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Complexation of Stereoregular Poly(methyl methacrylates). 8. Calorimetric Investigations

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ABSTRACT: The results of our calorimetric investigation of the complexation of long isotactic poly(methyl methacrylate) (it-PMMA) "matrices" with much shorter syndiotactic poly(methyl methacrylate) (st-PMMA) "oligomers" in a dilute solution of dimethylformamide (DMF) are presented. The heat of complexation at 30 °C and a total polymer concentration of 2.119×10^{-3} g/g is estimated to be 7.0 kJ/basemole of complex. Interpretation in terms of a simple model, discussed before, shows that complexation becomes more favorable for increasing degrees of occupancy of the matrix due to additional local ordering of occupied sections. Viscosity measurements confirm this conclusion. The critical chain length, defined as the chain length of the oligomers, below which no appreciable complexation takes place, is under the given circumstances shown to be approximately 60 monomer units. A continuous exchange and selection process is shown to be characteristic for the complexation of oligomers with a lower percentage of syndiotactic triads. This is apparent from (i) a shift in the position of the maximum of the heat of complexation to higher amounts of oligomers, (ii) a nonlinear dependence of the free energy of complexation on the degree of occupancy of the matrix, and (iii) an increased width at half-maximum of the calorimetric signal. Less heat per gram of polymer than expected is found for a lower total polymer concentration, especially for an excess of matrices. It is attributed to a suppressed local ordering due to the more swollen structure of the matrix. The reversed system of long syndiotactic matrices and isotactic oligomers as well as the influence of the matrix chain length is considered briefly.

Introduction

The existence of a stereocomplex, a concept introduced by Liquori et al.,[1] of isotactic and syndiotactic poly(methyl methacrylates) (it- and st-PMMA) was first demonstrated by Fox et al.[2] Recently, Vorenkamp et al.[3] showed that the stereocomplex has a composition of it/st = $^1/_2$. In dilute solutions with a suitable solvent, the maximum deviation of reduced viscosity and osmotic pressure as well as the maximum turbidity were all found at this composition. Moreover, DSC measurements showed a maximum crystallinity, after prolonged annealing of a mixture of it- and st-PMMA in the bulk at 140 °C, for the same composition.

Part of the interest in polymer complexes arises from the phenomenon of template polymerization. This refers to polymerizations characterized by propagation of active "oligomers" along macromolecular templates (matrices) for at least the greater part of their growth. A survey of various kinds of template systems has been given by Challa and Tan.[4] Template polymerizations can be classified according to two different types. The first type is characterized by preadsorption of monomer units on the template molecules. Hence initiation as well as propagation takes mainly place on the template. In the case of the second type, on the other hand, oligomeric radicals created in free solution grow until they reach some critical chain length, followed by complexation with the template, which from then on controls their growth. The radical polymerization of methyl methacrylate (MMA) in the presence of a long it-PMMA matrix in a suitable solvent is of the latter type. In this, as in most other template systems, the presence of the matrix leads to a rate enhancement, due to a delayed termination reaction of those growing chains which are bound to the matrix. Moreover, a promoted syndiotactic growth of PMMA radicals is observed once the oligomers are bound to the matrix.[5] The critical chain length, below which no appreciable complexation occurs, has in certain cases been estimated at less than 50 monomer units.[4] Although this number will depend on solvent, template concentration, and temperature, it is obvious that highly syndiotactic PMMA can only be obtained if the growth along the matrix proceeds for a long enough period. This requirement can only be met if a highly isotactic PMMA matrix of a high molar mass is used. The motivation of the present study of complexation between long it-PMMA matrices and much shorter st-PMMA oligomers is partly based on this observation.

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The most obvious way to study complexation quantitatively is by means of heat of complexation measurements. To date, only a few calorimetric studies on the complexation of it- and st-PMMA have been published. Biroš et al.[6] determined the heat of complexation for a 1 wt % solution of it- and st-PMMA of similar chain lengths in dimethylformamide (DMF) and toluene. They concluded that the *i*/*s* complexation stoichiometry lies between 1/1.5 and 1/2. Because the tacticity of it-PMMA was low (78% it triads) and because the polydispersities are unknown, more definite statements cannot be made. Recently, Killmann and Graun[7] measured the heat of complexation for it-PMMA ($\bar{M}_w = 30000$) and st-PMMA ($\bar{M}_w = 72000$) for a total polymer concentration of 2.2 and 0.22 g/L using carbon tetrachloride as solvent. Three different compositions corresponding to a ratio between the amount of isotactic and syndiotactic triads of 1/1, 1/2, and 1/18 were investigated. Of these, the greatest heat of complexation per gram of polymer was found for the first-mentioned composition. Since the tacticity of the st-PMMA used was rather low (79% st triads), this is, as will be argued further on, not necessarily in conflict with a 1/2 complexation stoichiometry. Moreover, carbon tetrachloride is a rather unsuited solvent as far as complexation is concerned. Spěváček and Schneider[8] found that st-PMMA with a molar mass of $\bar{M}_n = 170000$ could not even be dissolved in it, an observation confirmed by our own experience.

In a separate paper[9] a theoretical discussion, with the emphasis on the heat of complexation and critical chain length, for the complexation of a long it-PMMA matrix and much shorter st-PMMA oligomers was given. The starting point was the adaptation to the 1/2 complexation stoichiometry of a model, dealing explicitly with matrix–oligomer complexation, introduced by Khodakov et al.[10)] and reviewed by Kabanov and Papisov.[11] To obtain quantitative information about the extent of complexation it is necessary to know the heat of complexation per complex unit, which by definition consists of 1 monomer unit of it-PMMA and 2 monomer units of st-PMMA. In ref 9 it was shown that this can best be determined by taking an excess of matrix. An important result was the demonstration of the strong influence of the complexation stoichiometry on the ratio of the amount of oligomer and the amount of matrix for which the maximum heat of complexation per gram of total polymer occurs. In addition, the influence of the polydispersity of the oligomers thereupon was discussed. Moreover, a simple relation determining the critical chain length of the oligomers was derived, showing how it could be obtained from measurements with oligomers of a much longer chain length.

