

Dilute Solution Properties of Cyclized Polybutadiene

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ABSTRACT: Light scattering and viscosity measurements on dilute solutions of cyclized *cis*-1,4-polybutadiene polymers (CBR) with different degrees of cyclization (*DC*) and their fractions are reported in this paper. The data were obtained in both cyclohexane and mixed theta solvents at 30.0°C. The curves of the intrinsic viscosity $[\eta]_0$ in mixed theta solvents vs. the weight average molecular weight M_w for CBR with *DC* over 30% exhibited two distinct regions with slopes of 0.5 and less. Thus, the exponent in the viscosity equation is the same as that for the original uncyclized samples at M_w below the critical point M_{wc} and decrease with increasing *DC* at M_w above M_{wc} . The M_{wc} shifts to lower M_w as *DC* is increased. The relation of the molecular structure of CBR with *DC* is discussed. The results led to the conclusions that 1) at *DC* below 25%, the molecules are linear in the overall structure, but locally contain short intramolecular cyclic structures, *e.g.*, mono- and/or bicyclic structures, 2) at *DC* between 25 and 60%, the molecules are randomly branched, and 3) at *DC* over 80%, the molecules have probably very compact structure formed by internal crosslinks.

KEY WORDS Cyclized Polybutadiene / Degree of Cyclization / Intrinsic Viscosity / Weight Average Molecular Weight / Mean-Square Radius of Gyration / Mixed Theta Solvent / Dilute Solution /

The cyclized *cis*-1,4-polybutadiene (CBR) produced by Japan Synthetic Rubber Co., Ltd. shows characteristic properties of a photoresists, as has been reported elsewhere.¹ A variety of solution properties of cyclized polydienes, especially cyclized polyisoprene, have already been studied by a group of Czechoslovak Academy of Sciences,²⁻⁶ who found that the dependence of the limiting viscosity number and the GPC elution volume on the molecular weight is the same for both cyclo- and cyclized polydienes and that the structures of these two polydienes are very different from those of linear polydienes. Thus, the macromolecules of cyclo- and cyclized polydienes are compact and spherical in shape with extraordinarily small dimensions.

In this work, we have examined systematically the dilute solution properties of CBR with cyclization degrees from 0 to 80% in both good and theta solvents. The weight-average molecular weights, the mean-square radii of gyration, and the intrinsic viscosities of these CBR were determined by light scattering and viscosity measurements. On the basis

of the experimental data obtained, the relation between the intramolecular structure of CBR and the degree of cyclization is discussed.

EXPERIMENTAL

Materials

Five CBR samples with different cyclization degrees were used in the present work. They were prepared by cyclization of a butadiene polymer, JSR BR01 from our production plant. The details of the cyclization reaction were reported in a previous paper.¹ The conditions used for our cyclization reactions of the butadiene polymer were quite different from those employed by Bohackova *et al.*⁴ Several characteristic parameters of our samples are listed in Table I. The polydispersity of the samples increased considerably with increasing *DC*. More specifically, the number-average molecular weight M_n varied little with *DC*, while the weight-average molecular weight M_w increased considerably as *DC* is increased.

Table I. Characteristic properties of CBR

Sample	DC (%) ^a	$[\eta]/\text{dl g}^{-1\text{b}}$	$M_w \times 10^{-4\text{c}}$	$M_n \times 10^{-4\text{d}}$
CB-A	9	1.71	59.6	10.5
-B	31	1.32	83.3	11.5
-C	46	1.02	103.6	10.0
-D	63	0.58	115.2	9.9
-E	81	0.31	104.4	9.9

^a From NMR spectra.^b In cyclohexane at 30°C.^c By light scattering (cyclohexane, 30°C).^d By osmotic pressure (toluene, 37°C).

Fractionation

Each sample was fractionated by precipitation, using a column constructed at our laboratory.⁷ Elution of the polymer was made with benzene as the solvent and methyl alcohol as the nonsolvent, in such a way that the solvent composition in the mixture increased exponentially as the elution proceeded. Each sample was separated into about 15 fractions. Several fractions having suitable molecular weights were chosen for the present study.

