Dilute solution properties of poly(benzyl methacrylate)

R. W. Richards*

Deutsches Kunststoff Institut, Schlossgartenstrasse 6R D-6100, Darmstadt, West Germany

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A series of fractions of poly(benzyl methacrylate) have been prepared with weight-average molecular weights ranging from 0.19 x 10^6 to 1.74 x 10^6 g/mol. A theta temperature of 73.2°C was obtained from phase separation studies in cyclopentanol. Intrinsic viscosities have been measured in toluene and methyl ethyl ketone over a range of temperatures, as well as under theta conditions. Unperturbed dimensions and their temperature coefficient have been determined by a number of procedures. A value for the polymer solubility parameter has been calculated from the enthalpy parameter obtained from phase separation data.

INTRODUCTION

The unperturbed dimensions (*UD*) of a polymer chain and the temperature coefficient of the *UD* are of importance when comparing properties predicted by statistical mechanical theory with experimentally observed values[1–3]. A series of recent publications[4–6] has been concerned with the solution properties of methacrylates and has demonstrated the 'stiffening' effect on the *UD* of aromatic groups in the ester side chain. The present communication reports values of the *UD* and its temperature coefficient for poly (benzyl methacrylate) (PBMA), which also has an aromatic group in the ester side chain.

EXPERIMENTAL

Poly(benzyl methacrylate)

Benzyl methacrylate was prepared by esterification of methacrylic acid with benzyl alcohol. The crude product was neutralized, washed with water and dried over calcium chloride before being distilled from copper powder under a nitrogen atmosphere of reduced pressure (b.p. 85°C at 1.7 mmHg). Bulk polymerization was initiated at 60°C by azobisisobutyronitrile (0.15 mol %) immediately after redistilling the monomer once more. After 1 h the reaction was terminated, at which time the conversion was 12% by wt, the mixture was diluted with chloroform and the polymer precipitated by pouring into methanol. The polymer was redissolved and reprecipitated before drying under vacuum at 50°C.

Solvents

Methyl ethyl ketone (MEK), methanol and cyclopentanol were dried over anhydrous magnesium sulphate and distilled (b.p. 77°, 64.7° and 141°C respectively). Toluene was purified by the method described by Vogel[7] before being dried and distilled (b.p. 110.7°C).

Fractionation of PBMA

A dilute solution (1% w/v) of PBMA in MEK, containing 0.1% 2,6-di-t-butyl-*p*-cresol as antioxidant, was placed in a 4 l flask in a thermostat at 20°C. After equilibration, methanol was added until the solution became permanently turbid, the temperature was then raised to 35°C and maintained there until the solution became clear. The temperature was then slowly lowered to 20°C, stirring stopped and the polymer rich phase allowed to settle. After settling overnight the clear supernatant was rapidly decanted off and the precipitate redissolved in MEK and reprecipitated by dropwise addition of the solution to methanol. Nine fractions were obtained in this manner of which eight were used for measurements. All fractions were dried at 50°C under vacuum.

Molecular weights

Number-average measurements, $\bar{M}_n$, were obtained from osmotic pressure measurements using a Knauer dynamic membrane osmometer. Measurements were made in toluene at 30°C and results were interpreted by the procedure of Berglund–Larsson[8]. Weight-average molecular weights, $\bar{M}_w$, were obtained from light scattering measurements using a SOFICA photometer. The photometer was calibrated with toluene, a value of 49.3 x 10^{-6} cm^{-1} being used for R_{90} which was calculated from the theoretical Einstein–Cabannes equation[9]. Measurements were made at 25°C using a light wavelength of 435.8 x 10^{-7} cm and before use solutions, solvent and calibrant were filtered through Gelman membrane filters. The specific refractive index increment (ν) for PBMA in MEK was measured under the same conditions as for light scattering using a Shimadzu differential refractometer. Values of ν were measured for PBMA in a series of solvents, the dependence on refractive index ($\tilde{n}_0$) being described by the Gladstone–Dale equation below[10]:

$$\nu = 1.459 - 0.918\tilde{n}_0$$

Partial specific volumes

Specific volumes of PBMA in MEK, toluene and cyclo-

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* Present address: Department of Chemical Engineering and Chemical Technology, Imperial College, Prince Consort Road, London SW7 2BY, UK.

hexanone were measured using a Kratky[11] digital densitometer (Model DMS 10, A. Paar KG, Graz, Austria), capable of an accuracy of ±2.5 x 10^{-4} ml/g. For each solvent, measurements were made on five solutions with polymer weight fractions between 0.01 and 0.06 at temperatures of 25°, 35° and 45°C. Results were interpreted via equation (1):

$$V = (\bar{v}_2 - v_0)W_2 + v_0 \qquad (1)$$

where V and v_0 are the specific volumes of the solution and solvent, respectively, $\bar{v}_2$ is the polymer partial specific volume and W_2 the weight fraction of polymer in the solution. In fact, equation (1) yields an apparent partial specific volume, however, the difference between this and the true value is negligible[12].