In the present paper results for the heat of complexation of dilute solutions of it-PMMA matrices and st-PMMA oligomers in DMF will be presented. The organization is as follows. First the heat of complexation per complex unit will be determined. From this the degree of occupancy of the matrix in various very different cases can be calculated. Next the influence of the degree of occupancy of the matrix and of the chain length of the oligomers on the complexation will be discussed. An estimation of the critical chain length will be given. The reversed system of a long st-PMMA matrix and much shorter it-PMMA oligomers is discussed briefly. Finally the influence of the tacticity of the oligomers, the total polymer concentration, and the matrix chain length will be addressed.

Experimental Section

Table I
Molar Mass and Stereoregularity of PMMA Samples

polymer	$\bar{M}_n$	*D* ($\bar{M}_w/\bar{M}_n$)	*i*:*h*:*s*, %
i1	6.2×10^5	1.55	$i > 95$
i2	3.6×10^5	1.10	$i > 95$
i3	2.5×10^5	1.10	$i > 95$
i4	6.9×10^3	3.40	93:6:1
s1	5.4×10^5	1.30	0:13:87
s2	4.1×10^4	1.30	4:19:77
s3	3.8×10^4	2.25	2:7:91
s4	2.8×10^4	1.60	2:7:91
s5	2.7×10^4	1.30	5:30:65
s6	2.4×10^4	1.35	1:10:89
s7	2.1×10^4	1.55	1:5:94
s8	2.1×10^4	1.15	2:10:88
s9	1.9×10^4	2.25	2:7:91
s10	1.4×10^4	1.10	2:12:86
s11	6.4×10^3	1.30	2:12:86

Materials. Data on the PMMA samples used are listed in Table I. All it-PMMA's were synthesized in toluene with phenylmagnesium bromide as catalyst.[12] i1, i2, and i3 were obtained by means of fractionation of the same sample using acetone as solvent and water as precipitant. i4 was obtained from another sample by means of precipitation in hot methanol. s5 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 monomer). s1, s2, and s6 are fractions of products of Ziegler–Natta polymerizations in toluene with triethylaluminum and titanium tetrachloride as catalysts at −78 °C.[13] s3, s7, s8, s10, and s11 are fractions of samples which were prepared from st-poly(methacrylic acid) by methylization with diazomethane in DMF. These poly(methacrylic acid) samples were obtained directly by ^{60}Co radiation polymerization of the monomer in isopropyl alcohol.[14,15] s4 and s9 were obtained by means of ultrasonic degradation of sample s3. Ultrasonic irradiation of 3% by weight solutions in dichloromethane was carried out with a Branson Sonifier B12 operating at an intensity of 50 W nominally at 20 kHz. Tacticities 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 gel permeation chromatography (Waters ALC/GPC 150 C equipped with 2 TSK GMH 6 columns) using THF as an eluent, relative to polystyrene standards.

Calorimetry. Calorimetric measurements were carried out in a Setaram Calvet Type C80 twin microcalorimeter at 30 °C, using DMF as a 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 three times. Unless otherwise indicated, the total polymer concentration was 2.119×10^{-3} g/g.

Viscometry. Viscosities of mixtures of it- and st-PMMA in DMF (total polymer concentration 2.119×10^{-3} g/g) were measured at 30 °C, 10 min after mixing, using a micro-Ubbelohde viscometer (Schott KPG Type IC) in connection with a Lauda viscometer (Schott). Corrections for non-Newtonian effects and loss in kinetic energy were negligible.

Results and Discussion

In our previous paper[9] on the association of poly(methyl methacrylates) a model dealing with the complexation of long it-PMMA matrices and much shorter st-PMMA oligomers was introduced. As a straightforward extension to an it/st = 1/2 complex of a result obtained by Khodakov et al.[10] for a 1/1 complexation stoichiometry, the following expression for the degree of occupancy θ of the matrix by oligomers of chain length *n* was derived:

$$\frac{2\theta}{(1-\theta)m_{\text{o1}}} e^{\theta/(1-\theta)} = K_n \tag{1}$$

where

$$K_n = e^{-(n/2)\Delta G_1{}^\circ/RT} \tag{2}$$

m_{o1} is the basemole fraction of free oligomers in solution,

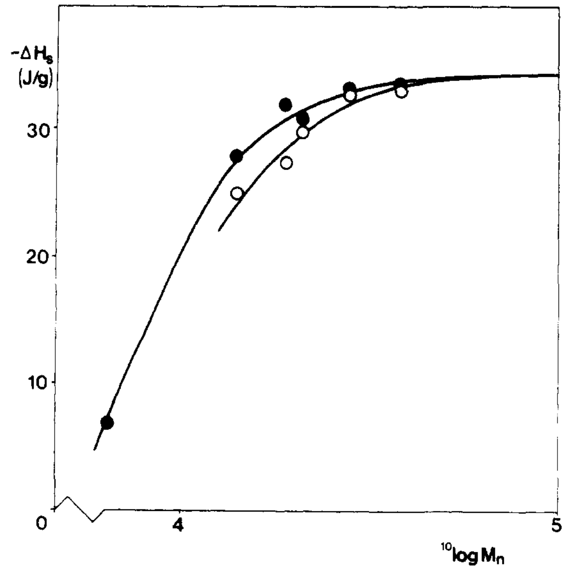

Figure 1. Effect of the molar mass of syndiotactic oligomers on the heat of complexation per gram of st-PMMA. Six different oligomers (s3, s4, s7, s9, s10, and s11) and one isotactic PMMA matrix (i1) were used. The experimental points correspond to two different fractions of oligomers: (○) $x_s = 0.2$ and (●) $x_s = 0.4$.

