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Preferential Solvation in Polymer–Monomer–Solvent Systems and Its Potential Effect on the Kinetics of Polymerization

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ABSTRACT: A model of the effect of preferential solvation of the polymer on the kinetics of polymerization in ternary polymer–monomer–solvent systems has been suggested. The extent of preferential solvation was measured by the light scattering and refractive index increment methods for a number of typical systems. In most cases, preferential solvation can be expected to change the rate of polymerization by a few percent. At low monomer concentrations, larger effects are more likely to occur than at high monomer concentrations.

One of the potential causes of frequently observed deviations of the real polymerization course in the presence of an inert solvent or solvent mixture from the classical kinetic scheme is seen in the preferential solvation of the propagating polymer chain by either monomer, or solvent, or some component of the solvent mixture.[1-3] It is known that, due to the preferential binding of some components of a multicomponent solvent by the polymer, in dilute polymer solutions the solvent composition within the domains of polymer molecules generally differs from its composition in volume elements of solution that remain unaffected by the force effects of segments of the polymer molecule.[4-6] Preferential binding of the monomer by the polymer may accelerate the polymerization compared with the rate corresponding to an average, analytically detectable monomer concentration in the system, and, vice versa, preferential sorption of the solvent on the polymer may slow down the polymerization. Similar reasonings hold for copolymerizations even in the absence of solvent; preferential sorption may also be one of the causes underlying the dependence of the monomer reactivity ratios on the nature of the solvent observed in some systems.

While the qualitative image of the effect is clear, its actual influence has so far been demonstrated rather by indirect experimental evidence, and a quantitative correlation between the magnitude of preferential solvation and effects upon the polymerization kinetics due to it is still lacking.

The influence of preferential sorption on the rate of propagation of a polymer chain has been analyzed theoretically by Kozlov and Enikolopyan.[7] They assumed that the thermodynamic behavior of the polymer solution in a monomer–solvent mixture is controlled by Flory–Huggins theory with binary interaction parameters and came to the conclusion that preferential sorption of the monomer or solvent may change the rate of polymerization up to a few tens of per cents.

Locatelli and Riess[8-11] investigated the effect of preferential sorption in the formation of graft copolymers of the ABS (acrylonitrile–butadiene–styrene) type in great detail. The finding that styrene–acrylonitrile chains grafted on polybutadiene have a higher content of styrene constitutional units than ungrafted molecules of a statistical copolymer of styrene and acrylonitrile formed in parallel with the grafts is consistent with a view that in a solution of polybutadiene in a styrene–acrylonitrile mixture polybutadiene is preferentially solvated with styrene. It seems that, in this reaction, the inititator is also nonuniformly distributed in the system owing to preferential sorption,[10] which affects the polymerization kinetics.

The extent of preferential sorption in a number of ternary polymer–monomer–solvent systems related to the formation of statistical copolymers of styrene and acrylonitrile in a toluene or dimethylformamide solution was measured by Pichot et al.,[12] who also compared their results with some phenomena observed in the copolymerization.

The dependence of the rate of polymerization of methyl methacrylate on the monomer concentration in a solution with cyclohexanone, preferentially bound by the polymer,[13]

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and with acetonitrile, in the presence of which, contrariwise, monomer is preferentially sorbed by the polymer,[14] approaches the classical kinetic relation if the monomer concentration in the immediate vicinity of the polymer is considered, instead of the average concentration. Also, in the polymerization of styrene[15] and methyl methacrylate[16] in the presence of precipitants, changes in the kinetic parameters are explained to a large extent by the effect of preferential sorption.

In this study, a simple model of the effect of preferential sorption on the polymerization kinetics is suggested, and the possible magnitude of the effect depending on the extent of preferential sorption is estimated. The magnitude of preferential sorption is determined experimentally for a number of common polymer–monomer–solvent systems, and the results are qualitatively interpreted in terms of the suggested model.

Theoretical Section

Coefficients of Preferential Sorption. Let us consider a solution of polymer P in a binary mixture of low molecular weight components J and K. In the thermodynamics of multicomponent polymer solutions, the coefficient of preferential sorption or binding, γ_J'', of the system component J (J being either monomer or solvent) on the polymer is represented by the derivative[5,17]

$$\gamma_J'' \equiv (\partial g_J/\partial g_P)_{T,\mu} \tag{1}$$

where g_J and g_P are the concentrations of J and P, respectively, in grams per gram of the low molecular weight component K $\neq$ J regarded as the principal solvent. The concentration g is the mass analogy of molality. The index μ means that changes in the concentrations of J and P proceed at fixed chemical potential of both low molecular weight components of the system, J and K, i.e., under the condition of osmotic equilibrium between the solution and the monomer–solvent mixture.

γ_J'' indicates what amount of component J should be added to the system if, at constant temperature, the polymer concentration is raised and if the chemical potential of both low molecular weight components J and K is to remain unchanged in this process. It may be visualized, somewhat schematically, that the polymer binds a certain amount of component J, thus reducing its chemical potential. In order to maintain the chemical potential of component J at the original level, this component must be added in an amount defined by γ_J''. Here, the term "binding" or "sorption" should be taken in the most general thermodynamic sense.[18] In domains of polymer molecules, the component J is present in excess compared with its concentration in the volume elements of the solvent with which polymer molecules do not interfere. The coefficient γ_J'' as a purely thermodynamic quantity cannot by itself provide any information on the mechanism of binding at the molecular level.

