Alternating copolymerization of 2-methyl-2-oxazoline with α-chloro- and α-bromoacrylic acids:

3. Synthesis, characterization and kinetics

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New 1:1 alternating copolymers of 2-methyl-2-oxazoline with (i) α-chloroacrylic acid and (ii) α-bromoacrylic acid were synthesized and characterized by i.r., n.m.r. and the products of alkaline hydrolysis. The copolymerization occurred at a temperature of 60°C without any added catalyst or initiator. The copolymerization kinetics were studied and the order with respect to each monomer was found to be unity. A scheme for the copolymerization involving a zwitterion intermediate is proposed.

Keywords Alternating copolymers; 2-methyl-2-oxazoline; zwitterion; copolymerization kinetics

INTRODUCTION

In an earlier paper we reported the synthesis, characterization and kinetics of the 1:1 alternating copolymerization of 2-methyl-2-oxazoline (MeOXZ) with methacrylic acid (MAA)[1]. The alternating copolymerization of 2-oxazoline and substituted oxazolines with β-propiolactone[2], acrylic acid[3,4] and acrylamide[5] are also reported in the literature. Here we report on the synthesis, characterization and kinetics of the copolymerization of 2-methyl-2-oxazoline with α-chloro- and α-bromoacrylic acids (ClAA and BrAA).

EXPERIMENTAL

MeOXZ was prepared by the method of Wenker[6] and dried by a final distillation from sodium[7]. The radical inhibitor, hydroquinone monomethyl ether, was purchased from Koch-Light Co., (L.R.) and was used without further purification. ClAA and BrAA were prepared using the procedure already reported in the literature[8].

Solvents

DMF was purified by distillation twice under nitrogen using KOH as the dehydrating agent. Acetonitrile and nitrobenzene were distilled over P_2O_5 under nitrogen. The other solvents were distilled before use.

Copolymerization procedure

A typical solution polymerization was carried out as follows. Equimolar quantities of MeOXZ and XAA (i.e. ClAA or BrAA) (15 mmol each) and ~0.1 g of hydroquinone monomethyl ether (radical inhibitor) were added at room temperature to acetonitrile (5.0 ml) in a polymerization tube. After passing nitrogen in for 30 min, the tube was sealed with rubber gaskets and kept at 60°C for 20 h. The reaction mixture was poured into diethyl ether (100 ml) to precipitate the copolymer. Unreacted MeOXZ and XAA were completely removed from the copolymer by repeated washing with ether. The copolymer was dried in vacuum and analysed by n.m.r., i.r. as well as by alkaline hydrolysis.

In a typical kinetic run, polymerization was conducted as above. From the weight of the copolymer, the rate of copolymerization, R_p was calculated using the formula,

$$R_p = \frac{1000\,w}{Vt(M_1 + M_2)}$$

where w = weight of the copolymer in g, V = volume of the reaction mixture which was taken for precipitation (in ml), t = time in seconds and M_1 and M_2 = molecular weights of the monomers.

Alkaline hydrolysis

To 0.5 g of the copolymer NaOH (0.5 g) was added in 5 ml of deuterated water. The reaction mixture was kept at 100°C for 10 h. The reaction mixture was then subjected to n.m.r. analysis.

Molecular weight determination

The number average molecular weight ($\bar{M}_n$) of the copolymers were determined in dimethyl formamide at 90°C employing a Knauer vapour pressure osmometer.

Viscosity measurement

The intrinsic viscosities $[\eta]$ of the copolymers were determined using an Ubbelohde viscometer thermostatically controlled at 25.0 ± 0.1°C.