NMR

The cyclization degree of each CBR sample was evaluated by means of ¹H-NMR. The measurements were carried out at room temperature using a JEOL 4H-100 spectrometer. A test solution of 10% polymer concentration was prepared in tetrachloroethylene with tetramethylsilane added as the internal standard.

Theta Solvents

We could not find for CBR a single (*i.e.*, pure) theta solvent suitable for dilute solution measurements. We found that a mixed theta solvent for CBR could be obtained by mixing cyclohexane ($n_{436}^{30} = 1.430$ — a good solvent) with dioxane ($n_{436}^{30} = 1.427$ — a poor solvent). The important reason for this selection was that the refractive indices of these solvents are almost identical. The weight-average molecular weight M_w , the second virial coefficient A_2 , and the mean-square radius of gyration $\langle s^2 \rangle_z$ could therefore be determined by conventional light scattering measurement. The composition of the mixed theta solvent at 30°C was determined as a function of the cyclization degree as described below.

Viscosity

Test solutions of several different concentrations were prepared in cyclohexane and in mixed theta solvents. Viscosity measurements were made at $30.0 \pm 0.1^\circ\text{C}$, using a capillary viscometer of the Ubbelohde dilution type. The kinematic energy and end-effect corrections were negligible.

Light Scattering

A Fica 50 automatic light scattering photometer was used, and the measurement was made over an angular range from 30 to 150° at $30.0 \pm 0.1^\circ\text{C}$. Vertically polarized light of wavelength 436 nm was used as the incident beam. Test solutions of different concentrations were made up from a 0.2% stock solution prepared by dissolving a given fraction in cyclohexane or in a mixed theta solvent. Each of these was filtered through a 0.45 μm Millipore filter and directly poured into a light scattering cell just before measurement. The specific refractive index increment of a given system was determined by a modified differential refractometer of the Schulz type.⁸

RESULTS AND DISCUSSION

NMR

The NMR spectra of the raw BR and the sample CB-D are illustrated in Figure 1. As seen from the figure, the intensity of the peak at 5.3 ppm decreases with cyclization and a new broad peak appears at near 1.5 ppm. From the area *A* for the proton $-\text{CH}=\text{}$ and the area *B* for the total saturated pro-

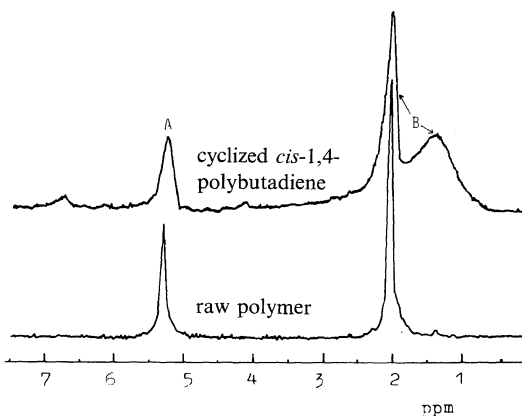
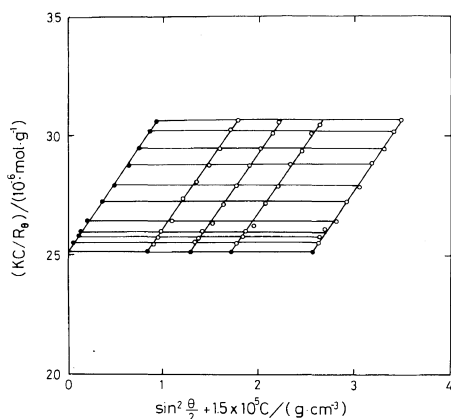
**Figure 1.** NMR spectra for cyclized polybutadiene and its starting polymer.

