

## Kinetics and Mechanisms of Zwitterionic Polymerizations of Alkyl Cyanoacrylates

D. C. PEPPER

Chemical Laboratory, University of Dublin,  
Trinity College, Dublin, Ireland.

(Received April 15, 1980)

**ABSTRACT:** The paper reviews work in the author's laboratory on the polymerization of alkyl cyanoacrylates, chiefly the butyl ester, in THF, by organic bases, phosphines and amines. It presents evidence that the bases initiate by addition, thus forming zwitterionic propagating species. Polymerizations initiated by  $\text{Ph}_3\text{P}$  are confirmed as "living polymerizations," but with *relatively* slow initiation (e.g.,  $k_i/k_p$ ,  $\sim 5 \times 10^{-5}$  at  $-80^\circ\text{C}$ ). Acid-inhibition studies of amine-initiated reactions show that rates of initiation are complex and have negative temperature dependence. This makes unnecessary an earlier postulate that these polymerizations involved a combination-termination process. A "slow-initiated, non-terminated" kinetic scheme quantitatively describes polymerizations by pyridine, 4-vinylpyridine, 2,6-lutidine, and benzyldimethylamine, yielding  $k_p$  values  $((2-8) \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$  at  $20^\circ\text{C}$ ) consistent among themselves and with that from the  $\text{Ph}_3\text{P}$ -initiated kinetics.

**KEY WORDS** Cyanoacrylates / Zwitterions / Phosphines / Tertiary Amines /  
Slow-Initiated-Non-Terminated Kinetics /

When these polymerizations were first reviewed in 1977,<sup>1</sup> the major unsettled questions were seen to be:

1) What is the electrochemical nature of the growing species when the polymerizations are initiated by covalent bases, amines or phosphines? Are they simple anions (with ammonium or phosphonium counter cations), as would follow if initiation somehow (not obviously) involved proton abstraction? Or are they, as expected, genuine *zwitterions*, formed by addition of the bases to the monomer?

2) What explains the striking difference between the overall kinetics of polymerizations initiated by phosphines (which appeared to be near-ideal "living polymerizations," *i.e.*, *terminationless*) and by amines, which showed a negative temperature coefficient of overall rate, at that time interpreted by the postulate of a highly temperature dependent (combination) termination process.

As will be described below, evidence for zwitterion formation has now been provided by spectroscopic demonstration of the presence of phosphonium, pyridinium and carbanion groups in the polymer<sup>2</sup> and by the demonstration that *graft*

copolymers are formed, when polymerization is by poly(vinylpyridine)<sup>3</sup> or poly(styryldiphenylphosphine).<sup>4</sup>

The different overall kinetics of phosphine- and amine-initiated polymerizations can now be reconciled by the conclusion that in neither case is there any intrinsic termination process, and that the differences arise from different *complexities* in the processes which generate the active species. This conclusion follows from the discovery that, under appropriate conditions in the presence of added strong acids, amine-initiated polymerizations showed clear-cut *inhibition periods*, from which the rates of chain-initiation could be deduced. These are found to have a negative temperature coefficient capable of explaining that of the overall rates, *i.e.*, permit evaluation of the concentration of active species, and hence of propagation rate constants, virtually identical with those observed from the simple kinetics of the phosphine-initiated polymerizations.

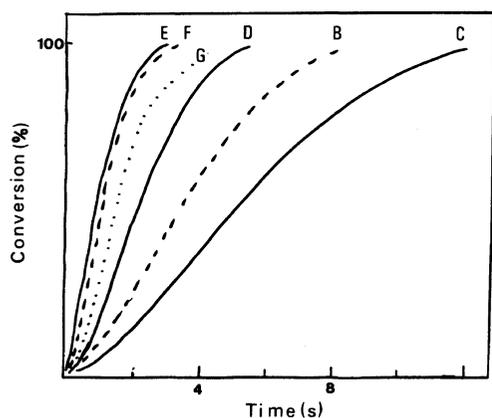
## EXPERIMENTAL PROBLEMS

The calorimetric technique for following the polymerization has been improved by the change from thermocouples to thermistors.<sup>5</sup> The much greater sensitivity attained has permitted study at lower reagent concentrations, thus avoiding excessively high rates which sometimes previously gave rise to ambiguities in interpretation.

