Stereocomplexation of stereoregular poly(methyl methacrylate)s: 9. Temperature and time dependence of the process of complexation

E. Schomaker, E. J. Vorenkamp and G. Challa
Laboratory of Polymer Chemistry, State University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

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The dependence on temperature, time and concentration of the process of stereocomplexation of it- and st-PMMA in dilute solutions in DMF was investigated by means of viscometry. On raising the temperature, DMF changes from a strongly complexing to a weakly complexing solvent and eventually into a non-complexing solvent. In a strongly complexing solvent the process of complexation consists of three stages: complexation, association of complexled chain sections and aggregation of particles containing associates. The first two stages, indistinguishable with viscometry in a strongly complexing solvent, can be observed separately at higher temperatures. In a weakly complexing solvent neither association nor aggregation occurs. In DMF st-PMMA has a more compact conformation in comparison with it-PMMA, which influences the symmetry of the process of complexation with regard to the stoichiometric ratio.

(Keywords: stereocomplexes; poly(methyl methacrylate); complexation time dependence; complexation temperature dependence)

INTRODUCTION

The phenomenon of stereocomplexation between isotactic (it) and syndiotactic (st) poly(methyl methacrylate) has been the subject of extensive investigations over a period of about 25 years[1-27]. Nevertheless, it was only recently that Vorenkamp *et al.* proved convincingly the complexation stoichiometry to be: it/st = 1/2[17].

Bosscher *et al.* found that the ester group of the isotactic chain and the α-methyl group of the syndiotactic chain are involved in the process of complexation and they suggested for the structure of the complex a double-helix, consisting of a 30/4 it-helix, surrounded by a 60/4 st-helix[19,23].

Stereocomplexes are formed in solution as well as in bulk. With respect to dilute solutions, one can distinguish three kinds of solvents: strongly, weakly and non-complexing, respectively called solvent types A, B and C[15].

From the results of recent investigations on the complexation between it- and st-PMMA in dilute solutions, one can deduce that in case of a strongly complexing solvent (type A) three stages can be distinguished:

(i) Complexation: When dilute solutions of it- and st-PMMA are mixed, stereocomplexes are formed locally, with a it/st = 1/2 stoichiometry[17].

(ii) Association: After complexation, the complexed chain sections associate, leading to very compact particles of an order of magnitude of some tenths of a nanometre[16,20,25,26].

(iii) Aggregation: The third stage is characterized by aggregation of the particles formed in stage two, eventually followed by flocculation[20].

Apart from the first stage of complexation this picture is almost identical to the one Sĕdláček *et al.* have proposed for the self-association of st-PMMA in dilute solutions[28].

In order to confirm the mechanism described above and to study the influence of temperature on the entire process of complexation, the viscosity of mixed dilute solutions of it- and st-PMMA was measured as a function of temperature, mixing ratio and time after mixing in dimethylformamide (DMF), which is a solvent of the strongly complexing type. Furthermore, in order to study the complexation behaviour at the borders of the regime of dilute solution, an area hitherto almost unexplored, we also measured the viscosity of mixed solutions of it- and st-PMMA as a function of concentration, up to the critical coil-overlap concentration.

EXPERIMENTAL

Materials

Data on the PMMA samples used are listed in *Table 1*. All it-PMMA's were synthesized in toluene with phenylmagnesium bromide as catalyst[29]. The syndiotactic samples were obtained by means of Ziegler–Natta polymerization in toluene using triethylaluminium and titanium tetrachloride as catalysts at −78°C [30]. It-1, it-2 as well as st-1 and st-2 were obtained by means of fractionation of synthesized samples using acetone as solvent and water as precipitant.

The tacticities were derived from the α-methyl peaks obtained for 3 wt% solutions in *o*-dichlorobenzene at 120°C by means of 200 MHz n.m.r. spectroscopy with a Nicolet NT-200. The molar masses were determined by gel permeation chromatography (Waters ALC/GPC 150 C equipped with 2 TSK GMH 6 columns) using THF as an eluent, relative to polystyrene standards.

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Viscometry

Viscosities of mixtures of it- and st-PMMA in DMF were measured using an Ubbelohde microviscometer (Schott KPG type Ic) in conjunction with a Lauda viscotimer (Schott). Corrections for non-Newtonian effects and loss in kinetic energy were negligible.

