

Sedimentation Analysis of 1,4-*cis*-Polybutadiene in a Theta Solvent, Diethyl Ketone at 10.3°C.

MITSUO ABE, YURIKO MURAKAMI, and HIROSHI FUJITA,
Department of Polymer Science, Osaka University, Osaka, Japan

Synopsis

A sedimentation and viscosity study of 1,4-*cis*-polybutadiene (having 95% 1,4-*cis* units) in a θ -solvent diethyl ketone (DEK) at 10.3°C. is reported. The limiting sedimentation coefficient s_0 and the limiting viscosity number $[\eta]_{\theta}$ of the *monodisperse* sample of this polymer in the given θ -solvent as functions of its molecular weight M are derived from data on polydisperse fractions by application of the method described by Homma et al. The results are: $s_0 = 0.530 \times 10^{-15} M^{1/2}$ (in sec.) and $[\eta]_{\theta} = 1.60 \times 10^{-2} M^{1/2}$ (in dl./g.). Substitution of the experimental data into the well-known Mandelkern-Flory equation yields 1.74×10^6 for the familiar parameter $\Phi^{1/2} P^{-1}$, which is about 30% lower than the usually accepted value (2.5×10^6).

INTRODUCTION

The recent success in synthesizing polybutadiene molecules of very high *cis* contents has provided the rubber industry and technology with a promising new material. Probably, Danusso et al.¹ were the first to report a θ -solvent for this synthetic rubber. It is isobutyl acetate (IBA) at 20.5°C. Recently, three more θ -solvents, methyl *n*-propyl ketone (MNPK) at 59.7°C., diethyl ketone (DEK) at 10.3°C., and methyl isoamyl ketone (MIAK) at 12.6°C., have been found by Abe and Fujita,² who extrapolated the critical consolute temperature to infinite molecular weight of the polymer by means of the familiar Shultz-Flory procedure. Parallel to this study, Fujita et al.³ have presented a viscosity-molecular weight relationship for a polybutadiene sample of about 95% *cis* content in one of these three θ -solvents, MIAK at 12.6°C., using the molecular weight values of fractions determined by light-scattering measurements in cyclohexane at 40°C.

The present study is concerned with sedimentation and viscosity of a similar *cis*-polybutadiene sample in another θ -solvent, DEK at 10.3°C. It purports to derive expressions which relate s_0 and $[\eta]$ of the monodisperse sample to the sample's molecular weight M . Here s_0 is the sedimentation coefficient at infinite dilution (referred hereafter to as the limiting sedimentation coefficient), and $[\eta]$ is the limiting viscosity number. The method used for this purpose is essentially the same as that which has been applied by Homma et al.^{4,5} in their recent studies on polystyrene and SBR

(styrene-butadiene copolymer rubber) in Θ -solvents. It consists of determinations of number-average and/or weight-average molecular weights of an appropriate number of fractions (of any molecular weight heterogeneity), and their limiting viscosity numbers $[\eta]_{\Theta}$ and distribution functions $G(s_0)$ of s_0 in the given Θ solvent.

EXPERIMENTAL

Materials

The starting polymer was prepared at the Research Laboratories of Japan Synthetic Rubber Company, Yokkaichi, by low-temperature homogeneous polymerization in benzene with the system $[(C_6H_5)_3P]_2CoBr_2-AlCl_3-AlEt_3$ as catalyst.⁶ The conversion ratio was limited to 10%. The resulting material was purified by repeated precipitations from benzene solutions, and then freeze-dried, with 1% (w/w) 2,2'-methylene-bis-(4-methyl-6-*tert*-butyl phenol) added. Unless otherwise stated, this antioxidant was added in the amount of 0.1% (w/v) to all the solvent and solutions to be used, except for those in light-scattering measurements, in which the addition was limited to 0.01% (w/v).

Diethyl ketone (DEK), chosen as the Θ -solvent for this study, was subjected to physical measurements after drying with molecular sieves and fractional distillation. Its density and viscosity coefficient at 10.3°C. were 0.8236 g./ml. and $5.35_3 \times 10^{-3}$ poises, respectively.

Fractionation

A 29.32-g. portion of the original polymer was dissolved in 3 liters of benzene and separated into 12 fractions by successive precipitation, either by addition of an appropriate amount of a precipitant methanol or by lowering the solution temperature by a relevant degree. The process followed is shown schematically in Figure 1. During the entire period of this process, pure nitrogen gas was constantly and slowly admitted into the fractionation vessel, which, in turn, was kept from exposure to light, so that degradation of the polymer might be minimized. Before use, both the original polymer and fractions were stored in a freezer at about -25°C.

