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Complexation of Stereoregular Poly(methyl methacrylates). 10. Influence of Polydispersity in Matrix–Oligomer Systems

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ABSTRACT: A simple model for the description of matrix–oligomer complexation reactions originally introduced by Khodakov et al. is adapted to describe the complexation of polydisperse oligomers with much longer macromolecules (matrices). A very strong selectivity with respect to oligomer chain length appears to be characteristic for these systems. This selectivity has a strong influence on the mixing ratio at which the maximum possible heat of complexation is found when calorimetric investigations are employed. The model is applied to experimental data on the isotactic poly(methyl methacrylate)–syndiotactic poly(methyl methacrylate) system previously published. It appears that the theoretical data are in agreement with the experimental data, considering the second-order cooperativity, i.e., further association of complexed chain sections, that is characteristic of this system.

Introduction

The existence of a stereocomplex, a concept introduced by Liquori et al.,[1] of isotactic (it) and syndiotactic (st) poly(methyl methacrylate) was first demonstrated by Fox et al.[2] Vorenkamp et al. proved the complexation stoichiometry to be 1 isotactic unit: 2 syndiotactic units.[3] On grounds of conformational energy calculations and X-ray diffraction data, Bosscher et al. suggested for the structure of the stereocomplex a 30/4 it-helix surrouneded by a 60/4 st-helix.[4]

Apart from the formation of the 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 it-PMMA matrix (also called template).[5,6] In this system oligomeric radicals created in free solution grow until they reach the so-called critical chain length, followed by complexation with the it-matrix. From then on, the matrix controls their growth, resulting in predominantly syndiotactic material.[7] Considering these observations, Schomaker et al. studied the complexation reactions between long isotactic matrices and much shorter syndiotactic oligomers[8] and interpreted the results in terms of a simple model originally developed by Khodakov et al.[9] and adapted by ten Brinke et al.[10] They found that the complexation appeared to be dependent of the occupancy of the matrix and the oligomer chain length. The dependence of the occupancy of the matrix was correlated to a second level of cooperativity due to further association of complexed chain sections, which was also found when both components of the complex are of high molar mass.[11-14] The dependence on oligomer chain length could not be explained satisfactorily.

In order to investigate the influence of polydispersity of the oligomers on the complexation properly, we now have adapted the model mentioned above. From simulations of ten Brinke et al. for the case of a mixture of two homodisperse oligomers[10] and from simulations of Papisov et al. for the case when the matrix is completely occupied,[15] a strong selectivity with respect to chain length is to be expected.

Theoretical Model

We will make the same assumptions as in the derivation of the complexation equation for the homodisperse case.[10] Thus the oligomers can exist in two states only, free in solution or completely bound to the matrix:

$$\text{oligomers} + \text{matrix} \rightleftarrows \text{polycomplex} \qquad (1)$$

Furthermore, we assume that the matrices are much longer than the oligomers, as it is then possible to neglect the change in the configurational (translational) entropy of the matrix upon complexation with respect to the change in the configurational entropy of the oligomers. Now the system can be treated as equilibrium adsorption of the oligomers to a one-dimensional matrix.

The change in free energy of the system ΔG can now be separated into two parts:

$$\Delta G = \Delta G_1 + \Delta G_2 \qquad (2)$$

$$\Delta G_1 = \Delta H_1 - T\Delta S_1 \qquad (3)$$

$$\Delta G_2 = -T\Delta S_2 \qquad (4)$$

ΔS_2 is the change in the configurational entropy whereas ΔH_1 and ΔS_1 are the changes in enthalpy and conformational entropy of the system, respectively. Neglecting the presence of the matrix in the system, which is permitted as long as the concentration is low enough, the number of states available to a system consisting of N_s solvent molecules and N_i oligomers of i segments ($i = 1, 2, 3, ..., \infty$) is according to Flory[16-19] given by

$$\Omega = (1/f_s)^{N_s}\prod_{i=1}^{\infty}(\omega_i/f_{\mathrm{ol}_i})^{N_i} \qquad (5)$$

Here ω_i is the number of states available to an i-mer in the close-packed state and is given by

$$\omega_i = (\delta_i/\sigma_i)i\exp(1-i) \qquad (6)$$

δ_i is a flexibility parameter and σ_i a symmetry number, related to the conformations of the oligomers. The site fractions are defined by

$$f_s = N_s/(N_s + \sum_{j=1}^{\infty} jN_j) \qquad (7)$$

$$f_{\mathrm{ol}_i} = iN_i/(N_s + \sum_{j=1}^{\infty} jN_j) \qquad (8)$$

So the configurational part of Ω in free solution, Ω^s, is given by

$$\Omega^s = \left(\frac{N_s + \sum_{j=1}^{\infty} jN_j}{N_s}\right)^{N_s}\prod_{i=1}^{\infty}\left[\left(i\exp(1-i)\times\left(\frac{N_s + \sum_{j=1}^{\infty} jN_j}{iN_i}\right)\right)^{N_i}\right] \qquad (9)$$

