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The Thermal Degradation of Polymers of *n*-Butylcyanoacrylate Prepared Using Tertiary Phosphine and Amine Initiators

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ABSTRACT

The thermal degradation of polymers of n-*butylcyanoacrylate, prepared using systems in which the propagating species is a macro-zwitterion, and of molecular weight from a few thousand to more than a million, have been examined by thermogravimetry, differential scanning calorimetry and pyrolysis–gas–liquid chromatography.*

In almost all cases quantitative conversion to monomer occurs and characterization of polymer thermally degraded to half its original mass shows that the molecular weight of the residual material is substantially the same as that of the original. The mechanism of degradation is considered to be chain unzipping with a zip length greater than the degree of polymerization of the longest chain examined; that is, 2350 units.

The stability of the polymer has been found to vary with both the nature of the polymerization initiator and the chain length. This implies that the depolymerization process is end initiated at the residue of the polymerization initiator. Polymers having pyridinium chloride salt ends are significantly more stable than those having phosphonium or quaternary ammonium ends. Kinetically, the degradation of the phosphine initiated polymers is a simple first-order process, but that of the pyridine initiated polymers shows an induction period, followed by a period of acceleration before reaching first-order behaviour in the later stages. The higher stability of the pyridinium

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salt end may be associated with an internal rearrangement of the end group, as a consequence of which the polymer chain becomes a substituent of the pyridinium ring.

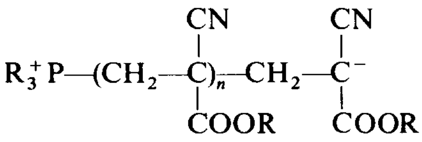
Degradation mechanism is also influenced by the nature of the salt anion. Replacement of the chloride by sulphate causes the depolymerization reaction to be accompanied by charring, indicating that the sulphate ion is extracting the elements of water from the polymer.

INTRODUCTION

The cyanoacrylate esters are well known for their ability to polymerize very rapidly to give hard glassy solids. This property, in conjunction with their high polarity, has resulted in their use as speciality adhesives. Polymerization mechanisms have been the subject of considerable study and are now well understood.[1-6] Degradation, however, has received relatively little attention, although results of a study of the thermal degradation of low molecular weight oligomers of the methyl and ethyl cyanoacrylates have been reported.[7] In this work the thermal stability of *n*-butylcyanoacrylate polymers of higher molecular weight produced using a range of initiator types is considered.

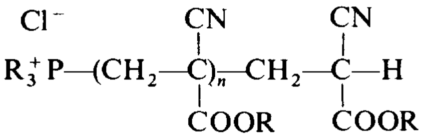
Commercial cyanoacrylate adhesive systems are usually based on the methyl or ethyl esters, but such materials are of limited value for laboratory study, being insoluble in the more common GPC solvents.[8] The *n*-butyl polymer is soluble in THF and is therefore preferred for both polymerization and degradation work.

Initiation by tertiary phosphines, pyridine and substituted pyridines, and by amines, results in the formation of zwitterions which may grow by successive insertion of monomer at the anion. Whilst there are considerable differences in the complexity of the actual initiation step, depending on precise choice of initiating species, in all cases initiators of the type mentioned result ultimately in macro-zwitterions:



$$R_3^{+}P{-}(CH_2{-}\overset{\displaystyle CN}{\underset{\displaystyle COOR}{C}})_n{-}CH_2{-}\overset{\displaystyle CN}{\underset{\displaystyle COOR}{C^-}}$$

Which, on killing with HCl, will give:



$$\overset{Cl^-}{R_3^{+}P}{-}(CH_2{-}\overset{\displaystyle CN}{\underset{\displaystyle COOR}{C}})_n{-}CH_2{-}\overset{\displaystyle CN}{\underset{\displaystyle COOR}{C}}{-}H$$

Spectroscopic and conductimetric evidence[3] obtained with triphenylphosphine and pyridine initiated systems supports the theoretical assumption that such polymers have phosphonium chloride and pyridinium chloride end groups, respectively.

