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Complexation of Stereoregular Poly(methyl methacrylates). 12. Complexation Process in Dilute Solution

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ABSTRACT: The process of stereocomplexation between isotactic and syndiotactic PMMA in dilute solution was studied by means of differential scanning calorimetry of isolated complexed material, solution viscometry, and isothermal mixing calorimetry. The results were combined with results of investigations previously published. It appeared that essentially the same mechanism as proposed for the complexation process in bulk can account for the observed phenomena, including the previously reported association and aggregation stages following complexation. Two main processes are distinguished: complexation and subsequent crystallization of complexed chain sections, leading to the formation of complex particles. With respect to crystallization, two modes are suggested: fringed-micellar and lamellar growth, depending on the so-called critical sequence length under the conditions employed and the mobility of the chain sections. These parameters appear to be influenced by various variables such as solvent quality, temperature, mixing ratio, and tacticity.

Introduction

Stereocomplexation of isotactic and syndiotactic poly(methyl methacrylate) (i- and s-PMMA) is possible in (dilute) solution as well as in bulk. In a companion paper the results were given of an investigation on the overall process in bulk and a mechanistic model which accounts for the observed phenomena was presented.[1]

With respect to dilute solution one can distinguish three kinds of solvents: strongly complexing, weakly complexing, and noncomplexing, respectively designated as solvent type A, B, and C.[2,3] In addition to this it was found that the "complexing ability" of a solvent can be changed from type A to eventually type C by raising the temperature.[2,4] Although various investigators have tried to correlate the complexing ability of solvents to solvent characteristics, a satisfactory correlation was not yet achieved.[2,3,5–7] In the case of strongly complexing solvents, complex particles are formed of about 10–30 nm,[4,8–11], consisting of a compact nucleus surrounded by a shell of noncomplexed chains.[4,9] In the case of an excess of one of the components this shell consists of the component in excess, leading to steric stabilization of the complex particles.[4,9] Schomaker et al. have given a phenomenological description of the process.[4] They showed that in case of solvents of type A, three stages can be distinguished: (i) complexation: (ii) association of complexed chain sections resulting in the formation of compact "complex particles"; (iii) aggregation of complex particles, eventually followed by flocculation.

As complexed material obtained from dilute solution also shows crystallinity,[5,12–16] and as also is found that on employing a strongly complexing solvent two melting points are found,[14,15] we investigated whether the same mechanism as proposed for complexation in bulk is followed in dilute solution.

In this paper the results of the present investigation on the complexation process in dilute solution are discussed, in combination with the results of previously published investigations, in terms of the mechanism proposed for the complexation in bulk.[1] First we show that the observed melting endotherms, shown by material obtained from

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Table I
Molar Mass and Stereoregularity of the PMMA Samples Used

polymer	$\bar{M}_w$	$\bar{M}_n$	i:h:s, %
i1	1.5×10^5	9×10^4	i, >95
i2	2.4×10^5	2.1×10^5	i, >95
i3	1.5×10^5	1.0×10^6	i, >95
i4	4.2×10^5	3.2×10^5	i, >95
i5	1.6×10^5	6.3×10^4	i, >95
s1	7.3×10^5	3.5×10^5	1:8:91
s2	2.4×10^5	1.4×10^5	3:12:85
s3	2.1×10^5	1.0×10^5	4:19:77
s4	2.4×10^5	1.9×10^5	5:30:65
s5	2.0×10^5	1.2×10^5	1:7:92
s6	3.5×10^5	2.6×10^5	1:8:91
s7	7.5×10^5	5.5×10^5	1:8:91
s8	3.3×10^5	7.5×10^4	1:10:89

dilute solution, have the same characteristics as the endotherms found when complexes obtained from bulk are investigated. Next the influence of the "complexing ability" of the solvent is discussed, and the predictions from the model in this respect are compared with the experimental results of de Boer et al.[15] and Katime et al.[14] Furthermore, the influence of complexation time, tacticity, and mixing ratio in relation with the proposed mechanism is investigated. Finally the relationship between the present mechanistic model and the previously published phenomenological description of the complexation process[4] is discussed.

Experimental Section

Materials. Data on the PMMA samples used are listed in Table I. All i-PMMA's were synthesized in toluene with phenylmagnesium bromide as initiator[17] and were subsequently fractionated, using acetone as solvent and water as nonsolvent. **s4** was obtained as a fraction of the product of an ordinary radical polymerization in DMF (monomer concentration 20 wt %), using *tert*-butylcyclohexyl peroxydicarbonate as initiator (0.5 mol % based on the monomer). **s1**, **s2**, **s3**, **s5**, **s6**, and **s7** are fractions of products of Ziegler–Natta polymerizations in toluene with triethylaluminum and titanium tetrachloride as catalysts at −78 °C.[18] **s8** is a fraction of a sample which was prepared from s-poly(methacrylic acid) by methylation with diazomethane in DMF. These poly(methacrylic acid) samples were obtained directly by ^{60}Co radiation polymerization of the monomer in isopropyl alcohol.[19,20]

Tacticities, based on triads, were derived from the α-methyl peaks obtained for 3 wt % solutions in *o*-dichlorobenzene at 120 °C by means of 200-MHz NMR spectroscopy with a Nicolet NT-200.