The choice of solvents that are themselves inert, and can be effectively freed from initiating impurities, remains a problem. All results reported below were from reactions in tetrahydrofuran (THF).

A still incompletely solved problem is purification of monomer sufficiently to obtain adequately reproducible samples. The butyl ester seems to present more difficulties than methyl or ethyl homologues. Chemical removal of the suspected impurities (cyanoacetic and cyanoacrylic acids) is difficult since any basic reagents or sorption agents tend to cause polymerization. Fractional distillation has its pro-

blems, since any portion of the equipment not previously acid-treated may cause uncontrollable polymerization. The resulting lack of uniformity in monomer samples is illustrated in Figure 1, which shows conversion curves for butyl cyanoacrylate (BCA) in THF initiated by pyridine (Py) at 20°C. The curves approximate in their later stages to 1st-order monomer consumption, and hence can be quantitatively compared by the ratio  $k_1/[Py]_0$ . As shown in the legend to Figure 3 these indicate a 3-fold extreme variation (between samples C and E). Most of the results quoted below were obtained with samples F and G, hence should be comparable within ~20%. The acid-inhibition effects were first characterised using sample C, the least active/most retarded—sample. However, later studies with the most “active” samples showed no effective differences in the inhibition periods, showing that the impurities in “inactive” samples are retarders, interfering weakly with the propagation but not with initiation.



**Figure 1.** Irreproducibility of BCA monomer samples to polymerization by  $[pyridine] = 5 \times 10^{-4}$  M in THF at 20°C, at  $[M]_0 = 0.065$  M

Sample	$k_1/[Py]_0$
	$l \text{ mol}^{-1} \text{ s}^{-1}$
B	1280
C	1040
D	2000
E	3700
F	3600
G	2460

## EVIDENCE FOR ZWITTERIONS

Most monomer samples so far prepared have impurity absorptions extending broadly over the near UV and masking absorptions of features in the polymer. One transparent sample, however, after polymerization showed spectra characteristic of the expected carbanion and of ionized initiating groups. Thus the polymerized solution (in THF) had an absorption edge starting near 300 nm which shifted to shorter wavelengths on “killing” with  $\text{CH}_3\text{SO}_3\text{H}$ , yielding a “difference spectrum” (Figure 2) close to that of the “model” carbanion  $^{\ominus}\text{CH}(\text{CN})\text{COOBu}$  (from sodium butyl cyanoacetate). Polymers initiated by  $\text{Ph}_3\text{P}$  or pyridine showed absorptions close to those of model phosphonium or pyridinium salts.

Further evidence that the initiating bases add to the monomer is provided by demonstrations that when the initiating base is itself polymeric, then *graft* copolymers are formed. Thus poly(vinylpyridine) (PVP) has been shown to polymerise BCA, forming copolymers in which pyridine groups of the PVP are converted to pyridinium.<sup>3</sup> Poly(styryldiphenylphosphine) has been found to initiate graft copolymers with ethyl cyanoacrylate.<sup>4</sup>

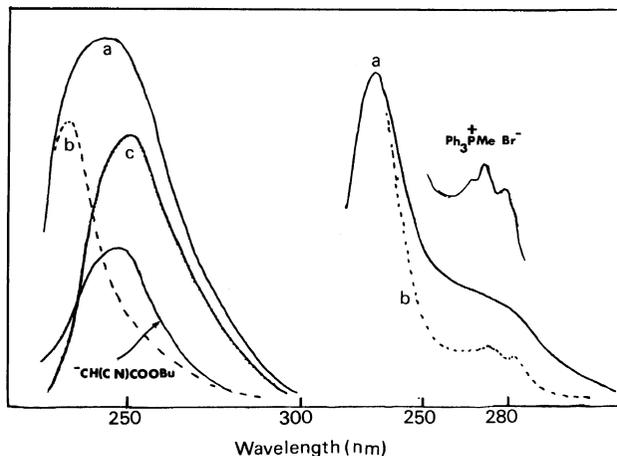
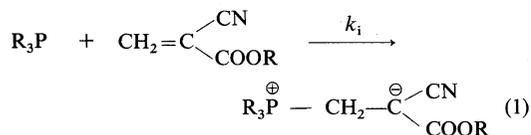


Figure 2. Spectra of polymerized solutions (a) before and (b) after killing with  $\text{CH}_3\text{SO}_3\text{H}$ : (c), difference spectrum, *i.e.*, of carbanion.

