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POLYMERIC SYSTEMS
AND TECHNOLOGIES

Concentration Effects in Homopolymerization of Amine- and Amide-Containing (Meth)acrylic Monomers in Organic Solvents

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Abstract—The dependences of the initial reduced rate of radical homopolymerization on the initial concentration of the monomers were studied for toluene and dimethylformamide solutions of four amine-containing (meth)acrylic esters and amides, and also for *N*-(*n*-butyl)acrylamide and *n*-butyl methacrylate taken for comparison. The concentration effects are similar for all the methacrylic monomers and are specific in the case of acrylamides {*N*-(*n*-butyl)acrylamide and *N*-[3-(dimethylamino)propyl]acrylamide}, which is associated with the specific features of the structure of the prereaction monomeric associates.

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Amphiphilic nitrogen-containing polymers based on (meth)acrylic monomers with amine and/or amide functional groups are used as flocculants [1, 2] and viscosity and dispersing additives to motor oils [3]; they are considered as promising temperature- and pH-sensitive media for targeted delivery of drugs to sick organs [4]. It has been shown recently that radical copolymerization of these types of monomers in water and organic solvents is characterized by strong concentration effects: The relative activities of the comonomers and the compositional heterogeneities of the copolymers formed depend on the initial monomer concentrations. This dependence was revealed, in particular, for copolymerization of amine-containing monomers with acrylamide and acrylonitrile [5] and with alkyl (meth)acrylates, [6], and also for copolymerization of *N*-alkylacrylamides with alkyl(meth)-acrylates [7]. The causes of these effects are a matter of discussion, although it is assumed in the above papers on the basis of the results obtained that these effects are associated with noncovalent interactions involving monomeric molecules.

Important information for elucidating the relationships of such interactions can be obtained by studying the concentration effects in the course of homopolymerization of amine- and amide-containing (meth)acrylic monomers, in which the set of possible kinds of noncovalent interactions is limited compared to the copolymerization. It was found previously that the relative initial homopolymerization rate of *N*,*N*-dimethylaminoethyl methacrylate (DMAEM) and *N*,*N*-diethylaminoethyl methacrylate (DEAEM) with increasing mole fraction of the monomers in solution exponentially decreases in ethyl acetate and passes through a pronounced maximum in ethanol. The position of this maximum is determined by the favorableness of the conditions for the formation of complexes of the monomer with the solvent [8]. In homopolymerization of *N*-octylacrylamide with linear or weakly branched alkyl fragment in toluene, as the initial concentration is increased, the reduced initial homopolymerization rate increases. This trend becomes considerably more pronounced in concentrated solutions [9].

Because toluene does not tend to form hydrogen bonds, these effects were attributed to the formation of hydrogen bonds between amide groups of the monomer, and in concentrated solutions, to additional cooperation of linear hydrocarbon fragments of *N*-octylacrylamides.

This assumption was based on the previously revealed “favorable” effect of the cooperation of linear alkyl groups on the reduced polymerization rate of higher *n*-alkyl acrylates [10]. Similar concentration effects in homopolymerization of cyclododecyl acrylate or cyclohexyl acrylate in benzene or tetrahydrofuran are probably also associated with the cooperation of hydrocarbon fragments of the monomers [11]. It should be noted that, for higher alkyl methacrylates, an increase in the initial concentration of the monomers does not noticeably influence the reduced homopolymerization rate [12]. This result was accounted for in [13, 14] by the fact that, in cooperative associates of methacrylates, the mutual location of vinyl groups is unfavorable for the reaction. Thus, depending on the features of noncovalent prereaction interactions involving the monomers and solvents, the dependences of the reduced homopolymerization rate on the monomer concentration can be diverse.