and the free energy of complexation, $\Delta G_1°$, is the change in free energy, due to the changes in enthalpy and conformational entropy, per mole of complex units as a result of complexation. Equation 1 is based on the assumption that an oligomer is either completely free or completely bound. m_{ol} is related to the fraction x_s of syndiotactic oligomers, defined as the fraction of the total amount of polymer, and to the total polymer concentration c by

$$m_{\text{ol}} \simeq c(x_s - 2\theta + 2\theta x_s) \qquad (3)$$

The consequences of eq 1 for the heat of complexation as a function of x_s as well as for the critical chain length were discussed thoroughly. Before we turn to the experimental results it is important to realize that the theoretical discussion concerned perfectly stereoregular matrices and oligomers. The samples used experimentally consist of it-PMMA matrices with a number of isotactic triads exceeding 95% and st-PMMA oligomers with a number of syndiotactic triads of about 90%. A detailed analysis of the stereoregular sequence length distribution, using a procedure introduced by Johnsen[16] and applied to poly(methyl methacrylates) by Spěváček and Schneider[17] and by Könnecke and Rehage,[18] is possible. However, the deviations from perfectness are small and will therefore in a first approximation be neglected.

Influence of Oligomer Chain Length and Matrix Occupancy. Figure 1 presents the heats of complexation per gram of st-PMMA, $-\Delta H_s$, for a total polymer concentration $c = 2.119 \times 10^{-3}$ g/g, using DMF as a solvent at 30 °C. The results are for the same matrices and six different oligomers of increasing chain lengths. Two different values for x_s, 0.2 and 0.4, are given. Previously, it was shown that for an excess of matrices and sufficiently long oligomers, nearly all oligomers are bound to the matrices.[9] This feature is also clearly present in Figure 1, which therefore enables us to conclude that for the given solvent and temperature, the heat of complexation per mole of complex units, $-\Delta H_c$, is to a good approximation given by

$$-\Delta H_c = 7.0 \text{ kJ/basemole of complex} \qquad (4)$$

Another conclusion that can be drawn from these results is that for $x_s = 0.4$ the critical chain length is approximately 60 units. Since the oligomers are not perfectly stereoregular the critical syndiotactic sequence length is certainly less. The explicit indication of the value of x_s for which the critical chain length is determined is necessary since it will in general be a function of x_s. Theoretically, a very simple expression implicitly determining the critical chain length can be derived in the limit $x_s \rightarrow 0$.[9]

$$cK_n^{\text{cr}} = 1/e^2 \qquad (5)$$

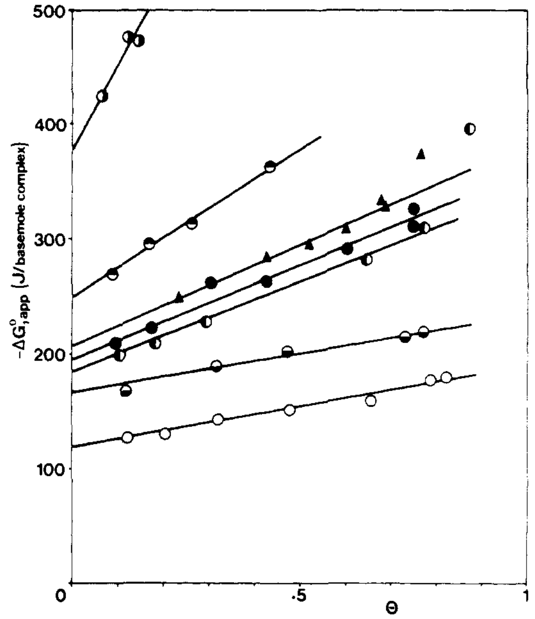

Figure 2. Effect of the degree of occupancy θ of the matrix i1 and of the molar mass of the oligomers on the free energy of complexation. The different lines correspond to the following oligomers: (○) s3, (⊖) s4, (◐) s7, (●) s9, (◒) s10, and (◑) s11. The results for the reversed system of a syndiotactic matrix s1 and isotactic oligomers i4 are also presented and are denoted by solid triangles.

Any application of eq 5 therefore determines the critical chain length of the oligomers for a large excess of matrices only. Spěváček and Schneider[17] reported a critical syndiotactic sequence length of about 10 units in various aromatic solvents. However, they employed concentrated solutions of about 10 wt % instead of the dilute solutions used in this investigation. In their case the change in configurational entropy is much smaller, making complexation more favorable. The importance of the concentration is also clearly illustrated by eq 5.

Once the heat of complexation per complex unit is known, the degree of occupancy θ of the matrix follows from the heat of complexation observed. Next, the free energy of complexation, $\Delta G_1°$, can be calculated from eq 1 for a given n, c, and x_s. The results of these calculations for the six different oligomers are presented in Figure 2, and two important observations can be made. The apparant values $|\Delta G°_{1,\text{app}}|$ increase as a function of the degree of occupancy θ of the matrix and decrease with increasing chain length n of the oligomers. The θ dependence will be considered first. As shown in the preceding paper,[9] a selection process due to polydispersity (or polytacticity) of the oligomers results in a nonlinear θ dependence of the apparent free energy of complexation. In our case a linear dependence is found. Moreover, most of the samples used have a narrow molar mass distribution and a limited polytacticity. But, it was already pointed out by Kabanov et al.[11] that all experimental evidence obtained so far shows that whenever cooperative interactions of oligomers and matrices occur, it is necessary to distinguish two levels of

