Aggregation behaviour of stereoregular poly(methyl methacrylates) in dilute solution: light scattering and proton n.m.r. study

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The aggregation behaviour of syndiotactic and isotactic poly(methyl methacrylate) in methyl ethyl ketone, n-butyl acetate, and 2-ethoxyethanol was investigated by light scattering and ^{1}H n.m.r. spectroscopy. Syndiotactic poly(methyl methacrylate) remains in its molecular form in solution at temperatures above $60°-70°C$; on cooling it undergoes aggregation followed by macroscopic separation (precipitation) of the polymer from solution. The rate of these processes depends on temperature, concentration of the polymer, and solvent. Molecular solutions of isotactic poly(methyl methacrylate) can be prepared only by long-term heating at temperatures above $100°-130°C$. During cooling, isotactic macromolecules prior to separation form stable associates in the region limited by discrete temperatures, and below this region polymer precipitates. The individual stereo forms of poly(methyl methacrylate) are separated from solution at different temperatures which are above the θ-temperatures of the atactic polymer.

INTRODUCTION

The properties of stereoregular poly(methyl methacrylate) (PMMA) in dilute solutions have been investigated for the last three decades[1-10]. The main topics were the effect of stereoregularity on the θ-temperature, unperturbed dimensions of macromolecules, and the dependence of intrinsic viscosity on molecular weight. In recent years, studies have appeared indicating the possibility of aggregation of both i-PMMA (cf. refs. 9, 11-16) and s-PMMA (cf. refs. 13-17), and even of a-PMMA[18,19] in solvents which with respect to a-PMMA are regarded as thermodynamically good.

This study demonstrates, by light scattering and ^{1}H n.m.r. spectroscopy, important differences in the behaviour of dilute solutions of i-, s- and a-PMMA in three solvents with a different 'solvent power'.

EXPERIMENTAL

Polymers and solvents

Conventional a-PMMA was prepared in toluene solution by radical polymerization initiated with 2,2'-azoisobutyronitrile at 60°C. Isotactic i-PMMA was prepared in benzene solution by anionic polymerization initiated with tertiary lithium butylate at 20°C. Syndiotactic s-PMMA was prepared in toluene solution by coordination polymerization catalysed with titanium(IV) chloride and triethyl aluminium at $-78°C$. All PMMA samples under investigation possess unimodal molecular weight distribution, and their molecular and structural parameters are given in *Table 1*. The purity of the solvents used, i.e. 2-ethoxyethanol (ethylcellosolve, ECS), n-butyl acetate(BAC), chloroform (CHF), methyl ethyl ketone (MEK), was checked by gas chromatography (content of impurities $<0.1\%$). The thermodynamic quality of the solvents with respect to a-PMMA is characterized by the exponents of the Mark–Houwink equation (*Table 2*).

Table 1 Molecular and structural characteristics of PMMA samples*

PMMA sample	$M_W \times 10^{-5}$	M_W/M_n	Content of triads (%)		
			syndio	hetero	iso
i	4.5	2.3	11	17	72
s	5.5	1.3	91.5	7.5	1
a	3.7	2.4	63	33	4

* M_W by light scattering in CHF at 25°C; M_W/M_n by g.p.c. in THF at 25°C. Tacticity determined from ^{1}H n.m.r. spectra in an equimolar mixture of o-dichlorobenzene and tetrachloroethylene at 140°C

Table 2 Exponent a in the Mark–Houwink equation and the refractive index increment dn/dc ($\lambda_0 = 546$ nm) for a-PMMA at 25°C