Approximate molecular weights of the unfractionated and fractionated samples were estimated from their limiting viscosity numbers in DEK at 10.3°C., assuming that the viscosity-molecular weight relation previously derived for this polymer in another Θ -solvent MIAK at 12.6°C.³ is applicable to this solvent system. The relative contents of 1,4-*cis*, 1,4-*trans*, and 1,2 vinyl units in each sample was evaluated from infrared data.⁷

Viscometry

Viscosity measurements were made in an Ubbelohde suspended-meniscus capillary viscometer, which had an upper bulb of ca. 2 ml. and a flow time

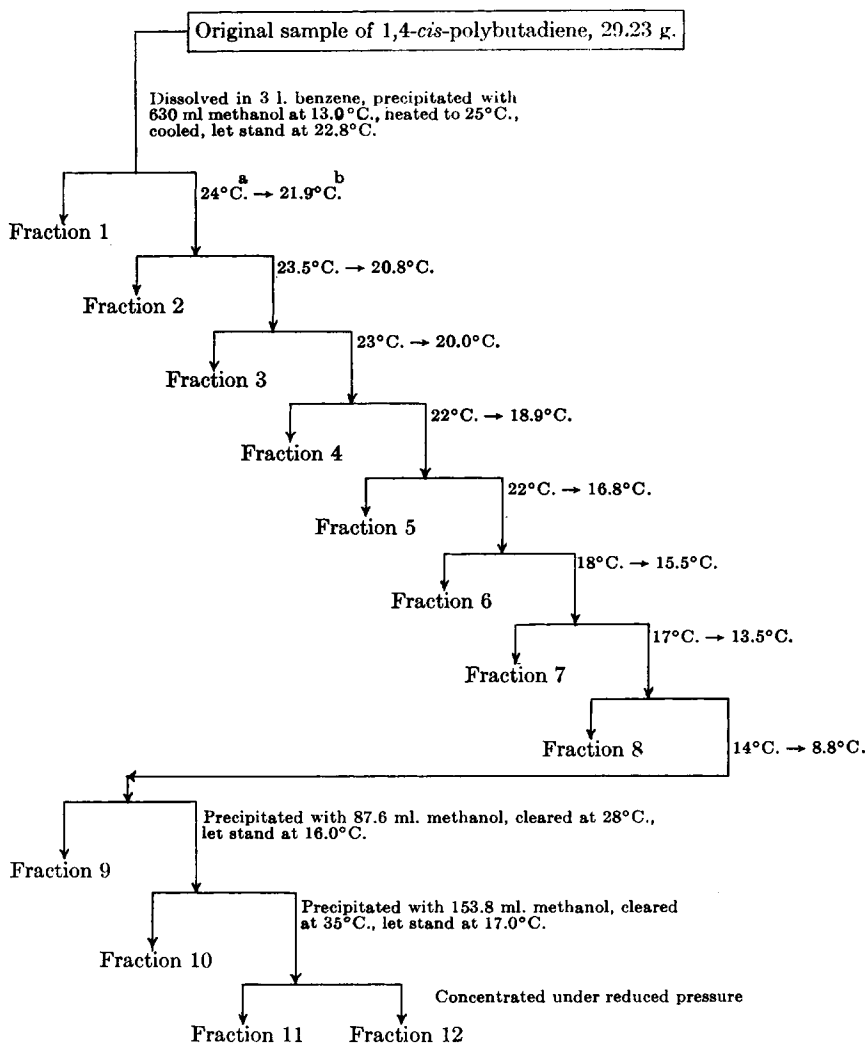


Fig. 1. Diagram of the fractionation process. The temperatures *a* and *b* denote those at which the solution cleared and at which phase separation began, respectively.

of 168.4 sec. for DEK at 10.3°C. Corrections for kinetic energy and shear rate were immaterial. Data were taken at four or five concentrations *c* (in grams/deciliter), and graphical extrapolation was made of both η_{sp}/c versus *c* and $(\ln \eta_{rel})/c$ versus *c* to zero concentration.

Osmometry

Glass osmometers of a modified Zimm-Myerson type, fitted with an adequately conditioned gel cellophane membrane (Tokyo Cellophane Co., pore size ca. 100 m μ , thickness 0.02 mm.), were used. Measurements were effected for 6 fractions (1, 3, 6, 7, 9, and 11) in cyclohexane at 35 \pm

0.01°C. The static method was used. Equilibrium osmotic heads from ascending and descending menisci agreed excellently in all the cases treated. The desired heads were read at least one day after equilibrium had been reached. In no case was leakage of the solute through the membrane detected.

Light Scattering

Six fractions (1, 3, 5, 6, 8, and 10) were subjected to light-scattering measurements in DEK at 10.3°C., first to determine their weight-average molecular weights \bar{M}_w and second to see if the second virial coefficient of *cis*-polybutadiene vanishes in this solvent medium. Measurements were made in a Shimadzu light-scattering photometer equipped with a cylindrical cell and a thermostating unit, unpolarized light of wavelength 436 m μ being used. The photometer assembly was calibrated in two ways, one with measurements on pure benzene and the other with measurements on methyl ethyl ketone solutions of an atactic polystyrene sample of known molecular weight (distributed by the Society of Polymer Science, Japan, for a cooperative development of light-scattering techniques). The constants of calibration from these two measurements agreed from one another to within $\pm 2\%$. The solvent and solutions to be examined were cleaned by spinning for 1.5–2.0 hr. at 13,500 rpm in a Phywe preparative centrifuge and directly put into the cell by means of a 50 ml. pipet fitted with a fine capillary at the tip. Data were taken at four polymer concentrations and in the range of angle of 35–140°, and were treated in terms of the Zimm procedure.

For the specific refractive index increment of the polymer in DEK, a value 0.15₆ ml./g., obtained at 25.0°C. for unpolarized light of wavelength 436 m μ ,⁸ was taken, ignoring the effect due to the difference of the measuring temperature from that at which the light-scattering experiment was conducted.