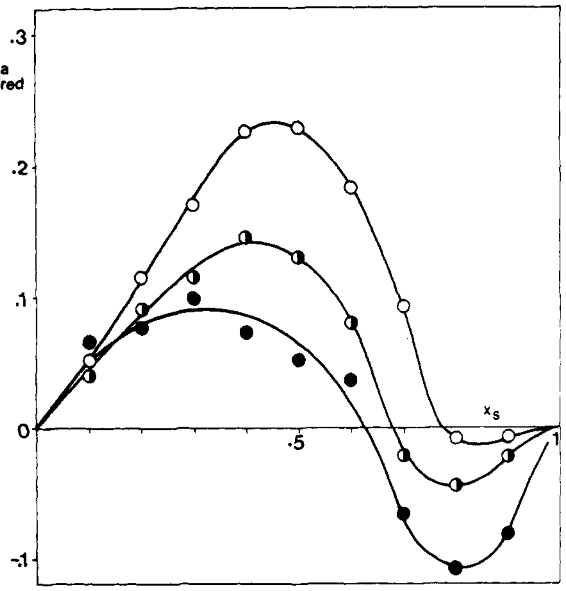

Figure 3. Reduced relative deviation from additivity of the viscosity $\eta_{red}{}^a$ as a function of the fraction of syndiotactic PMMA oligomers x_s using i2 as matrix and three different oligomers: (●) s3, (◑) s6, and (○) s8.

cooperation. The first level which is taken into account by the simple theory presented before is displayed by the strong dependence of K_n on the chain length n. However, a group of oligomers bound to the matrix can also act cooperatively if the occupied sections interact with each other. In this case the state of an oligomer bound to the matrix depends on whether other sections of the matrix are also occupied by oligomers or are free. This kind of behavior will also result in an apparent dependence of K_n on the degree of occupancy θ of the matrix. Our results point to the additional presence of the second level of cooperativity for the system of it-PMMA matrices and st-PMMA oligomers. This observation is in complete agreement with the results of light scattering experiments in DMF on the stereocomplex formation of it- and st-PMMA by Vorenkamp et al.[19] They concluded that the stereocomplex particles consisting of polymers of similar chain length mixed in a ratio it/st = $^1/_2$, consisted of double helices with local ordering in small "crystallites". It is our belief that this local ordering represents the driving force for the second level of cooperativity.

To investigate this suggestion, viscosity measurements with a long it-PMMA matrix and three different st-PMMA oligomers were performed. The reduced relative deviation from additivity of the viscosity, $\eta_{red}{}^a$, is defined by

$$\eta_{red}{}^a = \frac{1}{c}\left(\frac{\eta - \eta^a}{\eta^a}\right) \tag{6}$$

where η^a is the additive value of the viscosity given by

$$\eta^a = x_i\eta_i + x_s\eta_s \tag{7}$$

η_i and η_s are the viscosities of solutions of pure it- and st-PMMA, and $x_i = 1 - x_s$. Local ordering will result in a more compact structure, leading to lower values of $\eta_{red}{}^a$. For sufficient ordering $\eta_{red}{}^a$ should become negative. Figure 3 presents the behavior of $\eta_{red}{}^a$ as a function of x_s for the three st-PMMA samples of different chain length. An increased ordering as a function of the degree of occupancy is clearly indicated. Furthermore, longer oligomers give rise to a more compact structure for a given value of x_s. Since in this range of oligomer chain lengths, the n dependence of θ is mainly restricted to $x_s \leq 0.4$, this effect is due to an increased ordering of longer associated sections.

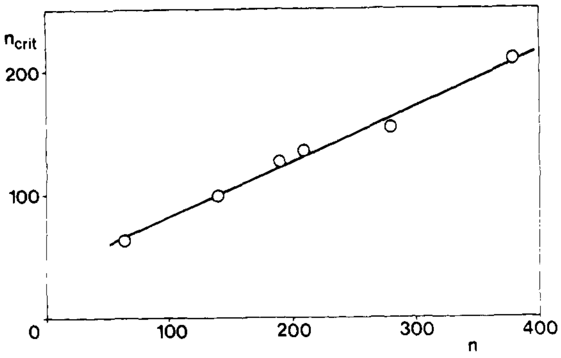

Figure 4. Critical chain length n_{crit} calculated with the help of eq 5, as a function of the chain length n of the oligomers used. Both matrix and oligomers used are the same as mentioned in the legend to Figure 1.

The decrease of the free energy of complexation as a function of the oligomer chain length is more puzzling. It is probably due to the inadequacy of the expression for the number of states available to oligomers in solution used in the derivation of eq 1.[9] This expression (eq 5 in ref 9) is only valid for a homogeneous segment distribution, which is not the case for the concentration and chain lengths of the oligomers employed in the heat of complexation measurements. Koningsveld et al.[20] studied the influence of this so-called dilute solution effect on the phase behavior in polymer solutions. Liquid–liquid equilibria in these systems involve a concentrated and a dilute phase. As a consequence of this dilute solution effect, miscibility is influenced unfavorably especially at the dilute solution side of the phase diagram. Moreover, the deviations from the Flory–Huggins predictions increase for decreasing degrees of polymerization. The Flory–Huggins theory is also based on a homogeneous segment distribution and in the case of complexation from dilute solution, similar deviations from eq 1 can be expected. The decrease of $\Delta G°_{1,app}$ for decreasing chain lengths implies that the complexation for small values of n is somewhat better than would be expected on the basis of the results for larger values of n. This is completely in line with the influence of the dilute solution effect discussed by Koningsveld et al.,[20] and we are inclined to attribute the chain length dependence of the free energy of complexation also to this effect.

Having obtained the free energy of complexation as a function of θ and n, we are now in the position to calculate the critical chain length, using eq 5, from the values of $\Delta G°_{1,app}$ extrapolated to $\theta = 0$. Clearly, the critical chain lengths thus calculated and presented in Figure 4 also depend on n.

The influence of the complexation stoichiometry and the oligomer chain length on the value of x_s for which $|\Delta H_p|$ has a maximum was extensively discussed in ref 9. For monodisperse samples the maximum should occur between the value of $x_s = 0.67$ for very strong complexation and $x_s = 0.5$ for very weak complexation. The experimental results for two st-PMMA samples of very different chain lengths and slightly different tacticities are presented in Figure 5. In agreement with the theoretical prediction, based on a 1/2 complex, the maximum occurs at approximately $x_s = 0.6$ for the longest oligomers and is shifted toward $x_s = 0.55$ for the shorter oligomers.

