Viscosity–Temperature Relationships for Dilute Solutions of Poly(cyclohexyl Methacrylate) in Methyl Isobutyl Ketone

Usually, the temperature dependence of the absolute viscosity η can be written as

$$\eta = A \cdot e^{(Q/RT)} \tag{1}$$

where RT is the thermal energy and Q is the apparent activation energy of viscous flow which is constant over a limited temperature range. The meaning of the preexponential term A is related to an activation entropy. This expression is of the Arrhenius form and has been called the Guzman–Andrade equation, which was theoretically derived by Eyring.[1] Thus, the absolute viscosity of a liquid is given by

$$\eta = (Nh/V) \cdot e^{-\Delta S/R} \cdot e^{Q/RT} \tag{2}$$

where N and h are, respectively, the Avogadro number and the Planck's constant, V is the molar volume of the liquid, and S is the entropy of activation of viscous flow.
From eqs. (1) and (2) we obtain

$$A = (Nh/V) \cdot e^{-\Delta S/R} \tag{3}$$

Measurements of absolute viscosities of dilute polymer solutions and their thermal variation are often employed as a way to characterize properties of macromolecules in solution.[1,2]
Moore et al.[4-6] have related the A and Q parameters of the Guzman–Andrade equation to the polymer flexibility and thermodynamic properties of polymer–solvent systems.
In this article, we have used eq. (1) to study the behavior of the poly(cyclohexyl methacrylate) (PCHM) in methyl isobutyl ketone on the temperature range 283–313 K.

EXPERIMENTAL

Cyclohexyl methacrylate (Fluka purum) was washed three times with sodium hydroxide followed by distilled water; it was dried over anhydrous Na_2SO_4 and distilled (<25 mm Hg) in pure dried nitrogen.
A sample of poly(cyclohexyl methacrylate) was obtained by radical polymerization using 1,2-azobisisobutyronitrile (Fluka puriss) as initiator in benzene, at 328 K. The polymer obtained was fractionated by solubility in the system p-dioxane/methanol. All fractions were purified by dissolving in benzene and reprecipitation with methanol. They were freeze-dried.
All solvents were analytical grade from Fluka.
Number average molecular weights $\overline{M}_n$ and weight average molecular weights $\overline{M}_w$ were determined by membrane osmometry and laser light scattering, respectively. In Table I, it can be seen the molecular weights and polydispersity index of the five fractions employed in this work.
Viscosities of both pure solvent and polymer solutions were measured, at several temperatures (283–313 K), by means of an modified Ubbelohde viscometer. The kinetic energy corrections were less than 0.2%. The bath temperature was regulated to ±0.02 K. Intrinsic viscosities were obtained by graphical extrapolation of both η_{sp}/c and $\ln \eta_r/c$ to zero concentration of polymer.

TABLE I
Molecular Weights and Polydispersity Index of Fractions of Poly(cyclohexyl Methacrylate)

Fraction	$M_n \times 10^{-5}$	$M_w \times 10^{-5}$	M_w/M_n
1A	3.29	3.95	1.20
2A	2.86	3.46	1.21
3A	1.47	1.75	1.19
4A	1.10	1.30	1.18
5A	0.73	0.85	1.16

RESULTS AND DISCUSSION

In eq. (1) both magnitudes A and Q depend on the solvent, on the concentration, and on molecular weight of the polymer, which makes necessary to use fractions with not too high polydispersity. For concentrations less than 1% we can write

$$Q = Q_0 + K_e Mc \qquad (4)$$

$$\ln(A/A_0) = K_\beta M^\beta c \qquad (5)$$

where K_e, K_β and β depend on the polymer–solvent system, and Q_0 and A_0 are characteristic magnitudes of the solvent.

Figure 1 shows an example of the ln η variation vs. $1/T$, at various concentrations, for a fraction of $\overline{M}_w = 395,000$ and, at constant concentration (0.3 g dL^{-1}), for different molecular weights. As can be observed in all cases, the plots are linear between 283 and 313 K.

From the slopes of ln η vs. $1/T$ plots we can calculate the apparent activation energy of viscous flow, Q. In Figure 2, we have plotted the Q values as a function of M_c. As it can be seen, this parameter is constant on the whole range of concentrations and molecular weights studied. Its value is equal to that of the pure solvent, $Q_0 = 9.16$ kJ mol^{-1}. This means that the K_e constant is practically equal to zero, which indicates that methyl isobutyl ketone behaves as an athermal solvent for poly(cyclohexyl methacrylate).