If the low molecular weight components of the system are liquids, the magnitude of preferential sorption may sometimes be expressed more graphically through the volume of the preferentially bound component J. The volume of the component J (related to 1 g of the principal solvent K) corresponding to its concentration g_J is $V_J = g_J\bar{v}_J$, where $\bar{v}_J$ denotes the partial specific volume of component J in the system of a given composition. We define the coefficient of preferential sorption γ_J' as

$$\gamma_J' \equiv (\partial V_J/\partial g_P)_{T,\mu} \tag{2}$$

γ_J' and γ_J'' are then related by

$$\gamma_J' = \bar{v}_J\gamma_J'' \tag{3}$$

The coefficients γ_J' and γ_J'' give a direct idea of the amount of component J preferentially bound by the polymer P.

For polymer solutions in multicomponent solvents, the polymer concentration c_P is usually given in grams of the polymer per milliliter of solution. The concentrations of components of the solvent are suitably expressed by their volume fractions, φ_J (or volume percent), related to the polymer-free solvent. Such a way of expressing concentration has the advantage that the volume fractions of solvent components do not change with the addition of the polymer. Hence, measurements carried out with constant volume fractions of solvent components thus defined are at the same time measurements at constant molality, which simplifies the determination of some thermodynamic quantities, including the coefficients of preferential sorption.

The coefficient of preferential sorption, γ_J, based on the concentrations c_P and φ_J is defined as

$$\gamma_J \equiv (\partial\varphi_J/\partial c_P)_{T,\mu} \tag{4}$$

The coefficient γ_J is the primary result of the measurement of preferential sorption of liquid components of a mixed solvent on the polymer by the usual methods, such as the method of refractive or density increments[20,21] or light scattering.[6,19]

The relations existing between γ_J, on the one hand, and γ_J' and γ_J'', on the other, are very simple for solutions infinitely dilute with respect to the polymer, dealt with below. The volume fraction φ_J of the component J of the binary solvent in which the concentration g_J is related to 1 g of component K is given by

$$\varphi_J = g_J\bar{v}_J/(g_J\bar{v}_J + \bar{v}_K) \tag{5}$$

The concentration of the polymer c_P at $c_P \rightarrow 0$ is expressed by means of g_P and g_J or φ_J by using eq 5 as

$$c_P = g_P/(g_J\bar{v}_J + \bar{v}_K) = g_P(1 - \varphi_J)/\bar{v}_K \tag{6}$$

By expressing relations between the differentials $d\varphi_J$ and dg_J and between dc_P and dg_P and by substituting them into eq 1 and 2, we obtain formulas for the recalculation of γ_J to γ_J' and γ_J''

$$\gamma_J' = (\partial V_J/\partial g_P)_{T,\mu} = (\partial\varphi_J/\partial c_P)_{T,\mu}/(1 - \varphi_J) = \gamma_J/(1 - \varphi_J) \tag{7}$$

and

$$\gamma_J'' = (\partial g_J/\partial g_P)_{T,\mu} = (\partial\varphi_J/\partial c_P)_{T,\mu}/\bar{v}_J(1 - \varphi_J) = \gamma_J/\bar{v}_J(1 - \varphi_J) \tag{8}$$

The numerical values of γ_J and their dependence on the composition of the solvent differ greatly from the values and similar dependences for γ_J' and γ_J''. Thus, e.g., while γ_J according to definition[6] assumes zero values for $\varphi_J = 0$ and $\varphi_J = 1$, γ_J' and γ_J'' are zero for $\varphi_J = 0$, but their limiting value for $\varphi_J \rightarrow 1$ may be nonzero.

The physical meaning of the coefficient γ_J defined on the basis of φ_J and c_P may be visualized in the following way: If the polymer concentration in a polymer solution in a binary solvent were to be changed by dc_P at fixed chemical potential of the solvent components, it would be necessary—along with the corresponding change in the osmotic pressure—to remove from each volume unit of the polymer-free solvent a volume of $\gamma_J\ dc_P$ of the preferentially unbound component K, and this volume would have to be replaced by the preferentially bound component J. A similar process takes place in the establishment of the osmotic equilibrium between a small volume of the polymer solution and a large volume of the binary solvent.

The physical meaning of variously defined coefficients of preferential sorption is dealt with here in greater detail, because the difference between their physical meanings is often left unrespected, which leads to quantitatively, and sometimes even qualitatively, incorrect conclusions. Not exceptionally, γ_J values are assigned the meaning of γ_J' values. When the potential influence of preferential sorption on the polymerization kinetics is discussed, more graphic results are obtained in terms of γ', although the results are expressed both in terms of γ_J' and γ_J, and in some cases only in terms of the primarily obtained coefficients γ_J.

Model of the Influence of Preferential Sorption on the Polymerization Kinetics. In the following we call the "analytical concentration" of a low molecular weight component of a system the average concentration of this component that results from an appropriate analytical determination. By the name "local concentration", the concentration of a component in the surroundings of the propagating chain end is meant.

The kinetics of polymerization is described in terms of the analytical concentration of the monomer. For instance, in the classical polymerization in the presence of an initiator, the polymerization rate is proportional to the molar concentration of the monomer. For this reason, the ratio between the local and analytical molar concentrations is probably a suitable criterion for an estimate of the magnitude of the effect of preferential sorption on the rate of polymerization. Below, the local monomer concentration in the immediate neighborhood of the whole propagating polymer molecule is considered, since this concentration may be assessed from the coefficient of preferential sorption.

It is possible that the monomer concentration in the closest vicinity of the reactive end of the propagating chain differs from the local concentration throughout the whole polymer molecule. However, the information on this effect, which very likely would also affect the polymerization kinetics, cannot be extracted from the measurement of preferential sorption. Unfortunately, no experimental technique for the direct determination of the local monomer concentration in the closest vicinity of the reactive end of a propagating chain is available. The reaction mechanisms, which probably involve solvation of the propagating chain end by low molecular weight components of the system, are usually described in terms of complex formation between the propagating chain end and the solvent or monomer. It is the kinetic aberrations that are used to estimate the stability constant for the complex formation, a parameter intimately, though not explicitly, related with the coefficient of preferential sorption.[3] Here, on the contrary, we attempt to predict kinetic effects on the basis of the independently determined extent of preferential sorption.

