

INFLUENCES OF WATER-SOLUBLE CATIONIC MONOMERS ON THE POLYMERIZATION RATE IN THE INVERSE EMULSION*

HOU Sijian (侯斯健) and HA Runhua (哈润华)

(Applied Chemistry Department, Tianjin University, Tianjin 300072)

ABSTRACT

This investigation deals with the free radical polymerization both of (2-methacryloyloxyethyl) trimethyl ammonium chloride (QACEMA) and of diallyldimethyl ammonium chloride (DADMAC) in inverse emulsion. The influences of some factors, such as the concentration of monomers, initiator and emulsifier are discussed. The polymerization rate equations of above two monomers can be written as follows:

$$R_p = k[M]^{1.21}[I]^{0.82}[E]^{0.57} \text{ (for QACEMA)}$$

$$R_p = k'[M]^{1.34}[I]^{0.90}[E]^{0.62} \text{ (for DADMAC)}$$

INTRODUCTION

There has been an increasing interest in water soluble cationic polymers during last a few decades. They are widely used in paper industry, waste water treatment, enhance oil recovery, cosmetics and other aspects^[1,2,8].

The properties of these cationic polymers have been described by some authors. Butler and Ingley reported the formation of water-soluble polymer from diallyl quaternary bromide in 1951^[3]. Only one report on the emulsion polymerization of DADMAC by Huang and Reichert^[4] and a few reports on solution and suspension polymerization of QACEMA and DADMAC^[5,6,7] have been made so far. But there are scarcely kinetics data available on inverse emulsion polymerization, especially with respect to the polymerization rate. This investigation was made emphatically on this aspect.

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EXPERIMENTAL

Reagents

Dimethylamino ethyl methacrylate (C.P.) was reacted with methane chloride, recrystallized, dried under the pressure of 8KPa and at 25°C for 48h, (2-methacryloyloxyethyl) trimethyl ammonium chloride was produced. Diallyldimethyl ammonium chloride, (A.R), 60% water solution. Sorbitan monooleate (SPAN80) and Nonyl-phenol polyoxyethylene ether (OP-4) as emulsifiers. $K_2S_2O_8$ and Na_2SO_3 , (A.R), as initiator. White oil, C_{12} - C_{16} saturated alkane, b.p> 240°C.

Polymerization and kinetics determination

The white oil containing emulsifiers and monomer solution are purged with purified nitrogen gas to remove the residual oxygen for 30 minutes, respectively, then mixed in a reactor for 30 minutes for being emulsified completely.

The polymerization was initiated by $K_2S_2O_8$ and Na_2SO_3 redox system at 30°C in a dilatometer and the polymerization rate (R_p) was determined dilatometrically.

RESULT AND DISCUSSIONS

Emulsion polymerization rate of QACEMA

Under the following conditions:

Monomer concentration: 20—40%(wt) (based on water)

Initiator concentration: 0.03—0.15%(wt) (based on monomer)

Emulsifier concentration: 4—12%(wt) (based on oil)

Water/Oil ratio: 1/1.2 (Vol.)

Temperature: $30 \pm 0.1^\circ\text{C}$

the inverse emulsion polymerization was carried out. During the polymerization, the height drop of emulsion in the capillary was determined consecutively, the data were treated differentially and the results are shown in Tables 1–3.

The data in Tables 1—3 were treated by least square method, the relationships of polymerization rate and concentration of reagents are obtained as follows:

$$R_p \propto [M]^{1.21} \text{ (correlation coefficient is 0.998)}$$

$$R_p \propto [I]^{0.82} \text{ (correlation coefficient is 0.994)}$$

$$R_p \propto [E]^{0.57} \text{ (correlation coefficient is 0.982)}$$

so the polymerization rate equation of QACEMA can be written as:

$$R_p = k[M]^{1.21}[I]^{0.82}[E]^{0.57}$$

Table 1 The influence of monomer concentration on the R_p

No.	[M] (wt%)	R_p	$-\ln[M]$	$-\ln R_p$
1	40	0.157	0.916	1.849
2	35	0.137	1.050	1.989
3	30	0.116	1.204	2.154
4	25	0.091	1.386	2.394
5	20	0.068	1.609	2.687

* Conditions: $[I] = 0.12\%$, $[E] = 12\%$, $T = 30 \pm 0.1^\circ\text{C}$ **Table 2** The influence of initiator concentration on the R_p

