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Dilute Solution Properties of Chlorosulfonated Polyethylene. I. Viscosity-Molecular Weight Relationship and Molecular Weight Distribution

B. Das[a]; B. B. Konar[a]
[a] Department of Applied Chemistry, Calcutta University, Calcutta, India

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Dilute Solution Properties of Chlorosulfonated Polyethylene. I. Viscosity-Molecular Weight Relationship and Molecular Weight Distribution

B. DAS and B. B. KONAR

Department of Applied Chemistry
Calcutta University
Calcutta, India

ABSTRACT

Chlorosulfonated polyethylene was fractionated and the different fractions in toluene were characterized by viscosity and light-scattering measurements. Values of ν and K in the Mark-Houwink relation were determined. The results indicate a tightly coiled structure for the polymer in the solvent studied. Integral and differential molecular weight distributions, the second virial coefficient, and the radius of gyration are also reported.

INTRODUCTION

Studies on the dilute solution properties of polymers have been quite exhaustive, and numerous investigations have been carried out. Studies on elastomers such as polybutadiene [1-6], polychloroprene [7-13], synthetic cis-polyisoprene [14], styrene-butadiene [15, 16], polyisobutylene [17-19], polysulfide [20], ethylene-propylene [21, 22], and on butyl [23], nitrile [24, 25], and silicone [26, 27] rubbers have been published. However, relatively little is known about the properties of chlorosulfonated polyethylene in dilute solution. There is only one report [27a] and that, too, deals merely

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with the viscosity-molecular weight relationship. The present work is a critical study on the dilute solution properties of this polymer.

EXPERIMENTAL

Materials

Standard commercial samples of chlorosulfonated polyethylene (Hypalon 40) having a Mooney viscosity (ML_4 at 100° C) of 54, specific gravity 1.18, chlorine content 34.2%, and sulfur content 0.95% was used. Commercially available toluene and methanol (BDH, Analar) were further dried and distilled before use.

Fractionation

Fractionation of the polymer was carried out by the usual precipitation method at 30° C using toluene as solvent and methanol as nonsolvent. In total, 18 fractions were collected.

Viscosity Measurements

These were carried out at 25 ± 0.1° C in toluene using Ubbelohde-type dilution viscometers. Intrinsic viscosities were obtained from η_{sp}/c vs c plots, and the results are shown in Table 1. Kinetic energy corrections were negligible.

Light-Scattering Measurements

A Brice-Phoenix Universal light-scattering photometer was used for light-scattering measurements. Vertically polarized light of wavelength 546 mμ was used and the intensity of the scattered light was measured at various scattering angles between 30 and 135°. Figure 1 shows a typical example of a Zimm plot where $R(\theta, c)$ represents the reduced scattering intensity as a function of the scattering angle θ and concentration c, and K represents a constant defined as $K = 2\pi^2 n_s^2 (dn/dc)^2 \lambda^{-4} N_A^{-1}$, n_s being the refractive index, λ the wavelength of light, and N_A the Avogadro number. The weight-average molecular weight $\overline{M}_w$ was obtained from the reciprocal of the intercept on the ordinate, $(K_c/R_\theta)_{c=0,\ \theta=0}$. From the slope of the zero angle line, A_2 values were calculated, and from the ratio

TABLE 1. Viscometric and Light-Scattering Data for Chlorosulfonated Polyethylene in Toluene

Fraction	Molecular weight, $M_w \times 10^{-5}$	$[\eta]$ (dL/g)	$\langle \bar{S}^2 \rangle_z^{1/2}$ (Å)	A_2 (cm^3/g^2 $\times 10^4$)
F-1	33.113	2.27	3493	0.755
F-2	25.000	1.75	3384	1.372
F-3	18.180	1.43	3226	0.333
F-4	9.120	1.17	3159	0.500
F-5	8.318	1.11	3046	0.833
F-6	5.405	0.84	2309	0.636
F-7	4.786	0.78	2236	0.636
F-8	4.545	0.73	2117	1.562
F-9	4.365	0.70	1704	3.171
F-10	3.311	0.65	1474	2.973
F-11	3.125	0.60	1292	1.212
F-12	2.777	0.56	1207	1.875
F-13	2.381	0.51	1167	0.428
F-14	1.905	0.47	1106	0.937
F-15	1.351	0.37	1057	1.256
F-16	1.031	0.34	941	1.786
F-17	0.909	0.28	729	2.000
F-18	0.667	0.27	701	1.667

