

Properties of Polyvinylchloride in Solution: An Hydrodynamic and Vibrational Spectroscopy Study

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ABSTRACT: The polymer polyvinylchloride has been studied in binary solvent mixtures and as a function of temperature in solution. A discontinuity of the polymer chain dimensions has been observed, as measured by hydrodynamic methods. This phenomenon is further examined by infrared and Raman spectroscopy. © 1999 John Wiley & Sons, Inc. *J Polym Sci B: Polym Phys* 37: 1351–1356, 1999

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INTRODUCTION

Several polymer solutions have been studied to date in which a discontinuity in the polymer chain dimensions, as measured by intrinsic viscosity, in a solvent mixture is observed. Discontinuities of this type are generally observed either in binary polymer mixtures where the only intensive parameter is the temperature^{1–9} or in ternary systems where the only intensive parameter is the solvent composition.^{10–18}

In the present work, the effect of the discontinuity in the intrinsic viscosity values of PVC in the binary solvent mixture of cyclohexanone + *n*-hexane and in THF at different temperatures is studied by infrared and Raman spectroscopy. The spectroscopic analysis has been focused on the configuration and conformational region of PVC, where the carbon–chlorine stretching vibrations (600–710 cm⁻¹) are sensitive to the rotational isomeric states.

EXPERIMENTAL

The PVC samples used in this work were obtained from B.D.H. and I.C.I. Molecular weights of the samples have been determined by light scattering (M_w : 185600, 98500, 65400, and 44500), using a model FICA 42000 P.G.D. instrument using the unpolarized green line at 546 nm of mercury. Scattered intensities were calibrated by using $R_B = 16.7 \times 10^{-6} \text{ cm}^{-1}$,¹⁹ the Rayleigh ratio of benzene at 25°C. Refractive index increments were determined at 25°C by means of a Brice-Phoenix model 2000V differential refractometer, using a 546 nm filter; dn/dc values of polymer solutions as a function of refractive index n have been found to obey the equation:

$$dn/dc = -0.77n + 1.18 \quad (1)$$

Intrinsic viscosity values $[\eta]$ (in ml g⁻¹) were obtained by measuring the specific viscosity of the polymer solutions, η_{sp} , using a modified Ubbelohde viscometer under constant pressure. The viscometer was positioned in a constant temperature bath. The intrinsic viscosity at each composition was calculated from the equation²⁰:

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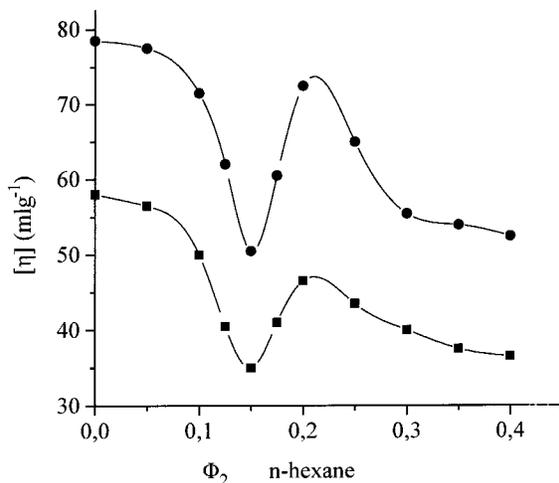


Figure 1. Intrinsic viscosity of PVC in cyclohexanone + *n*-hexane mixture, vs. composition in terms of volume fraction of *n*-hexane (■ $M_w = 44500$; ● $M_w = 65400$).

$$\eta_{sp}/c = [\eta] + k_\eta[\eta]^2c \quad (2)$$

where k_η is the Huggins coefficient.

The infrared spectra were obtained by a JASCO double beam model DS-701G spectrometer. The compensation technique is used in order to eliminate the influence of the solvent bands.

Raman spectra were obtained by means of a Spex Ramalog spectrometer fitted with a 1403 double monochromator. The light source was a Coherent Innova 90 argon-ion laser operating at 514.5 nm and 100 mW. Samples were enclosed in capillary tubes and held at a constant temperature ($\pm 1^\circ\text{C}$) in the temperature range 5–35°C by means of a Harney-Miller cell.