Phase separation (upper critical solution temperatures)

Upper critical solution temperatures were determined for four PBMA fractions in cyclopentanol. Initial solutions (containing 0.1% antioxidant) were prepared with PBMA concentrations approximately twice the critical volume fraction[13]. Critical solution temperatures were noted on both heating and cooling the solutions (at ~1°C/min), the difference between the two determinations for a particular PBMA concentration was never greater than 0.2°C. The solutions were diluted by adding a known volume of cyclopentanol.

Viscometry

Intrinsic viscosities were obtained by Huggins equation interpretations of measurements made in an Ubbelohde suspended level viscometer. End effect and kinetic energy corrections were negligible, additionally, shear effects were absent from all measurements. Intrinsic viscosities were measured in MEK at 15°, 25°, 35° and 50°C, in toluene at 25°, 40°, 55° and 70°C and in cyclopentanol under θ-conditions (73.2°C). All solutions contained 0.1% antioxidant and due notice was taken of the appropriate temperature corrections in calculating the polymer concentration.

RESULTS

Molecular weights

Values of $\bar{M}_n$ and $\bar{M}_w$ are given in *Table 1*, also included are second virial coefficients (A_2) and mean square end-to-end distances ($\langle r^2 \rangle_w$) obtained from Zimm plots. End-to-end distances were obtained from the z-average mean square radius of gyration after suitable heterogeneity correction[14]:

$$\langle r^2 \rangle_w = 6[\langle s^2 \rangle_z \, (h+1)/(h+2)]$$

Table 1 Molecular weights, second virial coefficients and end-to-end distances for poly(benzyl methacrylate)

$\bar{M}_n \times 10^{-6}$ (g/mol)	$\bar{M}_w \times 10^{-6}$ (g/mol)	$A_2 \times 10^4$ (cm^3 mol/g^2)	$\langle r^2 \rangle_w \times 10^{11}$ (cm^2)
–	1.74	0.89	16.62
–	1.35	1.24	11.76
0.84	1.08	1.26	8.58
0.65	0.81	1.39	6.00
0.39	0.57	1.39	4.78
0.30	0.43	1.23	2.94
0.26	0.36	1.40	2.46
0.11	0.19	1.54	1.20

where

$$h = [(\bar{M}_w/\bar{M}_n) - 1]^{-1}$$

$\bar{M}_n$ values could not be obtained for the two fractions of highest $\bar{M}_w$, the osmotic heights recorded were too small to be reliable. In calculating $\langle r^2 \rangle_w$ for these fractions, the mean value of h has been used i.e. 2.67. The relationship between A_2 and $\bar{M}_w$ is generally expressed by an equation of the form:

$$A_2 \propto \bar{M}_w^{-\gamma} \qquad (2)$$

Values of 0.15[14] and 0.25[15] have been theoretically derived for γ. Lines of each slope have been drawn through the present data (*Figure 1*), but the scatter in the values of A_2 is so great as to prevent justifiable discrimination between the two exponents.

No such difficulty is encountered in a similar plot (not shown here) for the dependence of $\langle r^2 \rangle_w$ on $\bar{M}_w$, which is described by the equation:

$$\langle r^2 \rangle_w \propto \bar{M}_w^{\,1.145} \qquad (3)$$

The exponent of this equation is related to the solvent power (*vide infra*).

Partial specific volumes

In accordance with equation (1), the experimental data gave straight line plots at all temperatures for all three solvents. The following relationships between $\bar{v}_2$ (ml/g) and temperature (T°C) were obtained:

MEK	$\bar{v}_2 = 0.840 + (T - 25)1.35 \times 10^{-3}$
Toluene	$\bar{v}_2 = 0.797 + (T - 25)4.45 \times 10^{-3}$
Cyclohexanone	$\bar{v}_2 = 0.760 + (T - 25)3.35 \times 10^{-3}$

