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Complexation of Stereoregular Poly(methyl methacrylates). 13. Influence of Chain Length on the Process of Complexation in Dilute Solution

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ABSTRACT: The complexation process between long *i* matrices and much shorter *s* oligomers was investigated by means of DSC on complexed material, isolated from dilute solution, as a function of *i/s* mixing ratio, time after mixing, and chain length of the oligomers. It was confirmed that the previously observed second level of cooperativity in this system is caused by subsequent crystallization of complexed sections. In line with the recently published general mechanism, two endotherms were found, originating from decomplexation of complexed sections, partly organized into fringed micellar clusters (T_m^1), and the simultaneous decomplexation and melting of lamellarly crystallized complexes (T_m^3). A dependence of T_m^3 on oligomer chain length was observed, suggesting that the (maximum) lamellar thickness was limited by this parameter. For the heat of complexation, a value of 20 kJ/base mol of complex was found, while further evidence was obtained that the additional heat of crystallization of complexed sections is negligible, compared to the heat of complexation.

Introduction

The process of stereocomplexation between isotactic (*i*) and syndiotactic (*s*) PMMA has been subject of extensive investigations ever since the first report of Fox et al. on mixtures of *i*- and *s*-PMMA showing anomalous WAXS patterns.¹ The investigations on this subject were reviewed by Speváček and Schneider.²

Very recently we published an investigation on the mechanism of the complexation process in bulk as well as dilute solution.^{3,4} The so-called critical sequence length for complexation, at the conditions employed, appears to be an important parameter in describing the overall process, which is mainly kinetically determined; i.e., a true thermodynamic equilibrium is not reached. The critical sequence length is defined as the minimum length of the complexed chain sections, above which the complexes are stable with respect to thermal fluctuations, and it is derived from the more familiar concept of critical chain length in complexation reactions.⁵⁻¹⁰ It appeared that in the overall process of stereocomplexation two processes can be distinguished:^{3,4} complexation of *i*- and *s*-PMMA, giving the well-known 1 *i*/2 *s* stereocomplex¹¹ and crystallization of complexed chain sections. With respect to crystallization, two modes were proposed: fringed micellar and lamellar growth, depending on the critical sequence length at the conditions employed and the mobility of the chain

sections. When a so-called strongly complexing solvent is employed, like DMF at room temperature,¹² the critical length for complexation is small. In that case, complexation proceeds much faster than lamellar crystallization, and the system will be immobilized quickly. Lamellar crystallization is hindered, resulting in a large amount of complex, only partly clustered into small fringed micellar crystallites. When the material obtained is isolated and dried and subsequently investigated by means of DSC, two main endotherms are detected, respectively, called T_m^1 and T_m^3 ,^{3,4} identified as (i) decomplexation of complexed sections, partly organized into small fringed micellar clusters of complexed sections; and (ii) melting and decomplexation of lamellar crystallites of complexed sections. In addition, it should be mentioned that it was postulated that the greater part of the heats involved should be ascribed to decomplexation, i.e., the heat of melting is negligible compared to the heat of decomplexation.^{3,4}

Apart from the formation of stereocomplex by mixing the components in bulk or in solution, the stereocomplex can also be formed *in situ* by free-radical polymerization of methyl methacrylate in the presence of an *i*-PMMA matrix.^{13,14} In this system, oligomeric radicals, created in free solution, grow until they reach the critical chain length, followed by complexation with the *i* matrix. From then on, the matrix controls their growth, resulting in predom-

Table I
Molar Mass and Stereoregularity of the PMMA Samples Used

polymer	\bar{M}_w	D	i:h:s, %
i-1	9.3×10^6	1.35	i > 95
i-2	1.1×10^6	1.5	i > 95
s-1	7.5×10^4	1.5	1:7:92
s-2	4.7×10^4	1.25	1:7:92
s-3	2.5×10^4	1.25	1:8:91
s-4	1.9×10^4	1.7	2:9:89
s-5	8.5×10^4	2.25	2:7:91
s-6	1.8×10^5	1.3	3:6:91

inantly syndiotactic material.¹³⁻¹⁵ Considering these observations, we studied the complexation reaction between long i matrices and much shorter s oligomers in dilute DMF solution, employing isothermal mixing calorimetry.^{5,9,10} It was found that, apart from the expected cooperativity with respect to oligomer chain length, the complexation appeared to be also dependent of the occupancy of the matrix, due to further association of complexed sections. In order to verify this mechanism, the i matrix/s oligomer system was investigated in more detail by DSC as a function of oligomer chain length, i/s mixing ratio, and time after mixing.