The solvents used in this work were all analytical grade from Merck or Aldrich with nominal purity 99+%.

RESULTS

Intrinsic Viscosity

PVC/Cyclohexanone + *n*-Hexane Ternary System

The intrinsic viscosity $[\eta]$ for two different molecular weights of PVC are shown in Figure 1 as a function of solvent mixture composition expressed as the volume fraction of *n*-hexane, ϕ_2 . We have observed a discontinuity in the intrinsic viscosity values at about $\phi_2 = 0.15$. The solvent mixture composition at which the discontinuity occurs

does not depend upon the molecular weight of the polymer.

The Huggins coefficient, k_η [eq (2)], which is a measure of solvent quality, also shows a dramatic variation with ϕ_2 (Fig. 2). Experiments show that k_η lies between 0.5–1 in poor solvents and may also indicate polymer aggregation,²¹ decreases monotonically to about 0.3 as solvent power improves.^{22,23}

We have used the extrapolation procedure of Stockmayer-Fixman²⁴ in order to obtain the unperturbed dimensions of the polymer, K_Θ (in $\text{ml g}^{-1} \text{mol}^{-1/2}$).

$$[\eta]/M^{1/2} = K_\Theta + 0.51 \Phi B M^{1/2} \quad (3)$$

where B is an interaction parameter and Φ is Flory's constant²⁵ ($\Phi = 2.87 \times 10^{-23} \text{ mol}^{-1}$). Figure 3 shows that the unperturbed dimensions also exhibit a discontinuity within the same region of the solvent mixture composition.

PVC/THF Binary System

The intrinsic viscosity $[\eta]$ of PVC in tetrahydrofuran as a function of temperature in the range 5–35°C is shown in Figure 4. We have observed a discontinuity at a temperature of about 23°C. Again, the temperature at which the discontinuity of the polymer chain dimensions occurs does not depend upon the molecular weight of the polymer.

Elastic Light Scattering

The experimental results of the light scattering are treated in the usual way to obtain the apparent molecular weight M^*

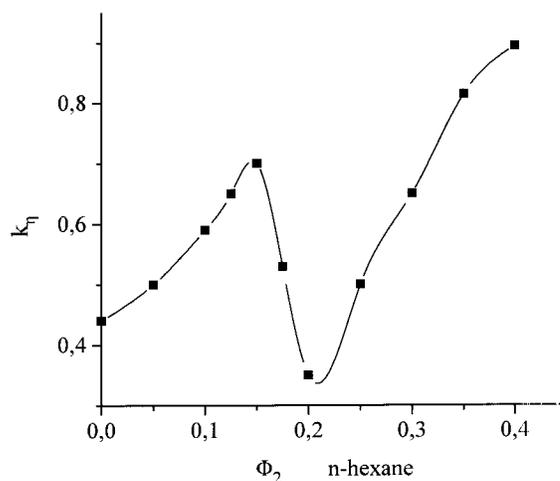


Figure 2. The Huggins coefficient of PVC in cyclohexanone + *n*-hexane mixture, vs. composition in terms of volume fraction of *n*-hexane ($M_w = 44500$).

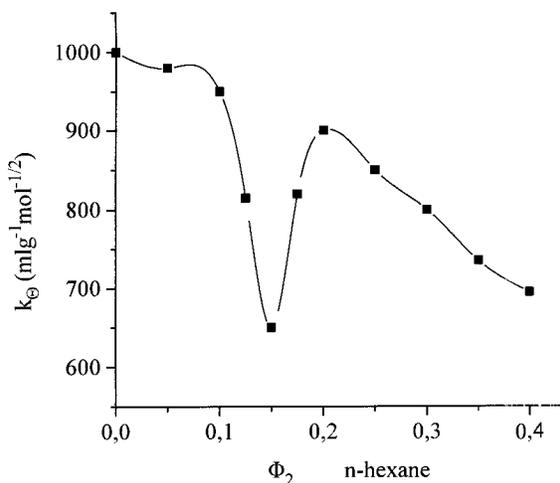


Figure 3. The unperturbed dimensions of PVC in cyclohexanone + *n*-hexane mixture, vs. composition in terms of volume fraction of *n*-hexane.

