Association of stereoregular poly(methyl methacrylates): 5. Stereo-complex formation in dilute solutions

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Further study was carried out on the stereocomplex formation in dilute solution using viscometry, osmometry, light scattering and gel permeation chromatography. It appears that the process can be divided in two steps. The primary step involves the formation of very compact particles by association of several isotactic and syndiotactic PMMA chains in a base-molar ratio of 1/2. The radius of gyration of these particles remains about the same as the additive value of the original components, whereas their molecular weight increases. The secondary step involves the aggregation of the particles which is reflected by an increase of the radius of gyration. It is proposed that this aggregation is caused by interparticle stereo-association of noncomplexed chain parts.

INTRODUCTION

The phenomenon of stereocomplex formation of isotactic and syndiotactic poly(methylmethacrylate) (it- and st-PMMA) has been much investigated in the past[1-14]. It has been established that the stereocomplex is formed by isotactic and syndiotactic sequences with a basemolar ratio iso/syndio of 1/2[15]. It has been found by Bosscher *et al.*[16] that the ester group of the isotactic chain and the α-methylgroup of the syndiotactic chain are responsible for the complex formation.

Stereocomplex formation occurs in bulk as well as in solution. In solution three solvent groups were distinguished[3]: the strongly complexing type A, the weakly complexing type B and the non-complexing type C.

In strongly complexing solvents it-PMMA can function as a template in the polymerization of MMA, which leads to the predominant formation of st-PMMA[17,18].

The stereocomplex recovered from mixtures in bulk or dilute solution appears to be partly crystalline, but until now it has not been possible to establish the exact crystal structure[19,20]. The difficulty in solving this problem is that the crystalline part is not sufficiently large due to interfering effects like gel formation. In the present study, investigations were carried out on the complex formation in dilute and very dilute solutions in order to get an idea about the structure under conditions where techniques like viscometry, osmometry, light scattering and gel permeation chromatography are applicable.

EXPERIMENTAL

Data on the PMMA polymers used are listed in *Table 1*. These polymers were prepared and characterized in the same way as described before[15]. Reduced viscosities of mixed solutions were measured shortly after mixing the separate solutions in a Lauda viscometer (Schott u. Gen., Mainz) at 25°C. The osmotic pressure measurements were performed with a Knauer automatic osmometer at 34°C. The light scattering experiments were performed at 25°C on very dilute solutions, freed from dust by normal procedures, with a Malvern light scattering photometer, equipped with a He–Ne laser. Corrections were made for the time difference between the measurements at different angles. The radius of gyration (R_g) of the complex was calculated from the angular dependence of the scattering at low concentration by using a Guinier plot[21], in which the logarithm of the Rayleigh ratio (ln R_θ) is plotted against $\sin^2(\theta/2)$. Because of the strong concentration dependence of the complex formation, it was not possible to apply the normal Zimm procedure of extrapolation to concentration zero for evaluation of R_g. However, because of the low concentrations we can assume the calculated radii of gyration to be correct within experimental error. The solvent used in all experiments was DMF, which is a strongly complexing solvent of type A. The refractive index increments (dn/dc) of the PMMA's and the stereocomplex were determined with a Zeiss–Jena interferometer. Gel permeation chromatography (g.p.c.) was performed on a Waters 150 C apparatus equipped with two μ-Bondagel columns (E-125, E-1000). The flow rate was kept at 1 ml/min and the temperature at 35°C.

RESULTS

To unravel the mechanism of the stereocomplex formation we measured the influence of the concentration of the components by different methods in dilute and very dilute solutions. *Figure 1* shows the viscosity vs. concentration of a mixture of it-1 and st-1 with ratio it/st $=1/2$ in DMF. We see that η_{sp}/c of the mixture is much lower than the additive value at low concentrations and increases at higher concentrations due to gel formation. Extrapolation towards $c=0$ leads to $[\eta]$ of the stereocomplex (*Table 2*). The measurements of the

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Table 1 Data of applied PMMA's