The molar masses were determined by means of gel permeation chromatography (Waters ALC/GPC 150 C equipped with 2 TSK GMH 6 columns) using THF as eluent relative to polystyrene standards, employing the method of universal calibration. The following Mark–Houwink constants were employed: polystyrene, $K = 1.64 \times 10^{-4}$ dL/g, $a = 0.702$;[21] i-PMMA, $K = 1.66 \times 10^{-4}$ dL/g, $a = 0.66$.[22] For s-PMMA the constants of a-PMMA were taken: $K = 1.28 \times 10^{-4}$ dL/g, $a = 0.702$.[23]

Differential Scanning Calorimetry. The samples were prepared by mixing dilute solutions of i- and s-PMMA in acetone or dimethylformamide (DMF), which are characterized as strongly complexing at room temperature.[2] After a given time of complexation, the turbid solutions were precipitated quickly in petroleum ether (bp 40–60 °C) in the case of the acetone solutions or in demineralized water in the case of the DMF solutions. The precipitated samples were obtained by centrifugation and subsequent drying at 50 °C in vacuo, for 2 days in the presence of P_2O_5. Unless otherwise stated, the DSC runs were performed employing a scan speed of 20 °C/min, using a Perkin-Elmer DSC-2. Temperature calibration of the calorimeter for all scan speeds used was performed with ICTA (the International Confederation for Thermal Analysis) certified reference materials. The heat of fusion of Indium was used for area calibrations.

Isothermal Calorimetry. Calorimetric measurements on mixing solutions of i- and s-PMMA were carried out in a Setaram Calvet Type C80 twin microcalorimeter using DMF as solvent. Corrections due to enthalpies of dilution appeared to be unnecessary. The precision of the equipment at the conditions employed was about 5 mJ. Each measurement was done at least 3 times for $T < 50$ °C and at least 10 times for $T \geq 50$ °C. The total polymer concentration was 0.25 g/dL.

Viscometry. Solutions of sterically stabilized complex particles, 0.2 g/dL, were prepared by adding slowly (during 1 h) 1 mL of solutions of both polymers (0.5 g/dL) simultaneously to 3 mL of DMF, while stirring vigorously. Viscosities of the solutions were measured as a function of the temperature by using a micro-Ubbelohde viscometer (Schott KPG type Ic) in connection with a Lauda viscotimer (Schott). Corrections for non-Newtonian effects and loss in kinetic energy were negligible.

Results and Discussion

The Endotherms. Complexed material obtained from dilute solution showed a WAXS pattern identical with the pattern of complexed material obtained from the bulk.[13] Furthermore it appeared that on investigating the samples, using DSC, one or two endotherms were detected, depending on the conditions employed.[2,13–15]

The following are some characteristic previous results of DSC investigations on complexed material obtained from dilute solution,[2,13–15] also found during this investigation:

The total heat involved is in general much larger than ever found in case of samples obtained by means of bulk annealing. The largest value measured during the present investigation was 50 J/g for the case of a 1:2 **i1**/**s1** sample obtained by precipitation from a 0.15 g/dL DMF solution, 2 days after mixing at room temperature. The maximum value obtained in the case of bulk samples was on the order of 20 J/g.[1]

Material from dilute solution shows in general higher values for the melting points.

Complex obtained from a so-called weakly complexing solvent (type B) shows only one endotherm, whereas material from solvents of type A shows two endotherms.[14,15]

In order to investigate whether the endotherms, in the case of samples obtained from dilute solution, have the same origin as the endotherms observed in case of bulk samples, we first have to show that the endotherms have the same characteristics. The main difference between the two main endotherms as found after bulk annealing (T_m^1 and T_m^3) is that T_m^1 shows a very strong superheating in contrast to T_m^3.[1,24] Solutions, 0.15 g/dL, of **i1** and **s1** in DMF were mixed 1:2. After 2 days the (partly) complexed material was precipitated and investigated by means of DSC as a function of scanning rate. As expected two endotherms were detected, from now on called T_m^1 and T_m^3, analogous to the endotherms found in case of bulk annealing. The results are given in Figure 1. It appears that only T_m^1 shows a very strong superheating, as also was found for the samples obtained from the bulk.

