

Viscosity–Temperature Relationship of Dilute Solution of Poly(vinyl chloride) in Cyclohexanone and in Its Blends with Xylene

KARTICK GUPTA, M. YASEEN

Organic Coatings and Polymers Division, Indian Institute of Chemical Technology, Hyderabad-500007, India

Received 11 October 1996; accepted 21 February 1997

ABSTRACT: Absolute viscosities of dilute solutions of poly(vinyl chloride) (PVC) in cyclohexanone and in its blends with xylene were determined at temperatures ranging from 5 to 50°C and in THF at 5–30°C. The simple Arrhenius reaction kinetics equation, used by Anrade to analyze the viscosity data of liquids and later by Moore for dilute polymer solutions, was used to estimate the thermodynamic parameters for the flow of PVC solutions and the quality of solvents. This relationship was also used to calculate thermodynamic parameters for PVC in binary solvent systems. The data of the activation energy of the viscous flow and preexponential factor were further analyzed by using the empirical relationships suggested by Moore for flexible polymer chains. The parameters obtained from these relationships are used to estimate and compare the solvency power of solvents and solvent blends. A blend of 1 : 1 cyclohexanone and xylene is found to have better dissolution characteristics for PVC than have cyclohexanone and other blends. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 2749–2760, 1997

Key words: absolute viscosity; poly(vinyl chloride); solvent blend; Moore's equation; solvency power

INTRODUCTION

Polymer molecules have an optimum degree of freedom or movement in a dilute solution. The average distribution of polymer segments depends on molecular chain length, temperature, and their thermodynamic interaction with solvent molecules. The change in temperature may produce extended uncoiled conformations or a collapsed globule state of polymer chains in solution or result in a contracted chain configuration of polymer molecules even in thermodynamically

good solvents due to unfavorable polymer–solvent interactions.¹ The solvency power of some solvents is enhanced by increasing the temperature, and in the case of some other solvents, this effect is favored at low temperatures. However, in the case of athermal solvents, the chain configuration remains unperturbed by a change in temperature.

The flow behavior of a solution is considered a rate-dependent phenomenon wherein the chain segment unit jumps from its potential energy well to the neighboring hole (i.e., one equilibrium position to another in the liquid). The motion of chain segments is not independent of one another as they are connected to each other by primary valance links (interaction) and by entanglements.

The variation in the viscosity of the polymer solution with a change in temperature is explained in two ways:

This is IICT Communication No. 3736.

Correspondence to: K. Gupta.

Contract grant sponsor: University Grants Commission, New Delhi, India.

Journal of Applied Polymer Science, Vol. 65, 2749–2760 (1997)

© 1997 John Wiley & Sons, Inc.

CCC 0021-8995/97/132749-12

1. Increase in temperature makes thermal energy available to individual segments to overcome the potential energy barrier against jumps.
2. At higher temperature, the available greater free volume reduces the potential energy barrier against jumps.

The empirical Arrhenius equation derived by Andrade² considering the viscosity–temperature relationship as the temperature dependence of the rate of chemical and physical processes is

$$\eta = Ae^{E/RT} \quad (1)$$

where η , A , E , and RT are the absolute viscosity, a preexponential factor related to activation entropy, the apparent activation energy of flow, and the thermal energy, respectively.

Eyring^{3,4} developed the absolute reaction rate theory in which he elaborated the preexponential factor, A :

$$A = (N_0h/V)e^{-\Delta S/R} \quad (2)$$

and

$$\eta = (N_0h/V)e^{-\Delta S/R}e^{E/RT} \quad (3)$$

where N_0 , h , V , and ΔS are Avogadro's number, Plank's constant, the molar volume of liquid, and the entropy of activation of flow, respectively. The parameter A primarily depends on ΔS as molar volume of solution in dilute polymer solution and differs very little from that of solvent.

Moore and coworkers^{5–10} demonstrated the application of the Arrhenius equation to dilute solutions of linear polymers and suggested the following equation:

$$\eta = Ae^{Q/RT} \quad (4)$$

where Q is the apparent activation energy of the viscous flow. They studied the dependence of A and Q on concentration, molecular weight of the polymer, and solvent quality. They also correlated these parameters to polymer flexibility and thermodynamic properties of polymer–solvent systems. Frisch and Simha¹¹ suggested that macromolecules could be characterized by using data on the thermal variation of the absolute viscosity of polymer solutions.

Moore's equations have been found to be valid for a wide variety of flexible and rather stiff linear polymers over a range of conditions of thermodynamic solvent quality. Liouni et al.¹² demonstrated for the first time that these expressions could be applied to data for 12-arm star polystyrene solutions in both cyclohexane (a poor to moderate solvent) and benzene (a good solvent). They¹³ also showed that Moore's equations are suitable for treating actual viscosity data obtained for dilute solutions of linear, 8- and 12-arm star polyisoprene solutions in a good solvent as well as in a poor to moderate solvent.

Ahmad et al.¹⁴ reported that reduced viscosity of dilute polyelectrolyte [poly(sodium 4-styrene sulfonate)] solutions increased with dilution and reached to a maximum and then decreased in the limit of infinite dilution. Moreover, the maximum reduced viscosity decreased and shifted toward a higher concentration of the polymer with an increase in temperature.

Some workers^{15–17} reported an anomalous viscosity–temperature relationship of ionomer solutions, different from that observed in the case of conventional polymer solutions. For example, Tant and Wilkes¹⁶ reported that the viscosity of a polyisobutylene telechelic ionomer solution increased with temperature. On the basis of FTIR and ESR studies of sulfonated EPDM ionomers in a xylene–alcohol blend, Eeng et al.¹⁷ reported that at the molecular level the solvation of the metallic ion with the cosolvent played a key role in influencing the viscosity–temperature behavior of ionomer solutions.