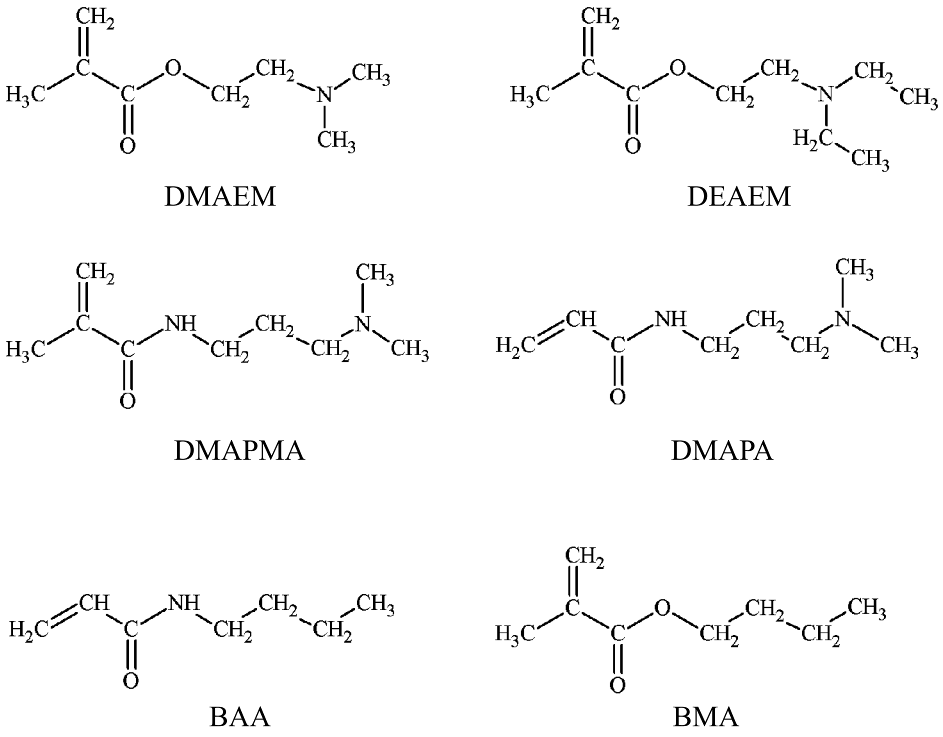
In this work, we performed a comparative study of the concentration effects in homogeneous radical homopolymerization of amphiphilic nitrogen-containing (meth)acrylic monomers containing polar amine and/or amide groups and nonpolar linear alkyl fragments in toluene and dimethylformamide (DMF) and analyzed how these effects correlate with differences in the tendency of the monomers to association.

The investigation objects were amine-containing (meth)acrylic esters (DMAEM and DEAEM) and amine-containing (meth)acrylamides {*N*-[3-(dimethylamino)propyl]methacrylamide (DMAPMA), *N*-[3-(dimethylamino)propyl]acrylamide (DMAPA)}; (meth)acrylic monomers containing alkyl and amide or ester groups but containing no amino groups [*N*-(*n*-butyl)-acrylamide (BAA) and n-butyl methacrylate (BMA)] were studied for comparison. The structural formulas of the monomers studied are shown in Scheme 1. The choice of the solvents was governed by the fact that toluene is a typical low-polarity solvent forming no strong hydrogen bonds, whereas DMF is a highly polar solvent capable of active participation in hydrogen bonding.

EXPERIMENTAL

DMAPMA, DMAEM, and DEAEM were purchased from Sigma–Aldrich, DMAPA and BAA were synthesized by the Schotten–Baumann reaction [14, 15], and BMA was prepared by esterification of methacrylic acid with butanol [19]. Prior to performing polymerization, all the monomers

Scheme 1. Structural formulas of the monomers studied.