#### POLYMERIZATIONS INITIATED BY PHOSPHINES

The *chemistry* of initiation by both phosphines and amines thus appear to be identical; in both cases it involves addition to the monomer. The kinetics of the processes are, however, very different, and as will appear below, it is these differences which are responsible for the different overall kinetic patterns.

For polymerization initiated by triethyl- and triphenyl-phosphines, we have found no reason to postulate other than the simplest rate equation



though with  $\text{Ph}_3\text{P}$  the rate constant for this addition must now be concluded to be very many times smaller than that for subsequent additions, *i.e.*, the propagation constant.

In the first explorations of these polymerizations,<sup>6</sup> with  $\text{Et}_3\text{P}$ , concentrations were used which gave extremely high rates, which were, within experimental error, of the first order from the beginning of the reaction. Subsequent studies, using  $\text{Ph}_3\text{P}$ , at lower phosphine concentrations and corresponding rates, show an initial acceleration in the 1st-order plots (of  $\ln[M]_0/[M]_t - t$ ). As illustrated in Figure 3(a), this acceleration has been attributed<sup>7</sup> to the growth in

population of active species as the *relatively* slow initiation process proceeds, and analysed by the plot of Figure 3(b) to yield the ratio of initiation to propagation rate constants,  $k_i/k_p \approx 5 \times 10^{-5}$  at  $-80^\circ\text{C}$ . It may seem surprising that such a low ratio is still compatible with near quantitative consumption of initiator (I) (shown by the observed near-ideal degree of polymerization  $\bar{P}_n \sim [M]_0/[I]_0$ ). However, the consumption of initiator is determined not by  $k_i/k_p$  alone but by the composite ratio,  $k_i[M]_0/k_p[I]_0$ , and in these extremely reactive systems only very low initiator concentrations can be used.

#### POLYMERIZATIONS INITIATED BY AMINES

A number of amines, including pyridine and derivatives and aliphatic amines, *e.g.*, triethylamine and benzyldimethylamine (BDMA) cause polymerization with very different overall kinetic features. The molecular weights produced are much larger, overall rates slower and anomalous in temperature dependence, *i.e.*, faster the lower the reaction temperature. The conversion curves, expressed as 1st-order plots, have much the same form as in Figure 3(a), *i.e.*, accelerate to apparent linearity, though usually more slowly. However, the final slope, *i.e.*, apparent 1st-order rate constant,  $k_1$ , does not correspond to complete utilisation of the initiator. Thus the ratio  $k_1/[I]_0$  varies with reagent

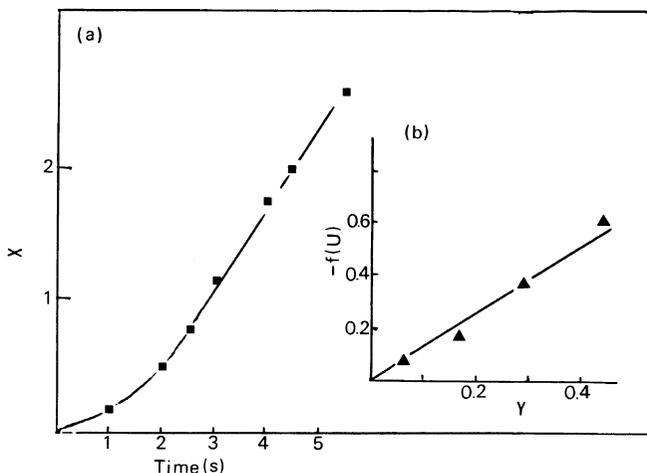


Figure 3. Derivation of  $k_i/k_p$  from  $f(U) = (-k_i[M]_0/k_p[I]_0)Y$  where  $Y = \Delta[M]/[M]_0$ ;  $U = dX/dt$ ;  $X = \ln [M]_0/[M]$ ;  $f(U) = [\ln(1 - U/U_t) + U/U_t]$  (see ref 7).

concentrations and is much lower than found in the phosphine-initiated polymerizations, where it can be identified with the propagation-rate constant (see Table II).