An attempt was made to analyze the absolute viscosity data of PVC solutions in cyclohexanone and in its blends with xylene as well as in tetrahydrofuran (THF) by using Moore's equation and establishing the solvent quality in terms of kinetic parameters. The apparent activation energy of the viscous flow, Q , and the preexponential factor, A , were derived by computing absolute viscosity data at different temperatures. The values of Q and A at different concentrations are used to calculate parameters like Q_0 , A_0 , KeM , and $K_\beta M^\beta$. The solvency power of cyclohexanone and cyclohexanone–xylene solvent systems for PVC was estimated and compared with the help of these parameters and also illustrated by the plots of KeM and $K_\beta M^\beta$ as function of the cohesion parameters of solvent systems.

EXPERIMENTAL

Polymer

Commercial PVC124, a product of Chemplast, Madras, used in the study was characterized by GPC using a polystyrene standard and found to have following molecular weights and polydispersity:

\bar{M}_w	\bar{M}_n	\bar{M}_z	Polydispersity
1,05,258	61,858	1,49,117	1.70

Solvents

AR-grade cyclohexanone (E. Merck India Ltd., Bombay), THF (Spectrochem Pvt. Ltd., Bombay), and distilled xylene were used.

Procedure

The flow time of dilute polymer solutions of concentrations in the range of 0.1–0.4 g/dL was measured at temperatures of 5, 10, 20, 30, 40, and 50°C by using a calibrated Ubbelohde capillary viscometer and an AVS 310 system (Schott Geräte thermostatic control) which automatically records the flow time of liquid to 0.01 of a second. In the case of PVC solutions in THF, the viscosity measurements were restricted up to 30°C because of its low boiling point. The density of individual solvents, solvent systems, and polymer solutions at temperatures mentioned above was determined by using a density meter DMA 48 (AP PAAR, Austria).

RESULTS

In all determinations, Ubbelohde capillary viscometers supplied by Schott Geräte, Germany, along with a viscosity measuring unit were used. The value of the viscometer constant engraved on each viscometer was rechecked with standard solvents of known viscosity. Hagenbach corrections were made in the efflux time according to the instructions given in the manual (supplied along with the capillary viscometer).

The absolute viscosity (at different temperatures) of solvents and polymer solutions was cal-

culated by multiplying the efflux time with the viscometer constant and density. For illustration, the viscosity data for PVC solutions at 30°C are plotted as function of concentration in Figure 1.

The values of the parameters A and Q for PVC solutions having 0.1–0.4 g/dL concentrations in different solvents and solvent systems were derived from the plots of $\ln \eta$ versus $1/T$ and are reported in Tables I and II, respectively. The values of A_0 and Q_0 for the solvents and solvent systems were also derived and reported. A set of representative plots of $\ln \eta$ versus $1/T$ for PVC solutions in the 1 : 1 cyclohexanone and xylene solvent system is presented in Figure 2.

The values of parameters A_0 and Q_0 for solvents and solvent systems were derived from the plots of A versus c and Q versus c (Figs. 3 and 4) as per the following equations suggested by Moore^{5–10}:

For flexible and stiff chains,

$$A = A_0 + K_\beta \times M^\beta \times c \tag{5}$$

where A_0 refers to the preexponential factor of pure solvent, K_β and β are constants for a given system, M is the molecular weight, and c is the concentration.

For flexible chains,

$$Q = Q_0 + Ke \times M \times c \tag{6}$$

where Q_0 is the activation energy of flow for the pure solvent, and Ke is a constant for a particular polymer–solvent system. The values of parameters KeM and $K_\beta M^\beta$ were also derived from plots in Figures 3 and 4 and are reported in Table III.

Cohesion parameters (δ_m) of the solvent systems reported in the table were calculated on the basis of single liquid approximation by Small¹⁸ and later used by Burrell¹⁹ in practical formulation:

$$\delta_m = \delta_1\phi_1 + \delta_2\phi_2 + \dots$$

Here, $\delta_1, \delta_2, \dots$ are cohesion parameters of individual solvents and ϕ_1, ϕ_2, \dots are their volume fractions.

The values of $K_\beta M^\beta$ and KeM for PVC solutions in different solvent systems are plotted as function of the cohesion parameters, δ_m , in Figures 5 and 6, respectively. The values of $(A - A_0)$ and $(Q - Q_0)$