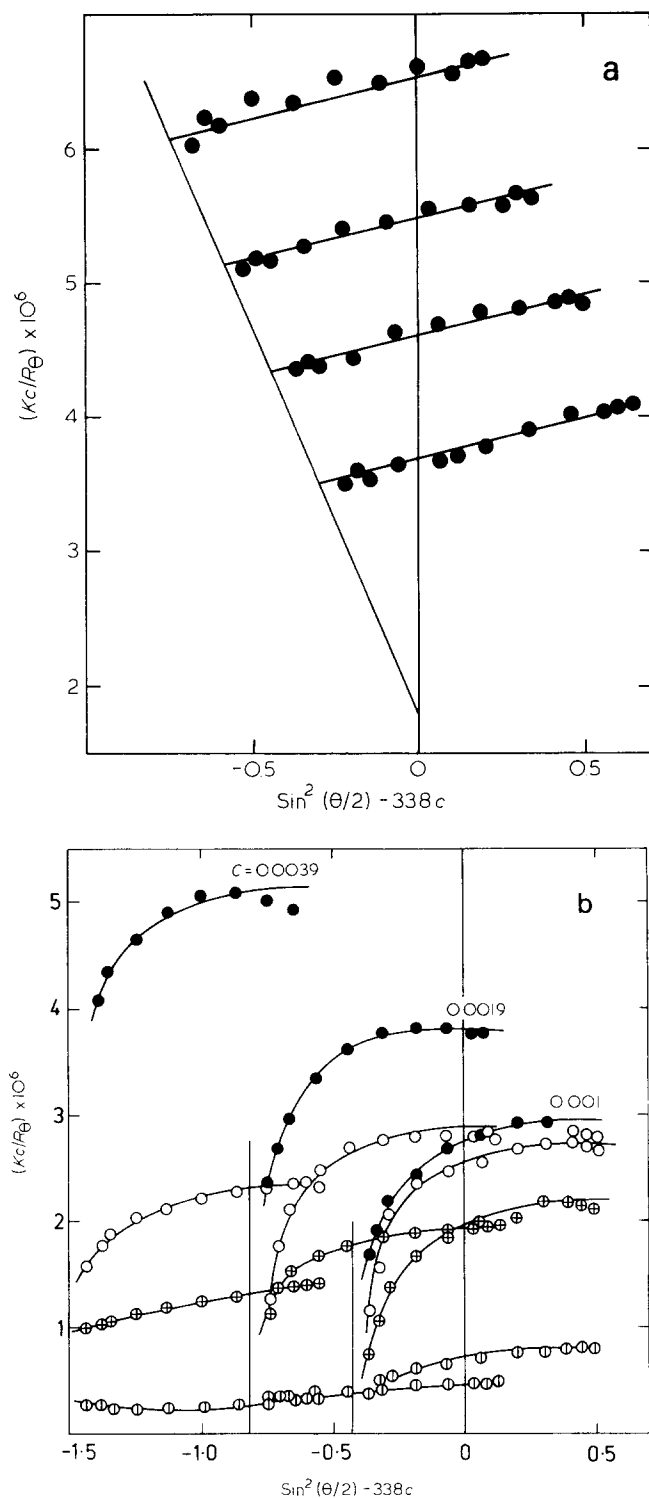| Solvent	a	dn/dc (cm³ g⁻¹)	Ref.
2-Ethoxyethanol (27°C)	0.51	0.076	20
Butyl acetate	0.60	0.097	21
Methyl ethyl ketone	0.72	0.112	22, 23
Chloroform	0.80	0.063	22, 24

Figure 1 Scattering diagrams of s-PMMA at 25°C: (a) in CHF; (b) in MEK, ● immediately after dissolution, ○ after four days, ⊕ after three weeks, ⊕ after six weeks at 25°C

Light scattering

The light scattering (LS) measurements were performed with a FICA 50 with an unpolarized light of wavelength 546 nm, and at temperatures between 25° and 120°C. For measurements at temperatures below 20°C, a SOFICA 42.000 was adapted.

The solutions at concentrations between 1×10^{-3} and 5×10^{-3} g cm^{-3} were purified by filtration through a sintered glass filter G4 (VEB Jenaer Glasswerk, GDR) with porosity about $3\,\mu m$, heated to 60°–80°C. The solutions were filtered at elevated pressure up to 10 kPa in an inert nitrogen atmosphere. Cells used in the measurements were sealed after filling.

Experimental data are presented in the usual Kc/R_θ vs. $\sin^2(\theta/2) + kc$ plot (K is the optical constant, θ is the angle of observation, R_θ is the so-called Rayleigh ratio at the angle θ, c is the concentration of the polymer, and k is an arbitrary constant).

Evaluation of the experimental data was carried out using refractive index increments, dn/dc, determined for a-PMMA (*Table 2*). The dependence of dn/dc on temperature t in BAC is given by the relation

$$dn/dc = 0.097 + 2.5 \times 10^{-4}(t - 25) \qquad (1)$$

calculated using the scattering data of a-PMMA and assuming that molecular weight does not change with temperature[25].

N.m.r. spectroscopy

Solutions of samples of stereoregular PMMA having the concentration 1×10^{-2} g cm^{-3} were prepared directly in measuring cells and homogenized in a bath at 100°C (BAC) or 70°C (MEK) for 5 days. After that, they were cooled to room temperature and after some days their ^{1}H n.m.r. spectra were recorded with a PS-JEOL spectrometer at 100 MHz. Integrated intensities were measured with a built-in integrator with an accuracy of $\pm 2\%$ (MEK) or $\pm 5\%$ (BAC). The absolute temperature values were calibrated by using n.m.r. spectra[26].

Viscometry

Viscosity was measured in capillary viscometers of the Ubbelohde type. The kinetic correction and non-Newtonian behaviour of solutions were negligible.

RESULTS AND DISCUSSION

The basic characteristics of the PMMA samples (*Table 1*) were determined by light scattering in chloroform (*Figures 1a* and *6*), which is a thermodynamically very good solvent; in this solvent all stereo forms of PMMA are molecularly dissolved and do not aggregate[13,14].

