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Water effects on the zwitterionic polymerization of cyanoacrylates

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SUMMARY:

This paper presents a number of qualitative and semi-quantitative observations on the effect of small concentrations of water on the polymerizations of butyl cyanoacrylates by tertiary amines in THF. It reports also that, in the absence of other bases, large concentrations (approx. 1 mol/l) of water can cause the polymerization of ethyl cyanoacrylate, in THF, even in presence of normally inhibiting amounts (10^{-5} mol/l) of *p*-toluenesulfonic acid. A formal kinetic scheme of a stationary-state polymerization, initiated by hydroxyl anions, is presented and discussed.

Introduction

In the 'classical' studies of carbanionic polymerization of styrene and other non-polar monomers, which led to the detailed understanding of the kinetics and mechanisms of 'living' polymerizations, consistent results were obtainable only after the most careful exclusion of traces of nucleophilic 'carbanion killers', notably water, which caused severe reductions in rate and molecular weight.

In contrast, the polymerizations of alkyl cyanoacrylates, also propagated by carbanionic species, show no such sensitivity, and can even be conducted in presence of high concentrations (e. g. ca. 1 mol/l) of water. An explanation that water reacts but causes transfer (since the hydroxyl ion is known to be a rapid initiator) is not adequate since molecular weights are also largely unaffected.

This inertness of the cyanoacrylate anion to potential reactants other than its monomer can be given a general explanation as the consequence of a very high stability conferred by the simultaneous presence of two electrophilic substituents, the CN and COOH groups. This insensitivity is, however, insufficient to resist interaction with appreciably acidic molecules, strong acids causing termination and weak acids transfer reactions. With water the interaction is weak enough to have been ignored as insignificant in the usual type of experiment using conventionally 'dry' solvents.

Nevertheless the potential roles of water deserve consideration if only to clarify the apparent paradox between the belief that water adsorbed on solid surfaces is the likely initiator of the rapid polymerization of the cyanoacrylate adhesives and the knowledge that the adhesive compositions contain up to 200 ppm of dissolved water (plus smaller concentrations of acidic stabilizers).

This paper presents a number of so far unpublished observations and partial investigations, and attempts a correlation in terms of a theory of orthodox character (hydroxyl ion-initiated, proton terminated), which is normally suppressed in stabilized, dry systems, but can become apparent at sufficiently high water concentration.

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Experimental part

The methods of purification and handling of reagents, monomers and solvents, etc., have been described in refs.[1-4]. Rates of polymerization were followed by the calorimetric method of refs.[2,3], and molecular weights derived from GPC[2].

Results

The effect of water on anion-initiated polymerizations of butyl cyanoacrylate (BCA)

Butyl lithium was the initiator with which the original observations of insensitivity to water were made[5]. These were semi-quantitative, in that they amounted to the finding of 'virtually identical' thermograms (ΔT vs. reaction time curves) when successive aliquots of monomer were added to a BuLi/THF solution, even though it had been exposed to intervening injections of water-saturated air.

Tetrabutylammonium acetate (TBAAc.) and *hydroxide* (TBAOH)[6]. These, and other TBA salts, are not easily dispensed into THF without also a small concentration of water, since the anhydrous salts are insufficiently soluble at 20 °C, and TBAOH is difficult to dehydrate from its normally-supplied 40% aqueous solution. Reassurance that the quantitative effects of these initiators were not significantly affected by approximately equivalent amounts of water was obtained by the following experiments:

With TBAAc. at $5{,}9 \cdot 10^{-5}$ mol/l and [BCA] = $5{,}2 \cdot 10^{-2}$ mol/l in THF at 20 °C, $[H_2O] \approx$ [TBAAc.] though uncontrolled within a factor of 2–3, three replicate experiments gave visually identical thermograms, i. e. overall rates. The derived values of the propagation rate constant differed by only 4%, to be compared with up to 50% variation commonly found as a result of imperfections in monomer purification and other experimental errors. To observe a substantial effect (30% reduction in rate) excess water up to 10^{-2} mol/l had to be added, — 170 times the concentration of the initiator!