Spectral studies

The n.m.r. spectra of the copolymers as well as the hydrolysis products were recorded with a Perkin Elmer

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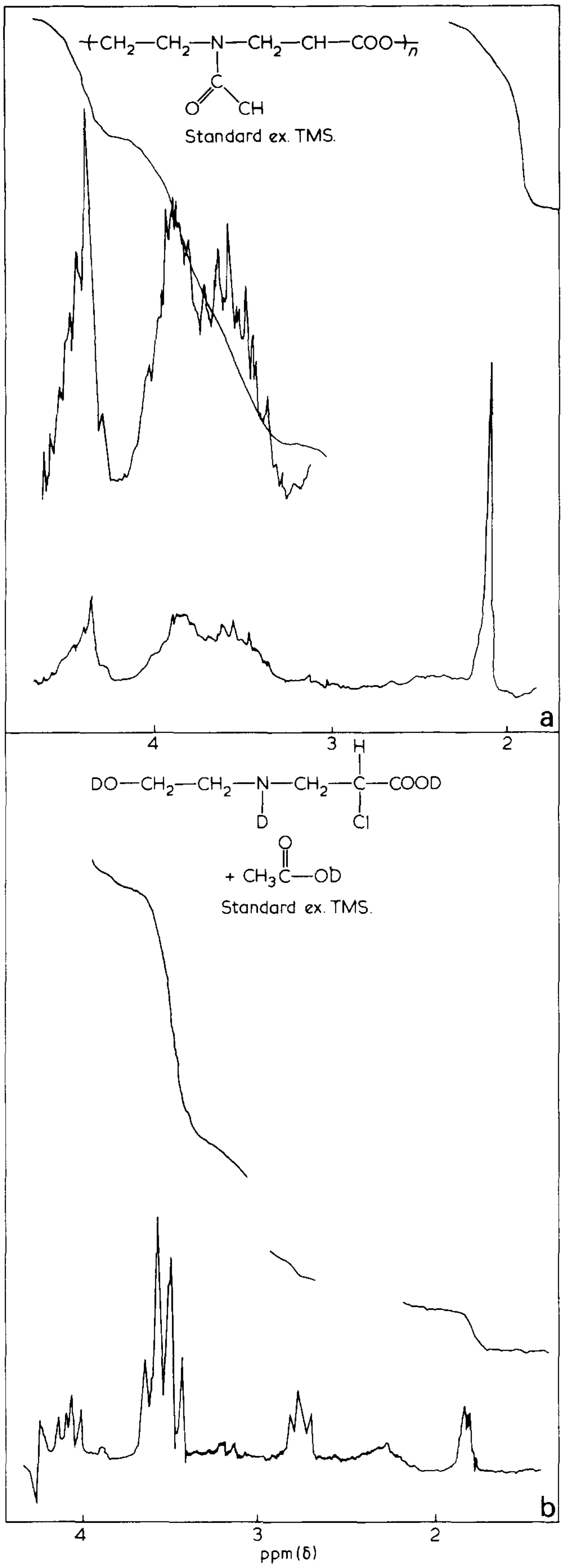


Figure 1 (a) ^1H n.m.r. spectrum of the copolymer, MeOXZ–ClAA: Solvent: D_2O, standard: external TMS; (b) ^1H n.m.r. spectrum of the hydrolysis product of the copolymer, MeOXZ–ClAA: solvent: D_2O, standard: external TMS

R-32 or a Varian T-60 spectrometer. The i.r. spectra of the copolymers were taken with a Perkin Elmer, model 337.

RESULTS AND DISCUSSION

The copolymers are a pale brown gummy material, differing from the homopolymers, poly(α-chloroacrylic acid) and poly(α-bromacrylic acid) (light yellow solids) and poly(*N*-acetyliminoethylene) (colourless resin).

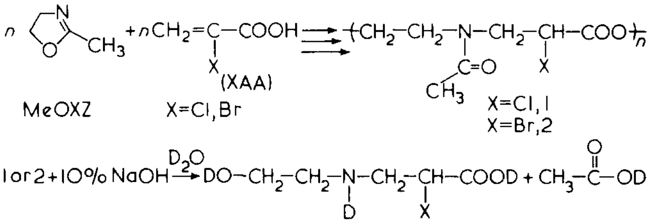
From solubility tests carried out on the copolymers with different solvents, it was observed that the copolymers were highly soluble in polar solvents like DMF, DMSO, acetonitrile, trifluoroacetic acid, methanol, ethanol, propanol, water, etc. and insoluble in non-polar solvents like CCl_4, benzene, etc.