Apart from the loss of configurational entropy on complexation of the oligomers with the matrix, also some

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configurational entropy is won, as the oligomers can be placed on the matrix in many ways. Assuming 1 matrix unit:2 oligomer units stoichiometry, as is the case for st-PMMA oligomers, and an it-PMMA matrix, this configurational term is given by[15,20]

$$\Omega^{\mathrm{m}} = \binom{N_{\mathrm{m}} - \sum_{i=1}^{\infty}[(i/2 - 1)N_i^{\mathrm{pc}}]}{N_{\mathrm{m}} - \sum_{i=1}^{\infty}(i/2)N_i^{\mathrm{pc}}} \left[\frac{(\sum_{i=1}^{\infty} N_i^{\mathrm{pc}})!}{\prod_{i=1}^{\infty}(N_i^{\mathrm{pc}}!)} \right] \tag{10}$$

Here N_i^{pc} stands for the number of oligomers with length i complexed with the matrix. This equation consists of two parts. The first part represents the number of ways one can distribute the oligomers over N_{m} matrix units without considering the distinguishability of the oligomers because of their difference in length.[20b] The second part of the equation takes account of this distinguishability.[15]

The final expression for ΔS_2 is given by

$$\Delta S_2 = R \ln \left(\frac{\Omega^{\mathrm{s}}(N_1^{\mathrm{s}},N_2^{\mathrm{s}},\ldots,N_\infty^{\mathrm{s}})\ \Omega^{\mathrm{m}}(N_1^{\mathrm{pc}},N_2^{\mathrm{pc}},\ldots,N_\infty^{\mathrm{pc}})}{\Omega^{\mathrm{s}}(N_1^0,N_2^0,\ldots,N_{\mathrm{s}}^0)} \right) \tag{11}$$

where N_i^{s} is the number of i-mers free in solution after complexation and N_i^0 the total numbers of i-mers in the system.

With respect to ΔG_1, we assume it to be linearly dependent on the chain length of the oligomers complexed to the matrix. Furthermore, we assume that there are no other interactions involved:

$$\Delta G_1 = \sum_{i=1}^{\infty}(i/2)N_i^{\mathrm{pc}}\Delta G_1{}^{\circ} \tag{12}$$

$\Delta G_1{}^0$ is the free energy of complexation per basemole complex, consisting of 1 isotactic unit and 2 syndiotactic units.

Minimization of the Gibbs free energy with respect to the number of complexed oligomers with length n is possible; assuming that $N_{\mathrm{s}} \gg \sum iN_i \gg \sum N_i$, the result is

$$\frac{2\theta_n}{m_n(1 - \sum_{i=1}^{\infty}\theta_i)} \left[\frac{1 + \sum_{i=1}^{\infty}(2/i - 1)\theta_i}{1 - \sum_{i=1}^{\infty}\theta_i} \right]^{n/2-1} = \exp(-n\Delta G_1{}^{\circ}/2RT) \tag{13}$$

where θ_n is the degree of occupancy of the matrix by oligomers of length n defined by

$$\theta_n = (n/2)N_n^{\mathrm{pc}}/N_{\mathrm{m}} \tag{14}$$

m_n is the basemole fraction of oligomer with chain length n free in solution, defined by

$$m_n = nN_n^{\mathrm{s}}/(N_{\mathrm{s}} + \sum_{i=1}^{\infty}iN_i^{\mathrm{s}}) = c(x_n - 2\theta_n x_{\mathrm{m}}) \tag{15}$$

Here c is the site fraction of the total amount of polymer in the system (matrix and oligomer), x_n is the weight fraction oligomer with length n with reference to the total amount of polymer in the system, and x_{m} is the weight fraction matrix. Assuming furthermore that $n \gg 1$ and $(\sum(\theta_i/i))/(1 - \sum\theta_i) \ll 1$ enables us to simplify eq 13:

$$\frac{2\theta_n}{m_n(1 - \sum_{i=1}^{\infty}\theta_i)} \exp\left(\frac{n\sum_{i=1}^{\infty}(\theta_i/i)}{1 - \sum_{i=1}^{\infty}\theta_i} \right) = \exp(-n\Delta G_1{}^{\circ}/2RT) \tag{16}$$

