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Dilute-Solution Properties of Chlorosulfonated Polyethylene. Il Theta Composition and Expansion Coefficient

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NOTE

DILUTE-SOLUTION PROPERTIES OF CHLOROSULFONATED POLYETHYLENE. II. THETA COMPOSITION AND EXPANSION COEFFICIENT

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INTRODUCTION

It is well recognized that a polymer is under theta conditions if the second virial coefficient A_2 is zero and the mean square radius of gyration of the polymer is proportional to the square root of its molecular weight. For any single solvent or a mixture of solvents, this condition prevails at a certain temperature, the theta temperature. Here, the polymer chains are said to be unperturbed as they are not affected by long-range interactions.

In this note we report the theta composition for chlorosulfonated polyethylene (CSP) in a solvent-nonsolvent mixture, viscometric data under theta conditions, and the expansion coefficients. Different theoretical expressions are also examined in terms of the present data.

EXPERIMENTAL/MATERIALS

As reported earlier [1], standard commercial samples of CSP and commercial solvents of highest purity were used. Details of fractionation, viscometry, and determination of $\bar{M}_w$ from light-scattering measurements in toluene, a nontheta solvent, have been described in a previous communication [1].

Determination of Theta Composition

A simple and rapid method, suggested by Elias [2-6], was used for the determination of theta compositions. Dilute polymer solutions of different compositions, maintained at a constant temperature, were titrated with a nonsolvent (methanol) until the first appearance of turbidity. The logarithm of the nonsolvent concentration at the cloud point was then plotted against the logarithm of polymer concentration at the cloud point and extrapolated to 100% polymer. The solvent-nonsolvent ratio at this point is the theta composition.

RESULTS AND DISCUSSION

The results of turbidimetric titration for CSP of various molecular weights are shown in Fig. 1 and Table 1 for the system toluene/methanol at 25°C.

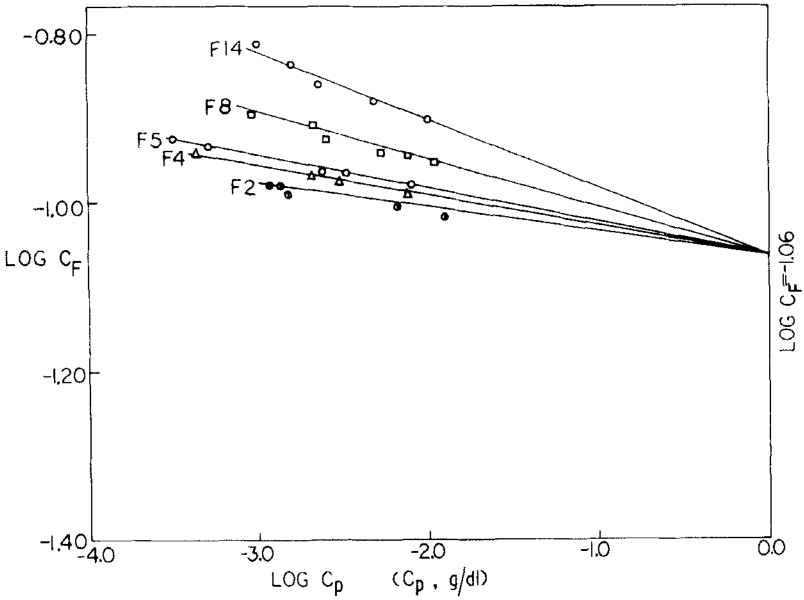

FIG. 1. Log-log plot of polymer vs nonsolvent concentration at the cloud point. $C_F = W_F/(V_L - V_F)$, where C_F = nonsolvent concentration, W_F = weight of nonsolvent, V_L and V_F are the volumes of solvent and nonsolvent, respectively, and C_P = polymer concentration.

TABLE 1. Viscosity-Molecular Weight Data for Chlorosulfonated Polyethylene

Fraction no.	$[\eta]$, dL/g	$[\eta]_\theta$, dL/g	α_η	$\bar{M}_w \times 10^{-5}$
F_1-1	2.270	1.800	1.080	33.1
F_1-2	1.750	1.400	1.077	25.0
F_1-3	1.430	1.160	1.072	18.2
F_1-4	1.170	0.960	1.068	9.12
F_1-5	1.110	0.920	1.064	8.32
F_1-6	0.840	0.720	1.063	5.41
F_1-7	0.780	0.660	1.057	4.79
F_1-8	0.730	0.620	1.056	4.55
F_1-9	0.700	0.600	1.052	4.37
F_1-10	0.650	0.560	1.052	3.31
F_1-11	0.600	0.515	1.051	3.13
F_1-12	0.560	0.485	1.049	2.78
F_1-13	0.510	0.450	1.043	2.38
F_1-14	0.470	0.420	1.038	1.91

The theta composition at 25°C thus obtained is methanol:toluene 11.0:89.0. Figure 1 shows that the lower the molecular weight, the greater is the slope of the straight line, as predicted by Elias.

Intrinsic viscosities measured under theta conditions for the fractions are shown in Table 1. The relationship between $\bar{M}_w$ and intrinsic viscosity at the theta point corresponds to $[\eta]_\theta = 0.912 \times 10^{-3}\ \bar{M}_w^{0.5}$. The expansion factors, α_η, evaluated from viscometric measurements, show a weak dependence on molecular weight and vary from 1.025 to 1.080, i.e., a variation of 5.4% over the molecular weight range studied (Table 1).