The coefficients of preferential sorption γ_J' and γ_J'' indicate what amount of the component J is preferentially bound by the polymer, but do not provide any information about the distance from the polymer chain within which changes in the local concentration of the component J due to preferential sorption still operate. Of course, the ratio between the local and analytical molar concentrations of component J markedly depends on the volume in which the preferentially sorbed amount of this component is dispersed.

Suppose that the volume of the solvation shell pertaining to 1 g of the polymer is s cm^3/g and that the preferentially sorbed amount of component J is uniformly dispersed in this volume. Outside the solvation shell, the concentration of component J is lower, and at infinite dilution of the polymer this external concentration is at the same time the analytical concentration of J. The volume of component J in the solvation shell may be thought of as consisting of two contributions (Figure 1): (i) the volume γ_J' given by that of the preferentially bound component J; (ii) in the remaining volume $(s - \gamma_J')$, the volume fraction of component J equals its volume fraction in the solvent with which polymer molecules do not interfere, φ_J, so that the volume of component J in the remaining volume $(s - \gamma_J')$ is $(s - \gamma_J')\varphi_J$. In the volume s of external solvent unaffected by preferential sorption, the component J occupies the volume $s\varphi_J$. Hence, for the ratio between the local and analytical molar concentrations of component J, $[J]_l/[J]_a$, we may write

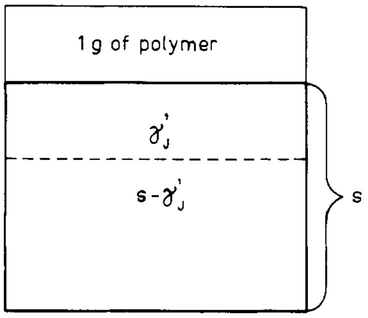

Figure 1. Schematic view of the division of the solvation shell of the polymer into two contributions.

$$\frac{[J]_l}{[J]_a} = \frac{\gamma_J' + (s - \gamma_J')\varphi_J}{s\varphi_J} = 1 + \frac{\gamma_J'}{s}\,\frac{1 - \varphi_J}{\varphi_J} \qquad (9)$$

or, if preferential sorption is expressed by the experimentally directly determined coefficient γ_J (eq 7),

$$\frac{[J]_l}{[J]_a} = 1 + \frac{\gamma_J}{s}\,\frac{1}{\varphi_J} \qquad (10)$$

Reasoning analogous to that leading to eq 9 and 10 yields for the ratio between the local and analytical molar concentrations of component K not sorbed preferentially by the polymer (which may equally be expressed by saying that component K is preferentially desorbed)

$$\frac{[K]_l}{[K]_a} = \frac{(s - \gamma_J')\varphi_K}{s\varphi_K} = 1 - \frac{\gamma_J'}{s} = 1 - \frac{\gamma_J}{s(1 - \varphi_J)} \qquad (11)$$

Analysis of the Model. The properties of the model are better dealt with by using eq 10, because the majority of experimental data on the preferential sorption on polymers in mixtures of low molecular weight liquids are expressed in terms of γ_J.

The ratio between the local and analytical concentrations of component J in the given system characterized by the composition of the binary mixture of low molecular weight compounds, φ_J, and by the coefficient of preferential sorption, γ_J, is basically affected by the volume of the solvation shell s. No method is available for a direct experimental determination of the volume s. Various estimates of the volume s lead to limiting values differing by more than 1 order of magnitude.

The estimate of the minimal s is based on an assumption that preferential sorption only operates in the monomolecular solvation shell surrounding the polymer chain. The volume of the monomolecular solvation shell may be estimated as 3–5 times that of the polymer chain. For instance, Lange[22] came to the conclusion that each constitutional repeating unit in a polystyrene chain is solvated in benzene solution with 3.1 ± 0.4 molecules of benzene. At a time when data on preferential sorption were first collected, the coefficient of preferential sorption seemed to be independent of the molecular weight of the polymer[23] and thus also of the polymer segment density in the domain of the polymer molecule. Hence, it was assumed that preferential sorption was limited to a narrow solvation shell enveloping the polymer chain.

Later on, it was found that in many polymer solutions in binary solvents preferential sorption did depend on the molecular weight of the polymer, and thus also on the density of polymer segments in the domain of the polymer molecule.[24,25] More compatible with this finding is the view that the preferentially sorbed molecules of a component raise its concentration throughout the domain of the polymer molecule. According to this concept, the volume of the solvation shell is much larger than in the preceding case, and the relative rise in the concentration of the preferentially sorbed component is proportionately smaller. The volume fraction of polymer segments in the domain of the macromolecule depends on its molecular weight and on the thermodynamic quality of the solvent, varying from values below 1% to a few volume percent.[26] High values of s between 90 and 100 comply with this argument. According to the present-day state of knowledge about preferential sorption, high s values seem more likely than low ones. In specific cases, some relative information on the decrease in concentration of the preferentially bound component with increasing distance from the polymer chain may be obtained by using labels sensitive to the composition of the solvent mixture and attached to the main chain by spacers of various length.[27]