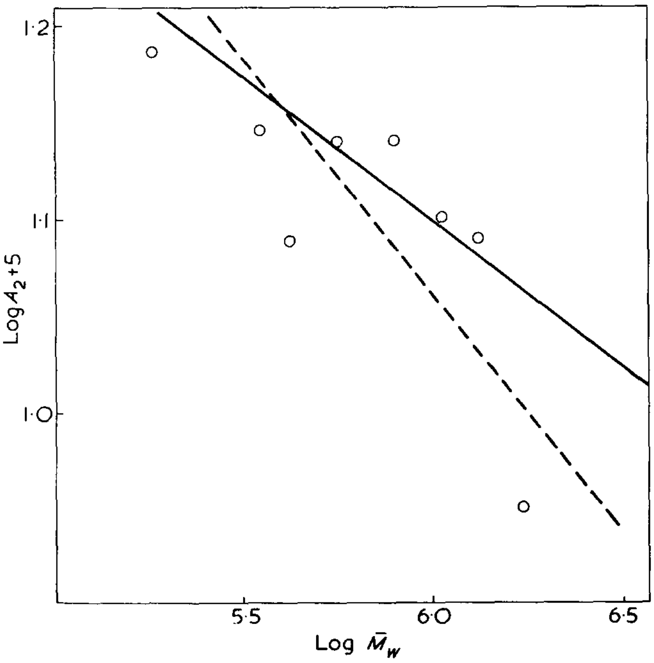

Figure 1 Dependence of A_2 on molecular weight. Experimental values: ——, γ = 0.15; – – –, γ = 0.25

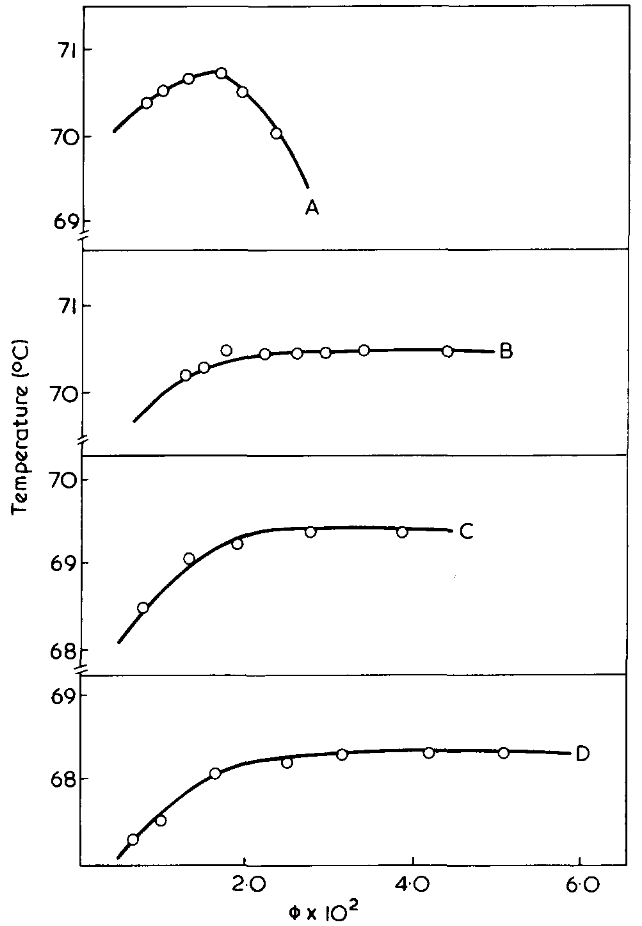

Figure 2 Phase separation curves of PBMA in cyclopentanol. A, $\bar{M}_w = 1.35 \times 10^6$; B, $\bar{M}_w = 1.08 \times 10^6$; C, $\bar{M}_w = 0.57 \times 10^6$; D, $\bar{M}_w = 0.36 \times 10^6$

Upper critical solution temperature

Phase separation curves for the four fractions investigated are shown in *Figure 2.* Maximum temperatures from these plots were plotted according to the Flory–Shultz equation[16],

$$1/T_c = 1/\theta\left[1 + \left(1/\psi\right)\left(x^{-1/2} + \frac{x^{-1}}{2}\right)\right] \qquad (4)$$

where T_c is the critical temperature in degrees Kelvin, θ is the theta or Flory temperature, ψ is the Flory entropy parameter, x is the $\bar{M}_w\bar{v}_2/V_1$ and V_1 the molar volume of the solvent.

In calculating x due notice has been taken of the temperature dependence of V_1 and $\bar{v}_2$, values of the latter parameter being those pertaining to solution in cyclohexanone. From the intercept of *Figure 3*, a θ-temperature of 73.2°C is obtained and a ψ_1 value of 1.22. Since $\theta = \kappa_1 T/\psi_1$, then $\kappa_1 = 422.55/T$, where κ_1 is the Flory enthalpy of dilution parameter. Although the exponent in the Kuhn–Mark–Houwink equation confirms the above temperature as the θ-temperature (*vide infra*), the maximum temperature may not correspond exactly to T_c. Consequently, the θ-temperature may be slightly lower than that quoted here.