The ^1H n.m.r. spectrum of the copolymer [oxyethylene (acetylimino)-2-chloro-3-oxotrimethylene], (1) from MeOXZ and ClAA in deuterated water shows a triplet at $\delta = 4.35$ (CO_2CH_2–), a multiplet centred at $\delta = 3.6$ (CH_2–N–CH_2– and –CHCOO–) and $\delta = 2.1$ (–$COCH_3$) (*Figure 1a*). The –CH peak is merged with –CH_2–N–CH_2– peak.

Similarly the ^1H n.m.r. spectrum of the copolymer, poly [oxyethelene(acetylimino)-2-bromo-3-oxotrimethylene], (2) obtained from MeOXZ and BrAA shows a triplet at $\delta = 4.4$–4.5, a multiplet at $\delta = 3.3$–4.0 and a singlet at $\delta = 2.1$. They are assigned to –CO_2CH_2, –CH_2–N–CH_2– and –CHBr and –$COCH_3$ (*Figure 2a*).

The i.r. spectra of the copolymers (1) and (2) show characteristic bands at 1720 cm^{-1} and 1650 cm^{-1}. They are assigned to the CO group of the ester and –N–CO–CH_3 (*Figure 3*). These copolymers therefore contain two different carbonyl groups, one from the substituted acrylic acids and the other from the ring opening of MeOXZ.

The alkaline hydrolyses of the copolymers were carried out to confirm the copolymer structure:



The ^1H n.m.r. spectrum of the hydrolysis products of copolymer (1) with 10% NaOH in D_2O showed that the products consisted of a 1:1 mixture of Na salts of *N*-(2[^2H]hydroxyethyl)-3-[^2H]amino-2-chloropropionic [^2H] acid and acetic [^2H] acid, i.e. n.m.r. peaks (*Figure 1b*) at $\delta = 4.1$ (–OCH_2), $\delta = 3.5$ (–CH_2–ND–CH_2), $\delta = 2.8$ (–CHCl) and $\delta = 1.9$ (–CO–CH_3).

Figure 2b shows the ^1H n.m.r. spectrum of the alkaline hydrolysis products of copolymer, (2). Peak assignment is as follows: Peak at $\delta = 4.4$ (methylene proton of –OCH_2), at $\delta = 3.5$ (methylene proton of –CH_2–N–CH_2–), at $\delta = 2.8$ (methine proton of –CH–COO–) and at $\delta = 2.0$ (–CO–CH_3).

From the above spectral data, the structure of copolymers (1) and (2) is confirmed.

Effect of reaction time, monomer composition and polarity of the medium on the copolymer yield

The rate of copolymerization, R_p, as a function of reaction time was studied and the results are collected in *Table 1*.