In polymer–binary solvent systems, in which no strong specific interactions between the components take place, the coefficient of preferential sorption, γ_J, defined in terms of concentrations c_P and φ_J has usually a simple course as a function of the solvent composition, starting from $\gamma_J = 0$ for $\varphi_J = 0$ through a maximum usually observed between $\varphi_J \simeq 0.3$ and $\varphi_J \simeq 0.7$ to $\gamma_J = 0$ for $\varphi_J = 1$.[28] Typical maximal values of the coefficient of preferential sorption, $\gamma_{J,m}$, in these systems are 0.1–0.2 cm^3/g. Also in systems with a more complicated dependence of γ_J on φ_J, e.g., in those with inversion of preferential sorption (i.e., such where in a certain region of φ_J the component J is preferentially bound and in another region of φ_J the second component of the solvent is preferentially sorbed), the maximal $\gamma_{J,m}$ values usually do not exceed 0.3 cm^3/g.[28] In less frequent systems with a strong specific interaction of components,[29,30] the maximal $\gamma_{J,m}$ reaches 0.6–1 cm^3/g; in some rare systems with extremely high preferential sorption, γ_J as high as 4 cm^3/g was also recorded.[31]

For further semiquantitative reasonings, we assume that the dependence of the coefficient of preferential sorption γ_J on the composition of the solvent φ_J may be described by a quadratic parabola with a maximum $\gamma_{J,m}$ at $\varphi_J = 0.5$,

$$\gamma_J = 4\gamma_{J,m}\varphi_J(1 - \varphi_J) \qquad (12)$$

This dependence gives a satisfactory qualitative description of the shape of the frequently observed simple dependences of γ_J on φ_J. By substitution for γ_J from eq 12 into eq 10 and 11, one obtains for the ratio between the local and analytical concentrations of the preferentially sorbed component J and desorbed component K

$$\frac{[J]_l}{[J]_a} = 1 + \frac{4\gamma_{J,m}}{s}(1 - \varphi_J) \qquad (13)$$

$$\frac{[K]_l}{[K]_a} = 1 - \frac{4\gamma_{J,m}}{s}\varphi_J \qquad (14)$$

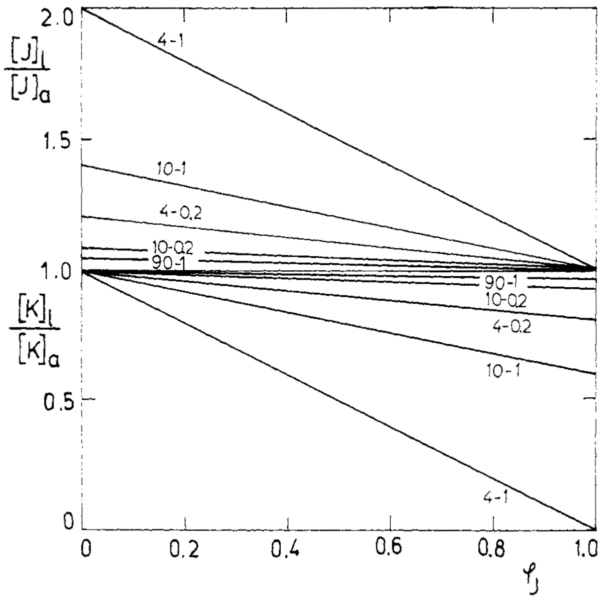

Figure 2. Dependence of the ratio between the local and analytical molar concentrations of components J and K, $[J]_l/[J]_a$ and $[K]_l/[K]_a$, on the volume fraction, φ_J, of the preferentially sorbed component J in the binary mixture of liquids J and K according to eq 13 and 14. The dependences are labeled by the volume of the solvation shell s (first value) and the maximal value of the coefficient of preferential sorption, $\gamma_{J,m}$ (second value).

The ratio $[K]_l/[K]_a$ is always nonnegative, and therefore $4\gamma_{J,m}\varphi_J/s < 1$. Hence, each $\gamma_{J,m}$ value has its corresponding minimal necessary value of the volume of the solvation shell s. Requirements corresponding to the extremely high ($\gamma_{J,m}$ = 4 cm^3/g), high ($\gamma_{J,m}$ = 1), and typical ($\gamma_{J,m}$ = 0.2) values of the coefficient of preferential sorption are, respectively, $s > 16$, $s > 4$, and $s > 0.8$ cm^3/g. Large minimal necessary volumes of the solvation shell correspond to strong specific interactions characterized by high coefficients of preferential sorption. It is not likely that weak nonspecific interactions characterized by low coefficients of preferential sorption would lead to smaller volumes of the solvation shell, in which differences between the local and analytical concentrations of the components could still be perceived, than strong specific interactions. It seems, therefore, that larger volumes of the solvation shell, say at least $s > 10$, are closer to physical reality. In principle, the volume of the solvation shell may vary with the composition of the monomer–solvent mixture. However, due to the absolute lack of information about this quantity, it is assumed below to be constant for the given monomer–solvent pair.

An analysis of properties of the present model of preferential sorption for the case of a simple γ_J vs. φ_J dependence given by eq 12 and of the volume of the solvation shell independent of the composition of the system leads to the following qualitative conclusions (Figure 2):

(1) The largest relative differences between the local and analytical monomer concentrations due to preferential sorption, and hence also the largest effect of preferential sorption on the polymerization kinetics, may be anticipated in the range of low monomer concentrations.

(2) At a magnitude of preferential sorption typical of systems with not too strong nonspecific interactions, the effect of preferential sorption on the polymerization kinetics is probably comparable with the experimental error of determination of the polymerization rate (±5%).

(3) With large volumes of the solvation shell s, which seem to be physically more acceptable, the effect of preferential sorption on the polymerization kinetics is experimentally perceptible only for high preferential

sorption values characterstic of strong specific interactions of the components of the system.

