rection-independent "expansion (or contraction) factor" for all values of $j - i$, in this case $s^2(R)/\langle s^2\rangle_0 = (s_{\parallel}{}^2(R) + 2s_{\perp}{}^2(R))/\langle s^2\rangle_0$. It turns out that these values, within the limits of accuracy, equal $-0.5k_{s^2}$. This result could have been easily derived in closed form under the assumption of Gaussian statistics and of a single expansion factor for all r_{ij}. Thus, the difference between columns 9 and 10 actually should represent the contribution of shape variation to the concentration dependence of r_h. Although these differences are by no means negligible, taking into account the variation of shape, in the way done by Akcasu, actually does not lead to an unanimous improvement: while there is a slight reduction of the difference between the data of columns 6 and 9 (over that between the data of columns 6 and 10) for Θ chains, the reverse is true for athermal systems. The *real* basic reason for the (partial) failure of Akcasu's treatment, however, appears to lie in the introduction of the assumption b of a d-independent (in the sense outlined above) "chain expansion" or "chain compression" caused by intermolecular interaction, which would lead to d-independent k_d values. Replacement of this "uniform expansion or contraction assumption" for all subchains by a more realistic one, therefore, invariably should lead to a substantial improvement of the Akcasu–Hammouda treatment. The inadequacy of this assumption which, for instance, may be easily extracted from our Figures 3 and 4, Figure 5, or Table II, apart from the distortions of the r_{ij} distributions on intermolecular interactions appears to be another example of the non-Gaussian character of intermolecular interaction effects between chain molecules regardless of thermodynamic conditions.

Acknowledgment. This paper is as an auxiliary contribution to the project (Grant No. 4309) sponsored by the "Fonds zur Förderung der wissenschaftlichen Forschung in Österreich", Vienna, Austria. We take this opportunity to gratefully acknowledge this support.

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(8) Admittedly, the value of ϕ that is necessary to make the excluded volume vanish is slightly dependent on n. Actually, the value chosen ($\phi = -0.255$), within statistical scatter, leads to a zero excluded volume for $n = 24$ and $n = 49$. Accordingly, there is a slightly positive excluded volume for $n = 99$ and $n = 199$, which, however, amounts to a few percent of that observed for athermal conditions only (3.5% and 6.5%, respectively).
(9) This is in qualitative accordance with the results of the first-order perturbation theory for $r_{ij}{}^2$ (Kurata, M.; Yamakawa, H.; Teramoto, E. *J. Chem. Phys.* **1958**, *28*, 785) and $r_{ij}{}^{-1}$ (Barrett, A. J. *J. Phys. A: Math. Gen.* **1983**, *16*, 2321), respectively.
(10) A detailed discussion of the chain length dependence of these quantities will be given together with a theoretical approach to the problem (Olaj, O. F.; Zifferer, G.; Mann, E., to be published).

Complexation of Stereoregular Poly(methyl methacrylates). 7. Theoretical Aspects

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ABSTRACT: In a suitable solvent isotactic (it) and syndiotactic (st) poly(methyl methacrylates) associate into a stereocomplex with an it/st = $^1/_2$ composition. A simple model, introduced by Khodakov et al., for the complexation of a long macromolecule (matrix) and much shorter macromolecules (oligomers) is adapted to this particular stoichiometry. It is shown that the heat of complexation per complex unit is determined experimentally by taking an excess of matrix rather than an excess of oligomers. The ratio of the amount of oligomer and the amount of matrix for which the maximum possible heat of complexation per gram of macromolecules occurs is shown to depend strongly on the chain length of the oligomers and on the stoichiometry of complexation. The influence of the polydispersity of the oligomers on the behavior of the heat of complexation as a function of the matrix/oligomer ratio is discussed. A simple relation for the critical chain length, defined as the chain length of the oligomers, below which no appreciable complexation takes place, is derived and is shown to be independent of the complexation stoichiometry.