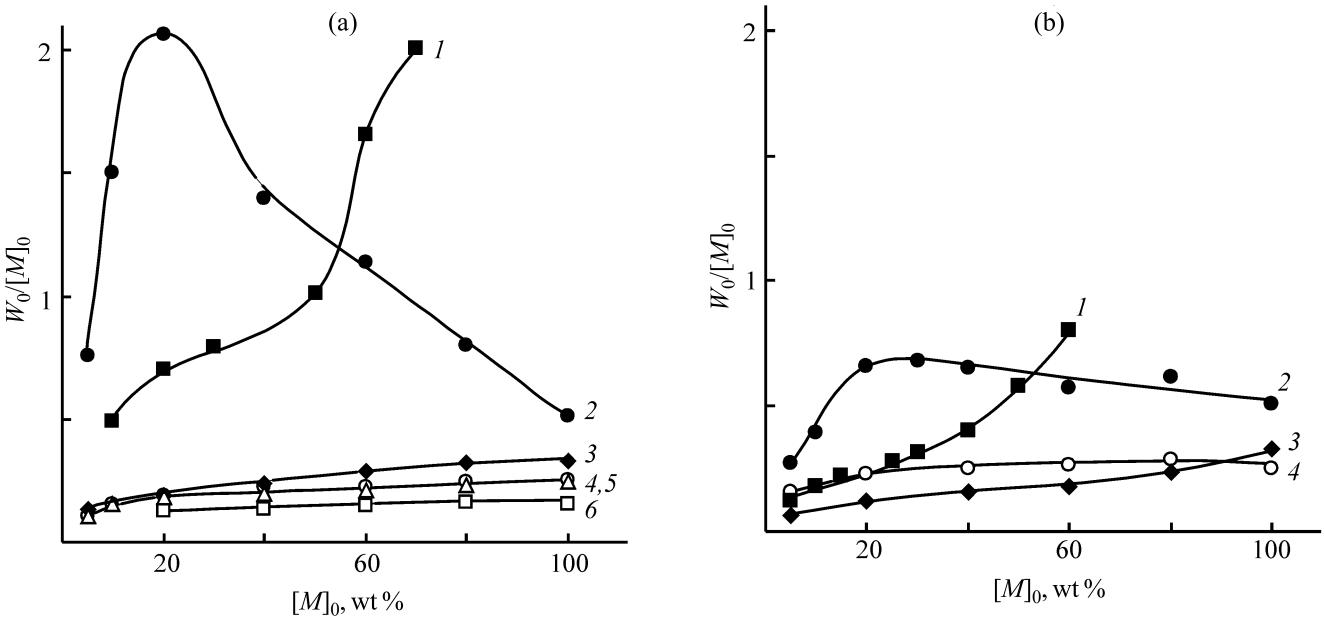


Fig. 1. Influence of the initial monomer concentration $[M]_0$ on the initial reduced rates $W_0/[M]_0$ of homopolymerization of (*1*) BAA, (*2*) DMAPA, (*3*) DMAPMA, (*4*) DMAEM, (*5*) DEAEM, and (*6*) BMA in (a) toluene and (b) DMF.

were vacuum-distilled. 2,2'-Azobis(isobutyronitrile) (AIBN) used as initiator was preliminarily recrystallized from ethanol.

Homopolymerization was performed in glass dilatometers at 60°C in the presence of AIBN in the solvent (toluene, DMF) or in the bulk. Prior to starting heating, the reaction mixtures were purged with nitrogen. The initial concentration of the monomers was varied from 5 to 100 wt %, and the AIBN concentration was 0.05 M.

The kinematic viscosity of the monomer solutions was determined with Ubbelohde viscometers with the capillary diameter of 0.34 and 0.56 mm at 25°C. The relative deviation of the viscosity of the monomer–solvent mixture from the calculated additive values (%) was estimated as follows [17]

$$\Delta\eta = 100(\eta_{\text{exp}} - \eta_{\text{calc}})/\eta_{\text{exp}},$$

where η_{exp} is the experimental viscosity of the monomer–solvent mixture, and η_{calc} is the calculated viscosity.

In accordance with [17], in the case when the viscosity of the monomer exceeded the viscosity of the solvent by a factor of more than 5, η_{calc} was determined by the Kendall equation (1), and at a smaller difference between these parameters, by the Kendall–Monroe equation (2):

$$\eta_{\text{calc}}^{1/3} = x_1\eta_1^{1/3} + x_2\eta_2^{1/3}, \tag{1}$$

$$\ln \eta_{\text{calc}} = x_1 \ln \eta_1 + x_2 \ln \eta_2, \tag{2}$$

where x_1 and x_2 are the mole fractions of the components in the mixture; η_1 and η_2 are the viscosities of the pure components.

The dielectric permittivity of the solutions of the monomer in toluene was measured with a BI-870 device (Brookhaven).

