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DETERMINATION OF THE ABSOLUTE RATE CONSTANTS IN FREE-RADICAL POLYMERIZATION OF ZWITTERIONIC SULFOBETAINE MONOMERS

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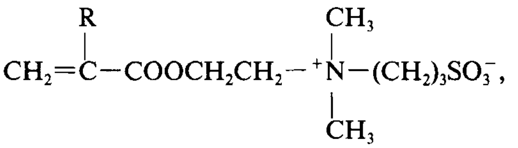
ABSTRACT

The absolute rate constants in the free-radical polymerization of zwitterionic sulfobetaine monomers [3-dimethyl(methacryloyloxyethyl) ammonium propane sulfonate (DMAPS) and 3-dimethyl(acryloyloxyethyl) ammonium propane sulfonate (DAAPS)] were investigated in formamide/dioxane cosolvent at 30°C. The rate of initiation (R_i) and k_p^2/k_t were determined using DPPH as the inhibitor. The propagation rate constant (k_p) and termination rate constant (k_t) were determined by intermittent illumination methods. The k_p values of DMAPS in the presence and absence of NaCl were determined to be 2760 and 1470 ($L \cdot mol^{-1} \cdot s^{-1}$), respectively. The enhanced polymerization rate of DMAPS in the presence of NaCl can be ascribed to the large k_p value, which may be due to the less electrostatic repulsive force and/or to the greater solubility in NaCl of the growing chain. The k_p of DMAPS was 50% lower than that of DAAPS, both in the presence and absence of NaCl, indicating that steric hindrance in the α-carbon position of DMAPS is important during polymerization. The termination rate constant is not significantly affected by the presence of NaCl.

INTRODUCTION

Sulfobetaine monomers, such as acryloyl or methacryloyl ammonium propane sulfonate,



$$CH_2{=}C(R){-}COOCH_2CH_2{-}{}^{+}N(CH_3)_2{-}(CH_2)_3SO_3^-, \quad R = H \text{ or } CH_3$$

are the functional monomers used as minor compounds for copolymers in various products, such as textiles, charge dispersing agents, medicals, membranes, adhesives, and latexes [1-7]. Recently, the solution properties of such zwitterionic polymers derived from sulfobetaine monomers were studied in our laboratory [8-14]. We reported that the minimum salt concentrations and intrinsic viscosities of these polyampholytes are related to the type and concentration of salt [9, 13].

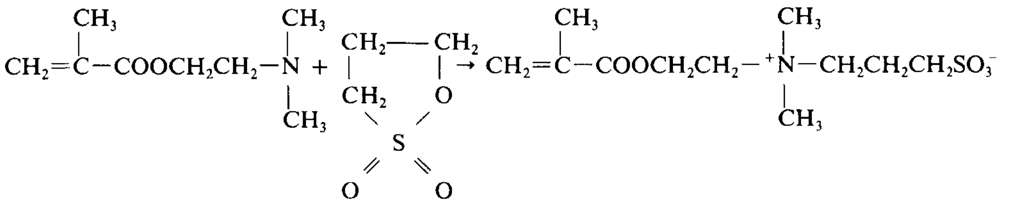
The kinetic features of the radical polymerization for zwitterionic monomers of the betaine type were rarely studied [15-19]. Earlier, Topchiev et al. [20] measured individual rate constants dilatometrically in the polymerization of carboxybetaine in the absence and presence of sodium chloride in aqueous solution. However, we found that polymerization is very difficult to carry out dilatometrically in aqueous solutions in which water-insoluble initiators such as 2,2′-azobisisobutyronitrile (AIBN) or 2,2′-azobiscyclohexane-carbonitrile (ACN) were used. Moreover, when the polymerization of zwitterionic sulfobetaine monomers is carried out in aqueous solution or in water-dioxane, the system becomes heterogeneous even at a low conversion because of limited solubility of the polymers. On the other hand, Gromov et al. [21] studied the kinetic data for water-soluble monomers, such as acrylamide and methacrylamide, by using formamide as a reaction medium.

It was found that the polymerization for zwitterionic sulfobetaines is carried out homogeneously in the formamide-dioxane cosolvent system at an early stage. The aim of the present paper was to investigate the absolute rate constant of two sulfobetaines in the absence and presence of NaCl in a formamide/dioxane cosolvent system. The propagation rate constant (k_p) and termination rate constant (k_t) were determined by the intermittent illumination method as reported previously [22-27].