On the other hand, according to Moore[7] and Niezette et al.,[8] if K_e values are ranged between 10^{-4} and 10^{-3}, it means that the polymer is flexible, while if they become greater than 10^{-2}, there is an increase in the rigidity of the macromolecular chain. In our case, the K_e value obtained for poly(cyclohexyl methacrylate) is zero, which indicates that poly(cyclohexyl meth-
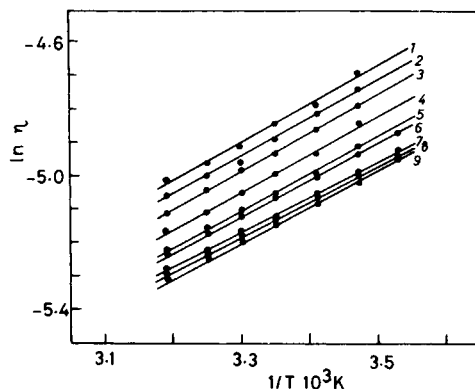

Fig. 1. ln η vs. $1/T$ for PCHM in methyl isobutyl ketone: (1) $M_w = 395,000$, $c = 0.7$ g dL^{-1}; (2) $M_w = 395,000$, $c = 0.6$ g dL^{-1}; (3) $M_w = 395,000$, $c = 0.5$ g dL^{-1}; (4) $M_w = 395,000$, $c = 0.4$ g dL^{-1}; (5) $M_w = 395,000$, $c = 0.3$ g · dL^{-1}; (6) $M_w = 346,000$, $c = 0.3$ g dL^{-1}; (7) $M_w = 175,000$, $c = 0.3$ g · dL^{-1}; (8) $M_w = 130,000$, $c = 0.3$ g dL^{-1}; (9) $M_w = 85,000$, $c = 0.3$ g dL^{-1}.
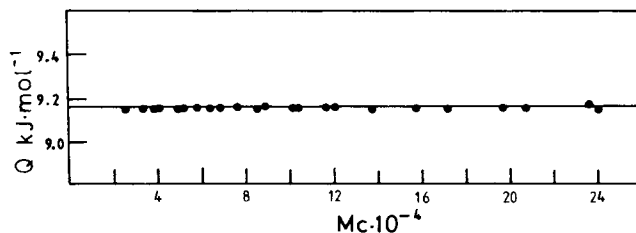
Fig. 2. Apparent activation energy of viscous flow Q against M_c for PCHM solutions in methyl isobutyl ketone.

acrylate) behaves as a flexible polymer in methyl isobutyl ketone. Some values of K_e for different polymers are given in Table II.

Another important magnitude of structural interest is the constant K_β. Its value can be calculated by ploting ln A in function of the concentration (Fig. 3). In this way, $K_\beta M^\beta$ is obtained from the slope and A_0 from the intercept. For our system we have obtained $A_0 = 1.36 \times 10^{-4}$ cP, value in accordance with the one theoretically calculated, taking into account the physical constants of the solvent. Both K_β and β constants are determined, respectively, from the intercept and the slope of the plot of ln K M vs. ln M. The values obtained are $K_\beta = 12.78 \times 10^{-5}$ dL g^{-1} and $\beta = 0.66$. These values agree with the ones obtained by Niezette et al.[8] for poly(β-naptyl methacrylate) and by Moore et al.[4] for other flexible polymers.

By using eqs. (1), (4), and (5), an expression of the intrinsic viscosity, $[\eta]$, as a function of temperature has been proposed by Moore et al.,

$$[\eta] = K_e M/RT + K_\beta M^\beta \tag{6}$$

Since in our system $K_e = 0$, we can write

$$[\eta] = K_\beta M^\beta \tag{7}$$

That is, in an athermal solvent the intrinsic viscosity does not depend on the temperature. In Figure 4 we have plotted $[\eta]$ against $1/T$ for two fractions of poly(cyclohexyl methacrylate). As can be seen, except in the temperature range (283–298 K) the intrinsic viscosity is constant when the temperature increases. The anomalous behavior observed in this interval of tem-