Kuhn–Mark–Houwink equations

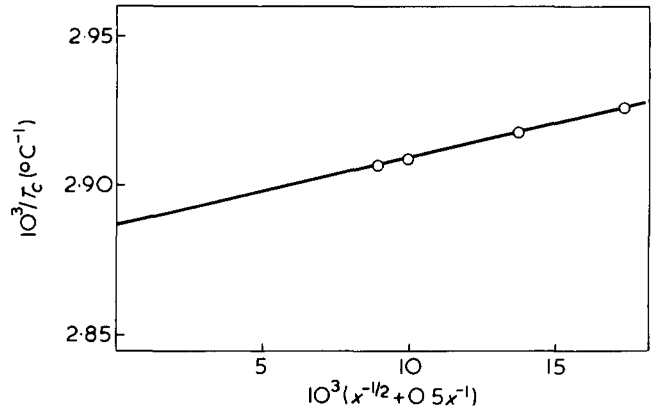

Figure 3 Flory–Shultz plot for PBMA in cyclopentanol

Linear log–log plots of $[\eta]$ as a function of $\bar{M}_w$ were obtained at all temperatures. The values of K and a in equation (5), obtained by least squares analysis, are given in *Table 2*. For cyclopentanol, a K value of 28.5×10^{-5} dl/g was obtained and an exponent of 0.5, the latter value being confirmation of θ-conditions.

$$[\eta] = K\bar{M}_w^a \qquad (5)$$

Unperturbed dimensions

The *UD* of a polymer chain are determined by the structural geometry specified by bond lengths and angles and on the conformation adopted by adjacent bond pairs. This latter factor determines the temperature coefficient of the *UD*, the value of which reflects the magnitude of the potential energy barrier to rotation about main chain bonds.

Polymer *UD* are generally obtained from dilute solution measurements but may also be obtained from neutron scattering measurements on bulk polymers[17–19]. Ideally, for the determination of *UD*, measurements should be made in θ-solvents. Where such solvents are not available, measurements made in good solvents may be used in conjunction with a suitable extrapolation procedure. Numerous procedures are available and have been reviewed by Cowie[20] and Yamakawa[21], the major difference between the procedures being the expression adopted for the dependence of α, the expansion coefficient, on z, the excluded volume parameter.

Six extrapolation methods have been used here. Methods A, B and C use data from Zimm plots, the remaining three being the more commonly encountered viscosity extrapolations.

Kurata plot (A)[22]

$$A_2\bar{M}_w^{1/2} = 1.65 \times 10^{23}A^3 + 0.968 \times 10^{23}B\bar{M}_w^{1/2}$$

$$A = (\langle r^2\rangle_{0w}/\bar{M}_w)^{1/2}$$

B = parameter characterizing polymer–solvent interactions.

Berry A_2 *plot (B)*[23]

$$1.42 \times 10^{-24}A_2\bar{M}_w^{1/2} = -A^3 + 6A(\langle s^2\rangle_w/\bar{M}_w)$$

Baumann plot (C)[24]

$$(\langle r^2\rangle_w/\bar{M}_w)^{3/2} = A^3 + B\bar{M}_w^{1/2}$$

Table 2 Kuhn–Mark–Houwink parameters for solutions of poly(benzyl methacrylate) in MEK and toluene at various temperatures

T (°C)	MEK $K \times 10^5$ (dl/g)	MEK a	Toluene $K \times 10^5$ (dl/g)	Toluene a
15	4.17	0.720	–	–
25	4.23	0.718	4.03	0.735
35	4.77	0.711	–	–
40	–	–	4.77	0.724
50	4.98	0.708	–	–
55	–	–	5.28	0.720
70	–	–	5.71	0.715