As eq 16 is true for each n (except for the cases stated above), it is in principle now possible to calculate the total degree of occupancy (θ_{t}), given the molar mass distribution of the oligomers. It is possible to reduce this indefinite set of equations to two equations with two unknowns. First we have to realize that

$$\sum_{i=1}^{\infty}(\theta_i/\mathrm{i}) = (\sum_{i=1}^{\infty}\theta_i)/\bar{n}_n{}^{\mathrm{c}} = \theta_{\mathrm{t}}/\bar{n}_n{}^{\mathrm{c}} \tag{17}$$

here $\bar{n}_n{}^{\mathrm{c}}$ is the number-average chain length of the complexed oligomers. Rearrangement of eq 16 now leads to

$$\theta_n = \frac{x_n}{2x_{\mathrm{m}} + \dfrac{2}{c(1 - \theta_{\mathrm{t}})} \exp\{n(\theta_{\mathrm{t}}/\bar{n}_n{}^{\mathrm{c}}(1 - \theta_{\mathrm{t}}) - \Delta G_1{}^{\circ}/2RT)\}} \tag{18}$$

Summation of both sides of this equation over all chain lengths gives us one equation. The other is obtained by summation, after both sides are divided by n. If we furthermore assume that $x_n \ll (1 - x_{\mathrm{m}})$ in the range $n \simeq 1$–10, then it is permitted to perform integrations instead of summations. This enables us to write finally

$$\theta_{\mathrm{t}} = \int_0^{\infty} \frac{x_n\,\mathrm{d}n}{2x_{\mathrm{m}} + \dfrac{2}{c(1 - \theta_{\mathrm{t}})} \exp\{n(\theta_{\mathrm{t}}/\bar{n}_n{}^{\mathrm{c}}(1 - \theta_{\mathrm{t}}) - \Delta G_1{}^{\circ}/2RT)\}} \tag{19}$$

$$\theta_{\mathrm{t}}/\bar{n}_n{}^{\mathrm{c}} = \int_0^{\infty} \frac{(x_{\mathrm{n}}/n)\,\mathrm{d}n}{2x_{\mathrm{m}} + \dfrac{2}{c(1 - \theta_{\mathrm{t}})} \exp\{n(\theta_{\mathrm{t}}/\bar{n}_n{}^{\mathrm{c}}(1- \theta_{\mathrm{t}}) - \Delta G_1{}^{\circ}/2RT)\}} \tag{20}$$

Selectivity with Respect to Chain Length

If the molar mass distribution of the oligomers is known, eq 19 and 20 can be numerically solved. Once the total amount of oligomer complexed and the number-average length of the complexed oligomers are known, it is possible to calculate the degree of occupancy of the matrix by the oligomers of each length n. So it is also possible to calculate the molar mass distribution of the oligomers complexed with the matrix and to compare these data with the original distribution. We have done this for a so-called log-normal distribution.[21] Expressed in terms of weight fractions as defined above ($\sum x_i = (1 - x_{\mathrm{m}})$)

$$x_n = \frac{1 - x_{\mathrm{m}}}{ns(2\pi)^{1/2}} \exp[-\ln^2 (n/n_0)/2s^2] \tag{21}$$

Here n_0 is the median value of the distribution and s is a measure of the width of the distribution and has the following connection with the dispersion number D:

$$D = \exp(s^2) \tag{22}$$

In terms of these parameters, the number-average chain length is expressed as

$$\bar{n}_n = n_0 \exp(-s^2/2) \tag{23}$$

In Figure 1 the total chain length distribution of the oligomers in the system with a number-average chain length of 100 and a dispersity number of 2 is presented ($x_{\mathrm{m}} = 0$), as well as the chain length distributions of the oligomers complexed to the matrix for the case of three weight fractions of oligomer at a total polymer concen-

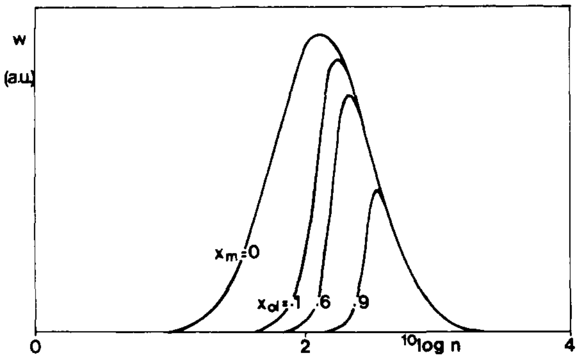

Figure 1. Chain length distribution of an oligomer of a number-average chain length of 100 and a dispersity number of 2 before complexation ($x_m = 0$) and three simulated distribution curves of the fraction bound to the matrix for an oligomer weight fraction (x_{ol}) of 0.1, 0.6, and 0.9. The free energy of complexation ($\Delta G_1°$) is 250 J/basemole complex, the temperature 300 K, and the concentration 0.2 g/dL.

