Stereo complexes in solutions of syndio- and isotactic poly(methyl methacrylate) mixtures: 1. Aggregation time and character of aggregated particles in different solvents

N. G. Belnikevitch
Institute of High Molecular Compounds, Academy of Sciences of the USSR, Leningrad, USSR

L. Mrkvičková and O. Quadrat
Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 *Prague* 6, *Czechoslovakia*

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The formation of stereo complexes in solutions of a mixture of syndiotactic and isotactic poly(methyl methacrylate) in dimethylformamide, dioxan and chlorobenzene was investigated viscometrically and by the light-scattering method as a function of time, of the ratio of stereo polymers and of their total concentration. It was found that the increase in molecular weight during growth of stereo complexes is accompanied by their contraction; the specific hydrodynamic volume of aggregates having molecular mass higher by two orders of magnitude may be considerably lower than the additive value of the hydrodynamic volumes of the pure polymer components.

Keywords Stereocomplexes; syndio- and isotactic poly(methyl methacrylate); aggregation time; solvent influence

INTRODUCTION

Gel formation on mixing of solutions of syndiotactic and isotactic poly(methyl methacrylate) ranks among the modes of behaviour of macromolecular systems which are still unexplained. The system obviously offers extraordinarily suitable conditions for the formation of aggregates. Formation of stereo complexes is assumed[1-21], but so far only hypotheses have been forwarded regarding the mechanism of this effect[1,14]. The existing papers reporting experimental studies of such solutions in the pre-gel stage or at a sufficiently large dilution when no gel has yet formed were mainly concentrated on an elucidation of conditions under which aggregation takes place. A number of physical methods were used, such as viscometry[3-14], light scattering[3,4] and turbidimetry[1,13], high-resolution and broad-line n.m.r.[16,17], sedimentation analysis[4,18], osmometry[13,15], calorimetry[19,20], X-ray diffraction[13] and dynamic measurements[20,21]. These studies are mainly concentrated on one solvent only and do not examine the phenomenon in a broader framework.

It was found that the ability to aggregate in a mixture of stereoregular poly(methyl methacrylates) depends on the solvent[5,8,11-13], on the concentration ratio of stereo polymers in the mixture, on their total concentration[4,15] and on time[8,11,15]. So far, the effect of solvents on the structure of the stereo complex has not been systematically investigated. Also, data on the optimal ratio between both components of the stereo complex are not uniform. The highest molecular mass of stereo aggregates determined by the light-scattering method[3] for the syndiotactic-to-isotactic polymer ratio was s:i = 2:1. In most papers dealing with the hydrodynamic behaviour, this ratio is also accompanied by an extreme value of the reduced[5,10,13] or intrinsic viscosity[3]. Some authors[4], however, report the optimal ratio of polymer components as being 1:2 or 1:1 (cf. ref. 10). An interesting, and still unexplained, feature is the character of the extremes of the dependences of viscosity on the composition of the polymer mixture. A minimum has been described in solutions in dimethylformamide for both the reduced[13] and intrinsic[3] viscosities, while a maximum has been reported for toluene and benzene solutions[5,10]. The investigation of reduced viscosity[8,11] and light scattering[15] showed that the formation of stereo complexes is time-dependent. Unfortunately, the results obtained by both methods were evaluated separately.

Based on this state of knowledge, we investigated systematically the process of formation of stereo complexes in several selected solvents. Owing to the good sensitivity of viscometry to interactions of polymer molecules in solutions and its simplicity, this method was advantageously used in our study and was supplemented by light-scattering measurements. Compared with studies published so far, such a combination allowed us to

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Table 1 Molecular and structural characteristics of PMMA samples

PMMA	$M_w \times 10^{-5}$ (g mol^{-1})	M_w/M_n	Content of triads (%)		
			Syndio	Hetero	Iso
Isotactic	4.5	2.3	11	17	72
Syndiotactic	5.5	1.3	91.5	7.5	1

analyse the hydrodynamic behaviour of stereo complexes more completely and at the same time to characterize their mass and dimensions.