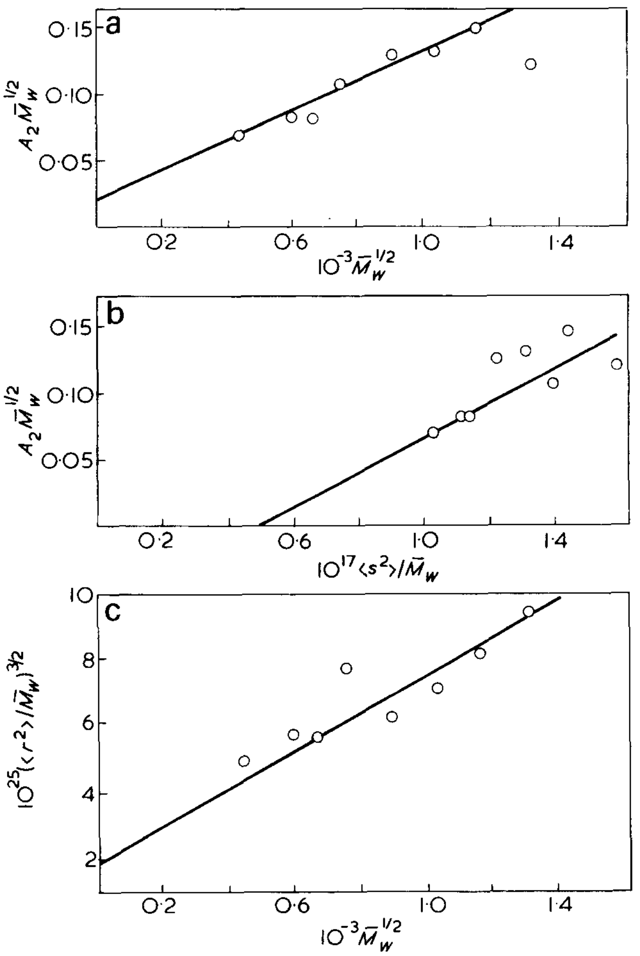

Figure 4 Extrapolation procedures using data from light scattering in MEK at 25°C. Units omitted to simplify appearance. (a) Kurata plot; (b) Berry A_2 plot; (c) Baumann plot

These three plots for PBMA in MEK at 25°C are shown in *Figure 4*, the straight lines being an empirical best fit to the data. The three viscosity plots used are methods D, E and F.

Modified Stockmayer–Fixman plot (D)[25]

$$[\eta]/\bar{M}_w^{1/2} = 1.05K_\theta + 0.287BK_\theta^{1/2}M_w^{1/2}$$

Berry viscosity plot (E)[26]

$$([\eta]/\bar{M}_w^{1/2})^{1/2} = K_\theta^{1/2} + 0.42_\theta^{1/2}\Phi B\bar{M}_w/[\eta]$$

Inagaki–Ptitsyn plot (F)[27]

$$[\eta]^{4/5}/\bar{M}_w^{2/5} = 0.786K_\theta^{4/5} + 0.454K_\theta^{2/15}\Phi B^{2/3}\bar{M}_w^{1/3}$$

For all the above plots $K_\theta = \Phi(\langle r^2\rangle_{0w}/\bar{M}_w)^{3/2}$ and Φ is the Flory viscosity constant. Plots according to methods D, E and F are given in *Figure 5* for PBMA in MEK and toluene at 25°C.

Whereas methods A, B and C provide values of the *UD* directly, methods D, E and F are dependent on the value of Φ used in those from K_θ. For $[\eta]$ in dl/g and in the non-free draining limit, theoretical values of $10^{-21}\,\Phi$ range from 1.81 to 2.87[28]. A value of 2.5 has been used here[26,29] which is reduced to 2.42 after correction for heterogeneity by the formula below[14]:

$$10^{-21}\Phi = 2.5\Gamma(h + 1.5)/[(h + 1)^{1/2}\Gamma(h + 1)]$$

where Γ is the gamma function and h has the value of 2.67. Ptitsyn and Eisner[30] concluded that Φ is also dependent on the solvent power and may be calculated from:

$$\Phi(\epsilon) = \Phi(1 - 2.63\epsilon + 2.86\epsilon^2) \qquad (6)$$

where Φ is the value pertaining to θ-conditions and ϵ is obtained from the exponent in the dependence of $\langle r^2\rangle_w$ on $\bar{M}_w$ which is $1 + \epsilon$. Furthermore, ϵ is related to the exponent a in the Kuhn–Mark–Houwink equation via:

$$a = (1 + 3\epsilon)/2 \qquad (7)$$

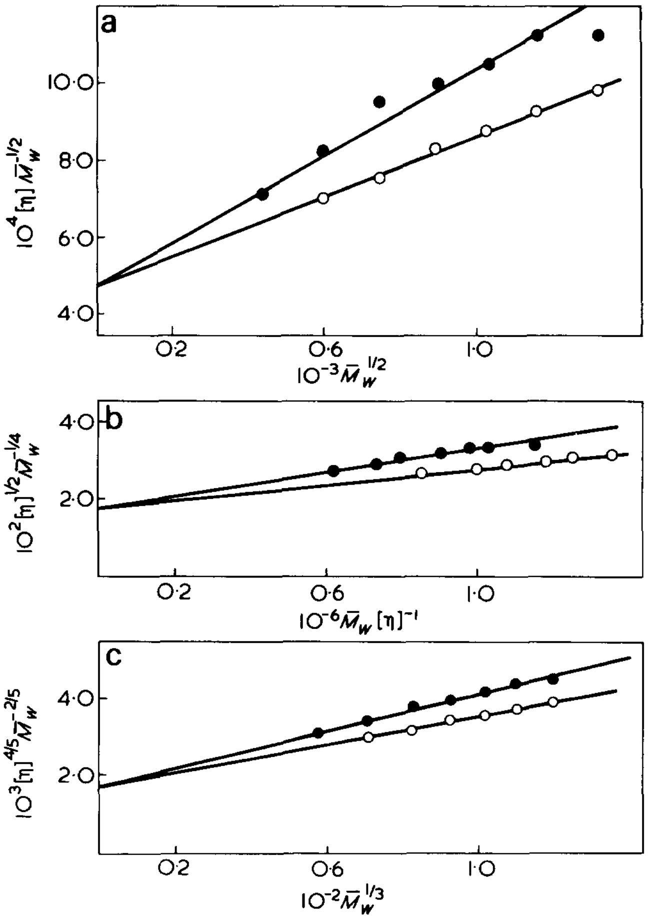

Figure 5 Extrapolation procedures using data from viscosity measurements at 25°C. Units omitted to simplify appearance. (a) Stockmayer–Fixman plot; (b) Berry plot; (c) Inagaki–Ptitsyn plot. ○, MEK; ●, toluene

Table 3 Unperturbed dimensions of poly(benzyl methacrylate) at 25°C from extrapolation methods

Plot	Solvent	$(\langle r^2\rangle_{0w}/\bar{M}_w)^{1/2} \times 10^9$ (cm mol$^{1/2}$/g$^{1/2}$)
A	MEK	4.73
B	MEK	5.53
C	MEK	5.72
D	MEK and toluene	5.74
E	MEK and toluene	4.92
F	MEK and toluene	5.73

For solutions of PBMA in MEK, both exponents in equations (3) and (5) yield a value of 0.145 for ϵ, whilst the value of a for PBMA in toluene yields an ϵ of 0.157. The best agreement with values of the *UD* from plots of methods A, B and C is obtained using $10^{-21}\Phi = 2.42$, the values for the *UD* obtained by the various extrapolation methods for data at 25°C are shown in *Table 3*. These values give an average of $(5.51 \pm 0.38) \times 10^{-9}$ cm mol$^{1/2}$/g$^{1/2}$. A value for the *UD* can also be obtained from the viscosity pre-exponential factor, K $(=K_\theta)$, for cyclopentanol, whereby a value of 4.9×10^{-9} cm mol$^{1/2}$/g$^{1/2}$ is obtained.

The temperature coefficient of the *UD* has been determined from data obtained in MEK and toluene at different temperatures. Since,

$$K_\theta = \Phi(\langle r^2\rangle_{0w}/\bar{M}_w)^{3/2}$$

then $\mathrm{dln}K_\theta/\mathrm{d}T = 3/2(\mathrm{dln}\,\langle r^2\rangle_{0w}/\mathrm{d}T)$. Plots of $\ln K_\theta$ as a function of T are shown in *Figure 6*, the average slope yields a value for the temperature coefficient of $(1.4 \pm 0.5) \times 10^{-3}\,\mathrm{K}^{-1}$. A value for the temperature coefficient may also be obtained by using equation (8) derived by Bohdanecky[31],

$$(P/Q)\mathrm{dln}\,[\eta]/\mathrm{d}T = (1/Q)\,\mathrm{dln}\,\langle r^2\rangle_{0w}/\mathrm{d}T + \mathrm{dln}\,(\bar{v}_2^2/V_1)/\mathrm{d}T + \mathrm{dln}\,(\tfrac{1}{2} - \chi_1)/\mathrm{d}T \qquad (8)$$

where

$$P = 2[(5\alpha^{2/3}) - 1]/[(5-\gamma)\alpha^2 - (3-\gamma)] \qquad (9a)$$

$$Q = (2\gamma/3)(\alpha^2 - 1)/[(5-\gamma)\alpha^2 - (3-\gamma)] \qquad (9b)$$

and α, the expansion coefficient, is defined by:

$$\alpha^\gamma = (\Phi_\theta/\Phi)[\eta]/[\eta]_\theta$$

which makes allowances for the fact that Φ may be different in theta and good solvents[26]. Values of γ range from 2.33 to 3.0[27]. Thus plotting (P/Q) dln $[\eta]/\mathrm{d}T$ as a function of $1/Q$, the temperature coefficient is obtained as the slope of the straight line. A similar plot can be derived using the Fixman[21] relationship between α and z. The factors P and Q are simpler, being,