The effect of stereoregularity of PMMA on the solution behaviour was studied in MEK, BAC and ECS (*Table 2*).

Syndiotactic PMMA

s-PMMA was macroscopically readily soluble in MEK at 60°C, and the solutions did not change their appearance during a long-term measurement (weeks) at 25°C. In spite of this, however, immediately after the solution temperature had dropped from 60° to 25°C, the light scattering measurements revealed the existence of curved envelopes in the low-angle range (*Figure 1b*), which suggests a low content of supermolecular structures. After four days of aggregation at 25°C the mutual position of scattering envelopes for the particular concentration was changed. In both cases, however, by extrapolating the scattering intensities from higher angles (i.e. neglecting the lower ones) to zero concentration, it was possible to obtain an approximate molecular weight of non-aggregated macromolecules. After six weeks the intensity of scattered light increased by an order of

magnitude, and the concave curvature of the envelopes mostly disappeared, as a consequence of increasing amount of aggregates (*Figure 1*). After half a year, s-PMMA started to separate out from the solutions.

Since aggregated monomeric units are not reflected directly in the high-resolution ^{1}H n.m.r. spectra[13-15], it is possible to determine their fraction p from the relation[14,15]
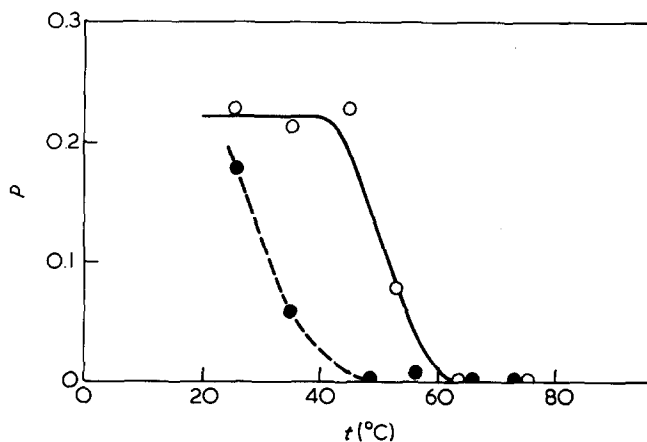
$$p = 1 - I/I_0 \qquad (2)$$

Figure 2 Temperature dependence of the fraction of aggregated monomeric units, for s-PMMA (O) and a-PMMA (●) in MEK; c = 1 x 10^{-2} g cm^{-3}

where I and I_0 are the integrated band intensities of high-resolution n.m.r. spectra of a system in which aggregation is investigated, and of the same system under conditions where no aggregation takes place. The I_0 values were determined in deuterated CHF, where stereoregular PMMA does not form aggregates, or by extrapolation of the temperature dependence of integrated intensities in the temperature range where aggregates are completely decomposed. We investigated only the integrated intensities of OCH$_3$ protons, because the bands of the CH$_2$ and α-CH$_3$ protons interfere with strong bands of the solvent. Since it is known that intensities of all proton bands behave in the same way[13-17], it is sufficient to investigate the OCH$_3$ bands. By using relation (2), it was found that $p \simeq 0.23$ at 25°C for s-PMMA in MEK approximately a week after complete dissolution. Aggregates of s-PMMA in MEK decompose at 45°–60°C as shown in *Figure 2*. The content of aggregates is approximately the same as that observed for this polymer in dimethylformamide[15], and their thermal stability resembles that in other solvents[14-16].

N.m.r. revealed a content of aggregates also in the case of a-PMMA in MEK ($p \simeq 0.18$); these aggregates decompose at temperatures of 25°–40°C (*Figure 2*). Light scattering of a-PMMA in MEK did not, however, show the presence of any aggregates. Therefore it might be possible that these aggregates are of an intramolecular character[16].