EXPERIMENTAL

Preparation of Monomers and Other Reagents

In a 0.25-L volume flask equipped with a stirrer, a cooler, and a thermometer, *N*,*N*-dimethylaminoethyl methacrylate (8.75 g) and acetone (20 g) were charged, and the contents were stirred at 30°C. A mixture of 1,3-propane sultone (6.8 g) and acetone (3 g) was added dropwise for 30 min. Upon completing the addition, the mixture was stirred at the same temperature for 4 h and then allowed to stand at room temperature for a week. The precipitated white crystals were collected by filtration, washed with dry acetone several times, and dried under reduced pressure to obtain 3-dimethyl(methacryloyloxyethyl) ammonium propane sulfonate (DMAPS), mp 280°C [8]. The reaction takes place according to Eq. (1):



(1)

The other monomer, 3-dimethyl(acryloyloxyethyl) ammonium propane sulfonate (DAAPS), was prepared from the corresponding acrylate, mp 145°C [10]. The monomer was characterized by elemental analysis techniques, IR, and NMR [8, 10].

The initiators, 2,2′-azobisisobutyronitrile (AIBN) and 2,2′-azobiscyclohexane-carbonitrile (ACN), were purified as described in previous papers [22–24]. 1,1-Diphenyl-2-picrylhydrazyl (DPPH) was used as an inhibitor. It was recrystallized as described previously [22–24].

Polymerization Procedure

The rate of polymerization at 30 ± 0.005°C was measured in a vacuum-sealed dilatometer. The rates of initiation (R_i) were determined by the inhibition method with DPPH in the presence and absence of NaCl. Photosensitized polymerization was carried out with ACN as an initiator to eliminate as much thermal decomposition as possible. The light source was an Ushio 250W high-pressure mercury lamp (Toshiba UV-D36C, UV-31, and IRA-25S) filtered at 3650 Å. Radical lifetime was determined by the rotating sector method as previously described [22–27].

Determination of the k_p^2/k_t Value

Rates of polymerization of DMAPS and DAAPS in the presence and absence of sodium chloride are presented in Table 1. It is observed that the rate of polymerization is enhanced in the presence of a salt for both DMAPS and DAAPS. This phenomenon may be due to there being less electrostatic repulsive force in the course of polymerization. In addition, the rate of polymerization of DMAPS, which has a methyl group in the α-carbon position, is smaller than that of DAAPS, indicating that steric hindrance of the methyl group in DMAPS is important.

The dependence of the polymerization rate (R_p) on the initiator and monomer concentration at 30°C was investigated in the presence and absence of NaCl. R_p was found to be proportional to the square root of the initiator concentration and to the monomer concentration, which is in good agreement with the general orders of a radical polymerization.

In order to clarify the cause of the enhanced polymerization rate in the presence of NaCl, elementary rate constants were determined by inhibition and by the intermittent illumination method. The former method is used to derive the k_p^2/k_t values and the latter to obtain the k_p/k_t values. DPPH was used as an inhibitor to determine the rate of initiation (R_i). The inhibition effect of DPPH on the polymerization of DMAPS is shown in Fig. 1.

The correlation between the duration of inhibition and the concentration of the inhibitor in formamide/1,4-dioxane cosolvent is shown in Fig. 2.

TABLE 1. Rate of Polymerization (R_p) and Rate of Initiation (R_i) in the Polymerization of Zwitterionic Monomers Initiated by AIBN in the Presence and Absence of NaCl at 30°C

Monomer	NaCl mol·L^{-1}	$R_p \times 10^5$ mol·L^{-1}·s^{-1} [a,b,d]	$R_i \times 10^9$ mol·L^{-1}·s^{-1} [a,b,c,d]	k_p^2/k_t, L·mol^{-1}·s^{-1}
DMAPS[e]	0.00	0.95	2.08	4.34
DMAPS	0.10	1.92	2.19	16.83
DAAPS[f]	0.00	1.46	2.11	10.10
DAAPS	0.10	3.50	2.06	59.47

[a] [Monomer] = 0.1 mol·L^{-1}.

[b] [AIBN] = 5×10^{-2} mol·L^{-1}.