Introduction

In certain solvents, the isotactic and syndiotactic sequences of it- and st-PMMA associate, leading to the formation of a stereocomplex, a concept first introduced by Liquori et al.[3] The composition of the stereocomplex has long been a point of controversy and only recently[4] was it shown unambiguously that both components are present in a ratio it/st = $^1/_2$. The structure of the stereocomplex is still not completely clear. Kusanagi et al.[5] suggested that it should be closely related to the double-stranded helix of it-PMMA. Then Bosscher et al.[6] concluded that the X-ray diffraction data and conformational energy calculations point to a double-stranded helix consisting of an isotactic 30/4 helix surrounded by a syndiotactic 60/4 helix, with an identity period of 73.6 Å.

Another remarkable observation is that the stereocomplex can be formed in situ by free-radical polymerization of methyl methacrylate to predominantly syndiotactic PMMA due to the presence of it-PMMA as a template.[7,8] Moreover, the presence of a template matrix leads to a rate enhancement, due to a delayed termination reaction of those growing chains which are bound to the matrix.[9]

Double-stranded helical structures are well-known for various synthetic polynucleotides as well as for natural DNA, and several models, e.g., the perfect-matching, the imperfect-matching, and the hairpin models, have been developed to describe the helix–coil transition in these systems.[10] Of these, the imperfect-matching model seems best suited to describe the dissociation of the stereocomplex. Our main interest is the complexation between a long macromolecule (matrix) and several much shorter complementary macromolecules (oligomers). A simple model describing this kind of a situation was developed by Khodakov et al.[1] and is based on the analogy between complexation and adsorption of oligomer chains on a one-dimensional lattice. They made the important assumption that oligomers can exist in two states only, free in solution or completely bound to the matrix. For simplicity it was also assumed that matrix and oligomers are present in the complex in a base molar ratio 1/1. This model with its straightforward extension to the actual stoichiometry of 1/2 will be outlined in the first section. The most important consequences of the model were summarized by Kabanov et al.[2] and we mention a few that are of special interest: (a) a strong dependence of the stability of the complex on the length of the oligomer chain and (b) a high selectivity to the length of the oligomer chain. The latter is especially important in the case of an excess of polydisperse oligomers.

In a companion paper,[11] the results of our calorimetric investigation of stereocomplex formation of it- and st-PMMA will be presented. It is the purpose of the present paper to develop a theoretical basis for the interpretation of those results. The main emphasis will therefore be on the heat of complexation and the influence of various factors, e.g., the ratio of the amount of matrix and oligomer or the polydispersity of the oligomers, thereupon.

Theoretical Model

As mentioned before, the main assumption in the theory of Khodakov et al.[1] for complexation of oligomers and a matrix in dilute solution is that an oligomer can exist in two states only, free in solution or completely bound. For isotactic and syndiotactic PMMA this is certainly not always the case and we will return to this complication where necessary. Due to this simplifying assumption, complexation is equivalent to the reaction

$$\text{oligomer} + \text{matrix} \rightleftharpoons \text{complex} \tag{1}$$

It will be treated as equilibrium adsorption of oligomers on a one-dimensional lattice. Apart from the polymer aspects, the treatment is the same as for Langmuir adsorption of low molecular weight substances on a surface.

The change in free energy of the system ΔG due to the complexation of $N_{\text{ol}}^{\text{pc}}$ oligomers can be separated into two parts:

$$\Delta G = \Delta G_1 + \Delta G_2 \tag{2}$$

$$\Delta G_1 = \Delta H_1 - T\Delta S_1 \tag{3}$$

$$\Delta G_2 = -T\Delta S_2 \tag{4}$$

ΔS_2 is the change in configurational entropy whereas ΔH_1 and ΔS_1 are the changes in enthalpy and conformational entropy. First an outline will be given on how to derive an expression for ΔS_2 for the case of a 1/2 complex; a detailed account of the derivation for the case of a 1/1 complex can be found in ref 2. Neglecting the presence of the long matrix, the total number of states Ω available to a system of N_{s} solvent molecules and N_{ol} oligomers of n segments each is according to Flory[12,13] given by

$$\Omega = (1/f_{\text{s}})^{N_{\text{s}}}(\omega/f_{\text{ol}})^{N_{\text{ol}}} \tag{5}$$