Code	$\bar{M}_w \times 10^{-5}$	$\bar{M}_n \times 10^{-5}$	$\bar{M}_v \times 10^{-5}$	*i–h–s*
it–1	5.8		5.4	94–4–2
it–2	1.5	0.7	1.2	96–3–1
it–3	2.0	1.0	1.6	96–3–1
st–1	5.0		3.7	1–10–89
st–2	1.5	0.74		1– 3–96

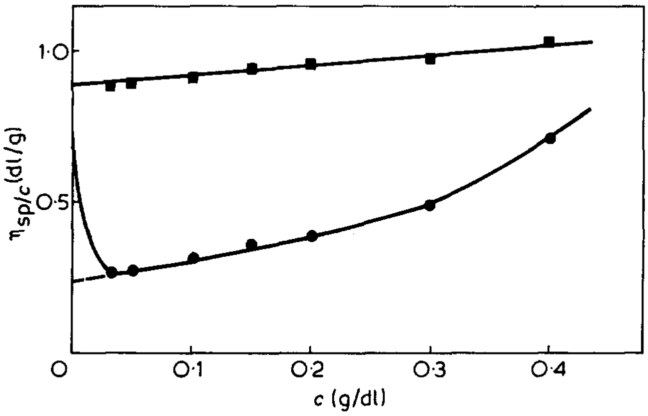

Figure 1 Reduced viscosity (η_{sp}/c) as a function of total concentration *c* for mixtures of it–1 and st–1 with ratio 1/2 in DMF at 25°C, measured 30 min after mixing. For comparison the additive values are also indicated (■)

Table 2 Data obtained by viscometry, light-scattering and osmometry on mixtures of it– and st–PMMA with a ratio of 1/2

	it–1/st–1	it–2/st–2
Additive value		
$[\eta]$ dl/g	0.895	0.31
$\bar{M}_w \times 10^{-5}$	5.3	1.5
$\bar{M}_n \times 10^{-5}$	–	0.72
R_g (nm)	34	27
1 hour after mixing		
$[\eta]$ dl/g	0.245	0.173
$(\bar{M}_w)_{app} \times 10^{-5}$	100*	12**
$(\bar{M}_n) \times 10^{-5}$	–	4.3
R_g (nm)	36	27
1 day after mixing		
$[\eta]$ dl/g	–	1.15
$(\bar{M}_w)_{app} \times 10^{-5}$	190*	29**
R_g (nm)	53	36

* Measured at $c = 0.06$ g/dl
** Measured at $c = 0.086$ g/dl

complex were performed 30 min after mixing and the results are typical for this kind of mixture within the first hour. It is known that η_{sp}/c will increase again with time and will finally rise above the additive value. This effect can also be attributed to gel formation.

In *Figure 2* the reduced osmotic pressure is plotted against the concentration for it-2, st-2 and their 1/2 mixtures. Measurements were done 45 min after mixing in DMF. Extrapolation towards $c = 0$ yields the value of $\bar{M}_n$ for the stereocomplex given in *Table 2*. *Figure 3* presents the apparent molecular weight, $(\bar{M}_w)_{app}$, of very dilute mixtures of it-1 and st-1 with ratio it/st = 1/2 vs. the concentration, 45 min after mixing. The influence of time on the complex formation can be seen from *Figure 4*. $(\bar{M}_w)_{app}$ increases rapidly within the first few minutes after mixing to a value which is a multiple of the additive one. However, the radius of gyration (R_g), calculated from the angular dependence of the scattered light intensity, does not increase (*Table 2*). Moreover, this intensity shows a linear dependence on the angle over the whole range ($\theta = 15°–140°$) during the first hour after mixing. After a long time R_g starts to increase and the Guinier plot shows an upward curvature at low angles (mixture it-1/st-1), which means that larger particles are formed (*Table 2*, after 1 day).