of the initial slope of the zero concentration line to the intercept, the Z-average radius of gyration $\langle \bar{S}^2 \rangle_z$ was obtained as

$$\frac{\text{Initial slope}}{\text{Intercept}} = \frac{16\pi^2}{3} \langle \bar{S}^2 \rangle_z \left(\frac{n}{\lambda_0} \right)^2$$

where λ_0 is the wavelength of light in a solution of refractive index n. The results are tabulated in Table 1.

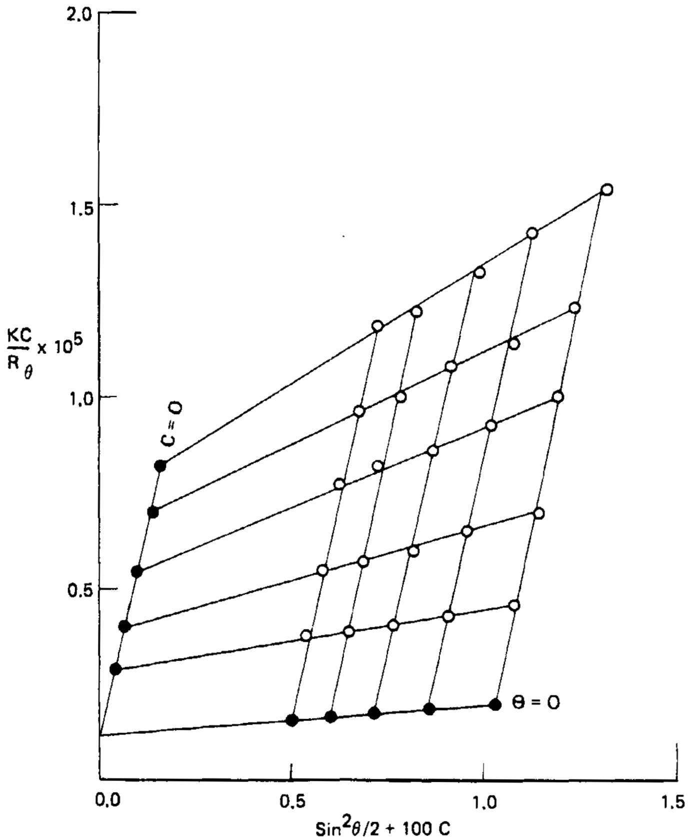

FIG. 1. Zimm plot for chlorosulfonated polyethylene (F-5) in toluene.

RESULTS AND DISCUSSION

The Mark-Houwink equation [28], which on empirical ground relates polymer molecular weight with intrinsic viscosity, is expressed as $[\eta] = K'M_w^{\nu}$ where K' and ν are constants independent of molecular weight for a specific polymer solvent system. Figure 2 shows the log-log plot of $[\eta]$ against M_w for chlorosulfonated polyethylene in toluene. The best-fit line with the range of molecular weight from 33.115×10^5 to 6.66×10^4 leads to $[\eta] = 5.2481 \times 10^{-4}\ M_w^{0.56}$. The ν-value of 0.56 for the polymer in toluene indicates a low hydrodynamic volume and a tightly coiled structure. Figure 2 also shows a linearity