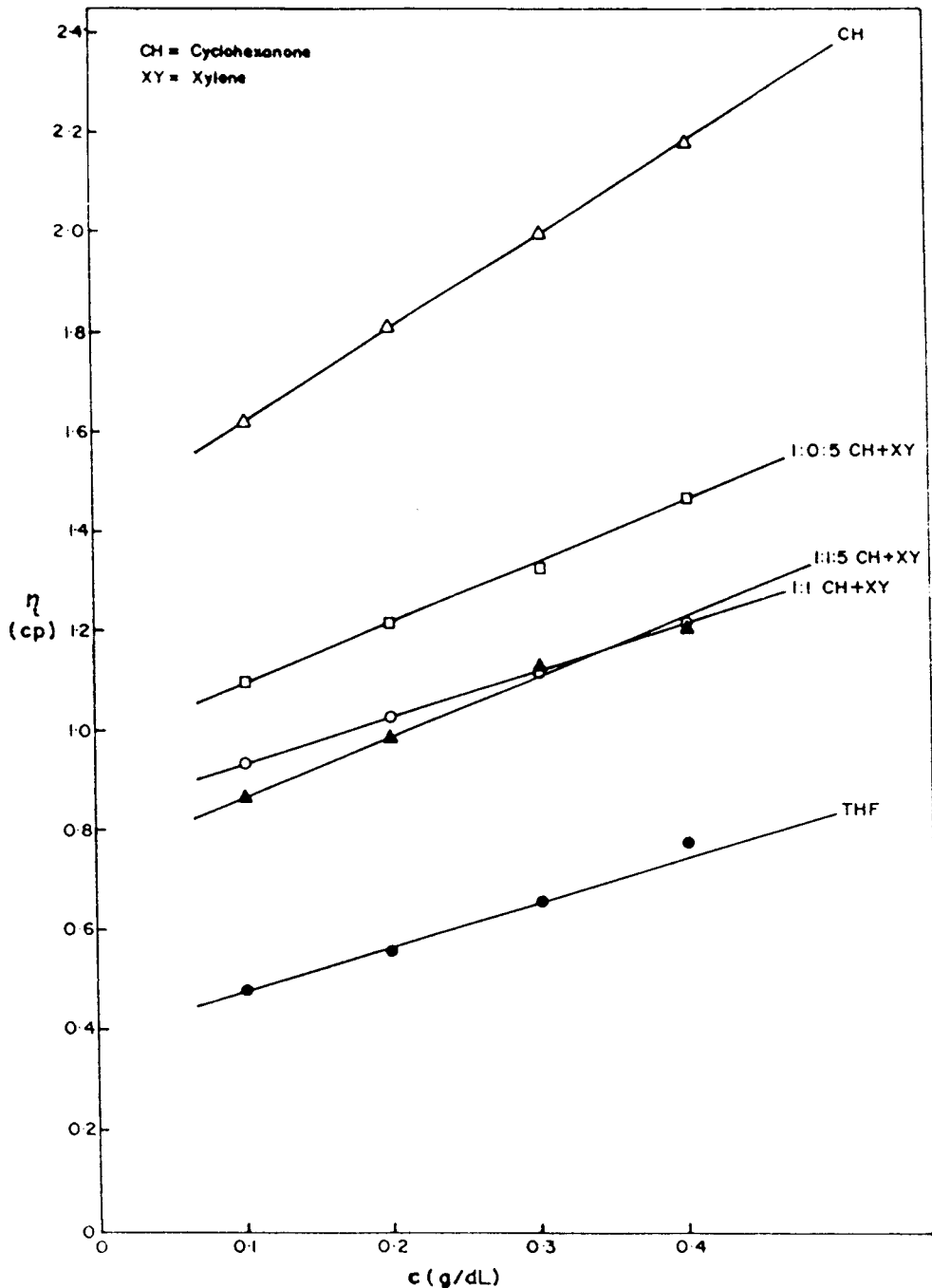


Figure 1 Absolute viscosity η versus c , concentration of PVC solution in different solvent systems at 30°C.

for PVC solutions in different solvents and solvent systems are reported in Tables IV and V.

DISCUSSION

The parameters derived by computing the data of the absolute viscosity of solvents and polymer

solutions as function of temperature are used to estimate the thermodynamic quality of solvents and solvent systems as well as the dissolution of PVC in them. The influence of polymer concentration and temperature on thermodynamic parameters (derived from the plots of viscosity data) has been interpreted.

Table I Preexponential Factor, A_0 , for Solvents and A for PVC Solutions in Different Solvents and Solvent Systems

Solvents and Solvent Systems	$A_0 \times 10^3$ (cp)	$A \times 10^3$ (cp)			
		0.1 ^a	0.2 ^a	0.3 ^a	0.4 ^a
Cyclohexanone	6.71	6.39	5.90	5.43	5.10
CH + XY (1 : 0.5)	7.63	7.15	6.75	6.34	5.82
CH + XY (1 : 1)	8.23	7.80	7.55	7.05	6.47
CH + XY (1 : 1.5)	9.19	8.13	6.80	5.62	4.32
CH + XY (1 : 2)	10.40	8.25	6.85	5.23	3.52
THF	22.00	22.60	23.40	23.80	24.20

CH, cyclohexanone; XY, xylene.

^a Concentration of PVC (g/dL).

Preexponential Factor, A

The term A , preexponential factor, is of activation entropy significance. Moore⁸ reported that the entropy of activation of the viscous flow, ΔS , of a dilute solution of a flexible chain high polymer decreased (i.e., A increased) with increasing concentration, whereas ΔS for a dilute solution of a cellulose derivative, having stiffer chains extended in solution, generally increased (i.e., A decreased) with increase of c . This has been explained with the help of two contributing factors to entropy: ΔS is for a single chain that may be written in a general form:

$$\Delta S = x - yf(M) \quad (7)$$

where x and y are constants for a given flexible chain polymer and $f(M)$ is a function of its molecular weight. The term x , which depends on the size of the segment, represents the gain in entropy

on activation of a segment and the term; $-yf(M)$ represents a loss in entropy arising from the necessity for cooperation between chain segments in order that the chain may move as a whole. In the case of a flexible chain polymer containing many segments per chain, x is likely to be small and will generally be exceeded by $yf(M)$. Consequently, ΔS for the solution decreases with an increase of c , increasing the number of chains, M , and increasing the number of chain segments.

In the case of stiff and extended cellulose derivatives, the size of the segment acting as a unit is relatively large and, therefore, the term x is likely to be greater than the factor $yf(M)$. Consequently, ΔS for such solutions is positive and increases with concentration.

The continuous decrease in the value of A (derived from the plot of $\ln \eta$ versus $1/T$) with an increase in concentration of PVC in cyclohexanone or in any one of the cyclohexanone-xylene

Table II Apparent Activation Energy, Q_0 , for Solvents and Q for PVC Solutions in Different Solvents and Solvent Systems

Solvents and Solvent Systems	Q_0 (kJ/mol)	Q (kJ/mol)			
		0.1 ^a	0.2 ^a	0.3 ^a	0.4 ^a
Cyclohexanone	13.60	14.02	14.37	14.83	15.28
CH + XY (1 : 0.5)	12.30	12.79	13.10	13.47	13.91
CH + XY (1 : 1)	11.69	12.08	12.39	12.77	13.14
CH + XY (1 : 1.5)	11.21	11.78	12.51	13.04	13.72
CH + XY (1 : 2)	10.91	11.77	12.51	13.42	14.01
THF	7.21	7.39	7.59	7.82	7.95

CH, cyclohexanone; XY, xylene.

^a Concentration of PVC (g/dL).