In the apparently analogous polymerization of nitroethylene by pyridine,<sup>8</sup> a similarly negative temperature coefficient of overall rate was explained by postulating a highly-temperature-dependent termination process. This explanation was tentatively advanced in our first interpretation of the BCA-amine polymerizations.<sup>1</sup> It can now be shown to be unnecessary, and the negative temperature dependence shown to have its origin in relatively slow and composite initiation processes.

#### Inhibition by Strong Acids

The evidence for the above assertion comes from the very striking effects observable when acidic substances (chain killers) are added to polymerizations of BCA initiated by pyridine and other amines. Increasing concentrations of *weak* acids (e.g., chloroacetic, cyanoacetic) simply cause progressively slower sigmoid conversion curves such as those of Figure 1, i.e., such acids would be classed as "retarders." Strong acids, however, (e.g., *p*-toluenesulphonic (TSA), picric, trichloroacetic) impose clear-cut inhibition periods ( $t_i$ ), proportional to the added concentrations, after which the polymerization "takes off" at a rate equal to, or greater than, that of the acid-free polymerization

(see Figure 4).

The three strong acids mentioned above all gave the same  $t_i/[HA]$  ratio (see Figure 5). It can be concluded therefore, that all these acids can kill chains as fast as they are generated by the initiator, i.e., that this ratio is an (inverse) measure of the rate of initiation ( $R_i$ ). Figure 5 includes results at three reaction temperatures and clearly shows that the induction periods fall (i.e.,  $R_i$  increases) the lower the temperature.

Such negative temperature coefficient of  $R_i$  implies that the process of chain initiation must be *composite*, a conclusion strengthened by determination of its monomer dependence, found to be

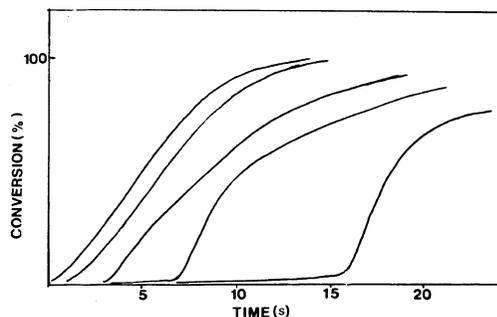


Figure 4. Induction periods in the polymerization of BCA by pyridine:  $[BCA]_0 = 0.065$  M;  $[Py]_0 = 5 \times 10^{-4}$  M in THF at 20°C;  $[TSA] = 0.15 \times 10^{-5}$  to  $4.6 \times 10^{-5}$  M.

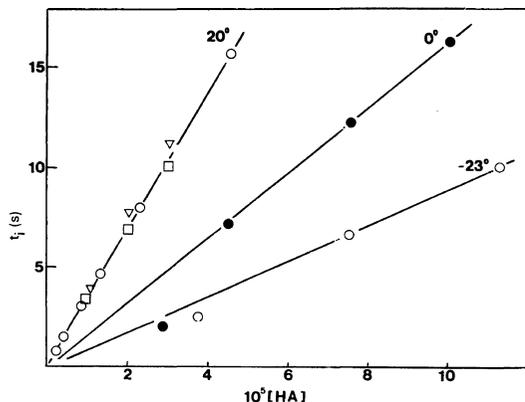
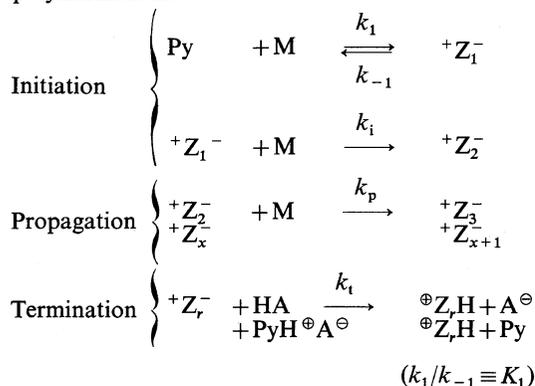


Figure 5. Acid-concentration dependence of induction periods:  $\circ$ , *p*-toluene sulphonic acid;  $\square$ , picric acid;  $\triangle$ , trichloroacetic acid. Conditions as for Figure 4.