Reversed System. In this section we consider briefly the reversed system of a long st-PMMA matrix and short it-PMMA oligomers. Since the complexation stoichiom-

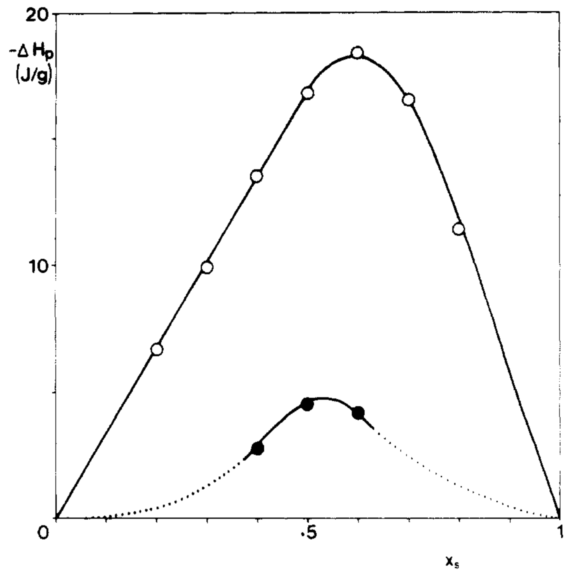

Figure 5. Influence of the molar mass of the oligomers on the location of the maximum of the heat of complexation per gram of total polymer, $-\Delta H_p$. The two different systems are (○) i1 and s3 and (●) i1 and s11.

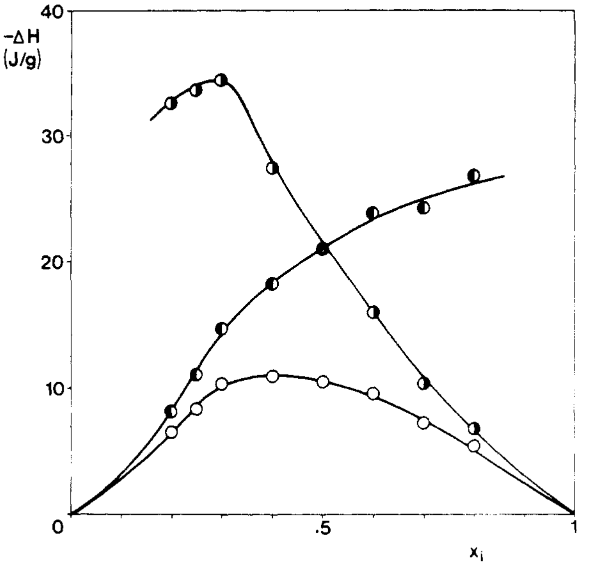

Figure 6. Heat of complexation as a function of the oligomer fraction x_i for the reversed system of a st-PMMA matrix s1 and it-PMMA oligomers i4. The heat of complexation is presented in three ways: per gram of oligomer (◑), per gram of matrix (◐), and per gram of total polymer (○).

etry is now 2/1 instead of 1/2, eq 1 is no longer valid and must be replaced by

$$\frac{\theta}{2(1-\theta)m_{\mathrm{ol}}}e^{\theta/(1-\theta)} = \bar{K}_{\mathrm{n}} \qquad (8)$$

where

$$\bar{K}_{\mathrm{n}} = e^{-n\Delta G_1{}^\circ/RT} \qquad (9)$$

m_{ol} is again the fraction of free oligomer in solution and the free energy of complexation $\Delta G_1{}^\circ$ is defined as before. Equation 9 predicts a maximum of the heat of complexation $|\Delta H_p|$ for x_i somewhere between the limiting values of $x_i = 0.33$ for very strong complexation and $x_i = 0.5$ for very weak complexation. The experimental results presented in Figure 6 show a maximum at $x_i \simeq 0.4$, in good agreement with these predictions. Using the value of the heat of complexation per complex unit, given by eq 4, one can again calculate the free energy of complexation as a function of θ. The results are also presented in Figure 2 and show an increase from 210 to 330 J/basemole of complex. Since in this case the molar mass of the oligomer it-PMMA is given by $\bar{M}_n = 6.9 \times 10^3$ it should be compared with the results of the foregoing section for st-PMMA oligomers with a molar mass of approximately $\bar{M}_n \simeq 1.4 \times 10^4$. The oligomers s10 (Table I) satisfy this requirement and Figure 2 shows that $|\Delta G^\circ{}_{1,\mathrm{app}}|$ increases from 250 to 400 J/basemole of complex as a function of θ. It is well-known that the behavior in solution of it- and st-PMMA is very different. it-PMMA is far more flexible than st-PMMA.[21] On the other hand, the characteristic ratio C_∞ defined by the unperturbed dimensions is much larger for it-PMMA than for st-PMMA.[22,23] Viscosity measurements as a function of temperature in DMF also show a large difference between the two tactic forms of PMMA.[24] Given, furthermore, the differences in tacticities, molar masses, and degrees of polydispersity between the various samples involved, the agreement between the reversed and the original system is more than satisfactory.

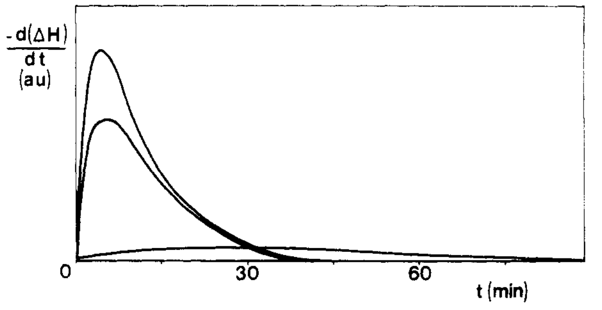

Figure 7. Influence of the tacticity of the oligomers on the calorimetric signal. In order of decreasing maximum of the signals the oligomers are s3, s2, and s5. In all cases the matrix is i1 and $x_s = 0.5$.