In BAC, s-PMMA can be molecularly dissolved only at elevated temperatures. The radiation envelopes measured above 60°C show no pronounced curvature, and the
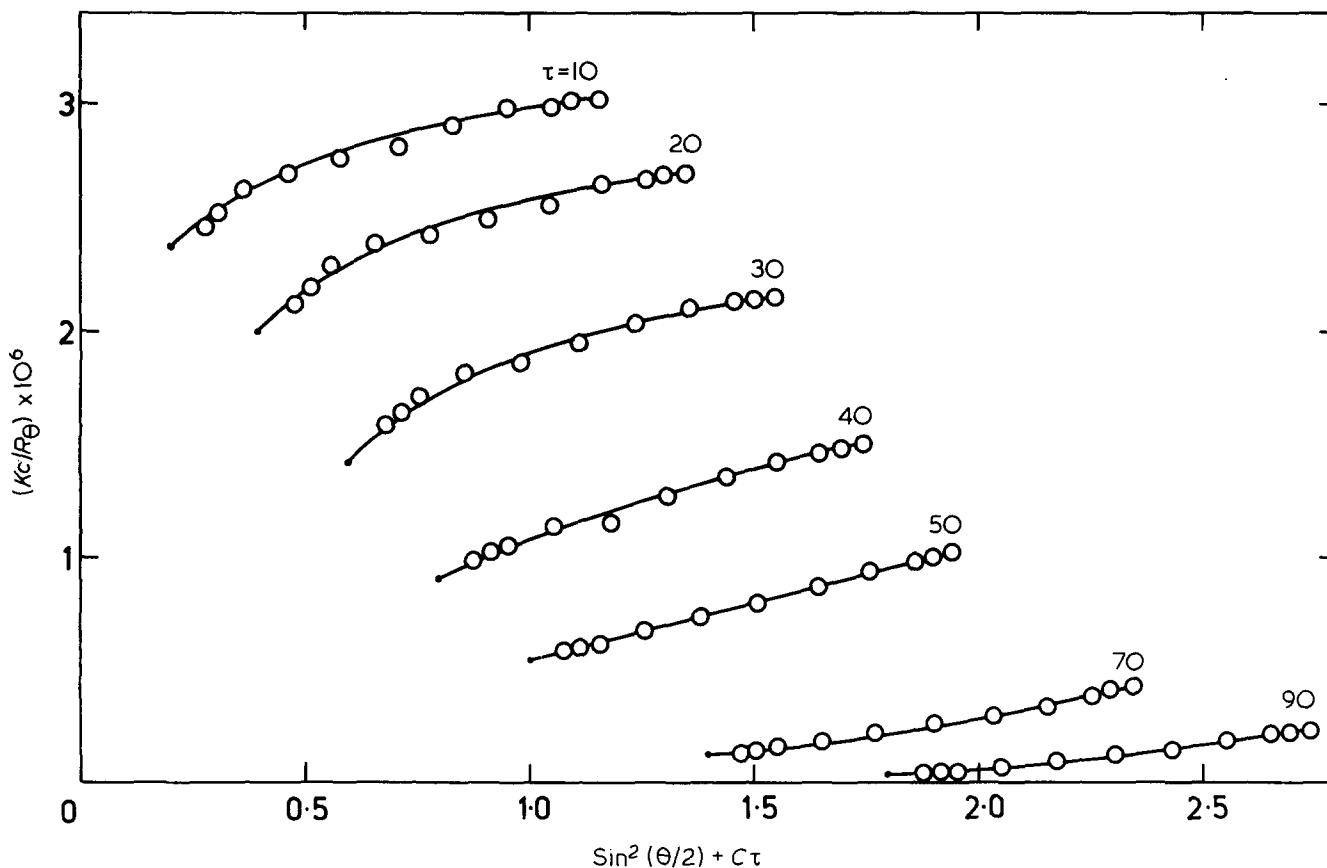
Figure 3 Dependence of the radiation envelopes of aggregating s-PMMA in BAC at 55°C on time τ (min); c = 5 x 10^{-3} g cm^{-3}, C = 0.02 min^{-1}

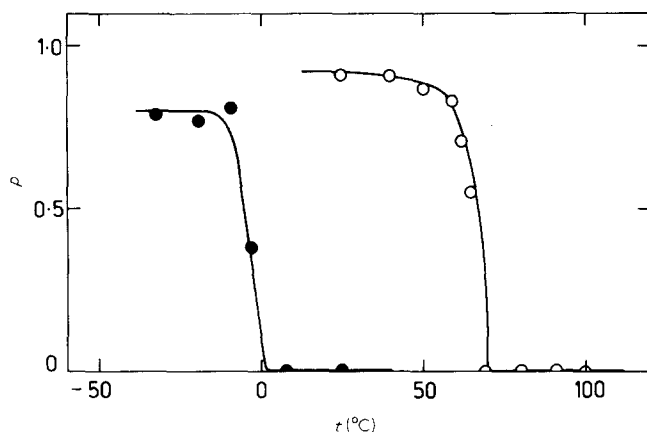*Figure 4* Temperature dependence of the fraction of aggregated monomeric units, for s-PMMA (○) and i-PMMA (●) in BAC; c = 10⁻² g cm⁻³
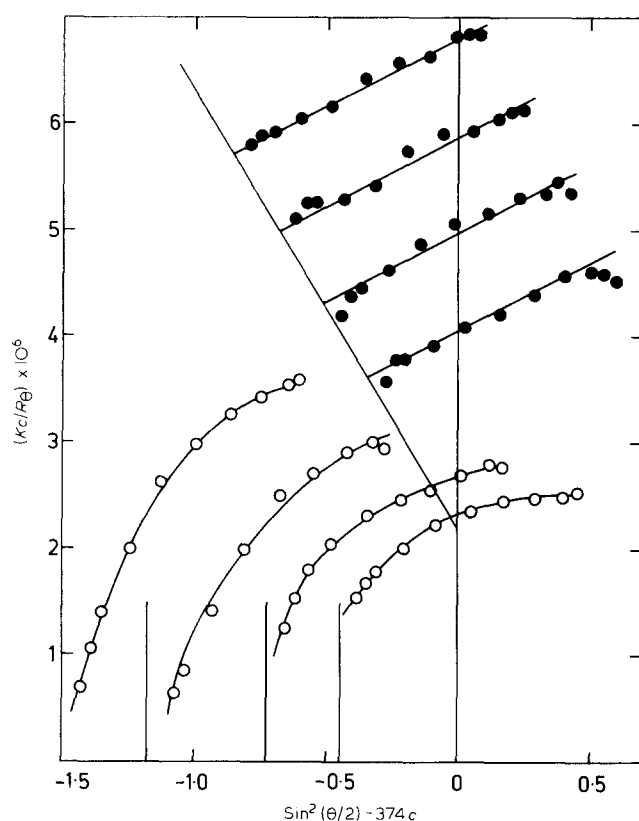