where $\omega = \delta n e^{1-n}/\sigma$, σ is a symmetry number, and δ is a flexibility parameter. ω is the number of states available to an n-mer in the close-packed pure state. δ is equal to the number of ways in which the oligomer can be arranged on the lattice after one of its segments has been fixed on a lattice site. It is a measure of the oligomer's conformational degrees of freedom. Its maximum value is given by

$$\delta_{\max} = z(z-1)^{n-2} \tag{6}$$

where z is the coordination number of the lattice. The site fractions f_{s} and f_{ol} are defined by

$$f_{\text{s}} = N_{\text{s}}/(N_{\text{s}} + nN_{\text{ol}}) \tag{7}$$

$$f_{\text{ol}} = nN_{\text{ol}}/(N_{\text{s}} + nN_{\text{ol}}) \tag{8}$$

The configurational part of Ω is given by

$$\Omega_1(N_{\text{ol}}) = n^{N_{\text{ol}}}\begin{pmatrix} N_{\text{s}}/n + N_{\text{ol}} \\ N_{\text{ol}} \end{pmatrix} \tag{9}$$

Because $N_{\text{ol}}^{\text{pc}}$ oligomers can be placed on the matrix in many ways, only part of the configurational entropy is lost upon complexation. Assuming that two units of the oligomer "react" with one unit of the matrix, as is the case for st-PMMA oligomers and the it-PMMA matrix, the number of ways $N_{\text{ol}}^{\text{pc}}$ oligomers can be placed on a matrix of N_{m} units is given by

$$\Omega_2 = \begin{pmatrix} N_{\text{m}} - (n/2 - 1)N_{\text{ol}}^{\text{pc}} \\ N_{\text{m}} - (n/2)N_{\text{ol}}^{\text{pc}} \end{pmatrix} \tag{10}$$

One way of understanding this expression is by realizing that it is precisely the number of ways of putting $N_{\text{m}} - (n/2)N_{\text{ol}}^{\text{pc}}$ "unreacted" indistinguishable matrix units into $N_{\text{ol}}^{\text{pc}} + 1$ cells (cf. ref 14, p 52). The final expression for ΔS_2 is given by

$$\Delta S_2 = R \ln \frac{\Omega_1(N_{\text{ol}}^{\text{s}})\Omega_2}{\Omega_1(N_{\text{ol}})} \tag{11}$$

where $N_{\text{ol}}^{\text{s}} = N_{\text{ol}} - N_{\text{ol}}^{\text{pc}}$ is the number of oligomers free in solution. Assuming ΔG_1 to be independent of the degree of occupancy of the matrix and of the chain length of the oligomers enables us to write

$$\Delta G_1 = (n/2)N_{\text{ol}}^{\text{pc}}\Delta G_1^{\circ} \tag{12}$$

For sufficiently large n, the proportionality to n is in agreement with eq 6.

Minimization of the Gibbs free energy with respect to the number of "reacted" oligomers is now possible, resulting in

$$\frac{2\theta}{(1-\theta)m_{\text{ol}}}e^{\theta/(1-\theta)} = K_{\text{n}} \tag{13}$$

where

$$K_{\text{n}} = e^{-(n/2)\Delta G_1^{\circ}/RT} \tag{14}$$

θ is the degree of occupancy of the matrix defined by

$$\theta = (n/2)N_{\text{ol}}^{\text{pc}}/N_{\text{m}} \tag{15}$$

and m_{ol} is the basemole fraction of free oligomer in solution given by

$$m_{\text{ol}} = nN_{\text{ol}}^{\text{s}}/(nN_{\text{ol}}^{\text{s}} + N_{\text{s}}) \tag{16}$$

Equation 13 is furthermore based on the assumptions that $n \gg 1$ and $n(1-\theta)/\theta \gg 1$ (cf. ref 15). It differs slightly from the expression given by Khadakov et al.,[1] due to the assumed 1/2 stoichiometry.