In order to investigate whether some kind of recrystallization occurs during scanning, we investigated the influence of a partial scan up to 190 °C and subsequent cooling (60 °C/min). As is shown in Figure 2, it appears that only the second endotherm (T_m^3) is still found and the heat involved is comparable to the case without a previous partial scan. So recrystallization during scanning was found not to occur. Nevertheless it appears that further crystallization is still possible as annealing for 30 min at 190 °C results in an increased heat effect (see Figure 2).

According to the model, as proposed for complexation and crystallization in bulk,[1] T_m^3 represents the simulta-

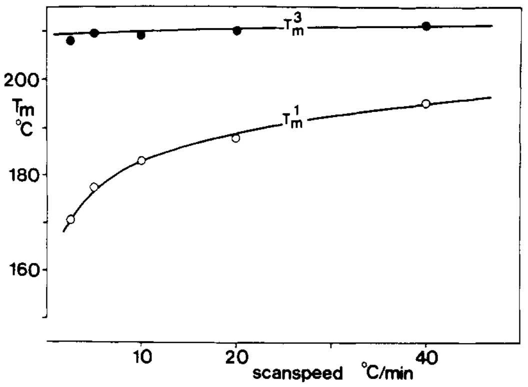

Figure 1. T_m^1 (○) and T_m^3 (●) as a function of scan speed, as found for samples obtained from 1:2 **il**/**sl** 0.15 g/dL DMF solutions, 2 days after mixing.

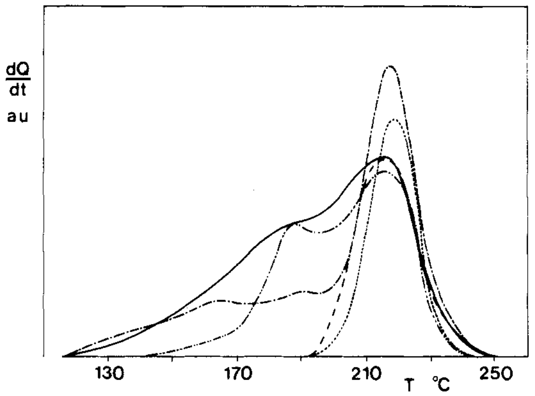

Figure 2. Influence of subsequent annealing of samples obtained from 1:2 **il**/**sl** 0.15 g/dL DMF solutions, 2 days after mixing. Solid line: DSC trace of a sample without further thermal treatment. Dashed line: The resulting DSC trace after a prescan up to 190 °C. Dotted line: DSC trace after annealing for 30 min at 190 °C. Dot–dash line: DSC trace of a sample which was annealed for 5 days at 120 °C after a pretreatment at 190 °C for 30 min. Dot–dot–dash line: DSC trace of a sample that was annealed for 5 days at 120 °C without a pretreatment at 190 °C. In all cases the same amount of material was used.

neous melting and decomplexation of lamellar crystallites of stereocomplexes. In that case, further annealing at low temperatures ($T_a < 140$ °C) of a sample from dilute solution showing only T_m^3 (after annealing at 190 °C) should result in the appearance of two extra endotherms origining from (fringed-micellar clusters of) stereocomplexes and lamellarly crystallized complexes formed in the amorphous matrix, during the additional bulk annealing. In Figure 2 the thermogram is shown of a sample obtained from a dilute solution, which was annealed for 30 min at 190 °C and subsequently annealed for 5 days at 120 °C. As expected two extra endotherms are found at temperatures comparable to those found during the bulk experiments employing an annealing temperature of 120 °C.[1] Furthermore we see a further increase of the intensity of the endotherm at 212 °C. So, there are three possible modes of growth: (i) growth of the existing lamellar crystallites, formed in dilute solution; (ii) complexation and fringed-micellar clustering of complexes in the amorphous matrix; (iii) lamellar growth in the amorphous matrix.

Next we studied the influence of annealing at 120 °C (for 5 days) without a previous thermal treatment at 190 °C. In this case only reorganization of (clusters of) complexes should be possible as the system remains completely immobilized. This expectation is confirmed by the experimental results (see Figure 2). The intensity and location of T_m^3 is almost unchanged, while T_m^1 has only sharpened, in particular because of the fact that low-melting material has disappeared.

Influence of Solvent. Now that we found that there are two independent endotherms with the same characteristics as those found after bulk annealing, we investigated whether the same mechanism, as proposed for complexation in bulk, is followed in dilute solution. An important difference is the time scale on which the processes take place. Another difference is that in the case of dilute solutions we deal with separate coils, whereas in case of a bulk system we deal with a homogeneous segmental distribution. Consequently, in principle much more and more perfect (crystallized) complexes can be formed, which also explains the fact that the melting points are found at higher temperatures and that the total heat involved is higher.