Table 1 Data on the PMMAs used

Polymer	$\bar{M}_w$	$D(=\bar{M}_w/\bar{M}_n)$	i:h:s (%)
it-1	6.8×10^5	1.40	i>95
it-2	4.0×10^5	1.10	i>95
it-3	3.8×10^5	4.90	94–4–2
st-1	7.5×10^5	1.40	1–8–91
st-2	3.2×10^5	1.20	0–13–87
st-3	3.3×10^5	4.30	1–10–89

Light scattering

Light scattering measurements were performed at 25°C using a Malvern light scattering photometer in combination with a He–Ne laser. The radius of gyration of the associates was calculated by means of a Guinier plot-procedure (see also ref. 20).

RESULTS AND DISCUSSION

Temperature dependence

In *Figures 1a–d* the reduced relative deviation from the additive value of the viscosity (η^a_{red}) is plotted as a function of time after mixing solutions of it-1 and st-1 at various temperatures at four different mixing ratios. η^a_{red} is defined as:

$$\eta^a_{red} \equiv (\eta - \eta^a)/\eta^a c \qquad (1)$$

wherein c stands for the total polymer concentration of

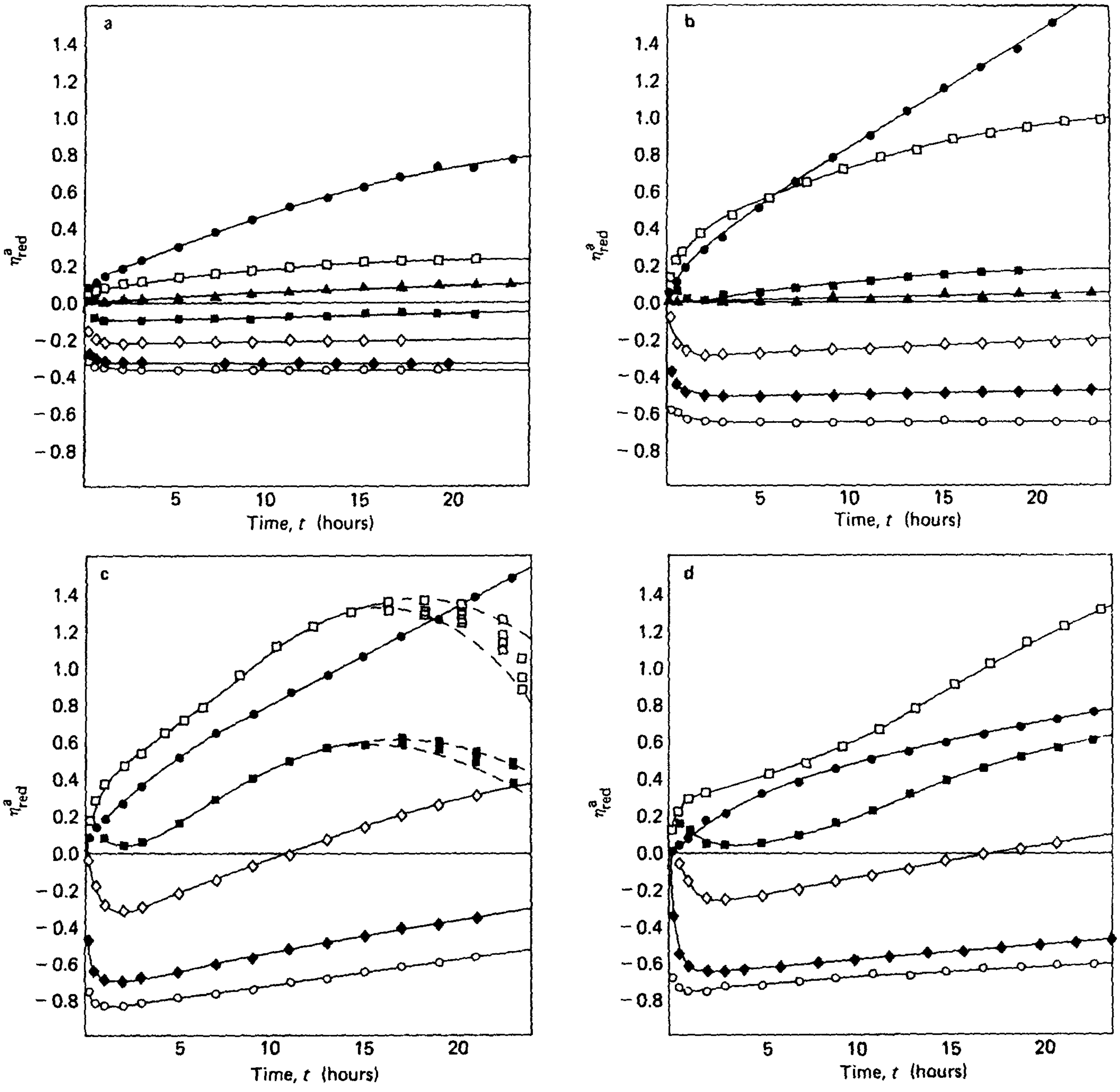

Figure 1 η^a_{red} as a function of time after mixing, at a mixing ratio of (a) it-st = 2:1, (b) 1:1, (c) 1:2, (d) 1:4 at temperatures of (○) 30°C; (◆) 40°C; (◇) 50°C; (■) 55°C; (□) 60°C; (●) 70°C; (▲) 80°C. The polymers used are it-1 and st-1. $c = 0.2$ g/dl DMF

the mixed solutions in DMF and η^a is the additive value of the viscosity defined as:

$$\eta^a = x_s\eta_s + (1-x_s)\eta_i \qquad (2)$$

Here η_i and η_s are the viscosities of the solutions of it- and st-PMMA respectively, of the same concentration c before mixing, and x_s is the fraction of st-PMMA in the mixed solutions, based on the total amount of polymer.

At low temperatures ($T \leqslant 40°C$) a strong decrease in η^a_{red} can be observed immediately after mixing dilute solutions of it-PMMA and st-PMMA in DMF. The reason is that DMF is a solvent of the strongly complexing type A at low temperatures, which means that DMF is neither a very good solvent for it- and/or st-PMMA, nor for the complex. Consequently after complexation, the complexed chain sections will immediately associate, leading to very compact particles. In case of an excess of one of the components with respect to the stoichiometric ratio the particles will be stabilized sterically, as the uncomplexed parts of the component in excess will be found at the outside of the particles, forming a shell preventing these particles from aggregating. Consequently