Polymer Bulletin 33, 167–173 (1994)

Polymer Bulletin

Polysoap-induced polymerization of methyl methacrylate and styrene by poly(sodium alkyl 2-hydroxy-3-methacryloyloxypropyl phosphate)s in water

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Summary

Poly(sodium alkyl 2-hydroxy-3-methacryloyloxypropyl phosphate)s as polysoap induced the radical polymerization of methyl methacrylate and styrene in the absence of an added radical initiator in water at 80℃. The polysoap having a C_{14} alkyl group showed the highest activity of all tested groups. The generalized initiation mechanism of the spontaneous polymerization in which the micellar aggregation state participates is discussed.

Introduction

We have previously found that some amphiphilic vinyl monomers, having polymerizable double bond, and hydrophilic and hydrophobic moieties, such as sodium alkyl 2-hydroxy-3-methacryloyloxypropyl phosphates (C_n-AHMP) and alkyl-2-methacryloyloxyethyldimethylammonium bromides, spontaneously polymerize through a radical mechanism in micellar solution [1~5]. As a feature of these polymerization systems, the monomer aggregation state has a very important role in controlling the generation of initiating radical species. A variation in alkyl chain length of the monomer and the addition of an inorganic electrolyte or unpolymerizable surfactant into the micellar solution modify the monomer aggregation state and vary the spontaneous polymerizability, i.e., the activity of generation of the initiating radical species.

On the other hand, during the emulsion polymerization of methyl methacrylate and styrene in which two desired functions, polymerization and surface activities, are separated into two kinds of molecules, a lipophilic vinyl monomer and a conventional surfactant, the spontaneous polymerization in the absence of a radical initiator [6~14] and the proposed thermal initiation process have been reported [10~14]. Imoto and Ouchi have investigated the polymerization of lipophilic vinyl monomers induced by water-soluble polymers in aqueous medium [15].

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The hydrophobic domain in the water-soluble polymer participates as a key factor for radical formation. The water-soluble polymer should be recognized as a kind of surface-active compound, polysoap, which forms a uni-molecular or plural-molecular micelle. From the viewpoint of micelle formation, conventional surfactants and water-soluble polymers belong in the same category.

Thus, the three kinds of spontaneous polymerization systems mentioned above show similar participation of the anisotropic reaction locus. In the case of the amphiphilic monomers, the formation of the monomer micelle is indispensable for the initiation of polymerization, and the modification of the aggregation state changes the polymerizability, indicating the existence of the most suitable state for radical generation. For the emulsion polymerization, the solubilization of a lipophilic monomer into the surfactant micelle or seed particle is required for the occurrence of spontaneous polymerization, and there is an appropriate combination of surfactant for each monomer. During the polymerization induced by the water-soluble polymer, the presence of a hydrophobic domain like a micelle core in water has a significant importance, and an appropriate combination of the polymer and the monomer is explained on the basis of a hard-soft concept relating to the hydrophilicity and hydrophobicity of the components.

The present paper deals with the spontaneous polymerization of methyl methacrylate (MMA) and styrene (St) in the presence of poly(C_n-AHMP) as a polysoap in aq. solution, and a generalized spontaneous initiation mechanism in the micellar organized systems is proposed.

Experimental

Materials

Poly(C_n-AHMP)s used were prepared by the polymerization of C_n-AHMP ($n=8,12,14,16$) previously characterized [1,2]: [C_n-AHMP] = 30 mmol/L, [Sodium peroxodisulfate] = 0.3 mmol/L in water at 70℃ for 4 h, and purified by repeated reprecipitation using the water-acetone system. The intrinsic viscosities of the poly(C_n-AHMP)s, determined in aq. NaCl (0.1 mol/L) at 25℃, were as follows; C_8: 3.54, C_{12}: 2.60, C_{14}: 1.40, C_{16}: 1.48 (dL/g). The monomers, MMA and St, were purified by the usual methods. Water was ion-exchanged; conductivity: 1×10^{-6} S/cm or lower. Other chemicals used were extra reagent grade.

Polymerization procedure

The polymerizations of MMA and St were carried out in a sealed glass tube with shaking at a given temperature. Before sealing, the tube was repeatedly degassed by a freeze-thaw technique.