Analogous to the annealing temperature in bulk, in solution the "complexing ability" of the solvent, also depending on temperature, is the most important factor with respect to the critical sequence length for complexation. When this critical length is large, in bulk at high annealing temperatures, lamellar growth is the predominant mode of growth. After the formation of a complex nucleus, having the dimensions of the critical sequence length, the growing complex will be directly stabilized by lamellar crystallization.[1] In case of dilute solutions the same should account for so called weakly complexing solvents (type B).

At low annealing temperatures in bulk, complexation proceeds much faster than (lamellar) crystallization, as the critical sequence length is much smaller. In this case the system will be immobilized very quickly and the predominant mode of crystallization will be clustering of complexed sections into fringed-micellar crystallites. In the case of dilute solutions we expect this scheme to be followed in strongly complexing solvents (type A).

In order to test this hypothesis, we have to study the influence of complexing ability of the solvent on the relative intensity of the endotherms and the temperatures at which they are found. In fact, this was already done by de Boer et al.,[15] by variation of the temperature, and more extensively by Katime et al.,[14] by variation of mixing ratio of binary solvent mixtures. Therefore we investigated whether their experimental results support our proposed model.[25]

Katime et al. investigated 1:2 i-/s-PMMA solutions using binary solvent mixtures of carbon tetrachloride, acetonitrile, and *n*-butyl chloride. All solvents are classified as strongly complexing, but mixtures of them appeared to have a varying complexing ability, depending on mixing ratio. The complexed material was separated from the solutions by centrifugation, 1 day after mixing. After drying, the material was characterized by using DTA, yielding the following results:[14]

On lowering the complexing ability of the solvent mixture, a lower yield was found until no more material could be separated from the solution (see Figure 1 in ref 14b). Nevertheless in these cases the viscosity of the solutions was still higher than the additive value.

The relative intensity of the second endotherm ($\Delta H_3/\Delta H_1$) increased whenever a less complexing solvent mixture was employed, until only T_m^3 could be detected.

The temperature at which T_m^3 was found was higher on lowering the complexing ability of the solvent mixture (see Figure 3, which was constructed from data of Katime et al.[14a]).

The dependency of T_m^1 is less simple and more difficult to explain. In the case of an extremely strongly complexing solvent (pure carbon tetrachloride or *n*-butyl chloride) we see that the temperature at which T_m^1 is found increases

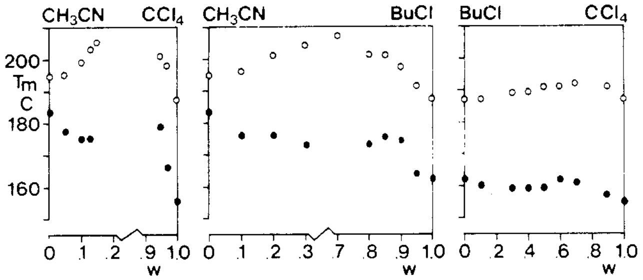

Figure 3. Influence of the complexing character of the solvent. T_m^1 (●) and T_m^3 (○), as a function of cosolvent weight fraction, for samples obtained from 1:2 i/t 0.2 g/dL solutions in binary cosolvent mixtures of acetonitrile, butyl chloride, and carbon tetrachloride, 1 day after mixing. This figure is constructed by using data of Katime et al.[14a]

on employing a less complexing solvent mixture. Whenever the starting point is acetonitril we see a decrease of T_m^1 (see Figure 3).

The predictions from our model are for the most part in line with these results. To separate material from solution, its density should differ sufficiently from that of the solution. In the case of a very weakly complexing solvent, the critical length is very large, which means that no complexes are formed that are stable with respect to thermal fluctuations. Only very weak temporary links between the components are formed, which explains the fact that a higher viscosity is found. However, separation from the solution by centrifugation is not yet possible. On employing a less weakly complexing solvent mixture, the critical sequence length lowers until it is small enough to make nucleation possible within the time scale of the experiment. Only the most perfect tactic sequences will form a complex nucleus, after which lamellar growth is possible. In this regime T_m^3 is found. The temperature at which the endotherm is found depends on the complexing ability of the solvent mixture, as the lamellar thickness will be determined by this parameter and also because of the fact that the most tactic sequences are selected.

On the other hand, in case of an extremely strongly complexing solvent, like carbon tetrachloride, the critical length is very small.[7] Complexation starts immediately all over the system. The formation of lamellar crystallites is hindered and the clustering of complexes into fringed-micellar crystallites becomes important. So, in this regime, two melting endotherms are found at relatively low temperatures, as the (clustered) complexes, giving rise to T_m^1, and lamellar crystallites of complexes, giving rise to T_m^3, formed are relatively small and will contain an important amount of defects. Reorganization is very difficult as the system is locally completely immobilized. The employment of a less strongly complexing solvent results in a larger critical sequence length and consequently it lasts longer before immobilization occurs. Lamellar growth becomes more important, resulting in a relative increase of the intensity of T_m^3. Furthermore the dimensions and quality of the complexes and crystals improve, resulting in an increase of the melting temperatures. The decrease of T_m^1 found for some cases is more difficult to explain and requires more research.