after the initial decrease, η^a_{red} remains constant. However, when dilute solutions of it- and st-PMMA are mixed in a stoichiometric ratio the particles formed will not be sterically stabilized and aggregation is possible. So, after the initial decrease η^a_{red} will increase again slowly, as observed. In addition we measured the radius of gyration of the (aggregated) particles by means of light scattering as a function of the mixing ratio and the time after mixing (*Figure 2*). As expected from the mechanism proposed above a strong increase in the radius of gyration is found around the stoichiometry ratio ($x_s = 0.67$).

At higher temperatures ($T \simeq 40°C$–$50°C$) the initial decrease of η^a_{red} after mixing is less pronounced because complexation as well as association are exothermic processes[26]. Complexation will produce less perfect complexes containing more loops and tails which, on the condition that they are long enough, can also complex with other complementary chain sections. Only when there are enough complexed chain sections sufficiently close to each other will association be favourable. Up to about 50°C association occurs rapidly enough for only an immediate decrease of η^a_{red} after mixing to be seen. However, between about 50°C–60°C, complexation and association become distinguishable and an initial increase in η^a_{red} due to complexation followed by a decrease due to subsequent association is observed. In dioxane which is known to be a moderately complexing solvent (between type A and B), the same phenomena are already observed at room temperature[25], which is completely in line with the above reasoning. At the aggregation stage a faster increase in η^a_{red} of the solutions is observed at higher temperatures up to 60°C. In the case of solutions with the stoichiometric mixing ratio the increase in η^a_{red} is eventually followed by a decrease, while the solution becomes inhomogeneous as a result of flocculation (see *Figure 1c*). These observations can be explained by the fact that at higher temperatures the particles formed, containing less complete complexes, have a less compact conformation. Aggregation of these particles with a larger hydrodynamic volume results in a faster and stronger increase in η^a_{red}, especially at the stoichiometric ratio, in which case steric stabilization is absent.