EXPERIMENTAL

Polymers

The polymer samples were obtained from the Laboratory for Research on Anionic Polymerizations at the Institute of Macromolecular Chemistry of the Czechoslovak Academy of Sciences. Isotactic poly(methyl methacrylate) (i-PMMA) was prepared by anionic polymerization in benzene solution initiated with lithium *tert*-butoxide at 20°C. Syndiotactic poly(methyl methacrylate) (s-PMMA) was obtained by coordination polymerization in toluene solution catalysed with titanium tetrachloride and triethyl aluminium at −78°C.

The tacticity of the polymers was determined from ^{1}H n.m.r. spectra recorded in an equimolar mixture of *o*-dichlorobenzene and tetrachloroethylene at 135°C with a JEOL PS-100 spectrometer at 100 MHz.

The weight average molecular weights, M_w, were determined by the light-scattering method in chloroform at 25°C. The number average molecular weights, M_n, or the M_w/M_n values used in the estimate of the distribution width, were obtained by g.p.c. measurements at 25°C in tetrahydrofuran with a standard Styragel packing calibrated with polystyrene standards. Molecular and structural parameters of the polymers are given in *Table 1*.

Solutions and solvents

Of the solvents reported in the literature as suited for an investigation of stereo complexes of PMMA, those chosen by us were dimethylformamide (a strongly complex-forming medium[12,13]), dioxan (a medium complex-forming medium) and chlorobenzene; the last of these had never been used before, and we assumed that it would possess a rather weak complex-forming effect. Our intention also to use benzene and toluene appeared to be unrealizable, since our sample of s-PMMA could not be dissolved in these solvents at room temperature. We were surprised by this finding, as in some studies[5,7-11] these solvents were used in the investigation of stereo complexes at 24°C as a weak complex-forming medium. The cause of the insolubility of our s-PMMA in benzene and toluene probably lies in its extremely high stereoregularity, while in the PMMA samples used in the papers referred to above the content of syndiotactic triads was lower. Obviously, the solubility of PMMA with high tacticity cannot be estimated at all from the thermodynamic quality of the solvent for an atactic polymer[26], if s-PMMA may become insoluble even in such good solvents as benzene and toluene. Difficulties connected with the solubility of s-PMMA are probably related to the unusual time dependences of viscosity observed[27] in toluene solutions and explained through the association of a pure stereoregular polymer.

Solutions of binary mixtures of s-PMMA and i-PMMA were prepared by mixing solutions of pure components. Both polymers dissolved quickly and without difficulties in dimethylformamide and dioxan, and somewhat more slowly in chlorobenzene.

The quality of the solvents used (Lachema, Brno) was checked chromatographically. Dioxan and chlorobenzene, both analytical grade, were simply redistilled before use. Dimethylformamide, analytical grade, was dried by distillation at reduced pressure with benzene.

Viscometry

The viscosity was measured at 25°C in capillary dilution viscometers of the Ubbelohde type with a closed circuit because of the high volatility of the solvent during disaggregation of the stereo complex, especially when heated to 90°C. The solutions were transferred into the measuring cell by using a vibrational electric pump. The flow time of the solvent was about 100 s. Both kinetic corrections and the non-Newtonian behaviour of the solvents were negligible. The intrinsic viscosity was extrapolated graphically by Heller's method[22] from the (c/η_{sp})–$(c/\ln \eta_r)/2$ vs. c plot for five concentrations.

Light scattering

The measurement was performed with a commercial Fica 40 apparatus in vertically polarized light, wavelength 546 nm, angular range 30–150°, temperature 25°C. The apparatus was calibrated with a benzene standard, the absolute scattering value of which at 90° was 21.8×10^{-6} cm^{-1}. Solutions of the individual stereo isomers were optically purified by filtration through a G5 glass filter, porosity about 1.5 μm, at elevated pressure in an argon atmosphere. The experimental data were evaluated using the respective refractive index increments dn/dc in dimethylformamide and dioxan, 0.062 and 0.07 cm^3 g^{-1}, determined for conventional PMMA (~60% syndiotactic triads). Chlorobenzene and PMMA are isorefractive; hence, observation of the formation of stereo complexes using the light-scattering method was ruled out in this case.