Figure 5 Scattering diagrams of i-PMMA at 25°C in CHF (●) and in MEK (○)

molecular weight ($M_w = (4.4–4.8) \times 10^5$) agrees satisfactorily with that determined in other solvents. A solution left at 60°C becomes turbid after a few days, although the second virial coefficient, $A_{2,s}$ measured directly after cooling to 60°C, was definitely positive. The kinetics of aggregation and incipient separation of s-PMMA from a solution in BAC at 55°C are shown in *Figure 3*. The time needed for the particle weight determined by light scattering to approach infinity was about 70 min. At 50°C, the whole process became faster, and the similar state was reached within some 20 min. In the last stages of the measurement the solution is slightly turbid, and the polymer separates out after a few hours. With decreasing

concentration of the polymer, the aggregation process followed by separation of the polymer from solution is slowed down. It is therefore not possible, by employing the usual procedure, to extrapolate the scattering data to zero concentration in order to determine the average dimensions and weight of the aggregated particles.

At 25°C, the integrated band intensity of OCH_3 protons in the n.m.r. spectra of s-PMMA in BAC is very weak, in accordance (cf. equation (2)) with a considerably high value of the fraction p (*Figure 4*). The majority of polymeric segments are part of aggregates which decompose in the temperature range 60°–70°C (some 55% of them decompose between 65° and 70°C). Such a distinct transition corresponds to the separation process of the polymer from solution with decreasing temperature, or to the dissolution of the polymer with increasing temperature.

With a-PMMA in BAC (unlike MEK) aggregation was not detected by any of the methods used.

In ECS, s-PMMA is macroscopically dissolved above 70°C. However, not even at 130°C does the sample show linear radiation envelopes. On cooling to 60°C the solution was not stable, its scattering behaviour being similar to that shown in *Figure 3*. At 27°C (θ-temperature of a-PMMA) the aggregation process was much faster. The state reached at 60°C within 20 h is found at 27°C already within 1.5 h. There does not seem to be any basic difference in the nature of aggregation processes leading to the separation of s-PMMA in ECS and BAC.

Isotactic PMMA

i-PMMA was macroscopically soluble in all solvents used above 40°C. However, scattering diagrams even at elevated temperatures (MEK, 0°–50°C; BAC, 25°–90°C) did not suggest molecular dissolution of the polymer (*Figures 5* and *6*). According to the reported data[11–15], i-PMMA is molecularly dissolved only at high temperatures (above 100°C) as checked in BAC. For solutions of i-PMMA prepared at 90°C, the diagrams obtained were similar to those of i-PMMA in MEK (*Figure 5*). When the temperature was raised to 120°C after cooling (first temperature cycle), the intensity of scattered light decreased and remained virtually unchanged on gradual cooling to 25°C (second cycle). After reproduction of the second cycle (third cycle), only insignificant changes with respect to the disaggregation behaviour were observed (*Figure 6*). The decrease in M_w (*Table 3*) with increasing temperature in the given cycle is probably an apparent one. The scattering data were evaluated with dn/dc calculated by means of equation (1) valid for a-PMMA. It is not ruled out, however, that the temperature dependence of dn/dc for i-PMMA may be somewhat different.