Another way to change the complexing ability of the solvent is by changing the temperature (see also "mechanism"). de Boer et al. have investigated 1:2 i/s samples obtained from acetone and DMF at different temperatures, 20 up to 70 days after mixing.[15] It appears that the temperatures at which T_m^1 and T_m^3 are found increase with the temperature of the solution, i.e., lowering the complexing ability of the solvent. Also the relative intensity of T_m^3 ($\Delta H_3/\Delta H_1$) is found to increase, until only T_m^3 is still found, analogous to the results of Katime et al. and in line with the present model.

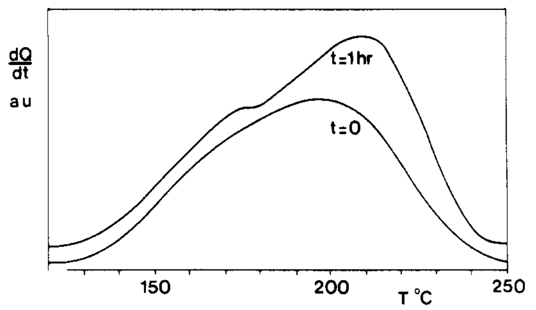

Figure 4. Influence of time. DSC traces as found for samples obtained from 1:1 i2/s1 0.2 g/dL DMF solutions immediately and 1 h after mixing.

Influence of Time. During the investigations, described above, very long complexation times were employed in order to reach quasi-equilibrium. In the present investigation, we have also studied the influence of "complexation time" (t_c). It appears that in the case of DMF solutions, one very broad endotherm is found with its maximum between T_m^1 and T_m^3, close to T_m^1, if the (partly) complexed material was isolated immediately after mixing at room temperature (see Figure 4). After 1 h the two endotherms can be identified.

According to the model, the first stage comprises the formation of complexed sections. Although the overall complexation process proceeds very fast in dilute solution, and therefore we cannot make a complete distinction between the two stages, we can still see that after short times T_m^1 is dominating the thermogram, representing the decomplexation of (clustered) complexed sections, not crystallized into lamellar crystallites.

If acetone is employed as solvent, the two endotherms are both found well separated, immediately after mixing. From this it appears that in acetone the process proceeds faster. This is also apparent from the fact that in the vicinity of the stoichiometric ratio ($0.5 < X_s < 0.8$) the amount of complexed material formed (measured as ΔH_{1+3}) is almost independent of the mixing ratio (see "influence of mixing ratio"), whereas in case of DMF a maximum is found, representing the stoichiometric ratio. Moreover it appears that in DMF, in contrast with acetone, more complex is formed (ΔH_{1+3} higher), employing longer complexation times ($t_c > 1$ h). So in acetone the system is immobilized more quickly than in DMF.

Influence of Tacticity. Lamellar crystallization of complexes requires polymers containing long perfect tactic sequences. Too many defects with respect to tacticity prevent lamellar growth principally. The influence of tacticity was investigated by using s-PMMA's of comparable molar mass, varying in tacticity. The results are given in Figure 5.

In agreement with expectations, the relative intensity of T_m^3 ($\Delta H_3/\Delta H_1$) decreases with tacticity, until only one broad endotherm is found with its maximum close to T_m^1.

Influence of the i/s Mixing Ratio. In case of strongly complexing solvents very compact "complex particles" are formed of about 10–30 nm.[4,8-11] Vorenkamp et al. used the term "microcrystallites" with respect to the nucleus of these particles.[9] These complex particles consist of a nucleus of (crystallized) complexed chain sections, surrounded by a shell of noncomplexed sections.[4,9] In the case of an excess of one of the components, this shell consists primarily of the component in excess, resulting in steric stabilization of the particles.[4,9] In the vicinity of the stoichiometric ratio, noncomplexed sections of both com-

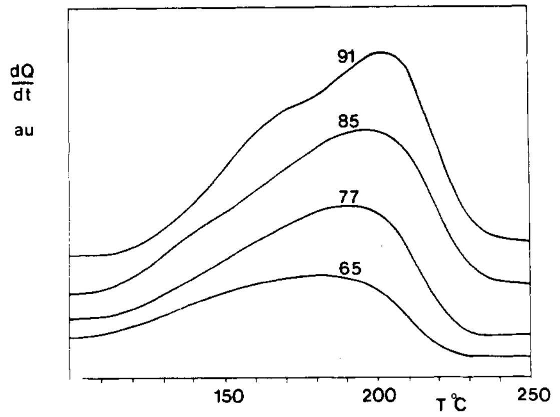

Figure 5. Influence of tacticity. DSC traces as found for samples obtained from 1:1 i/s 0.2 g/dL DMF solutions 1 h after mixing. In all cases **i2** was used. In order of decreasing tacticity, the s-polymers used are **s5**, **s2**, **s3**, and **s4**. The percentage of s-triads of the syndiotactic polymers are given in the figure.

