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I. C. Eromosele[a][b]
[a] University Chemical Laboratory, Trinity College, Dublin, Ireland [b] Department of Chemistry, Federal University of Technology, Yola, Nigeria

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EFFECT OF ACETIC ACID ON POLYMERIZATION OF BUTYLCYANOACRYLATE BY TETRABUTYLAMMONIUM ACETATE IN TETRAHYDROFURAN

I. C. EROMOSELE*

University Chemical Laboratory
Trinity College
Dublin, Ireland

ABSTRACT

Butylcyanoacrylate (BCA) was polymerized in tetrahydrofuran by tetrabutylammonium acetate (TBA^+Ac^-) in the presence of acetic acid. Large concentrations of acetic acid, several times the concentration of the initiator, TBA^+Ac^- did not stop the polymerization of BCA but showed an overall rate which decreased with increasing concentrations of the acid. The molecular weight of polymers, measured by gel permeation chromatography, decreased with increasing concentration of acetic acid. The corresponding molecular weight distribution is high but comparable to the value from acid-free polymerization. A retardation period, caused by methane sulfonic acid for BCA polymerized by TBA^+Ac^-, was extended in the presence of acetic acid. This is explained as arising from an enhanced equilibrium concentration of methane sulfonic acid from acetic acid protonated sulfonyl anions.

INTRODUCTION

Polymerizations of alkylcyanoacrylates by covalent bases have been studied extensively [1–5]. These polymerizations produce zwitterions which propagate anionically to yield high molecular weight polymers.

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*Present address: Department of Chemistry, Federal University of Technology, P.M.B. 2076, Yola, Nigeria.

Strong acids can inhibit the polymerization initiated by tertiary amines, permitting a quantitative study of the initiation processes [3, 5]. "Weak" acids, such as cyanoacetic and trichloroacetic acids, only retard the polymerization.

The zwitterions appear to be stable and insensitive to other anionic chain terminators such as water and carbon dioxide [1], which will readily terminate the growth of styryl anions, for example.

Polymerizations of butylcyanoacrylate (BCA) by tetrabutylammonium salts have been reported [6]. These polymerizations show well-defined retardation periods in the presence of toluene sulfonic acid (TSA) and methane sulfonic acid (MSA), permitting derivation of the rate constants for the initiation processes. Large concentrations of water have no apparent effect on rates of polymerization of BCA and the molecular weights of polymers [7].

This paper presents results of a study on the effect of acetic acid on MSA-retarded polymerization of BCA by tetrabutylammonium acetate in tetrahydrofuran (THF). The results of the effects of acetic acid on overall rates and molecular weights of MSA-free polymerizations are also presented and discussed.

EXPERIMENTAL

Polymerization was conducted in an adiabatic calorimeter whose design features were described by Pepper et al. [8].

Butylcyanoacrylate monomer was supplied by Loctite (Ireland), Ltd., and was purified by fractional distillation under reduced pressure.

Tetrabutylammonium acetate was prepared by reacting the corresponding hydroxide with acetic acid followed by recrystallization from *n*-butyl chloride. It was then stored in a dry nitrogen atmosphere.

Polymers were isolated by precipitation with acidified methanol followed by vacuum drying.

Molecular weight measurements were carried out by gel permeation chromatography (GPC) in THF using a calibration determined from narrow distribution polystyrene samples and the Mark-Houwink relationship for polystyrene [9] and poly(butylcyanoacrylate) [10].

Methane sulfonic acid (Koch Light Lab, Ltd.) was used as supplied.

Acetic acid was refluxed with acetic anhydride in the presence of chromium trioxide under nitrogen at approximately 98°C, and fractionally distilled twice under reduced pressure.

RESULTS AND DISCUSSION

Effect of Acetic Acid on MSA-Retarded Polymerization of BCA by TBA^+Ac^- in THF at 20°C