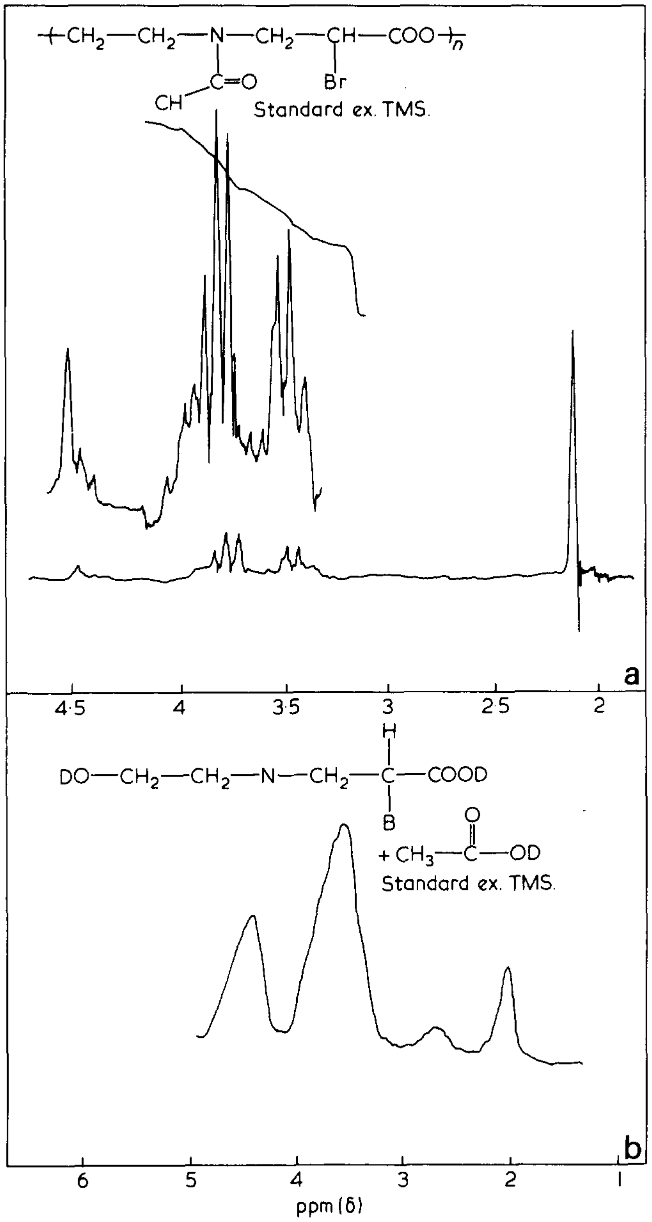


Figure 2 (a) ^1H n.m.r. spectrum of the copolymer, MeOXZ–BrAA: solvent: D_2O, standard: external TMS; (b) ^1H n.m.r. spectrum of the hydrolysis product of the copolymer, MeOXZ–BrAA: solvent: D_2O, standard: external TMS

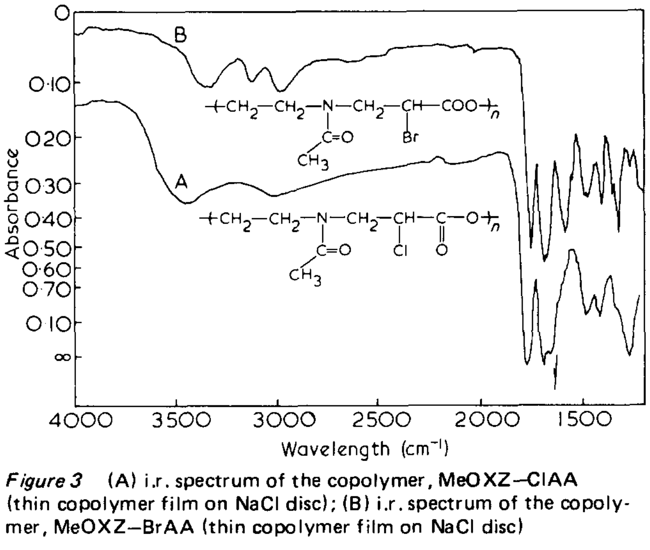


Figure 3 (A) i.r. spectrum of the copolymer, MeOXZ–ClAA (thin copolymer film on NaCl disc); (B) i.r. spectrum of the copolymer, MeOXZ–BrAA (thin copolymer film on NaCl disc)

It is clear from the experimental results that the R_p increases in the initial stages, reaches a maximum and decreases slowly afterwards. The initial increase in R_p may be due to the higher concentration of monomers available initially and the slow decrease of R_p indicates that the copolymerization is a growth step process.

The effect of mole fraction of MeOXZ on the copolymer yield with α-haloacrylic acids was also studied. The experimental data (*Table 2*) shows that the copolymer yield increases with increasing mole fraction of MeOXZ in the monomer mixture from 0.2 to 0.5 and, on further increase of MeOXZ, the copolymer yield decreases. The maximum copolymer yield was obtained by taking equimolar quantities (1:1) of the reactants.

By carrying out the copolymerization in various solvents, the effect of the polarity of the medium on the copolymer yield was assessed. The experimental results summarized in the *Table 3* emphasize the fact that increase in the polarity of the medium increases the copolymer yield.