By heating to 70°–80°C, the stereo complex undergoes decomposition, and a molecular solution is formed[4,7]. On mixing the basic solutions of polymer components of a corresponding concentration, the mixture was heated to 85°–90°C for 20 min directly in the viscometer or in the light-scattering measuring cell. The solution was then quickly cooled in a thermostat to 25°C, and the viscosity of light scattering was measured at suitable intervals.

RESULTS AND DISCUSSION

The dependences of intrinsic viscosity on the composition of a mixture of stereo polymers in dimethylformamide and dioxan had distinct extremes at the ratio between the syndiotactic and isotactic polymer 2:1. Since, under these circumstances, there is obviously maximal aggregation, the mixture of stereo polymers at this ratio was used in the measurement of the time dependence of stereo complex formation.

The viscosity was examined as a function of time (after the initial conditions had been adjusted by heating) at several concentrations in the range 2–5×10^{-3} g cm^{-3} in

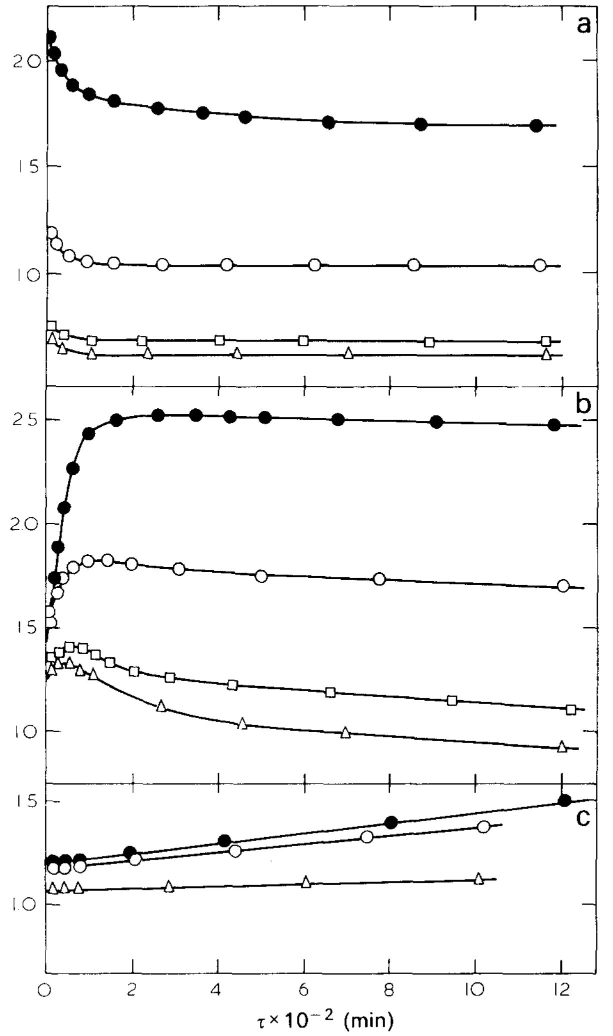

Figure 1 Dependence of reduced viscosity η_{sp}/c_m on τ at s:i = 2:1 in (a) dimethylformamide, (b) dioxan and (c) chlorobenzene for values of c_m: ●, 5×10^{-3}; ○, 4×10^{-3}; □, 3×10^{-3}; △, 2×10^{-3} g cm^{-3}

order to obtain, by extrapolating reduced viscosities, the time dependences of intrinsic viscosity as a measure of the hydrodynamic volume of aggregates. The concentration range was chosen so that the gel was still not formed at the highest concentration, while at the lowest concentration the time changes were still sufficiently large.