RESULTS AND DISCUSSION

To study the concentration effects, we chose as the parameter being estimated the initial reduced homopolymerization rate $W_0/[M]_0$:

$$W_0/[M]_0 = k_p(R_i/k_t)^{1/2}. \tag{3}$$

As seen from this equation, for radical homopolymerization processes at a constant initiation rate and an invariable ratio of the propagation and termination constants, the reduced initial rate should be constant at varied initial concentration of the monomers. Therefore, according to the classical concept that does not consider the effect of noncovalent interactions on the reactivity of the monomers, initiators, and propagating macroradicals, the

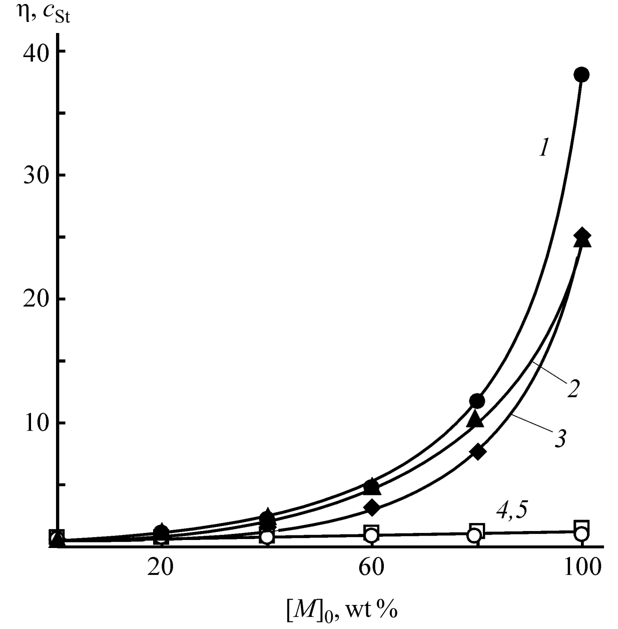


Fig. 2. Kinematic viscosity η of toluene solutions of (*1*) DMAPA, (*2*) BAA, (*3*) DMAPMA, (*4*) DMAEM, and (*5*) BMA as a function of the monomer concentration $[M]_0$.

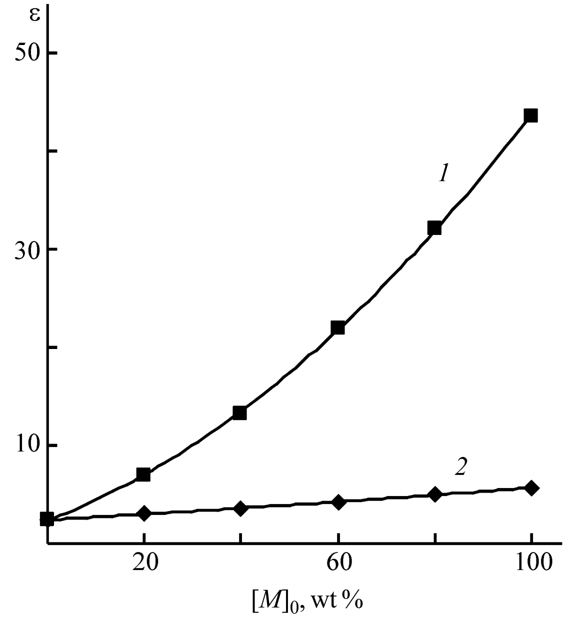


Fig. 3. Dielectric permittivity ε of toluene solutions of (*1*) DMAPMA and (*2*) DMAEM as a function of the monomer concentration $[M]_0$.

reduced rate should not vary with varying polymerization conditions. Therefore, as shown in [9, 10, 12], analysis of the influence of the initial monomer concentrations on $W_0/[M]_0$ can be used for evaluating the extent to which the polymerization in the given system deviates from “classical” polymerization and for performing comparative analysis of the effect of the prereaction interactions on the activity of monomers of different structures.

We determined the initial rates of the homopolymerization of the monomers and calculated the initial reduced rates at the initial monomer concentration varied and the initiator concentration and temperature kept constant. The data presented in Fig. 1a show that, for the homopolymerization of all the monomers under consideration in toluene, the initial monomer concentrations influence $W_0/[M]_0$. The monomers can be subdivided into three types in accordance with the character of the concentration effects. In the first group, which includes all the methacrylic monomers (BMA, DMAEM, DEAEM, DMAPMA), the reduced rates monotonically increase with increasing $[M]_0$. The increase in the rate is somewhat more pronounced in the concentration interval 5–20 wt %, and the total increase in the reduced rate in the concentration interval 5–100 wt % is from 25 (BMA) to 150% (DMAPMA).