Table II. Composition of mixed theta solvents for CBR

Sample	Cyclohexane/Dioxane (by volume)
CB-A	12/88
-B	17/83
-C	21/79
-D	30/70
-E	39/61

**Figure 2.** Zimm plot for CB-D-f13 in mixed theta solvents at 30°C.

tons, the degree of cyclization (DC —strictly apparent DC) was calculated using the following relation,

$$DC (\%) = \left(1 - \frac{3A}{A+B} \right) \times 100 \quad (1)$$

Composition of Mixed Theta Solvents

In order to determine the cyclohexane–dioxane ratio of the mixed theta solvent at 30°C (theta temperature) as a function of DC , light scattering measurements were carried out on the whole CBR polymers. Thus, A_2 for the sample CB-D vanished at 30°C when the volume ratio of cyclohexane to dioxane was 30/70. It was found from NMR data for fractionated CBR that DC of the low and high end fractions were somewhat different (about several per cent). However, their A_2 were nearly equal to zero under the same solvent conditions. In a similar way, the solvent composition leading to the theta at 30°C for all other CBR were finally determined as given in Table II.

Light Scattering and Viscosity

The customary extrapolations to zero concentration and scattering angle on the Zimm plot⁹ for CB-D-f13 in the mixed theta solvent are illustrated in Figure 2. Both angular and concentration extrapolations are practically linear. Similar Zimm plots were obtained for all other samples. The values of M_w , A_2 , and $\langle s^2 \rangle_z$ determined for each fraction are summarized in Table III.

For a given polymer, the same M_w should be obtained regardless of the solvent used. Figure 3 shows verification of the identity of two series of M_w , one determined in cyclohexane and the other in theta solvents.

Figure 4 represents the Mark–Houwink–Sakurada plots of $\log [\eta]_0$ against $\log M_w$ for the fractions in mixed theta solvents at 30°C. The plots are represented by the following equations,

$$[\eta]_0 = K_0 M_w^{0.5} \quad (\text{below } M_{wc}) \quad (2)$$

$$[\eta]_0 = K_0' M_w^a \quad (\text{above } M_{wc}) \quad (2)'$$

where K_0 , K_0' , and a are constants independent of M_w . The data points for the series CB-A fall on the straight line represented by eq 2. The plots for other series with DC over 30% begin to deviate from straight lines at a certain M_w (this is defined as the critical molecular weight M_{wc}) and, in each case, consists of two regions, one with a slope of 0.5 and other with a slope of a which is smaller than 0.5 for higher DC . Moreover, M_{wc} shifts to lower M_w as DC is increased. The fact that the data are expressed by eq 2 suggests that the molecule behaves hydrodynamically like a linear polymer. This does not always mean that the molecule is literally linear, but implies that, in the range of low DC , cyclization occurs in such a way that the molecule has no branches. The viscosity vs. molecular weight relations in cyclohexane at 30°C, though not given here, are represented by equations similar to eq 2 and 2' with larger exponents.

Figure 5 shows double-logarithmic plots of $\langle s^2 \rangle_{0z}^{1/2}$ against M_w in mixed theta solvents at 30°C. We see that the dependence of $\langle s^2 \rangle_{0z}^{1/2}$ on M_w resembles that of $[\eta]_0$, but shows no critical molecular weight. The data points for the series CB-A and those for other series are respectively represented by the equations,

$$\langle s^2 \rangle_{0z}^{1/2} = k_0 M_w^{0.5} \quad (\text{for the series CB-A}) \quad (3)$$

$$\langle s^2 \rangle_{0z}^{1/2} = k_0' M_w^b \quad (\text{for other series}) \quad (3)'$$

