Unperturbed dimensions of poly(phenyl acrylate)

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Thirteen fractions of poly(phenyl acrylate) have been prepared with weight-average molecular weight ranging from 0.158×10^6 to 2.57×10^6 g mol^{-1}. The temperature coefficient of the unperturbed dimensions and the glass transition temperature were found to be -1.8×10^{-3} deg^{-1} and 55.6°C respectively. Good accord was obtained among different methods for establishing θ-conditions of 11.5°C in ethyl lactate. From viscometry, osmometry and light scattering under θ-conditions, as well as in a good solvent, the unperturbed dimensions were determined via several procedures yielding a value of $[\langle r^2\rangle_{0w}/\bar{M}_w]^{1/2} = 6.0\ (\pm 0.2) \times 10^{-9}$ cm $\mathrm{g}^{-1/2}$ $\mathrm{mol}^{1/2}$. This corresponds to a steric factor $\sigma = 2.37$ ($\pm$0.08) and a characteristic ratio $C_\infty = 11.3$ ($\pm$0.8). The polymer chain is thus more rigid than poly(methyl acrylate), but less rigid than poly(phenyl methacrylate). With respect to its T_g and flexibility, poly(phenyl acrylate) bears a strong similarity to poly(benzyl methacrylate).

INTRODUCTION

The influence of the size of the group R on the chain flexibility of poly(methacrylates), $-\!\!\![CH_2{-}C(CH_3)COOR]\!\!\!-$, has been studied in detail, but less attention has been paid to the series of poly(acrylates), $-\!\!\![CH_2{-}CHCOOR]\!\!\!-$. In the present work we present data on poly(phenyl acrylate) (PPA), which bears the large phenyl group as substituent R. Since information on the polymerization of the liquid monomer phenyl acrylate is rather scant, preliminary experiments (not reported here) were conducted, therefore, in order to optimize conditions for obtaining high molecular weight PPA suitable for subsequent fractionation and characterization. In this connection, the tendency of acrylates to undergo branching at high conversion was borne in mind.

EXPERIMENTAL

Materials

The monomer (Polysciences Inc.) was vacuum-distilled in the presence of hydroquinone and Cu turnings, only the major middle cut being retained. After redistillation, the fraction boiling at 72°C (at 4.5 mmHg press.) was kept. Its refractive index was $n_D^{20} = 1.5215$, in good accord with the literature value[1]. The initiator AIBN (Koch Labs. Ltd.) was crystallized from methanol. Toluene, methyl ethyl ketone and ethyl lactate were dried over anhydrous $MgSO_4$ and distilled at atmospheric pressure.

Polymerisation

With toluene as solvent, [monomer] = 4 mol dm^{-3} and [initiator] = 1×10^{-4} mol dm^{-3}, polymerization in outgassed, sealed ampoules was carried out for different times at 60°C. The percentage conversion was determined gravimetrically after precipitating diluted solution into cyclohexane. (Difficulties in obtaining a fine, easily filterable, precipitate were encountered with other precipitants). The rate of conversion was 2.2×10^{-3} % s^{-1}.

Fractionation

A sample of polymer was prepared to 17% conversion. G.p.c. analysis (RAPRA, Shawbury, Shropshire, England: courtesy of Mr. L. J. Maisey) yielded $\bar{M}_w = 1.86 \times 10^6$ and $\bar{M}_n = 0.72 \times 10^6$. It was dissolved in toluene to give a 1.5% w/v solution, with 0.015% w/v 2:6 di-tert-butyl *p*-cresol being incorporated as antioxidant. Isothermal fractionation at 28°C using methanol as non-solvent produced seven fractions, some of which were refractionated to give a final total of thirteen fractions. The overall recovery amounted to 97% of the initial weight of polymer.

Characterization

Membrane osmometry[2], light scattering[2,3,4], differential refractometry[2,3,4] and viscometry[2,3] were used according to techniques already described.