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 initiator¹⁶ and were subsequently fractionated, using acetone as solvent and water as nonsolvent. s-6 is a fraction of a product of a Ziegler-Natta polymerization in toluene with triethylaluminum and titanium tetrachloride as catalysts at -78°C .¹⁷ The other s samples are fractions of samples which were 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.^{18,19}

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 two TSK GMH 6 columns) using THF as eluent, relative to polystyrene standards, employing the method of universal calibration. The Mark-Houwink constants employed were for polystyrene, $K = 1.64 \times 10^{-4} \text{ dL/g}$, $a = 0.702$,²⁰ and for i-PMMA, $K = 1.66 \times 10^{-4} \text{ dL/g}$, $a = 0.66$.²¹ For s-PMMA, the constants were taken as $K = 1.28 \times 10^{-4} \text{ dL/g}$, $a = 0.702$.²²

Differential Scanning Calorimetry. The samples were prepared by mixing 0.2 g/dL solutions of i- and s-PMMA in dimethylformamide (DMF). After a given time of complexation, the turbid solutions were precipitated quickly in demineralized water, while stirring vigorously. The precipitated samples were obtained by membrane filtration ($4.5 \mu\text{m}$) and subsequent drying at 20°C in vacuo, during 2 days in the presence of P_2O_5 . The DSC runs were performed employing a scan speed of $20^\circ\text{C}/\text{min}$, using a Perkin-Elmer DSC-2. Temperature calibration of the calorimeter for all scan speeds used was performed with ICTA (International Confederation for Thermal Analysis) certified reference materials. The heat of fusion of indium was used for area calibrations.

Results and Discussion

Influence of Mixing Ratio. From previous studies on the i matrix/s oligomer systems, we know that in the limit of an infinite excess of i matrices, i.e., in case of zero degree of occupancy of the matrix, the critical syndiotactic chain length in DMF at 30°C , employing a concentration of 0.2 g/dL, is about 70 units.^{5,9,10} We also know that because of the so-called second level of cooperativity, which is now to be ascribed to the subsequent crystallization of com-

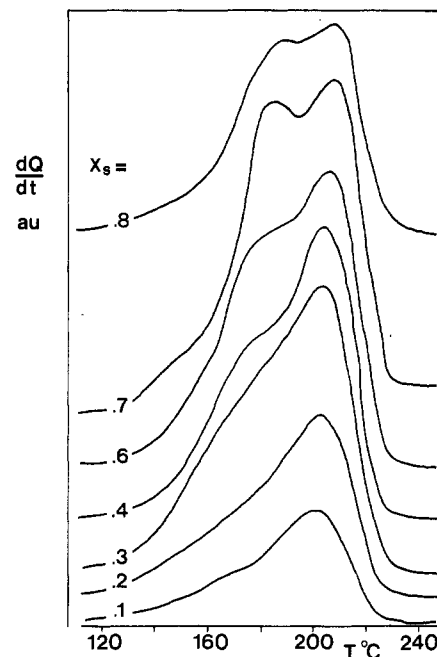


Figure 1. Influence of i/s mixing ratio. DSC traces of complexed material from 0.2 g/dL of DMF solutions of i-1 and s-1, obtained by precipitation 3.5 h after mixing at 20°C . The base mole fraction of s-PMMA employed, based on the total amount of polymer in the system, is given as x_s . See also Table II.

Table II
Influence of Mixing Ratio, Given as Base Mole Fraction of s Oligomer, x_s , on T_m^1 and T_m^3 . The Samples Were Obtained by Mixing 0.2 g/dL of i-1 and s-1 DMF Solutions at 20°C , Worked up 3.5 h after Mixing

x_s	$T_m^1, ^\circ\text{C}$	$T_m^3, ^\circ\text{C}$	x_s	$T_m^1, ^\circ\text{C}$	$T_m^3, ^\circ\text{C}$
0.2	173	203	0.6	182	205
0.3	175	203	0.67	183	206
0.4	180	204	0.7	185	208
0.5	178	204	0.8	189	208

plexed sections, the real value of the critical chain length will be smaller for higher degrees of complexation and the value mentioned is only a maximum, which may be interpreted, in line with the proposed mechanism, as the minimum size for nucleation.