Table 1 Rate of copolymerization with reaction time: MeOXZ = ClAA = 15 mmol. Acetonitrile = 5 ml. MeOXZ = BrAA = 15 mmol. Temperature = 60° + 0.1°C

MeOXZ–ClAA system		MeOXZ–BrAA system	
Reaction time (hours)	R_p (m l^{-1} s^{-1})	Reaction time (hours)	R_p (m l^{-1} s^{-1})
0.08	61.97×10^{-5}	1.0	12.28×10^{-5}
0.17	74.02×10^{-5}	1.5	14.26×10^{-5}
0.25	80.83×10^{-5}	2.0	15.46×10^{-5}
0.50	65.65×10^{-5}	2.5	16.84×10^{-5}
1.00	36.95×10^{-5}	3.0	17.71×10^{-5}
1.50	26.23×10^{-5}	6.0	9.49×10^{-5}
2.00	19.86×10^{-5}	9.0	6.69×10^{-5}
		12.0	5.14×10^{-5}
		15.0	4.11×10^{-5}

Table 2 Effect of mole fraction of MeOXZ on the copolymer yield: acetonitrile = 5 ml, temperature = 60 ± 0.1°C

Mole fraction of MeOXZ	Copolymer yield (%)	
	MeOXZ–ClAA system	MeOXZ–BrAA system
0.2	22.59	32.27
0.3	30.98	60.00
0.4	62.95	68.92
0.5	82.48	96.82
0.6	81.94	86.57
0.7	75.97	74.16
0.8	44.85	63.43

Table 3 Effect of solvent nature on the copolymer yield: [MeOXZ] = [ClAA] = 15 mmol. Solvent = 5 ml. [MeOXZ] = [BrAA] = 15 mmol. Temperature = 60 ± 0.1°C

Solvent	Polarity of the medium (Debye units)	Copolymer yield (%)	
		MeOXZ–ClAA system	MeOXZ–BrAA system
Toluene	0.36	40.59	12.33
1,2-Dichloroethane	1.60	50.87	71.40
DMF	3.82	61.78	84.57
Acetonitrile	3.92	66.93	85.98
Nitrobenzene	4.22	82.68	94.00

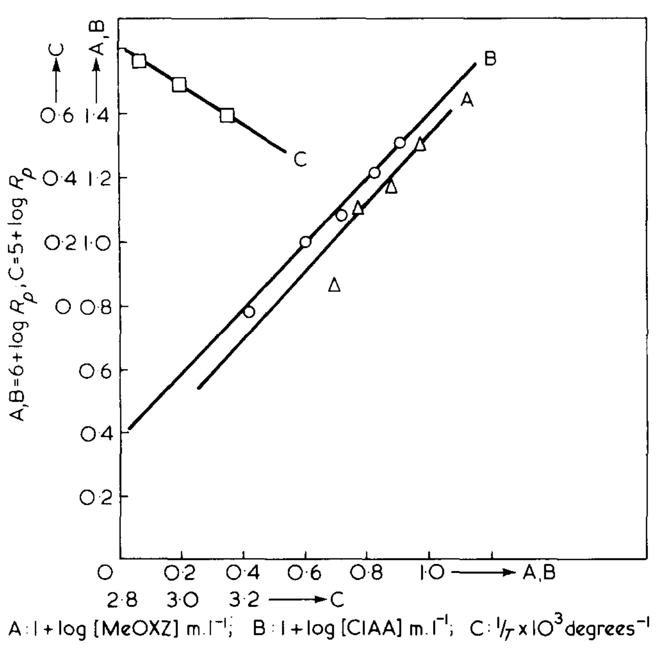


Figure 4 2-Methyl-2-oxazoline: α-chloroacrylic acid system: (i) order with respect to each monomer. Plots: A, B . . . 6 + log R_p vs. 1 + log [Monomer]. (A), 2-Methyl-2-oxazoline; (B), α-chloroacrylic acid. (ii) Energy of activation. Plot: (C), 5 + log R_p vs. 1/T . 10^3