Ultracentrifugation

Sedimentation experiments were performed on the original sample and its 11 fractions in DEK at 10.3 \pm 0.1°C., by use of a Spinco Model E analytical centrifuge equipped with a phase plate and a temperature-regulating unit. All measurements were effected with a 12-mm. double-sector cell at the maximum angular velocity 59,780 rpm. Schlieren photographs of sedimentation boundaries were magnified by a factor of 20 and traced on transparent millimeter graph papers by means of a universal contour projector (Nippon Kogaku Co., Tokyo).

Pycnometric measurements, made on DEK solutions of the original unfractionated sample at 10.3°C., yielded a linear plot for the inverse density ρ^{-1} versus the weight fraction of the solute w_2 in the range examined (w_2 from zero to 0.03). From its slope (determined by least-square treatment) a value of 0.11₄ was obtained for the buoyancy factor $1 - \rho_0\bar{v}$,

where ρ_0 is the density of pure solvent and \bar{v} the partial specific volume of solute at infinite dilution. This relatively small buoyancy factor is unfavorable for sedimentation analysis of *cis*-polybutadiene to be effected in DEK at 10.3°C. as a Θ -solvent.

RESULTS

Fractionation Data

Table I summarizes the results from successive fractionations. It was found (Table II) that the relative contents of 1,4-*cis*, 1,4-*trans*, and 1,2 vinyl units showed no systematic variation from fraction to fraction. The integral distribution $F(M)$ of molecular weight M in the original unfractionated sample calculated from these fractionation data by the use of the standard Schulz procedure is shown in Figure 11.

TABLE I
Fractionation Data

Fraction	$[\eta]_{\Theta}$, dl./g. ^a	$\bar{M}_n \times 10^{6b}$	Weight, g.	Cumulative weight fraction, % ^c
12	0.344	0.462	1.21	2.20
11	0.487	0.888	1.76	7.59
10	0.580	1.32	2.55	15.41
9	0.660	1.70	3.05	25.58
8	0.724	2.05	2.42	35.60
7	0.767	2.30	2.36	44.18
6	0.812	2.58	2.27	52.58
5	0.847	2.80	1.44	59.32
4	0.870	2.95	1.89	65.34
3	0.900	3.16	3.60	75.32
2	0.939	3.45	2.67	86.60
1	0.974	3.70	2.33	95.77
			Total	27.55 ^d

^a Limiting viscosity number in diethyl ketone at 10.3°C.

^b Viscosity-average molecular weight calculated in terms of eq. (11) in the text.

^c $\left[\sum_{i=12}^j \text{weight fraction of fraction } i + \frac{1}{2} (\text{weight fraction of fraction } j) \right] \times 100$.

^d Recovery = 27.55/29.32 = 0.943.

Osmotic Pressure Data

Figure 2 shows plots for π/c versus c on the six fractions examined, where π is the equilibrium osmotic pressure and c the polymer concentration. The number-average molecular weights \bar{M}_n obtained from the ordinate intercepts of the indicated lines are recorded in Table II. Values of the osmotic second virial coefficient derived from the slopes of these lines are nearly the same for the six fractions, giving 1.35×10^{-3} mole-ml./g.² as an average.

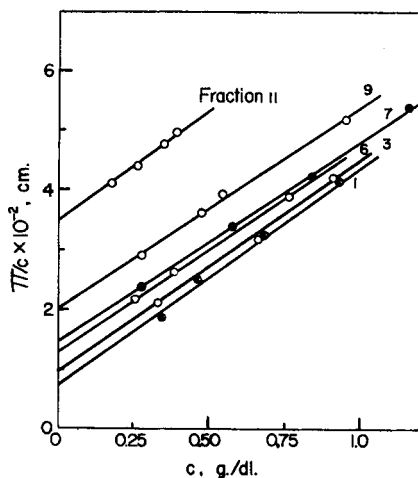


Fig. 2. Osmotic pressure plots for six fractions in cyclohexane at $35 \pm 0.01^\circ\text{C}$. (except for fraction 7, for which the temperature is $30 \pm 0.01^\circ\text{C}$.)

Light-Scattering Data

By way of example, Figure 3 shows Zimm plots for fraction 3. The corresponding plots for other five fractions examined are essentially similar in nature to this graph and are not reproduced here. It is seen that the 1,4 *cis*-polybutadiene molecule doubtlessly comes to the theta state in DEK at 10.3°C ., in conformity to the previous finding of Abe and Fujita² from measurements of the critical solution temperature. The values of \bar{M}_w obtained are given in Table II. The values of $\langle S^2 \rangle_z$, the *z*-average square radius of the polymer coil, for the fractions were too small to be determined with precision, excepting those of fractions 1 and 3. Table II also includes the viscosity-average molecular weights \bar{M}_v of the original polymer and its 12 fractions calculated from limiting viscosity numbers in DEK at 10.3°C . by means of a viscosity-molecular weight relationship

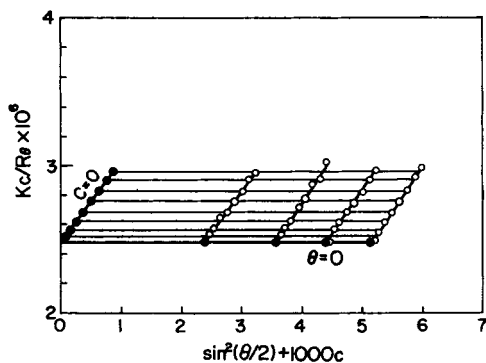


Fig. 3. Zimm plots for light-scattering data on fraction 3 in diethyl ketone at 10.3°C .

to be derived below. Comparison of \bar{M}_n , \bar{M}_w , and \bar{M}_v listed in Table II gives qualitative information about the molecular weight heterogeneity of respective fractions.