Values of $(\alpha^5 - \alpha^3)/\bar{M}_w^{1/2}$ for CSP are plotted against $\bar{M}_w^{1/2}$ in Fig. 2, which shows an appreciable variation in this quantity, an observation also

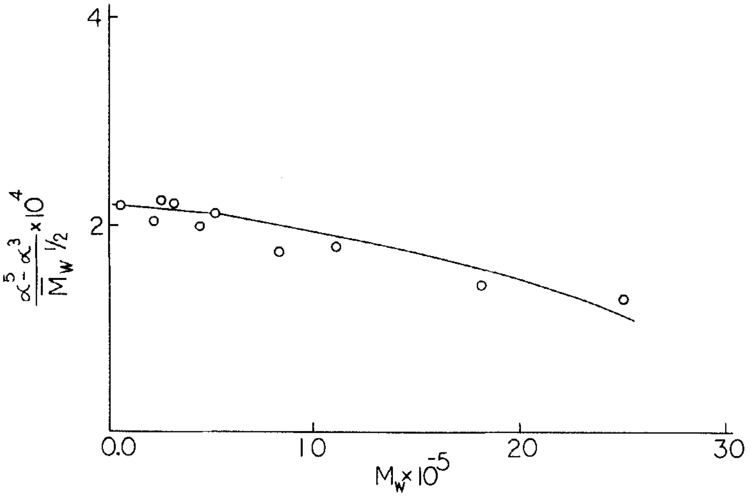

FIG. 2. Plot of $(\alpha^5 - \alpha^3)/\bar{M}_w{}^{1/2}$ vs $\bar{M}_w$.

reported by other workers [7, 8]. This is contrary to the prediction of the Flory theory, according to which:

$$\alpha^5 - \alpha^3 = CZ.$$

On the other hand, the Stockmayer-Fixman theory predicts

$$\alpha^3 - 1 = 1.9Z,$$

with

$$Z = B(\langle S_0{}^2 \rangle / M)^{-3/2} \cdot M^{1/2}$$

and

$$B = \left(\frac{1}{4}\right)^{3/2} \cdot \left(\frac{1}{m_s}\right)^2 \beta$$

where β is the binary cluster integral and m_s is the molecular weight of the segment.

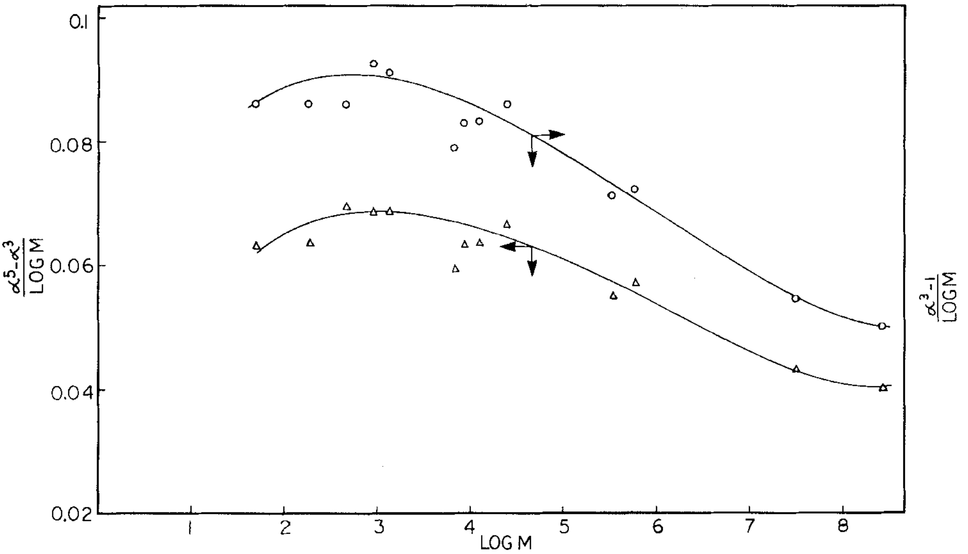

FIG. 3. Plot of $(\alpha^5 - \alpha^3)/\log M$ or $(\alpha^3 - 1)/\log M$ vs $\log M$ for different fractions of CSP.

Berry [9] assumed a linear dependence of B on $(1 - \theta/T)$ over a considerable temperature range, and he observed that the Flory theory, as modified by Flory and Fisk [10], was valid over the molecular weight range studied. Norisuye et al. [11] on the other hand, held that this assumption may not be valid over a wide temperature range and that the molecular weight dependence of Z is a more reliable criterion.

Nagasawa et al. [12], however, pointed out that the proportionality of Z to $N^{1/2}$ may not be sensitive enough to distinguish among the theories, particularly in the low molecular weight range and extended their studies to the range of $\bar{M}_w \approx 10^6$.

In the present work, both theories were initially examined on the basis of the molecular weight dependence of Z. Accordingly, plots of $(\alpha^5 - \alpha^3)/M^{1/2}$ vs $\log M$ and $(\alpha^3 - 1)/M^{1/2}$ vs $\log M$ are shown in Fig. 3. Neither of the two theories seems to fit the data throughout the entire molecular weight range, both the functions showing a maximum around $\log M \approx 3$. Similar behavior for polyisobutylene has been reported by Flory and Krigbaum [13].

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