The dependence of reduced viscosity η_{sp}/c (where η_{sp} is the specific viscosity and c is the total polymer concentration in the mixture) on time differs for the various solvents used (*Figure 1*). With solutions in dioxan, at lower polymer concentrations the reduced viscosity increased at the beginning, reached its maximum and then decreased below the initial value. The higher the concentration of the polymer, the steeper was the initial increase in viscosity, and the maximum was shifted to longer times. In contrast, the reduced viscosity of solutions in dimethylformamide gradually decreased from the beginning of the measurement, and the decrease was steeper, the higher the concentration of the polymer. With solutions in chlorobenzene, η_{sp}/c obeyed the similar time dependence as in dioxan with the difference that the increase in viscosities was much smaller, and the maximum at the highest concentration under investigation was reached only after ten days.

Unfortunately, the time change of reduced viscosity for the particular concentrations was not uniform, and, as is pointed out below, the size of the associates depended on the total polymer concentration. This ruled out the possibility of applying both the usual experimental technique (i.e. dilution of the basic solution) and extrapolation of the time dependences of reduced viscosities of separately prepared solutions in *Figure 1* to zero concentration in order to obtain intrinsic viscosity during stabilization of the stereo complex.

The time dependences of increase in the particle mass, $M_{w,app}$, and in the apparent size (radius of gyration), $R_{z,app}$, differed depending on the solvent used (*Figure 2*). The values of the apparent parameters were determined at final concentrations given in *Table 2*. In dimethylformamide, where the complex was stabilized almost instantaneously, a very steep rise in $M_{w,app}$ was measured, while the size increase was negligible. In dioxan, both parameters were increasing more slowly, so that both the mass and size of the stereo complexes took at least two days to become stabilized (*Table 2*).

The intrinsic viscosities measured after the solutions in dimethylformamide and dioxan had been stabilized for two days lie below the additive dependence of intrinsic viscosities of pure components on the composition of the mixture (*Figure 3*) and have a minimum at the syndiotactic-to-isotactic polymer ratio of 2:1. The intrinsic viscosities of solutions in chlorobenzene, also determined after two days, lie above the additive dependence on a curve with a very flat maximum which, compared with dioxan and dimethylformamide, is shifted towards higher fractions of the isotactic polymer.

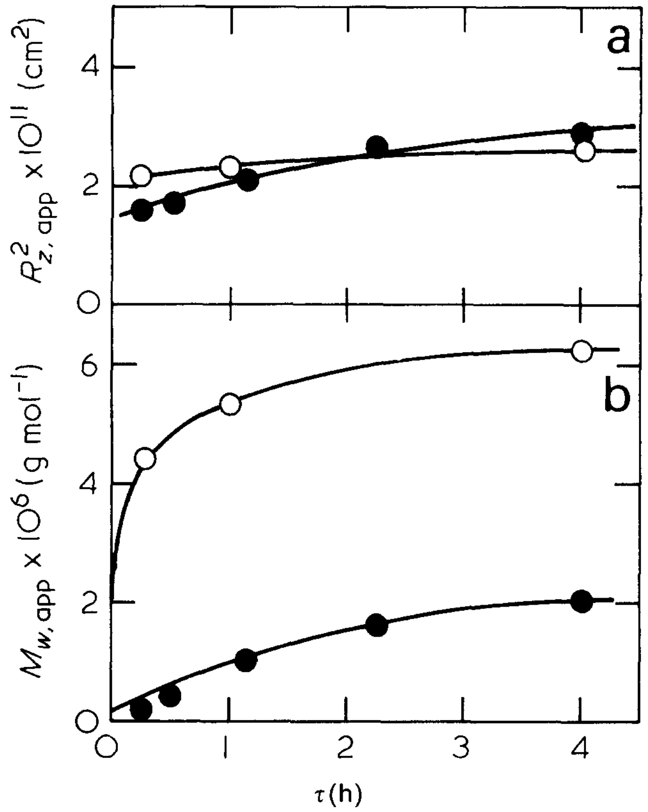

Figure 2 Dependence of (a) the apparent radius of gyration $R^{z}_{2,app}$ and (b) of the apparent particle mass $M_{w,app}$ on ψ: dioxan ($c^m \geqslant 4 x 10^{\theta 3}$ g cm$^{\theta 3}$); –, dimethylformamide ($c^m \geqslant 1 \leqslant 10^{\theta 3}$ g cm$^{\theta 3}$)