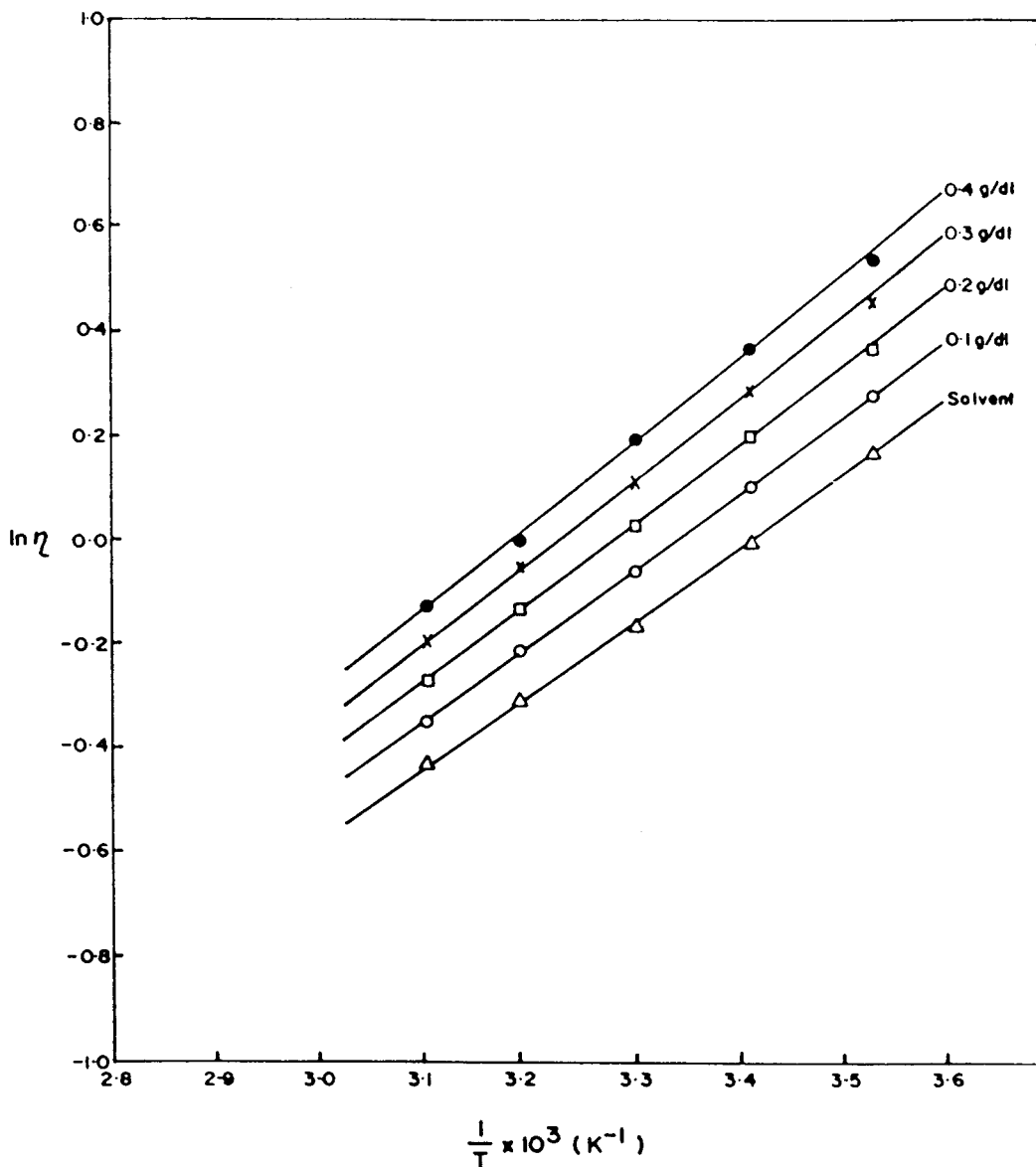


Figure 2 $\ln \eta$ versus $1/T$ plots for different concentrations of PVC in the 1 : 1 cyclohexanone and xylene blend.

systems indicates the stiffness of polymer molecules and a lesser degree of freedom at higher concentration (Table I). Primarily, the value of A decreases exponentially with the entropy of activation of the viscous flow ΔS . The high value of A indicates the good quality of the solvent system, whereas a low value of A reflects the relatively low interaction of the solvent with polymer molecules. In solutions having 0.2, 0.3, and 0.4 g/dL of PVC in solvent systems, the value of A was observed to increase to an optimum value and then to decrease with the content of xylene in the

solvent system. The optimum value of A observed in the 1 : 1 cyclohexanone and xylene solvent system indicates its better solvency power for PVC.

In a very dilute solution of PVC (0.1 g/dL), the continuous increase in values of A observed with the content of the xylene in the blend indicates the greater degree of freedom of PVC molecules. The values of A for the PVC solution in THF are also reported at the bottom of Table I. There is an increase in A values with the increase in concentration, indicating that polymer chains are flexible in THF. The other interesting feature is