The heat of complexation is defined as the heat produced during the complexation process and is therefore positive. One of the most important quantities to determine experimentally is the heat of complexation per unit complex, which by definition consists of one monomer unit of it-PMMA and two monomer units of st-PMMA. At first sight, a possible way seems to be given by measuring the heat of complexation for an excess of oligomers. However, as in the case of adsorption, this does not necessarily lead to a saturation of the matrix but rather to some maximum value of θ, which might be smaller than 1. Basically this is due to the fact that the number of ways of putting oligomers on a matrix decreases strongly when θ approaches 1. The opposite situation of an excess of matrix, on the other hand, offers better prospects. In the limit of very small oligomer concentration, but fixed total polymer (=matrix + oligomer) concentration eq 13 becomes

$$\frac{N_{\mathrm{ol}}^{\mathrm{pc}}}{N_{\mathrm{ol}}^{\mathrm{s}}} \simeq \frac{N_{\mathrm{m}} + nN_{\mathrm{ol}}}{N_{\mathrm{s}} + N_{\mathrm{m}} + nN_{\mathrm{ol}}} \equiv cK_{\mathrm{n}} \tag{17}$$

where N_{m} is the number of units of the matrix. The total polymer concentration c, defined as the site fraction, is usually of the order 10^{-3}, whereas a reasonable value for K_{n} is 10^6 (see ref 11). In this case, nearly all oligomers will be bound to the matrix, permitting a reasonable estimate of the heat of complexation per complex unit. For the same values of c and K_{n} the maximum possible degree of occupancy of the matrix is only about 0.82.

Maximum Heat

A simple way to get information about the stoichiometry of complexation by calorimetric investigations is to look for the ratio $r_{\max}$ between the amount of oligomer and the amount of matrix for which the maximum heat of complexation per gram polymer (=matrix + oligomer) is found. This will be shown by comparing a 1/2 and 1/1 complexation stoichiometry. By definition

$$r = nN_{\mathrm{ol}}/N_{\mathrm{m}} \tag{18}$$

and we are looking for the maximum, as a function of r, of the heat of complexation per gram polymer, which is proportional to

$$\frac{(n/2)N_{\mathrm{ol}}^{\mathrm{pc}}}{nN_{\mathrm{ol}} + N_{\mathrm{m}}} = \frac{\theta}{r + 1} \tag{19}$$

$r_{\max}$ is therefore the solution of the equation

$$(r + 1)\theta'(r) - \theta(r) = 0 \tag{20}$$

where $\theta'(r)$ denotes the first derivative with respect to r of $\theta(r)$. An expression for $\theta'(r)$ in case of a 1/2 stoichiometry can be derived from eq 13 by realizing that m_{ol} is given by

$$m_{\mathrm{ol}} = \frac{c(r - 2\theta)}{(1 - c)(1 + r)} \tag{21}$$

The final result is

$$\theta'(r)\left[(r + 1)\left(1 + \frac{\theta}{(1 - \theta)^2}\right)e^{\theta/(1-\theta)} + \frac{1}{2}cK_{\mathrm{n}}(r + 2 - 4\theta)\right] = -\theta e^{\theta/(1-\theta)} + \frac{1}{2}cK_{\mathrm{n}}(1 - \theta) \tag{22}$$

For a given cK_{n} and r, $\theta(r)$ and $\theta'(r)$ can be calculated numerically from eq 13 and 22. In this way $r_{\max}$ is found as the solution of eq 20. Figure 1 presents $x_{\mathrm{ol}}^{\mathrm{m}} = r_{\max}/(1 + r_{\max})$, which is the value of $nN_{\mathrm{ol}}/(nN_{\mathrm{ol}} + N_{\mathrm{m}})$ for which the maximum occurs, as a function of ln (cK_{n}). By choosing cK_{n} as a variable, we obtain a master curve valid at all concentrations. We observe that, only for very large values of cK_{n}, $x_{\mathrm{ol}}^{\mathrm{m}}$ approaches 0.67. For realistic values ($K_{\mathrm{n}} \simeq 10^6$ and $c \simeq 0.001$) the maximum occurs for $x_{\mathrm{ol}}^{\mathrm{m}} \simeq 0.6$. The same analysis can be given for a 1/1 complexation stoichiometry. The results are plotted in Figure 1. For similar values of K_{n} and c the maximum now occurs at $x_{\mathrm{ol}}^{\mathrm{m}} \simeq 0.45$. In both cases $x_{\mathrm{ol}}^{\mathrm{m}}$ approaches 0.5 in the limit of small cK_{n}. This happens because, as will be shown further on, complexation becomes independent of the complexation stoichiometry in this limit.

