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Dilute Solution Properties of Poly(Vinyl Chloride)

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Dilute Solution Properties of Poly(Vinyl Chloride)

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ABSTRACT

Light scattering and viscosity studies were made on dilute solutions of poly(vinyl chloride) (PVC) in three solvents: cyclohexanone, cyclopentanone, and tetrahydrofuran. Eight samples of PVC (M_w = 25,400 to 145,000) were used to determine the intrinsic viscosities, molecular weights, and the polymer-solvent interaction parameters over a range of temperatures. The solutions were found to behave normally and to exhibit no evidence of aggregate formation. The molecular weights obtained in all three solvents were independent of temperature and agreed well within the experimental errors. The interaction parameters observed were independent of concentration and molecular weight, and functions only of temperature. The intrinsic viscosities were related to molecular weight by the Mark-Houwink equation between 20 and 50°C. The temperature coefficient of the interaction parameter obtained by light scattering agrees well with that found by viscometry. Cyclohexanone, cyclopentanone, and tetrahydrofuran are all good solvents for PVC, and the order of solvent quality is cyclohexanone > cyclopentanone > tetrahydrofuran.

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INTRODUCTION

In the past, several researchers [1-12] have studied the dilute solution behavior of poly(vinyl chloride) (PVC) in various organic solvents, using osmotic pressure, viscosity, and light-scattering techniques. These studies give conflicting values, for any given solvent and temperature, of the constants K_m and a of the Mark-Houwink-Sakurada (M.H.S.) equation:

$$[\eta] = K_m M^a. \tag{1}$$

For example, the values of K_m and a reported in tetrahydrofuran between 20 and 30°C vary from 0.36×10^{-4} to 21.9×10^{-4} and from 0.54 to 0.92, respectively. The possible causes for these inconsistent values may be the effects of polydispersity, incorrect dissymmetry correction, and inadequate solution clarification.

The present investigations were carried out in order to clarify this confused situation and to establish a reliable relationship between $[\eta]$ and M_w for a wide range of molecular weights by viscosity and light-scattering techniques. These measurements were made in three solvents, cyclohexanone, cyclopentanone, and tetrahydrofuran, at 32.4°C. The light-scattering data were analyzed according to the Zimm method [13].

EXPERIMENTAL

Sample

The PVC samples used were obtained from Scientific Polymer Products, Inc. PVC was fractionated by fractional precipitation, using tetrahydrofuran and carbon disulfide as solvent and nonsolvent, respectively. Eight fractions, ranging in molecular weight from 22,500 to 165,000, were obtained.

Viscosity Measurements

The viscosities of the solutions were measured at 32.4°C with an Ubbelohde-type viscometer and corrected for kinetic energy effects. Fluctuations of the temperature were less than 0.04°. The intrinsic viscosity $[\eta]$ was calculated from the reduced viscosity by means of the Huggins [14] equation:

$$\eta_{sp}/C = [\eta] + k_1[\eta]^2 C. \quad (2)$$

Light-Scattering Measurements

Light-scattering measurements were performed in the three solvents at 32.4°C, using a universal light-scattering photometer (C. N. Wood Manufacturing Co., Newton, Pennsylvania, Model 300), which was calibrated with Cornell standard polystyrene and pure, dust-free benzene [15]. Scattering intensities were measured at 11 angles ranging from 30 to 150°, using unpolarized light of wavelength 435.8 nm. A cylindrical cell was used throughout the work.

The interpretation of the light-scattering data was based on the Zimm method, expressed in the general form

$$KC/R_\theta = (1/\bar{M}_w)\left[1 + \frac{16\pi^2}{3\lambda^2}\langle \bar{S}^2 \rangle_Z \sin^2\frac{\theta}{2}\right] + 2A_2C + \cdots, \quad (3)$$

where K is an optical constant and is equal to $2\pi^2 n_0^2 (dn/dc) N_A \lambda^4$, C is the concentration in g/mL, R_θ is the difference between the Rayleigh ratio of the solution and that of the pure solvent, $\bar{M}_w$ is the weight-average molecular weight, $\langle \bar{S}^2 \rangle_Z^{1/2}$ is the Z-average mean-square radius of gyration, θ is the scattering angle, λ is the wavelength of light in the medium, A_2 is the second viral coefficient, and N_A is Avogadro's number.

The solutions were clarified by filtering under nitrogen pressure through Millipore filters. Values of (dn/dc) of the polymer solutions were measured in a Brice-Phoenix differential refractometer previously calibrated with aqueous solutions of KCl [16]. The measurements were carried out at the same wavelength (λ = 435.8 nm) and same temperature (T = 32.4°C) as the light-scattering measurements.

