BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 2570—2574 (1968)

Unperturbed Dimension of Poly(butylene oxide)

Masahiro MATSUSHIMA, the late Masaaki FUKATSU and Michio KURATA
Institute for Chemical Research, Kyoto University, Uji, Kyoto

(Received April 5, 1968)

Viscosity and light scattering measurements of poly(butylene oxide) were carried out in various solvents, including a theta solvent, isopropanol. The intrinsic viscosity *vs.* molecular weight relationships obtained in the range of molecular weight from 2.1×10^5 to 2.3×10^6 were:

$$[\eta]=3.39\times10^{-5}\,M_w{}^{0.84} \text{ in benzene at } 30^\circ\text{C},$$

$$[\eta]=4.08\times10^{-5}\,M_w{}^{0.79} \text{ in methyl ethyl ketone at } 30^\circ\text{C},$$

$$[\eta]=8.65\times10^{-4}\,M_w{}^{0.50} \text{ in isopropanol at } 29.8^\circ\text{C}.$$

The ratio σ between the end-to-end distance of the polymer chain in the unperturbed state and that in the freely rotating state was estimated to be 1.66.

As the second part of a series of papers on the dilute solution properties of polyoxides,[1] we here report the results of light scattering and viscosity measurements performed on poly(butylene oxide).

Experimental

Polymer Sample. Poly(butylene oxide) was a gift from Dr. Yutaka Matsui of the Takeda Chemical Industries, Ltd., which was polymerized in *n*-hexane at 60°C using a zinc diethyl complex catalyst with butylene glycol.[2] The polymer was dissolved in acetone to make an original solution for the fractionation. The

---

[1] Part I of this series: M. Kurata, H. Utiyama and K. Kamada, *Makromol. Chem.*, **88**, 281 (1965).

[2] Y. Matsui, N. Hashimoto, T. Saegusa and J. Furukawa, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **69**, 1375 (1966).

concentration was 0.8 g/d*l*. To the solution, methanol was added at 34°C until the solution became turbid. Then, the solution was cleared at an elevated temperature, cooled again and stood at 34°C at which phase separation was proceeded. After removal of the solution phase by siphoning, the precipitate was dissolved in benzene, and dried, and dissolved again in benzene with a small amount (about one hundredth of polymer weight) of antioxidant, *p*-benzylamino phenol. This solution was freeze-dried, and stored in a freezer at about −20°C. The removed solution phase was subjected to the next cycle of the fractionation. The procedures described above were repeatedly applied until the original polymer was separated into 20 fractions. Nine of these fractions were put in light scattering and viscosity measurements.

Solvents. Benzene, methyl ethyl ketone and isopropanol were used as solvents. These solvents were put in physical measurements after dried with drying agents and fractionally distilled. The drying agents used were sodium metal for benzene, active anhydrous calcium sulfate for methyl ethyl ketone and anhydrous copper sulfate for isopropanol, respectively.

Theta Temperature. The theta temperature was found to be 29.8°C in isopropanol by light scattering measurements. Figure 1 shows the apparent second virial coefficient for the whole polymer plotted against the temperature. In the figure, an arbitrary scale is used for the ordinate, since the refractive index increment was not determined in this solvent.

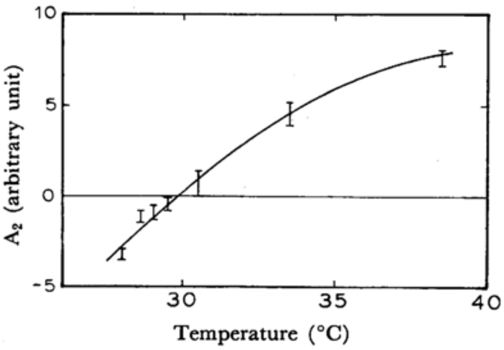

Fig. 1. Determination of the theta temperature.

