Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Aoki, Shuzo and Nakamae, Satoshi(1994) 'Polymerization of Methyl Methacrylate Induced by Micellar Solution of Cationic Surfactants', Journal of Macromolecular Science, Part A, 31: 5, 573 — 579

To link to this Article: DOI: 10.1080/10601329409349739

URL: http://dx.doi.org/10.1080/10601329409349739

J.M.S.—PURE APPL. CHEM., A31(5), pp. 573–579 (1994)

POLYMERIZATION OF METHYL METHACRYLATE INDUCED BY MICELLAR SOLUTION OF CATIONIC SURFACTANTS

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ABSTRACT

The polymerization of methyl methacrylate was induced by a micellar solution of cationic surfactants, such as benzyldimethylphenylammonium chloride, dodecyltrimethylammonium chloride, and cetyltrimethylammonium chloride, in the absence of added initiator to yield a high molecular weight polymer at 60–80°C. The initiation mechanism was compared with other spontaneous polymerization systems. The monomer-solubilized micelle as the reaction locus was emphasized to facilitate the production of the initiating radical species.

INTRODUCTION

Several research groups have reported that the emulsion polymerizations of methyl methacrylate (MMA) and styrene can proceed spontaneously without added radical initiators [1–4]. The polymerizabilities of these monomers were associated with the kind of surfactant used. Combinations of styrene–fatty acid alkali metal salts and MMA–alkali metal salts of alkylbenzene sulfonic acid or alkylsulfuric acid showed high activities. A thermal initiation process in analogy to thermally-induced bulk polymerization was proposed [2, 4].

The participation of surface-active quaternary ammonium salts on the initiation process of the radical polymerization of vinyl monomers has been known in some cases. Benzyldimethylphenylammonium chloride (BDPA) can initiate the polymerization of MMA in methanol or ethanol through the thermal or redox decomposition of BDPA to produce the radical species [5, 6]. Water-soluble polymers having quaternary ammonium side groups can also induce the polymerization of vinyl monomers in aqueous media [7, 8]. We have recently found that a surface-active monomer, alkyldimethylmethacryloyloxyethylammonium bromide, polymerizes spontaneously in micellar solution [9].

The present article concerns the aqueous polymerization of MMA induced by surface-active quaternary ammonium salts, BDPA and other conventional cationic surfactants, in the absence of added initiator.

EXPERIMENTAL

Materials

BDPA was prepared from benzyl chloride and dimethylaniline, and recrystallized from ethanol containing a small amount of water as monohydrated salt [5]. Reagent-grade dodecyltrimethylammonium chloride (DTMA) and cetyltrimethylammonium chloride (CTMA) were obtained commercially and recrystallized from acetone. MMA was distilled under reduced pressure prior to use. Water was distilled after deionization.

Polymerization

The polymerization was carried out in a sealed tube after oxygen had been removed by repeated freeze–thaw under vacuum, with shaking in the dark. The resulting polymer was separated by pouring the polymerization mixture into a large amount of methanol as a nonsolvent for the polymer and as a good solvent for the surfactant and the monomer, and dried under vacuum.

Measurements

The number-average molecular weight ($\overline{M}_n$) was determined by Tosoh 8000 series gel-permeation chromatography at 38°C using tetrahydrofuran as the eluent.

The relative viscosity (η_{rel}) of the MMA–quaternary ammonium salt–water system was estimated by its effusion time from a pipet of constant volume at room temperature.

RESULTS AND DISCUSSION

Polymerization in Methanol

As shown in Table 1, BDPA showed an exceptionally high initiating activity in methanol, as reported previously [5, 6]. Polymerization with other quaternary salts gave a polymer in rather low yields. The polymerization systems were apparently homogeneous before and after the reaction, because only a small amount of methanol was used.