In BAC the dissolution process of PMMA was also investigated by measurement of specific viscosity η_{sp} in the temperature range 40°–100°C. While in the case of a-PMMA and s-PMMA the increase in η_{sp} was monotonic (*Figure 7*), η_{sp} of i-PMMA reached its maximum approximately at 70°–75°C and after that decreased. On cooling to the initial temperature 45°C, the η_{sp} was lower by 6.7% than the original one. The repeated temperature cycle led to the dependence of η_{sp} on temperature with a much lower maximum than in the first cycle; at the same time, η_{sp} at 100°C was the same in both cycles. The following temperature cycles were reproductions of the second
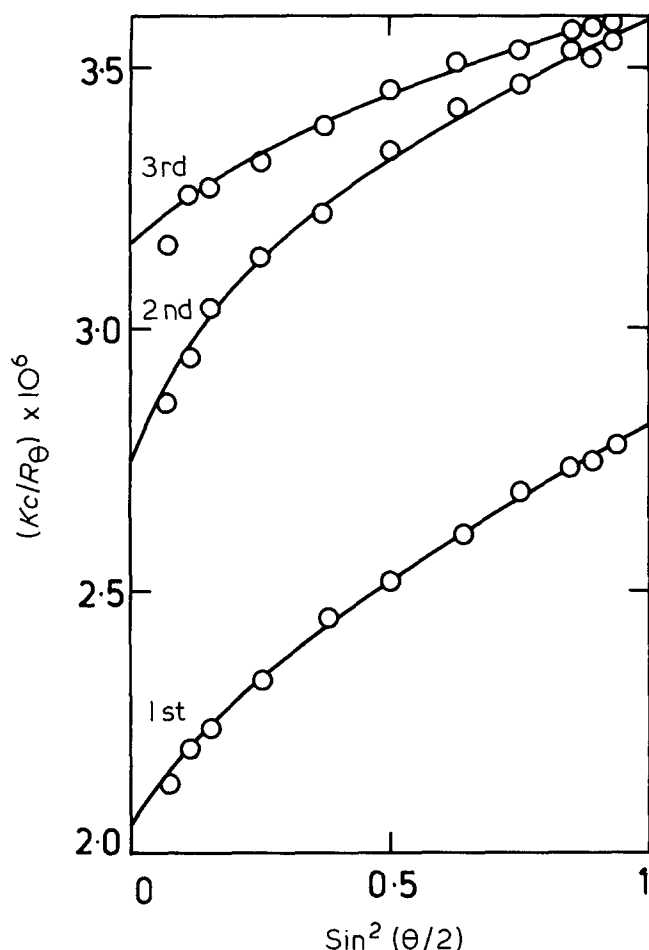
Figure 6 Shapes of the angular dependence of scattered light from i-PMMA in BAC at 80°C in the first, second and third temperature cycle; $c = 3 \times 10^{-3}$ g cm^{-3} (cf. *Table 3*)

Table 3 Molecular weights, M_w, of i-PMMA in BAC determined at various temperatures and with various histories of the samples*

Temperature (°C)	$M_w \times 10^{-5}$		
	I	II	III
120	—	4.2	3.0
100	—	4.3	3.4
90	7.0	—	—
80	7.0	5.2	3.3
70	6.6	—	—
60	7.4	5.6	4.2
50	7.8	—	—
40	8.2	6.2	4.3
25	—	—	4.7

* The samples were heated to 90°C and light scattering was measured at this and at a gradually decreasing temperature (I). After that, the sample was again heated to 120°C and the following measurement was made at decreasing temperature (II and III)

cycle. Viscosity became immediately constant on reaching 100°C and did not change for 12 h, which suggests that these effects cannot be explained by degradation of the polymer. The lower viscosity on return to 45°C after the first cycle indicates, similarly to the light scattering results, decomposition of supermolecular formations, originally present in the solution.

No such effects appeared with the other two polymers; the solutions were molecularly dissolved (with s-PMMA, only above 70°C). The plateau on the temperature dependence of η_{sp} in a-PMMA reported in the literature[27] and attributed to the configurational transition has not been observed.

When cooling a molecular solution of i-PMMA in BAC an increase in the intensity of scattered light was observed below 5°C. In the range 0°–5°C, the polymer forms stable associates (*Figure 8*). At 0°C fast spontaneous separation of i-PMMA from BAC was observed. This was also indicated by n.m.r. spectroscopy through a steep increase in the fraction p in the range 0° to -10°C (*Figure 4*).

In ECS the association of i-PMMA and separation of the polymer from solution was also observed by light scattering. A sample was molecularly dissolved at 90°C. At a temperature below 70°C i-PMMA in ECS forms stable associates. On cooling to 38°C the polymer precipitates from solution.