In TBAOH solutions, dispensed as the 40% aqueous solution, the ratio of $[H_2O]/[TBAOH]$ is ≈ 21. In a series of reactions in THF at 20 °C, with [BCA] = $0{,}6 - 1{,}3 \cdot 10^{-2}$ mol/l, and [TBAOH] = $0{,}6 - 4{,}5 \cdot 10^{-6}$ mol/l, it was found necessary to add extra water up to ca. 10^{-2} mol/l (ca. $18000 \cdot$ [TBAOH]) before appreciable consequences (20% reduction in rate) could be detected. At $[H_2O]/[TBAOH] > 10^6$, the rate was still 20% of the 'dry' value, and the polymer molecular weight unaffected. At the highest $[H_2O]$, 3 mol/l, water alone caused polymerization.

Water effects on initiation by tertiary amines

Limited results so far suggest different responses from the two cyanoacrylate esters, ethyl and butyl, in that no clear-cut effects have been observed with BCA, but quite striking behaviour with ECA in THF initiated by triethylamine or by pyridine.

Thus Johnston[1] reported no effect of H_2O up to 1 vol.-% on the rates of polymerization of BCA in THF by Et_3N or by pyridine. With ECA he found a small *increase* of rate, with Et_3N, as $[H_2O]$ was increased up to approximately $1/2[Et_3N]$, but no further effect beyond this ratio.

With ECA and pyridine, and considerably higher concentrations of water, Ryan[7] found a slight accelerating effect on the overall rate but a surprisingly strong influence on the rate of *initiation*, as judged by a sharp reduction in the inhibition periods (t_i) in acid-inhibited reactions. The results are shown in Tab. 1. If interpreted by the theory developed for the 'dry' reactions[2], they would imply a strong effect of water to increase the rate constant of the composite initiation process by pyridine, and little effect, possibly a small decrease, in the propagation rate constant.

Initiation by addition of pyridine to form zwitterion might certainly be expected to be accelerated by water through a purely physical effect, since it must increase the dielectric constant of the medium and favour the necessary charge-separation. But it seems likely that the large, more than fortyfold, increase indicated in Tab. 1 is more than should be expected from this source. A more plausible interpretation may be that there is a shift in the chemistry of the initiation towards the mechanism suggested by Johnston for the water effect in the Et_3N/ECA system, i.e. water-cocatalysed initiation by OH^-, giving in the present case:

$$\mathrm{Py} + \mathrm{H_2O} \rightleftharpoons \mathrm{PyH^+} + \mathrm{OH^-} \xrightarrow{\mathrm{M}} \mathrm{HOM^-}$$

Apart from its interest as the anionic analogue of water-cocatalysed cationic polymerization by Friedel-Crafts halides, this suggestion deserved further consideration since it would imply also a change in the propagating species, now a simple carbanion not a zwitterion. The polymer product, after acidification in work-up, would be a neutral macromolecule and not a salt. There would also be expected to be kinetic consequences. These are considered in detail in a later section.

The effect of water alone, i.e. in the absence of other bases

Information to date is confined to a single observation with BCA and a short series of experiments with ECA both in THF at 20 °C[7].

With BCA (containing ca. 10^{-6} mol/l TSA as stabilizer), no reaction was observed on addition of 'traces' of water, and only a very slow (days) polymerization in presence of 10 vol.-% of water giving polymer of molecular weight ca. 20000.

ECA at similar high concentrations of water gave measurable rates even in presence of higher acidic concentrations. Quantitative interpretation is however difficult, since under these conditions the systems tend to become inhomogeneous, i.e. a polymer-rich phase separates as the reaction proceeds. This tendency was found to be reduced when a slightly unconventional method of preparation was used, i.e. by the addition of dry acidified THF/monomer to the aqueous THF mixture. Tab. 2 summarizes the findings.