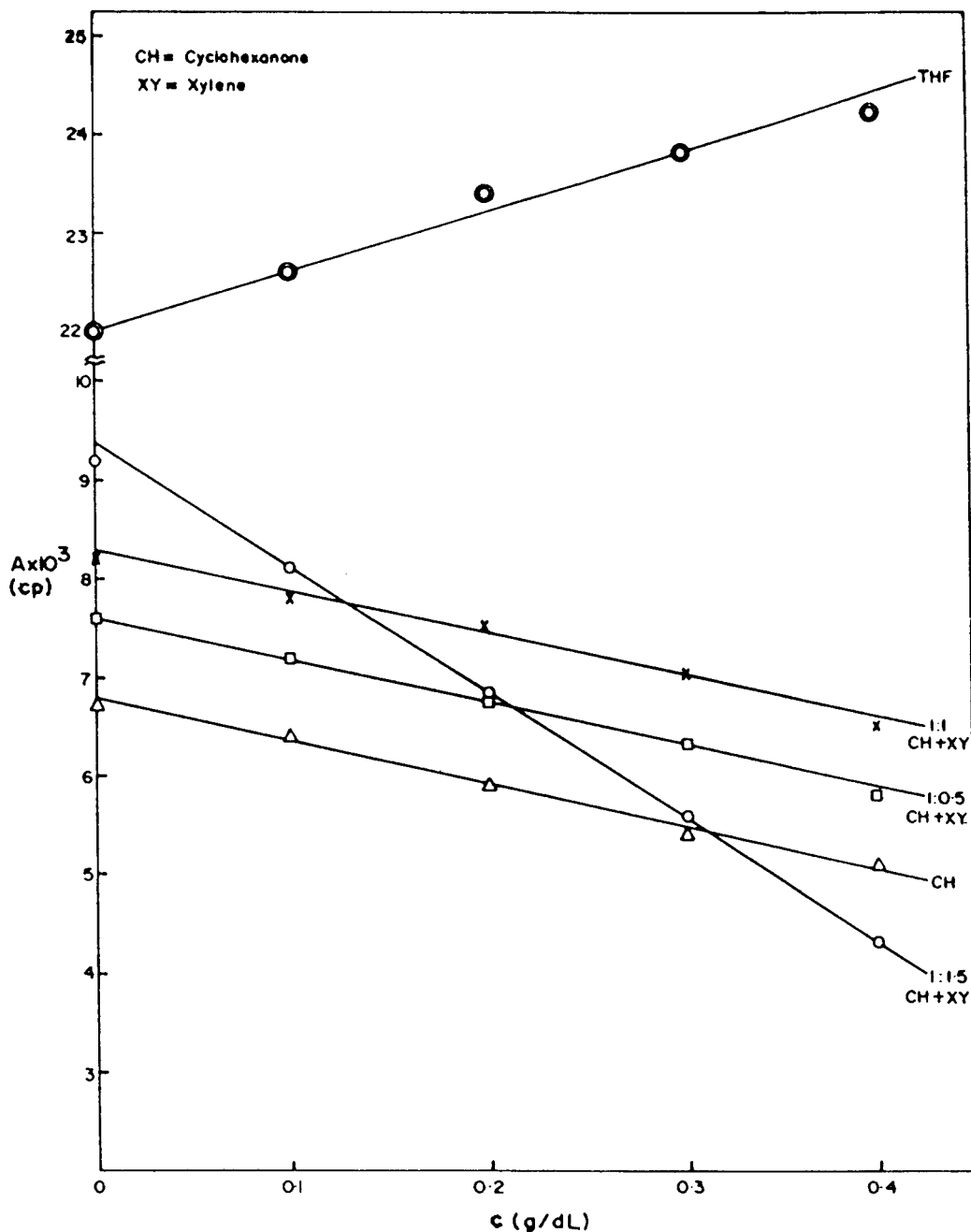


Figure 3 Preexponential factor A versus c of PVC in different solvent systems.

that the values of A for PVC solutions in THF are much higher than those in cyclohexanone and cyclohexanone-xylene solvent systems. This indicates the better solvency power of THF for PVC.

The plots of A as a function of concentration in Figure 3 are representative of the data reported in Table I. The steep downward trend of the plots for PVC solution in 1 : 1.5 and 1 : 2 cyclohexanone

and xylene blends indicates their poor solvency power for PVC. On the other hand, the plots for PVC in cyclohexanone as well as in its 1 : 0.5 and 1 : 1 combination with xylene being not so steep show their moderate solvency power for PVC. The upward trend of plot for PVC in THF indicates its good solvency power.

The value of $(A - A_0)$ is a measure of flexibility

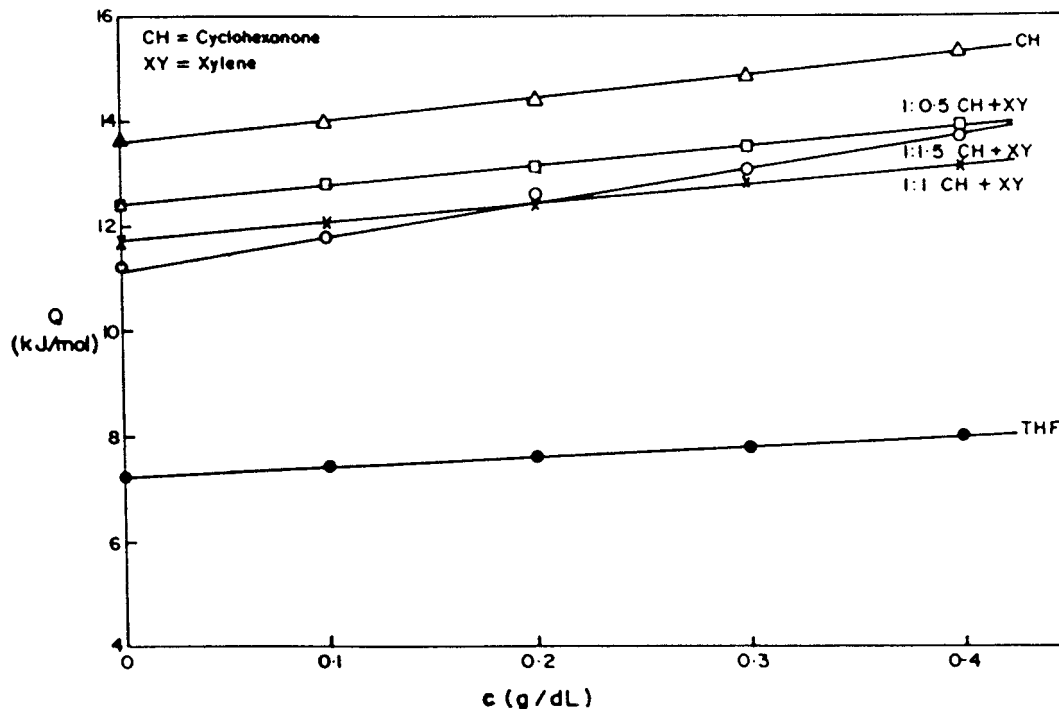


Figure 4 Apparent activation energy of viscous flow Q versus c of PVC in different solvent systems.

of polymer chains in a solution. Moore reported⁵ that the positive value of $(A - A_0)$ for cellulose nitrate with 12.2% nitrogen content indicates the flexible nature of the chains in the solution. The data reported in Table IV indicate that $(A - A_0)$ is negative for PVC solutions in cyclohexanone as well as in its blends with xylene. However, the negative value of $(A - A_0)$ for PVC in the 1 : 1 blend of cyclohexanone and xylene is of lower order. The increase in the magnitude of value of $(A$

$- A_0)$ with content of xylene above 50% in the blend indicates that PVC chains are less flexible in 1 : 1.5 and 1 : 2 blends of cyclohexanone and xylene. The positive values of $(A - A_0)$ for PVC in THF indicate the good flexibility of PVC chains in it.