$$P = 2\alpha^3/[(3-\gamma)\alpha^3 + \gamma] \qquad (10a)$$

$$Q = (2\gamma/3)(\alpha^3 - 1)/[(3-\gamma)\alpha^3 + \gamma] \qquad (10b)$$

For a given solvent and taking $\gamma = 3$ and $\Phi_\theta = \Phi$, no difference in the value of the temperature coefficient was found using either expressions (9) or (10). Furthermore, changing the values of Φ or γ produced no change in the value of the temperature coefficient. The type of plot obtained is shown in *Figure 7* for PBMA in MEK. For both MEK and toluene, the average value of the temperature coefficient of the *UD* for PBMA in both MEK and toluene obtained by this plot is $(1.1 \pm 0.2) \times 10^{-3}\,\mathrm{K}^{-1}$.

Thermodynamic parameters and the solubility parameter

The quantity B appearing in methods A to F is related to the Flory–Huggins interaction parameter, χ, via equation (11):

$$B = (\bar{v}_2^2/V_1N_a)(1 - 2\chi_1) \qquad (11)$$

Additionally, χ_1 is composed of enthalpic and entropic terms[33],

$$\chi_1 = \chi_H + \chi_S$$

In terms of Flory's notation $\chi_H = \kappa_1$ and $\chi_S = (\tfrac{1}{2} - \psi_1)$, furthermore, χ_H is related to the solubility parameters of the polymer–solvent system by equation (12):

$$\chi_H = V_1/RT(\delta_1 - \delta_2)^2 \qquad (12)$$

Values of χ_H for PBMA in MEK and toluene calculated from χ_1 $[\chi_H = -T(\mathrm{d}\chi_1/\mathrm{d}T)^{33}]$ using plots of methods D, E and F are all negative. Hence, equation (12), which in its strictest sense only applies to endothermic systems, cannot be used for these values. However, no such obstacle appears for the value of χ_H from phase separation in cyclopentanol. At a standard temperature of 25°K, χ_H for this system is 1.42.

A value of δ_1 for cyclopentanol is not available in the literature but may be calculated from various physical properties[34,35], the average value so obtained is 11.6 (cal/cm^3)$^{1/2}$. Depending on which root of the equation is taken, using these values results in PBMA solubility parameters of 8.4 or 15.0 (cal/cm^3)$^{1/2}$. The latter can certainly be rejected, since this value is commensurate with values for cellulose and polyacrylonitrile, i.e. polymers wherein strong specific intermolecular forces occur in solution.

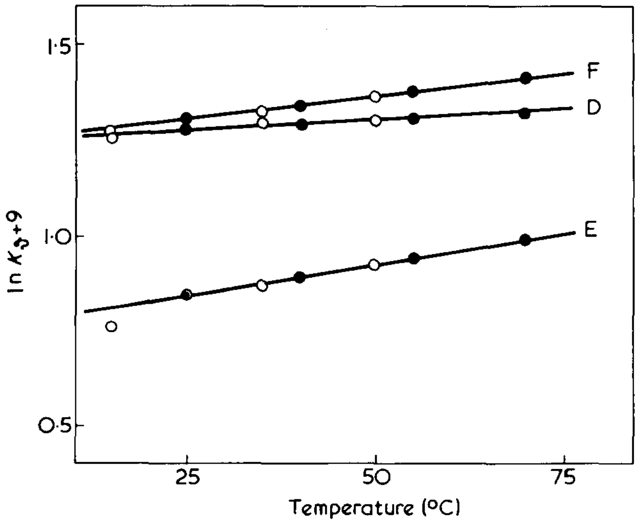

Figure 6 Determination of the temperature coefficient of the *UD* of PBMA from dependence of K_θ on temperature. ○, MEK; ●, toluene