CONCLUSION

In the solvents under investigation (MEK, BAC, ECS), syndiotactic (s-)PMMA is dissolved molecularly only above ~70°C, regardless of the thermodynamic quality of the solvent used. If the temperature of the solution is lower, the particle weight increases (aggregation), which is finally followed by the precipitation of s-PMMA from solution. The rate of aggregation increases with increasing polymer concentration in solution and with decreasing temperature, being different in the individual solvents. It is noteworthy that this occurs in spite of the similar tacticities of s- and a-PMMA (cf. *Table 1*), high above the
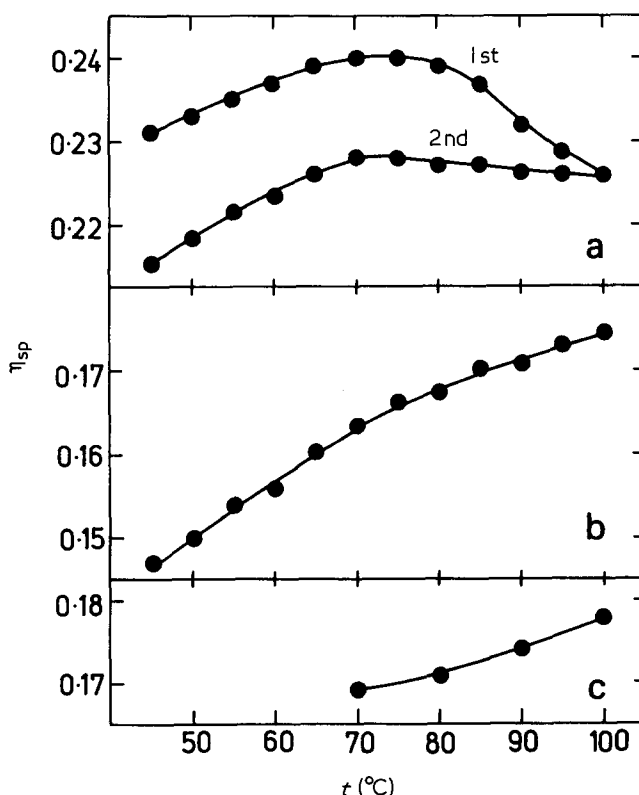

Figure 7 Dependence of specific viscosity, η_{sp}, in BAC on temperature t (°C): (a) i-PMMA in first and second temperature cycle; (b) a-PMMA; (c) s-PMMA; $c = 3 \times 10^{-3}$ g cm^{-3}
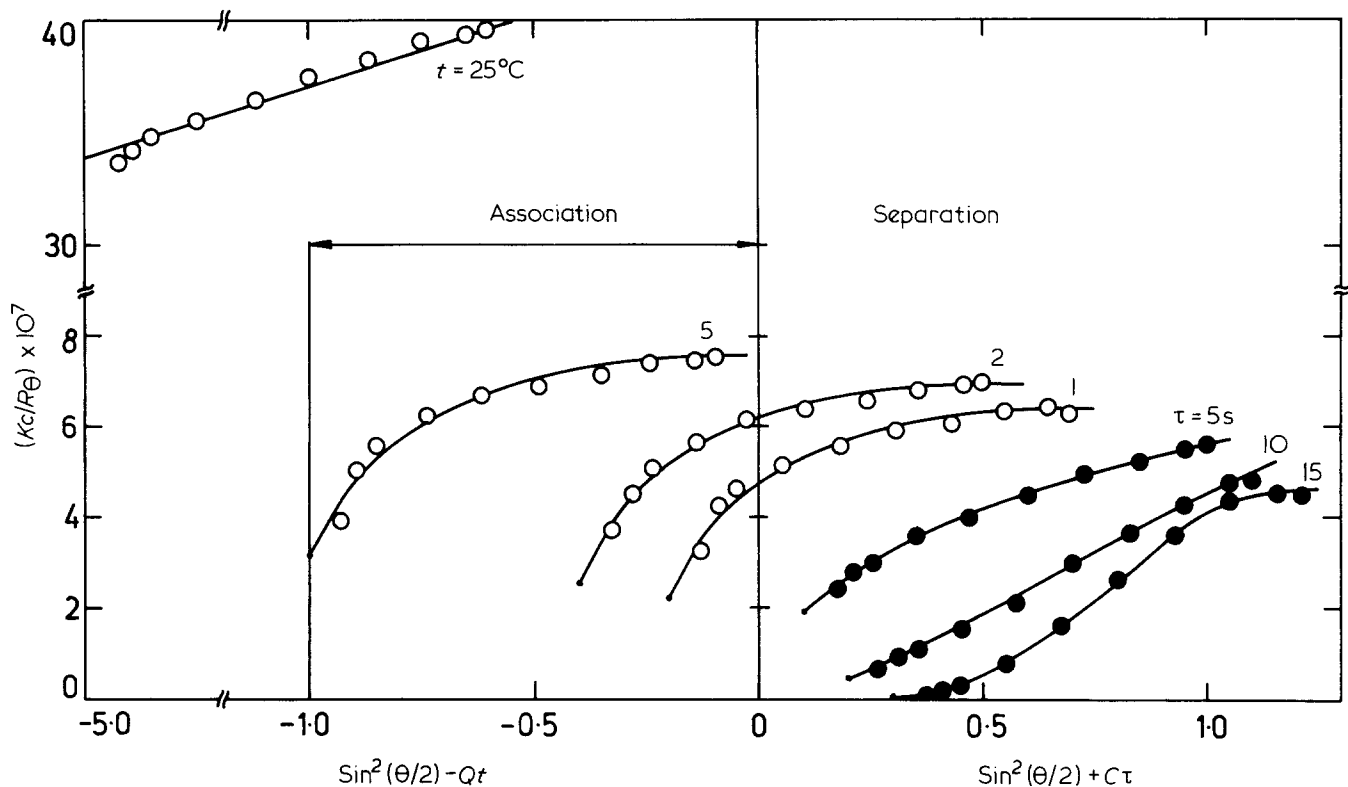
Figure 8 Dependence of the radiation envelopes of i-PMMA in BAC on temperature t (°C) (O) and time τ (s) (●) at 0°C; c = 5 x 10^{-3} g cm^{-3}; Q = 0.2°C^{-1}; C = 0.02 s^{-1}