Experimental Section

Light Scattering. The intensity of scattered light was measured with a photogoniodiffusometer Sofica in the range of scattering angles 30–150° with a vertically polarized primary beam with the wavelength in vacuo of 546 nm. The reduced intensities of scattering for zero angle and infinite dilution were obtained by the Zimm method.[32] Most of the measurements were carried out at 25 °C; for one system, the temperature dependence of scattering was measured in the temperature range 25–70 °C. Solutions of various polymer concentrations were prepared by gradual dilution of solutions with the highest concentration. Prior to each measurement, the solutions were clarified of dust particles by Jena bacterial filters, density G5. All solutions containing the monomer as a component of the solvent were stabilized with hydroquinone.

Equilibrium Dialysis. The polymer solution at 25 °C was put in osmotic equilibrium with the corresponding binary solvent by a one-step nonexhaustive dialysis in simple dialyzers using a procedure described earlier[19] with Ultracellafilter allerfeinst membranes (Membranfiltergesellschaft, Göttingen, West Germany). The dialyzers were made of brass with golded surfaces in contact with solution or solvent or of glass. Although also in the dialysis monomer-containing systems were stabilized with hydroquinone, considerable difficulties emerged due to the fact that during the time needed for the establishment of osmotic equilibrium a part of the monomer often polymerized. These complications occur more frequently with metal dialyzers than with glass ones. Of all the monomers taken for investigation, styrene was the most sensitive; for systems containing styrene, most of the data on preferential sorption had to be obtained by the light scattering method. Among the monomers studied, methyl methacrylate was the least liable to polymerization during the dialysis. Pichot et al.[12] used dialysis techniques similar to ours, but did not mention difficulties due to the polymerization of the monomer.

Refractive Index Increments. The refractive index increments were measured at 25 °C and for one system in the temperature range[33] 25–70 °C for the wavelength in vacuo of 546 nm with a Brice-Phoenix Model BP-2000-V differential refractometer and expressed in cm^3/g. The apparatus was calibrated with aqueous potassium chloride solutions.

Coefficients of Preferential Sorption. The coefficients of preferential sorption were determined either by light scattering or by the refractive index increment method.

The coefficient of preferential sorption γ_J is calculated from the light scattering data by use of the relation[19]

$$\gamma_J = \frac{(\mathrm{d}n/\mathrm{d}c_P)_\varphi[(M_{ap}/M)^{1/2} - 1]}{\mathrm{d}n_0/\mathrm{d}\varphi_J} \tag{15}$$

where M is the molecular weight of the polymer; M_{ap} is the apparent molecular weight of the polymer in the given multicomponent solvent, i.e., a value calculated by means of the relations valid for light scattering from polymer solutions in one-component solvents, in which the effect of preferential sorption on the intensity of scattered light need not be considered; $(\mathrm{d}n/\mathrm{d}c_P)_\varphi$ is the refractive index increment in a mixed solvent determined at the same ratio of solvent components in solution and solvent, i.e., an increment determined by the usual procedure; $\mathrm{d}n_0/\mathrm{d}\varphi_J$ is the refractive index increment of the solvent component J in the mixed solvent of the given composition without polymer. $\mathrm{d}n_0/\mathrm{d}\varphi_J$ values of many two-component solvents used are virtually independent of the composition of the mixture, whence $\mathrm{d}n_0/\mathrm{d}\varphi_J = n_J - n_K$, where n_J and n_K are refractive indices of pure components of the solvent.

In the refractive index increment method, the coefficient of preferential sorption γ_J is given by[19]

$$\gamma_J = \frac{(\mathrm{d}n/\mathrm{d}c_P)_\mu - (\mathrm{d}n/\mathrm{d}c_P)_\varphi}{\mathrm{d}n_0/\mathrm{d}\varphi_J} \tag{16}$$

where $(\mathrm{d}n/\mathrm{d}c_P)_\mu$ is the refractive index increment of the polymer in a mixed solvent determined at equal chemical potentials of the solvent components both in solution and in the polymer-free solvent, i.e., after the establishment of osmotic equilibrium between solution and solvent; the other two refractive index increments have been defined above.

Relative Rates of Polymerization. The monomer in the presence of the same volume of solvent was polymerized in sealed ampules at 60 °C, using azobisisobutyronitrile as initiator up to a conversion of 2–3%. The relative rates of polymerization are defined as ratios between the conversions of systems polymerized in parallel in the presence of various solvents under otherwise identical conditions.

Polymers and Chemicals. The polymers used were prepared by radical polymerization to a low or medium conversion. Their weight-average molecular weights were of the order of magnitude of 10^5, specifically $M_w = 1.92 \times 10^5$ for polystyrene, 1.10×10^5 for poly(methyl methacrylate), 2.02×10^5 for poly(hydroxyethyl methacrylate), and 3.30×10^5 for polyacrylonitrile; for the statistical copolymers of styrene and 2-methoxyethyl methacrylate with the weight fraction of styrene in the copolymer 0.226, 0.426, and 0.655, $M_w = 2.14 \times 10^5$, 1.20×10^5, and 0.96×10^5, respectively. These values are well suited for the given type of measurements, because in the light scattering method extrapolation of the measured values to zero angle of observation is accurate, and in the refractive index increment method no polymer molecules penetrate through the semipermeable membrane during the dialysis. For polymers with molecular weights of the order of magnitude 10^5, the molecular weight dependence, if any, of the coefficient of preferential sorption would be virtually negligible.

Monomers and solvents were commercial reagent grade chemicals, freshly redistilled before use.

Results and Discussion

It might seem that the number of systems suited for an investigation of the preferential solvation of polymers in solutions of a mixture of the monomer and solvent is virtually unlimited. Determination of the coefficient of preferential sorption both by the light scattering and the refractive index increment methods requires, however, that both low molecular weight components of the system differ sufficiently in their refractive indices. This considerably reduces the number of systems, allowing a tolerably accurate study of the effect.