The complication of phase-separation must mean that these results have little quantitative significance, but *qualitatively* they seem definitely to imply that water can both start and stop polymerization chains. The obvious first postulate to make is that of a hydroxyl ion-initiated polymerization terminated by the conjugate acid H_3O^+. Under neutral conditions, when these are equivalent, one might expect relatively slow initiation and fast terminations, and hence a stationary state polymerization. In

Tab. 1. Effect of water on polymerization of ECA by pyridine in THF. $[ECA]_0 = 0{,}083$ mol/l, $[Py]_0 = 5 \cdot 10^{-5}$ mol/l, $T = 20\,°C$. TSA = *p*-toluenesulfonic acid

Vol.-% H_2O	$\frac{10^5 \cdot [TSA]}{mol \cdot dm^{-3}}$	t_i/s	$\frac{k_i}{l^2 \cdot mol^{-2} \cdot s^{-1}}$ [a]	U_f/s^{-1} [b]	$\frac{10^{-5} \cdot k_p}{l \cdot mol^{-1} \cdot s^{-1}}$ [c]	$10^{-6} \cdot M_p$ [d]
0	1,0	21,8	1,66	—	—	2,6
1,0	1,0	12,6	2,88	—	—	—
2,0	1,0	8,2	4,42	—	—	—
10	1,0	0,5	72	—	—	0,94
0	0	—	—	0,30	1,9	—
1,0	0	—	—	0,34	1,8	—

[a] Initiation constant in $R_i = k_i [Py] [M]^2$, where $k_i = [TSA]_0/(t_i [Py]_0 [M]_0^2)$, (cf. ref.[2]).

[b] U_f = final gradient of 1st order plot.

[c] k_p = propagation rate constant = $u_f/(k_i [Py]_0 \int [M]^2 dt)$.

[d] M_p = 'peak' mol. wt. (relative, i.e. = M_p of poly(BCA) having same GPC elution volume).

Tab. 2. Polymerization of ECA in THF by water

$10^2 \cdot$ [ECA] / $mol \cdot dm^{-3}$	$10^5 \cdot$ [TSA] / $mol \cdot dm^{-3}$	Vol.-% H_2O	U_f [a] / s^{-1}	M_p [b]	Remarks
(A) ECA added to THF/H_2O/*p*-tol. SO_3H (TSA):					
6,5	0	10	v. low	—	—
8,3	0	30	2,06	—	Polymer separates
8,3	0	20	0,6	—	Polymer separates
8,3	0,1	20	0,35	—	Polymer separates
8,3	1,0	20	0,08	8 200	Homogeneous up to ca. 20%
(B) ECA/THF/TSA added to THF/H_2O:					
8,3	0,1	10	v. low	95 000	Homogeneous
8,3	0,1	15	0,02	22 000	Homogeneous
8,3	0,1	16,2	0,15	50 000	Homogeneous
8,3	0,1	17,5	0,20	43 000	Homogeneous [c]
8,3	0,1	20	0,24	39 000	Homogeneous [c]

[a] U_f = 'final' gradient of 1st order plot, but gives an approximate half-life of the whole reaction, i.e. $t_{1/2} \approx 0{,}7/U_f$.

[b] M_p = peak mol. wt. on GPC trace.

[c] Till late in reaction.

presence of other acidic or basic species, the ionization equilibria and consequential rates will be profoundly affected. The kinetic scheme given below attempts to formulate some of these possibilities.

Theory of stationary state polymerization by water

Two simplifying assumptions are postulated:

1) The concentrations of initiating and terminating ions are determined simply by the water-ionization equilibria.
2) The re-initiation process after transfer is sufficiently fast to permit the stationary concentration of propagating species to be determined simply by the balance of initiation and termination.