In Table 1, it can be seen that the retardation period (t_r) increases with increasing concentration of acetic acid. At a fixed concentration of MSA of 0.73×10^{-5} mol/L, a fivefold increase in the concentration of acetic acid yielded a threefold increase in t_r. As shown later, acetic acid itself did not exhibit a clear-cut retardation period for the polymerization of BCA. Its effect in prolonging the retardation period in the presence of MSA may be rationalized in terms of an equilibrium arising from protonation of methane sulfonyl anion by acetic acid, i.e.,

$$MSAH \rightleftharpoons MSA^- + H^+ \qquad (1)$$

$$HAc \rightleftharpoons Ac^- + H^+ \qquad (2a)$$

$$TBA^+Ac^- \rightleftharpoons TBA^+ + Ac^- \qquad (2b)$$

From the above scheme, the acetate salt in Eq. (2b) is not completely dissociated in THF, as explained in a previous paper, and initiation of BCA polymerization by the salt is chiefly by ion-pairs [6]. In addition, the total concentration of the acetate anion may remain virtually unchanged since Ac^- from Eq. (2a) must, in principle, alter the effective concentration of Ac^- derived from Eq. (2b). Results from the retardation of polymerization of BCA by MSA [6] also indicate that there is complete utilization of the acid at the end of the retardation period since the overall rate of postretardation polymerization is approximately equal to that of a corresponding acid-free polymerization of BCA. Thus, in the presence of acetic acid, the conjugate bases, MSA^- and Ac^-, must compete for the hydrogen ion in Eq. (2a) derived by the equilibrium dissociation of acetic acid. Consequently, the equilibrium in Eq. (2a) must shift to the right, resulting in a net protonation of the sulfonyl anion by acetic acid as summarized by

$$MSA^- + HAc \rightleftharpoons MSAH + Ac^- \qquad (2c)$$

The prolongation of the retardation period is, by this postulate, caused by termination of the initiated chains by the conjugate acid of sulfonyl anion.

TABLE 1. Effect of Acetic Acid on Retardation, t_r, by MSA for Polymerization of BCA by TBA^+Ac^- in THF at 20°C

$[M]_0 \times 10^2$ mol/L	$[TBAAc]_0 \times 10^4$ mol/L	$[MSA]_0 \times 10^5$ mol/L	$[HAc]_0 \times 10^4$ mol/L	t_r, s	$[Acid]_{Tot} \times 10^5$ mol/L[a]	$\overline{M}_n \times 10^{-6}$	$\overline{M}_w/\overline{M}_n$
5.16	2.33	0.73	–	8	0.73	0.97	1.3
5.16	2.33	0.73	34.3	18	1.64	0.42	1.5
5.16	2.33	0.73	68.6	30	2.73	0.30	1.8
5.16	2.33	0.73	102.6	42	3.83	0.26	1.9
5.16	2.33	0.73	136.0	47.2	4.30	0.062	6.4
5.16	2.33	0.73	171.0	62.6	5.71	0.053	6.5
5.16	1.79	0.70	–	12.3	0.70	0.45	2.3
5.16	1.79	0.70	3.4	13.6	0.77	0.32	2.1
5.16	1.79	0.70	34.6	27.3	1.55	0.12	2.4
6.50	2.0	1.0	5.0	11.4	–	–	–
6.50	2.0	1.0	50.0	24.0	–	–	–
6.50	2.0	1.0	500	173.0	–	–	–

[a] Total acid, $[Acid]_{Tot}$, calculated from the length of the retardation period.

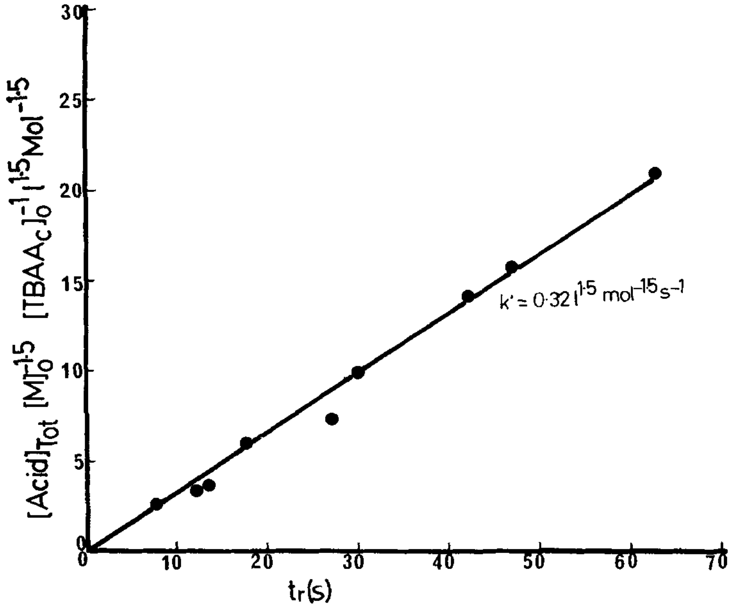

FIG. 1. Plot of $[\mathrm{Acid}]_{\mathrm{Tot}}$ $[\mathrm{M}]_0^{-1.5}$ $[\mathrm{TBAAc}]_0^{-1}$ vs t_r for MSA-retarded polymerization of BCA in THF by $\mathrm{TBA^+Ac^-}$ in the presence of acetic acid.