The results show (Table I) that, in most systems under investigation, the coefficients of preferential sorption, γ_J, have low or medium values. If the model suggested by us for the mechanism of effect of preferential sorption on the polymerization kinetics reflects physical reality, at least aproximately, no effects considerably exceeding experimental error involved in the usual determinations of the rate of polymerization can be expected for these systems (Figure 2). Similar effects may be anticipated in the copolymerization of common monomers as a result of the preferential solvation of propagating copolymer chains by one of the comonomers. An example of such a system is given in Table II; to some extent, the solution of poly(methyl methacrylate) in a mixture of methyl methacrylate and styrene may also be regarded as a system of this type (Table I).

Pichot et al.[12] have observed in ternary systems containing styrene or acrylonitrile as the monomer, toluene or dimethylformamide as the solvent, and polystyrene, polyacrylonitrile, or their copolymers as the polymer coefficients of preferential sorption γ_J assuming absolute values up to 0.17, 0.25, and 0.43 cm^3/g at a monomer content in a mixture with the solvent of a mere 1, 2.5, and 5 vol %. These are anomalous dependences of the coefficient of preferential sorption on the composition of the liquid mixture reaching a comparatively high maximum in the range of very low monomer contents. These systems cannot be adequately described, even qualitatively, by eq 13 and 14 and Figure 2 derived from them. However, eq

Table I

Coefficients of Preferential Sorption γ_J and γ_J' Defined by Eq 4 and 2 for Ternary Polymer-Monomer-Solvent Systems

solvent	φ^a	t, °C	bound component[b]	method[c]	$(\frac{dn}{dc_P})_\varphi{}^d$	$(\frac{dn}{dc_P})_\mu{}^e$	$\frac{dn_0}{d\varphi_J}{}^f$	$\gamma_J{}^g$	γ_J'
				Polystyrene					
cyclohexane	0.15	25	M	LS	0.075	(0.086)	0.120	0.09	0.60
cyclohexane	0.30	25	M	LS	0.092	(0.112)	0.120	0.16	0.54
cyclohexane	0.40	25	M	LS	0.104	(0.129)	0.120	0.21	0.52
cyclohexane	0.50	25	M	LS	0.120	(0.152)	0.120	0.27	0.53
cyclohexane	0.60	25	M	LS	0.129	(0.160)	0.120	0.26	0.44
cyclohexane	0.70	25	M	LS	0.138	(0.166)	0.120	0.23	0.33
cyclohexane	0.85	25	M	LS	0.155	(0.173)	0.120	0.15	0.17
dioxane	0.15	25	M	LS	0.076	(0.084)	0.123	0.065	0.43
dioxane	0.30	25	M	LS	0.092	(0.102)	0.123	0.08	0.27
dioxane	0.40	25	M	LS	0.104	(0.112)	0.123	0.065	0.16
dioxane	0.50	25	M	LS	0.116	(0.129)	0.123	0.11	0.22
dioxane	0.60	25	M	LS	0.126	(0.138)	0.123	0.10	0.17
dioxane	0.70	25	M	LS	0.137	(0.147)	0.123	0.08	0.11
dioxane	0.85	25	M	LS	0.155	(0.163)	0.123	0.065	0.08
n-heptane	0.10	25	M	LS	0.075	(0.089)	0.158	0.09	0.90
n-heptane	0.20	25	M	LS	0.091	(0.109)	0.158	0.11	0.55
n-heptane	0.30	25	M	LS	0.106	(0.136)	0.158	0.19	0.63
n-heptane	0.40	25	M	LS	0.122	(0.162)	0.158	0.25	0.62
n-heptane	0.50	25	M	LS	0.137	(0.191)	0.158	0.34	0.68
n-heptane	0.60	25	M	LS	0.154	(0.195)	0.158	0.26	0.43
butanone	0.50	25	M	LS	0.140	(0.149)	0.167	0.06	0.12
methyl methacrylate	0.50	25	(S)	RI	0.122	0.122	−0.132	0.00	0.00
				Poly(methyl methacrylate)					
acetonitrile	0.17	25	S	RI	0.094	0.078	−0.070	0.23	0.28
acetonitrile	0.32	25	S	RI	0.100	0.085	−0.070	0.23	0.34
acetonitrile	0.50	25	S	RI	0.110	0.097	−0.070	0.18	0.36
acetonitrile	0.68	25	S	RI	0.119	0.113	−0.070	0.09	0.28
benzene	0.30	25	M	RI	0.061	0.054	−0.089	0.075	0.25
benzene	0.50	25	M	RI	0.046	0.044	−0.089	0.025	0.05
benzene	0.70	25	M	RI	0.033	0.032	−0.089	0.00	0.00
acetophenone	0.50	25	(M)	RI	0.034	0.033	−0.121	0.00	0.00
benzyl alcohol	0.50	25	(S)	RI	0.026	0.027	0.129	0.00	0.00
styrene	0.50	25	(S)	RI	0.025	0.025	0.132	0.00	0.00
trichlorobenzene	0.50	25	S	RI	0.014	0.021	0.154	0.04	0.08
				Poly(hydroxyethyl methacrylate)					
methanol	0.25	25	S	RI	0.078	0.070	−0.115	0.07	0.09
methanol	0.35	25	S	RI	0.090	0.081	−0.115	0.08	0.12
methanol	0.50	25	S	RI	0.110	0.093	−0.115	0.15	0.30
methanol	0.625	25	S	RI	0.120	0.107	−0.115	0.11	0.30
methanol	0.75	25	S	RI	0.135	0.122	−0.115	0.11	0.45
methanol	0.875	25	S	RI	0.151	0.140	−0.115	0.10	0.77
water	0.20	25	S	RI	0.068	0.049	−0.088	0.21	0.26
water	0.20	25	S	LS	0.068	(0.050)	−0.088	0.21	0.26
water	0.20	30	S	LS	0.069	(0.051)	−0.087	0.21	0.26
water	0.20	40	S	LS	0.071	(0.053)	−0.085	0.22	0.27
water	0.20	50	S	LS	0.074	(0.055)	−0.082	0.23	0.29
water	0.20	60	S	LS	0.076	(0.057)	−0.080	0.24	0.30
water	0.20	70	S	LS	0.079	(0.059)	−0.077	0.26	0.32
water	0.60	25	M	RI	0.103	0.143	0.126	0.32	0.53
water	0.60	25	M	LS	0.103	(0.143)	0.126	0.32	0.53
water	0.60	30	M	LS	0.104	(0.144)	0.125	0.30	0.50
water	0.60	40	M	LS	0.107	(0.147)	0.122	0.31	0.53
water	0.60	50	M	LS	0.109	(0.149)	0.119	0.34	0.56
water	0.60	60	M	LS	0.111	(0.151)	0.115	0.34	0.57
water	0.60	70	M	LS	0.114	(0.154)	0.112	0.36	0.59
tetrafluoropropanol	0.50	25	S	RI	0.105	0.083	−0.121	0.18	0.36
				Poly(acrylonitrile)					
dimethyl sulfoxide	0.65	25	S	LS	0.061	(0.067)	0.086	0.07	0.20
dimethyl sulfoxide	0.73	25	S	LS	0.055	(0.062)	0.086	0.08	0.30
dimethyl sulfoxide	0.82	25	S	LS	0.048	(0.053)	0.086	0.06	0.32
dimethyl sulfoxide	0.91	25	S	LS	0.040	(0.044)	0.086	0.05	0.51