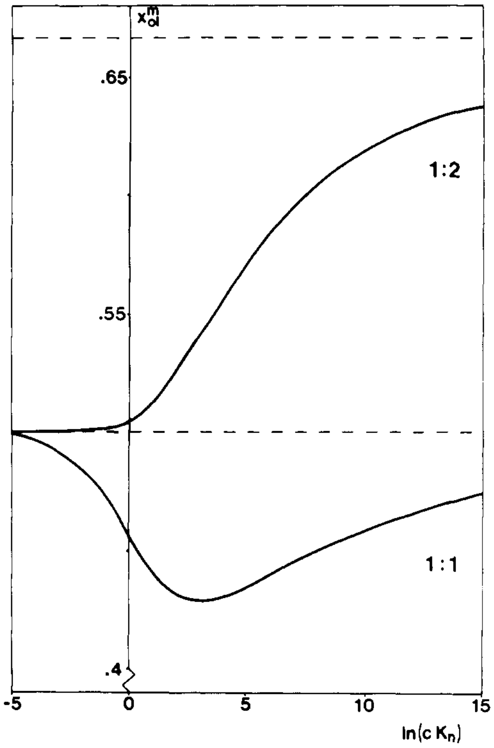

Figure 1. Oligomer fraction $x_{\mathrm{ol}}^{\mathrm{m}}$, for which the maximum heat of complexation per gram of polymer will be obtained, as a function of ln (cK_{n}) in the case of 1/2 and 1/1 complexation.

Critical Chain Length

An important parameter controlling template polymerization is the critical chain length, loosely defined as the lower bound of the chain length of the oligomers below which no appreciable complexation takes place. Since initiation, in the case of template polymerization of methyl methacrylate in the presence of isotactic PMMA matrices, starts in solution[21] and since the most important effect of the matrix on the polymerization rate of methyl methacrylate is the delayed termination reaction of those growing chains which are bound to the matrix, the importance of the critical chain length is obvious. The initial stages of template polymerization are characterized by an excess of matrix. The degree of occupancy θ of the matrix is still small and the discussion becomes more simple in terms of the fraction p of the total number of oligomers that is bound to the matrix:

$$p = N_{\mathrm{ol}}^{\mathrm{pc}}/N_{\mathrm{ol}} \tag{23}$$

In terms of r and θ this can be rewritten as

$$p = 2\theta(1 - r)/r \tag{24}$$

Using this expression one can eliminate θ from the original equation (13). Figure 2 presents p as a function of ln (cK_{n}) in the limit $r \rightarrow 0$. Clearly, complexation depends strongly on cK_{n} and hence on the chain length of the oligomers and increases rapidly beyond a certain degree of polymerization (cf. ref 1, 2, and 15). The transition point, defined as the inflection point of the function $p(cK_{\mathrm{n}})$, is given by

$$cK_{\mathrm{n}} = 1 \tag{25}$$

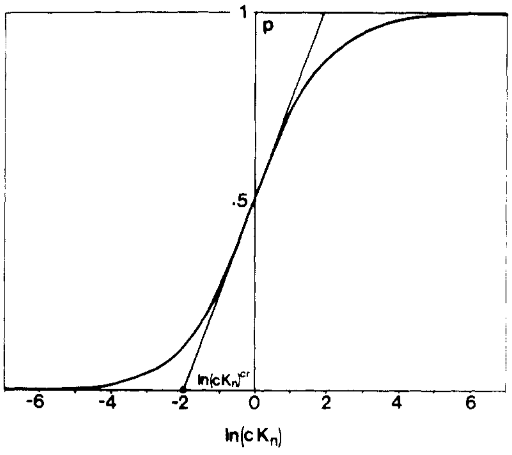

Figure 2. Fraction p of all oligomers that is bound to the matrix as a function of ln (cK_n).