In Figure 1, the DSC traces of complexed material, obtained 3.5 h after mixing 0.2 g/dL solutions of i-1 and s-1, are given for different mixing ratios. Comparable results were obtained for mixtures with other oligomers. It appears that again two main endotherms are detected, identified as T_m^1 and T_m^3 . The temperatures at which the maxima are found are given in Table II. As was also found for samples where both have high molar mass,⁴ the relative intensity of T_m^3 versus T_m^1 ($\Delta H_3/\Delta H_1$) depends on the mixing ratio. Because, in case of an excess of matrices, T_m^3 is found almost exclusively, in combination with the fact that T_m^3 corresponds to the decomplexation and melting of lamellarly crystallized complexes, it is concluded that indeed the subsequent crystallization of complexed oligomers causes the observed second level of cooperativity.^{5,9,10} From this, it is suggested that the complexed oligomers are not distributed randomly over the matrices, where in that case almost exclusively T_m^1 should be found, but are organized into lamellar crystallites of complexes, consisting of several s oligomers, in which at least the i matrices make tight folds. The nonrandom distribution is not unique to this system. Kabanov et al. have already shown that the same occurs in case of complexation between poly(methacrylic acid) matrices and poly(vinyl-

pyrrolidone) or poly(ethylene glycol) oligomers.^{8,23}

On approaching the stoichiometric ratio, the relative intensity of T_m^1 is found to increase strongly. As we deal with a strongly complexing solvent, complexation proceeds very fast (see also Time Dependence section). Consequently, in the vicinity of the stoichiometric ratio, the system will be immobilized quickly, and further reorganizations are more or less prevented. So, the formation of lamellar crystallites is strongly hindered, resulting in a relative increase of ΔH_1 , representing the noncrystallized and fringed micellarly crystallized complexed chain sections.

The temperature at which the maximum of the first endotherm is found (Table I), which is, according to our model, dependent on the mean sequence length of the complexed sections that are not crystallized lamellarly, appears also to be dependent on mixing ratio. This is also partly due to the increasing immobility in the system. For an excess of matrices, lamellar crystallites are formed almost exclusively; the remaining part of the complexed material, giving rise to T_m^1 , consists most probably of complexed chains of inferior tacticity and interlamellar complexed material, possibly partly clustered into fringed micellar crystallites. On approaching the stoichiometric ratio, the system is immobilized more quickly and further reorganization into lamellar crystallites is prevented on the time scale of the experiment, resulting predominantly in the formation of longer complexed sections. Therefore, the maximum of the first endotherm is shifted toward higher temperatures. In addition to this immobilization effect, there is also the effect of selection with respect to chain length and tacticity, which becomes especially important beyond the stoichiometric ratio as was apparent from earlier investigations.^{5,9,10} This explains why, also beyond the stoichiometric ratio, the maximum still shifts toward higher temperatures, on increasing the amount of oligomer in the system.

This selection effect is also reflected in the dependency of T_m^3 on mixing ratio. Since the temperature at which the maximum of T_m^3 is found is dependent of the chain length of the oligomers, as will be shown later, selection of the longest oligomers in case of an excess will result in a shift of T_m^3 toward higher temperatures beyond the stoichiometric ratio.

According to our model, the heat involved with the overall process of decomplexation and melting can be almost exclusively ascribed to the falling apart of the double helices, i.e., decomplexation.^{3,4} In Figure 2 the total heat of decomplexation (ΔH_{1+3}) is given as a function of oligomer base mol fraction (with respect to the total amount of polymer). ΔH_{1+3} is given per gram of i matrix, per gram of s oligomer, and per gram of both polymers in the system, respectively. Within experimental error, no dependency on chain length was observed, in line with expectations, as all oligomers used have chain lengths exceeding the critical length. So, the results for the four polymer pairs were taken together.

Until now, the heat of complexation was only measured, mixing dilute solutions of the components, by using microcalorimetry.^{5,24,25} However, the resulting values were strongly dependent on the solvent used, as the heats of desolvation of the i and s chains, the heat of complex solvation, and in some cases even the heat of dilution also contribute to the overall heat measured. A more straightforward and simple method is to derive the heat of complexation from the heat of decomplexation as measured by means of DSC, provided that the heat of melting of the crystallites themselves is negligible com-