Table 2 Dependence of the apparent mass and size of stereo complexes on time τ

Solvent	$c_m \times 10^3$ (g cm^{-3})	τ (day)	$M_{w,\mathrm{app}} \times 10^{-6}$	$\overline{R^2_{z,\mathrm{app}}} \times 10^{11}$ (cm^2)	$\overline{R^2}/M$ (cm^2 g^{-1} mol)
Dioxan	2	0.17	1.8	2.15	0.12
		1	4.4	4.02	0.09
		2	7.4	5.10	0.07
		3	8.7	6.24	0.07
	4	0.01	0.4	1.7	0.42
		0.17	2.0	2.8	0.14
		1	7.0	6.4	0.09
		2	9.0	7.5	0.08
		3	10.0	8.3	0.08
Dimethylformamide	1	0.01	4.5	2.1	0.05
		0.17	6.0	2.6	0.04
		3	9.0	2.8	0.03

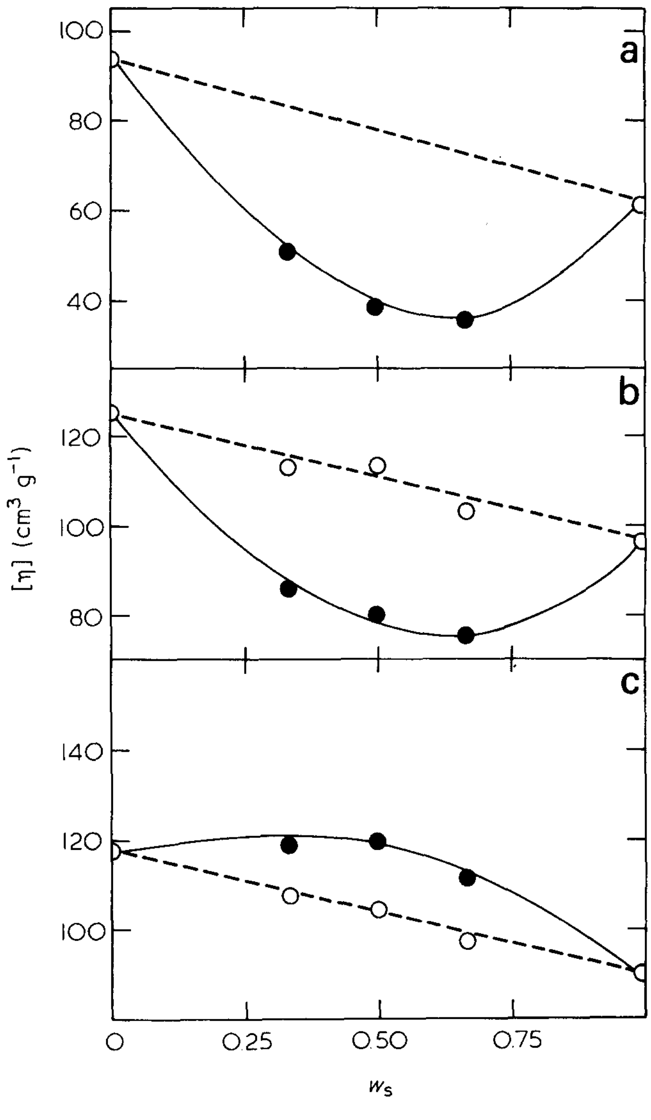

Figure 3 Dependence of the intrinsic viscosity of a mixture of polymer stereo isomers on the weight fraction of the syndiotactic component w_s at $c_m = 2 \times 10^{-3}$ g cm^{-3} in (a) dimethylformamide (b) dioxan and (c) chlorobenzene: ●, after stabilization for two days; ○, on heating; - - - -, additive dependence of intrinsic viscosities of polymer components