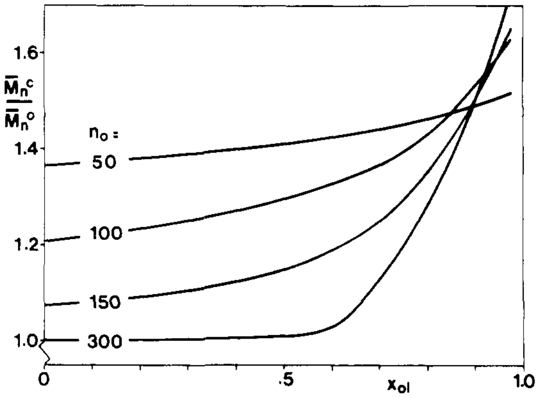

Figure 2. Selectivity expressed in terms of the ratio of the number-average molar mass ($\bar{M}_n^c$) of the complexed fraction and that of the total amount of oligomer in the system ($\bar{M}_n^o$) as a function of the oligomer weight fraction for a median molecular chain length (n_0) of 50, 100, 150, and 300. The dispersity number is in all cases 1.1. The free energy of complexation ($\Delta G_1°$) is 300 J/basemole complex, the temperature 300 K, and the concentration 0.2 g/dL.

tration of 0.2 g/dL, a temperature of 300 K, and a free energy of complexation of 250 J/basemole complex. As also found by Papisov et al. for the case of full occupancy of the matrix[15] and by ten Brinke et al. for the case of two homodisperse fractions,[10] a very strong selectivity with respect to the chain length of the oligomers is apparent, especially for the case of an excess of oligomers. This selectivity is based on the cooperative character of these complexation reactions, which is expressed by eq 12.

In Figure 2 this selectivity is expressed in terms of the ratio of the number-average molar mass of the complexed fraction and the total amount of oligomer. This ratio is plotted as a function of the oligomer weight fraction for four oligomers only differing in median chain length, n_0, with a dispersity number of only 1.10. One can see that for the case of long chains, selection does not occur up to about the stoichiometric ratio, because essentially all the oligomers in the system are complexed with the matrix. At higher weight fractions only the longest oligomers will be selected. This is also apparent from Figure 3, in which the ratio of the dispersity number of the oligomers bound to the matrix and of the total amount of oligomer is plotted as a function of the oligomer weight fraction.

When an essential part of the molar mass distribution of the oligomer has a chain length of the order of magnitude or lower than the so-called critical chain length,

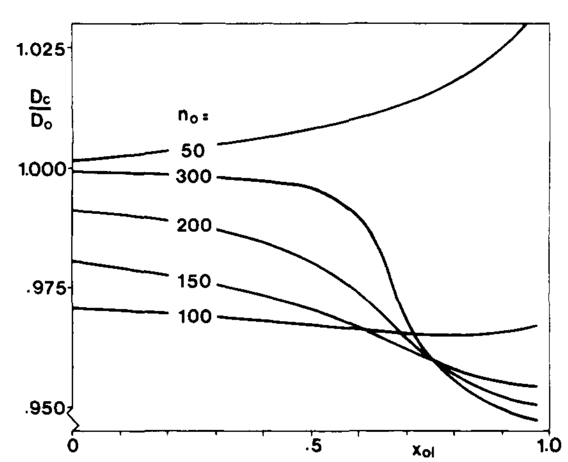

Figure 3. Ratio of the dispersity numbers of the oligomers bound to the matrix (D_c) and the total amount of oligomer in the system (D_0) as a function of the oligomer weight fraction for a median molecular chain length (n_0) of 50, 100, 150, 200 and 300. The dispersity number is in all cases 1.1. The free energy of complexation ($\Delta G_1°$) is 300 J/basemole complex, the temperature 300 K, and the concentration 0.2 g/dL.

selection occurs also at lower oligomer weight fractions. Given the temperature and concentration, this critical chain length n_c is defined as[10]

$$n_c = -(\ln c + 2)2RT/\Delta G_1° \tag{24}$$

Employing the same data we used to construct Figures 2 and 3, we find the critical chain length has in this case a value of 67. In Figure 2 it is shown that the selectivity for the case of an oligomer with a median chain length $n_0 = 50$ is almost independent of the weight fraction oligomer in the system. The reason is that as the greater part of the oligomer has a chain length that is shorter than the critical chain length, only (part of) the very longest oligomers are complexed with the matrix. Figure 3 shows that in this case the dispersity number of the complexed part is higher than that of the original oligomer sample.