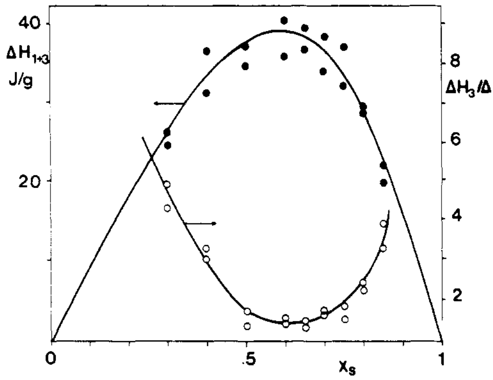

Figure 6. Total heat involved, ΔH_{1+3}, and the ratio $\Delta H_3/\Delta H_1$ as a function of the weight fraction of s-PMMA, X_s, as found by DSC for samples obtained from 0.2 g/dL **i3**/**s6** acetone solutions, 1 h after mixing.

ponents will remain at the outer side of the particles. In this case further complexation is possible, resulting in aggregation of the particles.[4,9] Nevertheless, from the present model we expect that further lamellar crystallization is strongly hindered, as we deal with chains which already make part of other (crystallized) complexed sequences. On the basis of this mechanistic picture we expect a relative decrease of the heat involved with T_m^3 in the vicinity of the stoichiometric ratio.

In order to verify this expectation, the influence of mixing ratio on the relative intensities of T_m^3 and T_m^1 ($\Delta H_3/\Delta H_1$) was studied. Acetone was used as solvent, as the endotherms are less overlapping in that case (see "influence of time"). One hour after mixing, the solutions were precipitated quickly in petroleum ether 40–60. The results are given in Figure 6.

We see that in the vicinity of the stoichiometric ratio ($0.5 < X_s < 0.8$) the total heat involved (ΔH_{1+3}) is almost independent of the mixing ratio, which is characteristic of a quickly immobilized system. Moreover, it appears that in this region the relative intensity of T_m^3 ($\Delta H_3/\Delta H_1$) is at a minimum, in line with the expectation formulated above.

Next, nonstoichiometric complex solutions, $X_s = 0.4$ and $X_s = 0.85$ ($t_c = 1$ h), were mixed in the solute ratio 1:2, resulting in a total base mole fraction s-PMMA of $X_s = 0.67$. Immediately after mixing the solutions were precipitated, in order to prevent reorganization processes to occur. From the thermograms it appeared that the heat involved with T_m^1 was larger for the mixed solution ($\Delta H_3/\Delta H_1 = 2.0$) than for the original solutions $X_s = 0.4$ and 0.85 ($\Delta H_3/\Delta H_1 = 3.3$ and 3.9, respectively). This result is in line with the results presented above. The original solutions contain "complex particles", sterically stabilized by noncomplexed chain sections of the component in excess. On mixing, additional complexation occurs between the complementary particles. However, lamellar crystallization is strongly hindered in this case, resulting predominantly in an increase of ΔH_1 and thus a decrease of $\Delta H_3/\Delta H_1$.

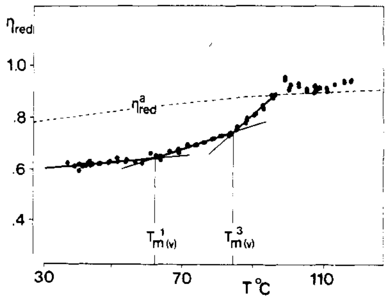

Figure 7. Reduced viscosity as a function of temperature for a 1:1 **i4**/**s7** 0.2 g/dL DMF solution of so-called "sterically stabilized complex particles". The heating rate was 3.0 °C/h. The onsets of the melting trajectories are indicated as $T_m^{1}{}_{(v)}$ and $T_m^{3}{}_{(v)}$.