Table III. Results of viscosity and light scattering measurements^a

Fracion	Mixed theta solvents				Cyclohexane			
	$[\eta]_0$	$M_w \times 10^{-4}$	$\langle s^2 \rangle_{0z}^{1/2} \times 10^{10}$	$[\eta]$	$M_w \times 10^{-4}$	$A_2 \times 10^4$	$\langle s^2 \rangle^{1/2} \times 10^{10}$	
CB-A	9	0.59	10.8	146	0.79	9.5	10.8	170
	10	0.71	16.1	170	1.09	14.9	10.4	196
	11	0.88	20.4	210	1.40	19.6	8.65	256
	12	1.10	36.2	255	1.82	35.9	8.24	336
	13	1.45	51.8	311	2.75	58.7	6.30	398
-B	7	0.35	6.2	—	0.50	6.7	9.13	130
	8	0.41	8.7	—	0.65	8.9	7.87	150
	9	0.45	11.8	146	0.73	11.7	7.08	165
	10	0.55	17.2	171	0.88	17.2	5.70	230
	11	0.60	20.5	175	1.08	21.4	5.65	240
	12	0.70	29.9	201	1.48	31.5	5.85	270
	13	0.89	55.0	238	1.92	61.0	3.05	390
	14	1.14	116	324	2.54	121	2.15	570
-C	7	0.24	4.8	—	0.34	5.3	7.09	—
	9	0.28	7.4	—	0.44	8.2	6.31	122
	10	0.33	10.1	125	0.52	9.9	6.55	150
	11	0.34	12.2	147	0.59	12.8	5.26	154
	12	0.38	17.0	150	0.67	17.8	3.85	184
	13	0.41	23.0	150	0.77	23.3	4.00	218
	14	0.47	34.6	182	0.97	39.5	2.62	266
-D	5	0.18	3.6	—	0.22	3.3	3.75	—
	7	0.21	5.3	—	0.28	5.3	3.74	—
	9	0.25	10.8	115	0.32	10.3	3.98	129
	11	0.28	18.7	135	0.42	17.3	2.98	179
	13	0.33	39.7	160	0.54	39.1	1.70	264
	15	0.39	110	221	0.72	115	1.27	366
-E	7	0.17	5.5	—	0.22	5.7	1.89	—
	9	0.19	12.9	110	0.26	10.6	1.44	120
	11	0.20	23.5	116	0.28	20.4	1.35	155
	13	0.21	51.0	151	0.32	49.0	0.95	260
	15	0.22	86.0	174	0.37	82.0	0.74	310

^a $[\eta]_0$ and $[\eta]$, dl g⁻¹; $\langle s^2 \rangle_{0z}^{1/2}$ and $\langle s^2 \rangle^{1/2}$, m; A_2 , mol cm g⁻¹.

where k_0 , k_0' , and b are constants independent of M_w . The exponent b is also seen to decrease with increasing DC .

The above results indicate that the molecular structures of CBR in the regions below and above M_{wc} are quite different from each other. In particular, the molecule above M_{wc} behaves like a branched polymer. This behavior is discussed in detail below.

Molecular structures at M_w below M_{wc}

The relation between K_0 and DC is shown in

Figure 6. It is seen that with increasing DC , K_0 initially decreases monotonically and appears to be constant for DC above 50%. The mechanism of cyclization and the structure of the product are fully understood for *cis*-BR. However, the formation of a six-membered ring (cyclic structure) which is much the same as that in cyclized polyisoprene appears to have been established.¹⁰ The behavior of K_0 for DC below 50% may be explained by a theory analogous to that known for short branching in polyethylene.¹¹ Thus, the formation of a short cyclic structure like a mono- and/or bicyclic structure does

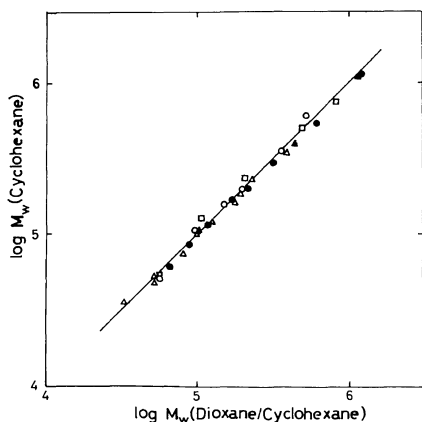


Figure 3. Experimental verification of the M_w values determined in cyclohexane and in mixed theta solvents: ○, CB-A; ●, CB-B; △, CB-C; ▲, CB-D; □, CB-E.

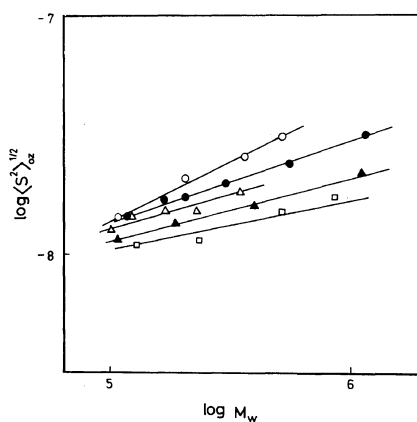


Figure 5. Double logarithmic plots of $\langle s^2 \rangle_{0z}^{1/2}$ against M_w for each CBR. Symbols are the same as in Figure 3.