$$Kc/\Delta R = 1/M^* + 2A_2^*c \quad (4)$$

where K is a constant and ΔR is the difference of Rayleigh ratios of solution, and solvent, and A_2^* is the apparent second virial coefficient. The coefficient of preferential adsorption λ' was calculated by the equation²⁶:

$$\lambda' = [(M^*/M)^{1/2} - 1][(dn/dc)/(dn/d\varphi_1)] \quad (5)$$

The coefficient λ' is defined as:

$$\lambda' = [x_1/M]V_1 \quad (6)$$

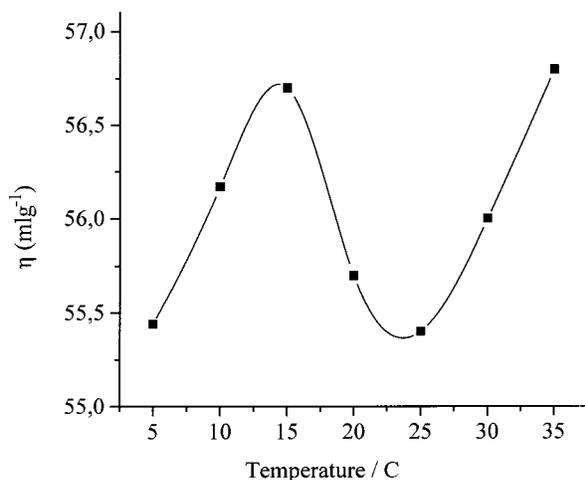


Figure 4. Intrinsic viscosity of PVC in THF vs. temperature ($M_w = 44500$).

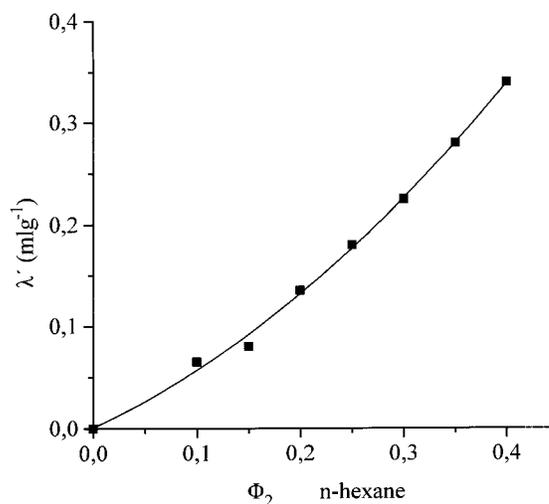


Figure 5. Coefficient of preferential solvation of PVC in cyclohexanone + *n*-hexane mixture, vs. composition in terms of volume fraction of *n*-hexane ($M_w = 44500$).

where x_1 is the number of molecules of solvent-1 in the neighborhood of the macromolecular chain. From eq. (6), it is concluded that cyclohexanone (solvent-1) is preferentially adsorbed by the polymer (Fig. 5).

Infrared and Raman Spectroscopy

IR and Raman frequencies for solid PVC in the 600–710 cm^{-1} region are listed in Table I. IR spectra of solid PVC as well as in solution in cyclohexanone + *n*-hexane solvent mixture are shown in Figure 6. The bands at 612 cm^{-1} and 695 cm^{-1} on the IR spectrum of PVC in cyclohexanone are considered to correspond to the 613 cm^{-1} and 696 cm^{-1} bands, respectively, of the PVC solid film spectrum. Pure cyclohexanone in the region 600–710 cm^{-1} has a band at 650 cm^{-1} , while pure *n*-hexane has a weak absorption band at 675 cm^{-1} .