In polymerization of the acrylic *N*-alkylamide, BAA, an increase in the monomer concentration from 10 to 50 wt % led to an increase in the rate by a factor of 2, but with a further increase in the concentration from 50 to 70% $W_0/[M]_0$ increased considerably more rapidly (by a factor of 2 more). This behavior essentially differs from the behavior of the methacrylic monomers, for which the rate in this interval of $[M]_0$ increased by no more than 10%. Finally, for the amine-containing acrylamide, DMAPA, the dependence passes through a maximum: $W_0/[M]_0$ increases by a factor of 2.7 in the concentration interval 5–20 wt % and then decreases to approximately the same extent with a further increase in the initial monomer concentration. DMAPA appeared to be the only monomer for which the reduced polymerization rate in the bulk was lower than in the 5% toluene solution. On replacement of toluene by DMF, the shape of the concentration dependences changed only slightly for the methacrylic monomers (Fig. 1b, curves *3* and *4*), whereas for the acrylic monomers the dependences became considerably less pronounced, with the overall trend preserved (Fig. 1b, curves *1* and *2*).

In analysis of such differences in the behavior of the monomers of different structures, let us consider in succession the probability of the influence of different

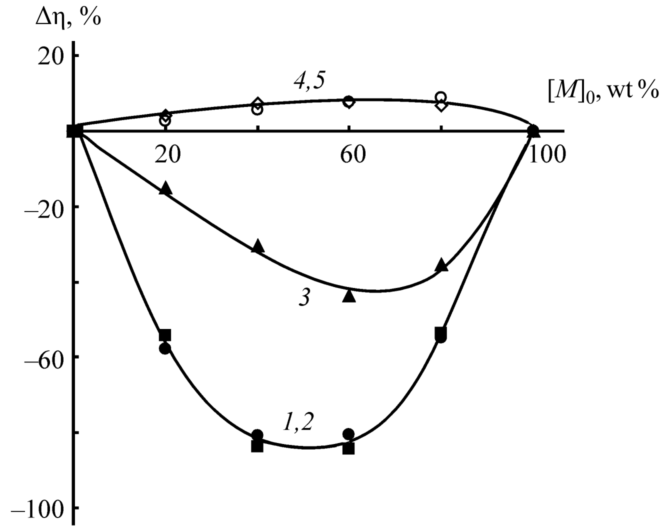


Fig. 4. Relative deviation of the kinematic viscosity, Δη, of monomer solutions as a function of the monomer concentration $[M]_0$. Monomers: (*1*) DMAPA, (*2, 3*) DMAPMA, and (*4, 5*) DMAEM; solvents: (*1, 2, 4*) toluene and (*3, 5*) DMF.

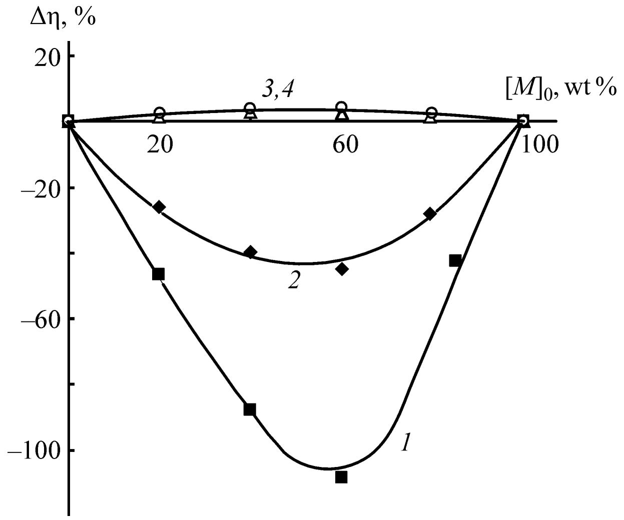


Fig. 5. Relative deviation of the kinematic viscosity, Δη, of monomer solutions as a function of the monomer concentration $[M]_0$. Monomers: (*1, 2*) BAA and (*3, 4*) DMA; solvent: (*2, 3*) toluene and (*1, 4*) DMF.

factors on the manifestation of the concentration effects. The most apparent factor is the viscosity of the initial monomer solutions, which differs in our experiments very strongly. It is known that the radical polymerization rate strongly depends on the viscosity of the reaction mixtures, which influences both the initiation rate and the ratio of the propagation and termination rate constants (which ensures, in particular, the manifestation of the gel effect) [18, 19]. Therefore, we obtained isotherms of the kinematic viscosity of the toluene solutions of the monomers (Fig. 2). For the ester monomers, the kinematic viscosities of the solutions only slightly depend on the monomer concentrations, whereas for the amides the viscosities sharply increase in the concentrated solutions. When comparing the essentially different character of the concentration effects in the homopolymerization of the three amides (BAA, DMAPA, and DMAPMA) with small differences in their viscosity isotherms, it is logical to conclude that variation of the viscosity of the initial mixtures cannot be the major factor responsible for the revealed kinetic features of the homopolymerization of these monomers.