Intrinsic Viscosity. Viscosity measurements were made in three solvents, *i. e.,* benzene at 30.0°C, methyl ethyl ketone at 30.0°C and isopropanol at 29.8°C, using dilution viscometers of the Ubbelohde type. Corrections for kinetic energy and shear rate were both immaterial. The intrinsic viscosities $[\eta]$ and the Huggins constants k′ were determined by extrapolating the plots of η_{sp}/c *vs.* c, and of $(\ln \eta_{\mathrm{rel}})/c$ *vs.* c to zero concentration in such a manner that both plots gave the same ordinate intercept. In such a case that the η_{sp}/c *vs.* c plot displayed a marked curvature, the plot of η_{sp}/c *vs.* η_{sp} was used for the extrapolation.

Refractive Index Increments. Measurements were made in a differential refractometer of the Debye type (Shimadzu Seisakusho, Ltd., Kyoto) which was calibrated against aqueous potassium chloride. Five solutions with different concentrations were prepared by dilution from two initial solutions whose concentrations were determined by weighing the dried amount of polymers recovered from a known volume of the solutions. The refractive index increment obtained for the light of 436 mμ wavelength was 0.0863 m*l*/g in methyl ethyl ketone at 30°C.

Light Scattering. Measurements were made on nine fractions of the polymer in methyl ethyl ketone at 30°C by using a light scattering photometer of the Brice type (Shimadzu Seisakusho, Ltd., Kyoto). The calibration of the photometer was made against pure benzene using the Rayleigh ratio determined by Carr and Zimm. The test solutions were cleaned by spinning for 1.5 hr at 22000 rpm in a preparative centrifuge (type 55P, Hitachi Ltd., Tokyo). Vertically polarized light of 436 mμ wavelength was used as the incident beam, and the vertical component of the scattered light was measured at various scattering angles between 30° and 140°. The weight average molecular weight M_w, the second virial coefficient A_2 and the *z*-average value of the mean-square statistical radius $\langle S^2\rangle_z$ were determined by the standard method.

Results and Discussion

Intrinsic Viscosity *vs.* Molecular Weight Relationships. The results of the light scattering and viscosity measurements are summarized in Table 1. These data of the intrinsic viscosities are plotted in Fig. 2 against the molecular weight using the double logarithmic scale. The following relationships are obtained between these two quantities in the range of molecular weight from 2.1×10^5 to 2.3×10^6:

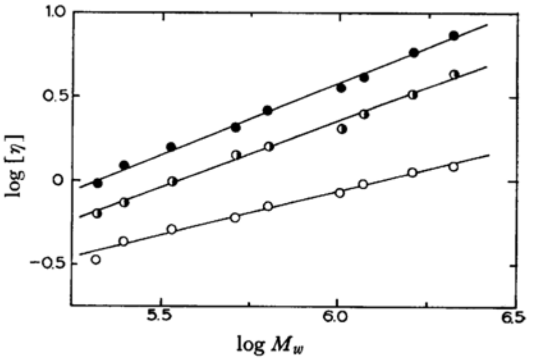

Fig. 2. Intrinsic viscosity *vs.* molecular weight relationships for poly(butylene oxide). White circles, in isopropanol at 29.8°C; half-filled circles, in methyl ethyl ketone at 30.0°C; black circles, in benzene at 30.0°C.

$$[\eta]=3.39\times10^{-5}\,M_w^{\,0.84}$$
(in benzene at 30.0°C),

$$[\eta]=4.08\times10^{-5}\,M_w^{\,0.79}$$
(in methyl ethyl ketone at 30.0°C),

$$[\eta]=8.65\times10^{-4}\,M_w^{\,0.50}$$
(in isopropanol at 29.8°C).