In this context we want to recall the results of de Boer et al. who also studied the influence of mixing ratio on $\Delta H_3/\Delta H_1$, employing complexation times of 20 days instead of 1 h.[15] They found that $\Delta H_3/\Delta H_1$ was at a minimum for an excess of s-PMMA, beyond the stoichiometric ratio. From our viscometric investigations, previously published, we know that an excess of i-PMMA is much more effective than an excess of s-PMMA with respect to steric stabilization of the complex particles.[4] The reason might be that as the complexation stoichiometry is 1:2, the critical sequence length for i-PMMA is only half the critical length for s-PMMA. Consequently the probability that in the case of an excess of i-PMMA complementary s-PMMA sequences exceeding the critical length are available is smaller than for the opposite case. As aggregation of complex particles takes place over longer periods of time and is detected as a decrease of $\Delta H_3/\Delta H_1$, we can understand that the minimum is shifted toward an excess of s-PMMA on employing much longer complexation times.

Decomplexation in Dilute Solution. It is possible to make a dilute solution of sterically stabilized complex particles in DMF and consequently heat it in order to detect both melting points. This can be done by registration of the viscosity of the solution as a function of the temperature. Always, two discontinuities in the reduced viscosity versus temperature curves were registered (see Figure 7). After the second discontinuity the viscosity of the solution increased to somewhat higher values than the additive value, followed by a decrease toward the additive value. The additive value of the reduced viscosity was calculated as

$$\eta_{red}{}^{a} = X_s \eta_{red,s} + (1 - X_s)\eta_{red,i} \qquad (1)$$

Here $\eta_{red,i}$ and $\eta_{red,s}$ are the reduced viscosities of the solutions of i- and s-PMMA of the same concentration as the total concentration after mixing. X_s is the base mole fraction s-PMMA in the mixed solutions, based on the total amount of polymer. These results may be interpreted as follows. We start with a solution of sterically stabilized complex particles with a viscosity far below the additive value. On heating, at the onset, $T_m^{1}{}_{(v)}$, of the viscometrically detected melting trajectory, the complexed sections, which are not crystallized lamellarly, start to decomplex, resulting in the swelling of the particles. At the onset,

$T_{\mathrm{m}}{}^{3}{}_{(\mathrm{v})}$, of the second melting trajectory, also the complexes which are crystallized lamellarly start to decomplex, resulting in a further increase of the viscosity, until there is only still a weak interaction between i- and s-PMMA, responsible for the slightly increased viscosity with respect to the additive value. A further increase of the temperature, finally, results in additive behavior.

Mechanism. Now we want to discuss the relationship between our present model and the phenomenological description of the process, comprised of three stages: complexation, association, and aggregation.[4] First, we have to conclude that the driving force for association of stereocomplexes is crystallization. The present model gives in fact a more fundamental specification of the association process.

At low temperatures ($T < 50$ °C) in DMF, the observed association resulting in the formation of complex particles is, according to the proposed model, caused by clustering of complexed sections into fringed-micellar crystallites, next to the formation of lamellar crystallites of complexes. In addition to this, the driving force for the third stage, aggregation of complex particles, is complexation between noncomplexed chain sections at the outer side of the complex particles. As stated above ("influence of mixing ratio"), lamellar crystallization is strongly hindered in this case; only some clustering may be possible.

On raising the temperature, the critical sequence length increases and complexation proceeds less fast. Fringed-micellar growth becomes less important, until only lamellar growth is possible. In a previous paper, we have shown that in the case of temperatures T = 50–70 °C, an induction period is found with respect to association.[4] This observation has now to be interpreted as the formation of a complex nucleus of critical dimensions, after which lamellar growth is possible. At still higher temperatures, the critical sequence length is not in reach of the system anymore. Only very weak temporary links between the components are formed, which are not stable with respect to thermal fluctuations. This regime was found in DMF at about 70–80 °C, showing viscosities above the additive value.[4] Above this regime, no interaction could be detected anymore. These findings are in agreement with the present results of the viscometric detection of the melting trajectories.

In order to support this picture of the complexation process in dilute (DMF) solution, which is based on viscometric investigations, we have also studied the process calorimetrically, as a function of temperature. Dilute solutions of i- and s-PMMA were mixed and the heat of complexation (and crystallization) was detected. The results are summarized in Figure 8. For $T \geq 50$ °C, no significant differences were found for X_{s} = 0.4, 0.5, 0.6, and 0.7 and the results were taken together.

At about 50 °C, a discontinuity is found in the ΔH versus temperature curves. Much more heat is detected in the lower temperature region ($T < 50$ °C) than expected on the basis of extrapolation from the higher temperature region ($T > 50$ °C). Another important observation is that the overall process proceeds much slower above 50 °C, as is shown by an increased width of the calorimetric signal. Also the maximum of the signal is shifted toward longer times after mixing (t_{m} in Figure 8).