TABLE II
Values of K_e Parameter for Several Polymers

| Polymer	K_e(cal dL g^{-1} mol^{-1})
Poly(cyclohexyl methacrylate)[a]	0 (methyl isobutyl ketone)
Poly(β-naphtyl methacrylate)[8]	0 (p-dioxane)
	-5.0×10^{-4} benzene)
	-1.0×10^{-3} (toluene)
Poly(isobutylene)[4]	7.8×10^{-4} (cyclohexane)
Polyvinyl formol[6]	2.3×10^{-3} (chloroform)
Cellulose trinitrate[9]	2.8×10^{-2} (acetone)
Ethyl cellulose[9]	3.2×10^{-2} (MEK)
	3.2×10^{-2} (nitroethane)
	3.3×10^{-2} (benzene)
	3.1×10^{-2} (ethyl acetate)
	3.2×10^{-2} (butyl acetate)
	2.9×10^{-2} (chloroform)
Polyvinyl acetate[4]	2.0×10^{-3} (chloroform)
Polybutadiene[10]	1.3×10^{-3} (toluene)
	0 (decaline)
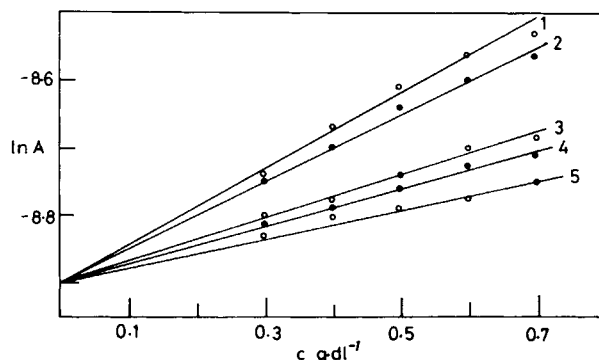
Fig. 3.   ln A as a function of concentration. M_w: (1) 395,000; (2) 346,000; (3) 175,000; (4) 130,000; (5) 85,000.

perature can be explained, bearing in mind that poly(cyclohexyl methacrylate) undergoes a conformational transition, such as has been shown by Katime et al.[11]

As we have already seen above, the activation energy of viscous flow, Q, in this system is equal to that of the solvent. Likewise, in this system, the intrinsic viscosity does not depend on the temperature, except in the temperature interval lies between 283 and 298 K. Therefore, it seems clear that the differences in the activation energy of viscous flow between solvent and solutions are related to dependence of coil expansion coefficient on temperature. In effect, from eqs. (4)–(6) and taking into account that the linear expansion coefficients, α_η^3, are obtained from the Fox–Flory equation[12]

$$[\eta] = K_\theta M^{\frac{1}{2}}\alpha_\eta^3 \tag{8}$$

we can write

$$[\eta] = \Delta Q/cRT + \ln(A/A_0)/c = K_\theta M^{\frac{1}{2}}\alpha_\eta^3 \tag{9}$$

Assuming that the K_θ parameter, which characterizes the unperturbed dimensions of the polymer, is constant, we can derive with respect to $1/T$

$$\Delta Q/Rc = -|\eta|(d \ln \alpha_\eta^3/dT)T^2 \tag{10}$$

In this equation we can observe the relationship which exists between the variation of the apparent activation energy of viscous flow and the expansion of the polymer coil with temperature.

In this way, it should be possible to detect by means of variation in Q the conformational transition observed for poly(cyclohexyl methacrylate) in methyl isobutyl ketone between 283
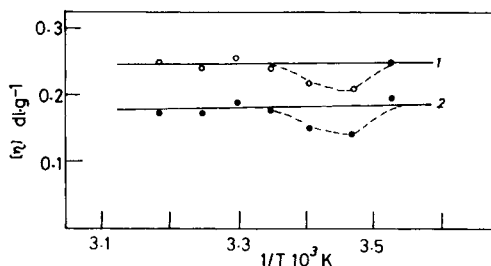

Fig. 4.   Plots of $|\eta|$ against $1/T$: (1) $M_w = 130,000$; (2) $M_w = 85,000$.

and 298 K (Fig. 4, Ref. 11). However, in Figure 1 we can see that the slopes of $\ln \eta$ vs. $1/T$, and therefore Q, do not undergo any sharp variation. Consequently, Q is not a convenient parameter to detect conformational transitions in synthetic polymers perhaps due to the fact the accuracy in the viscosity data has to be very high to find sharp variation in the $\ln \eta$ vs. $1/T$ curves (Fig. 1). On the other hand, the decrease in intrinsic viscosity observed in the transition interval may be compensated by the increase of the linear expansion coefficient, α_η^3, in this same range.[13]

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I. KATIME
J. R. OCHOA

Grupo de Propiedades Termodinámicas
   de Macromoléculas en Disolución
Departamento de Química Física
Facultad de Ciencias
Universidad del País Vasco
Apartado 644, Bilbao, Spain