polymer reports

Intrinsic viscosity–temperature relationships

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INTRODUCTION

During studies on the intrinsic viscosity–temperature relationship for poly(methyl methacrylate) in acetone, Kawai *et al.*[1] found that the intrinsic viscosities [η] of several fractions of different molecular weights exhibited a maximum at about 30°C. Since similar intrinsic viscosity–temperature behaviour was observed for polyethylenes in xylene[2], Kawai and Ueyama tried to interpret this phenomenon and derived an equation which gives the condition for the existence of the temperature T_m at which the [η] vs. temperature curve exhibits a maximum. They concluded that such behaviour is in no way specific to poly(methyl methacrylate) in acetone but should be observed generally for polymer solutions when intrinsic viscositites are measured over sufficiently wide ranges of temperature.

Kawai's treatment leads to the existence of a characteristic temperature T_m for a given polymer–solvent combination as for the θ-temperature[3]. However, the polymer molecules take on the most expanded conformation at this temperature, whereas they take on the most compact conformation at the θ-temperature.

Whereas the θ-temperature depends only on thermodynamic properties of the solution, T_m is also affected by the chain flexibility. The measurement of T_m thus provides a method for determining a parameter which gives a measure of the chain flexibility. In this report we present data on the viscometric behaviour of two systems: poly(4-tert-butylcyclohexyl methacrylate) (PBCy) in cyclohexane and poly(pentachlorophenyl methacrylate) (PPClPh) in *o*-dichlorobenzene. In both systems we have found similar viscosity–temperature behaviour, namely maxima in curves [η] vs. temperature.

EXPERIMENTAL

The polymer fractions used here have been described previously[4-6].

RESULTS AND DISCUSSION

Figure 1 shows the dependence of ln [η] on temperature for four fractions of poly(4-tert-butylcyclohexyl methacrylate) in cyclohexane. A change of dln[η]/dT is observed at $T \sim 25$°C.

In *Figure 2* we can see the dependence of ln [η] on temperature for three fractions of poly(pentachlorophenyl methacrylate) in *o*-dichlorobenzene. A maximum in the curve is observed at $T \sim 30$°C as reported previously[6].

In *Table 1* we summarize the molecular characteristics of the fractions of the two polymers and the range of the temperatures studied.

The maxima in the temperature behaviour can be analysed in the light of the interpretation of the Kawai temperature, T_m, as poly(methyl methacrylate) in acetone and polyethylenes in xylene.

We have applied the Kawai treatment, which can be summarized in the following equations which show that the effect of temperature on [η] depends on the temperature coefficient of K and α, where K and α are as defined by Flory–Fox equations[7].

Kawai obtained an approximate solution for the dependence of K_θ and α on temperature. The following equation describes this situation:

$$[\eta] = J(1 - bT)M^{1/2}[(20/27) + (c + A/9)^{1/2}]^3 \qquad (1)$$

where J and b are constants characteristic of the particular polymer chain, $c = 0.02276$ and $A = A^*(1 - bT)^{-1} \times (1 - \theta/T)$. The expression for A^* is: $A^* = 2C_M{}^* M^{1/2}\varphi$ and

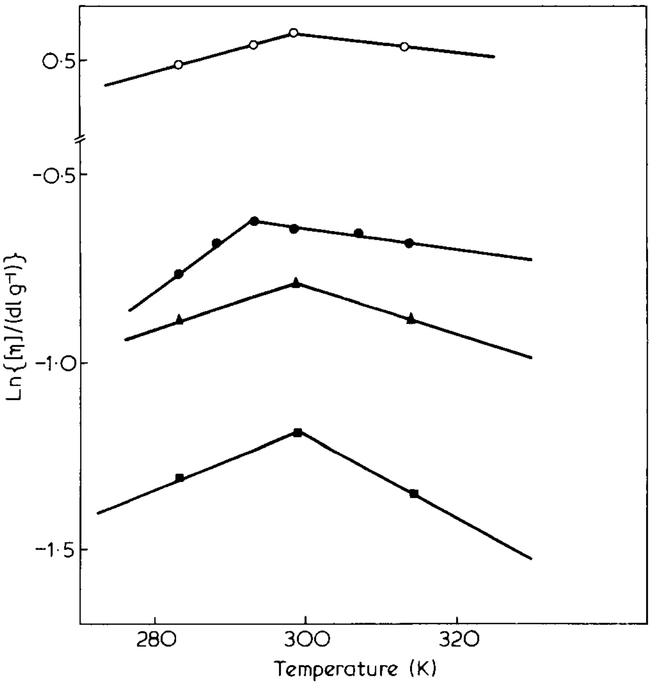

Figure 1 Plot of ln [η] *versus* temperature for four fractions of poly(4-tert-butylcyclohexyl methacrylate) in cyclohexane. ○, Fraction F-1; ●, F-6; ▲, F-8; ■, F-10

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Table 1 Molecular characteristics of the fractions of the two polymers and the range of temperature studied