Figure 5 shows the g.p.c. chromatograms of it-3, st-2 and the 1/2 mixture, respectively. It appears that the complex-peak does not stay at the same place, but moves slowly towards shorter elution times. After complexation times longer than 1 h the particles are completely

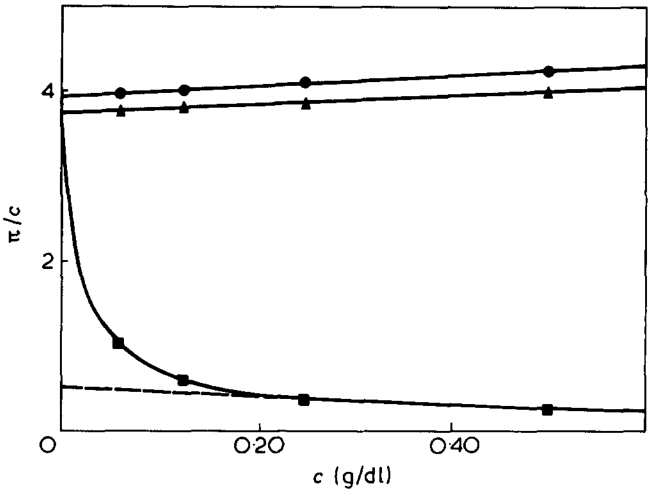

Figure 2 Reduced osmotic pressure π/c as a function of total concentration *c* for it–2 (●), st–2, (▲) and their 1/2 mixtures (■), in DMF at 35°C, 45 min after mixing

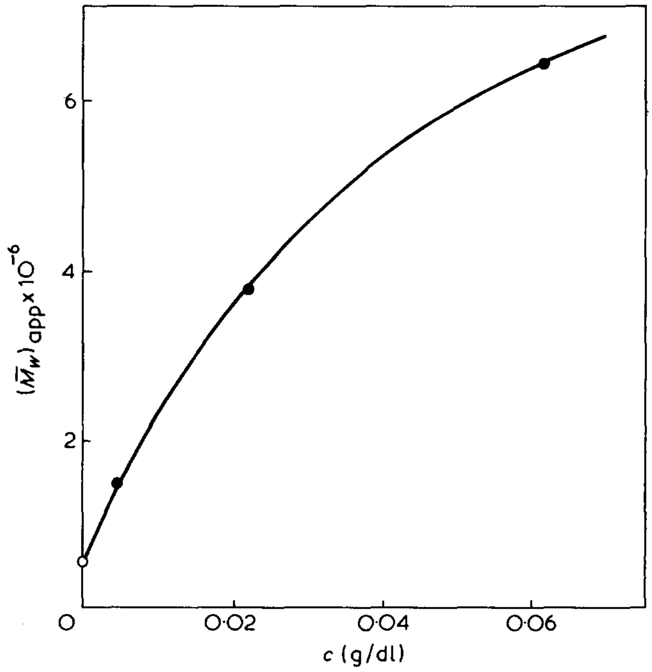

Figure 3 Apparent weight average molecular weight $(\bar{M}_w)_{app}$ vs. concentration for mixtures of it–1 and st–1 with ratio 1/2 in DMF at 25°C, measured 45 min after mixing. ((○) calculated additive value)

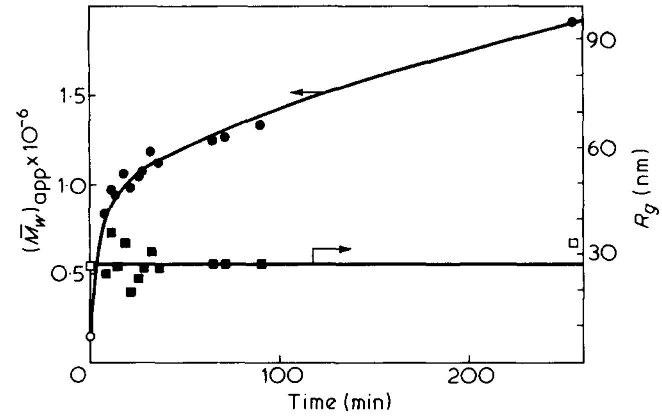

Figure 4 Apparent weight average molecular weight $(\bar{M}_w)_{app}$ and radius of gyration (R_g) plotted against time after mixing it–2 and st–3 with ratio 1/2 at 0.086 g/dl (25°C, DMF, (□, ○): calculated additive values)