A significant difficulty with work on cyanoacrylate polymers arises from the very high monomer reactivity precluding the production of low molecular weight polymer by simple stoichiometric control of the reactants. Low molecular weight material can, however, be prepared by the use of strong acid inhibitors.

The technique of acid inhibition has proved extremely useful in the elucidation of the kinetic and mechanistic detail of the polymerization reactions.[5] Polymerization behaviour suggests that the end groups of acid inhibited polymers produced with any particular initiator are similar in structure to those produced in the absence of acid by that initiator. Polymers initiated by pyridine and inhibited by sulphuric acid and by hydrochloric acid have been examined in this work, allowing evaluation of the role of the associated anion in the degradation behaviour.

Chain regularity of all polymers is believed to be very high, and, in the absence of transfer or inhibition processes, molecular weight distributions, as measured by GPC, are narrow, M_w:M_n usually being in the range 1·5 to 2·0.

EXPERIMENTAL

All but two of the polymers described in this work were prepared by solution polymerization in THF, the exceptional materials being polymerized in diethyl ether. The requisite quantity of distilled monomer was dissolved in solvent, agitated under nitrogen and initiator solution rapidly injected. Polymerization, evident by a slight exotherm, was complete within seconds. As previously stated, the very high monomer reactivity prevents the production of low molecular weight polymer by this method, the overall conversion being far faster than the rate at which large quantities of initiator can be introduced and dispersed. Acid inhibition of pyridine initiated systems was therefore used to give the low molecular weight polymers.[9] All polymers were precipitated by methanol acidified with HCl.

Initiators giving the zwitterion mechanism and used to produce the polymers whose behaviour is described here include triethylphosphine, triphenylphosphine, pyridine, 4-vinyl pyridine, lutidine, triethylamine and benzenedimethylamine.

The techniques used to study thermal stability and degradation kinetics were thermogravimetry, differential scanning calorimetry and pyrolysis–gas–liquid chromatography. A Du Pont 990 system was used for thermal analysis. Dynamic thermogravimetry was carried out with a sample size of 6 mg and a heating rate of 10°C min^{-1}. Isothermal work was conducted using the same sample size. For calorimetry a 2-mg sample and a heating rate of 20°C min^{-1} were used, this somewhat high rate being found to give optimum peak definition. Both thermogravimetry and calorimetry were carried out under a flow of 50–60 ml min^{-1} of nitrogen.

With a small number of polymers an interfaced TG–IR spectroscopy technique was used to examine the volatile products of degradation. A heated gas cell of the White type[10] was connected via a heated line to the eflux port of the TG, and by adjustment of the temperature of the cell and line to match that of the TG, volatile products were examined at the temperature of their formation. This technique was preferred to simple low temperature trapping because of the reactive nature of the likely products of degradation. Molecular weight characterization of residual polymer was conducted following degradation to 50% mass loss at 180°C on the TG, a 20-mg sample being found sufficient for this purpose.

Pyrolysis–gas–liquid chromatography was carried out on a Pye–Unicam GCV instrument fitted with a Curie point pyrolysis system and a flame ionization detector. Sample was loaded onto the pyrolysis wire by preparing a concentrated polymer solution into which the tip of the wire was dipped, the solvent being allowed to dry off before insertion into the apparatus. The chromatograph was operated isothermally with the column at 160°C, the injector at 200°C and detector at 240°C. Carrier gas flow was 40 ml min^{-1} of N_2. Pyrolysis at 358°C for 4 s was followed by separation on a 2 m 4 mm inside diameter 3% OV17 on PPQ column. The retention time of monomer was determined by injection of stabilized monomer solution.