Polymer	Solvent	Temperature range	$\bar{M} \times 10^{-5}$
PBCy	Cyclohexane	25°–40°C	$\bar{M}_w \times 10^{-5}$
F_1			19.30
F_6			6.00
F_8			2.90
F_{10}			1.50
PPClPh	*o*-Dichlorobenzene	8°–50°C	$\bar{M}_n \times 10^{-5}$
F_A			2.39
F_B			1.44
F_C			0.16

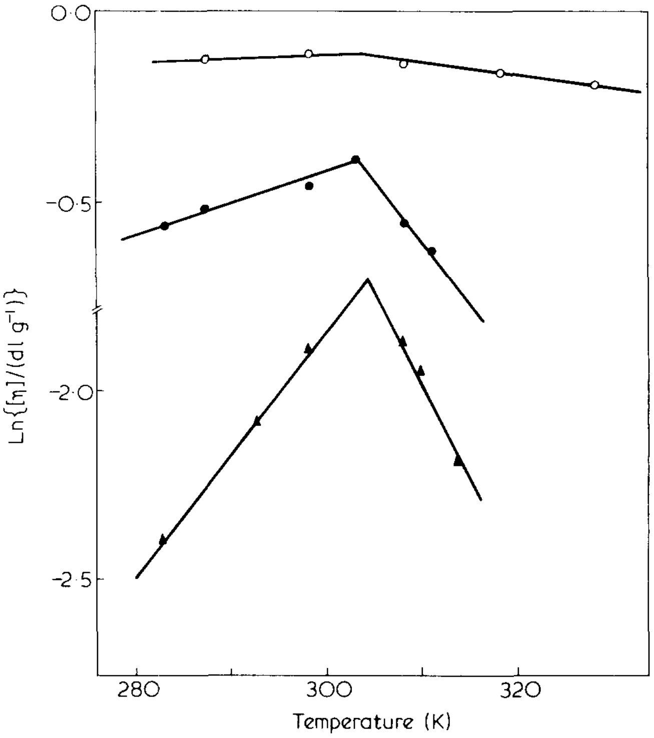

Figure 2 Plot of ln [η] *versus* temperature for three fractions of poly(pentachlorophenyl methacrylate) in *o*-dichlorobenzene. ○, Fraction A; ●, fraction B; ▲, fraction C

the asterisk denotes the value extrapolated to $T = 0$K.

Taking into account that the condition which gives T_m as a maximum in the [η] vs. T curves is $d[\eta]/dT = 0$ and neglecting c, the following relationship can be deduced from equation (1):

$$(1-\theta/T_m)^{2/3}/(\theta/T_m) = (27/20)(A^*/9)^{1/3}(1-bT_m)^{2/3}/bT_m \tag{2}$$

Since T_m is also affected by the chain flexibility, its measurement will provide a method for determining the constant b, which gives a measure of the chain flexibility.

In the special case when $(27/20)(A^*/9)^{1/3} = 1$, equation (2) becomes, according to Kawai:

$$T_m^{\,2} = \theta/b \tag{3}$$

We have estimated b using equation (3) by measuring T_m.

In *Table 2* we summarize the b values, Mark-Houwink exponent a, θ and T_m temperature for different polymer–solvent systems. The b values for poly(4-tert-butylcyclohexyl methacrylate) and poly(pentachlorophenyl methacrylate) seem a little low to be consistent with the information on their molecular flexibility[4,5], in view of the magnitude of b obtained for poly(methyl methacrylate).

Table 2 Mark–Houwink exponent a, and b values, θ and T_m for different polymer–solvent systems

System					
Polymer	Solvent	a	θ (K)	b	T_m (K)
PMMe	Acetone	0.70[7]	147	0.00177	303
PS	Benzene	0.74[8]	100	0.00125	283
PS	Cyclohexane	0.50[8]	307	0.00125	496
PS	Dichloroethane	0.66[9]	190	0.00125	390
PBCy	Cyclohexane	0.75[4]	142	0.00160	298
PBCy	n-Butanol	0.50[4]	313	0.00160	442
PPClPh	*o*-Dichlorobenzene	0.67[5]	147	0.00160	303
PPClPh	Ethyl benzene	0.50[5]	298	0.00160	432

However, it is necessary to consider that since the thermodynamic properties of poly(4-tert-butylcyclohexyl methacrylate)–cyclohexane and poly(pentachlorophenyl methacrylate)–*o*-dichlorobenzene are not known, we could not estimate the θ-temperature. Nevertheless since the solvent in the systems analysed is chemically similar to the monomeric unit we have compared the Mark–Houwink exponent a in order to estimate the solvent power. This is shown in *Table 2*, column 3. In addition, we give the θ temperatures in other solvents. From experiment we could give approximate T_m values knowing the θ-temperatures or θ values when measuring T_m. Knowing T_m and θ and with the assumption that equation (3) applies, we have estimated b. The value derived for b should be taken only as orientative, owing to the limitations of the calculations. However, $b = 0.0160$ is a reasonable value compared with the value estimated for poly(methyl methacrylate) in acetone by Kawai and Ueyama.

In conclusion, the particular viscometric behaviour of two polymers is one demonstration that this behaviour with maxima in [η] vs. temperature curves should be observed generally for polymer solutions, and may be considered a general phenomenon.

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