These results are in line with the hypothesis that above 50 °C the critical sequence length is so high that only lamellar crystallites of complexes are stable, while at lower temperatures the critical length is low enough that also (fringed-micellar clusters of) complexes are formed, which are not crystallized lamellarly, resulting in the detection of an additional heat effect in the lower temperature region. The observation that the overall process proceeds much slower at temperatures over 50 °C confirms the isothermal viscometric data, in which case an induction period was found, and it is in line with the hypothesis that at these conditions lamellar crystallites are formed, in which case an induction period is also expected. In the case of temperatures over 70 °C, no more heat could be detected, within the time scale of the experiment, also in agreement with the viscometric data.[4]

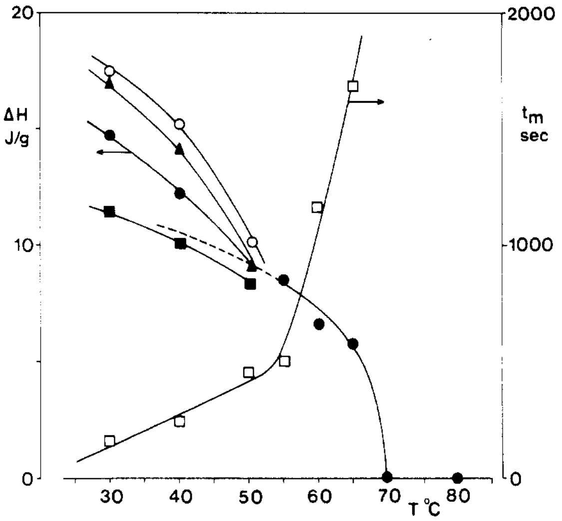

Figure 8. Heat of mixing, ΔH, of 0.25 g/dL solutions of i- and s-PMMA, and the time after which the maximum of the calorimetric signal, t_{m}, is detected, as a function of temperature. The polymers used were **i5** and **s8**, employing weight fractions of s-PMMA, with respect to the total amount of polymer in the system, of X_{s} = (■) 0.4, (●) 0.5, (○) 0.6, and (▲) 0.7. For $T >$ 50 °C the results for $0.5 \leq X_{\mathrm{s}} \leq 0.7$ were taken together (●). t_{m} is given for X_{s} = 0.5 (□).

Concluding Remarks

The present investigation of the complexation process in dilute solution and previous work in bulk[1] have resulted in a mechanistic model, which makes it possible to explain the most important observations with respect to the stereocomplexation process. In bulk as well as in dilute solution there are in principle two main processes, complexation and crystallization of complexed chain sections. With respect to the bulk process two mechanisms for complexation were proposed:[1] (i) a double-helix is formed by twisting the chains around each other, in which case the chain ends have to be free to move; (ii) a right-handed as well as a left-handed double helix is formed next to each other by forming a kink of s-PMMA which subsequently wraps around the i-chain, followed by a rotation. The "kink-nucleated" mode explains the fact that complexation in bulk is almost independent of chain length (entanglements).

Although one may expect that in dilute solution as compared to bulk the first mode is less hindered, it is not possible to make a more definite statement on the relative importance of the proposed complexation mechanisms.

With respect to crystallization, two modes are possible, fringed-micellar and lamellar growth, depending on the critical sequence length and the mobility of the chain sections. These parameters are influenced by various variables such as temperature, mixing ratio, complexing ability of the solvent, and tacticity.

Although no systematic study was done on the complexation in more concentrated systems in connection with the present model, we may expect that the same mechanism is followed. For example Ryan et al. have already found that in case of gelation of concentrated solutions of i- and s-PMMA, crystallites are formed.[26] Liu et al. have studied the melting process in benzene gels by means of NMR.[6] It appeared that two stages could be distinguished. Between 35 and 60 °C the mobility of the methyl ester protons was continuously increasing, followed by an extra increase between 60 and 70 °C up to the level of uncomplexed material. This observation points again to the existence of two morphologies. The group of Rehage et al. published various papers on the complexation in concentrated systems,[27-32] using only weakly complexing solvents. Considering these conditions, their results support the present model. For example, they studied the gelation process in *o*-xylene at high temperatures.[29] In this case we expect only lamellar growth, which is in agreement with their observation of a nucleation stage.

Finally we want to remark that from this work it appears that a suitable method to investigate the complexing ability of solvents involves the investigation of material, precipitated from dilute solution, by means of DSC. In this way it is possible to characterize the solvent by means of the ratio $\Delta H_3/\Delta H_1$, the total heat involved (ΔH_{1+3}) and the melting temperatures (T_m^1 and T_m^3). Additional information could be obtained by variation of complexation time. From this study we already know and understand that type-A solvents are characterized by two melting points (T_m^1 and T_m^3), whereas weakly complexing, type-B solvents are characterized by one melting point (T_m^3).

Registry No. i-PMMA, 25188-98-1; s-PMMA, 25188-97-0.

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