$\alpha[M]_0^2$  for pyridine (and 4-vinylpyridine) and  $\alpha[M]_0^3$  for 2,6-dimethylpyridine (2,6-lutidine) and BDMA. Table I gives extensive results for the induction periods induced by TSA in the polymerization of BCA in THF by these four amines.

#### Kinetic Scheme

The quantitative relationships of Table I can be rationalised by the postulate that the zwitterions are rapidly killed by the acid but only relatively slowly generated by initiation processes which (according to the amine) require two or three stages of monomer addition before the zwitterion is capable of rapid propagation. Thus for pyridine-initiated polymerizations:



When  $K_1$  is small (or more strictly,  $k_{-1} \gg k_1[M]$ ) and  $k_t[\text{HA}] \gg k_p[\text{M}]$ , a stationary state will be established in which  $[\text{M}]$  and  $[\text{Py}]$  remain approximately constant until virtually all HA has been

consumed, *i.e.*,

$$\begin{aligned}
 d[\text{Z}]/dt &\equiv R_i - R_t \\
 &\approx K_1 k_1 [\text{Py}][\text{M}]^2 - k_t [\text{Z}][\text{HA}] = 0 \text{ in ss} \\
 [\text{Z}]_{\text{ss}} &= K_1 k_1 [\text{Py}][\text{M}]^2 / k_t [\text{HA}] \\
 -d[\text{HA}]/dt &= k_t [\text{HA}][\text{Z}]_{\text{ss}} \\
 &\approx K_1 k_1 [\text{Py}][\text{M}]^2 \approx K_1 k_1 [\text{Py}]_0 [\text{M}]_0^2
 \end{aligned}$$

The acid-consumption rate is thus of zero order and  $\approx [\text{HA}]_0/t_i$ , giving

$$t_i \approx [\text{HA}]_0 / K_1 k_1 [\text{Py}]_0 [\text{M}]_0^2 \quad (2)$$

The constancy shown in Table I of the ratio  $k_2 = [\text{HA}]_0/t_i [\text{Py}]_0 [\text{M}]_0^2$  supports this interpretation of pyridine initiation and identifies the experimental constant  $k_2$  with the composite initiation rate constant in

$$R_i = K_1 k_1 [\text{Py}][\text{M}]^2 \quad (3)$$

The negative temperature coefficient is now easily understood as arising from an *exothermic* equilibrium constant  $K_1$ .

In polymerizations where the initiator is 2,6-lutidine or benzyltrimethylamine, and  $t_i$  is found  $\propto (1/[\text{M}]_0^3)$ , the analogous kinetic scheme would require two successive quasi-equilibria (in successive additions of monomer) before the chain-initiating species (here  ${}^+Z_2^-$ ) is formed, and the composite initiation rate constant would have three components (*i.e.*,  $k_3 = K_1 K_2 k_1$ ).

#### Acid-Free Polymerization by Amines—"SINT" Kinetics

It is now possible to test whether the above-demonstrated negative temperature dependence of initiation rates is sufficient to explain that of the overall rates. If so, it becomes unnecessary to postulate any termination in acid-free polymerizations—a much-to-be-desired simplification of theory since it is already clear that none need be invoked for the phosphine-initiated reactions.