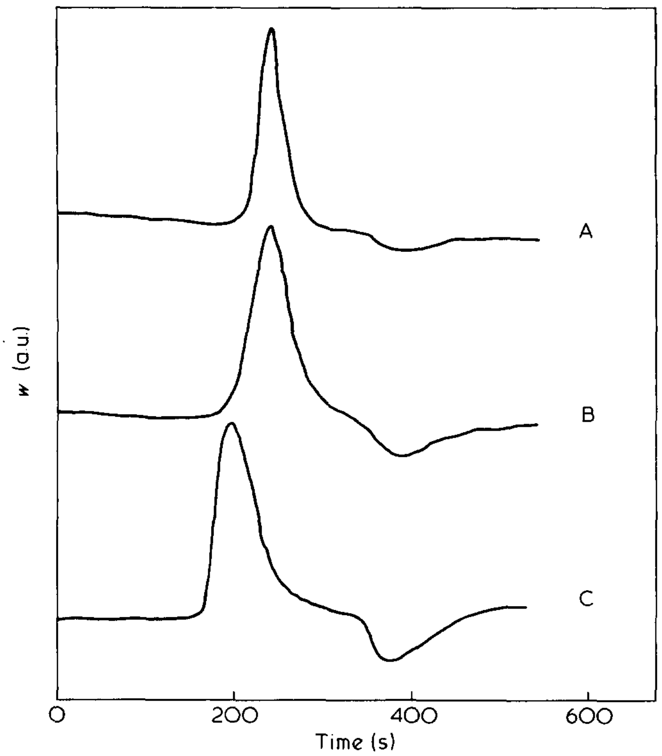

Figure 5 G.p.c. chromatograms of it–3, (A); st–2, (B) and their 1/2 mixture (C)

excluded from the column. From the column capacities (maximum pore size) we could estimate the radius of the excluded complex particles to be above 50 nm.

DISCUSSION

When it- and st-PMMA coils penetrate each other, segments of stereocomplex are formed initiated by cooperative attractive van der Waals forces between complementary it- and st-segments. Consequently, the interaction with the solvent deteriorates and shrinkage of the coils takes place. So, compact particles are formed which leads to a reduction of the measured viscosity of the solution (*Figure 1*).

From the increase of $\bar{M}_n$ (*Figure 2*) and $\bar{M}_w$ (*Figure 3*) we see that several it- and st-PMMA chains are involved in the formation of one primary particle. In spite of this increase in molecular weight the radius of gyration of the particles does not increase. The shift of the peak in the g.p.c. chromatogram indicates that the particles are larger than the coils of it- and st-PMMA themselves. This seems to be in contradiction with the constancy of the radius of gyration. However, in the calculation of $R_g \equiv(\Sigma m_i r_i^2/\Sigma m_i)^{1/2}$, with m_i the weight segment i at distance r_i from the centre of gravity, the heaviest parts of the particle contribute most, whereas in g.p.c. the hydrodynamic volume of the whole particle is important. If we assume that the primary complex particles consist of a core in which the chains are packed close together to start a kind of crystallization of stereocomplex and an outer sphere in which chains are still free, this implies that R_g can be small compared to the enveloping dimensions of the whole particle.

Figure 6 depicts a sketch of this so-called primary stereocomplex particle. We consider such a particle to be composed of double helices in which the radius of the st-PMMA helix is larger than that of it-PMMA, in accordance with the stereocomplex composition it/st $= 1/2$. As complementary chains never completely cover each other, more it- and st-chains enter the particle in order to associate with complementary free chain parts. In this way about a 10-fold increase in molecular weight is possible (see *Table 2*, after 1 h). Parts of the chains which are protruding into the solution can be non-associated and interparticle stereo-association of these parts will probably start the secondary process: aggregation of particles to larger ones. In this process step the association is much weaker, as can be seen from the study of De Boer[20], who showed that it was possible to break the contacts between the primary particles by ultrasonic waves. The secondary process is accompanied by an increase of viscosity and radius of gyration (*Table 2*, after 1 day). The same phenomenon is observed from the