We also tried to measure the intrinsic viscosities at the very beginning of the time dependence after the stereo complexes had been destroyed by heating, immediately before each particular measurement. It appeared that the $[\eta]$ values measured in dimethylformamide were very close to those obtained after stabilization for two days; in dioxan and chlorobenzene the values obtained on heating lay on the additive dependence of the intrinsic viscosities of polymer components.

It can be seen from the time dependences of the particle mass and size and from the viscosity of solutions that the formation of stereo complexes in dimethylformamide proceeds very quickly. As the intrinsic viscosity measurement in this solvent, even if carried out immediately on heating, is obviously already affected by the formation of stereo complexes, the resulting values of intrinsic viscosity cannot be regarded as the additive ones. Even though the extrapolation dependences of reduced viscosity on concentration were linear, the extraordinary situation was indicated by an unusually high Huggins constant (3.4). In the other cases the Huggins constants were only slightly higher, corresponding to a polymer with flexible chain in a thermodynamically poorer solvent.

The position of intrinsic viscosities after stabilization of the dimethylformamide solution in *Figure 3* suggests that the hydrodynamic volume of stereo complexes is smaller than would correspond to a mixture of non-interacting polymer components according to the additive dependence. This means that particles of the stereo complexes are desolvated in this medium, compared with macromolecules of poly(methyl methacrylate). Scattering measurements in this solvent showed that with considerably increased mass the size of aggregates remains unchanged, i.e. that the density of monomer units increases with time, and the aggregates probably become more compact.

The intrinsic viscosity of dioxan solution on heating coincides with the additive value of the intrinsic viscosities of polymer components, which indicates that in this case aggregation is not as fast as in dimethylformamide and that the results of measurement are still adequate to characterize molecular solution without aggregates. Similarly to dimethylformamide, the intrinsic viscosity of the stabilized solution is lower than the additive value. The size of the stereo complexes, similarly to their mass, increases with time in dioxan, unlike in dimethylformamide, because desolvation of aggregates after stabilization is weaker.

The maximum which appears on the time dependences of reduced viscosity in dioxan may be explained so that the initial increase in the hydrodynamic volume due to the increasing particle mass is gradually compensated by the increasing compactness of the stereo complexes caused as a consequence of desolvation. After that, the effect of desolvation prevails and the reduced viscosity decreases.