As expected, the intrinsic viscosity in the theta solvent was proportional to the square-root of

TABLE 1. MOLECULAR WEIGHTS AND INTRINSIC VISCOSITIES OF POLY(BUTYLENE OXIDE)

Fraction No.	M_w $\times 10^{-5}$	Benzene (30°)		MEK (30°C)		Isopropanol (29.8°)	
		$[\eta]$ a)	k'	$[\eta]$ a)	k'	$[\eta]$ a)	k'
2	21.0	7.21	0.29	4.27	0.32	1.24	0.55
3	16.1	5.79	0.32	3.24	0.44	1.14	0.57
5	11.8	4.14	0.33	2.47	0.41	0.955	0.48
7	10.2	3.56	0.32	2.10	0.40	0.851	0.56
9	6.34	2.60	0.31	1.60	0.43	0.704	0.51
10	5.16	2.05	0.32	1.41	0.36	0.596	0.51
11	3.43	1.58	0.32	0.985	0.41	0.509	0.41
14	2.50	1.23	0.33	0.724	0.39	0.429	0.42
15	2.09	0.953	0.33	0.623	0.48	0.334	0.54

a) expressed in dl/g.

TABLE 2. UNPERTURBED DIMENSIONS OF POLY(EPOXIDES)

Polymer	Temp. (°C)	$(\langle L^2\rangle_0/M)^{1/2}$ (Å)	σ	Reference
Poly(ethylene oxide)	35	0.790	1.46	5), 7)
Poly(propylene oxide)	39.5	0.735	1.56	6), 7)
	38	0.792	1.68	unpublished
Poly(butylene oxide)	30	0.700	1.66	this work
Poly(styrene oxide)	25	0.640	1.95	8)

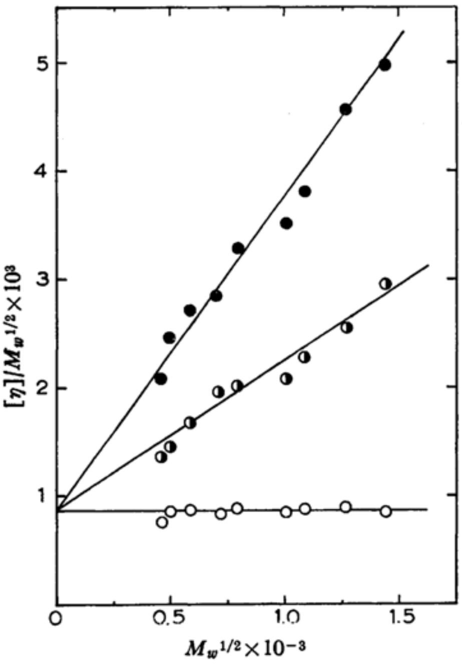

Fig. 3. Plots of $[\eta]/M_w^{1/2}$ vs. $M_w^{1/2}$ on poly(butylene oxide) in three solvents. The same marks as those in Fig. 2 are used.

the molecular weight. On the other hand, the intrinsic viscosity in benzene was proportional to as high the power of the molecular weight as 0.84, indicating benzene was an extremely good solvent.

Unperturbed Dimension. The viscosity data given in Table 1 are replotted in Fig. 3 according to the Kurata-Stockmayer-Fixman theory:[3,4]

$$[\eta]/M^{1/2} = K + 0.51\,\Phi_0\,BM^{1/2} \tag{4}$$

$$K = \Phi_0(\langle L^2\rangle_0/M)^{3/2} \tag{5}$$

Here $\langle L^2\rangle_0$ is the mean-square end-to-end distance of the unperturbed chain, B is a parameter representing the thermodynamic interaction between polymer segments, and Φ_0 is the Flory universal constant. As shown in Fig. 3, we can determine three straight lines with a common ordinate intercept, showing that the value of K, and hence the unperturbed dimension of the chain, is essentially independent of the solvents. It has recently been pointed out by various investigators that the $[\eta]/M^{1/2}$ vs. $M^{1/2}$ plots for the good solvent systems often display downwards curvature in the region of high molecular weights. Such a tendency, however, was not observed in the present systems.