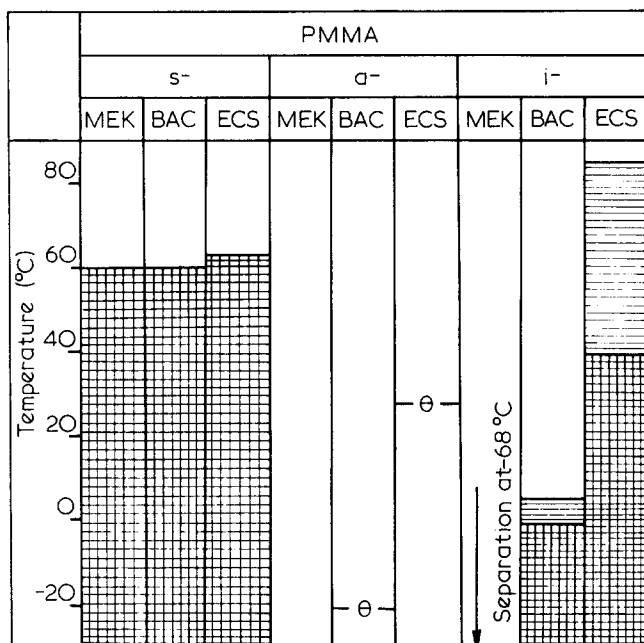*Figure 9* The scheme of behaviour of different PMMA stereoregular forms in dilute solution: molecular solution ☐ reversible association ▤, separation (precipitation) of polymer from solution ▦

θ-temperatures of a-PMMA[20,28] (BAC, $-20°C$; ECS, 27°C). Here, it should be stressed that a-PMMA does not precipitate from the solvents used even on cooling to $-70°C$.

Preparation of a molecular solution of i-PMMA requires long-term heating of the sample to high tempera-

tures (100°–130°C). In the following cooling of the solution the range of reversible stable association is found above the separation temperature (*Figure 9*). When the temperature is increased, the weight of the associates decreases and weight increase is observed on cooling. At a given concentration of the solution, the weight of these associates is unambiguously determined by temperature. Below this range i-PMMA separates from solution, also above θ-temperature of a-PMMA. Temperatures of separation of i- and s-PMMA differ by approximately 130°C in MEK, by 60°–70°C in BAC and by 20°–30°C in ECS (cf. *Figure 9*).

It should be stressed that the kinetics of all processes may also be affected by the molecular weight of stereoregular polymers; this aspect has not been examined in this study.

If macroscopic separation of the polymer was observed, both light scattering and ^1H n.m.r. spectroscopy gave consistent information. However, in a long-term separation, e.g. of s-PMMA in MEK, when only the aggregation stage was investigated, the observed increase in particle weight by light scattering would correspond to a very small number of spot intermolecular contacts ($<0.1\%$ chain units). This could not be reflected in a decrease in the intensities of the n.m.r. spectra. Since the fraction of aggregated monomeric units in MEK given by n.m.r. is larger by an order of magnitude ($p \simeq 0.23$), sequential intramolecular contacts were suggested to be the structural basis of the aggregates[17]. Different evidence of both methods regarding the mode of aggregation was also provided by an investigation of the behaviour of a-PMMA in MEK. In this case, a not-negligible fraction of aggregated monomeric units was determined at 25°C by n.m.r. ($p \simeq 0.18$), while light scattering failed to reveal any joining of the macromolecules.

In our opinion, the aggregation and separation processes observed might also be explained, for example, by crystallization of stereoregular PMMA from solution. A more detailed study of this phenomenon is required.

ACKNOWLEDGEMENT

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