The total concentration of acid, i.e., $[\mathrm{Acid}]_{\mathrm{Tot}}$, may be calculated from the length of the retardation period by comparison with that caused by MSA only. Values from this calculation permit the plot shown in Fig. 1 whose slope yields the rate constant for initiation $k' \simeq 0.32$ $\mathrm{L}^{1.5}\cdot\mathrm{mol}^{-1.5}\cdot\mathrm{s}^{-1}$, which conforms to the value of k' earlier reported for retardation of BCA caused by MSA [6].

As expected, the average molecular weight, $\overline{M}_n$, of polymer for polymerization conducted at fixed concentrations of monomer, initiator, and MSA, and at varying concentrations of acetic acid as shown in Table 1, decreases with increasing concentration of total acid, $[\mathrm{Acid}]_{\mathrm{Tot}}$. Consistent with this trend is the increase in value of the corresponding molecular weight distribution function, $\overline{M}_w/\overline{M}_n$, which may be associated with the formation of an increasing amount of low molecular weight oligomers as the retardation period increases.

Calculation of Propagation Rate Constant, k_p

Theoretical Part

In a previous paper [6] it was mentioned that a knowledge of the initiation rate, R_i, may permit calculation of the concentration of the growing polymeric species, $[P^-]$, generated over the time course of the polymerization, i.e.,

$$[P^-] = \int_0^t R_i dt$$

and

$$R_i = k'[I]_0[M]_0^{1.5}$$

where k' = initiation rate constant, $[I]_0$ = initiator concentration, and $[M]_0$ = monomer concentration. Thus,

$$\begin{aligned} [P^-]_t &= \int_0^t k'[I][M]_0^{1.5} dt \\ &= k'[I]_0 \int_0^t [M]_0^{1.5} dt \\ [I] &\cong [I]_0 \end{aligned}$$

since the fractional consumption of initiator deduced from molecular weight is low.

$$-d[M]/dt = R_i + R_p$$

However, since the rate of initiation is very low, the bulk of the monomer is consumed by the propagating species, hence,

$$-d[M]/dt \cong R_p = k_p[P^-][M]$$

$$\frac{-d \ln [M]}{dt} = k_p[P^-] = U \qquad (3)$$

or

$$\frac{\ln [M]_0}{[M]_t} = Ut$$

Thus, a first-order plot in [M] vs t is initially curved but becomes linear to yield a value for U, the first-order rate constant. The initial curvature has been explained as arising from the initial slow build-up of the concentration of the propagating species $[\mathrm{P}^-]$ which becomes virtually constant as the polymerization progresses [3].

The rate of propagation may thus be calculated from values of $[\mathrm{P}^-]$ and U, as shown in Eq. (3).

Calculation of Transfer Rate Constant, k_{tr}

Approximate values of k_{tr}/k_p were calculated by Pepper [11] for BCA polymerized in the presence of acetic acid by using

$$\frac{k_{tr}}{k_p} = -\frac{1}{5} \ln \left[1 - \frac{[\mathrm{M}]_0}{[\mathrm{T}]_0} \cdot \frac{M_m}{M_n(\mathrm{th})} (R - 1) \right] \tag{4}$$

where $[\mathrm{M}]_0$ = monomer concentration
$[\mathrm{T}]_0$ = concentration of transfer agent
M_m = theoretical number-average molecular weight
$R = \overline{M}_n(\mathrm{th})/\overline{M}_n$

From the values of k_{tr}/k_p and a knowledge of k_p, approximate values of k_{tr} were deduced.