Phase separation

Exhaustive tests yielded only two liquids, *n*-butyl lactate and ethyl lactate, offering potential as θ-solvents for PPA. Since the θ-temperature in *n*-butyl lactate appeared to lie below 0°C, attention was focussed solely on ethyl lactate, which gave indications that the θ-temperature would lie between 0°C and room temperature. Accordingly, six fractions covering the range $\bar{M}_w = 0.16 \times 10^6$–$2.5 \times 10^6$ were used in phase separation experiments according to the Shultz–Flory method[5], the procedures being as described before[3,6]. The turbidimetric technique of Cornet and Ballegooijen[7] (valid if $M \geqslant c.\ 2 \times 10^4$) does not invoke

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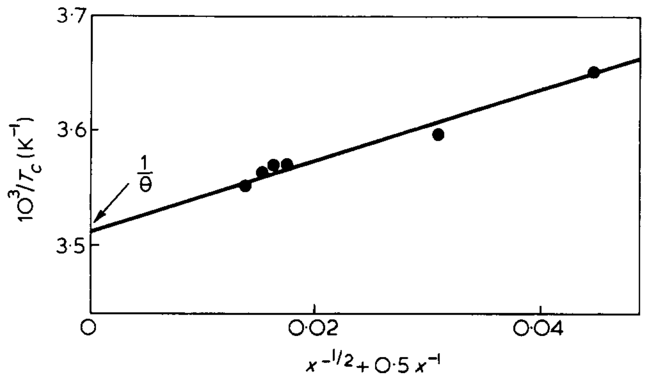


Figure 1 Determination of θ-temperature in ethyl lactate via the Shultz–Flory method[5]. T_c is the critical miscibility temperature and x is the weight average degree of polymerization of the polymer

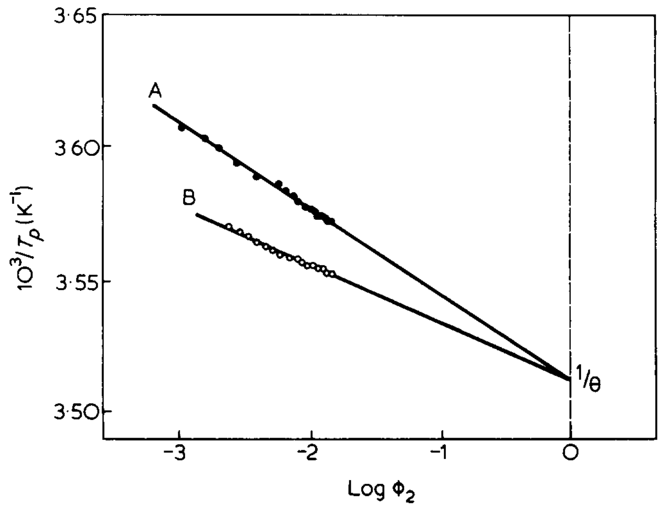


Figure 2 Determination of θ-temperature in ethyl lactate via the Cornet and Ballegooijen method[7] applied to samples: A, $\bar{M}_w$ = 0.88 × 10^6; B, $\bar{M}_w$ = 2.2 × 10^6. T_p is the incipient precipitation temperature and ϕ_2 is the volume fraction of polymer

the molecular weight and, moreover, requires only one polymer sample. However, as a check on consistency, previously described procedures[3] were employed with two fractions of different molecular weights.

RESULTS

Molecular weights

Values of $\bar{M}_w$ measured by light scattering in methyl ethyl ketone at 30°C ($d\tilde{n}/dc$ = 0.183 $cm^3\,g^{-1}$; λ_0 = 436 nm) agreed to within 5% with those measured under θ-conditions, i.e. at 11.7°C in ethyl lactate. The average values were compared with the number average molecular weights $\bar{M}_n$ determined by osmometry at 30°C. The resultant range of $\bar{M}_w$ was 2.57 × 10^6–0.158 × 10^6 and the corresponding one of $\bar{M}_n$ was 1.28 × 10^6–0.077 × 10^6. The mean polydispersity of all the fractions ($\bar{M}_w/\bar{M}_n$ = 2.0) was disappointingly high and is possibly due to insufficiently dilute fractionation solution.