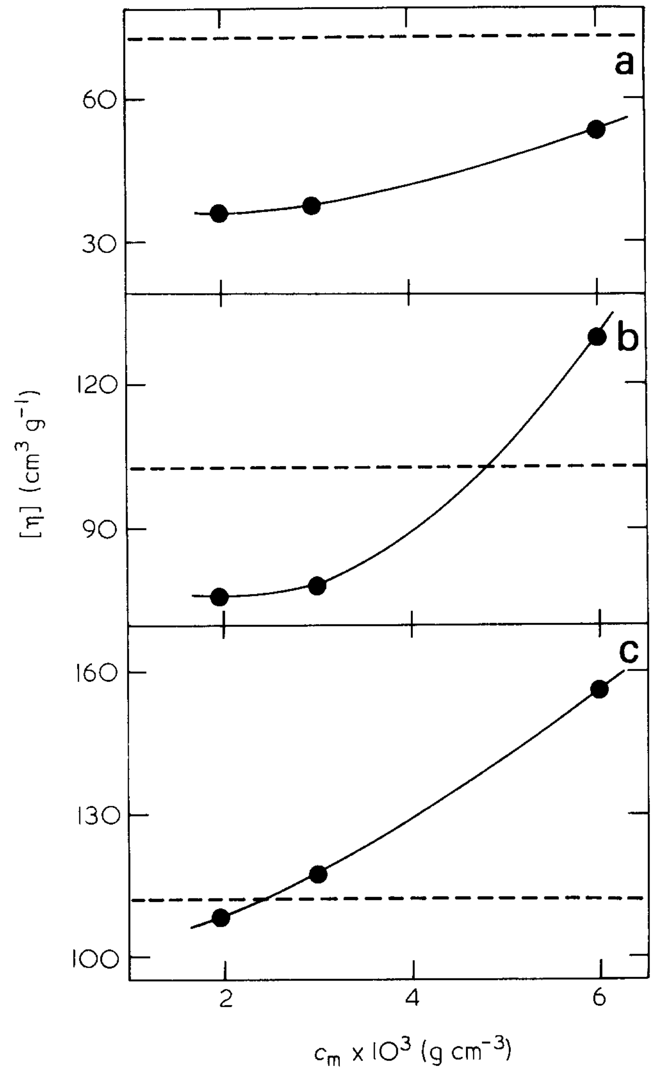

Figure 4 Dependence of the intrinsic viscosity of solutions of a mixture of polymer stereo isomers on the total initial concentration c_m at s:i = 2:1 in (a) dimethylformamide, (b) dioxan and (c) chlorobenzene: - - - -, additive value

In dimethylformamide the maximum cannot be perceived, because the complex is formed very quickly. The slight increase in reduced viscosity with time in chlorobenzene indicates that the complex formation in this solvent is much slower still than in dioxan, and that the effect of desolvation appears only after ten days. The intrinsic viscosity of solution measured immediately on heating lies on the additive dependence, similarly to dioxan (*Figure 3*). Standing for two days is not sufficient to bring about stabilization of stereo complexes in chlorobenzene. The intrinsic viscosity of the chlorobenzene solution after standing for two days represents the hydrodynamic volume of aggregates with increased particle mass in which desolvation has not yet occurred.

It would seem that deviations of the intrinsic viscosities measured in stabilized solutions of stereo polymers from the additive values may indicate the formation of stereo complexes or its intensity in various solvents. This assumption is not correct, however, as one should bear in mind that the size of stereo complexes, and hence the intrinsic viscosity, also depend on the total polymer concentration at mixing, c_m. It has been reported[15] that, according to light-scattering measurements, the apparent mass of aggregates in dimethylformamide increases with c_m. Also, the intrinsic viscosity[4] determined in the same solvent (but at a reverse ratio of the polymer components) has been found to be higher, the higher the initial concentration. Our solutions behaved similarly in all the solvents used (*Figure 4*).

Figure 4 shows that the position of the point corresponding to the $[\eta]$ value of the stereo complex determined after stabilization may be arbitrary with respect to the additive value of pure polymer stereo isomers, depending on the chosen c_m; the agreement between $[\eta]$ and the additive value does not mean that no aggregation occurred.

A complete idea about the hydrodynamic behaviour of the stereo complex can be obtained only by correlating the intrinsic viscosity $[\eta]$ with the real mass M_w and with the real value of the radius of gyration R_z as the dependence on the total polymer concentration in solution after mixing c_m (*Table 3*). When determining both $[\eta]$ and M_w and R_z, extrapolations to infinite dilution were carried out, because the stabilized stereo complex is not disaggregated by dilution (the second virial coefficient is positive and the character of scattering envelopes remains unchanged by dilution (*Figure 5*)). The dependence of desolvation of stereo complexes on the solvent used and on the total concentration of polymers in the mixture can be seen in *Table 3*. While the additive values of both quantities ($[\eta]$, R_z) for pure components are higher than those calculated for the θ-temperature, the values for the stereo complexes are lower.