The ternary system PVC/THF + *n*-hexane was also studied by IR spectroscopy. In our previous study,¹⁶ we have observed a discontinuity in the intrinsic viscosity values at $\varphi_2 = 0.15$ (volume fraction of *n*-hexane). Pure THF has no bands in the region 620–690 cm^{-1} . We have observed in solution the bands at 612 cm^{-1} and 690 cm^{-1} which correspond to the 613 cm^{-1} and 696 cm^{-1} , respectively, of the solid film. Addition of *n*-hexane in the mixture for the last two ternary systems, leaves the conformation sensitive region of the spectrum quite unaffected.

Table I. C—Cl Frequency Region (in cm^{-1}) of Solid PVC^a

Pohl and Hummed ³⁸ Jackson et al. ⁴¹	This Work	Pohl and Hummed ³⁸ Robinson et al. ³⁹ Rubic and Zerbi ⁴⁰	This Work	Configuration ^b
IR		RAMAN		
603		608	609	s
613	613	614	615	s
624		623		i
633	636	634	635	i
639		637		s
647		647		s
677	680	680		s
696	696	692	693	i
		704	702	s

^a Uncertainty in frequency: $\pm 1 \text{ cm}^{-1}$.^b (s) = syndiotactic; (i) = isotactic.

In the Raman spectrum of solid PVC we have observed five bands which are listed in Table I. We have studied PVC in THF in the temperature range 5–35°C (THF has two weak bands at about 595 cm^{-1} and 650 cm^{-1}). The band at 618 cm^{-1} corresponds to the 615 cm^{-1} of the solid. Examples of spectra for three different temperatures

are shown in Figure 7. No changes were observed in the conformationally sensitive spectra region.

DISCUSSION

It was the discontinuity in the polymer chain dimensions as expressed by intrinsic viscosity of

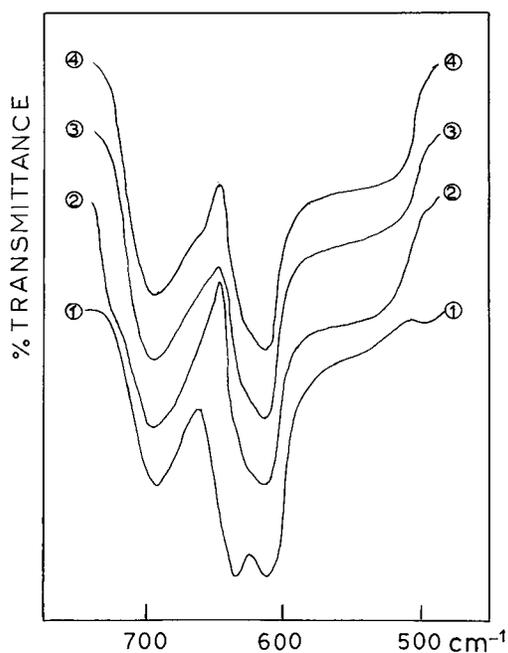


Figure 6. IR spectra ($450\text{--}750 \text{ cm}^{-1}$) of PVC in cyclohexanone + *n*-hexane mixture. Composition in terms of volume fraction of *n*-hexane (1 : PVC film; 2 : $\varphi_2 = 0.00$; 3 : $\varphi_2 = 0.15$; 4 : $\varphi_2 = 0.30$).

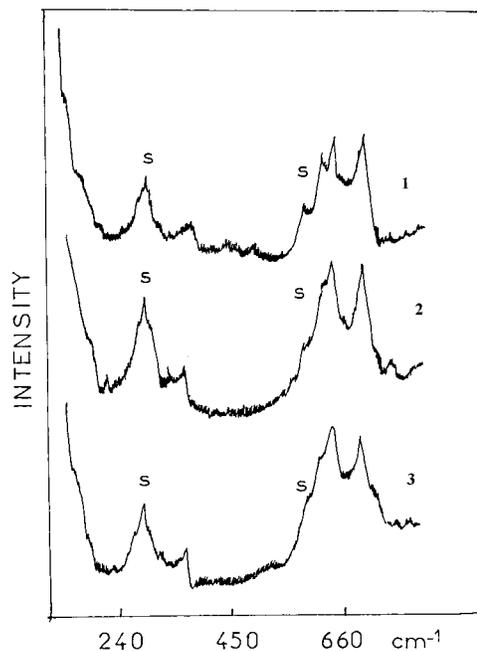


Figure 7. Raman spectra ($100 \text{ cm}^{-1}\text{--}800 \text{ cm}^{-1}$) of PVC in THF (s : solvent bands) (1 : 5°C; 2 : 25°C; 3 : 35°C).