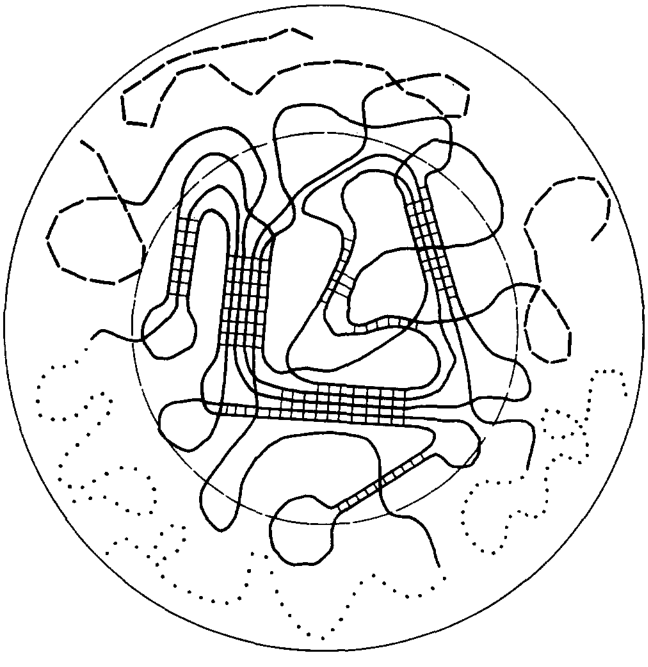

Figure 6 Schematic drawing of a primary stereocomplex particle. The solid lines represent double helices of stereocomplex showing local ordering in small 'crystallites'. The dotted and broken lines are free chain parts of it– and st–PMMA, respectively, which protrude from the ends of the double helices

beginning when larger concentrations are used, which is quite understandable.

REFERENCES

1 De Boer, A. and Challa, G. *Polymer* 1976, **17**, 633
2 Feitsma, E. L., de Boer, A. and Challa, G. *Polymer* 1975, **16**, 515
3 Challa, G., de Boer, A. and Tan, Y. Y. *Int. J. Polym. Mater.* 1976, **4**, 239
4 Liu, H. Z. and Liu, K. I. *Macromolecules* 1968, **1**, 157
5 Van den Berg, W. B., Hymans, B., Piet, P. and Heikens, D. *Nature* 1968, **217**, 949
6 Borchard, W., Pyrlik, M. and Rehage, G. *Makromol. Chem.* 1971, **145**, 449
7 Liquori, A. M., de Santis, P., Savino, M. and D'Alagni, M. *Polym. Lett.* 1966, **4**, 943
8 Chiang, R., Burke, J. J., Threlkeld, J. O. and Orofino, T. A. *J. Phys. Chem.* 1966, **70**, 3591
9 Spěvăcek, J. and Schneider, B. *Makromol. Chem.* 1974, **175**, 2939
10 Spévácek, J. and Schneider, B. *Makromol. Chem.* 1975, **176**, 729
11 Dayantis, J., Reiss, C. and Benoit, H. *Makromol. Chem.* 1968, **120**, 113
12 Biros, J., Mása, Z. and Pouchlý, J. *Eur. Polym. J.* 1974, **10**, 629
13 Pyrlik, M., Borchard, W., Rehage, G. and Uerpmann, E. P. *Angew. Makromol. Chem.* 1974, **36**, 133
14 Borchard, W., Kalawrytinos, G., Mohadjer, B., Pyrlik, M. and Rehage, G. *Angew. Makromol. Chem.* 1973, **29/30**, 471
15 Vorenkamp, E. J., Bosscher, F., Challa, G. *Polymer* 1979, **20**, 59
16 Bosscher, F., Keekstra, D. W. and Challa, G. *Polymer* 1981, **22**, 124
17 Buter, R., Tan, Y. Y. and Challa, G. *J. Polym. Sci., Polym. Chem. Edn.* 1973, **11**, 2975
18 Gons, J., Vorenkamp, E. J. and Challa, G. *J. Polym. Sci., Polym. Chem. Edn.* 1975, **13**, 1699
19 Liquori, A. M., Anzuino, G., Coiro, V. M., D'Alagni, M., de Santis, P. and Savino, M. *Nature* 1965, **206**, 358
20 De Boer, A., *Thesis*, Groningen, 1976
21 Guinier, A. and Fournet, G., 'Small Angle Scattering of X-rays', John Wiley, New York, 1955, p 126