Maximum Heat

To determine the stoichiometry of complexation, often calorimetric investigations are employed. The mixing ratio at which a maximum heat of complexation is found is then taken as the stoichiometric ratio.

In a previous paper we have shown that in the homodisperse case with a complexation stoichiometry of 1 matrix unit: 2 oligomer units, the maximum heat of complexation will always be found at a weight fraction oligomer of less than $^2/_3$.[10] It is to be expected that the selectivity in the case of heterodisperse samples might influence the dependence of the weight fraction oligomer at which the maximum is found (x_{ol}^{max}) on variables like chain length, temperature, and concentration. The heat of complexation (ΔH_c) can be defined as

$$\Delta H_c = 3\theta_t x_m \tag{25}$$

Here we have normalized ΔH_c so that the maximum value equals unity (at $\theta = 1$ and $x_m = {}^1/_3$). Substituting this expression into eq 19 and 20 and subsequently differentiating both expressions with respect to x_m (or x_{ol}) result in four equations with four unknowns which can be solved numerically.

In Figure 4 x_{ol}^{max} is plotted as a function of the median chain length for four different dispersity numbers. From this figure we can conclude that the dispersity of the oligomers has a great influence on the mixing ratio at which the maximum occurs. Again the selectivity with respect

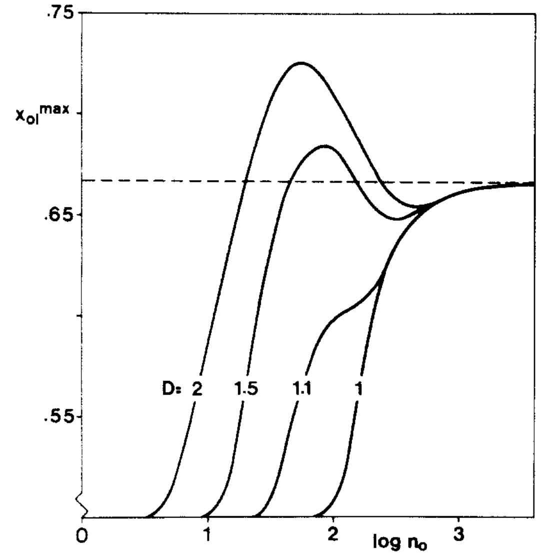

Figure 4. Oligomer weight fraction (x_{ol}^{max}) for which a maximum heat of complexation will be obtained as a function of the median molecular chain length (n_0) for four different dispersity numbers. The free energy of complexation ($\Delta G_1°$) is 300 J/basemole complex, the temperature 300 K, and the concentration 0.2 g/dL.

to the chain length is responsible for this effect. Three regions can be distinguished. When complexation is weak, i.e., when n_0 is relatively low, only (part of) the longest chains available will be bound to the matrix, and the maximum is found before the stoichiometric ratio is reached. Eventually in the limit of no complexation the maximum is independent of complexation stoichiometry and will always be found at a mixing ratio of 1:1.[10] In the case of moderate complexation, the maximum can be shifted far beyond the stoichiometric ratio, depending on the polydispersity of the oligomer sample. When finally very long chains are employed, all chains available will be bound to the matrix up to the stoichiometric ratio. Consequently, the polydispersity effect will vanish and the maximum will eventually be found at a mixing ratio of 1:2.

Apart from the free energy of complexation and the chain length, the other two important parameters are the temperature and the concentration. Depending on the sign of the free energy of complexation, raising the temperature will of course increase or decrease the degree of complexation and the curves in Figure 4 will be shifted to shorter or longer chain lengths, respectively. An increase of the concentration will also improve the degree of complexation as the number of states available to the oligomers free in solution will be relatively lower so complexation is more favorable (quantitatively this is expressed in eq 24). Consequently, the concentration also influences the weight fraction at which the maximum is found.

Comparison with Experimental Results

In a previous paper we published our results of a calorimetric investigation of the complexation of it-PMMA matrices with various st-PMMA oligomers differing in chain length.[8] Using the model for the description of the complexation in the homodisperse case, we calculated the (apparent) free energy of complexation per basemole complex ($\Delta G_1°_{app}$) from the experimental results. It appeared that $\Delta G_1°_{app}$ depended on the oligomer chain length as well as the occupancy of the matrix. Especially the dependence on the chain length could not be explained satisfactorily. Now that the polydisperse model is available, we have reconsidered the data.