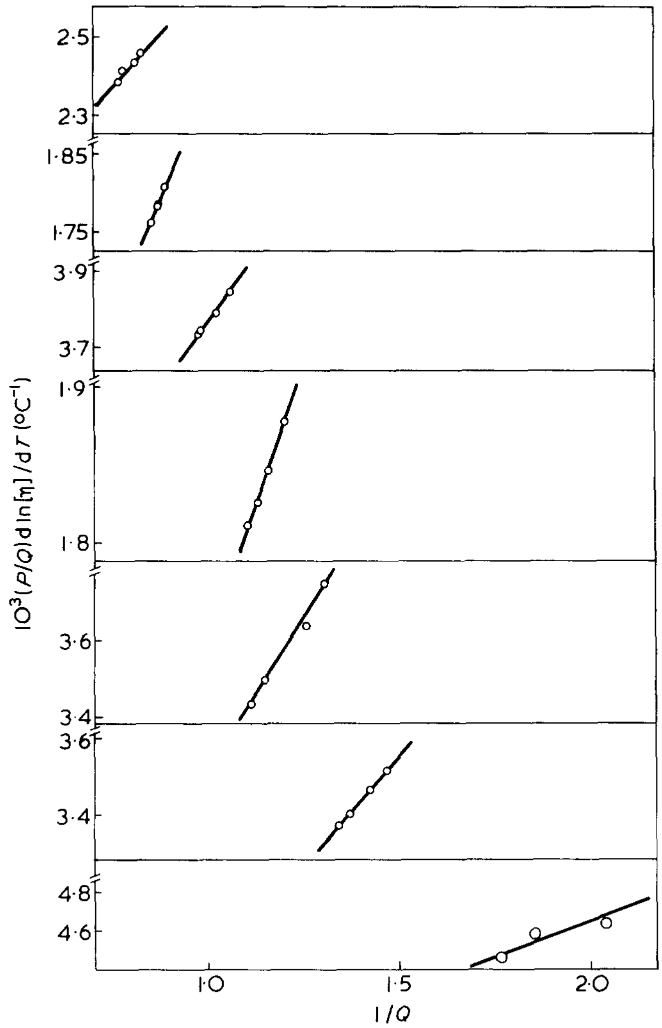

Figure 7 Application of the Fixman modification of the Bohdanecky procedure for the determination of the temperature coefficient

DISCUSSION

From the positive temperature coefficient it would be expected that a larger *UD* would prevail in cyclopentanol compared with the values in MEK and toluene at lower temperatures; such is not the case. This disparity may be attributable to the so called specific solvent effect. Although such effects are well documented[37,38], the causes are not so clear. It has been suggested that the cause may lie in a dependence of the chain conformational energy on the solvent dielectric constant[39], or in a direct interaction of the solvent with the polymer[40,41]. Dielectric constants for MEK and toluene are 18.5 and 2.38[42] and whilst that of cyclopentanol is not known it is probably close to that of cyclohexanol (15.0). These values do not reflect the change in *UD*. Although possible hydrogen bonding between the carbonyl groups in PBMA and the hydroxyl groups in the alcohol can be envizaged, it is not clear how this would affect the *UD*. Similar hydrogen bonding could be present in the system poly(cyclohexyl methacrylate)–butyl alcohol (θ-solvent), but no difference was noted between the *UD* in this and other solvents[5]. For the purpose of comparison with other methacrylates it is more convenient to use the characteristic ratio, C_∞, defined as:

$$C_\infty = (\langle r^2\rangle_{0w}/\bar{M}_w)M_b/l^2$$

Table 4 Characteristic ratios at 25°C for a series of methacrylates

Methacrylate	C_∞	Reference
Methyl	6.8	1
Cyclohexyl	10.6	5
Tetrahydrofurfuryl	11.7	44
Decahydro-β-naphthyl	13.5	4
Phenyl	12.9	5
β-Naphthyl	16.2	4
Benzyl	10.0	This work

where M_b is the molecular weight per skeletal bond of length l.

Such values are given in *Table 4* for PBMA and a series of methacrylates with bulky ester groups, as a comparison the value for poly(methyl methacrylate) is included. A theoretical study[45] of the latter has shown that first order interactions i.e. those between adjacent segments, are the major factors determining C_∞. The larger values predominating in *Table 4* probably reflect the greater steric interactions due to the bulkier ester groups. A lower value of C_∞ for PBMA when compared to that for poly(phenyl methacrylate) is attributable to relief of steric hindrance by the additional CH_2 group in PBMA providing another rotation centre. Since the *trans* state of a polymer chain is that of maximum extension, it is clear that the population of this rotational state must increase with temperature to account for the positive value of the temperature coefficient for PBMA obtained. Hence the equilibrium conformation for PBMA is not the *trans* state. This conclusion agrees with a theoretical study of poly(methyl methacrylate)[45] where the configuration of minimum energy about skeletal bonds was found to be at positions ±15°C from the *trans* state.

Available experiment values for the solubility parameter of PBMA range from 9.8 to 10.0 (cal/cm^3)$^{1/2}$ [47], whilst from molar attraction constants a value of 9.5 (cal/cm^3)$^{1/2}$ is obtained. The value obtained from phase separation studies [8.4 (cal/cm^3)$^{1/2}$] in cyclopentanol does not agree with any of these values. It is unfortunate that the solubility parameter for cyclopentanol is not available in the literature, however, the equations used to calculate δ_1 are known to yield reasonably accurate values. One reason for the low value of δ_2 derived from cyclopentanol results may be an erroneously high value for the entropy parameter ψ_1 from the Flory–Shultz plot[48].

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