[c] Inhibitor: DPPH.

[d] Solvent: Formamide:1,4-dioxane = 3:1 (v/v).

[e] DMAPS: 3-Dimethyl(methacryloyloxyethyl) ammonium propane sulfonate.

[f] DAAPS: 3-Dimethyl(acryloyloxyethyl) ammonium propane sulfonate.

Similar behaviors were observed in the initiator polymerization in the presence of NaCl.

R_i can be calculated from the reciprocal of the slope in Fig. 2 according to Eq. (2). The rate of initiation is also shown in Table 1.

$$R_i = \frac{\text{initial concentration of inhibitor}}{\text{length of inhibition period}} \tag{2}$$

R_i values were hardly affected by the salt, indicating that the decomposition

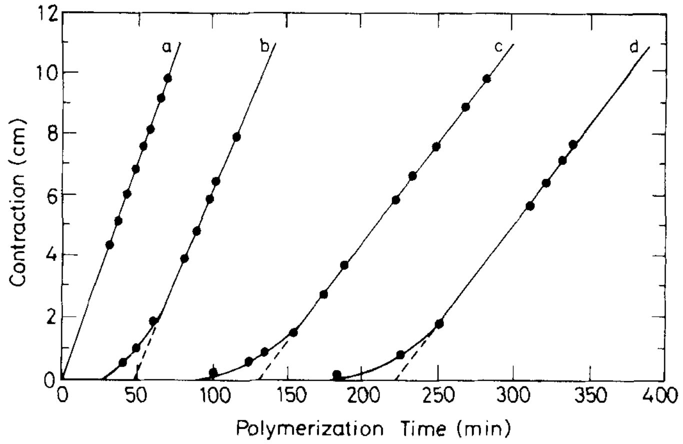


FIG. 1. The DPPH inhibition effect on the polymerization of 3-dimethyl(methacryloyloxyethyl) ammonium propane sulfonate initiated by AIBN at 30°C. [DMAPS] = 0.1 mol·L^{-1}, [AIBN] = 5×10^{-2} mol·L^{-1}, [DPPH] = (a) 0; (b) 0.5; (c) 1; (d) 2×10^{-5} mol·L^{-1}.

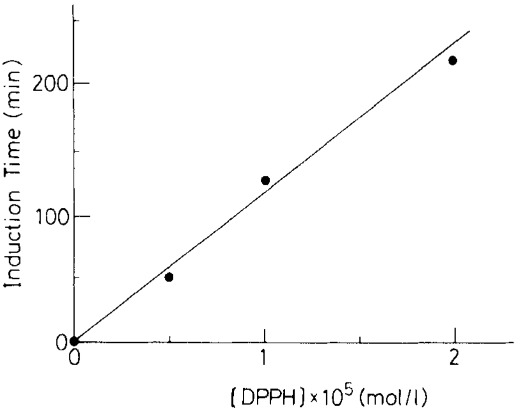


FIG. 2. Relationship between induction time and DPPH concentration for polymerization of 3-dimethyl(methacryloyloxyethyl) ammonium propane sulfonate initiated by AIBN at 30°C. [DMAPS] = 0.1 mol·L^{-1}, [AIBN] = 5 × 10^{-2} mol·L^{-1}.

rate of AIBN was not influenced by the presence of NaCl. The value of k_p^2/k_t can be derived by using Eq. (3) [26, 27].

$$\frac{k_p^2}{k_t} = \frac{R_p^2}{R_i[\mathrm{M}]^2} \tag{3}$$

It can be seen from Table 1 that the polymerization rate in the presence of NaCl is about 100% higher than that in the absence of NaCl, the observed variation in the polymerization rate arising from a variation of k_p^2/k_t.