Given the molar mass and the dispersity of the samples used and furthermore assuming that the molar mass distribution of the samples may be represented as a log-normal distribution, it is possible to simulate the complexation experiments and to evaluate the theoretical results again with the homodisperse model. In Figure 5 the simulated curves are presented for an adopted value for the free energy of complexation of 250 J/basemole complex, as well as the original experimental data. It is evident that the dependence on chain length and θ is predicted qualitatively correctly.

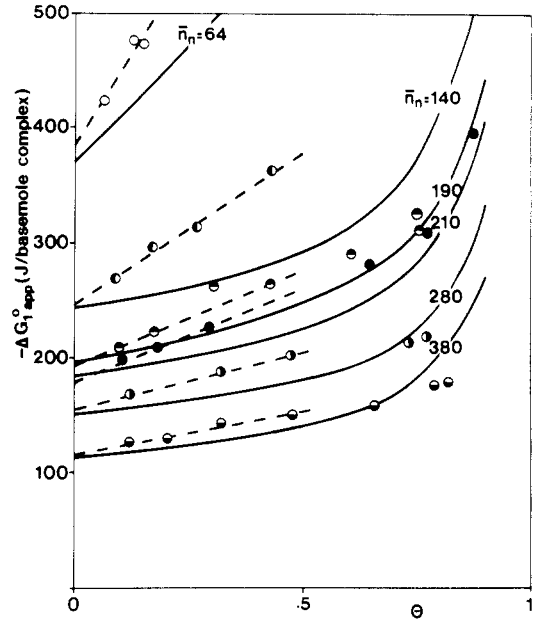

Figure 5. Apparent free energy of complexation $\Delta G_1°$ as a function of the occupancy of the matrix (θ) as obtained by evaluating former experimental results[8] in terms of the homodisperse model (---) compared with simulated curves employing the heterodisperse model using a value of the free energy of complexation $\Delta G_12°$ of 250 J/basemole complex (—). The temperature was 300 K and the concentration 0.2 g/dL. The oligomers employed are as follows: (○) $\bar{M}_n = 6400$, $D = 1.3$; (◐) $\bar{M}_n = 14000$, $D = 1.1$; (◓) $\bar{M}_n = 19000$, $D = 2.25$; (●) $\bar{M}_n = 21000$, $D = 1.55$; (◑) $\bar{M}_n = 28000$, $D = 1.6$; (◒) $\bar{M}_n = 38000$, $D = 2.25$. For further experimental details see the paper of Schomaker et al.[8]

The apparent dependence on chain length can be explained again in terms of selection. When a sample is used with a number-average chain length of the order of magnitude of the critical chain length, the longest chains will be selected and the occupancy of the matrix is higher than would be expected on grounds of the number-average chain length. Consequently, the apparent free energy of complexation will be overestimated. Whenever a sample is used with a higher number-average chain length, containing a small fraction having chain lengths of the order of magnitude or lower than the critical chain length, the greater part of this fraction will stay free in solution and the occupancy of the matrix will be lower than expected. In this case the free energy of complexation will be underestimated.

The theoretically predicted dependence on θ is also based on the selection principle and can be explained in a comparable way. If the oligomer weight fraction in the system increases, i.e., θ increases, the longest chains available will be selected. Consequently, $\Delta G_1°$ apparently increases as a function of θ. This increase will be strongest when there is an excess of oligomers in the system with respect to the stoichiometric ratio as is shown in Figure 5 at high values of θ.

Comparison of the experimental data with the theoretical curves reveals a systematic positive deviation. At low values of θ this deviation increases with θ. At higher