Effect of Acetic Acid on Polymerization of BCA by TBA$^+$Ac$^-$ in THF at 20°C

Table 2 is a collection of the results of polymerization of BCA by TBA$^+$Ac$^-$ in THF in the presence of acetic acid. The following features are evident:

1. Overall rate of polymerization decreases with an increase in acetic acid concentration as also shown by a first-order plot in Fig. 2.
2. Molecular weight, $\overline{M}_n$, of the polymer decreases as the acetic acid concentration increases.
3. Apart from values of $\overline{M}_w/\overline{M}_n$ marked with an asterisk in Table 2, values for acetic acid-containing polymerization differ by ±19% from the value for acetic acid-free polymerization. In addition,

TABLE 2. Effect of Acetic Acid on Rates and Molecular Weights for BCA Polymerized by TBA^+Ac^- in THF at 20°C

$[HAc]_0 \times 10^4$ mol/L	$\underline{U}$, s^{-1}	$[P^-] \times 10^7$ mol/L	$k_p \times 10^{-5}$ L/mol·s	$k_{tr} \times 10^{-3}$ L/mol·s	$R_p \times 10^3$ L/mol·s	M_n (th) $\times 10^{-6}$	$\overline{M}_n \times 10^{-6}$	$\overline{M}_w/\overline{M}_n$
—	0.32	6.41	5.0	—		12.3	0.79	2.1
—	0.33	—	—	—		—	—	—
0.16	0.39	—	—	—		—	0.86	1.7
0.51	0.36	—	—	—		—	0.45	3.3[a]
2.5	0.36	—	—	—		—	0.47	2.5
3.4	0.37	6.28	5.9	4.9	3.79	12.7	0.53	2.2
5.2	0.47	—	—	—		—	0.59	2.0
6.8	0.48	5.98	8.0	3.4	3.70	13.2	0.53	1.9
17.0	0.41	—	—	—		—	0.30	2.3
17.0	0.44	5.4	8.0	1.8	2.79	14.9	0.40	2.1
34.6	0.43	5.6	7.7	1.7	1.40	14.1	0.19	2.7[a]
34.6	0.40	—	—	—		—	0.12	4.2[a]
144	0.17	11.2	1.5	0.16	0.69	7.1	0.10	1.8
173	0.13	13.0	1.0	0.13	0.48	6.1	0.07	2.0

[a] $[M]_0 = 5.16 \times 10^{-2}$ mol/L; $[TBAAc]_0 = 0.59 \times 10^{-4}$ mol/L.

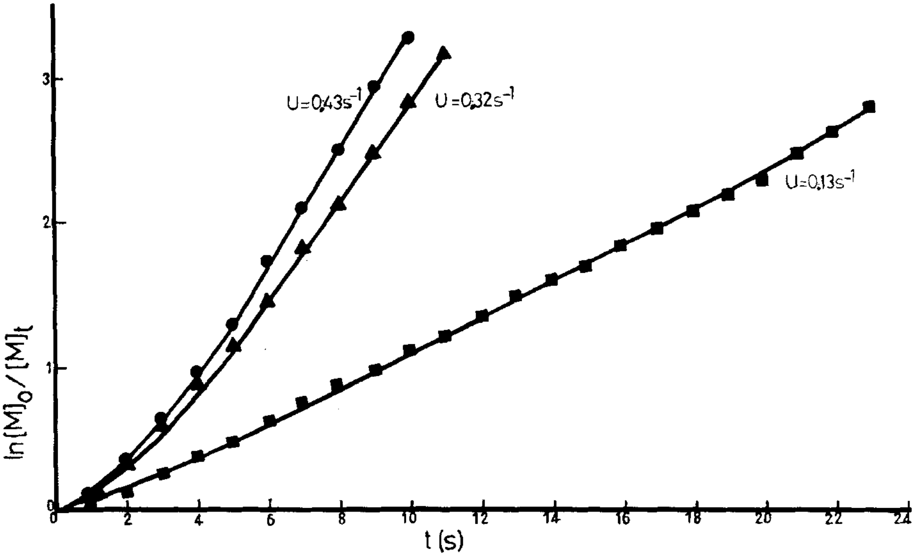

FIG. 2. Plots of ln $[M]_0/[M]_t$ vs t, showing the effect of acetic acid on the overall rate of polymerization of BCA by TBA^+Ac^- in THF at 20°C. $[M]_0 = 0.16 \times 10^{-2}$ mol/L, $[TBAAc]_0 = 0.59 \times 10^{-4}$ mol/L. (▲) $[HAc]_0 = 0$, (●) $[HAc]_0 = 34.6 \times 10^{-4}$ mol/L, (■) $[HAc]_0 = 173.0 \times 10^{-4}$ mol/L.

values for $\overline{M}_w/\overline{M}_n$ show no clear-cut trend with the concentrations of acetic acid.