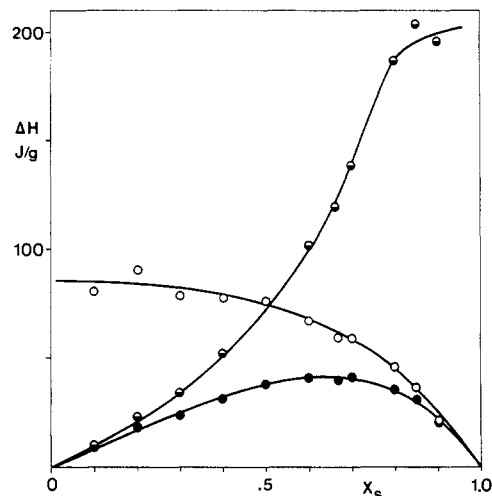


Figure 2. Overall heat of decomplexation (and melting) ΔH_{1+3} per gram of i (●) s (○), and both (●) polymers in the system, as a function of base mole fraction s-PMMA, x_s . Within experimental error, no significant differences were found for polymer pairs i-1/s-1, i-1/s-2, i-1/s-3, i-1/s-5, and i-2/s-5, and consequently the results were taken together. The investigated material was precipitated 1 h after mixing it with 0.2 g/dL of DMF at 20 °C.

pared to the heat of decomplexation, which is the case according to our model.^{3,4} In the next two paragraphs, more experimental evidence is presented to support this thesis.

The fact that all oligomers used have chain lengths exceeding the critical length enables us to determine the heat of complexation, as in the case of an excess of one of the components; in principle, the complementary component will be complexed completely. From the heat of decomplexation per gram of s oligomer in the limit of an infinite excess of matrices (Figure 2), we obtain for the heat of complexation a value of about -17 kJ/base mol of complex, consisting of one i unit and two s units. On the other hand, we obtain a value of -20 kJ/base mol of complex from the heat of decomplexation per gram i matrices, in the limit of an infinite excess of oligomers. This discrepancy can be explained by the fact that the overall tacticity of the oligomers is less perfect than the tacticity of the i matrices. In the case of an excess of oligomers, the best ones will be selected, so in principle more perfect complexes are formed when there is an excess of oligomers. Therefore, the value of -20 kJ/base mol of complex is the most reliable one, although the real value might be somewhat higher as a degree of complexation of 100% will never be attained in practice. Bosscher et al. suggested for the structure of the complex a 30/4 i helix, surrounded by a 60/4 s helix.²⁶ On the grounds of conformational energy analysis, the energy of stabilization of this double helix was calculated as -30 kJ/base mol of complex,²⁷ which is of the same order of magnitude.

Time Dependence. The overall process of complexation and crystallization was studied as a function of time after mixing solutions of i matrices and s oligomers. The mixing ratio employed was 1 i/2 s, which is the stoichiometric ratio of the complex at the level of monomeric units. After a given time, the mixed solutions were precipitated quickly. After drying carefully, the samples were studied by means of DSC. The results are summarized in Table III and Figure 3.

With respect to the overall heat of decomplexation (and melting) (ΔH_{1+3}), it appears that within experimental error the final value was reached within 30 min. However, the shape of the endotherms, the locations of the maxima of the endotherms, T_m^1 and T_m^3 , and the ratio $\Delta H_3/\Delta H_1$

Table III
 ΔH_{1+3} , T_m^1 , T_m^3 , and T_e as a Function of Time after Mixing 0.2 g/dL of DMF Solutions of i-1 and s-1, s-2, or s-3 at 20 °C. The Base Mole Fraction of s Oligomer, x_s , Was 0.67

time	s-1				s-2				s-3			
	ΔH_{1+3} , J/g	T_m^1 , °C	T_m^3 , °C	T_e , °C	ΔH_{1+3} , J/g	T_m^1 , °C	T_m^3 , °C	T_e , °C	ΔH_{1+3} , J/g	T_m^1 , °C	T_m^3 , °C	T_e , °C
1 min	32.0	176	201	221	33.0	175	201	219	31.2	174	201	212
15 min	37.0	180	205	225	38.1	180	204	220	36.6	182	202	212
30 min	39.0	180	206	225	39.3	182	204	219	39.2	185	202	213
1 h	40.1	181	206	225	39.4	182	206	220	39.7	185	202	214
3.5 h	39.3	183	206	225	40.2	185	206	221	39.5	186	202	214
21 h	39.7	184	207	225	39.1	185	207	221	38.9	186	203	214
92 h	39.5	184	207	225	38.8	186	207	221	39.9	187	203	214