No.	$[I](\text{wt}\%)$	R_p	$-\ln[I]$	$-\ln R_p$
6	0.15	0.173	6.502	1.755
2	0.12	0.137	6.725	1.989
7	0.09	0.124	7.013	2.085
8	0.06	0.084	7.419	2.480
9	0.03	0.045	8.112	3.097

* Conditions: $[M] = 35\%$, $[E] = 12\%$, $T = 30 \pm 0.1^\circ\text{C}$ **Table 3** The influence of emulsifier concentration on the R_p

No.	$[E](\text{wt}\%)$	R_p	$-\ln[E]$	$-\ln R_p$
2	12	0.137	2.120	1.989
10	10	0.117	2.303	2.148
11	8	0.096	2.526	2.345
12	6	0.089	2.813	2.416
13	4	0.071	3.219	2.642

* Conditions: $[M] = 35\%$, $[I] = 0.12\%$, $T = 30 \pm 0.1^\circ\text{C}$ *Emulsion polymerization rate of DADMAC*

Under the same conditions as those of QACEMA, the inverse emulsion polymerization was carried out. The same methods were adopted and the results are shown in Tables 4—6.

The data in Tables 4—6 were treated by least square method, the relationships of polymerization rate and concentration of reagents are obtained as follows:

$$R_p \propto [M]^{1.34} \text{ (correlation coefficient is 0.993)}$$

$$R_p \propto [I]^{0.90} \text{ (correlation coefficient is 0.993)}$$

$$R_p \propto [E]^{0.62} \text{ (correlation coefficient is 0.991)}$$

the polymerization rate equation of DADMAC can be expressed as:

$$R_p = k'[M]^{1.34}[I]^{0.90}[E]^{0.62}$$

The homopolymerization of QACEMA and DADMAC in emulsion exhibits similar kinetic characteristics. It means that the polymerization process has not been affected by the cationic environment.

Table 4 The influence of monomer concentration on the R_p

No.	[M](wt%)	R_p	$-\ln[M]$	$-\ln R_p$
1	40	0.131	0.916	2.033
2	35	0.112	1.050	2.189
3	30	0.092	1.204	2.387
4	25	0.076	1.386	2.572
5	20	0.050	1.609	2.988

* Conditions: $[I] = 0.12\%$, $[E] = 12\%$, $T = 30 \pm 0.1^\circ\text{C}$

Table 5 The influence of initiator concentration on the R_p

No.	[I](wt%)	R_p	$-\ln[I]$	$-\ln R_p$
6	0.15	0.166	6.502	1.872
1	0.12	0.131	6.725	2.033
7	0.09	0.119	7.013	2.125
8	0.06	0.075	7.419	2.585
9	0.03	0.038	8.112	3.260

* Conditions: $[M] = 40\%$, $[E] = 12\%$, $t = 30 \pm 0.1^\circ\text{C}$

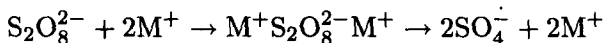
Table 6 The influence of emulsifier concentration on the R_p

No.	[E](wt%)	R_p	$-\ln[E]$	$-\ln R_p$
1	12	0.131	2.120	2.033
10	10	0.119	2.303	2.125
11	8	0.095	2.526	2.354
12	6	0.083	2.813	2.487
13	4	0.067	3.219	2.702

* Conditions: $[M] = 40\%$, $[I] = 0.12\%$, $T = 30 \pm 0.1^\circ\text{C}$

The scales of R_p to monomer concentration are both larger than unity. The

reason may be that the monomer participates in the initiation process, such as DADMAC reacts with the potassium persulfate^[2] through the following reaction:



so the sensibility of R_p to the monomer concentration increases.

The relationships of R_p to initiator concentration are much higher than the theoretical value of radical polymerization. Usually this phenomenon was explained according to the monoradical termination process. Although the viscosity influences (gel effect) on R_p during the initial period of polymerization is not notable, the radical at the end of macromolecule can hardly be terminated through the radical combination due to the steric effect.

The exponents with respect to the emulsifier concentration for both cationic monomers are almost the same. This result also shows that the R_p has been affected by the type and concentration of emulsifier system, but not influenced by the monomer structure.

Keywords:

(2-methacryloyloxyethyl) trimethyl ammonium chloride; Diallyldimethyl ammonium chloride; Polymerization rate; Inverse emulsion

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