[a] Volume fraction of the solvent in a mixture with the monomer. [b] M and S indicate that monomer and solvent are preferentially bound by the polymer, respectively; symbols in parentheses define the component J of systems with virtually zero γ_J and γ_J' values. [c] LS and RI indicate that the coefficients of preferential sorption were determined by the light scattering and by the refractive index increment methods. [d] Refractive index increment of the polymer in cm³/g determined at the same ratio of both low molecular weight components in solution and in a monomer-solvent mixture. [e] Refractive index increment of the polymer in cm³/g determined at equal chemical potentials of the monomer and solvent in solution and in a monomer-solvent mixture; values in parentheses were calculated from the known molecular weight of the polymer and the measured intensity of scattered light. [f] Refractive index increment of the component J sorbed preferentially by the polymer in a monomer-solvent mixture of the given composition. For hydroxyethyl methacrylate-water mixtures the values were determined experimentally; for the other systems they are virtually independent of the composition of the mixture and were calculated from tabulated refractive index values for pure monomers and solvents. [g] γ_J and γ_J' are in cm³/g.

Table II
Coefficients of Preferential Sorption γ_J and γ_J' Defined by Eq 4 and 2 for a Ternary System Statistical Copolymer of Styrene and 2-Methoxyethyl Methacrylate–Styrene–2-Methoxyethyl Methacrylate[a]

w_s[b]	φ_s[c]	$(\frac{dn}{dc_P})_\varphi$[d]	$(\frac{dn}{dc_P})_\mu$[e]	$\frac{dn_0}{d\varphi_J}$[f]	γ_J[g]	γ_J'
0.226	0.17	0.052	0.052	−0.132	0.00	0.00
0.426	0.44	0.057	0.056	−0.132	0.00	0.00
0.655	0.76	0.056	0.054	−0.132	0.01	0.05

[a] In the mixture of both monomers, a copolymer was dissolved having composition that in the given mixture of monomers is formed in the initial stage of polymerization; γ_J was determined by the refractive index increment method at 25 °C; 2-methoxyethyl methacrylate is regarded as the component J preferentially bound by the copolymers. [b] w_s gives the weight fraction of styrene in the copolymer. [c] φ_s denotes the volume fraction of styrene in the mixture of monomers. [d-g] Cf. the respective notes in Table I.

10 and 11 hold generally for the suggested model, and one can see at a glance that the relative differences between the local and analytical concentrations of the solvent component present in a small amount may be considerable, if this component in spite of its small content is rather strongly sorbed or desorbed by the polymer. In systems of this type, an important effect of preferential sorption on the polymerization kinetics may be expected in the range of low monomer concentrations. Let it be noted, however, that systems of the above type seem to be rather rare. No such behavior has ever been detected with ternary systems investigated in this study, and neither has such an anomalous dependence of the coefficient of preferential sorption on composition been observed in our earlier studies in similar nonaqueous systems not containing monomers.

Most of the coefficients of preferential sorption were determined at 25 °C. Radical-initiated polymerizations are usually carried out at elevated temperatures, and a question arises as to the extent of the effect of temperature on the coefficient of preferential sorption. Our earlier unpublished experience with systems not containing monomers indicates that the coefficient of preferential sorption is mostly little temperature dependent. For the system poly(2-hydroxyethyl methacrylate)–2-hydroxyethyl methacrylate–water, the coefficients of preferential sorption were measured in the range 25–70 °C in mixtures with 20 and 60 vol % water (Table I). Here, too, the unpronounced temperature dependence of γ_J for a system with 20 vol % water and the independence of this quantity of temperature for a system with 60 vol % water suggest that the difference between the temperature of measurement of the coefficient of preferential sorption and the polymerization temperature does not virtually affect the qualitative conclusions.