For the amine-initiated polymerizations the assumption of no intrinsic termination processes could be called a "slow initiation, no termination" kinetic scheme. It would clearly lead to a non-stationary situation. This might be thought unrealistic since at first sight it might seem to imply an explosive, *i.e.*, ever-increasing rate. However, since initiation rates have been shown to be highly

**Table I.** Inhibition of BCA polymerization by *p*-toluene-SO<sub>3</sub>H (HA) in THF at 20°C

Initiator, I	10 <sup>4</sup> [I] <sub>0</sub>	$\frac{[M]_0}{\text{mol dm}^{-3}}$	10 <sup>5</sup> [HA] <sub>0</sub>	$\frac{t_i}{\text{s}}$	$\frac{[HA]_0^a}{t_i[I]_f[M]_0^2} \equiv k_2$	$\frac{[HA]_0^a}{t_i[I]_f[M]_0^3} \equiv k_3$
Pyridine	1.25	0.065	2.28	31.7	1.40	
	5	"	0.45	1.5	1.40	
	"	"	1.34	4.1	1.55	
	"	"	2.28	7.2	1.50	
	"	"	4.56	15.4	1.40	
	"	0.091	2.28	3.7	1.47	
	"	0.052	"	11.5	1.47	
	297	0.110	970	16.5	1.63	
4-Vinylpyridine	5	0.065	4.0	4.4	4.30	
	5	0.039	"	14.4	3.65	
Benzyltrimethylamine (BDMA)	10	0.104	0.5	18.4		0.242
	20	0.065	"	37.5		0.243
	"	0.078	"	20.5		0.257
	"	0.104	"	8.5		0.261
	"	0.131	"	4.5		0.244
	40	0.039	0.1	18.2		0.231
2,6-Dimethylpyridine (2,6-Lutidine)	345	0.065	4.0	11.7		0.361
	"	0.039	"	36.3		0.347

<sup>a</sup> [I]<sub>f</sub> = [I]<sub>0</sub> - [HA]<sub>0</sub>

monomer-dependent, it can be seen qualitatively that the rate of initiation must fall more steeply with conversion than that of propagation, so that something approximating to a quasi-stationary state may result. Quantitatively, for pyridine-initiated polymerizations,

$$-d[M]/dt = 2R_i + k_p[M][^+Z^-] \sim k_p[M][^+Z^-] \quad (\text{since } R_i \ll R_p)$$

or

$$-d \ln[M]/dt (\equiv dX/dt \equiv U) = k_p[^+Z^-] \quad (4)$$

where

$$[^+Z^-]_t = \int_0^t R_i dt = K_1 k_i \int_0^t [Py][M]^2 dt \approx K_1 k_i [Py]_0 \int_0^t [M]^2 dt \quad (5)$$

(since Py consumption very small)

When the amine (A) is benzyltrimethylamine or lutidine

$$[^+Z^-]_t \approx K_1 K_2 k_i [A]_0 \int_0^t [M]^3 dt \quad (6)$$

Given previous determination of the composite initiation-rate constants, the values of  $[^+Z^-]_t$  are thus calculable at any stage in the polymerizations from the observed monomer-conversion curves. Also predictable are the average molecular weights, since the number-average degree of polymerization of the product at any conversion should be simply the ratio  $\Delta[M]_t / [^+Z^-]_t$ .

#### Quantitative Verification of SINT Postulates

Figure 6 shows plots of  $[^+Z^-]_t$  calculated according to eq 5 and 6 from the conversion curves of four polymerizations at 0°C, two initiated by pyridine and two by BDMA. Also shown are the logarithmic forms of the conversion curves ( $X \equiv \ln[M]_0/[M]_t - t$ ). It can be seen that the  $[^+Z^-]_t$  values do indeed converge to approximate constancy, and that the gradients of the logarithmic conversion curves ( $dX/dt \equiv U$ ) appear to correlate as required by eq 4. This correlation is quantitatively

