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Radical polymerization of 2-methacryloyloxyethyl phosphorylcholine in water: kinetics and salt effects

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Abstract

The homogeneous polymerization of 2-methacryloyloxyethyl phosphorylcholine (MPC) as betaine monomer with potassium peroxydisulfate (KPS) was kinetically investigated in water by means of FT-near IR spectroscopy. The overall activation energy of the polymerization was estimated to be 12.8 kcal/mol. The initial polymerization rate (R_p) at 40 °C was given by $R_p = k[\text{KPS}]^{0.98}[\text{MPC}]^{1.9}$. The presence of alkaline metal halides accelerated the polymerization. The larger the radius of metal cation or halide ion was, the larger the accelerating effect was. The accelerating salt effect was explained by interactions of salt ions with ionic moieties of the propagating polymer radical and/or the MPC monomer. A kinetic study was also performed on the polymerization of MPC with KPS in water in the presence of NaCl of 2.5 mol/l. R_p at 40 °C was expressed by $R_p = k[\text{KPS}]^{0.6}[\text{MPC}]^{1.6}$. A very low value of 4.7 kcal/mol was obtained as the overall activation energy of the polymerization.

Keywords: Radical polymerization; Kinetic study; Phosphorylcholine; Betaine monomer; Salt effect

Betaine monomers having covalently bound positive and negative charges and their polymers show water solubility and dispersibility, intermolecular association through charges, and high affinity for metal salts. Although many types of betaine monomers including phosphorylcholine [1–5], sulfobetaine [6–12], and carbobetaine [13–15] monomers have been synthesized and polymerized and their polymers and copolymers have been characterized, there have been only a few kinetic studies of radical polymerization behaviors of such betaine monomers [2,12,13]. In previous papers [2,12], we kinetically investigated the polymerizations of 3-(*N*-2-methacryloyloxyethyl-*N*,*N*-dimethyl)ammonatopropanesulfonate (MDAPS) as a sulfobetaine with potassium peroxydisulfate (KPS) in water and of 2-methacryloyloxyethyl phosphorylcholine (MPC) with dimethyl 2,2′-azobisisobutyrate (MAIB) in ethanol, where the polymerization rates (R_p) were expressed by $R_p = k[\text{KPS}]^{0.65}[\text{MDAPS}]^{1.0}$ at 40 °C and $R_p = k[\text{MAIB}]^{0.54}[\text{MPC}]^{1.8}$ at 50 °C, respectively.

In this communication, we carried out a kinetic study of the polymerization of MPC with KPS in water by

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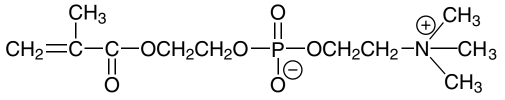
means of FT-near infrared spectroscopy (FT-NIR). The salt effect on the polymerization was also examined.



$CH_2{=}C(CH_3){-}C({=}O){-}OCH_2CH_2O{-}P({=}O)(O^{\ominus}){-}OCH_2CH_2{-}N^{\oplus}(CH_3)_3$

(MPC)

MPC was supplied by Nippon Oil & Fats Company, Ltd. KPS was recrystallized from water. Ion-free water was used.

The polymerization of MPC with KPS in water was conducted in a degassed and sealed Pyrex tube (5 mm diameter) in a custom-made aluminum furnace, in which FT-NIR measurements were performed [12,16]. The polymerization proceeded homogeneously. The conversion of MPC was monitored in situ by the absorption at 6150 cm^{-1} as the overtone absorption due to the =C–H stretching vibration.

Fig. 1 shows time-conversion curves obtained at different temperatures, where the concentrations of KPS and MPC were 5.00×10^{-4} and 1.00 mol/l, respectively. The initial polymerization rate (R_p) at each temperature was determined from the corresponding time-conversion curve in Fig. 1. From the Arrhenius plot of R_p, the overall activation energy of the present polymerization was estimated to be 12.8 kcal/mol. This value is fairly lower than 16.0 kcal/mol observed for the polymerization of MDAPS with KPS in water [12].

In order to clarify the relationship between R_p and the initiator concentration, the polymerization was performed at 40 °C on varying the KPS concentration at a fixed MPC concentration of 1.00 mol/l. R_p increased in proportion to the 0.98 power of the initiator concentration. The nearly first order dependence of R_p on the initiator concentration suggests that a unimolecular termination occurs in the present homogeneous polymerization. The propagating center of the polymer radicals may be occluded in zwitterionic polymer associations through charges so that the MPC monomer is no longer accessible to the growing active center. When the MPC concentration was changed keeping the KPS concentration constant at 5.00×10^{-4} mol/l, R_p at 40 °C was proportional to the 1.9th order of the monomer concentration. Such high order of the monomer concentration comes probably from association of the monomers in water which is enhanced with increasing MPC concentration [17].