Kinetic Scheme:

Ionization $$2\,H_2O \overset{K_w}{\rightleftarrows} H_3O^+ + OH^-$$

$$[OH^-] = [H_3O^+] = K_w^{1/2}\,[H_2O]$$

Initiation $$OH^- + M \xrightarrow{k_i} P_1^-$$

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

$$P_x^- + M \xrightarrow{k_p} P_{x+1}^-$$

Transfer $$P_r^- + H_2O \xrightarrow{k_{tr}} P_rH + OH^-$$

Termination $$P_s^- + H_3O^+ \xrightarrow{k_t} P_sH + H_2O$$

A stationary concentration in $[P^-]$ would be determined by:

$$d[P^-]/dt = k_i[OH^-][M] - k_t[P^-][H_3O^+] = 0$$

$$\text{i.e. } [P^-]_{ss} = (k_i/k_t)[M][OH^-]/[H_3O^+]$$

giving a stationary rate of monomer consumption:

$$-d[M]/dt = (k_i k_p/k_t)[M]^2[OH^-]/[H_3O^+]$$

and 'instantaneous' degree of polymerization:

$$\overline{DP}_n = k_p[M]/(k_t[H_3O^+] + k_{tr}[H_2O])$$

Different consequences must be expected when the ionization is influenced by the presence of acid (HA) of base (B), thus:

Case 1. Neutral conditions (as above)

Here $[OH^-] = [H_3O^+] = K_w^{1/2}[H_2O]$

$$\text{Rate} = (k_i k_p/k_t)[M]^2 \quad \text{independent of } [H_2O] \tag{1}$$

$$\overline{DP}_n = k_p[M]/(k_t K_w^{1/2}[H_2O] + k_{tr}[H_2O]) \tag{2}$$

The same form of equation for rate could be expected to apply to polymerization in any solvent (S) sufficiently basic to make the preferred ionization process:

$$H_2O + S = SH^+ + OH^-$$

giving $[OH^-] = [SH^+] = K_s^{1/2}([H_2O][S])^{1/2}$, cancelling in the rate equation, but the equation for $\overline{DP}$ should have mixed exponents in $[H_2O]$

$$\text{i.e. } \overline{DP} = k_p[M]/(k_t K_s^{1/2}[S]^{1/2}[H_2O]^{1/2} + k_{tr}[H_2O]) \tag{3}$$

Case 2. In presence of strong acid, HA

Here $[H_3O^+] \approx [HA]$; $[OH^-] + K_w[H_2O]^2/[HA]$

giving
$$\text{Rate} = (k_i k_p/k_t)[M]^2 K_w[H_2O]^2/[HA]^2 \tag{4}$$

$$\overline{DP}_n = k_p[M]/(k_t[HA] + k_{tr}[H_2O]) \tag{5}$$

Case 3. Both acid, HA, and base, B, present

Here the equilibria must also satisfy:

$$B + H_2O \overset{K_b}{\rightleftarrows} BH^+ + OH^-$$

and the general case will give complicated equations. But under most practical conditions, where $[H_2O] \gg [B]_0 > [HA]_0 \approx [BH^+]$, they will reduce to $[B] \approx ([B]_0 - [HA]_0) \approx [B]_0$ and

$$[OH^-] = K_b[B]_0[H_2O]/[BH^+] = K_b[B]_0[H_2O]/[HA]$$

and $$[P^-]_{ss} = (k_i/k_t)[M]\,K_b[B]_0[H_2O]/[HA]$$

giving $$\text{Rate} = (k_ik_p/k_t)[M]^2\,K_b[B]_0[H_2O]/[HA]^2 \qquad (6)$$

$$\overline{DP}_n = k_p[M]/(k_t[HA] + k_{tr}[H_2O]) \qquad (7)$$

Effects of conversion

The above equations refer to the instantaneous rates and degrees of polymerization at the concentrations specified, i.e. are appropriate for the initial behaviour in slow reactions but not for the high conversions in the rapid cyanoacrylate polymerizations.