## Zwitterionic Polymerizations of Cyanoacrylates

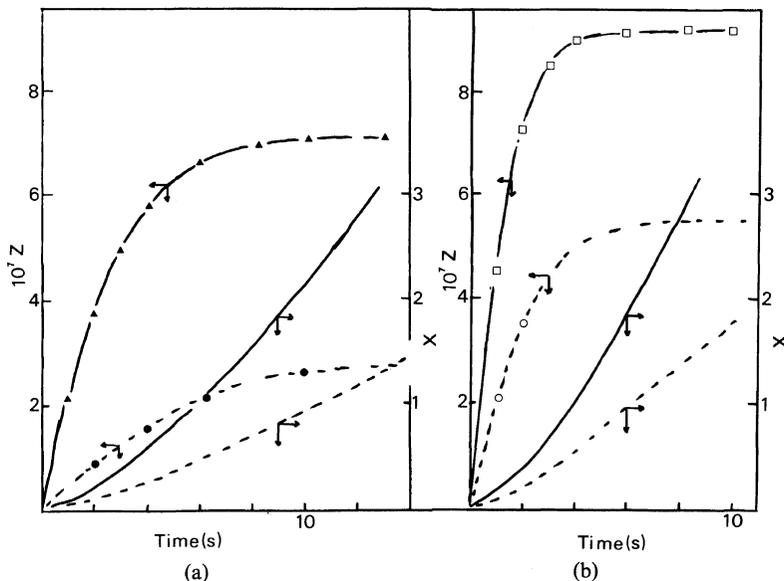


Figure 6. Calculated  $[Z]_t$  compared with  $X = \ln[M]_0/[M]_t$  at  $0^\circ\text{C}$ :  $\blacktriangle$ ,  $[\text{BCA}]_0 = 0.039$ ,  $[\text{pyridine}] = 5 \times 10^{-5} \text{ M}$ ;  $\bullet$ ,  $[\text{BCA}]_0 = 0.013$ ,  $[\text{pyridine}] = 1 \times 10^{-4} \text{ M}$ ;  $\square$ ,  $[\text{BCA}]_0 = 0.065$ ,  $[\text{BDMA}] = 1 \times 10^{-3} \text{ M}$ ;  $\circ$ ,  $[\text{BCA}]_0 = 0.039$ ,  $[\text{pyridine}] = 2 \times 10^{-3} \text{ M}$ .

tested in Figure 7, which shows that all four experiments are described by the theory with the same value of  $k_p$ , even though the evaluation of  $[^+Z^-]$  in the experiments having different initiators required different initiation-rate constants and integrations of the monomer conversion.

Further corroboration of the theory is illustrated in Table II which compares the whole range of present results for polymerizations at  $20^\circ\text{C}$  by  $\text{Ph}_3\text{P}$  and four different amines. The ratio  $k_1/[I]_0$  is, for the rapidly initiating phosphines, identifiable with  $k_p$ . For the amines it is only an empirical indicator of their initiating efficiency, which differs according to the amine (and varies with  $[M]_0$  and  $[I]_0$ ). The values derived for  $k_p$ , through eq 5 or 6 and 4 are, however, closely comparable in all systems.

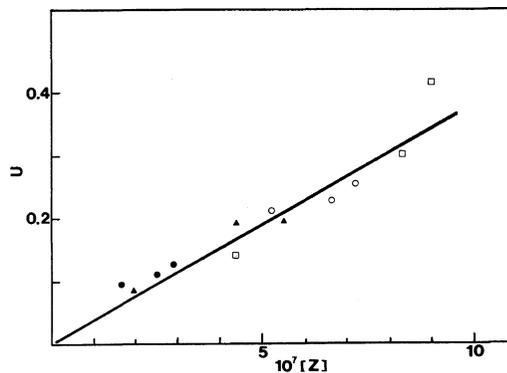


Figure 7. Results of Figure 6, plotted to test equation 4: solid points, pyridine-initiated; open points, BDMA-initiated.

Table II.  $k_p$  values at  $20^\circ\text{C}$  for BCA in THF by SINT analysis

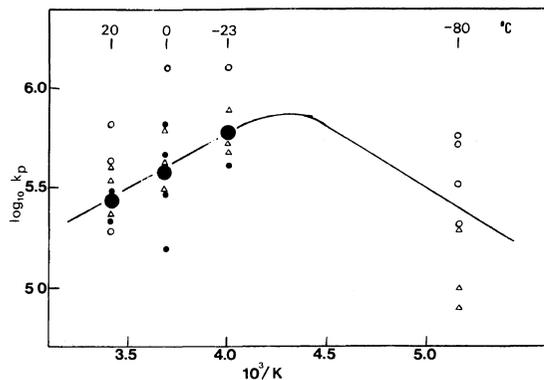
Initiator, I	$\text{Ph}_3\text{P}$	4-Vinyl-Py	Py	Lutidine	BDMA
$(k_1/[I]_0)/l \text{ mol}^{-1} \text{ s}^{-1a}$	$(2-6) \times 10^5$	$(12-15) \times 10^3$	$(1-8) \times 10^3$	67	7-230
$10^5 k_p/l \text{ mol}^{-1} \text{ s}^{-1}$	2-6	3-4	4-5	2-3	2-3