Influence of Oligomer Tacticity. The presence of a highly isotactic PMMA matrix promotes the syndiotactic growth of PMMA radicals along the it-PMMA chain if a suitable solvent, e.g., DMF, is employed. Prior to association the oligomeric PMMA radicals consist of approximately 65% syndiotactic triads only. It is therefore of interest to investigate the influence of the tacticity of st-PMMA oligomers on the complexation with the it-PMMA matrix in more detail. Three different oligomers of similar molar masses ($\bar{M}_n \simeq (3\text{–}4) \times 10^4$) and a decreasing percentage of syndiotactic triads (91%, 77%, and 65%) were used. Characteristic results of the calorimetric measurements are presented in Figure 7. For the sample with the smallest amount of syndiotactic triads the signal is weak and very broad. In this case an accurate determination of the heat of complexation is no longer possible. The increased width is characteristic for a selectivity with respect to the syndiotactic sequence length. As time goes on, the equilibrium state is approached more closely. A detailed comparison between the two other samples will accordingly show that the continuing exchange and selection process is more manifestly present for the lower syndiotactic sample s2 than for the high syndiotactic sample s3.

Figure 8 shows the heat of complexation for these two samples expressed as J/g of st-PMMA and as J/g of total polymer. As expected, the heat of complexation per gram of st-PMMA, $-\Delta H_s$, is much smaller for the s2 sample than for the s3 sample as long as there is an excess of matrix. The fact that ΔH_s remains approximately constant up to $x_s \simeq 0.65$ for the lower syndiotactic sample compared to 0.5 for the other sample is a clear manifestation of the selectivity with respect to the syndiotactic sequence length.

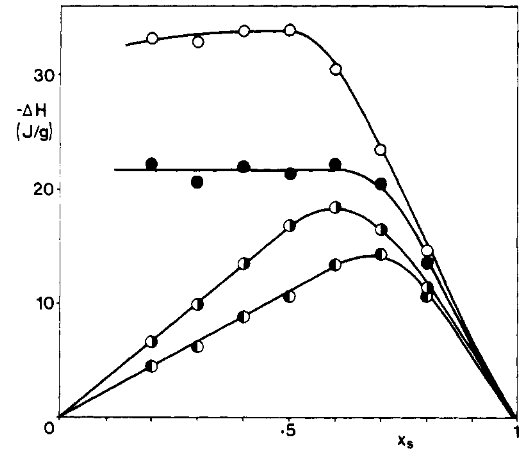

Figure 8. Influence of the amount of syndiotactic triads of the oligomers on the heat of complexation, which is presented in two ways; per gram of total polymer [(◑) i1 and s3; (◐) i1 and s2] and per gram of oligomer [(○) i1 and s3; (●) i1 and s2].

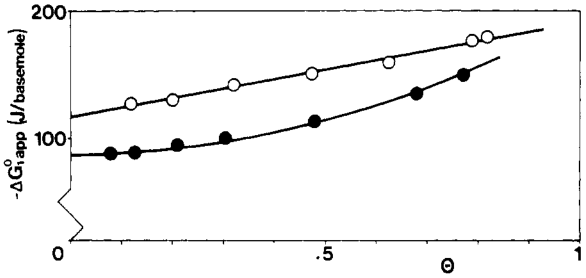

Figure 9. Influence of the tacticity of the oligomers on the free energy of complexation. The different systems are (○) i1 and s3 and (●) i1 and s2. The nonlinearity of the free energy of complexation as a function of θ, of the latter system, is characteristic for the selectivity with respect to the syndiotactic sequence length.

For perfectly stereoregular samples, $|\Delta H_s|$ decreases strongly beyond a certain value of x_s because additional complexation becomes entropically less and less favorable.[9] For the lower syndiotactic oligomers this is also the case except that now additional heat may still be produced by selecting the longest syndiotactic sequences. As a consequence, $|\Delta H_s|$ starts to decrease at higher x_s values and the maximum possible heat of complexation per gram of total polymer is observed at a value of x_s exceeding the limiting value 0.67, for very strong complexation of monodisperse highly stereoregular polymers. This behavior is similar to the predicted effect of polydispersity of oligomers,[9] where the selection is with respect to oligomer chain length rather than syndiotactic sequence length.

The application of the simple theoretical model discussed before to the complexation involving the lower syndiotactic oligomers is rather questionable, since the model is based on the assumption that an oligomer is either completely free or completely bound. Nevertheless, the results obtained by neglecting this complication are revealing. The free energy of complexation calculated with the help of eq 1 and the known heat of complexation ΔH_c (eq 4) as a function of θ is presented in Figure 9. For small values of θ, $|\Delta G^\circ_{1,\mathrm{app}}|$ is somewhat smaller for the lower syndiotactic sample because the local ordering depends on the lengths of the associated sections. The presence of a pronounced selection effect is demonstrated by the nonlinearity of the free energy of complexation for $\theta > 0.5$ for the s2 sample. At higher θ values the free energies approach each other.

Finally, Figure 10 presents the width at half-maximum of the calorimetric signal for the lower syndiotactic sample compared to the average value for the four longest oligomers of high syndiotacticity used in the study on the influence of the oligomer chain length on the complexation behavior. A pronounced broadening of the former is observed. In all cases, the width is a function of x_s, with a maximum in the neighborhood of $x_s = 0.7$ (for the reversed system treated in the last section this maximum occurs at $x_i \simeq 0.3$). During the complexation reaction a continuing exchange and selection process takes place in order to minimize the total free energy. This rearrangement process will be relatively easy for an excess of one of the components and easiest for an excess of highly stereoregular matrices. Since the width of the calorimetric signal is a measure for the time necessary to reach equilibrium, a maximum around $x_s \simeq 0.7$ is expected. The shift to $x_s \simeq 0.8$ for the lower syndiotactic sample is a further indication for the importance of the selection of the longest syndiotactic sequences.