Activation Energy of Viscous Flow, Q

The activation energy of viscous flow Q indicates the amount of energy required for the flow of poly-

Table III Values of Parameters A_0 , Q_0 , $K_\beta M^\beta$, and KeM for PVC in Various Solvents and Solvent Systems

Solvents and Solvent Systems	Cohesion Parameter, δ_m (J/cm^3) ^{1/2}	$A = A_0 + K_\beta \times M^\beta \times c$		$Q = Q_0 + Ke \times M \times c$	
		$A_0 \times 10^3$ (cp)	$K_\beta M^\beta \times 10^3$	Q_0 (kJ/mol)	KeM
Cyclohexanone	20.25	6.79	-4.34	13.57	4.24
CH + XY (1 : 0.5)	19.48	7.61	-4.40	12.39	3.37
CH + XY (1 : 1)	19.11	8.34	-4.49	11.71	3.56
CH + XY (1 : 1.5)	18.88	9.37	-12.61	11.18	6.35
CH + XY (1 : 2)	18.74	9.92	-15.81	11.02	7.63
THF	19.52	22.20	5.20	7.21	1.91

CH, cyclohexanone; XY, xylene.

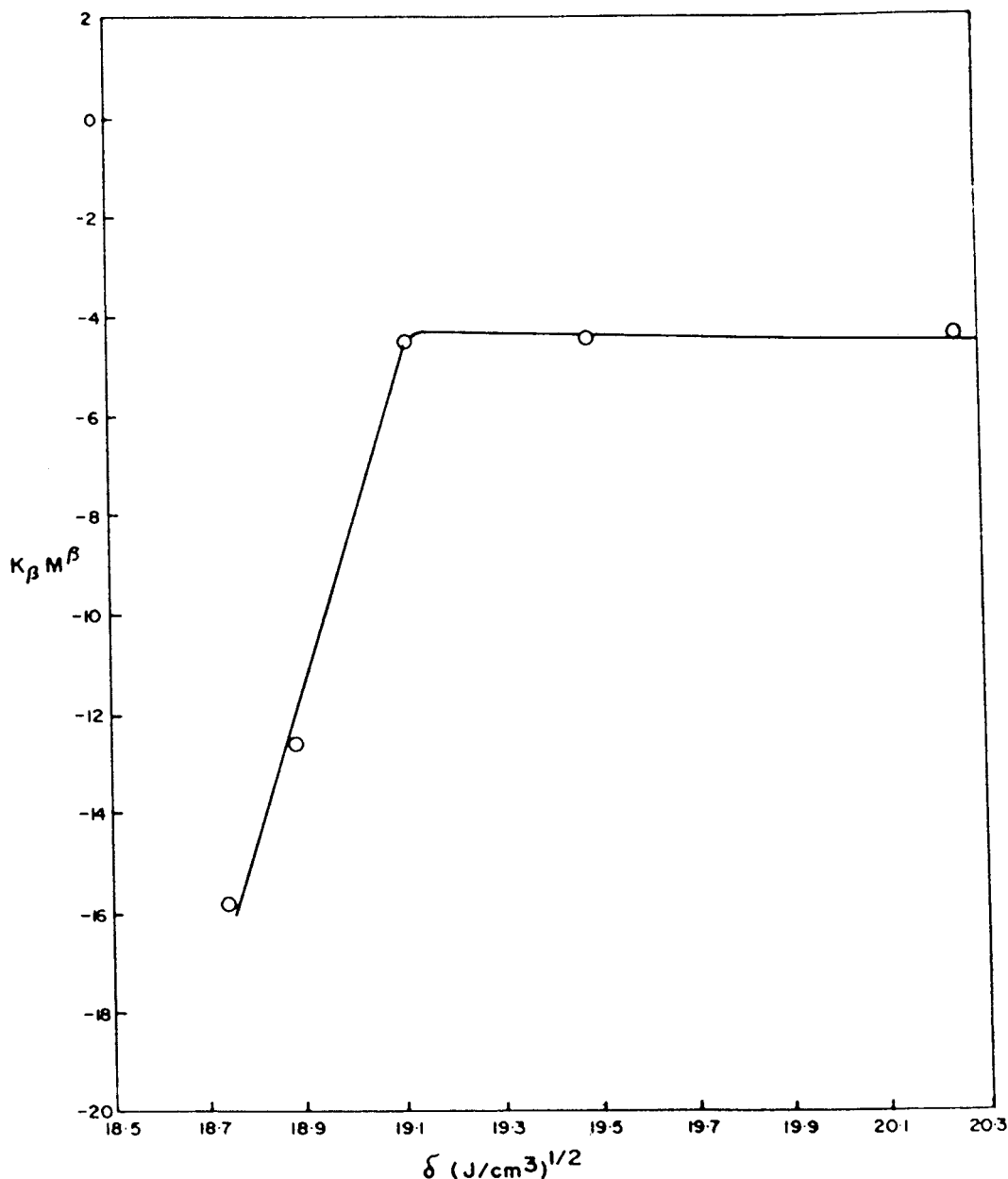


Figure 5 Plot of $K_{\beta}M^{\beta}$ versus δ_m , the cohesion parameter of solvent systems.

mer solution in a particular solvent. The quantum of Q required for viscous flow also corresponds to the compatibility of the solvent with the polymer. The lower amount of Q required indicates good interaction between solvent and polymer as well as flow property. The continuous increase in activation energy of flow of the PVC solution in a solvent system with concentration indicates that PVC molecules remain relatively coiled and have a compact configuration in solution of higher concentration.