Monomer conversion: If all other concentrations remain unaltered, the equations are simply adapted by integration over the fall in [M] giving the fractional conversion, $Y = 1 - [M]/[M]_0$, and the integrated $\overline{\overline{DP}}_n$ over conversion Y, related to its initial value $\overline{DP}_n(0)$ in the ratio $Y/\ln(1 - Y)^{-1}$ (ref.[8]), e.g.

$$\begin{array}{lll} \text{at } Y = 0{,}5 & \overline{\overline{DP}}_n = & 0{,}721 \cdot \overline{DP}_n(0) \\ \phantom{\text{at } Y = }0{,}9 & & 0{,}390 \cdot \overline{DP}_n(0) \\ \phantom{\text{at } Y = }0{,}99 & & 0{,}215 \cdot \overline{DP}_n(0) \end{array}$$

Acid consumption: Here, since $[HA]_0$ is normally very small, and yet $k_t[HA] \gg k_p[M]$, the consequence is virtually complete suppression of $-d[M]/dt$ until all [HA] has been consumed, i.e. an *inhibition* period, after which the kinetics should rapidly converge to those of the neutral condition. The rate of acid consumption during the inhibition period has an unusual *inverse* form, viz.:

$$\begin{aligned} -d[HA]/dt &= k_t[HA][P^-] \\ &= k_i[M]K_w[H_2O]^2/[HA] \\ \text{or in presence of B} \quad &= k_i[M]K_b[B]_0[H_2O]/[HA] \end{aligned}$$

which integrates to

$$[HA]_0^2 - [HA]_t^2 = 2kt, \text{ where } k = k_i[M]_0K_w[H_2O]^2$$
$$\text{or} \qquad = k_i[M]_0K_b[B]_0[H_2O]$$

giving a definite inhibition period, t_i, at which $[HA] \to 0$

$$t_i = [HA]_0^2/2k = [HA]_0^2/(2k_i[M]_0K_w[H_2O])^2 \qquad (8)$$

$$\text{or} = [HA]^2/(2k_i[M]_0K_b[B]_0[H_2O]) \qquad (9)$$

Note the unusual form, t_i proportional to the square of [HA], differing from the *inverse* first power found when initiation involves addition of base, B, to the monomer[2].

Application of experimental results

(i) Tab. 1, B = pyridine

Here most of the information relates to the effect of water on the inhibition time, t_i. As already noted, analysis according to the pyridine-initiation theory of ref.[2] would imply initiation rates at the highest $[H_2O]$ perhaps too great to be plausible. Analysed by the present theory, the value of t_i can be seen in Fig. 1 to vary approximately with $1/[H_2O]$, as required by Eq. (9) above, with a gradient yielding a value for the product $k_i K_b \approx 1{,}6 \cdot 10^{-6}\ l \cdot mol^{-1} \cdot s^{-1}$. Whether this is a plausible figure can only be guessed, but it can be recalled that k_i for initiation by Ph_3P, expected to be less than for OH^-, has been estimated at $100\ l \cdot mol^{-1} \cdot s^{-1}$ at 20 °C, and K_b is quoted at $2 \cdot 10^{-9}$ in aqueous solution.

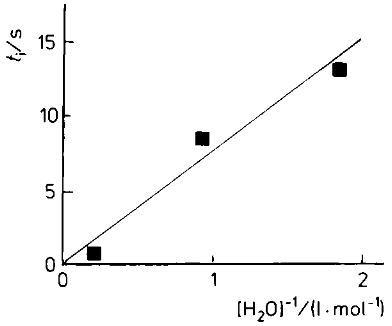

Fig. 1. Polymerization of ECA by pyridine/water: Effect of $[H_2O]$ on inhibition by *p*-toluenesulfonic acid (10^{-5} mol/l). [ECA] = 0,083 mol/l, [Py] = $5 \cdot 10^{-3}$ mol/l, T = 20 °C

For the effect of water on the rate in nominally acid-free condition, Tab. 1 provides only one measurement. The slight increase observed is in qualitative accord with Eq. (6) but can be no real test. An inference that 1% $[H_2O]$ is inadequate to make an appreciable change of initiator from Py to OH^- could be drawn from the finding that the results in this reaction could still be analysed by the 'slow initiation-no termination' theory of ref.[2] to provide a k_p value.