TABLE II
Molecular Characteristics of Samples Studied

Fraction	$\bar{M}_n \times 10^5$	$\bar{M}_w \times 10^5$	$\bar{M}_v \times 10^5$	1,4- <i>cis</i> , %	1,4- <i>trans</i> , %	1,2- <i>vinyl</i> , %
1	3.60	5.78	3.70	94.6	2.4	2.8
2	—	—	3.45	95.3	2.1	2.4
3	2.72	4.02	3.16	94.8	2.3	2.8
4	—	—	2.95	95.7	1.9	2.4
5	—	3.05	2.80	95.4	2.1	2.5
6	2.01	2.86	2.58	95.0	2.1	2.7
7	1.76	—	2.30	95.8	1.8	2.4
8	—	2.25	2.05	95.5	2.0	2.5
9	1.31	—	1.70	95.7	1.9	2.4
10	—	1.43	1.32	95.3	2.1	2.6
11	0.75	—	0.888	95.2	2.2	2.6
12	—	—	0.462	94.8	2.4	2.8
Original (unfractionated)	—	—	2.18	94.6	2.3	2.9

Sedimentation Data

First, to examine how much the sedimentation behavior of *cis*-polybutadiene in this Θ -solvent medium is affected by the concentration of the solution, we chose three fractions (2, 6, and 9) and determined, at three or four initial concentrations c_0 , their apparent sedimentation coefficients s_m in the usual manner, i.e., from measurements of the position of maximum refractive index gradient as a function of time. The results are indicated in Figure 4. It is seen that the concentration dependence of s_m in this synthetic rubber- Θ -solvent system is not altogether negligible, even at low concentrations. In the concentration range examined, the behavior of s_m appears to be fitted by a linear equation of the form: $s_m = s_{m_0} (1 - k_s c_0)$. Values of k_s for the three fractions are plotted against s_{m_0} in Figure 5, where the marks of the plotted points correspond to those of Figure 4.

Next, with fraction 6 chosen as a representative, we calculated its $G^*(s)$ functions at four initial concentrations by application of the method of sedimentation analysis described by Homma et al.^{4,5} Here $G^*(s)$ denotes the apparent integral distribution of sedimentation coefficient s in a given solvent (DEK at 10.3°C. in the present case) that has been defined previously.^{4,5} The results are shown in Figure 6. The effect of the initial concentration on $G^*(s)$ is apparent. Therefore, in order for the distribution function of limiting sedimentation coefficient s_0 to be found, it is imperative that the function $G^*(s)$ be determined for at least three or four initial concentrations, and the results be extrapolated to

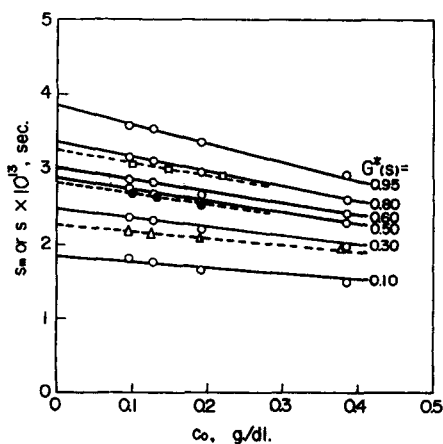


Fig. 4. Plots of s_m vs. initial concentration c_0 : (\square) fraction 2, (\bullet) fraction 6, (Δ) fraction 9; plots of (\circ) s at various fixed $G^*(s)$ vs. c_0 (taken with fraction 6). All plotted points refer to diethyl ketone at 10.3°C.

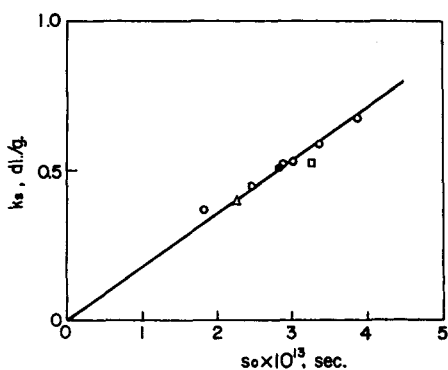


Fig. 5. Linear relation between k_s and s_0 (and also s_{m0}) deduced from Figure 4.