Another possible cause of the concentration effects in polymerization is variation of the overall polarity of the medium. Indeed, variation of the initial ratio of (meth) acrylic monomers and toluene cannot but lead to a change in the polarity of the medium, especially for such polar molecules as amine-containing amides DMAPA and DMAPMA. It is known that the polarity of the medium can influence the radical polymerization by varying the extent of stabilization of the intermediate species; for the majority of vinyl monomers, this factor, however, is believed to be relatively insignificant [20]. As applied to the systems under consideration, this conclusion is confirmed by essential difference in the kinetic data obtained for DMAPA and DMAPMA, which have the same set of polar groups and cannot significantly differ in the polarity. Furthermore, the dielectric permittivity of the monomer solutions varies approximately proportionally to the monomer concentration (Fig. 3), which does not correspond to the trends in the variation of the initial reduced polymerization rate with the concentration.

According to published data, in solution polymerization of polar vinyl monomers, the polymerization kinetics in many cases is strongly influenced by the formation of prereaction complexes or associates of the monomer–monomer and monomer–solvent types [20–22]. The viscosity is one of the most sensitive parameters associated with intermolecular interactions in solutions [23]. Therefore, analysis of the deviations of the experimental viscosity values from the values calculated by the additive equations is often used for evaluating the extent to which various parameters influence the properties of solutions of (meth)acrylic monomers [24, 25].

Figure 4 shows the corresponding data obtained for amine-containing monomers, and Fig. 5, the data for the monomers containing no amino groups. It follows from the results obtained that amino groups weakly influence the viscosity characteristics of the monomer solutions. Small positive deviations from the calculated additive viscosity values ($\Delta\eta$, the procedure for calculating this parameter is given in the Experimental) are observed for methacrylic esters with the amino group (DMAEM) and without it (BMA), with the results only slightly changing on replacement of toluene by DMF. Considerably stronger deviations are observed for all the amide monomers. The maximal values of $\Delta\eta$ in toluene were –85 for the amine-containing amides DMAPA and DMAPMA and –110 for the amide containing no amino groups (BAA). In the amide-containing solvent, DMF, the maximal values of $\Delta\eta$ decrease by a factor of 2–2.5.

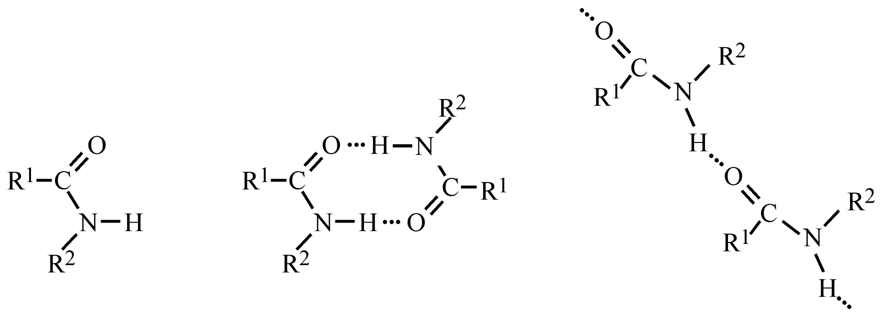
These data show that strong noncovalent bonds are formed in the initial reaction solutions of the three monomeric amides. For monosubstituted amides, the tendency to intermolecular association via hydrogen bonds involving amide groups is well known [26]. Cyclic dimers and linear polyassociates consisting of different numbers of molecules (Scheme 2) can exist in solutions along with the monomeric form of the amides. It is known [27–29] that the ratio of the monomeric and various associated species depends on the structure of the amides, on their concentration, on the solvent, and on other factors. As shown previously [30], participation of the carbonyl groups of the amide and ester acrylic and methacrylic monomers in hydrogen bonding accelerates their radical polymerization owing to an increase in the extent of polarization of the vinyl group. In addition, the polymerization rate should be influenced by the type of the associate (linear or cyclic) and by the mean number of associated amide molecules linked in a pseudopolymer chain.