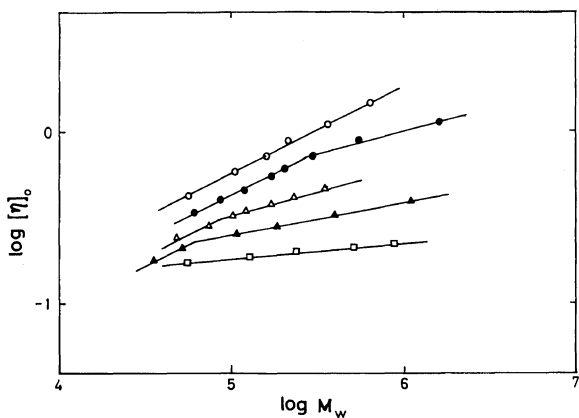


Figure 4. Double logarithmic plot of $[\eta]_0$ vs. M_w for each CBR. Symbols have the same meaning as in Figure 3.

not essentially alter the linearity of the polymer molecule, but shortens its contour length, giving rise to a decrease in K_0 , as observed here. The constant K_0 for DC above 50% indicates that the content of short cyclic structure attains a limiting value when DC exceeds 50%.

Molecular structures at M_w above M_{wc}

The procedure most frequently used for the estimating the degree of branching of a polymer is to compare the theta state values of $[\eta]_0$ and $\langle s^2 \rangle_0$ between branched and linear polymers of the same molecular weight. For this purpose it is convenient

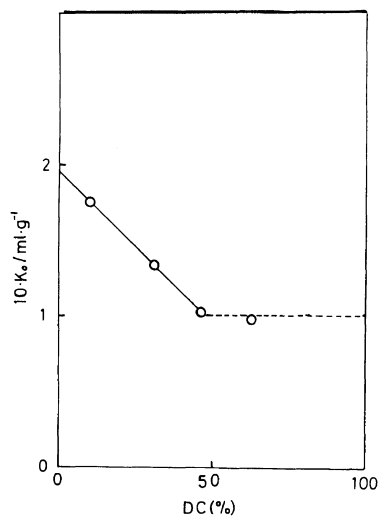


Figure 6. Dependence of K_0 values on cyclization degree for CBR.

to define three dimensionless parameters G , g , and ν by,

$$G = [\eta]_{0b} / [\eta]_{0l} \quad (4)$$

$$g = \langle s^2 \rangle_{0b} / \langle s^2 \rangle_{0l} \quad (5)$$

$$G = g^\nu \quad (6)$$

where the subscripts b and l indicate branched and linear polymers, respectively. The exponent ν is roughly equal to 0.5 in most cases.¹² Table IV gives the theoretical values of the parameters G , g , and ν

Table IV. Theoretical viscosity relations for various molecular structures

Type of structure	Relation	References
Branched		
Star	$G \propto g^{0.5}$	13
Comb	$G \propto g^{0.5}$ (low branching) $G \propto g^{1.5}$ (high branching)	14
Random	$G \propto g^{0.5-0.6}$, $g \propto M^{-0.5}$, $[\eta]_0 \propto M^{0.2-0.25}$	12
Ring		
Single	$G \propto g^{0.633}$	16

for various types of branched and ring polymers.

In evaluating G and g for CBR, $[\eta]_{ob}$ and $\langle s^2 \rangle_{ob}$ in eq 4 and 5 should be the intrinsic viscosity and the mean-square radius of gyration of a real CBR sample in the mixed theta solvent, while $[\eta]_{ol}$ and $\langle s^2 \rangle_{ol}$ should represent these values of a hypothetical linear CBR having the same M_w as the real CBR. The $[\eta]_{ol}$ for a series of samples with a fixed DC can be estimated by extrapolating the $[\eta]_0$ versus M_w relationship for low M_w samples to the region of high M_w . The DC dependence of K_0 shown in Fig. 6 may be used for this purpose. On the other hand, k_0 in eq 3 could not be experimentally determined except for the series CB-A. Therefore, we estimate $\langle s^2 \rangle_{ol}$ from $[\eta]_{ol}$ by using the familiar Flory-Fox relation,