PVC that led us to look at the problem from a spectroscopic point of view. Vibrational spectroscopy showed that in the conformation-sensitive region where the C—Cl stretching band appears, no changes are observed, either upon addition of a nonpolar solvent, such as *n*-hexane or with temperature change.

In general, strong solvents for PVC should: (a) have a high electron donor, (b) have no significant steric hindrance so that the solvent molecules can easily approach the polymer chain, and (c) have sufficient bulk for effectively separating the polymer chains and reducing interchain forces.²⁷ According to this discussion cyclohexanone solvates PVC mainly through C=O . . . Cl—C complex formation.²⁸ On the other hand, THF solvates PVC through O . . . Cl—C.

It is well known^{29–31} that a carbonyl compound normally exhibits its highest frequency in the vapor phase, while in solution the highest values are observed in solvents of low polarity. Such frequency shifts can be satisfactorily explained by dielectric constant effects. We use this in our attempt to account for the behavior of such systems. The addition of a nonpolar solvent seems to break these dielectric constant effects of pure cyclohexanone and this effect yields an increase of the polymer chain dimensions in the short region of discontinuity.

A sufficient concentration of *n*-hexane in the mixture THF + *n*-hexane yields similar results on the dimensions of the polymer.

On the other hand, PVC forms associations in solution with dioxane, methyl acetate, cyclohexanone, and THF.³² The presence of *n*-hexane in the solution dissolves the associations, as one can see from the results of k_η and λ' where in the latter, cyclohexanone is preferentially strongly adsorbed by the polymer.

From a spectroscopic view, Shimanouchi et al.^{33–35} and Krimm^{36,37} have assigned the band at 696 cm^{-1} of PVC to the C—Cl stretching vibration of the S_{CH} structure, in which a chlorine substituent is situated in a position *trans* to a carbon; this band corresponds to a folded, mainly isotactic structure. The band at 613 cm^{-1} is assigned to the C—Cl stretching vibration of the S_{HH} structure, in which the chlorine substituent is *trans* to a hydrogen substituent in the polymer chain and corresponds to the extended, mainly syndiotactic structure. On the other hand, it is considered that the band at 613 cm^{-1} is due to the disordered part of the S_{HH} structure. The absorbance ratio of the bands at about 696 cm^{-1} and

613 cm^{-1} should be related to the ratio of the amount of S_{CH} arrangement to that of S_{HH} arrangement in the polymer chain in solid or in solution. In the solid state, this ratio was found to be about 0.70, while in the cyclohexanone + *n*-hexane mixture, it remains unchanged throughout the concentration range at about 0.81. In the case of the THF + *n*-hexane mixture, this ratio is about 0.72. The later result enhanced the aspect that the conformation of the macromolecular chain remains unchangeable.

From the above discussion, it is concluded that the observed discontinuity in the intrinsic viscosity values of PVC in solution either in a binary solvent mixture or with temperature is related to the influence of the polymer–solvent interaction and not to any conformational change of the macromolecular chain.