In the heterogeneous polymerization, the polymer produced was recovered by precipitation in a diethyl ether-methanol (2:1 by volume) mixture for polyMMA or acetone for polySt together with poly(C_n-AHMP) initially added. The conversion of the monomer-to-polymer was calculated according to the following equation.

$$\text{Conversion (\%)} = \frac{\text{Precipitated polymer (g)} - \text{Added poly(}C_n\text{-AHMP) (g)}}{\text{Added monomer (g)}} \times 100$$

The homogeneous polymerization system was prepared in the following manner. The prescribed amount of MMA, A: 0.15 mL (140 mg) or B: 0.30 mL (280 mg), was added with a microsyringe to the solution containing dissolved poly(C_n-AHMP) (0.1 g) in water (10 mL). The mixture was then sonicated for 10 mins. After standing overnight at room temperature, the lower clear phase was pipetted out for use in subsequent polymerizations. The amount of solubilized monomer in the solution was determined by UV absorption at 210 nm, excepting for C_8-AHMP solution giving smaller values than in pure water. The monomer-to-polymer conversion was calculated from the ratio of the UV absorbance before and after the polymerizations.

Fractionation of polymer mixture

The polymer mixture (0.5 g) recovered from the polymerization system, poly(C_{14}-AHMP)-polyMMA or -polySt, was dissolved or swollen in 20 mL of dimethylformamide, and poured into a large amount of methanol, a good solvent for poly(C_{14}-AHMP) but a non-solvent for polyMMA and polySt. After evaporation of the soluble part, only a trace amount of polymeric compounds remained.

Results and discussion

The activity of polysoap as a polymerization inducer is presumed to be governed by the solubilization capacity for the monomer and its solubilized state. The chemical structure of polysoap, especially its hydrophobic nature, can be expected to change the capacity and the activity as an inducer. In the present work, poly(C_n-AHMP) with different alkyl chain lengths was used as a polysoap with varying hydrophobicity.

Polymerization of MMA and St in a heterogeneous system

Figure 1 shows the results of polymerization of MMA and St in an aq. solution of poly(C_n-AHMP), in which an excess amount of the monomer for the solubilization capacity of the polysoap used was introduced. All of

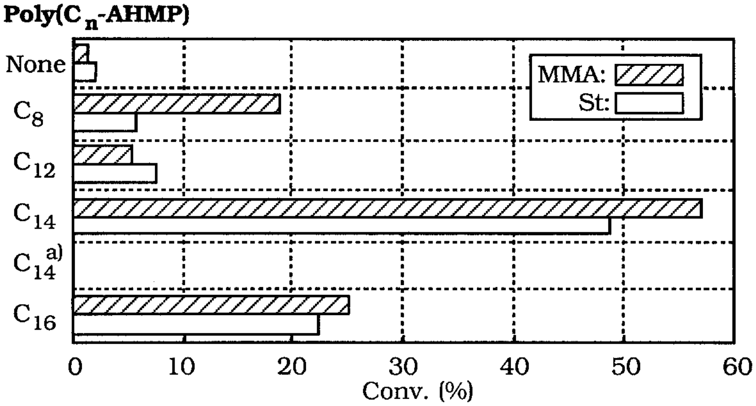

Figure 1. Polymerization of MMA and St in an aq. solution of poly(C_n-AHMP) at 80℃ for 5 h: poly(C_n-AHMP) = 0.1 g, monomer = 3.0 mL and water = 10 mL

[a] *p*-Benzoquinone (1000 ppm) was added.

the polymerization proceeded heterogeneously to give milky white emulsions when the conversion exceeded about 19%. The polysoap significantly promoted polymerization in both systems, and the conversion remarkably changed with alkyl chain length in the order: $C_{14} > C_{16} > C_8 \sim C_{12}$. The addition of a free-radical inhibitor, *p*-benzoquinone, entirely inhibited the polymerization, proving that the polymerization proceeded through a radical mechanism. The results lead to the conclusion that poly(C_n-AHMP) induces the polymerization of MMA and St in water similar to the case of conventional water-soluble polymers [15]. The attempted separation of polyMMA or polySt from the recovered polymer mixture was unsuccessful as described in the experimental section, suggesting that graft polymerization would take place as reported in similar polymerization systems [15]. Further confirmation of graft polymerization by GPC analysis failed owing to the lack of a suitable solvent for both components, because poly(C_{14}-AHMP) was soluble only in water and methanol [2].

Polymerization of solubilized MMA

Three different monomer states, a solubilized monomer in the hydrophobic domain of the polysoap, a dissolved monomer in water and a dispersed monomer droplet exist in the heterogeneous polymerization system described above. Therefore, in order to ascertain the locus of formation of the initiating radical species by excluding the contribution of monomer droplet, the polymerization of MMA solubilized in the aq. polysoap solution was carried out. The results are shown in Table 1.