$$[\eta]_{ol} = 6^{3/2} \Phi_0 \frac{\langle s^2 \rangle_{ol}^{3/2}}{M} \quad (7)$$

where Φ_0 is a constant which is the same for all flexible linear polymes under the theta condition. The Φ_0 for CB-A was estimated from the experimental values of $[\eta]_{ol}$ and $\langle s^2 \rangle_{ol}$ to be $1.76 \times 10^{23} \text{ mol}^{-1}$. This value is somewhat smaller than the typical theoretical value, but the deviation may be attributed to the molecular weight distributions in

Table V. Structural parameters estimated of CBR

Sample	$M_w \times 10^{-4}$	G	g	v	λM	$\lambda^{-1} \times 10^4$
CB-B	51.0	0.92	0.80	0.39	2.8	18
	116	0.75	0.65	0.67	6.8	17
-C	23.3	0.87	0.82	0.68	2.6	9.0
	39.5	0.81	0.71	0.60	5.0	7.9
-D	19.2	0.67	0.70	1.1	5.0	3.8
	44.0	0.55	0.45	0.74	20	2.2
	115	0.39	0.40	1.0	28	4.1
-E	23.5	0.42	0.49	1.2	15	1.6
	51.0	0.30	0.39	1.3	30	1.7
	86.0	0.24	0.31	1.2	54	1.6

the present samples.¹⁵ In fact, $\langle s^2 \rangle_{oz}$ calculated for CB-B-f9 below M_w was in very good agreement with the measured one. The values of G , g , and v thus obtained by eq 4, 5, and 6 are shown in Table V. It can be seen that 1) G and g decrease with increasing M_w at constant DC and that they decrease with increasing DC at constant M_w , and 2) v increases as DC is increased. Thus, the shrinkage of chain dimensions should be attributed to chain branching due either to intramolecular reaction or to crosslinking within the molecule.

As shown in Table I, when cyclization is made on the same unfractionated BR01, M_n remains essentially unchanged, while M_w increases considerably with increasing DC . We made a check of this phenomenon using two fractionated samples of BR01. The results are shown in Table VI, where M_n of CBR is almost the same as that of the original BR and M_w increases by a factor of 2 or 3. Thus, we can conclude that the cyclization reaction is accompanied by polymer chain scission and recombination. Hence, it may be appropriate to assume a randomly branched form for the molecular struc-

Table VI. Change in molecular weight by cyclization for BR fractions

Sample	BR			CBR			
	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	M_w/M_n	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	M_w/M_n	DC (%)
F1	2.4	2.6	1.1	2.6	5.7	2.2	52
F2	4.7	5.2	1.1	5.0	14.1	2.8	60

ture of CBR.

For a randomly branched molecule, the theory¹² gives,

$$g = \left[\left(1 + \frac{\lambda M}{7} \right)^{1/2} + \frac{4M}{9\pi} \right]^{-1/2} \quad (8)$$

which is strictly applicable to a sample with a narrow distribution of molecular weight. Here the parameter λM represents the number of branch units in the molecule. By substituting g in Table V into eq 8, we calculated λM and obtained the results given in Table V. It is seen that λ^{-1} is essentially independent of M_w but decreases with increasing DC . This implies that for a given M_w the number of branch units increases with increasing DC . Since the cyclization reaction involves both intra- and intermolecular reactions, the latter of which leads to branching, the chance of chain branching may increase as the reaction proceeds.

The values of ν and a obtained for CBR with DC lower than 50% are in agreement with the theoretical values $\nu=0.6$ and $a=0.2\sim 0.25$ for randomly branched polymers. For DC larger than 50%, especially for the sample CB-E, ν is larger than unity and is smaller than 0.2. These values differ considerably from the theoretical values, indicating that the behavior of CB-E in solution cannot be explained by branched structure only. For these high DC , a highly compact structure formed by intramolecular crosslinking may appear during the cyclization reaction, as has been pointed out in regard to cyclized polyisoprene.⁵

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