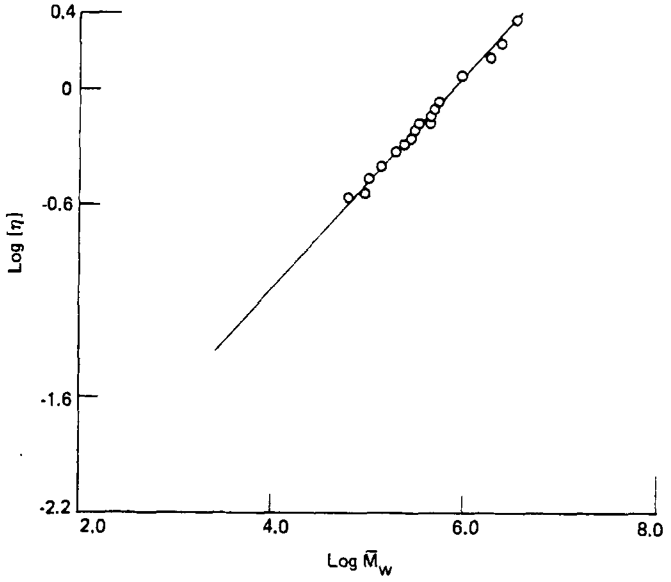

FIG. 2. Log-log plot of [η] vs $\overline{M}_w$ for chlorosulfonated polyethylene.

extending up to the high molecular weight region studied, thus indicating little evidence of branching.

Integral and differential molecular weight distribution for this polymer were calculated by the methods of Schulz [29] and Tung [30] and are shown in Figs. 3 and 4. From these two distribution curves it is seen that 50% of the chlorosulfonated polyethylene has a molecular weight over 5.321 × 10^5 and the most abundant species is of 1.905 × 10^5 molecular weight. The differential molecular weight distribution curve also shows the long extension at high molecular weights that appears to be typical of diene polymers.

The second virial coefficient A_2 and the radius of gyration generally show a downward trend with molecular weight. However, no definite trend could be detected in the A_2 values listed in Table 1. It should be remembered that the experimental determination of A_2 from light-scattering data is rather hazardous and irregularities have often been reported [31-33].

Attempts have been made to explain the [η]-M relations on the basis of various models [34]. In the bead and spring model, a proposed Gaussian chain of n + 1 beads, each with mass m_n, radius R_s, and separated from its neighbors by a spring with a rest length b, leads to the relation $[\eta] = \phi'(Xh^*)\langle S^2\rangle^{3/2}/M$ with X, a draining

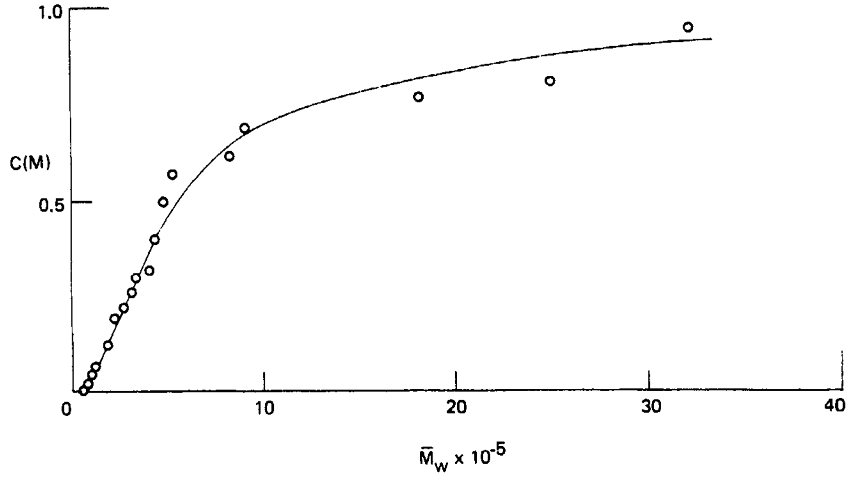

FIG. 3. Integral molecular weight distribution curve for chlorosulfonated polyethylene.