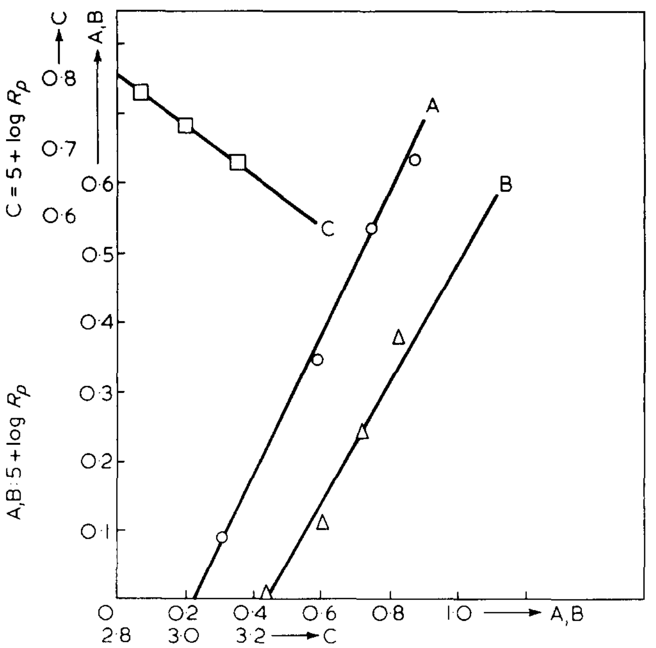
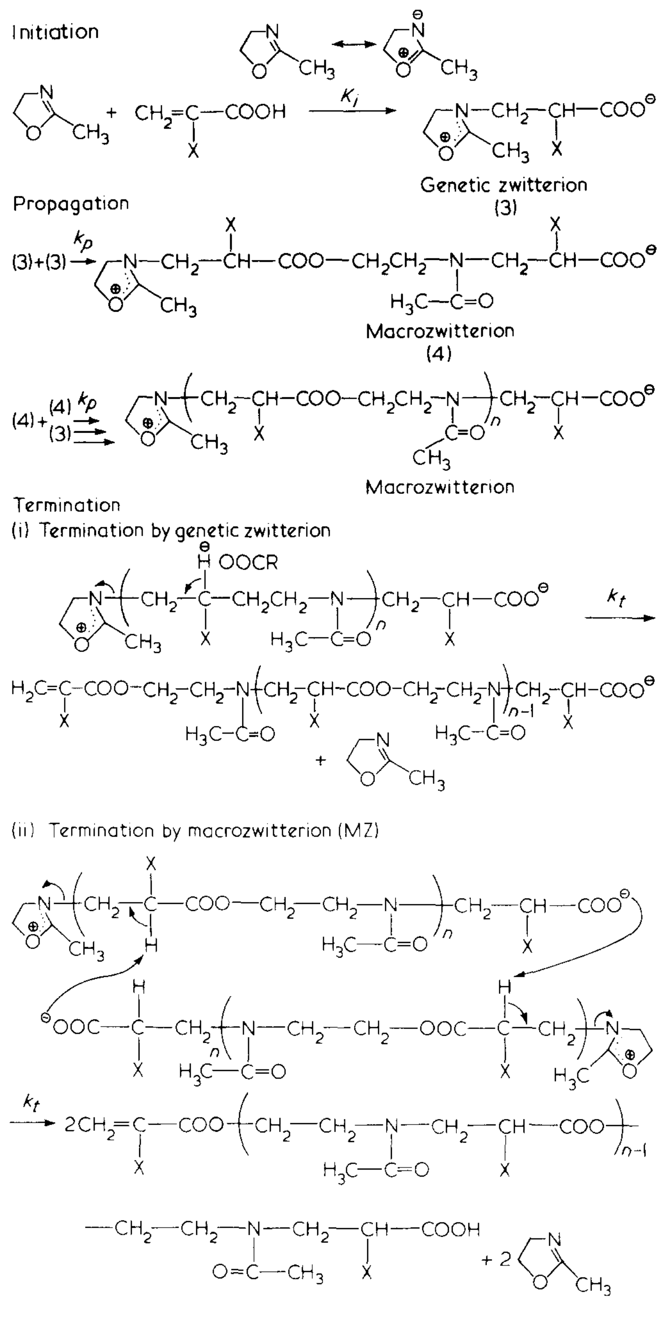