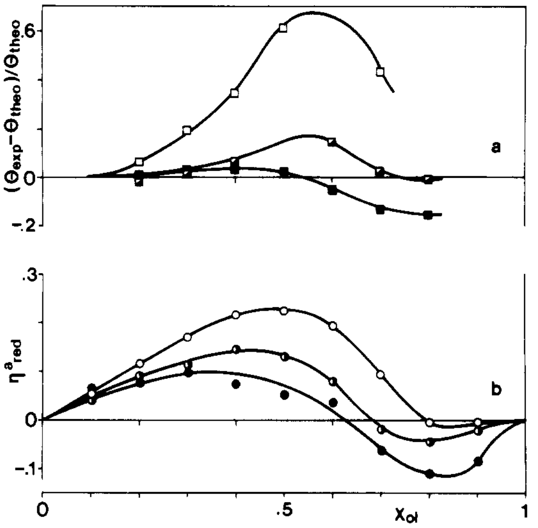

Figure 6. (a) $(\theta_{\text{exptl}} - \theta_{\text{theor}})/\theta_{\text{theor}}$ as a function of the oligomer weight fraction (x_{ol}) for three samples taken from Figure 5. The oligomers employed are as follows: (□) $\bar{M}_n = 14000$, $D = 1.1$; (◪) $\bar{M}_n = 21000$, $D = 1.55$; (■) $\bar{M}_n = 38000$, $D = 2.25$. For further experimental details see the paper of Schomaker et al.[8] (b) Reduced relative deviation from additivity of the viscosity of mixed solutions of the same matrix with three different oligomers as a function of the weight fraction oligomer in the system. The oligomers employed are as follows: (○) $\bar{M}_n = 21000$, $D = 1.15$; (◑) $\bar{M}_n = 24000$, $D = 1.35$; (●) $M_n = 38000$, $D = 2.25$. For further experimental details see the paper of Schomaker et al.[8]

values this deviation becomes negative, particularly in the case of the samples with the highest molar masses. In Figure 6a this deviation is plotted for some samples in terms of $(\theta_{\text{exptl}} - \theta_{\text{theor}})/\theta_{\text{theor}}$ as a function of x_{ol}. This deviation should be ascribed to the so-called "second level of cooperativity" that is characteristic for this system. When both components of the stereocomplex are of high molar mass, very compact stereocomplex particles are formed in a strongly complexing solvent like DMF, consisting of double helices with locally associated small "crystallites" surrounded by the uncomplexed chains in excess with respect to the stoichiometric ratio.[12,14] Schomaker et al. found that this association of complexed chains also occurs in matrix–oligomer systems, increasing with the degree of occupancy of the matrix and the chain length of the oligomers.[8] This is shown in Figure 6b, where the reduced relative deviation from additivity of the viscosity of mixed solutions of the same it-matrix and three different st-oligomers is plotted as a function of x_{ol}. This viscosity function is defined as

$$\eta_{\text{red}}{}^{\text{a}} = (\eta - \eta^{\text{a}})/c\eta^{\text{a}} \qquad (26)$$

Here η^{a} is the additive value of the viscosity of the two solutions. In this figure it is shown that a negative deviation from additivity, which is characteristic for the association phenomenon,[8,12,14] is found at high values of x_{ol}. Furthermore, we can conclude from this figure that association is stronger when the chain length is longer.

From these results it is to be expected that ΔG_1 is not linearly dependent on the oligomer chain length as assumed in eq 12. As a consequence of the second-order cooperativity in this system, ΔG_1 is also a function of θ. In the limit of no complexation, $\theta = 0$, the theoretical data coincide with the experimental values as is shown in Figure 5 because association of the complexed sections is then principally not possible. When occupation of the matrix increases, association becomes increasingly important. Because of this extra interaction term complexation will become relatively more favorable and the occupancy of the matrix will be found higher than expected on theoretical grounds as shown in Figure 6a. Whenever long oligomers are employed and $\theta > 0.5$ (or at high weight fractions oligomer), association can become very strong as shown in Figure 6b. Under these conditions exchange and selection processes are prevented on the time scale of the experiment. Equilibrium will not be reached, and θ will eventually be found lower than expected theoretically. Comparison of parts a and b of Figure 6 confirms this picture.

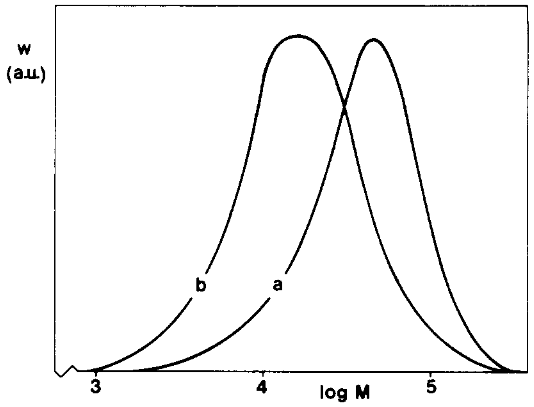

Figure 7. Molar mass distributions of (a) the oligomers complexed with the matrix and (b) the oligomers free in DMF solution. The oligomer sample employed had $M_n = 19000$, and $D = 2.25$. The matrix employed had $\bar{M}_n = 1650000$, and $D = 1.35$. The total polymer concentration was 0.2 g/dL, $x_{\text{ol}} = 0.6$, and the temperature was 20 °C.