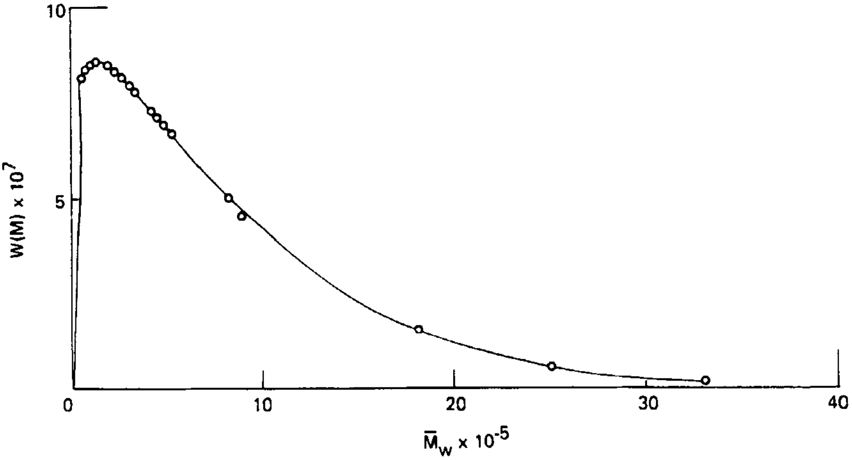

FIG. 4. Differential distribution curve for chlorosulfonated polyethylene.

TABLE 2. Parameters Derived from the Dependence of $[\eta]$ on M_w

Polymer	Solvent	$(S^2/N)_n$ $\times 10^{16}$	A	10^3 h^+	10^8 R_s	λ
Chlorosulfonated polyethylene	Toluene	4.47	177	5.47	0.33	0.11

parameter, defined as $X = 2^{1/2}h^+M^{1/2}$ where $h^+ = (R_s/m_n)(2\pi\langle S^2\rangle/M)^{-1/2}$ and $h^* = h^+\sqrt{m_n}$. The quantity (R_s/m_n) is related to Ξ_{FD}, the friction factor in the absence of hydrodynamic interaction, by $R_s/m_n = \Xi_{FD}/6\pi M\eta_0$. For infinitely long chains, Pyun [35] obtained the relation

$$\lim_{n=0} 10^{-23}\phi'(X, h^*) = 9.67X/(1 - 1.414h^*)$$

Again, the expressions for ϕ' have been put in a form such that the molecular weight dependence of $[\eta]$ can be put in the form

$$M^{1/2}/[\eta] = [K'(\langle S^2\rangle/M)^{3/2}]^{-1}[1 + (A/M^{1/2})]$$

and adequately represents the molecular weight dependence of $[\eta]$, at least over a reasonable span in M. Evaluation of $\langle S^2\rangle/M$ from the intercept of a plot of $M^{1/2}/[\eta]$ vs $M^{-1/2}$ requires the use of a model to give a value for K'. Similarly, interpretation of A in terms of the parameters h^+, h^*, and λ requires the use of a model. Data on chlorosulfonated polyethylene has been analyzed, and the results for $(\langle S^2\rangle/N)_\eta$ and A are shown in Table 2. The subscript η signifies that the estimate derives from data on intrinsic viscosity as a function of molecular weight. Further analysis of these data with the value of A leads to the estimates for h^+ given in Table 2. This value of h^+ can be used to compute the value of R_s shown in Table 2. The value of λ obtained from $\ell_n\lambda^{-1} = 2.22 + [(\sqrt{2}h^+ A - K)/2.27]$ is also shown in Table 2.

To analyze the data shown in Table 2, it can be stated that the positive value of A indicates a deviation from nondraining hydrodynamic behavior. However, the decrease in $(\langle S^2\rangle/N)_\eta$ value is sufficient to increase h^+ to the range where nondraining behavior is to be expected under the conditions of this study. The very low value of $[\langle S^2\rangle/N]_\eta$ indicates a high degree of coiling, resulting in solvent immobilizing behavior.