Figure 5 2-Methyl-2-oxazoline: α-bromoacrylic acid system: (i) order with respect to each monomer. Plots: A, B . . . 5 + log R_p vs. log [Monomer]. (A) 2-Methyl-2-oxazoline; (B) α-bromoacrylic acid. (ii) Energy of activation. Plot: (C) 5 + log R_p vs. 1/T . 10^3

Kinetics of copolymerization

All copolymerizations occurred at measurable rates in the temperature range 45°–75°C. The steady state is where the concentration of the formation of the macro-zwitterions is equal to the concentration of the termination of the macro-zwitterions. In the case of the MeOXZ–ClAA system, the steady state is attained in about 15 minutes whereas for the MeOXZ–BrAA system the steady state is reached in about 3 h. The order with respect to each of the monomers is determined by an isolation method. The plot of log R_p *versus* log [monomer] is linear with slope of unity suggesting a first order process with respect to each of the monomers (*Figures 4* and *5*).

Based on the experimental results and by analogy to the mechanistic studies of Saegusa *et al.*[3], a mechanism with formation and propagation *via* zwitterion (3), formed in a Michael type addition and hydrogen transfer from MeOXZ and XAA, is proposed. Reaction of two molecules of zwitterion (3), leads to the dimeric zwitterion (4) which in turn reacts with zwitterion (3) to give the trimeric zwitterion. Two trimeric zwitterions also lead to a hexameric zwitterion while a dimeric and trimeric zwitterion give a pentameric zwitterion, etc. The propagation consists of the nucleophilic attack of the carboxylate group at the electrophilic carbon adjacent to the oxygen atom in the 2-methyl-2-oxazolinium ring. This propagation reaction may occur at both the ends of the growing zwitterion. The chain may be terminated either by genetic or macrozwitterion.



Assuming steady state approximation for charge neutralization and k_i and k_t independent of chain length the following rate expression for R_p is derived.

$$R_p = \frac{k_i k_p}{k_t}[\mathrm{MeOXZ}][\mathrm{XAA}]$$

The copolymerization was carried out at three different temperatures and the R_p was calculated. From the slopes of the plots of log R_p *versus* $1/T$ (*Figures 4* and *5*), the overall energies of activation, E_{R_p} were computed as being 2.75 and 2.40 kcal mol^{-1} for MeOXZ–ClAA and MeOXZ–BrAA copolymerizations respectively E_{R_p} for free radical polymerization is about 20 kcal mol^{-1} [9] and for the ring opening polymerization initiated by $BF_3.H_2O$ is 18 kcal mol^{-1} [10]. So E_{R_p} for our systems are much lower than those of free radical polymerization as well as ring opening polymerization.

The intrinsic viscosities, $[\eta]$, and the number average molecular weights of the copolymers are given below:

$\bar{M}_{n\,\mathrm{MeOXZ-ClAA}} = 2585$ $\quad [\eta]_{\mathrm{MeOXZ-ClAA}} = 0.062$

$\bar{M}_{n\,\mathrm{MeOXZ-BrAA}} = 4043$ $\quad [\eta]_{\mathrm{MeOXZ-BrAA}} = 0.074$

The $\bar{M}_n$ and $[\eta]$ values for the MeOXZ–BrAA copolymer are higher than for the MeOXZ–ClAA copolymer. The rates of copolymerization, R_p, for the two systems, MeOXZ–ClAA and MeOXZ–BrAA ($[\mathrm{MeOXZ}] = [\mathrm{XAA}] = 15$ mmol, Reaction time = 9 h) under identical conditions are 4.92×10^{-5} and 6.69×10^{-5} m l^{-1} s^{-1} respectively. The high electronegativity of chlorine in ClAA, although it seems to impart greater initiating power than the bromine in BrAA, results in the rate of propagation of copolymerization, R_p (which is in fact the rate determining step in the copolymerization) for the MeOXZ–BrAA system to exceed MeOXZ–ClAA owing to its effect on the first two steps in the proposed mechanism (see earlier). The more electronegative chlorine reduces the negative charge on the carboxylate group of the zwitterion more effectively than the corresponding bromine, thus reducing the attacking power of this carboxylate group to the incoming zwitterion.

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