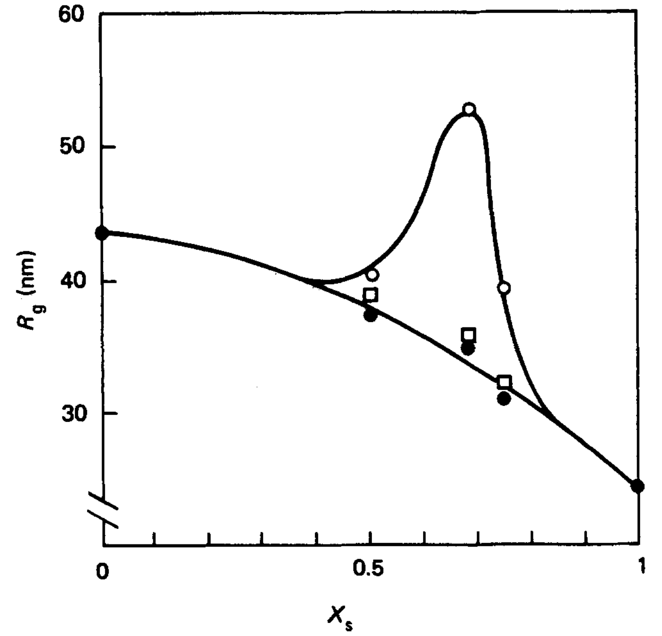

Figure 2 Radius of gyration of the (aggregated) associates at 25°C, 10 min (●), 90 min (□) and 1 day (○) after mixing. The polymers used are it-3 and st-3. $c = 0.62$ g/dl DMF

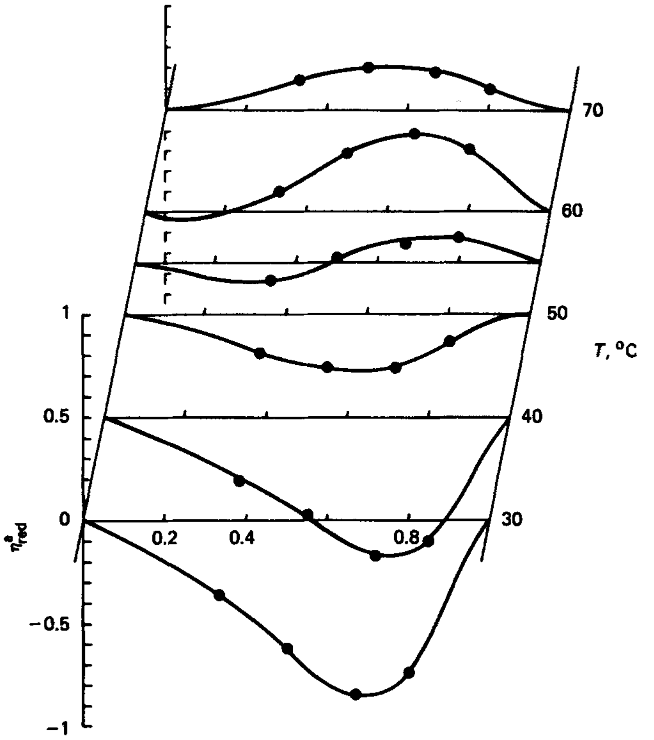

Figure 3 η^a_{red} as a function of mixing ratio and temperature, measured one hour after mixing solutions of it-1 and st-1. $c = 0.2$ g/dl

At still higher temperatures ($T \simeq 60°C$–$80°C$) only a continuous increase in η^a_{red} is observed whilst the deviation from additivity has a maximum at a mixing ratio approaching it/st = 1:1, as shown in *Figure 3*. Both observations are characteristic of complexation in a solvent of the weakly complexing type B[15]. In such a solvent only relatively short sequences of the chains will complex, whilst the remaining sections form loops and tails, which can complex with complementary chain sections of other chains. Consequently a network with relatively loose junctions is formed. Association is no longer favourable, which accounts for the continuous increase in η^a_{red}. Under these conditions, one can expect a maximum complexation at a mixing ratio of it/st = 1/1, as shown by ten Brinke *et al.*[27]. Lastly, at temperatures above 80°C, no further interaction is observed and DMF has become a solvent of type C.

Asymmetry of dependence on mixing ratio

The influence of the mixing ratio was partly discussed in the previous section; however, a remarkable feature so far has been neglected. The behaviour of a (it/st = 1/4) mixture with respect to viscosity appears to be comparable with the behaviour of a 1/2-mixture rather than a 1/1 mixture, which would be expected on account of symmetry with respect to the stoichiometry ratio (1/2). However, it is well known that the behaviour, in solution, of it- and of st-PMMA are very different, it-PMMA being far more flexible than st-PMMA[31]. On the other hand the characteristic ratio c_∞, defined by the unperturbed dimensions, is much larger for it-PMMA than for st-PMMA[32-36]. Depending on temperature, values of c_∞ in the case of it-PMMA vary between 9.2 and 10.2 whereas for st-PMMA values between 7.3 and 8.4 are found. On account of these values one can expect a difference of a factor 1.25–1.75 in the intrinsic viscosity under θ-conditions.