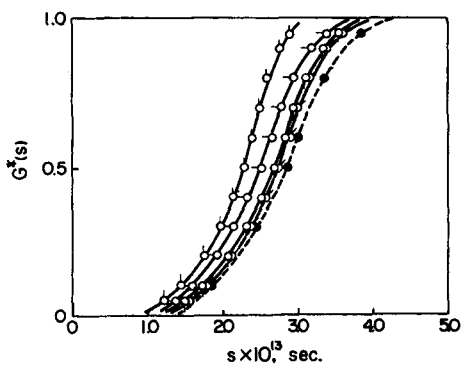


Fig. 6. Apparent integral distributions $G^*(s)$ of sedimentation coefficient s of fraction 6 in diethyl ketone at 10.3°C. for various initial concentrations c_0 : (\diamond) 0.386 g./dl.; (\circ) 0.193 g./dl.; (\square) 0.129 g./dl.; (\odot) 0.097 g./dl.; (\bullet) 0.000 (extrapolated).

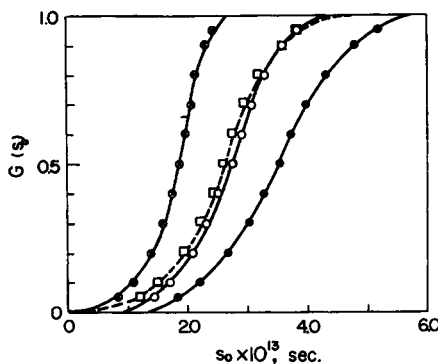


Fig. 7. Integral distributions $G(s_0)$ of limiting sedimentation coefficient s_0 : (□) original unfractionated sample; (●) fraction 1; (○) fraction 6; (⊗) fraction 11. All in diethyl ketone at 10.3°C.

infinite dilution by using, for example, an empirical procedure described previously.⁴ Unfortunately, a great many experiments have to be performed for this procedure to be carried through. So, in this study, the following convention was adopted to estimate the distribution function of s_0 , $G(s_0)$, from the experimental determination of $G^*(s)$ at one initial concentration.

If the values of s for various fixed $G^*(s)$ and for different c_0 are read off the system of curves shown in Figure 6 and are plotted against c_0 , the results indicated by open circles in Figure 5 are obtained. It is observed that the plots for any fixed $G^*(s)$ follow a straight line in the range of c_0 indicated and thus are represented by the equation $s = s_0 (1 - k_s c_0)$. Values of k_s so obtained for several fixed $G^*(s)$ are plotted against the corresponding s_0 values in Figure 4 (open circles). From this graph it would be legitimate to assume that there is a linear correlation between k_s and s_0 , expressed by the equation $k_s = 0.17_9 \times 10^{13} s_0$ when c_0 is expressed in grams/deciliter. Such a linear relation, in turn, implies that under Θ conditions the quantity k_s varies linearly with the square root of the polymer's molecular weight M , since, according to current theory, s_0 of a linear flexible macromolecule in a Θ -solvent should be a linear function of $M^{1/2}$. Pyun and Fixman,⁹ and independently Yamakawa,¹⁰ have recently presented theoretical calculations which lead to the linear correlation between k_s and $M^{1/2}$ under Θ conditions. Our conventional procedure for the derivation of $G(s_0)$ makes recourse to such an empirically obtained relation between k_s and s_0 . That is, we transform a $G^*(s)$ curve determined at an appropriately chosen c_0 by changing the abscissa from s to s_0 by using the relation:

$$s = s_0 (1 - 0.17_9 \times 10^{13} s_0 c_0) \quad (1)$$

and regard the resulting curve on the s_0 axis as the desired $G(s_0)$. Except for that of fraction 6, we have evaluated the $G(s_0)$ functions of all other

fractions and the original sample from sedimentation data taken at one initial concentration relevant to each (about 0.2 g./dl.), by applying the method described above. By way of example, the $G(s_0)$ curves thus obtained for the original polymer and fractions 1, 6, and 11 are shown in Figure 7.

In all the cases treated, the centrifugal edges of the observed sedimentation boundary curves did not travel beyond about 40% of the length of the solution column in the maximum interval of each run. In other words, all sedimentation patterns from which data for s_m and $G(s_0)$ were derived were confined to the region in the cell where hydrostatic pressures caused by the high-speed spinning of the rotor are not as high as to produce appreciable changes in viscosity and density of solvent and partial specific volume of solute. In view of this behavior, corrections for pressure effects on s_m and $G(s_0)$ were ignored in the present study.

DISCUSSION

Basic Relationships

Current theory¹¹ of dilute polymer solutions indicates that under Θ conditions the limiting viscosity number $[\eta]_{\Theta}^m$ and the limiting sedimentation coefficient s_0 of a monodisperse sample of a linear polymer molecule are related to its molecular weight M by the equations:

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

$$s_0 = kM^{1/2} \quad (3)$$

where K and k are parameters characteristic of the given polymer-solvent system and also of temperature. If these relations are combined with the relation:

$$f(M)dM = g(s_0)ds_0 \quad (4)$$

where $f(M)$ is the differential distribution of M and $g(s_0)$ is the differential distribution of s_0 , the following equations, valid for any polydisperse sample of the given polymer in the given Θ -solvent, are readily derived:

$$\bar{s}_v = (k/K)[\eta]_{\Theta} \quad (5)$$

$$\bar{s}_n = k\bar{M}_n^{1/2} \quad (6)$$

$$\bar{s}_w = k\bar{M}_w^{1/2} \quad (7)$$

Here \bar{s}_n , \bar{s}_v , and \bar{s}_w are the average sedimentation coefficients of the given polydisperse sample defined by the equations:

$$\bar{s}_n = \left\{ \int_0^{\infty} [g(s_0)/s_0^2] ds_0 \right\}^{-1/2} \quad (8)$$

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

$$\bar{s}_w = \left[\int_0^\infty s_0^2 g(s_0) ds_0 \right]^{1/2} \quad (10)$$

and $[\eta]_\theta$ is the limiting viscosity number of the same sample in the θ -solvent considered. The $g(s_0)$ in eqs. (8)–(10) also refers to the same solvent. Equation (7) is due originally to McCormick,¹² while eqs. (5) and (6) may be attributed to Homma et al.^{4,5} The application of these equations to our *cis*-polybutadiene data is presented in the following.