Table 1. Polymerization of MMA solubilized in aq. poly(C_n-AHMP) without added initiator: poly(C_n-AHMP) = 0.1 g and water = 10mL

Poly (C_n-AHMP)	Solubilized MMA mg	Temp. (℃)	Time (h)	Conv. (%)
	Prescription A[a]			
None	141	60	7	0
C_8	—			0
C_{12}	141			0
C_{14}	141			0
C_{16}	141			0
None	141	80	5	5
C_8	—			10
C_{12}	141			9
C_{14}	141			67 [b]
C_{16}	141			7
	Prescription B[a]			
None	134	80	5	4
C_8	—			57 [b]
C_{12}	156			23
C_{14}	191			84 [b]
C_{16}	297			13

[a] See experimental section.

[b] Polymerization system became turbid at the end point of polymerization.

Poly(C_{14}-AHMP) exhibited an exceptionally high initiating activity even at a lower monomer concentration level, although it required a rather higher polymerization temperature of 80℃. Other polysoaps gave higher polymer yields than that in pure water at a higher level of monomer concentration. In these systems, the amount of solubilized MMA means the sum of MMA truly solubilized in the hydrophobic domain and MMA dissolved in water. At a lower monomer concentration level, the amount of added MMA was within its solubility in pure water, and a part of MMA would be solubilized in the hydrophobic domain. Further, the addition of MMA should increase the amount of truly solubilized MMA until the capacity limit of the polysoap, and the polymer yield at a higher monomer concentration increased in practice. Although the amount of solubilized MMA was dependent on the alkyl chain length of poly(C_n-AHMP), poly(C_{16}-AHMP) which solubilized the largest amount of MMA produced rather small amount of polyMMA. These results emphasize that the hydrophobic domain solubilized MMA is the locus of formation of the initiating radical species in aq. polysoap solution, and C_{14} is the best fit alkyl chain length in this polysoap series, suggesting both amount and organized structure of solubilized monomer in the hydrophobic domain of the polysoap are important factors of the polymerization inducer.

In the case of heterogeneous system in where excess amounts of MMA exist as monomer droplets, it is assumed that the monomer is supplied, like in emulsion polymerization, by diffusion from the monomer droplets to the hydrophobic domain as the reaction locus with the progress of polymerization.

Initiation mechanism

Lingnau and Meyerhoff have proposed a mechanism for the thermal polymerization of MMA, in which the dimer biradical is spontaneously formed from the monomer molecules followed by a chain-transfer reaction producing the dimer monoradical as the initiating species, and pointed out an important role of the chain-transfer agent during the initiation [16,17]. The micelle from a conventional surfactant exists in a dynamic equilibrium with the monomeric surfactant molecule in the solution, and the exchange rate is very fast [18]. If MMA solubilized in the micelle thermally produces the dimer biradical, the transfer from the biradical to the surfactant molecule would occur and leave the monoradical in the micelle and remove the transferred surfactant radical to the solution by the dissociation of the micelle in order to avoid termination and facilitate propagation in the micelle. This would be a reason for the facile thermal polymerization in the emulsion state as compared with the bulk reaction. Further, the arrangement and orientation of the monomer molecule in the micelle would be possible to facilitate a monomer-monomer interaction. Because, in the case of polysoap, the polymer micelle can not dissociate, the polysoap radical produced by transfer in the same manner as the conventional surfactant remains in the micelle and could initiate the polymerization of MMA to give the graft copolymer. The initiation mechanism of MMA in the micellar organized system is generally given by the following scheme.

$2\,M \rightarrow \cdot M_2 \cdot$ (M: MMA monomer, M_2: MMA dimer)

$\cdot M_2 \cdot$ + Surfactant or Polysoap $\rightarrow$ $M_2 \cdot$ + Surfactant $\cdot$ or Polysoap $\cdot$

$M_2 \cdot + n\,M \rightarrow (M)_{2+n}$

Polysoap $\cdot$ + nM $\rightarrow$ Graft polymer

The surfactant radical that escapes from the micelle could initiate the polymerization of dissolved MMA in water. The spontaneous polymerization of the amphiphilic vinyl monomers having a methacrylate moiety previously reported [1~5] would proceed through a similar initiation mechanism.

In the case of St polymerization, the same mechanism seems to be applicable except for the monomer radical formation during the first stage [19].

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Accepted May 6, 1994 Shi