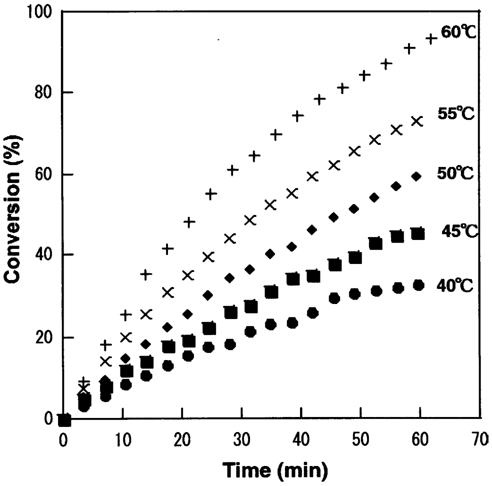


Fig. 1. Time-conversion curves in the polymerization of MPC with KPS at different temperatures in water: [MPC] = 1.00 mol/l, [KPS] = 5.00×10^{-4} mol/l.

Thus we obtained the following rate equation for the polymerization of MPC with KPS at 40 °C in water:

$$R_p = k[\mathrm{KPS}]^{0.98}[\mathrm{MPC}]^{1.9}$$

This rate equation is considerably different from that ($R_p = k[\mathrm{KPS}]^{0.65}[\mathrm{MDAPS}]^{1.0}$) for the polymerization of MDAPS as a sulfobetaine monomer with KPS in water at 40 °C [12].

The salt effect on the polymerization of MPC with KPS was examined because MPC as betaine monomer and its polymer were expected to have strong interaction with the metal salts through charges. Alkaline metal salts were reported to exert accelerating effects on the radical polymerizations of anionic and cationic monomers in water [10,18,19], where the acceleration was explained by the fact that the ionic monomers and polymers could be neutralized by the salt, resulting in a decrease in the electrostatic repulsive forces. However, there were few papers on the salt effect on the radical polymerization of betaine (zwitterionic) monomers in water except for our previous paper [12].

The polymerization of MPC with KPS was performed in water at 40 °C in the presence of various alkaline metal salts, where the concentrations of MPC and KPS were 1.00 and 5.00×10^{-4} mol/l, respectively. The salts used were LiCl, NaCl, KCl, CsCl, KF, CsF, and Na_2SO_4.

Table 1 summarizes the R_p values estimated from the time-conversion curves observed in the polymerizations in the presence of the salts. Thus the presence of any salts used here was found to cause an increase in R_p. The addition of CsCl of 2.5 mol/l increased R_p by a factor of about 8. As shown in Fig. 2(a), R_p showed an exponential increase with increasing salt concentration for NaCl, KCl, and CsCl, while a linear increase in R_p was observed for LiCl, suggesting that LiCl interacts with MPC and its propagating polymer radical in a different manner from the other metal chlorides. The order

Table 1
Initial polymerization rate (R_p) in the polymerization of MPC with KPS at 40 °C in water in the presence of salts[a]

[Salt] (mol/l)	$R_p \times 10^4$ (mol/l s)						
	LiCl	NaCl	KCl	CsCl	KF	CsF	Na_2SO_4
0.00	1.25	1.25	1.25	1.25	1.25	1.25	1.25
0.50	2.20	1.37	1.77	1.90	1.29	1.29	1.45
1.00	2.70	1.76	2.30	2.59	1.31	1.47	2.97
1.50	3.57	2.45	3.63	3.97		1.72	
2.00	4.43	3.38	4.37	6.80	1.45	2.21	
2.50		5.00	6.47	10.10	1.54	2.61	
3.00		6.55			1.65		

[a] [MPC] = 1.00 mol/l, [KPS] = 5.00×10^{-4} mol/l.