The data reported in Table V indicate that the value of $(Q - Q_0)$ is lower for the PVC solution in the 1 : 1 cyclohexanone and xylene blend compared to in cyclohexanone alone and in its other blends with xylene. The reason for such differences may be considered in terms of differences in chain flexibility and extension. Stiff, extended chains, which are likely to overlap at the concentrations considered, might be expected to cause greater interference with flow, leading to larger values of $(Q - Q_0)$ than in the case of less ex-

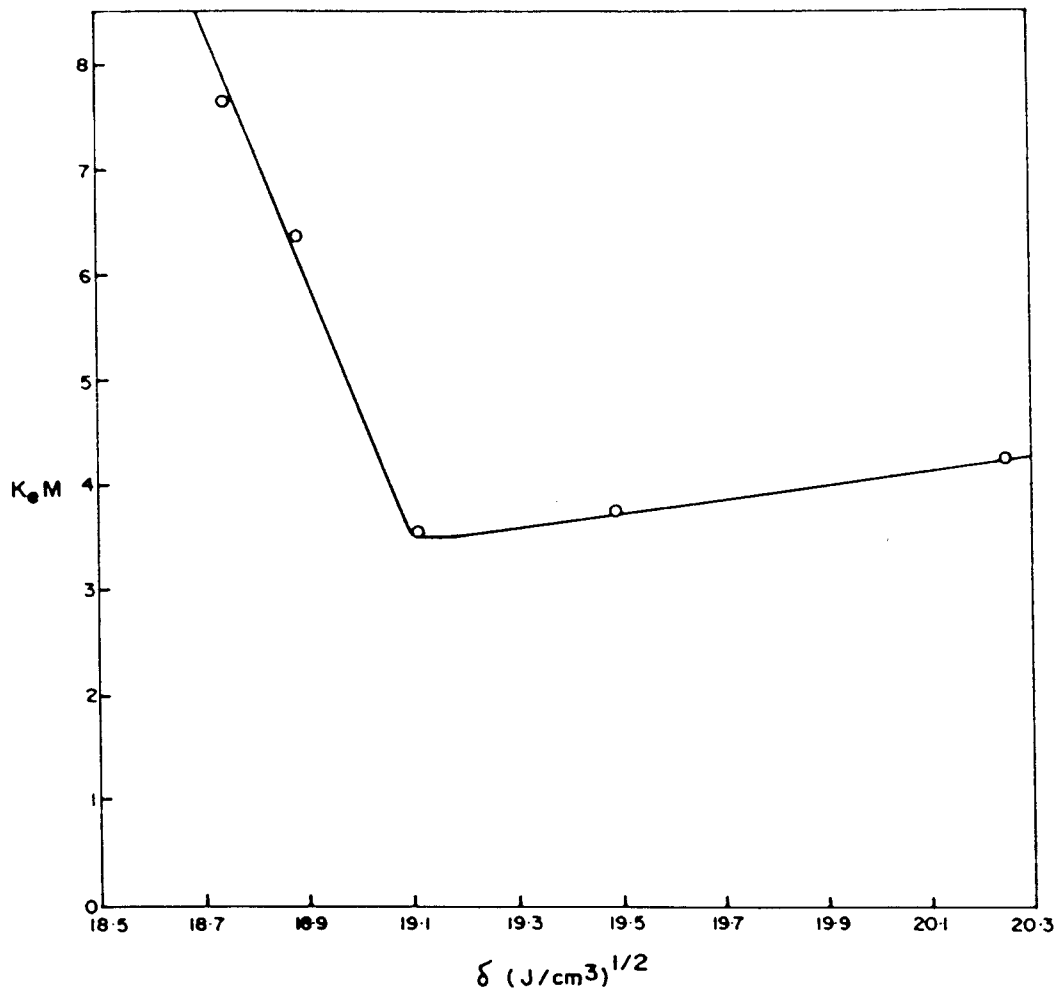


Figure 6 Plot of KeM versus δ_m , the cohesion parameter of solvent systems.

tended flexible chains.⁵ The fairly low value of $(Q - Q_0)$ for the PVC solution in THF indicates the good solvent quality of THF.

The plots of Q versus c of PVC solutions in

cyclohexanone and in its various combinations with xylene as well as in THF are linear (Fig. 4). The KeM derived from these plots is the rate of change of Q with concentration and is a measure

Table IV Values of $(A - A_0)$ for PVC in Different Solvents and Solvent Systems

Solvents and Solvent Systems	$(A - A_0)$ (cp)			
	0.1 ^a	0.2 ^a	0.3 ^a	0.4 ^a
Cyclohexanone	-0.32	-0.81	-1.28	-1.61
CH + XY (1 : 0.5)	-0.48	-0.88	-1.29	-1.81
CH + XY (1 : 1)	-0.43	-0.68	-1.18	-1.76
CH + XY (1 : 1.5)	-1.06	-2.39	-3.57	-4.87
CH + XY (1 : 2)	-2.15	-3.55	-5.17	-6.88
THF	0.60	1.40	1.80	2.20

CH, cyclohexanone; XY, xylene.

^a Concentration of PVC (g/dL).

Table V Values of $(Q - Q_0)$ for PVC in Different Solvents and Solvent Systems

Solvents and Solvent Systems	$(Q - Q_0)$ (kJ/mol)			
	0.1 ^a	0.2 ^a	0.3 ^a	0.4 ^a
Cyclohexanone	0.42	0.77	1.23	1.68
CH + XY (1 : 0.5)	0.49	0.80	1.17	1.61
CH + XY (1 : 1)	0.39	0.70	1.08	1.45
CH + XY (1 : 1.5)	0.57	1.30	1.83	2.51
CH + XY (1 : 2)	0.86	1.60	2.51	3.10
THF	0.18	0.38	0.61	0.74

CH, cyclohexanone; XY, xylene.