In *Figure 4* the intrinsic viscosity of solutions of it- and st-PMMA of comparable molar masses is shown as a function of temperature. Although the considerations in terms of c_∞ given above are fundamentally valid only under θ-conditions, they suffice to explain the large difference in intrinsic viscosity.

It should be noted that in some solvents like toluene, *o*-dichlorobenzene and butyl acetate, it- and/or st-PMMA has a tendency for self-association[28], which might also give rise to a difference in the hydrodynamic behaviour. However Spěváček found at a rather high concentration of 1 g/dl in DMF only a slight and comparable tendency to form self-associates for both it-PMMA and st-PMMA[37]. Consequently self-associatuion cannot be the explanation for the large difference observed in intrinsic viscosity.

Another indication that the explanation in terms of c_∞ given above is correct is the fact that while the intrinsic viscosity of it-PMMA remains almost constant with rising temperature, the intrinsic viscosity of st-PMMA increases. Sundararajan and Flory have calculated that $d\ln c_\infty/dT$ is negative in the case of it-PMMA and positive in the case of st-PMMA[35]. Taking into account that no θ-conditions were employed, the difference in behaviour is in agreement with their calculations.

The observed difference in hydrodynamic volume will also influence the process of complexation. In the case of an excess of one of the components with respect to the stoichiometric ratio, chain sections of the component in excess will be found at the outside of the particles formed. As this shell contributes considerably to the hydrodynamic volume of the entire particle, it is to be expected that particles with a mainly syndiotactic shell will have a relatively smaller hydrodynamic volume than those with a shell of mainly isotactic chain sections, especially at low temperatures. This might explain the fact that the decrease in viscosity at low temperatures is stronger in case of an 1 it/4 st mixing ratio, compared with a 1/1 mixing ratio.

Dependence on concentration

It is well known that on raising the concentration of mixtures of it- and st-PMMA in DMF the viscosity eventually rises above the additive value, whilst the minimum at a 1/2 mixing ratio eventually changes into a maximum at a mixing ratio of about 1/1[20,22]. The reason for this is that when the concentration of the solution approaches the critical coil-overlap concentration, locally a network is formed which extends over the entire solution when the critical concentration is exceeded. The junctions of the network are formed, according to Rehage *et al.*, by microcrystallites[22], which should be interpreted

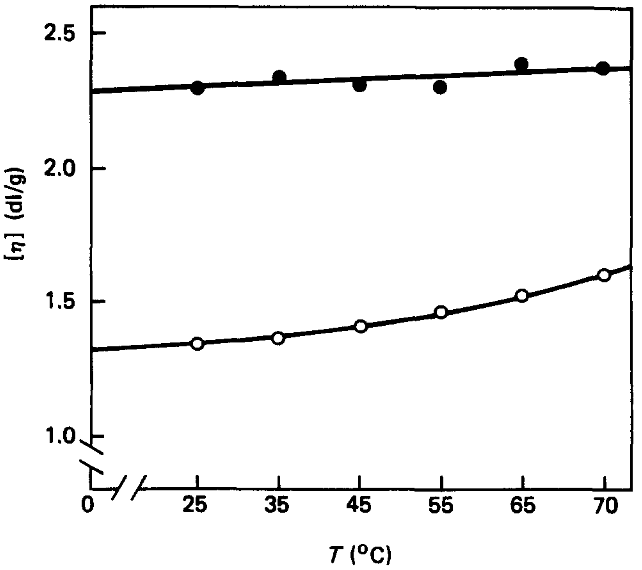

Figure 4 Intrinsic viscosity of it-2 (●) and st-2 (○) as a function of temperature