Finally, we have tried to verify experimentally the occurrence of the selection process in this system. Centrifugation of a solution of complexes, matrices, and oligomers followed by separate characterization of the material separated and the material still in solution might seem a suitable procedure. However, centrifugation induces a concentration gradient in the solution, and the concentration is a very important parameter in these complexation reactions as expressed by eq 24. So a redistribution of oligomers over the matrices as a function of the position in the centrifugation tube (concentration) can be expected. Sometimes even a mixture of solvents is used in centrifugation experiments in order to create a density gradient.[23,24] In these cases one essentially introduces also a gradient in the free energy of complexation. Consequently, in principle, centrifugation experiments cannot give a correct picture of the complexation equilibrium.

As at the moment no technique more suitable is available to verify the selection process, we employed the centrifugation procedure as described above. To prevent reorganization during centrifugation we studied an it-matrix/st-oligomer solution with a composition near the stoichiometric ratio of the complex ($x_{\text{ol}} = 0.6$). It is known that in this case, aggregation and eventually flocculation of stereocomplex particles take place,[12,14] marked by an increasing turbidity of the solution. One day after mixing the components the complexed material was separated easily from the turbid solution by centrifugation. Reorganization of oligomers is assumed not to occur on the time of scale (of minutes) of this procedure as a consequence of the formation of aggregated stereocomplex particles.

In Figure 7 the results of this experiment are presented. The materials separated from and still in solution were characterized by means of gel permeation chromatography (Waters ALC/GPC 150C equipped with one TSK GMH 6 column) relative to polystyrene standards using chloroform as eluent. In this noncomplexing solvent the separated stereocomplexes dissolve and decomplex. The existence of the selection process is clearly confirmed by this experiment.

Concluding Remarks

From the results presented above it is concluded that selection processes in matrix–oligomer complexation reactions are far more important than expected. As a result, it is principally not possible to evaluate these reactions correctly in terms of a homodisperse model when heterodisperse samples are employed. With respect to the system under consideration, even the complexation behavior of oligomers with a dispersity number of 1.1 is not predicted correctly by the homodisperse model.

As a result of these selection processes, it is not possible to correlate directly the mixing ratio, at which a maximum heat of interaction is found, to the stoichiometric ratio of complexation, in the case of calorimetric investigations of matrix–oligomer systems. No problems of these kind will be met when only components of high molar mass are employed.

The selectivity of this kind of complexation reaction can be used to fractionate heterodisperse samples with respect to chain length as shown above for the case of the it-PMMA–st-PMMA system. In principle, to obtain the highest degree of selectivity, one has to use an excess of oligomers with regard to the matrix as shown above. However, in this system, showing second-order cooperativity, the associates formed tend to immobilize the system, preventing the exchange processes from occurring. As this second-order cooperativity is not unique to this system,[22] it might sometimes be better in practice to employ an excess of matrices to prevent this immobilization. In that case highest selectivity is met at the critical conditions as defined by eq 24. Finally, it should be mentioned that in this system, it is also possible to fractionate with respect to tacticity as shown by Schomaker et al.[8]

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Registry No. 1 isotactic PMMA:2 syndiotactic PMMA complex, 79616-50-5.

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On the Chain Length Dependence of the Dynamics of Coil Expansion of Poly(methacrylic acid)

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ABSTRACT: The rate of chain expansion of poly(methacrylic acid) (PMA) in methanol solutions containing 4,4′-bis(dimethylamino)triphenylmethane leucohydroxide (I) was measured by following the change in the light scattering intensity (LSI). Chain expansion was induced by the photolysis of I by a 20-ns flash of 265-nm light. OH^- ions generated in this way led to an increase in the degree of ionization of the PMA. The half-life of the LSI decrease reflecting the chain expansion depended on the molecular weight as $\tau_{1/2} \propto M^x$, with $x = 0.9$. On the basis of the Rouse–Zimm theory, $x = 1.5$ was expected. The discrepancy is explained in terms of the neutralization of PMA being a stepwise noncooperative process. Initially, the hydroxyl ions react almost exclusively with carboxylic groups in the outer regions of the rather compact PMA coils. Subsequently, the ionized sites equilibrate and thus become statistically distributed along the chains.

Introduction

The dynamics of conformation changes of polyelectrolytes can be measured conveniently with the aid of a technique based on a UV light induced pH jump accomplished by laser flash photolysis of an OH^- emitter such as the substituted triphenylmethane leucohydroxide I. This was recently demonstrated by Irie and Schnabel,[1] who investigated the chain expansion of poly(methacrylic acid) (PMA). Prior to that it was shown by Irie[2] that upon continuous irradiation of triphenylmethane leuco-

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