In order to verify the effect of preferential sorption on the rate of polymerization of a typical system, we determined the relative polymerization rates of styrene in the presence of cyclohexane and dioxane as solvents. In mixtures of styrene with each of these solvents, polystyrene is preferentially solvated with the monomer; the coefficient of preferential sorption of styrene in mixtures with cyclohexane assumes medium values, being approximately twice that observed in mixtures with dioxane (Table I). There were, however, no differences between the relative polymerization rates of both systems.

In polyacrylonitrile solutions in mixtures of acrylonitrile and dimethyl sulfoxide we detected a not too large preferential solvation of the polymer with solvent (Table I). The values of the coefficients of preferential sorption would indicate a decrease in the local monomer concentration in the domains of polymer molecules by a few percent compared with the analytical concentration (Figure 2). This effect may produce a similar relative decrease in the overall rate constant of polymerization with decreasing monomer concentration. Czajlik et al.[34] have observed in this system and in the interval of compositions investigated by us a decrease in the overall rate constant of polymerization with decreasing monomer concentration by approximately 20%. It seems, therefore, that the preferential solvation of polyacrylonitrile with dimethyl sulfoxide somewhat enhances the considerable kinetic effect whose main cause lies elsewhere.

It has been pointed out in the Theoretical Section that in polymerization reactions the local concentration of low molecular weight components of the system in the immediate vicinity of the propagating chain end may differ from the local concentration in the domain of the whole polymer molecule. In this case, the experimentally determinable coefficient of preferential sorption would not be a quantity suited for correction of the kinetic constants for the difference between the local and analytical monomer concentrations. However, in our opinion the suggested model of the kinetic effect of preferential sorption adequately explains the situation arising in nonradical reactions of the modification of polymers, e.g., substitution reactions on polymer chains. A considerable effect of preferential sorption on the kinetics of reactions of polymers has been predicted theoretically[35] and is an object of our attention.

It may be said, in conclusion, that in typical monomer–solvent systems preferential sorption occurring in polymerizations in the presence of a solvent may cause changes in the rate of polymerization amounting to several percent. The potential effect of preferential sorption ought to be considered when correlating exact kinetic data. On the other hand, it is not likely that preferential sorption is the decisive cause underlying the frequently observed and considerable influences on the polymerization kinetics from the part of the solvent.

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Registry No. Polystyrene, 9003-53-6; poly(methyl methacrylate), 9011-14-7; poly(hydroxyethyl methacrylate), 25249-16-5; polyacrylonitrile, 25014-41-9; styrene–2-methoxyethyl methacrylate copolymer, 61735-85-1; styrene, 100-42-5; acrylonitrile, 107-13-1.

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Adsorption of Ionizable Polymers on Ionic Surfaces: Poly(acrylic acid)

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ABSTRACT: The adsorption behavior of ionized poly(acrylic acid) on tribasic calcium phosphate surfaces from aqueous solutions has been studied by Fourier transform infrared spectroscopy. Measurements included the amount adsorbed, a parameter proportional to fraction of surface-bound repeating units, and the extent of water-induced desorption. Results indicate that the cationic nature of the adsorbing surface is the main driving force for the intense and largely irreversible adsorption of the anionic polyelectrolyte. Another important factor in the adsorption behavior is the collective drag of macromolecules toward the surface through segmental interactions in solution. Collective surface migration of chains is most prominent in solutions of high concentration or molecular weight. Such adsorbates are partly desorbable and contain low fractions of surface-bound repeating units. The intensity of collective drag decreases significantly in concentrated solutions with ionization of side groups and screening of the surface potential by addition of monovalent ions to the solvating medium.

Introduction

The adsorption of polymer molecules on surfaces has been a phenomenon of scientific and technological interest over the past few decades. The problem has been analyzed experimentally with different techniques for various substrate/adsorbate systems. An extensive review of experimental work has been organized by Lipatov and Sergeeva. Several authors have made important contributions in the theoretical treatment of the problem but primarily for the case of adsorption from dilute solutions.[2–14] The issues of scientific concern include (1) the amount of macromolecular material that is isothermally adsorbed by substrates from melts or solutions, (2) the intensity of substrate/adsorbate interaction and its relation to adsorption stability, (3) the conformational transitions undergone by chains in the adsorbed layer and their effect on molecular motion, and (4) the substrate properties and macromolecular variables that control all of the above features of adsorption. The adhesion of organic macromolecules to metals, ceramics, and biological tissues and the control of interface-related properties in composite materials are two examples where adsorption phenomena become technologically relevant.

The classical hypothesis of polymer adsorption from solution on impenetrable surfaces envisions the process as one involving conformational distortion of molecular coils. This distortion is caused by interactions between repeating units and surface sites and is accompanied by a loss of entropy in the polymeric coil. An example is the elongation and lateral contraction of a Gaussian chain as it spreads to interact with the substrate's active sites. There is a great deal of discussion in the literature concerning the nature of the adsorbed film based on experiments that measure its thickness and weight. One concept proposed is that of multilayer adsorption, in which chains do not necessarily change their shape. A similar idea is the adsorption of macromolecular aggregates rather than single molecules.[16,17] Others have envisioned the formation of attached segments and unadsorbed loops[18] explaining why the thickness of the adsorbed layer exceeds that of a monolayer of flatly attached chains. Conformational distortion into a rather elongated state has been supported by experimental measurements[19] of the fraction of functional groups attached to the surface (e.g., more than 30%). The effect of solution variables (solvent, temperature, and molecular weight) and nature of the substrate on amount adsorbed has also been investigated (e.g., see ref 20–27). Even though there are exceptions, adsorption usually increases with molecular weight, and it is inversely proportional to solution intrinsic viscosity (it decreases with solvent power). Generally speaking, experimental work on adsorption has been more common in nonionic polymers. Earlier experimental work on polyelectrolyte adsorption has been reviewed by Fontana.[28] For adsorption of ionic polymers,

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