The unperturbed dimension $(\langle L^2\rangle_0/M)^{1/2}$ is determined to be 0.700×10^{-8} (cm·mol$^{1/2}$·g$^{-1/2}$), assuming that $\Phi_0=2.5\times10^{21}$. The conformational parameter σ which is defined as the ratio of the end-to-end distance of the unperturbed chain to that of the freely-rotating chain is then evaluated as 1.66×0.05.

---

[3] M. Kurata and W. H. Stockmayer, *Fortschr. Hochpolymeren-Forsch.*, **3**, 196 (1963).

[4] W. H. Stockmayer and M. Fixman, *J. Polymer Sci.*, **C1**, 137 (1963).

TABLE 3. STATISTICAL RADII AND THE SECOND VIRIAL COEFFICIENTS OF POLY(BUTYLENE OXIDE) IN METHYL ETHYL KETONE AT 30°C

Fraction No.	M_w $\times 10^{-5}$	From $[Kc/R(\theta)]^{1/2}$ plot				From $Kc/R(\theta)$ plot		
		$\langle S^2\rangle_z^{1/2}$ a)	$\Phi\times 10^{-21}$ b)	$A_2\times 10^4$ c)	$A_2M_w/[\eta]$	$\langle S^2\rangle_z^{1/2}$ a)	$A_2\times 10^4$ c)	$A_2M_w/[\eta]$
2	21.0	645	2.27	2.3	113	790	3.0	148
3	16.1	540	2.24	2.4	119	640	3.2	160
7	10.2	400	2.27	2.3	110	460	3.2	155
9	6.34	310	2.32	2.2	87	320	4.0	158
10	5.16	285	2.13	1.7	63	300	4.1	150
11	3.43	245	1.68	1.8	56	260	3.8	133

a) expressed in Å unit. b) $\Phi=[\eta]M_w/6^{3/2}\langle S^2\rangle_z^{3/2}$. c) expressed in mol·m$l$·g^{-2}.

The unperturbed dimensions of various poly(epoxide) chains given in literature are listed in Table 2. The data show that the side group of poly(butylene oxide) gives rise to an enlarging effect on the unperturbed chain dimension to the same degree as that of the methyl group in poly(propylene oxide).5-7) The effect is clearly smaller than that of the phenyl group in poly(styrene oxide).8) The similar trend can be found within the group of vinyl polymers, in which polypropylene and polybutene show approximately the same value of σ, 1.6—1.8, while polystyrene a relatively high value, 2.3.3,7)

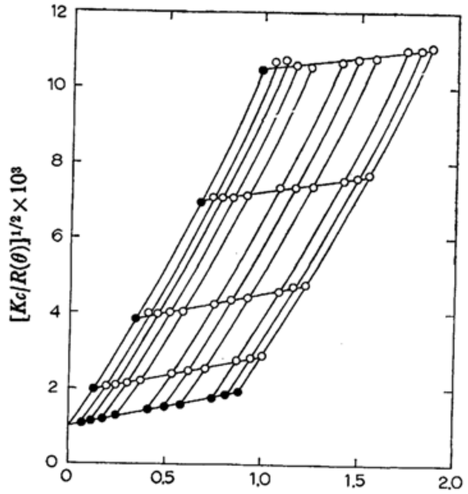

Fig. 4. Plots of $Kc/R(\theta)$ vs. $\sin^2(\theta/2)+100c$ for the sample, fraction 7. The polymer concentrations c are 0.00991, 0.00671, 0.00345 and 0.00128 g/ml from top to bottom. The scattered angles θ are 30, 40, 50, 60, 80, 90, 100, 120, 130 and 140° from left to right. Black circles represent the values of $Kc/R(\theta)$ extrapolated to $\theta=0$ or $c=0$.