TABLE 1. Polymerization of MMA Induced by Cationic Surfactants in Methanol at 60°C

Surfactant,	g/mL CH_3OH	MMA/CH_3OH, vol/vol	Time, hours	Polymer yield, %	$\overline{M}_n$ ($\times 10^{-3}$)
BDPA	0.75	2.5	6	100	257
DTMA	0.13	2.5	6	2.5	–
CTMA	0.32	2.5	6	1.8	–
CTMA	0.64	2.5	6	2.5	–

Polymerization in Water

The polymerization was conducted in binary systems consisting of MMA and a concentrated aqueous solution of the quaternary salts. A stable emulsion did not result. Accordingly, the polymerization proceeded to an unstable suspension state consisting of an MMA phase and an aqueous phase of solubilized MMA, which turned out to be a non-fluid gel-like state with progress of the polymerization.

All the quaternary salts examined showed initiating activity for the polymerization of MMA at 60°C (Table 2). The molecular weights of the polymers obtained in aqueous media were characteristically higher than those obtained in methanol. Although DTMA and CTMA are conventional cationic surfactants widely used for a variety of purposes, they are not known to produce radical species.

Polymerization Induced by BDPA/Water

Figure 1 shows the results of polymerization with BDPA in water. The polymer yield increased with an increase in the amount of BDPA and increasing temperature.

Polymerization Induced by CTMA/Water

Figure 2 shows the typical time course of polymerization with CTMA in water, in which the so-called gel-effect was observed and an almost quantitative polymer yield was attainable with prolonged time.

TABLE 2. Polymerization of MMA Induced by Cationic Surfactants in Water at 60°C

Surfactant,	g/mL H_2O	MMA/H_2O, vol/vol	Time, hours	Polymer yield, %	$\overline{M}_n$ ($\times 10^{-3}$)
BDPA	0.40	1	6	7.2	–
BDPA	0.53	1	6	11.5	1630
DTMA	0.13	1	6	8.7	2740
CTMA	0.24	1	6	18.8	3140

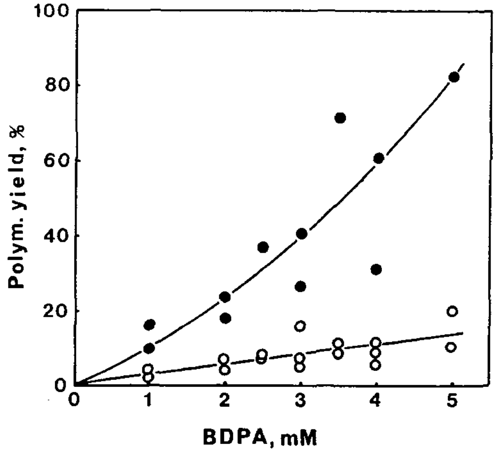

FIG. 1. Polymerization of MMA with varying amount of BDPA in water: MMA, 2 mL; water, 2 mL; 6 hours; (○) 60°C, (●) 80°C.

CTMA showed a higher activity than BDPA based on the results obtained in methanol (Fig. 3). The change of volume ratio of MMA and water (1/1-1/3) did not affect the polymer yield at 60°C. The unsatisfactory reproducibility of the data obtained was considered to result from the inhomogeneity of the polymerization systems and the gel-effect, especially at higher conversion.

Viscosity of MMA/CTMA/Water System

The MMA/CTMA/water system became highly viscous with an increasing CTMA content, as shown in Fig. 4. No abrupt change of the viscosity of CTMA/water was observed in the concentration range used for polymerization. CTMA

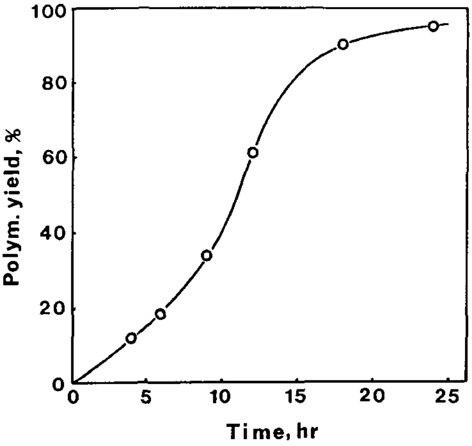

FIG. 2. Time course of polymerization of MMA with CTMA at 60°C: MMA, 2 mL; water, 2 mL; CTMA, 1.5 mM.