Values of k and K for the System 1,4-*cis*-Polybutadiene–DEK at 10.3°C.

Table III lists the values of \bar{s}_n , \bar{s}_v , and \bar{s}_w calculated from the $G(s_0)$ curves obtained. Values of \bar{s}_n and \bar{s}_w were calculated only for fractions whose \bar{M}_n or \bar{M}_w were actually determined. This table also includes the s_{m_0} values of the three fractions, for which the apparent sedimentation coefficient s_m was measured as a function of the initial concentration c_0 .

TABLE III
Various Average Sedimentation Coefficients (at Infinite Dilution) of *cis*-Polybutadiene Fractions in Diethyl Ketone at 10.3°C.

Fraction	$\bar{s}_n \times 10^{13}$, sec.	$\bar{s}_w \times 10^{13}$, sec.	$\bar{s}_v \times 10^{13}$, sec.	$s_{m_0} \times 10^{13}$, sec. ^a
1	3.0 ₄	3.7 ₀	3.5 ₇	—
2	—	—	3.2 ₈	3.2 ₇
3	2.7 ₂	3.3 ₈	3.1 ₂	—
4	—	—	3.0 ₃	—
5	—	2.9 ₈	2.9 ₂	—
6	2.3 ₂	2.7 ₈	2.7 ₄	2.8 ₂
7	2.2 ₆	—	2.5 ₇	—
8	—	2.5 ₄	2.5 ₂	—
9	1.9 ₇	—	2.2 ₀	2.2 ₆
10	—	2.0 ₂	1.9 ₆	—
11	1.3 ₉	—	1.8 ₀	—

^a Determined in the usual manner from the position of the maximum refractive index gradient as a function of time.

Figure 8 shows plots for \bar{s}_v versus $[\eta]_\theta$. If eq. (5) is valid, these plots should form a straight line passing through the coordinate origin, and this should be the case regardless of the molecular weight heterogeneities of respective samples appearing in the plot. It is seen that our data obey this prediction, except in the region of relatively high $[\eta]_\theta$, where the plotted points deviate systematically upward from the straight line fitting the points for the lower $[\eta]_\theta$. This upward deviation appears due to increasing branching of the molecules in high molecular weight fractions. The slope of the straight line drawn is 3.32×10^{-13} , which, according to eq. (5), may be taken as the value of k/K for the polymer–solvent system studied.

Plots for \bar{s}_n versus $\bar{M}_n^{1/2}$ and for \bar{s}_w versus $\bar{M}_w^{1/2}$, derived from the numerical values given in Tables II and III, are shown together in Figure 9. Equations (6) and (7) predict these two plots to fall on a common

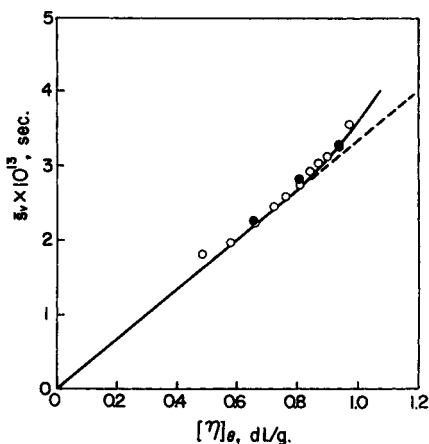


Fig. 8. Plots of (O) \bar{s}_v vs. $[\eta]_\theta$ in diethyl ketone at 10.3°C. and (●) s_{m_0} vs. $[\eta]_\theta$ in the same solvent medium.

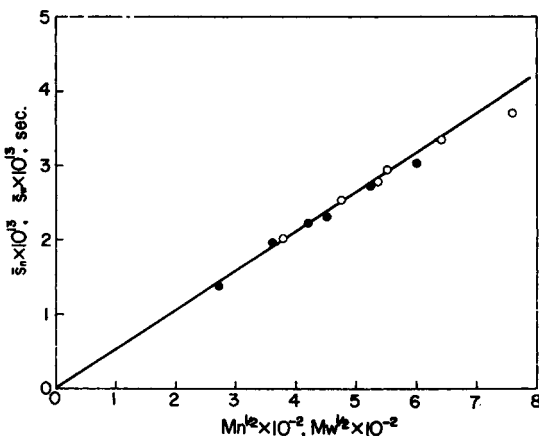


Fig. 9. Plots of (●) \bar{s}_n vs. $\bar{M}_n^{1/2}$ and (O) \bar{s}_v vs. $\bar{M}_w^{1/2}$ in diethyl ketone at 10.3°C.

straight line passing through the coordinate origin, regardless of the polydispersities of respective samples. It is observed that, except for one point at the extreme right, this theoretical prediction is excellently borne out by our experimental results. The slope of the line drawn is 5.30×10^{-16} , which, in accordance with eq. (6) or (7), may be taken as the k value for the system considered. When this is substituted into $k/K = 3.32 \times 10^{-13}$ found above, the value 1.60×10^{-3} is obtained for the parameter K .