^a Concentration of PVC (g/dL).

of flexibility of the polymer in a solvent system. The plot of KeM versus δ_m cohesion parameters of the solvent systems passes through a minimum ($KeM_{\min} = 3.56$), indicating the optimum flexibility of PVC chains in the 1 : 1 cyclohexanone and xylene blend compared to other blends (Fig. 6).

$K_\beta M^\beta$ is the rate of change of A with concentration. The higher the negative value of $K_\beta M^\beta$, the less is the polymer-solvent interaction. The plot of $K_\beta M^\beta$ vs. δ shows an abrupt fall in solvent quality when the blend contains more than 50% xylene (Fig. 5). The value of $KeM = 1.91$ and $K_\beta M^\beta = 5.2 \times 10^{-3}$ for the PVC-THF system indicates a very good interaction of THF with PVC (Table III).

While discussing the results with the help of the Arrhenius equation, the binary solvent blends or systems were treated as a single solvent for the polymer. The interaction between a binary solvent system and a polymer is somewhat different from that of a polymer in a single solvent. The hydrodynamic properties of the polymer coil are influenced by the synergistic action of the components of the binary solvent system.

The synergistic behavior of the solvents in a binary solvent system can be considered and explained on the basis of the Dondos and Patterson²⁰ concept of the free energy of the mixing of liquids. In a binary solvent system, the polymer coil provides a number of potential interaction sites which, as such, are not available in an individual solvent. The polymer coil develops potential contact sites, which, in turn, interact with appropriate solvent molecules and the combined S_1-P and S_2-P contacts which lead to enhance the solvation of the polymer chains. It can be suggested from the observation that almost all binary solvent systems could be characterized by excess

Gibb's free energy of mixing, implying that S_1-S_2 solvent contacts are energetically unfavorable.^{21,22,23} When $G_m^E > 0$, the two solvents are relatively incompatible and S_1-P-S_2 contacts are favored. The solvency power is explained by the incompatibility between the solvents of the binary solvent system which prefer to interact with polymer molecules than with themselves. Coil expansion is likely to be optimum when the polymer-binary solvent system interactions are maximum because of the balancing action of hydrogen bonding in the polymer and solvent molecules. The dissolution of a polymer in a binary solvent system takes place as molecules of the two solvents tend to solvate the polymer at different sites along the chain and result in reinforcement of solvation.

CONCLUSIONS

The analysis of the viscosity data of dilute PVC solutions by using Moore's equations provided quantitative data to estimate the solvent quality. THF was found to be a better solvent for PVC. However, on account of the high cost of dry THF (free from water), it is not economical to use it in the preparation of PVC films by the solution-casting technique for commercial production. The presence of water in THF makes the film hazy in appearance because of the formation of microvoids by slower evaporation of water in comparison to that of THF.

PVC was also found to be soluble in cyclohexanone. With a view to improve the dissolution characteristics of cyclohexanone and to reduce the cost, the dissolution characteristics of various blends of cyclohexanone and xylene were studied.

A blend of 1 : 1 cyclohexanone and xylene was found to have better solvency power for PVC in comparison to that of cyclohexanone alone or its other blends with xylene.

One of the authors, K.G., is grateful to University Grants Commission, New Delhi, for financial support in the form of a research fellowship and to the Director of this institute for providing him facilities for research work for the Ph.D. degree.

REFERENCES

1. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953.
2. E. N. Da Costa Anrade, *Nature*, **125**, 309, 582 (1930).
3. H. Eyring, *J. Chem. Phys.*, **4**, 283 (1936).
4. W. Kauzmann and H. Eyring, *J. Am. Chem. Soc.*, **62**, 3113 (1940).
5. W. R. Moore, *Nature*, **191**, 1292 (1961).
6. W. R. Moore and M. Murphy, *J. Polym. Sci.*, **56**, 519 (1962).
7. W. R. Moore, R. J. Hutchinson, R. J. Fort, and M. Murphy, *Polymer*, **4**, 35 (1963).
8. W. R. Moore, *Nature*, **206**, 184 (1965).
9. W. R. Moore and M. A. Uddin, *Eur. Polym. J.*, **3**, 673 (1967).
10. W. R. Moore, *Physical Chemistry*, 5th ed., Prentice-Hall, Englewood Cliffs, NJ, 1981.
11. H. L. Frisch and R. Simha, in *Rheology, Theory and Applications*, F. R. Eirich, Ed., Academic Press, New York, 1956, Vol. I.
12. M. Liouni, C. Touloupis, N. Hadjichristidis, and J. W. Mays, *J. Appl. Polym. Sci.*, **37**, 2699 (1989).
13. M. Liouni, C. Touloupis, N. Hadjichristidis, and J. W. Mays, *Eur. Polym. J.*, **26**, 479 (1990).
14. N. Ahmad, A. Saeed, K. Ahad, and M. S. Khan, *J. Chem. Soc. Pakistan*, **16**(2), 91 (1994).
15. R. D. Lundberg and H. S. Makowski, *J. Polym. Sci. Polym. Phys. Ed.*, **18**, 1821 (1980).
16. M. R. Tant and G. L. Wilkes, *J. Appl. Polym. Sci.*, **37**, 2873 (1989).
17. K. Eeng, Z. Zeng, W. Ouyang, and Z. Li, *J. Appl. Polym. Sci.*, **61**, 729 (1996).
18. P. A. Small, *J. Appl. Chem.*, **3**, 71 (1953).
19. H. Burrell, *Off. Dig.*, **27**, 226 (1955).
20. A. Dondos and D. Patterson, *J. Polym. Sci. Part A-2*, **7**, 209 (1969).
21. J. M. G. Cowie and I. J. Mcewen, *Polymer*, **24**, 1449 (1983).
22. B. A. Wolf and G. Blaum, *J. Polym. Sci. Polym. Phys. Ed.*, **13**, 1115 (1975).
23. I. Fernandez-Pierola and A. Horta, *J. Chem. Phys.*, **77**, 271 (1980).