Furthermore, the critical chain length, defined by the onset of the complexation, follows from

$$cK_n^{cr} = 1/e^2 \tag{26}$$

This relation is based on the assumption that an oligomer can exist in two states only, free in solution or completely bound to the matrix. The possibility of loops and tails is disregarded and deviations from the theoretical predictions can therefore be expected, especially in the transition region. Nevertheless, it enables a reasonable estimation of the critical chain length from a value of $\Delta G_1°$, determined by heat of complexation measurements involving much longer oligomers. This is of practical importance, because the heat of complexation can be determined accurately for sufficiently long oligomers only.

The very simple result of eq 25 can easily be understood on the basis of a Flory–Huggins type argument. According to this theory, the entropy of mixing for a low concentration of oligomers, neglecting the influence of the matrix, is given by

$$\Delta S_m \simeq N_{ol}^{pc} \ln (N_s/nN_{ol}^{pc}) \tag{27}$$

In the case of complexation the number of states is reduced, compared to the close-packed pure state, by an additional factor $n^{N_{ol}^{pc}}$ (cf. eq 5). To calculate the total amount of entropy lost upon complexation the increase in the number of states due to the many ways of placing N_{ol}^{pc} oligomers on the matrix also has to be taken into account. In the case of a low occupancy of a long matrix of N_m units, N_{ol}^{pc} indistinguishable oligomers can be placed in

$$(N_m)^{N_{ol}^{pc}}/N_{ol}^{pc}! \simeq (N_m/N_{ol}^{pc})^{N_{ol}^{pc}} \tag{28}$$

ways on the matrix. This result is independent of the stoichiometry of complexation and explains why the relation for the critical chain length does not contain this stoichiometry explicitly. It also explains the limiting behavior, found in the last section, of r_{max} for small values of cK_n. The statistical weight of the system with N_{ol}^{pc} oligomers bound to the matrix relative to the completely unbound system is therefore

$$\exp\left[N_{ol}^{pc}\left(\ln\left(\frac{N_m}{N_{ol}^{pc}}\right) - \ln\left(\frac{N_s}{N_{ol}^{pc}}\right) - \frac{1}{2}n\Delta G_1°/RT\right)\right] = (cK_n)^{N_{ol}^{pc}} \tag{29}$$

As expected, the transition point corresponds precisely to the point where the statistical weight of a unit bound to the matrix equals that of a unit free in solution.

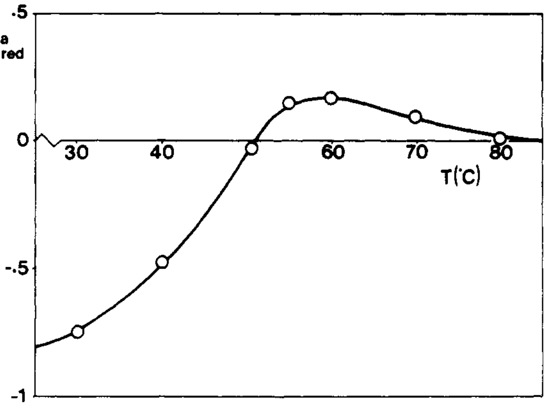

Figure 3. Reduced relative deviation from additivity of the viscosity, defined as $\eta_{red}^a = (1/c)[(\eta - \eta^a)/\eta^a]$, where η^a is the additive value of the viscosity, of a 1:2 mixture of it- and st-PMMA in DMF as a function of temperature. (Total polymer concentration 0.2 g/dL; st-PMMA, $\bar{M}_w = 7.5 \times 10^5$, $D = 1.4$, i:h:s = 1:8:91%; it-PMMA, $\bar{M}_w = 6.8 \times 10^5$, $D = 1.4$, $i > 95\%$.)