θ-conditions

The Shultz–Flory method gave θ = 11.4°C (*Figure 1*), the entropy of dilution parameter ψ_1 and the enthalpy parameter κ_1 being respectively 1.07 and 305.5/T (temperature T in degrees Kelvin). The Cornet and Ballegooijen method yielded θ = 11.6°C and 11.7°C for the two fractions used (*Figure 2*). The second virial coefficient, A_2, was determined at different temperatures by light scattering on solutions of a fraction of $\bar{M}_w$ = 1.47 × 10^6. Extrapolation to $A_2 = 0$ gave θ= 11.5°C (*Figure 3*). The mean value of θ is therefore 11.5°C but, to allow for the uncertainty in it and consequent possibility of precipitation of high molecular weight fractions, the temperature was maintained at 11.7°C during measurements of viscosity and light scattering under θ conditions.

Unperturbed dimensions (u.d.)

Both direct and indirect means have been used to evaluate the u.d. of PPA, which is defined as $\{\langle r^2\rangle_{0w}/\bar{M}_w\}^{1/2}$, where the mean square end-to-end distance $\langle r^2\rangle$ is expressed in cm^2.

A Mark–Houwink relationship in terms of $\bar{M}_w$ was established in ethyl lactate at 11.7°C. The exponent ν and constant K_θ in equation (1) were 0.50 (±0.01) and 5.52 × 10^{-2} $cm^3\,g^{-3/2}\,mol^{1/2}$:

$$[\eta] = K_\theta \bar{M}_w^{\nu} \tag{1}$$

U.d. were obtained from equation (2) in which Φ is the universal Flory constant corrected[8] for heterogeneity to 2.35 × 10^{21} mol^{-1} from its uncorrected value. The latter was taken as 2.5 × 10^{21} mol^{-1}:

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

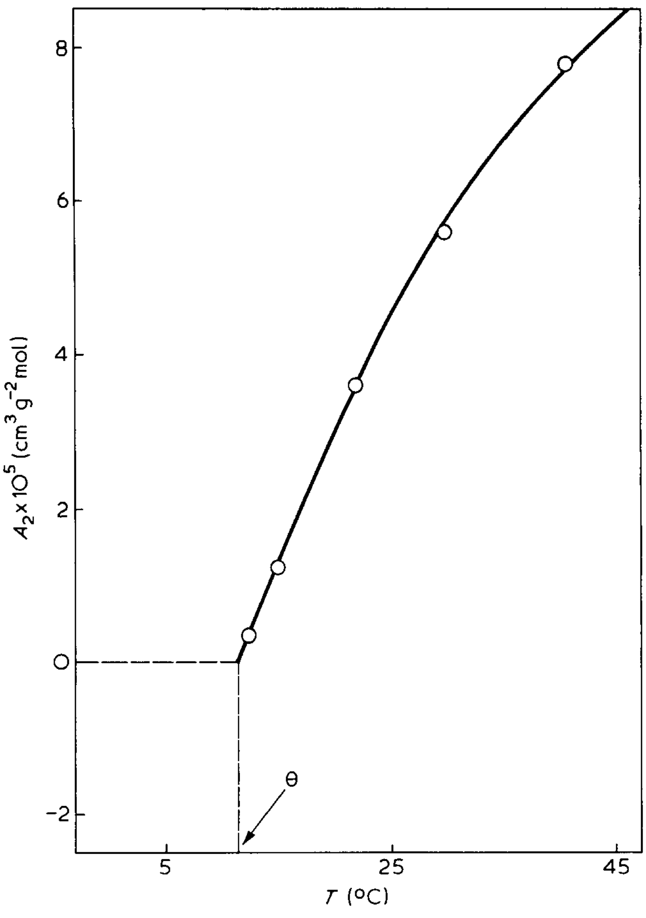


Figure 3 Location of θ-temperature from the variation of the second virial coefficient with temperature

Table 1 Values of $\{\langle r^2\rangle_{0w}/\bar{M}_w\}^{1/2} \times 10^9$ expressed in cm g$^{-1/2}$ mol$^{1/2}$ for PPA, according to different procedures