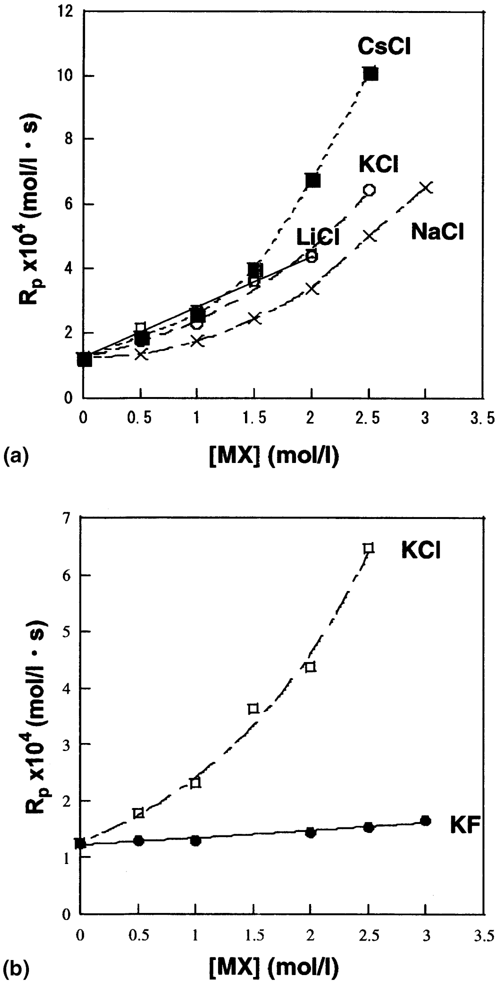


Fig. 2. Initial polymerization rate (R_p) in the polymerization of MPC with KPS at 40 °C in water in the presence of metal salts (MX): [MPC] = 1.00 mol/l, [KPS] = 5.00×10^{-4} mol/l.

of accelerating effect was CsCl > KCl > NaCl when chloride salts were employed. Thus, the larger the radius of metal cation was, the larger the accelerating effect was.

Fig. 2(b) compares the results for KCl and KF. The R_p value was much higher in the presence of KCl than in the presence of KF. A similar tendency was observed for the polymerizations in the presence of CsCl and CsF (Table 1). Thus, also for the anion, the larger ion caused the more acceleration of the polymerization of MPC as betaine monomer. The same acceleration order with respect to the kind of ion was previously observed for the polymerization of MDAPS as sulfobetaine monomer with KPS in water although the accelerating salt effect was much lower for the polymerization of MDAPS compared to that of MPC [12].

"Salting in" effects were observed for some zwitterionic polymers from betaine monomers [10,20,21]. The intra- and inter-ionic associations between the cationic and anionic groups cause compact conformation and/or insolubility of the zwitterionic polymers in aqueous solution. The addition of salt hinders such associations by interactions of salt ions with ionic moieties of the polymers, leading to expanded conformation of the betaine polymer chains which makes them more soluble [7,10,20–22]. As a result, the solution viscosity and the hydrodynamic diameter of the zwitterionic polymer increase with increasing salt concentration. Such effects by the salt are greater for the larger and less hydrated ion because the larger ion can more strongly interact with the ionic part of betaine polymers.

The exposed radical center of the expanded propagating polymer chain is expected to react more rapidly with another monomer compared with the covered growing end of the contracted polymer chain with a compact conformation [23–25]. Thus, the addition of salt results in expanded conformations of the MPC propagating polymer radical chains, leading to enhancement of propagation rate and then acceleration of the polymerization. The loosening of the compact structure of the propagating polymer chains by the salt may retard occlusion of the active sites in the polymer chains, resulting in a decrease in termination rate and then in an increase in R_p. The observed accelerating order of alkaline metal salts is the same as those reported for viscometric effects and hydrodynamic radius enlargement by metal salts in the aqueous zwitterionic polymer solutions [20].

"Salting out" effects may be more important for LiCl as a salt of smaller and more hydrated lithium ion, causing enhancement of the MPC monomer associations which can also accelerate the polymerization. This is probably a reason for the different salt effect above observed for LiCl.

$R_p = k[\mathrm{KPS}]^{0.6}[\mathrm{MPC}]^{1.6}$ was obtained as the rate equation for the polymerization of MPC with KPS at 30 °C in water in the presence of NaCl of 2.5 mol/l. Thus, the presence of NaCl caused bimolecular termination probably by loosening of the compact structure of the propagating polymer chains. The overall activation energy of the polymerization was 4.7 kcal/mol being much lower compared with that (12.8 kcal/mol) in the absence of the salt.

Na_2SO_4 of 1.00 mol/l accelerated the polymerization more than NaCl of 1.00 mol/l (Table 1). This is because the former is a salt of divalent sulfonate ion carrying two Na^+ ions [26].

The interaction of MPC monomer with NaCl was examined at 40 °C in water by means of ^{13}C-NMR (100 MHz for ^{13}C) spectroscopy. Relative intensities of peaks due to the carbonyl carbon (171.6 ppm) of the ester group and the α-carbon (138.2 ppm) of the vinyl group of MPC were observed to decrease with increasing NaCl concentration (0, 1.00, and 2.00 mol/l) although their chemical shifts were almost independent of the salt concentration, suggesting that the phosphonate ion moiety of MPC binds Na^+ ion.

The interaction of MPC monomer with the salts may suppress the above-mentioned association of the monomers, leading rather to a decease in R_p. The decreased order (from 1.9th to 1.6th) with respect to the monomer concentration observed in the presence of NaCl comes probably from the interaction of MPC monomer with the salt.

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