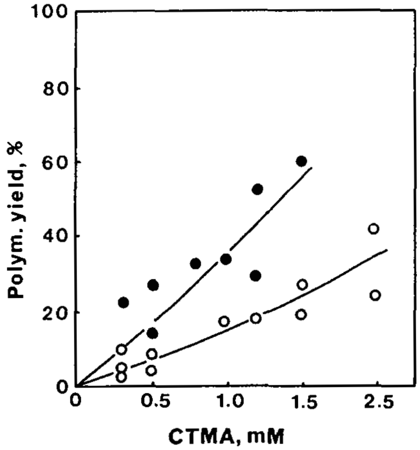

FIG. 3. Polymerization of MMA with varying amount of CTMA in water: MMA, 2 mL; water, 2 mL; 6 hours; (○) 60°C, (●) 80°C.

forms a spherical micelle in the concentration range from 5 to 38% by weight [10, 11]. Thus, the high viscosity of the MMA/CTMA/water system seems to be attributable to the solubilization of MMA into the micelle.

Initiation Mechanism

Fueno et al. proposed that the polymerization of MMA with BDPA in methanol was initiated by the alkyl radical produced by thermal homolysis of BDPA [5]. Further investigation by Otsu et al. revealed that the initiation was brought about

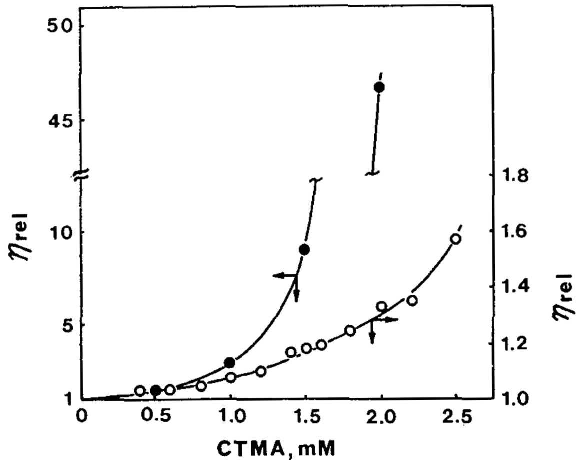

FIG. 4. Relative viscosity: (○) CTMA in 2 mL water; (●) CTMA in 2 mL MMA and 2 mL water.

by the methyl or phenyl radical provided by the redox reaction between BDPA and dimethylaniline produced by thermal dissociation of BDPA [6]. However, this redox mechanism is neglected in water because the dissociation of BDPA did not occur in water [6]. Conventional cationic surfactants are also stable in water at the temperature used for polymerization.

In water, the surface-active quaternary ammonium salt forms an aggregate with an organized structure such as a micelle and liquid crystal, above the cmc, and it is able to solubilize the oil-soluble monomer. The monomer-solubilized aggregate is considered to be the reaction locus. This is very similar to the polymerization of vinyl monomers with water-soluble polymers as a micelle-forming polysoap, in which the presence of a hydrophobic area in the polymer agglomerate in water, corresponding to the inside of a micelle, is indispensable as the reaction locus [7, 8, 12]. Further, the spontaneous polymerization of surface-active monomers takes place only above the cmc, i.e., the formation of a monomer micelle is the key factor for initiation [9, 13, 14].

Thus, these three kinds of the spontaneous polymerization systems, surfactant-induced and polysoap-induced polymerizations of vinyl monomers, and the polymerization of surface-active monomers, are classified in the same category. The initiating radical species is assumed to be produced by the reaction between monomer molecules, at least for the methacrylic acid derivatives, through the mechanism proposed for the thermal polymerization of MMA in bulk by Lingnau and Meyerhoff [15]. The role of the micelle as the reaction locus facilitates the reaction by organizing the solubilized monomer molecules.

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Received June 18, 1993