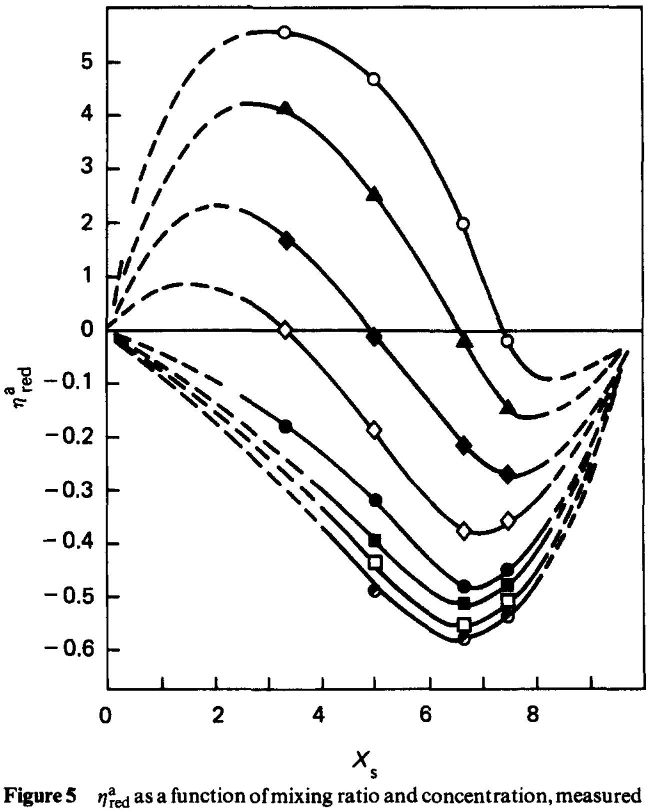

Figure 5 η^a_{red} as a function of mixing ratio and concentration, measured 30 min after mixing at 25°C. (◐) c = 0.05; (□) c = 0.1; (■) c = 0.15; (●) c = 0.2; (◇) c = 0.3; (◆) c = 0.4; (▲) c = 0.5; (○) c = 0.6 g/dl. The polymers used are it-3 and st-3

within the framework of the present work, as associates of complexed chain sections.

So far no investigations covering the concentration dependence up to the critical concentration have been reported. In *Figure 5* the results of our investigations on the concentration dependence at 25°C are presented. In addition it ought to be mentioned that measurements of the viscosity at concentrations of 0.8 g/dl were impossible, because of inhomogeneties, caused by gelation. The behaviour of the mixtures that differ in concentration appears to be strongly asymmetric. This observation also can be explained by the difference in hydrodynamic volume of the components. The critical coil-overlap concentration, c^*, as calculated by the empirical relation of Simha[38]

$$c^* = [\eta]^{-1} \qquad (3)$$

is 0.43 for it-2 and 0.75 for st-2 at 25°C. Therefore, on raising the concentration, the critical coil-overlap concentration will be approached earlier in the case of an excess of it-PMMA, as demonstrated by the location of the maximum in *Figure 5*. The same effect is observed when samples with a higher molar mass are used[39].

CONCLUSIONS

The viscometric investigations confirm that the entire process of complexation of it- and st-PMMA in a strongly complexing solvent consists of three stages: (1) complexation, (2) association of complexed chain sections and (3) aggregation of the particles formed.

On raising the temperature, DMF changes from a strongly complexing solvent into a weakly complexing solvent and eventually into a non-complexing solvent.

In DMF, st-PMMA has a more compact conformation in comparison with it-PMMA. On raising the temperature the hydrodynamic volume of the syndiotactic coils increases, whereas the hydrodynamic volume of the isotactic coils remains almost the same. These differences influence the symmetry of the process of complexation with regard to the stoichiometric ratio.

Finally we want to remark that it is not surprising that the stoichiometry of the stereocomplex has been a point of controversy for such a long time, as a considerable part of the investigations were based on viscometry. Depending on temperature, concentration, solvent, time after mixing, etc. it is possible to obtain maxima or minima in the viscosity *versus* mixing ratio curves at almost every value of the mixing ratio, as shown by the present investigation.

REFERENCES

1 Fox, T. G., Garrett, B. S., Goode, W. E., Gratch, S., Rincaid, J. F., Spell, A. and Stroupe, J. D. *J. Am. Chem. Soc.* 1958, **80**, 1768