The apparent effect of acetic acid on the overall rate of polymerization of BCA by TBA^+Ac^- and on the molecular weight of the polymer is expected if it is reasoned that the acid is acting as a chain transfer agent. The finding, however, that $\overline{M}_w/\overline{M}_n$ for the polymers shows no clear-cut trend with increasing acetic acid concentration is inconsistent with this expectation. Furthermore, values of $\overline{M}_w/\overline{M}_n$ for acetic acid-containing polymerization are in some cases lower than 2.1—the value for acetic acid-free polymerization. This may seem spurious, but it can be accommodated by understanding that values of $\overline{M}_w/\overline{M}_n$ from identical polymerizations of BCA may differ by up to 10% and that $\overline{M}_w/\overline{M}_n$ which are much higher than 2.0 have been reported for BCA polymerized by tertiary amines [3, 5] and various ionic initiators [13] in the absence of added acid. For these cases, varying levels of cyanoacrylic acid, suspected to be present in the monomer and acting as transfer agent, were adduced to be responsible for the high distribution function and degree of reproducibility [13, 14]. To the extent that these findings are correct, the values for $\overline{M}_w/\overline{M}_n$, as indicated in Table 2, are not significantly affected by a large concentration of acetic acid when compared to the acid-free value of 2.1.

It might thus seem inconsistent that $\overline{M}_n$ of the polymers and their corresponding $\overline{M}_w/\overline{M}_n$ should exhibit a contrasting response to acetic acid. This apparent inconsistency can be reconciled by the fact that values for the propagation rate constant are several orders of magnitude larger than those for the transfer constant, as can be seen in Table 2. Consequently, the effect of transfer reaction on the distribution function is expected *a priori* to be relatively small compared with its effect on molecular weight. In addition, experimental conditions for the polymerization were contrived to generate only a few propagating chains such that overall rates may be low enough to be measured by a calorimetric technique earlier described by Pepper et al. [8].

This argument is strengthened by reference to the values of $\overline{M}_w/\overline{M}_n$ in Table 1, which increase consistently with increasing acetic acid under constant concentrations of monomer, initiator, and methane sulfonic acid. For this case, however, the predominant chain-terminating process is caused by methane sulfonic acid and not by a chain transfer reaction by acetic acid.

Reaction Mechanism

Initiation:

$$\mathrm{TBA^+Ac^-} + \mathrm{M} \xrightarrow{k_i} \mathrm{P_1^-}$$

Propagation:

$$\mathrm{P_1^-} + \mathrm{M} \xrightarrow{k_p} \mathrm{P_2^-}$$

$$\mathrm{P_n^-} + \mathrm{M} \xrightarrow{k_p} \mathrm{P_{n+1}^-}$$

Transfer by Acetic Acid:

$$\mathrm{P_n^-} + \mathrm{HAc} \xrightarrow{k_{tr}} \mathrm{P_nH} + \mathrm{Ac^-}$$

if $\mathrm{TBA^+AC^-}$ is taken as I, then

$$R_i = k_i[\mathrm{M}][\mathrm{I}]$$
$$R_p = k_p[\mathrm{M}][\mathrm{P}_n^-]$$

and

$$R_{tr} = k_{tr}[\mathrm{P}_n^-][\mathrm{HAc}]$$

In a previous paper [6] the complex nature of the initiation process was explained and an empirical equation for R_i was shown to be $R_i = k'[\mathrm{I}][\mathrm{M}]^{1.5}$.

Thus, on the assumption of a steady state, the expression for the overall rate of polymerization, R_p, from the above scheme becomes

$$R_p = \frac{k_p k'[\mathrm{I}][\mathrm{M}]^{2.5}}{k_{tr}[\mathrm{HAc}]}$$

CONCLUSION

Polymerization of BCA by $\mathrm{TBA^+Ac^-}$ in THF is not stopped by large concentrations of acetic acid but can proceed with an overall rate and molecular weight of polymer which decrease with increasing concentrations of acetic acid. The distribution function $\overline{M}_w/\overline{M}_n$ of the polymers from acetic acid-containing polymerization is high but comparable to the acid-free value. This is attributable to chain propagation being much greater by several orders of magnitude than chain transfer.

In the presence of acetic acid, methane sulfonic acid exhibits a prolonged retardation period for BCA polymerized by $\mathrm{TBA^+Ac^-}$. This is postulated as arising from an enhanced equilibrium concentration of methane sulfonic acid by protonation of its conjugate base by acetic acid.

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