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REFERENCES AND NOTES

1. Reiss, C.; Benoit, H. CR Hebd Seanc Acad Sci Paris 1961, 253, 268.
2. Dondos, A. Makrom Chem 1970, 135, 181.
3. Noël, C.; Platzer, N.; Monnerie, L.; Basselier, J. S. J Chim Phys 1970, 67, 558.
4. Dondos, A.; Rempp, P.; Benoit, H. Makrom Chem 1973, 171, 135.
5. Katime, I.; Roig, A.; Cabanas, P. G. Eur Polym J 1974, 10, 897.
6. Gargallo, L.; Guenes, C. L.; Radic, D. Eur Polym J 1984, 20, 483.
7. Simionescu, B. C.; Ioan, S.; Chirias, A.; Simionescu, C. I. Polym Bull 1987, 17, 439.
8. Sarabia, C.; Radic, D.; Gargallo, L. Makrom Chem 1981, 182, 2517.
9. Katime, I.; Cabanas, P. G.; Vera, C. R. Polym Bull 1981, 5, 25.
10. Viras, F.; Viras, K.; Aroni, F.; Dondos, A. Eur Polym J 1974, 10, 891.
11. Lin, K.; Parson, J. L. Macromolecules 1969, 2, 529.
12. Dondos, A. Makrom Chem 1972, 162, 113.
13. Gargallo, L. Makrom Chem 1976, 177, 233.
14. Dondos, A.; Havredaki, V.; Mitsou, A. Makrom Chem 1975, 176, 1481.
15. Katime, I.; Strazielle, C. Makrom Chem 1977, 178, 2295.
16. Mitsou-Clappas, A.; Viras, K. Eur Polym J 1980, 16, 205.
17. Palaiologou, M.; Viras, F.; Viras, K. Eur Polym J 1988, 24, 1191.

18. Molinou, I.; Palaiologou, M.; Viras, F.; Viras, K. *Eur Polym J* 1991, 27, 277.
19. Carric, J.; Zimm, B. H. *J Chem Phys* 1950, 18, 1616.
20. Huggins, M. L. *J Am Chem Soc* 1942, 64, 2716.
21. Elias, H. G. *Makrom Chem* 1942, 99, 291.
22. Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper and Row: New York, 1971.
23. Mays, J. W.; Hadjichristidis, N. in H. G. Barth and J. W. Mays, Eds., *Modern Methods of Polymer Characterization*; New York: John Wiley & Sons, 1991.
24. Stockmayer, W. H.; Fixman, M. *J Polym Sci* 1963, Part C-1, 137.
25. Flory, P. J. *Statistical Mechanics of Chain Molecules*; Interscience: New York, 1969.
26. Strazielle, C.; Benoit, H. *J Chim Phys* 1961, 58, 675, 678.
27. Small, P. A. *J Appl Chem* 1953, 3, 71.
28. Tabb, D. L.; Koenig, J. L. *Macromolecules* 1975, 8, 929.
29. Bellamy, L. J.; Williams, R. L. *Trans Faraday Soc* 1959, 55, 14.
30. Brooks, C. J.; Eglinton, G.; Hanaineh, L. *Spectrosc Acta* 1966, 22, 131.
31. Engberts, J. B.; Perjessy, A.; Blandamer, M. J. *J Chem Soc Faraday Trans* 1993, 89, 4199.
32. Gautron, R.; Wippler, C. *J Chim Phys* 1961, 58, 754.
33. Shimanouchi, T.; Tsuchiya, S.; Mizushima, S. *J Chem Phys* 1959, 30, 1365.
34. Shimanouchi, T.; Tasumi, M. *Bull Chem Soc Jpn* 1961, 34, 359.
35. Mizushima, S.; Shimanouchi, T.; Nakamura, K.; Hayashi, M.; Tsuchiya, S. *J Chem Phys* 1957, 26, 970.
36. Krimm, S. *Pure Appl Chem* 1968, 16, 369.
37. Krimm, S. *J Polym Sci* 1963, Part C-7, 3.
38. Pohl, H. U.; Hummel, D. O. *Makrom Chem* 1968, 113, 190, 203.
39. Robinson, M. E. R.; Bower, D. I.; Maddams, W. F. *Polymer* 1978, 19, 773.
40. Rubic, A.; Zerbi, G. *Macromolecules* 1974, 7, 754, 759.
41. Jackson, R. S.; Bower, D. I.; Maddams, W. F. *J Polym Sci, Polym Phys Ed* 1990, 28, 837.