Plot	Relevant parameters	Measurements in MEK at 30°C		Measurements in ethyl lactate at 11.7°C	
		Direct	Via K_θ	Direct	Via K_θ
Berry[9]	$[\eta], \bar{M}_w$	–	5.77	–	6.04
Mark–Houwink	$[\eta], \bar{M}_w$	–	–	–	6.12
Bohdanecký[10]	$[\eta], \bar{M}_w$	–	6.20	–	6.08
Inagaki, Suzuki and Kurata[11]	$[\eta], \bar{M}_w$	–	6.21	–	6.70
Flory, Fox and Schaefgen[12]	$[\eta], \bar{M}_w$	–	5.62	–	6.07
Kurata–Stockmayer[8] (iterative)	$[\eta], \bar{M}_w$	–	6.06	–	6.11
Stockmayer–Fixman[13] (modified)	$[\eta], \bar{M}_w$	–	6.16	–	6.05
Kurata *et al.*[14]	$A_2, \bar{M}_w$	5.81	–	–	–
Baumann[15]	$\langle r^2\rangle, \bar{M}_w$	5.83	–	5.83	–
Berry[16]	$A_2, \langle r^2\rangle, \bar{M}_w$	5.50	–	–	–

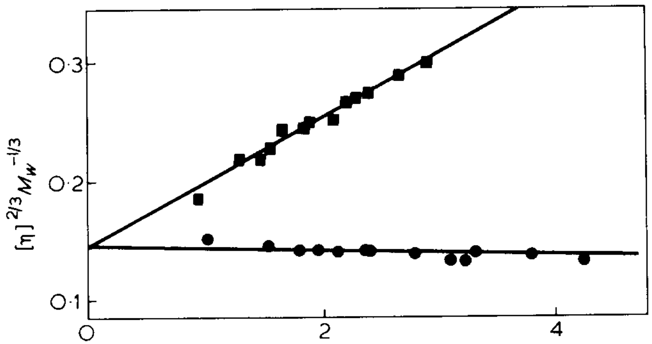


Figure 4 Determination of K_θ by Kurata–Stockmayer iterative procedure[8]. ■, in methyl ethyl ketone at 30°C; ●, in ethyl lactate at 11.7°C. Intrinsic viscosity is expressed in cm^3 g^{-1} and g (α) is a function[8] of the expansion factor α

Values of K_θ, and hence the u.d., are also obtainable from several extrapolation procedures. The relevant equations are not reproduced here, but the references are quoted in *Table 1*, where the resultant values of the u.d. are listed. Plots are also available which yield the u.d. directly without recourse to Φ. These involve measurements of A_2 and $\bar{M}_w$ or $\langle r^2\rangle_w$ and $\bar{M}_w$ or A_2, $\langle r^2\rangle_w$ and $\bar{M}_w$. The heterogeneity correction needed is the conversion of z-average mean square radius of gyration (from light scattering) – to $\langle r^2\rangle_w$, the relevant equation being quoted previously[3,8]. Resultant values of the u.d. are also listed in *Table 1*. Examples of plots involving an indirect procedure and a direct one are given in *Figures 4* and *5* respectively.

A slight trend is apparent in *Table 1* for the u.d. derived indirectly to be slightly greater than the directly obtained values. This difference would be effectively eliminated by the use of 2.6×10^{21} mol^{-1} in place of 2.5×10^{21} mol^{-1} as the uncorrected Φ. However, the overall range of the u.d. is not wide and we have averaged all seventeen results to yield a value of 6.01 (±0.20) × 10^{-9} cm g$^{-1/2}$ mol$^{1/2}$. The steric factor σ is defined as:

$$\sigma = \{\langle r^2\rangle_{0w}/\bar{M}_w\}^{1/2}/\{\langle r^2\rangle_{0f}/M\}^{1/2} \tag{3}$$

where $\langle r^2\rangle_{0f}$ is the mean square end-to-end distance for a freely rotating chain. Calculation involving accepted values[17] for bond length and bond angle gives $\{\langle r^2\rangle_{0f}/M\}^{1/2} = 2.53 \times 10^{-9}$ cm g$^{-1/2}$ mol$^{1/2}$ and hence, from equation (3), $\sigma = 2.37$ (±0.08). An alternative expression of chain stiffness is the characteristic ratio C_∞ defined as:

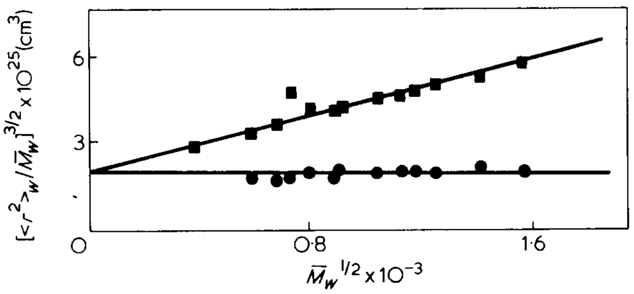


Figure 5 Determination of the unperturbed dimensions via Baumann plot[15]. ■, in methyl ethyl ketone at 30°C; ●, in ethyl lactate at 11.7°C. The mean square end-to-end distance is expressed in cm^2

$$C_\infty = \{\langle r^2\rangle_{0w}/\bar{M}_w\}(M_u/2l^2) \tag{4}$$

where l is the skeletal bond length and M_u is the molecular weight of the segment in PPA. The average value of the u.d. in conjunction with equation (4) gives $C_\infty = 11.3$ (±0.8).

Temperature dependence of the unperturbed dimensions

For each fraction, the intrinsic viscosity $[\eta]$ was measured in methyl ethyl ketone at 10°, 20°, 30° and 40°C. The plots of ln $[\eta]$ *versus* T were all linear and of negative slope, essentially independent of molecular weight. An example is provided in *Figure 6a* for the fraction of highest molecular weight. In general the slope is expressible as follows, where α is the viscometric expansion factor:

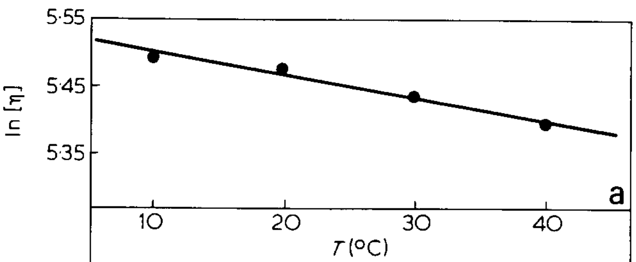
$$\mathrm{d}\ln[\eta]/\mathrm{d}T = (3/2)\,\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T + 3\,\mathrm{d}\ln\alpha/T \tag{5}$$

As discussed previously[18], refined analysis based on equation (5) is necessary when dln $[\eta]$/dT is temperature dependent. However, under the present circumstances, the system is displaced considerably from θ conditions (in the vicinity of which α changes markedly). Hence the constant value of the left-hand side of equation (5) may be equated with $(3/2)\,\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T$. The average value of dln $[\eta]$/dT was thus used to calculate the temperature coefficient of the unperturbed dimensions.

Another route to this coefficient is due to Bohdanecký[19] According to his analysis, a linear plot of slope equal to $\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T$ is obtained when $(P/Q)\,\mathrm{d}\ln[\eta]/\mathrm{d}T$ is plotted *versus* $(1/Q)$. The quantities P and Q are defined as follows:

$$P = (5\alpha^2 - 3)/3\alpha^2$$

$$Q = (\alpha^2 - 1)/\alpha^2$$



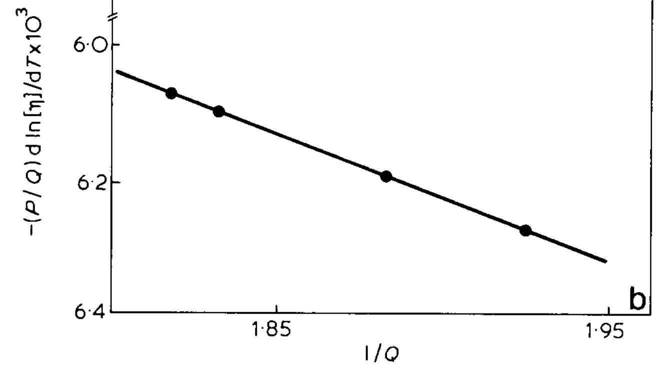


Figure 6a Variation of ln[η] with temperature for fraction of $\bar{M}_w$ = 2.57 x 10^6 in methyl ethyl ketone