Thus for monodisperse linear 1,4-*cis*-polybutadiene in DEK at 10.3°C. we arrive at the following relationships:

$$[\eta]_\theta^m = 1.60 \times 10^{-3} M^{1/2} \text{ (in dl./g.)} \quad (11)$$

$$s_0 = 5.30 \times 10^{-16} M^{1/2} \text{ (in sec.)} \quad (12)$$

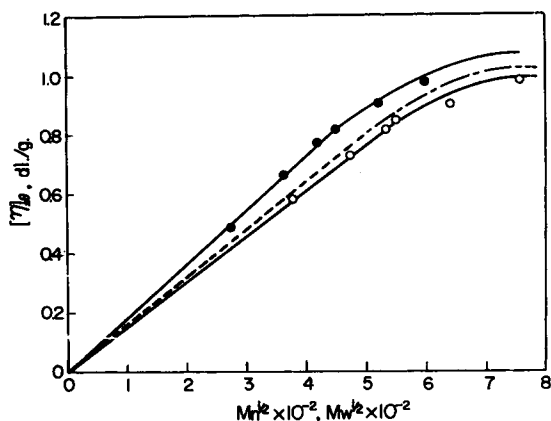


Fig. 10. Plots of (●) $[\eta]_{\theta}$ vs. $\bar{M}_n^{1/2}$ and (○) $[\eta]_{\theta}$ vs. $\bar{M}_w^{1/2}$ in diethyl ketone at 10.3°C.; (—) relation given by eq. (11) in the text; (---) curve drawn rather arbitrarily to account for molecular branching of high molecular weight samples.

Equation (11) may be compared with a previously derived relation of Fujita et al.:³

$$[\eta]_{\theta} = 1.30 \times 10^{-3} \bar{M}_w^{1/2} \quad (13)$$

which refers to a θ -solvent, MIAK at 12.6°C. Probably it is more legitimate to compare eq. (13) with a relation between $[\eta]_{\theta}$ and $\bar{M}_w^{1/2}$ for our polybutadiene fractions, rather than with eq. (11). The open circles in Figure 10 indicate such a relation. This figure also indicates the corresponding relation between $[\eta]_{\theta}$ and $\bar{M}_n^{1/2}$ (closed circles). For $[\eta]_{\theta}$ below 0.85 dl./g: the plots are linear, yielding the equations:

$$[\eta]_{\theta} = 1.52 \times 10^{-3} \bar{M}_w^{1/2} \quad (14)$$

$$[\eta]_{\theta} = 1.81 \times 10^{-3} \bar{M}_n^{1/2} \quad (15)$$

The difference between eqs. (13) and (14) is rather large and appears to suggest a difference of specific effects of DEK and MIAK on the unperturbed dimensions of 1,4-*cis*-polybutadiene. However, recent viscosity measurements by one of us (M. A.) for the present polybutadiene fractions in MIAK at 12.6°C. have yielded a relation essentially identical to eq. (14). Hence it must be concluded that eq. (13) is not correct and there is no essential difference in specific effects of DEK and MIAK. Danusso et al.¹ had earlier deduced the following relation for high-*cis*-polybutadiene in a θ -solvent IBA (isobutyl acetate) at 20.5°C.:

$$[\eta]_{\theta} = 1.85 \times 10^{-3} \bar{M}_n^{1/2} \quad (16)$$

This coefficient is quite close to that appearing in eq. (15), but the agreement is presumably somewhat accidental.

The two plots in Figure 10 bend downward rather sharply at $[\eta]_{\theta}$ above 0.85 dl./g. Fujita et al.³ observed similar behavior for *cis*-polybutadiene in

MIAK as Θ -solvent and interpreted it in terms of the increased molecular branching in samples of higher molecular weight. This interpretation again may apply here. It also accounts for the fact that, as in Figure 8, plots for \bar{s}_v versus $[\eta]_\Theta$ systematically bend upward at $[\eta]_\Theta$ above 0.8–0.85 dl./g. However, it is not consistent with the plots of Figure 7, which apparently exhibit no detectable curvature over the molecular weight range indicated; if samples of higher molecular weight are molecularly branched, these plots should be more or less curved upward at molecular weights above a certain value. The need for further study is thus indicated.