<sup>a</sup>  $k_1 \equiv (-\text{dln}[M]/\text{dt})_t \equiv (\text{d}X/\text{d}t)_t \equiv U_f$ .

## REMAINING UNCERTAINTIES

Experiments at temperatures down to  $-80^{\circ}\text{C}$  have permitted similar derivations of  $k_p$  which are shown as an Arrhenius plot in Figure 8. The scatter of values at any one temperature, which includes variations associated with different monomer preparations, obscures the small temperature variation, but the tentative curve drawn with a shallow maximum is based on three self consistent sets of values using a single monomer sample (shown as heavy points in Figure 8). If it is confirmed it may be evidence of increasing participation at low temperatures of free as distinct from paired ions.

However it is still premature to make detailed deductions, since there is good reason to believe that the derived values of  $k_p$  are still to some degree distorted by the retarding effect on the overall rates of still unremoved traces of weak acids in the monomer samples. This is illustrated clearly in the results from the poorest monomer sample (C of Figure 1). With this sample the acid-inhibition results are "normal," *i.e.*, the impurities are not affecting initiation, and the calculation of  $[^+Z^-]$  is still valid. The overall rates of monomer consumption are, however, much depressed and the derived  $k_p'$  an order of magnitude less than the values of Table II. Even the best monomer samples so far produced must contain some transfer agents, since the polymer molecular weights obtained are still some 2–3 times lower than the theoretical values calculable from  $[M]_0/[^+Z^-]_f$ .

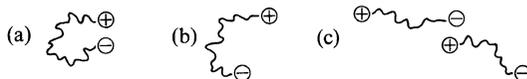


**Figure 8.** Arrhenius plot for  $k_p$  results from all initiators:  $\circ$ ,  $\text{Ph}_3\text{P}$ ;  $\triangle$ , pyridine;  $\bullet$ , BDMA. Heavy points averaged as in Figure 7.

## MECHANISMS

The assignment of precise chemical mechanisms to the proposed elementary steps in the chain polymerization still presents difficulties.

A zwitterionic propagating species may, according to its chain length and concentration, be expected to exist in various conditions, cyclic, unfolded or associated, *i.e.*,



Derived  $k_p$  values must in principle contain contributions from all three species. Present experimental values are expected to refer mainly to (b) since chain lengths are very great, which should favour (b) over (a), and concentrations very low, which should discourage (c).

The composite processes envisaged for chain-initiation must at present be taken as kinetic postulates only, *i.e.*, schemes which account for the negative temperature coefficients and orders in monomer concentration. The observation that 2,6-dimethyl substitution into pyridine greatly reduces the initiation rate and increases its complexity, naturally focusses attention on steric effects. The effect of these on the rate is to be expected, but it is not obvious how they could impose a change in mechanism. It is hoped that spectroscopic studies, and further exploration of the temperature dependence of the initiation rates, may provide evidence by which the situation may be clarified.

The conclusion that, in acid-free conditions, these polymerizations have no termination mechanisms must be qualified. What is here demonstrated is that any such reactions have no kinetic importance, *i.e.*, are slow compared to the very high rates of propagation. However the earlier-proposed termination reaction in pyridine-initiated polymerizations, namely loss of pyridine to yield either oligomeric rings or chain extended polymers<sup>1</sup> must still be regarded as a possibility at high temperatures, by analogy with the production of cyclic dimers and trimers in the pyridine-initiated polymerization of isocyanates.<sup>9</sup>

*Acknowledgment.* The experimental work of Mr. Bernard Ryan and (in smaller but important part) Miss Sandra Townsend, and the earlier studies of Dr. D. S. Johnston have provided the basis for

the ideas developed here and to them I express my thanks.

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