(ii) Tab. 2, water alone

The main importance of these results is the clear qualitative indication that, even in presence of appreciable concentrations of acid, water in sufficient quantities can cause polymerization. The complication of phase separation rules out firm quantitative interpretation, but at a tentative level it might be speculated that the large effect between 10 and 30% H_2O might result from the squared dependence required by Eq. (4).

The effect on polymer molecular weight described in the second section of Tab. 2 seems systematic enough to warrant a tentative analysis. The degree of polymerization,

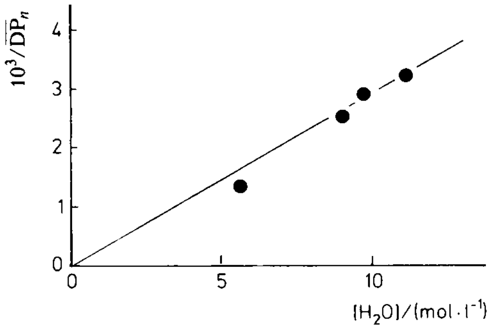

Fig. 2. Polymerization of ECA by water alone: Effect of $[H_2O]$ on degree of polymerization, $\overline{DP}_n$. [ECA] = 0,083 mol/l, [TSA] = 10^{-6} mol/l, T = 20 °C

calculated crudely from $M_p/125$, can be seen from Fig. 2 to lie close to the reciprocal relationship with $[H_2O]$ required by Eq. (7) (with one exception, the result at 15% H_2O). The gradient would correspond to a value for k_{tr}/k_p of $2{,}4 \cdot 10^{-5}$ from the crude results, or $8{,}3 \cdot 10^{-6}$ if all samples are (plausibly) taken to have reached the same 95% conversion. Such figures may seem very low, but do not appear out of the question when compared with $k_{tr}/k_p \approx 10^{-3}$ deduced for CH_3COOH in the polymerization of BCA by TBAAc[9].

General conclusions

This collection and review of information, fragmentary though it is, permits a clearer, if still tentative, understanding of a number of features of these systems.

The demonstration that very large concentrations of water are needed before any strong effect can be seen should help to lay any fears of some investigators that their results may have been invalidated by neglect of the extreme precautions (vacuum handling, etc.) found necessary in the analogous polymerization of non-polar monomers.

A second point is that the relative insensitivity of these polymerizations to water is best understood not as an insensitivity of the carbanion but as a consequence of the extreme reactivity of the monomer, which results in propagation being favoured over other reactions to which the carbanion may also be susceptible. It is relevant to note that, while CH_3COOH is a quite active transfer agent, concentrations as high as 0,2 mol/l do not totally suppress the rate of polymerization by TBAAc in THF[10].

With hind-sight it is obvious that, in any ionic reaction involving water, acid-base equilibria must be important. It seems likely that in the stabilizing action of acid in water-containing monomer samples, its role as a suppressor of OH^- initiation is more important than that of inhibitor. How stabilized monomer solutions may nonetheless be polymerized on surfaces still remains unclear, unless it is because in a surface multilayer the local concentration of water is in fact very high.

The formal theory here is obvious but may serve to correlate any future systematic studies. These are certainly needed to provide more extensive tests than available from the few experiments considered here. One feature of particular interest to test is the predicted inverse square dependence of the inhibition period in presence of both water and base. There is one unpublished report of such behaviour in the quinoline/ECA system, but further confirmation of such unusual effect is much needed.

The most direct test of the ideas advanced here would of course be the chemical identification of the polymer end-group, which should change for example, from Py^+- to HO- as the water content of reaction mixture was increased.

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