Whether complexation will occur clearly depends on the value of $\Delta G_1°/RT$. The enthalpic part $\Delta H_1°/RT$ is the equivalent of the adsorption energy parameter χ_s, defined as the difference in adsorption energies of a solvent molecule and a polymer segment divided by RT.[16] As is well-known, adsorption only occurs beyond a certain critical value of the adsorption energy parameter. For weak adsorption loops and tails are very important. Moreover, tails give the most important contribution to the adsorption layer except close to the surface, where loops dominate.[17] The concentration profile due to loop segments decays exponentially with increasing distances.[18] The same holds for the concentration profile due to tail segments, except that the exponent is reduced by a factor of 2. These results are valid for Θ-solvents, in which case the root-mean-square layer thickness is proportional to the square root of molar mass.[19] These properties are derived for adsorption on a flat surface but are not expected to change essentially in the case of a long cylinder. The analogy between adsorption and complexation is important in understanding the influence of temperature on the complexation of it-PMMA and st-PMMA in a dilute solution and the corresponding viscosity. For sufficiently high temperatures the situation resembles weak adsorption and the presence of loops and tails will result in an expanded structure which manifests itself by an increased viscosity. At lower temperatures the complexation will be nearly complete and a collapsed structure[20] with a lower viscosity will result. It was suggested before that the imperfect-matching model is best suited to describe the dissociation of the complex. Whereas the perfect-matching model leads to a true higher order phase transition, the imperfect-matching model predicts a broad transition region, due to the increased entropy from the number of ways of forming loops. This broad transition region is exactly what is found for the stereocomplex. Figure 3 shows the reduced relative deviation from additivity of the reduced viscosity of a dilute solution of it-PMMA and st-PMMA of similar chain lengths and a ratio it/st = $^1/_2$ in dimethylformamide as a function of temperature. It indicates a broad transition region of about 40 °C.

Polydispersity

The presence of oligomers of different chain length leads to preferential complexation of the longest oligomer chains. It was already shown by Papisov and Litmanovich[15] that cooperative reactions between macromolecules are characterized by high selectivity with respect to chain length.

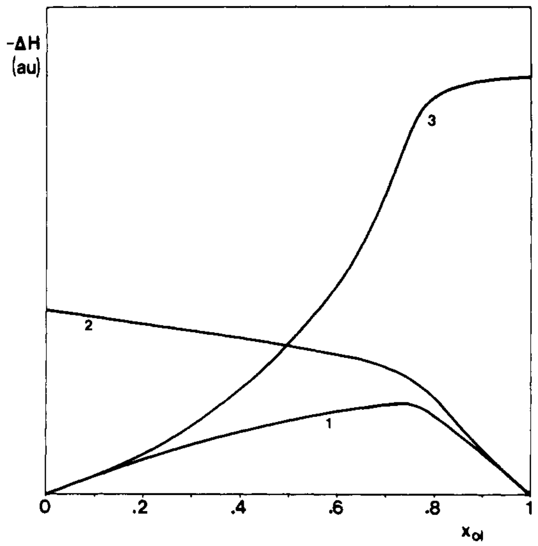

Figure 4. Heat of complexation per gram of polymer (curve 1), per gram of oligomer (curve 2), and per gram of matrix (curve 3) as a function of the oligomer fraction x_{ol} for a sample consisting of two equal fractions of oligomers of different chain length.

In the case of two narrow fractions of oligomers of chain lengths n_1 and n_2 respectively and a 1/1 complexation they showed

$$\theta_1/\theta_2 = (m_{ol}{}^1/m_{ol}{}^2)(K_{n_1}/K_{n_2}) \qquad (30)$$

where θ_1 and θ_2 are the degrees of occupancy of the matrix. $m_{ol}{}^1$ and $m_{ol}{}^2$ are the concentrations of the free oligomers in solution. This expression is based on the assumption $\theta_1 + \theta_2 = 1$, which requires an excess of oligomer and a sufficiently large K_{n_1} or K_{n_2}.

We will start from two narrow fractions and a 1/2 complexation stoichiometry, implying that two oligomer units "react" with one matrix unit, without making any further assumptions. The analysis of the first section can be repeated and results in two equations for the two unknowns θ_1 and θ_2. The first one is given by

$$\theta_1 e^{(\theta_1+(n_1/n_2)\theta_2)/(1-\theta_1-\theta_2)} - cK_{n_1}(1 - \theta_1 - \theta_2)(r_1 - 2\theta_1)/2(r_1 + r_2 + 1) = 0 \qquad (31)$$