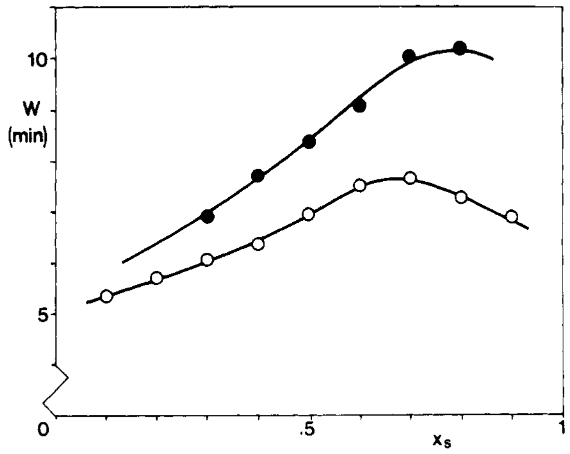

Figure 10. Influence of the tacticity of the oligomers on the width at half-maximum of the calorimetric signal. The matrix in all cases is i1. The two curves correspond to (●) average value for the oligomers s3, s4, s7, and s9 and (○) s2.

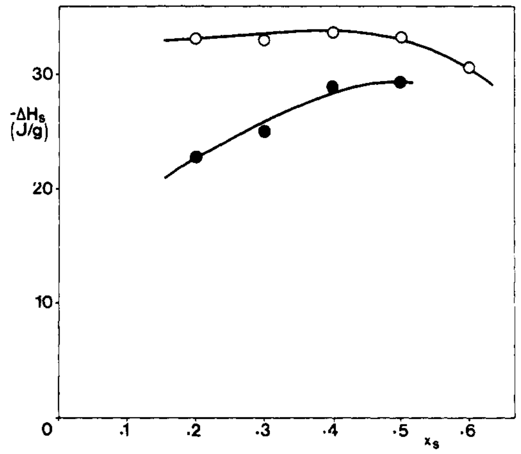

Figure 11. Effect of the total polymer concentration on the heat of complexation per gram of oligomer for the system i1 and s3. Total polymer concentrations employed are (○) $c = 2.119 \times 10^{-3}$ g/g and (●) $c = 1.060 \times 10^{-3}$ g/g.

Polymer Concentration and Matrix Length. As part of the present investigation two more parameters, the total polymer concentration c and the matrix length, were varied. Theoretically, the complexation depends on c through the combination cK_n. The effect of a smaller polymer concentration is predicted to be similar to the effect of a reduced oligomer chain length. For a small amount of oligomers (excess of matrix) the equilibrium between free and bound oligomers is shifted somewhat toward the free oligomer side and less heat will be produced. Figure 11 presents the heat of complexation per

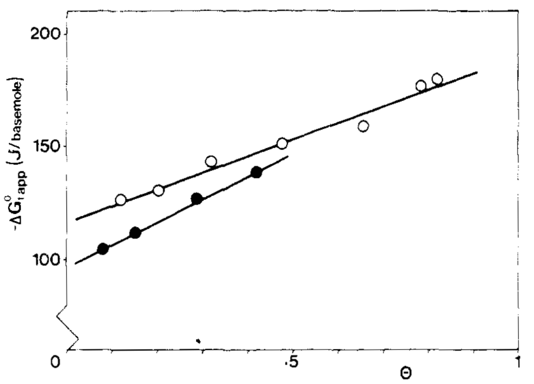

Figure 12. Calculated effect of the total polymer concentration on the free energy of complexation. The system consists of i1 and s3 and the polymer concentrations are (○) $c = 2.119 \times 10^{-3}$ g/g and (●) $c = 1.060 \times 10^{-3}$ g/g.

gram of oligomer, $-\Delta H_s$, as a function of x_s for the original polymer concentration of 2.119×10^{-3} g/g and a reduced polymer concentration of 1.060×10^{-3} g/g. Two observations can be made. First, for an excess of matrix the heat of complexation lessens considerably and secondly, the difference diminishes gradually as x_s increases. Again on the basis of the estimated heat of complexation per complex unit (eq 4) and the actual heat of complexation found, the free energy was calculated and is presented as a function of θ in Figure 12. Rather than being independent of concentration $|\Delta G^\circ_{1,\mathrm{app}}|$ is smaller for a lower total polymer concentration, although the difference diminishes as a function of x_s. This implies that the simple theoretical model would on the basis of the results for the original polymer concentration predict a larger heat of complexation than actually observed, expecially for an excess of matrix. This is another indication of the importance of the local ordering for the complexation process, as can be seen in the following way. For the high molar mass of the matrix ($\bar{M}_n \simeq 6.2 \times 10^5$), the original polymer concentration is in the case of an excess of matrices estimated to be very close to the critical overlap concentration. Both, light scattering measurements and intrinsic viscosity measurements in DMF at 25 °C point to a critical overlap concentration of about 0.25×10^{-3} g/g, as far as the isotactic PMMA matrices are concerned. For low values of the oligomer fraction, a reduction of the overall concentration will result in far more swollen conformations of the matrices.[5] As a consequence, the local ordering will be suppressed and the complexation will be reduced even more than predicted by eq 1. For larger values of x_s, the degree of occupancy of the matrix increases and the solvation of the unoccupied parts becomes less important.

The configurational entropy of the matrix is neglected in the derivation of the expression for the degree of occupancy of the matrix. As long as the matrix is very long only a small error is introduced in this way. Complexation between a shorter matrix and oligomers will result in a greater loss of configurational entropy, especially for low degrees of occupancy. To investigate the influence of the matrix chain length an isotactic PMMA matrix of a molar mass of $\bar{M}_n \simeq 2.5 \times 10^5$ was taken. The heats of complexation for this matrix and for the original matrix are presented in Figure 13. Qualitatively the behavior is as expected and indicates that a correct description for matrices of a somewhat lower molar mass must also take the loss of configurational entropy of the matrix into account.