Figure 6b Determination of dln $\langle r^2\rangle_0$/dT according to Bohdanecký plot[19] for sample of $\bar{M}_w$ = 2.57 x 10^6 in methyl ethyl ketone

The values of α were obtained from equation (6) in which $[\eta]_\theta$ is the intrinsic viscosity measured under θ conditions:

$$\alpha^3 = [\eta]/[\eta]_\theta \qquad (6)$$

Bohdanecký plots were constructed separately for each fraction (*Figure 6b* is an example for the same sample as in *Figure 6a*). The slopes were almost the same for all fractions, the mean differing by only 1% from the value yielded by plots of ln $[\eta]$ *versus T, viz.* $\mathrm{dln}\langle r^2\rangle_0/\mathrm{d}T = -1.8 \times 10^{-3}$ deg^{-1}.

DISCUSSION

Since the molecular weight of the segment varies according to the polymer, chain flexibility is expressible most appropriately in terms of σ or C_∞, rather than $\{\langle r^2\rangle_{0w}/\bar{M}_w\}^{1/2}$. Here we shall consider C_∞.

There is a rough parallel between this dilute solution parameter and the bulk property parameter T_g (the glass transition temperature), both of which increase with increase in chain stiffness. Among the factors influencing stiffness are the polarity and bulkiness of the ester group –COOR. Thus, in the poly(methacrylates), T_g^{20} and C_∞^{21} fall as the length of the alkyl group increases. With respect to T_g the same applies to the poly(acrylates)[20], but literature values of C_∞ for them are too few and insufficiently self-consistent to allow similar conclusions to be drawn with any degree of confidence. When R comprises large aliphatic or aromatic rings, the enhanced steric hindrance is reflected in large values of T_g and C_∞. Values of the latter ranging from 10.0 to 16.2 in the poly(methacrylates) have been collated by Richards[22].

A further increase in steric hindrance is imposed by the substitution of an α-hydrogen atom with an α-methyl group. Thus, for poly(methyl acrylate) and poly(methyl methacrylate), the values of T_g are 2°C and 105°C respectively. Although one might anticipate the C_∞ value for poly(methyl methacrylate) to exceed slightly that for poly(methyl acrylate), there is scatter among the literature values for these polymers and the average C_∞ is actually 8.0 for each of them.

With regard to PPA, we have measured the specific volume at different temperatures. The derived T_g of 55.6°C lies in good accord with reported values of 56.5°C[23] and 55.0°C[24]. Hence T_g and C_∞ (=11.3 ± 0.8) are both displaced in the expected direction from the corresponding values for poly(methyl acrylate). The influence of the α-methyl group is also evident in the value of C_∞ = 12.9 obtained by Desreux and co-workers[25] for poly(phenyl methacrylate). The T_g of the latter polymer, 110°C[24], is also higher than that of PPA.

Finally, it appears that, within the groups of polymers considered, PPA has characteristics closest to those of poly(benzyl methacrylate). For this latter polymer, Richards[22] has obtained unperturbed dimensions = 5.5 (±0.4) x 10^{-9} cm $\mathrm{g}^{-1/2}$ $\mathrm{mol}^{1/2}$ and C_∞ = 10.0; Krause *et al.*[24] quote T_g = 54°C. Hence the additional constraint to flexibility (*cf.* PPA) imposed by the α-methyl group is counterbalanced by the simultaneous relief of steric hindrance provided by the methylene group, with the result that the above values are very close to those already quoted here for PPA.

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