Evaluation of Parameters Φ and P

Under Θ -conditions the well-known Flory-Mandelkern equation¹³ may be put in the form:

$$\Phi^{1/3}/P = N_A \eta_0 k K^{1/3}/(1 - \rho_0 \bar{v}) \quad (17)$$

where N_A is Avogadro's number, η_0 is the viscosity coefficient of the solvent, k and K are the coefficients appearing in eqs. (2) and (3), $1 - \rho_0 \bar{v}$ is the buoyancy factor, and finally Φ and P are the parameters familiar in the current theory of dilute polymer solutions.¹¹ Substituting our experimental values for these quantities into eq. (17), we obtain

$$\Phi^{1/3} P^{-1} = 1.74 \times 10^6 \quad (18)$$

If the widely accepted empirical value of 5.1 is inserted for P , we obtain $\Phi = 0.720 \times 10^{21}$, which is only one third of the standard empirical value.¹¹ Homma and Fujita⁵ encountered a similar discrepancy in their recent study on SBR (styrene-butadiene copolymer rubber), but they were unable to explain it. Probably one of the causes of these discrepancies is in that both the polybutadiene and SBR samples used in the present and previous studies may have been branched, even at molecular weights lower than those at which the existence of branching was apparent from the viscosity behavior observed. Recently Hearst¹⁴ corrected the incomplete averaging process of the Oseen tensor which appears in the Kirkwood-Riseman theory for $[\eta]$ of flexible chain molecules and obtained a value 2.2×10^{21} for Φ . If this value is inserted into eq. (18), we obtain $P = 7.5$, which is 40% larger than the currently accepted theoretical value 5.3. However, it may be noted that this theoretical value is based on an incomplete averaging of the Oseen tensor in the Kirkwood-Riseman theory for the frictional coefficient of flexible chain molecules.

Comparison of Integral Distributions $F(M)$ of Molecular Weight M

Figure 11 compares the $F(M)$ curve for the original unfractionated sample derived from sedimentation analysis with that obtained from the fractionation data given in Table I. It is seen that the two curves agree well with one another up to M of about 3.2×10^5 . The marked divergence of them beyond this limit is attributed to the fact that, as shown in Figure 10, eq. (11) is presumably no longer applicable in the region of M above

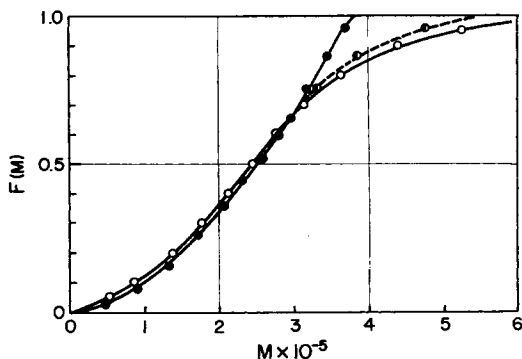


Fig. 11. Comparison of integral distributions $F(M)$ of molecular weight M obtained for the original unfractionated sample by: (O) sedimentation analysis and (●) fractionation; (●) result which would be obtained if the viscosity-molecular weight relation were corrected for molecular branching in the manner shown by the chain line in Figure 10.

about 3.5×10^5 . It appears reasonable to assume that in such a region of M the correct relation between $[\eta]_0$ and M would follow a downward curve shown by a chain line. The dashed curve in Figure 11 is the distribution curve which would be obtained if the chain line in Figure 10 were actually followed. With this device the agreement between the two $F(M)$ curves, one from ultracentrifugation and the other from fractionation, is appreciably improved. Finally, we wish to note that, by using the sedimentation method employed here, the desired $F(M)$ curve for a given 1,4-*cis*-polybutadiene sample can be derived in two or three days.

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Résumé

On fait une étude par sédimentation et viscosité du 1,4-*cis*-polybutadiène (ayant 95% d'unités 1,4-*cis*) dans un solvant- Θ , la diéthyl cétone (DEK) à 10,3°C. Le coefficient de sédimentation limite s_0 et la viscosité limite $[\eta]_{\Theta}$ de l'échantillon *monodispersé* de ce polymère dans le solvant Θ donné, en fonction de son poids moléculaire M sont obtenus à partir des résultats des fractions polydispersées en appliquant la méthode décrite par Homma et al. Les résultats sont: $s_0 = 0.530 \times 10^{-15} M^{1/2}$ (en sec.) et $[\eta]_{\Theta} = 1.60 \times 10^{-3} M^{1/2}$ (en dl/g). L'introduction des résultats expérimentaux dans l'équation bien connue de Mandelkern-Flory, donne 1.74×10^6 pour le paramètre habituel $\Phi^{1/2}P^{-1}$, qui est environ 30% plus bas que la valeur habituellement admise (2.5×10^6).

Zusammenfassung

Eine Sedimentations- und Viskositätsuntersuchung wurde an 1,4-*cis*-Polybutadien (mit 95% 1,4-*cis*-Bausteinen) in einem Θ -Lösungsmittel, Diäthylketon (DEK), bei 10,3°C durchgeführt. Der Grenzsedimentationskoeffizient s_0 und die Grenzviskositätszahl $[\eta]_{\Theta}$ werden für eine monodisperse Probe dieses Polymeren in dem gegebenen Θ -Lösungsmittel als Funktion ihres Molekulargewichtes M aus Daten für polydisperse Fraktionen unter Verwendung der von Homma et al. beschriebenen Methode abgeleitet. Die Ergebnisse sind: $s_0 = 0,530 \times 10^{-15} M^{1/2}$ (in sek.) und $[\eta]_{\Theta} = 1,60 \times 10^{-3} M^{1/2}$ (in dl/g). Einsetzen der Versuchsdaten in die wohlbekanntete Mandelkern-Flory-Gleichung liefert für den Parameter $\Phi^{1/2}P^{-1}$ den Wert $1,74 \times 10^6$, was um ungefähr 30% niedriger ist als der allgemein angenommene Wert ($2,5 \times 10^6$).

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