Conclusions

The main subject of this paper as well as the previous paper[9] is the complexation of a long it-PMMA matrix and much shorter st-PMMA oligomers. Theoretically[9] the "oligomeric" character of one of the components implies that the maximum heat of complexation per gram of polymer will be found at a value of x_s which is somewhat smaller than the value of 0.67 corresponding to an it/st = 1/2 complexation stoichiometry. On the other hand, we showed that polydispersity or lower tacticity of the oligomers may shift the maximum to values of x_s exceeding 0.67 due to a selectivity of the complexation process with respect to the syndiotactic sequence length. Experimentally, the location of the maximum was found to vary between 0.55 and 0.7 depending on the oligomers used. It can be concluded that reliable information with respect to the complexation stoichiometry can only be obtained from calorimetric measurements on matrix/oligomer systems if highly stereoregular samples of a narrow molar mass distribution are used. The oligomer effect can be avoided by taking samples of similar chain length. However, the necessity of highly stereoregular samples remains. A low tacticity implies that the macromolecule contains mainly stereoregular sequences of only a small number of units. In this way another kind of oligomer effect is introduced, although admittedly in a far more complicated form, since many of the stereoregular "oligomers" are mutually connected. Still, the experience with the matrix/oligomer systems suggests that also in such a case a definite statement about the location of the maximum of the heat of complexation per gram of polymer is impossible. Biroš et al.[6] and Killman et al.'s[7] results mentioned before are striking examples.

An important conclusion from the present work is that under the given circumstances the critical chain length is about 60 monomer units of st-PMMA. As far as template polymerization is concerned this seems a rather large number, because in the latter case the growing active oligomers are also of a much lower tacticity. In fact, on the basis of this observation hardly any template effect would be expected. However, it is important to realize that the critical chain length is strongly dependent on the total polymer concentration (eq 5), which for an excess of matrices is approximately equal to the template concentration. Gons et al.[26] (cf. ref 4) studied the influence of the template concentration on the relative polymerization rate of MMA. They observed an increasing template effect as a function of the template concentration. And, indeed, hardly any template effect was observed at concentrations in the neighborhood of 0.2 g/dL. A much stronger effect was found near the critical overlap concentration of the template molecules, which for the molar masses used is

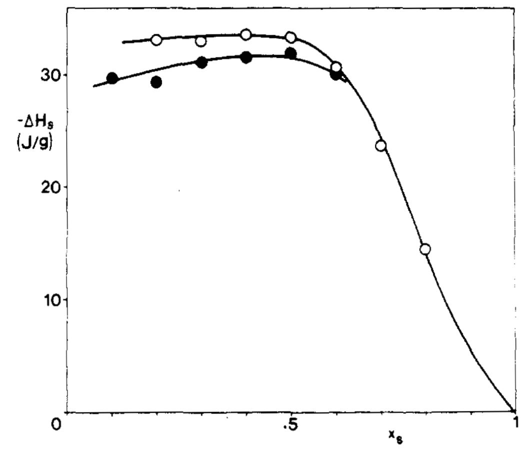

Figure 13. Influence of the molar mass of the matrix on the heat of complexation per gram of oligomer. The two different systems are (○) i1 and s3 and (●) i3 and s3.

about 1 g/dL. A simple argument based on eq 5 and a critical chain length of 60 units for a polymer concentration of 2.119×10^{-3} g/g shows that the critical chain length is about 30 units in this case. Moreover, realizing that the apparent free energy of complexation decreases strongly for oligomers of decreasing molar mass (Figure 2), the real critical chain length is probably still smaller. The basic reason for this pronounced effect of the template concentration on the critical chain length is that complexation of an oligomer at higher template concentrations is accompanied by a smaller decrease in configurational entropy of the system because more places on the matrices are available to a particular oligomer. Although the real situation in the case of template polymerization is, due to growing chains jumping from one template to another, far more complicated, the increasing template effect as a function of template concentration is at least partly due to the reduced critical chain length.

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Experimental Simulation of the Effect of Intramolecular Repulsion on the Heat of Mixing for Polymer Blends

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ABSTRACT: Random copolymers are sometimes known to form miscible blends, over a certain window of comonomer contents, with other polymers even though neither limiting homopolymer does so. Binary interaction models that consider intramolecular interactions have been introduced, and these models predict that the necessary exothermic mixing can occur when the intramolecular interaction between comonomers is sufficiently repulsive relative to the repulsive intermolecular interactions. An experimental simulation of this effect is given here using low molecular weight liquids that approximately model the monomer residues in the blend system poly(methyl methacrylate)/poly(styrene-*co*-acrylonitrile). All three binary combinations exhibit endothermic mixing; however, exothermic behavior is observed when certain premixes of the analogues of styrene and acrylonitrile are mixed with the methyl methacrylate analogue. Agreement between experimental and calculated results is good.

Introduction

The equilibrium-phase behavior of polymer–polymer mixtures is governed primarily by the heat of mixing contribution to the free energy since the combinatorial entropy change is usually very small. In fact, in the limit of high molecular weights, typical of most commercial polymers, an exothermic heat of mixing is needed to satisfy the necessary and sufficient thermodynamic conditions for miscibility. Exothermic mixing is usually thought to result from some specific interaction between certain groups, e.g., OH and C═O, in the two molecules being mixed, although the interactions among all other moieties contribute to the heat of mixing as well. Recently it has been recognized that *intramolecular* interactions among units within the molecules being mixed may also make an important contribution to the heat of mixing and can be the cause of exothermic mixing. This point of view has been incorporated into binary interaction models independently by Kambour, Bendler, and Bopp,[1] ten Brinke, Karasz, and MacKnight,[2] and Paul and Barlow.[3] This paper reports a direct experimental simulation, using low molecular weight compounds, which shows that because of repulsive

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