Mean-square Statistical Radius and the Second Virial Coefficient. The z-average value of the mean-square statistical radius $\langle S^2\rangle_z$ can be estimated from the angular dependence of the scattered light intensity using the plots either of $Kc/R(\theta)$ or of $[Kc/R(\theta)]^{1/2}$ vs. $\sin^2(\theta/2)$. Here K is an optical constant, $R(\theta)$ is the reduced intensity of scattered light at the scattering angle θ, and c is the polymer concentration. The former ordinate $Kc/R(\theta)$ is known to be appropriate to ordinary polymer samples, especially to the samples with the most probable distribution of the molecular weight, while the latter ordinate $[Kc/R(\theta)]^{1/2}$ to the monodisperse polymers.9) Since the present

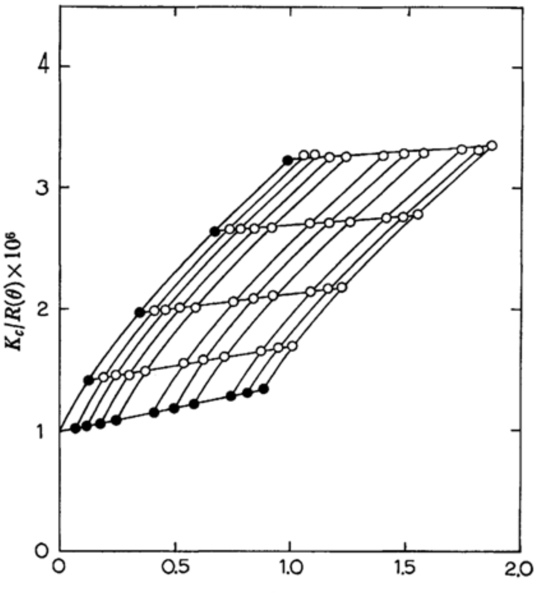

Fig. 5. Plots of $[Kc/R(\theta)]^{1/2}$ vs. $\sin^2(\theta/2)+100c$ for the sample, fraction 7. The polymer concentrations and scattering angles are the same as those in Fig. 4.

---

5) F. E. Bailey, Jr., and R. W. Callard, *J. Appl. Polymer Sci.*, **1**, 56 (1959).

6) J. Moacanin, *ibid.*, **1**, 272 (1959).

7) See also, M. Kurata, M. Iwama and K. Kamada, Table IV-D in "Polymer Handbook," ed. by J. Brandrup and E. H. Immergut, Interscience Pub., New York (1966).

8) G. Allen, C. Booth, S. J. Hurst, M. N. Jones and C. Price, *Polymer*, **8**, 391 (1967).

9) G. C. Berry, *J. Chem. Phys.*, **44**, 4550 (1966).

polymer samples are intermediate in the nature between the two above, we tried the two plots and obtained the results given in Table 3. For illustration, the two plots for fraction 7 are shown in Figs. 4 and 5. These plots lead to the same value of molecular weight, but to rather different values of $\langle S^2 \rangle_z$. As is seen from the table, the $\langle S^2 \rangle_z$ values obtained by the $[Kc/R(\theta)]^{1/2}$ plot lead to values of Φ close to the widely accepted value, $2.1—2.2 \times 10^{21}$, while those by the $Kc/R(\theta)$ plot to lower values of Φ.

As for the concentration dependence of the scattered light intensity, the plot of $Kc/R(\theta)$ *vs.* c gave correlation curves with curvature less than the plot of $[Kc/R(\theta)]^{1/2}$ *vs.* c does. The second virial coefficients A_2 evaluated from the ordinary $Kc/R(\theta)$ plot were found to be larger by a factor about 1.5, on the average, than those evaluated from the $[Kc/R(\theta)]^{1/2}$ plot. Because of the uncertainties involved in the estimates of $\langle S^2 \rangle_z$ and A_2, we here avoid further discussions on these quantities.

This work was supported in part by a grant from the Takeda Chemical Industries, Ltd. Kind help of Dr. Yutaka Matsui of this industries in supply of the original polymer samples is gratefully acknowledged.