Therefore, one of the most probable causes of essential differences in the character of the concentration dependences of the initial polymerization rates of the monomeric amides (DMAPA, DMAPMA, and BAA) is the difference in their association equilibria. The specific features of the behavior of the two amino amides can be attributed only to the presence of the methyl substituent in the vinyl group of the DMAPMA molecule (because this is the only difference between these monomers). This methyl group, apparently, affects the equilibrium between the three forms of amide associates shown in Scheme 2 (depending on the overall monomer concentration in the solution) and/or the mutual steric arrangement of the vinyl groups in these associates. Pronounced increase in the initial polymerization rate in solutions of the two acrylic amides in definite concentration intervals (up to 20 wt % for DMAPA, above 50 wt % for BAA) is probably associated with the fact that the mutual arrangement of the vinyl groups in the monomer associates prevalent under these conditions is favorable for the reaction.

The assumption that the prereaction monomer association plays the decisive role accounts for a decrease in the concentration effects for the amide monomers on replacing toluene by DMF. Owing to the participation of a part of amide groups of the monomers in hydrogen bonding with amide groups of the solvent, the number of monomer–monomer bonds decreases; i.e., the fraction of associates of types (b) and (c) decreases (Scheme 2). A decrease in the polymerization rate of all the amides in DMF indicates that the polymerization is accelerated to a greater extent by hydrogen bonding between the monomer molecules than by hydrogen bonding with the solvent. Hence, not only the very fact of the participation of amide groups in hydrogen bonding, but also the structure of the monomer associates plays an important role. In the DMF–ester monomer systems, as well as in toluene–ester monomer systems, there are no labile hydrogen atoms required for the formation of strong hydrogen bonds. Therefore, the solvent replacement does not noticeably influence the concentration effects in such systems.

It can also be noted that, in solutions of methacrylic esters (DMAEM, BMA) in DMF, in contrast to their toluene solutions, the polarity of the medium decreases as the monomer concentration is increased, because the dielectric permittivity of DMF (ε = 36.7 [31]) is considerably higher than that of methacrylates. Hence, in these systems the polarity and initial reduced polymerization rate vary in opposite directions. This fact confirms the above conclusion that variation of the polarity of the medium influences the homopolymerization rate insignificantly. The more probable cause of the increase in the initial reduced homopolymerization rate of the methacrylic esters is a change in the initiation efficiency due to an increase in the solution viscosity, occurring to a greater or lesser extent in all the systems under consideration with increasing $[M]_0$. As shown previously, in styrene polymerization in benzene, the initiation efficiency with AIBN can decrease with decreasing monomer concentration, especially at a styrene concentration lower than 1.0 M [32]. This is caused by an increase in the contribution of the recombination of primary radicals when high initiation rate is combined with low monomer concentration. Thus, the shape

Scheme 2.



(a) (b) (c)

(a) Monomeric form of the amides, (b) cyclic amide dimer, and (c) fragment of linear amide polyassociate.

of the dependence of the initiation efficiency on the monomer concentration, obtained in [31], is similar to the shape of the concentration dependence of the reduced polymerization rate of methacrylic esters in toluene, obtained in this study. Apparently, the initiation factor can exert effect in all the systems under consideration. However, in the case of methacrylic esters, for which there are no conditions for the monomer association, this factor determines the shape of the concentration dependence of the initial reduced rate. For acrylamide monomers, the initiation factor is not decisive but only supplements the effect of the monomer association, which actually determines the specific shape of the concentration dependences.

CONCLUSIONS

In homopolymerization of amine-containing (meth)-acrylic esters and amides, *N*-(*n*-butyl)acrylamide, and *n*-butyl acrylate in toluene and dimethylformamide, the initial monomer concentrations influence the reduced initial homopolymerization rate. The character of the concentration effects is similar for methacrylic monomers and is considerably more pronounced for acrylamides {*N*-(*n*-butyl)acrylamide and *N*-[3-(dimethylamino)-prolyl]acrylamide}. This fact is due to the prereaction monomer association involving amide groups. Certain increase in the initial reduced homopolymerization rate of methacrylic esters may be due to a change in the initiation efficiency with increasing solution viscosity.

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