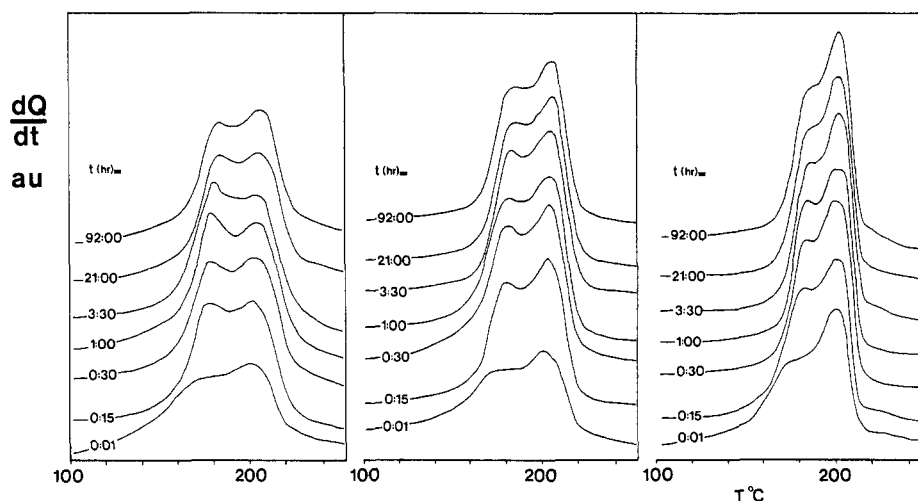


Figure 3. Influence of time after mixing. DSC traces of complexed material from 0.2 g/dL of DMF solutions of i-1 and s-1, s-2, or s-3, obtained by precipitation after a given time after mixing, as indicated in the figure, at 20 °C, employing an s base mole fraction of $x_s = 0.67$. See also Table III.

appeared to be dependent on time up to days after mixing.

From the thermograms we see that after 1 min after mixing lamellar crystallites are formed next to noncrystallized complexes and fringed micellar clusters. About 80% of the final amount of complex is then already formed, so the system is for the major part already strongly immobilized. Further lamellar growth is hindered, so further complexation results in a stronger increase of ΔH_1 , compared to ΔH_3 , for $t < 30$ min. Apart from this also some reorganization is found to occur, resulting in the formation of (crystallites of) complexes of better quality. Improvement of the quality of the complexes, i.e., complexed sections consisting of more units and with less defects, is easier to attain than further growth of lamellar crystallites, as in that case reeling in of the chains is necessary. From this we understand that for $t > 30$ min, during the first hours, the maximum of the first endotherm, T_m^1 , is shifted toward higher temperatures, as complexed material with a relatively low melting point reorganizes into material which melts at some higher temperature. This is also apparent from the fact that also the width of the endotherm decreases, while the total heat involved, ΔH_{1+3} , is roughly the same.

Further growth of lamellar crystallites at the expense of complexed material, which was not crystallized lamellarly, is found to occur on the time scale of days, as is apparent from the fact that the relative intensity of ΔH_3 increases. From the fact that the total heat involved (ΔH_{1+3}) remains the same within experimental error, while more lamellarly crystallized complexes are formed, the conclusion can be drawn again that the additional heat of melting of the lamellar crystallites is negligible in comparison with the heat of decomplexation.

Influence of Chain Length. As was also mentioned earlier, all oligomers used have chain lengths exceeding the

critical length. Therefore, within experimental error, no differences were found with respect to the overall heat of complexation (ΔH_{1+3}). Nevertheless, a distinct dependency on chain length is observed, with respect to the shape, the maxima, and the relative intensities of the endotherms (Table III and Figure 3). This again points to the conclusion that indeed the additional heat of melting of the lamellar crystallites is negligible in comparison with the heat of decomplexation.

From Figure 3 we see that, while the total amount of complex is the same (ΔH_{1+3}), in case of longer chains less lamellarly crystallized complexes are formed. The reason may be that, in case of longer oligomers, there is an enhanced chance that the same oligomers make up part of different complexed sections, making lamellar crystallization more difficult to occur. Moreover, detailed inspection of the thermograms reveals that the reorganization processes mentioned above proceed faster in the case of shorter chains (Figure 3). This is also apparent from the fact that the shift of T_m^1 toward higher temperatures proceeds faster in the cases of shorter chains (Table III). This observation is also in line with the idea that for longer oligomers the system is immobilized more strongly.