RESULTS AND DISCUSSION

The relationships between the weight-average molecular weight $\bar{M}_w$ and intrinsic viscosity $[\eta]$ for PVC in cyclohexanone, cyclopentanone, and tetrahydrofuran at 32.4°C are shown in Fig. 1 and can be represented by Eqs. (4), (5), and (6), respectively:

$$[\eta] = 1.72 \times 10^{-4} \bar{M}_w^{0.79}, \quad (4)$$

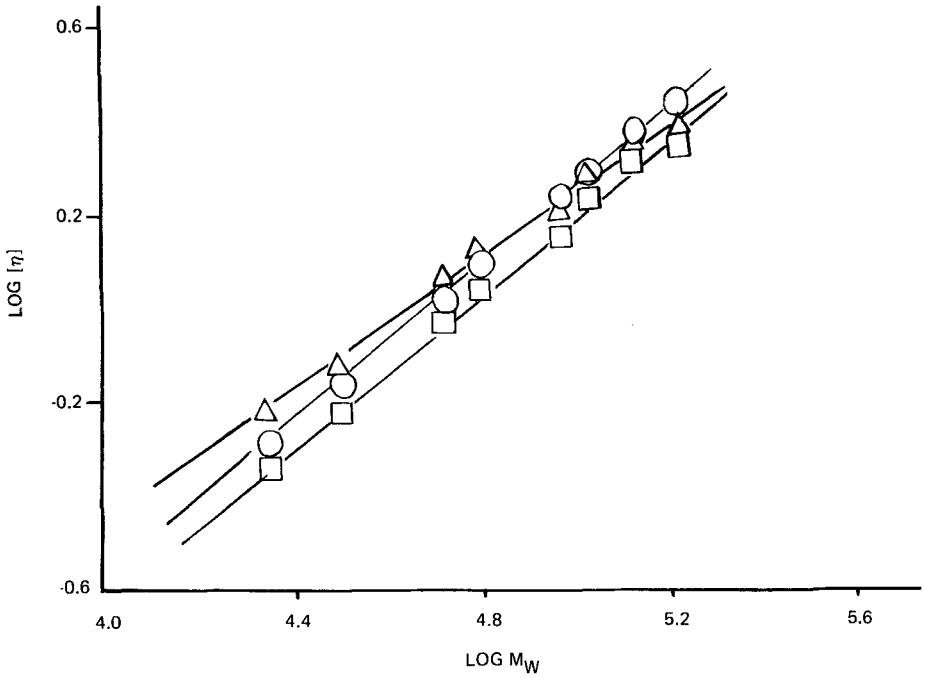

FIG. 1. Mark-Houwink-Sakurada plots for poly(vinyl chloride) in cyclohexanone (○), cyclopentanone (□), and tetrahydrofuran (△) according to Eq. (1); $[\eta]$ in dL/g.

TABLE 1. Comparison of Molecular Weight of PVC in Cyclohexanone, Cyclopentanone, and Tetrahydrofuran

	$M_W \times 10^{-3}$		
Fraction	Cyclohexanone	Cyclopentanone	Tetrahydrofuran
1	22.45	21.96	22.09
2	36.29	36.48	37.38
3	54.08	53.27	52.86
4	69.56	68.34	67.29
5	94.30	94.78	94.17
6	131.52	131.09	129.65
7	143.23	142.82	141.52
8	165.18	164.20	162.34

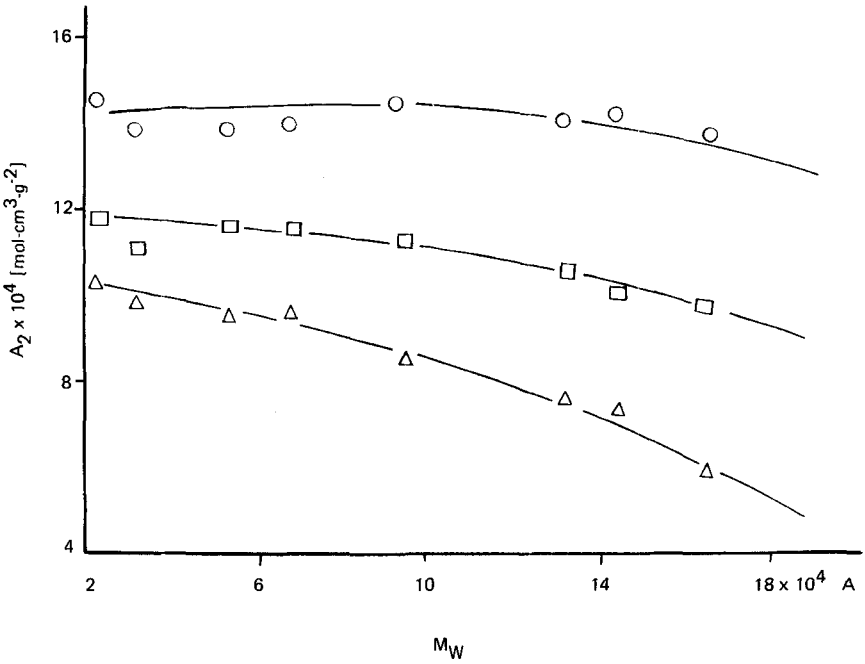

FIG. 2. Second virial coefficient versus molecular weight for poly(vinyl chloride) in cyclohexanone (□), cyclopentanone (△), and tetrahydrofuran (●).

$$[\eta] = 1.04 \times 10^{-4} \quad \overline{M}_w^{0.84} \tag{5}$$

$$[\eta] = 8.63 \times 10^{-5} \quad \overline{M}_w^{0.87} \tag{6}$$

The molecular weight of PVC obtained in the three solvents are in good agreement within experimental error, as shown in Table 1. This close agreement in molecular weights rules out the possibility of aggregate formation since it is improbable that aggregation would be identical in the three solvents investigated.

Figure 2 shows a plot of the second virial coefficient, A_2, as a function of molecular weight $\overline{M}_w$ in the three solvents. It indicates that the interaction between polymer and any given solvent decreases with increasing molecular weight, which is according to expectation.

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