2 Liquori, A. M., Anzuino, G., Coiro, V. M., D'Alagni, M., de Santis, P. and Savino, M. *Nature* 1965, **206**, 358

3 Liquori, A. M., de Santis, P., Savino, M. and D'Alagni, M. *Polym. Lett.* 1966, **4**, 943

4 Chaing, R., Burke, J. J., Threlkeld, J. O. and Orofino, T. A. *J. Phys. Chem.* 1966, **70**, 3591

5 Liu, H. Z. and Liu, K. I. *Macromolecules* 1968, **1**, 157

6 Dayantis, J., Reiss, G. and Benoit, H. *Makromol. Chem.* 1968, **120**, 113

7 Borchard, W., Pyrlik, M. and Rehage, G. *Makromol. Chem.* 1971, **145**, 449

8 Borchard, W., Kalawrytinos, G., Mohadjer, B., Pyrlik, M. and Rehage, G. *Angew. Makromol. Chem.* 1973, **29/30**, 471

9 Pyrlik, M., Borchard, W., Rehage, G. and Uerpmann, E. P. *Angew. Makromol. Chem.* 1974, **36**, 133

10 Biroš, J., Máša, Z. and Pouchlý, J. *Eur. Polym. J.* 1974, **10**, 629

11 Spěváček, J. and Schneider, B. *Makromol. Chem.* 1974, **175**, 2939

12 Spěváček, J. and Schneider, B. *Makromol. Chem.* 1975, **176**, 729

13 Feitsma, E. L., de Boer, A. and Challa, G. *Polymer* 1975, **16**, 515

14 de Boer, A. and Challa, G. *Polymer* 1976, **17**, 633

15 Challa, G., de Boer, A. and Tan, Y. Y. *Int. J. Polym. Mater.* 1976, **4**, 239

16 Mekenitskaya, L. I., Amerik, Yu. B. and Golova, L. K. *Vysokomol. Soyed.* 1979, **A21**, 1334; *Polym. Sci. USSR* 1980, **21**, 1463

17 Vorenkamp, E. J., Bosscher, F. and Challa, G. *Polymer* 1979, **20**, 59

18 Spěváček, J. and Schneider, B. *Coll. Polym. Sci.* 1980, **258**, 621

19 Bosscher, F., Keekstra, D. W. and Challa, G. *Polymer* 1981, **22**, 124

20 Vorenkamp, E. J. and Challa, G. *Polymer* 1981, **22**, 1705

21 Könnecke, K. and Rehage, G. *Colloid Polym. Sci.* 1981, **259**, 2062

22 Rehage, G. and Wagner, D. *Polym. Prepr.* 1982, **23**, 29

23 Bosscher, F., ten Brinke, G. and Challa, G. *Macromolecules* 1982, **15**, 1442

24 Dybal, J., Štokr, J. and Schneider, B. *Polymer* 1983, **24**, 971

25 Belnikevitch, N. G., Mrkvičková, L. and Quadrat, O. *Polymer* 1983, **24**, 713

26 Schomaker, E., ten Brinke, G. and Challa, G., *Macromolecules* 1985, **18**, 1930

27 ten Brinke, G., Schomaker, E. and Challa, G. *Macromolecules* 1985, **18**, 1925

28 Sedláček, B., Spěváček, J., Mrkvičková, L., Stejskal, J., Horská, J., Baldrian, J. and Quadrat, O. *Macromolecules* 1984, **17**, 825 and references therein

29 Goode, W. E., Owens, F. H., Feldman, R. P., Snijder, W. H. and Moore, J. H. *J. Polym. Sci.* 1960, **46**, 317

30 Abe, H., Imai, K. and Matsumoto, M. *J. Polym. Sci.* (*C*) 1968, **23**, 469

31 Lyerla, J. R., Jr., Horikawa, T. T. and Johnson, D. E. *J. Am. Chem. Soc.* 1977, **99**, 2463

32 Schulz, G. V. and Kirste, R. *Z. Phys. Chem., N.F.* 1961, **30**, 171

33 Schulz, G. V., Wunderlich, W. and Kriste, R. *Makromol. Chem.* 1964, **75**, 22

34 Sakurada, I., Nakajima, A., Yoshizaki, O. and Nakamae, K. *Kolloid Z.* 1962, **186**, 41

35 Sundararajan, P. R. and Flory, P. J. *J. Am. Chem. Soc.* 1974, **96**, 5025

36 Katime, I., Gutierrez Cabañas, P., Ochoa, J. R., Garay, M. and Ramiro Vera, C. *Polymer* 1983, **24**, 1015

37 Spěváček, J. *J. Polym. Sci., Polym. Phys. Edn.* 1978, **16**, 523

38 Simha, R. *J. Chem. Phys.* 1945, **13**, 188

39 Schomaker, E., unpublished