama, H., M. Kurata, K. Kajitani, M. Tamura, and M. Sugimoto, *Repts. Progr. Polymer Phys. Japan*, **6**, 29 (1963).

Résumé

On a trouvé que la méthyl-*n*-propyl-cétone (MNPK) à 21°C. et la méthyl-isobutyl-cétone (MIBK) 46°C. représentent des conditions thèta pour des copolymères caoutchou-teux de styrène–butadiène appelés SBR 1500 dans le commerce. Des données pour l'incrément spécifique de l'indice de réfraction et de densité indiquent que ces solvants sont adéquats pour la centrifugation de ce polymère par la méthode optique des "schli-eren." On a effectué des mesures de sédimentation sur le polymère global et sur six fractions dans le MNPK à 21°C. On a démontré qu'on peut dans des solvants thèta pour un polymère SBR 1500 déterminer les coefficients *s* de la distribution de sédimenta-tion (à la limite de la concentration zéro) à partir d'une série d'expériences de sédimenta-tion à une concentration au-dessus de 0.4 g./dl. et plus grande que zéro et ceci avec une bonne exactitude. La relation entre *s* et le poids moléculaire *M*, nécessaire pour trans-former la distribution de *s* en distribution de *M*, est obtenue par la théorie de Flory, qui donne une relation entre *s*, l'indice viscosimétrique limite et *M*. On croit que les condi-tions thèta et le processus d'analyse précité peuvent être utilisés facilement pour des études d'hétérogénéité spécilement dans le cas de ce type de coutchouc synthétique SBR 1500.

Zusammenfassung

Methyl-*n*-propylketon (MNPK) bei 21°C und Methylisobutylketon (MIBK) bei 46°C bilden Thetabedingungen für den handelsüblich als SBR 1500 bezeichneten Styrol-Butadiencopolymerkautschuk. Das spezifische Brechungsindexinkrement und die Dichte zeigen, dass diese Lösungsmittel zu Ultrazentrifugenmessungen an diesem Poly-meren nach der schlierenoptischen Methode geeignet sind. Sedimentationsmessungen am Gesamtpolymeren und sechs Fraktionen werden in MNPK bei 21°C durchgeführt. Es wird gezeigt, dass in diesem Theta-Lösungsmittel die Verteilung des Sedimentations-koeffizienten *s* (in der Grenze für Konzentration Null) einer gegebenen SBR-1500-Probe mit guter Genauigkeit aus einem einelnen Sedimentationsversuch bei einer Konzentra-tion zwischen Null und 0,4 g/dl bestimmt werden kann. Die zur Umwandlung dieser Verteilung von *s* in die Verteilung von *M* benötigte Beziehung zwischen *s* und dem

Molekulargewicht M wird mit Hilfe der durch die Theorie von Flory gegebenen Beziehung zwischen s, Grenzviskositätszahl und M abgeleitet.   Die Theta-Bedingungen gemeinsam mit dem in dieser Arbeit beschriebenen analytischen Verfahren scheinen in einfacher Weise Heterogenitätsuntersuchungen an synthetischem Kautschuk vom speziellen Typ SBR 1500 zu ermöglichen.