Combination of the Meyerhoff[24] and Flory theories[25] shows that the ratio between the hydrodynamic volume and the particle size $[\eta]M/(\overline{R^2})^{3/2}$ may be regarded as a criterion of compactness or of the hydrodynamic character of the particle. For a compact sphere this ratio is roughly 3.5 times higher than for a non-draining polymer coil. In the concentration range in dioxan under in-

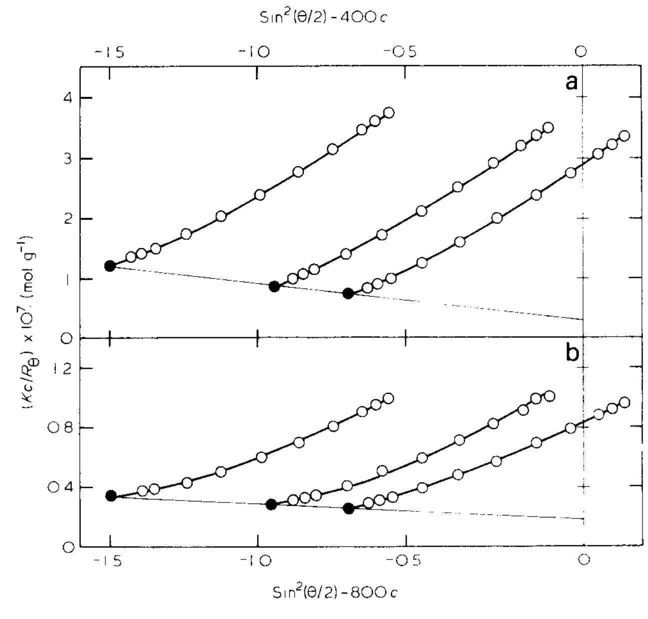

Figure 5 Scattering diagram of stabilized stereo complexes in (a) dioxan (c_m = 4 x 10^{-3} g cm^{-3}) and (b) dimethylformamide (c_m = 2 x 10^{-3} g cm^{-3})

Table 3 Characteristics of stabilized stereo complexes

Solvent	$c_m \times 10^3$ (g cm^{-3})	$M_w \times 10^{-6}$ (g mol^{-1})	$R_z^2 \times 10^{11}$ (cm^2)	$[\eta]$ (cm g^{-1})	$R_{z,\theta}^2 \times 10^{11}$ (cm^2)	$[\eta]_\theta$ (cm g^{-1})	$\frac{[\eta]M}{(R_z^2)^{3/2}} \times 10^{-24}$ (mol^{-1})
Dioxan	Additive	0.525	1.25	127	0.45	41	1.51
	2	9.0	5.71	75	7.83	172	1.56
	4	33.3	15.48	88	29.20	338	1.51
Dimethylformamide	Additive	0.525	0.94	94	0.45	41	1.7
	1	10	3.0	37	8.70	182	2.3
	2	50	7.3	36	43.95	414	2.9

Values under θ-conditions calculated for PMMA with normal distribution (M_w/M_n = 2) in 2-ethoxyethanol at 27°C (cf. ref.23)
Additive (R_z^2) values calculated for PMMA with given M_w and normal distribution

vestigation ($2\times10^{-3} \leqslant c_m \leqslant 4\times10^{-3}$), $[\eta]M/(\overline{R^2})^{3/2}$ is constant. This means that the hydrodynamic character of stereo complexes remains unchanged by desolvation in this case. In dimethylformamide where c_m is lower ($1\times10^{-3} \leqslant c_m \leqslant 2\times10^{-3}$), $[\eta]M/(\overline{R^2})^{3/2}$ increases (*Table 3*). Desolvation renders the particles more compact and their hydrodynamic character changes.

Since, as has been shown, stereo complexes differ in their desolvation from the linear coil and, moreover, in the particular solvents the measure of their desolvation and the hydrodynamic character (compactness of the particles) may be different, the only reliable criterion of their formation or of its intensity in various solvents appears to be the mass value of stabilized stereo complexes, M_w.

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