REFERENCES

[1] R. L. Cleland, J. Polym. Sci., 27, 349 (1958).
[2] Ph. Ribeyrolles, A. Guyol, and H. Benoit, J. Chim. Phys., 56, 377 (1959).
[3] V. G. Vinogradov, Ya K. Malkin, and V. G. Kulichikin, Vysokomol. Soedin., 10(11), 2522 (1968).
[4] G. Kraus and T. J. Gruver, Rubber Chem. Technol., 41(5), 1256 (1968).
[5] V. W. Smith and S. Thiruvengoda, Ibid., 43(6), 1439 (1970).
[6] J. N. Anderson, S. K. Baczak, H. E. Adams, and L. E. Vescelius, J. Appl. Polym. Sci., 19(8), 2255 (1975).
[7] W. E. Mochel, J. B. Nichols, and C. J. Mighton, J. Am. Chem. Soc., 70, 2185 (1948).
[8] W. E. Mochel and J. B. Nichols, Ind. Eng. Chem., 43, 154 (1951).
[9] J. T. Maynard and W. E. Mochel, J. Polym. Sci., 13, 251 (1954).
[10] W. E. Mochel and J. B. Nichols, J. Am. Chem. Soc., 71, 3435 (1949).
[11] A. V. Gevorkyan, E. S. Egiyan, and L. G. Melkonyan, Vysokomol. Soedin., B, 9(9), 674 (1967).
[12] W. Scholtan, H. Lange, Sie Ying Lie, K. Dinges, and R. Mayer-Mader, Angew. Makromol. Chem., 14, 43 (1970).
[13] Y. Kato and T. Hashimoto, J. Appl. Polym. Sci., 18(4), 1239 (1974).
[14] N. Kovalev and I. M. Trypkina, Kauch. Rezina, 9, 32 (1973).
[15] I. Ya. Poddudnyi, V. A. Grechanovskii, M. I. Mosevitskii, and A. V. Podalinskii, Vysokomol. Soedin., 5(7), 1042 (1963).
[16] H. A. Scheraga and L. Mandelkern, J. Am. Chem. Soc., 75, 179 (1953).
[17] P. J. Flory, Ibid., 65, 372 (1943).
[18] W. R. Krigbaum and P. J. Flory, Ibid., 75, 1775 (1953).
[19] R. A. Komoroski and L. Mandelkern, J. Polym. Sci., Polym. Symp., 54, 201 (1976).
[20] A. N. Genkin, T. P. Nasonova, I. Ya. Poddubnyi, and R. A. Shlyakhtar, Vysokomol. Soedin., 4, 1088 (1962).
[21] V. P. Mironyuk, V. N. Reikh, L. M. Ivanova, and Yu. G. Kamenev, Kauch. Rezina, 7, 12 (1974).
[22] M. Uhniat, M. Rubay, T. Marciniak, and J. Bankiewicz, Polymeri, 17(3), 141 (1972).
[23] O. P. Singhal, K. Lal, and L. H. Bhatnagar, Indian J. Chem., 9(4), 355 (1971).
[24] V. P. Shaboldin, A. G. Sukhomudrenko, A. I. Krasheninnikov and A. V. Morozov, Vysokomol. Soedin., A, 14(7), 1462 (1972).
[25] W. Scholtan, H. Lange, R. Casper, U. Pohl, D. Wendisch, and R. Mayer-Mader, Angew. Macromol. Chem., 27, 1 (1972).

[26] J. Esnerova, O. Vilim, and J. Novak, Plasty Kauc., 13(9), 271 (1976).

[27] L. Mandik, J. Eichler, and J. Foltyn, Makrotest, Sb. Prednasek, Celostatni Konf., 5, 161 (1978).

[27a] N. M. Tretyakova, L. V. Monomerov, and R. G. Romanova, Vysokomol. Soedin., B, 16(6), 438 (1974).

[28] P. J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, New York.

[29] G. V. Schulz, Z. Phys. Chem., B47, 155 (1940).

[30] L. H. Tung, J. Polym. Sci., 20, 495 (1956).

[31] M. M. Huque, D. A. I. Goring, and S. G. Mason, Can. J. Chem., 36, 952 (1958).

[32] J. Oth and V. Desreux, Bull. Soc. Chim. Belg., 63, 285 (1954).

[33] R. St. John Manley, Arkiv. Kemi., 9, 519 (1956).

[34] H. Yamakawa, Modern Theory of Polymer Solutions, Harper & Row, New York.

[35] C. W. Pyun, J. Chem. Phys., 49, 2875 (1968).

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