The second one is obtained by interchanging the subscripts 1 and 2. r_1 and r_2 are defined by

$$r_i = n_i N_{ol}{}^i/N_m; \quad i = 1, 2 \qquad (32)$$

The influence of the polydispersity on the heat of complexation is of special interest. To see the effect most clearly an extreme case of very different K_n values will be considered. Figure 4 presents the heat of complexation per gram of matrix, per gram of oligomer, and per gram of total polymer for a concentration $c = 10^{-3}$. Furthermore, $r_1 = r_2$, $K_{n_1} = 10^7$, and $K_{n_2} = 10^3$. The variable x_{ol} is now defined by

$$x_{ol} = \frac{n_1 N_{ol}{}^1 + n_2 N_{ol}{}^2}{n_1 N_{ol}{}^1 + n_2 N_{ol}{}^2 + N_m} \qquad (33)$$

There are a few striking features. First, the heat of complexation per gram of matrix for an excess of oligomer is more than twice the heat of complexation per gram of oligomer for an excess of matrix. This occurs because in the case of an excess of matrix most of the long oligomers are bound to the matrix, but many of the short ones stay free in solution, whereas for an excess of oligomers the longer ones are selected and the matrix becomes filled to a degree determined by the long oligomers only. Secondly, and related, the heat of complexation per gram of total polymer has a maximum for a value of x_{ol} exceeding 0.67, which is, as shown before, the upper bound in the case of one narrow fraction of oligomers. Another important consequence of this selection process is that the apparent free energy of complexation, calculated on the basis of eq 13 and 14, becomes a nonlinear function of the degree of occupancy of the matrix. Figure 5 demonstrates this for the specific example considered above.

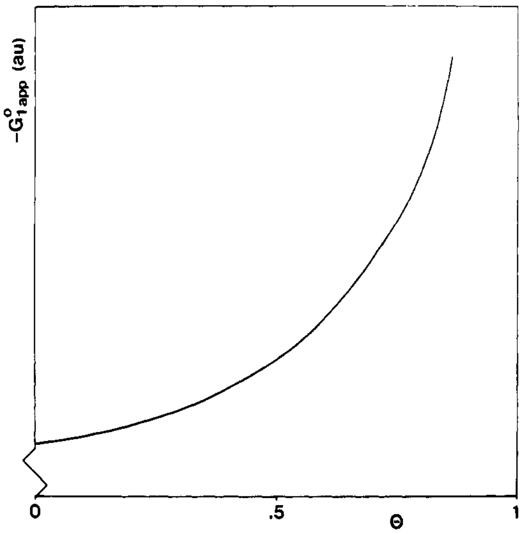

Figure 5. Apparent free energy of complexation calculated from eq 13 and 14 as a function of the degree of occupancy of the matrix for a sample consisting of two equal fractions of oligomers of very different chain length.

Concluding Remarks

The results of this paper are based on two important assumptions. One of them, that an oligomer is either completely free or completely bound, should be valid far away from the dissociation region. Far less clear is the assumed independentness for $\Delta G_1°$ of the chain length and of the occupancy of the matrix. Kabanov et al.[2,22] showed that in the case of complexation of poly(methacrylic acid) as matrix and poly(vinylpyrrolidone) or poly(ethylene glycol) as oligomer, the oligomers are not distributed randomly among the matrices. For an excess of matrices, some of them are practically filled whereas others are nearly free. Hence, due to another kind of cooperativity, again an all-or-nothing situation occurs. In such a case, the simple model will not be valid anymore, since random distribution of oligomers is essential in translating the results obtained for one matrix to the case of many matrices.

McGhee and von Hippel[23] investigated cooperative and noncooperative binding of large ligands to a one-dimensional lattice. Using a somewhat different approach, they found an expression for noncooperative binding identical with Khodakov's result. Cooperativity was included by assuming that ligands bound to the lattice interact favorably with their nearest neighbors. We have reason to believe that in the case of it- and st-PMMA there is also a weak cooperativity with respect to the number of oligomers bound, due to the association and local ordering of different occupied sections of the matrix.[11] But, as long as the cooperativity is weak, the simple model presented provides a most convenient starting point for understanding the experimental results and for discussing deviations from the theoretical predictions.

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

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Received November 21, 1984

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.