Another important observation is that T_m^3 also depends on chain length. After 1 min all three samples appear to show identical values for T_m^3 , but after several days there is a significant difference between the sample of the smallest molar mass and the other two. In addition to this, it appears that also more lamellar material is formed with a high melting point, whenever oligomers with longer chain lengths are employed. This appears from the fact that the location of the end of the endotherm, T_e , depends on chain length. Some additional measurements were performed, employing other chain lengths. In Figure 4 the results are summarized. In principle, the melting temperature of

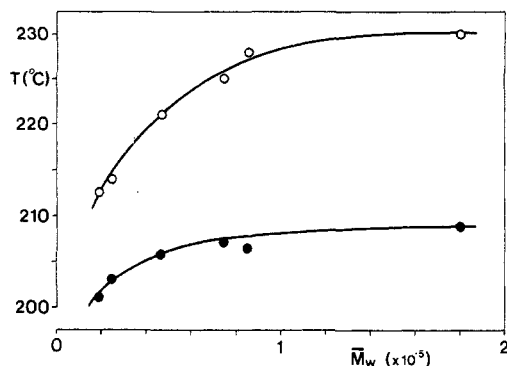


Figure 4. Influence of oligomer chain length. T_m^3 (●) and T_g (○) as a function of \bar{M}_w of the oligomer employed. T_g is defined as the temperature at which the tangent through the inflection point between the maximum and the end of the endotherm crosses the base line. The samples were obtained by precipitation 21 h after mixing 0.2 g/dL of DMF solutions of i-1 and s-1, s-2, s-3, s-4, s-5, or s-6 at 20 °C, employing an s base mole fraction of $x_s = 0.67$.

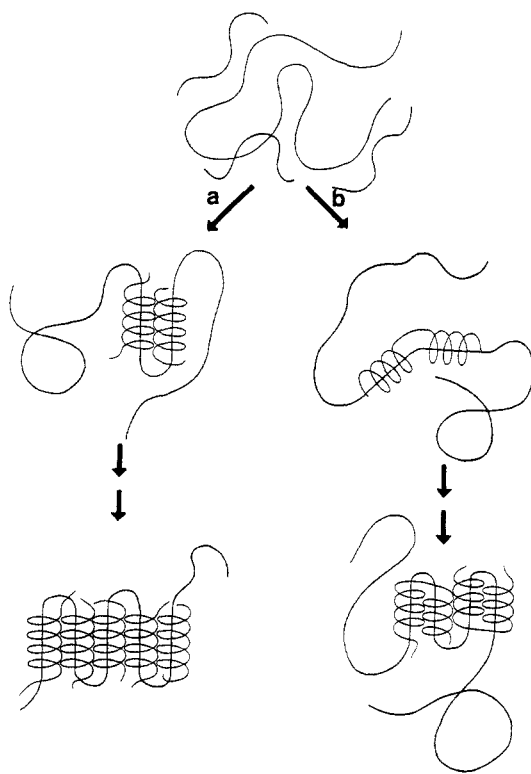


Figure 5. Mechanistic interpretation of the observed dependence of T_m^3 and T_g on the chain length of the oligomers employed (see text).

lamellar crystallites depends on the lamellar thickness, i.e., the length of the complexed sections between two folds. When i- as well as s-PMMA is of high molar mass, both chains will fold back,^{3,4} which explains the fact that for "oligomers" with molar masses over 1×10^5 no dependency on chain length is observed. The observed dependency on chain length of T_m^3 and especially T_g for oligomers with smaller molar masses suggests that at least the maximum lamellar thickness is limited by the chain length of the oligomers.

The interpretation might be that the lamellar thickness is of the order of magnitude of the oligomer chain in its complex conformation; i.e., only the i matrix folds back (cf. Figure 5a). However, in a paper on complexation in bulk, we proposed a mechanism to explain the fact that

complexation proceeds very fast, independent of the chain length of the components.³ In this mechanism, a right-handed helix as well as a left-handed double helix is formed next to each other starting from a kink of s-PMMA which subsequently wraps around the i chain, followed by a rotation. If these two complementary helices are bent to each other, a small lamellar crystallite is formed with one tight fold. It is possible that this mechanism is also followed (by oligomers) in dilute solution,⁴ and then the (maximum) lamellar thickness would be of the order of magnitude of half the oligomer chain in its complex conformation (cf. Figure 5b).

Concluding Remarks

We have established that the second level of cooperativity in this system is caused by the subsequent crystallization of complexed sections and that the oligomers will not be distributed randomly over the matrices. So, we understand why the theoretical model, developed for complexation between matrices and oligomers in general, was only correct (quantitatively) in describing the complexation between i-PMMA matrices and s-PMMA oligomers, in the limit of an infinite excess of matrices.¹⁰

Another important result is the fact that we are able to explain the observed phenomena again in terms of the same mechanistic model as proposed for the overall complexation process between long i and s chains in bulk as well as in solution.^{3,4}

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

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