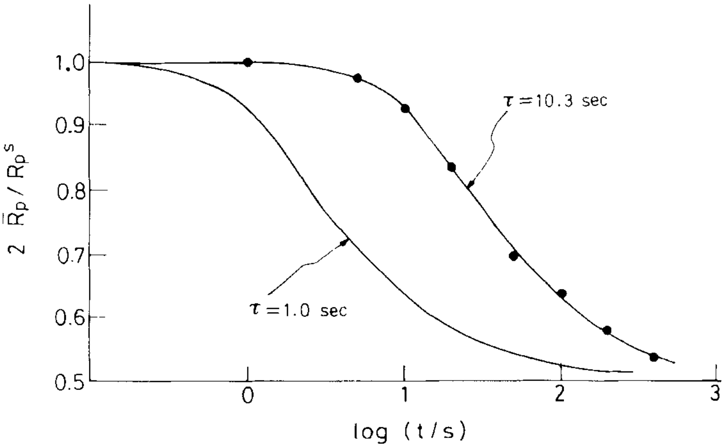


FIG. 3. Determination of the average lifetime of propagating radicals from DMAPS in formamide/dioxane cosolvent at 30°C; $\bar{R}_p$ = rate of overall polymerization at intermittent illumination time; R_p^S = rate at stationary state under continuous irradiation; t = intermittent illumination time; ratio of dark to light = 3; [DMAPS] = 0.1 mol·L^{-1}; [2,2′-azobiscyclohexanecarbonitrile] = 2 × 10^{-3} mol·L^{-1}.

TABLE 2. Rate Constants for the Polymerization of Zwitterionic Monomers at 30°C

Monomer	NaCl $\mathrm{mol \cdot L^{-1}}$	$R_p \times 10^5$ $\mathrm{mol \cdot L^{-1} \cdot s^{-1}}$[a]	τ,[a,b] s	$k_p/k_t \times 10^3$	k_p $\mathrm{L \cdot mol^{-1} \cdot s^{-1}}$	$k_t \times 10^{-5}$ $\mathrm{L \cdot mol^{-1} \cdot s^{-1}}$[a]
DMAPS[c]	0.0	2.86	10.3 ± 1.2 (6)	2.95	1470 ± 170	4.99 ± 0.58
DMAPS	0.1	5.81	10.5 ± 1.3 (7)	6.10	2760 ± 342	4.52 ± 0.56
DAAPS[d]	0.0	4.24	10.1 ± 1.0 (6)	4.31	2330 ± 230	5.40 ± 0.53
DAAPS	0.1	11.10	9.59 ± 1.1 (6)	10.64	5590 ± 641	5.25 ± 0.60

[a] [Monomer] = 0.1 $\mathrm{mol \cdot L^{-1}}$. [2,2-Azobiscyclohexane carbonitrile] = 2×10^{-3} $\mathrm{mol \cdot L^{-1}}$. Solvent: Formamide:1,4-dioxane = 3:1 (v/v).

[b] Number of runs.

[c] DMAPS: 3-Dimethyl(methacryloyloxyethyl) ammonium propane sulfonate.

[d] DAAPS: 3-Dimethyl(acryloyloxyethyl) ammonium propane sulfonate.

Determination of the k_p/k_t Value

In order to obtain the individual k_p and k_t values, the average lifetime (τ) of propagating radicals was determined by the rotating sector method. Figure 3 shows the variation of the polymerization rate (R_p) with illumination time (t) for the radical polymerization of DMAPS in the absence of NaCl. The k_p/k_t value can be derived by using Eq. (4) [26, 27].

$$\frac{k_p}{k_t} = \frac{R_p\tau}{[\mathrm{M}]} \tag{4}$$

The k_p value for DMAPS was determined to be 1470 $\mathrm{L \cdot mol^{-1} \cdot s^{-1}}$ in the absence of NaCl and 2760 $\mathrm{L \cdot mol^{-1} \cdot s^{-1}}$ in the presence of NaCl. The results are shown in Table 2. The rate of polymerization is enhanced when NaCl is added to the reaction system. The difference in the rate of polymerization in the absence and presence of NaCl can be mainly ascribed to the variation in k_p. The large k_p value in the presence of NaCl may be due to less electrostatic repulsive force in the course of polymerization, since both the zwitterionic monomer and polymer could be neutralized by NaCl aqueous solution [12, 20]. Other explanations for the observed enhanced k_p might be that the growing chain is more soluble in salt [9, 16–19] and/or a simple salt effect is operative, although the latter is small. The k_p of DMAPS was 50% lower than that of DAAPS, both in the presence and absence of NaCl, indicating that steric hindrance in the α-carbon position is important during polymerization. The termination rate constant is not significantly affected by the presence of NaCl. A similar result was also observed by Topchiev et al. [20] and Liaw et al. [26, 27].

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