RESULTS

Figure 1(a)–(h) illustrates the isothermal thermogravimetric response of one example of each of the various types of polymer examined. Initial rates of mass loss from these curves have been used with the Arrhenius equation to calculate activation energies. Pyrolysis–gas–liquid chromatography results are most conveniently expressed as % monomer and % non-monomer, and are listed in Table 1 along with the details of polymer preparation, the number average molecular weight, the initial rate of mass loss at 180°C, and the activation energy for the overall degradation process. Also given in the Table is the temperature at which the dynamic TG run displays 2% mass loss, this value providing a convenient, though arbitrary, indication of degradation onset. Figure 2(a)–(d) illustrates the calorimetry

TABLE 1
Effect of Initiator on Degradation Characteristics

Initiation system	M_n	*Temperature at 2% mass loss (°C)*	*Rate at 180°C* ($\%s^{-1}$)	E_a (*kcal mole*$^{-1}$)	*Pyrolysis–gas–liquid chromatography (% monomer)*
Triphenylphosphine	$1{\cdot}07 \times 10^{6}$	158	$1{\cdot}35 \times 10^{-1}$	20·03	—
Triphenylphosphine	$3{\cdot}07 \times 10^{5}$	145	$1{\cdot}64 \times 10^{-1}$	19·62	98·48
Triphenylphosphine	$2{\cdot}44 \times 10^{5}$	155	$2{\cdot}02 \times 10^{-1}$	23·86	98·91
Triphenylphosphine	$7{\cdot}00 \times 10^{4}$	135	$2{\cdot}08 \times 10^{-1}$	20·95	—
Triethylphosphine	$4{\cdot}40 \times 10^{4}$	140	$2{\cdot}45 \times 10^{-1}$	20·22	—
Pyridine	$5{\cdot}00 \times 10^{6}$	185	$7{\cdot}43 \times 10^{-3}$[a]	24·79	99·95
Pyridine	$1{\cdot}76 \times 10^{6}$	217	$6{\cdot}11 \times 10^{-3}$[a]	14·49	97·87
Pyridine	$3{\cdot}60 \times 10^{5}$	200	$5{\cdot}00 \times 10^{-3}$	14·31	—
Pyridine HCl inhibited	$4{\cdot}45 \times 10^{4}$	194	$6{\cdot}60 \times 10^{-3}$[a]	21·72	—
Pyridine HCl inhibited	$4{\cdot}20 \times 10^{3}$	167	$9{\cdot}78 \times 10^{-3}$	28·00	99·65
Pyridine H_2SO_4 inhibited	$3{\cdot}60 \times 10^{5}$	176	$6{\cdot}41 \times 10^{-2}$	18·71	—
Pyridine H_2SO_4 inhibited	$2{\cdot}40 \times 10^{3}$	145	$1{\cdot}72 \times 10^{-1}$	18·36	97·18
Pyridine H_2SO_4 inhibited	$3{\cdot}00 \times 10^{3}$	137	$2{\cdot}43 \times 10^{-1}$	11·32	94·56
Lutidine	$5{\cdot}80 \times 10^{5}$	160	$1{\cdot}17 \times 10^{-1}$	23·77	99·46
4-Vinylpyridine	$5{\cdot}30 \times 10^{5}$	175	$1{\cdot}17 \times 10^{-2}$	18·74	87·43
Benzenedimethylamine	$2{\cdot}00 \times 10^{6}$	170	$1{\cdot}83 \times 10^{-2}$	6·40	99·76
Triethylamine	$7{\cdot}00 \times 10^{5}$	181	$1{\cdot}95 \times 10^{-2}$	9·86	99·74
Pyridine in diethylether	$4{\cdot}20 \times 10^{5}$	148	$1{\cdot}39 \times 10^{-1}$	14·29	98·08
Pyridine in diethylether	$6{\cdot}90 \times 10^{4}$	150	$1{\cdot}19 \times 10^{-1}$	18·40	—

[a] Rates calculated by application of the Arrhenius equation to data obtained at higher temperatures.

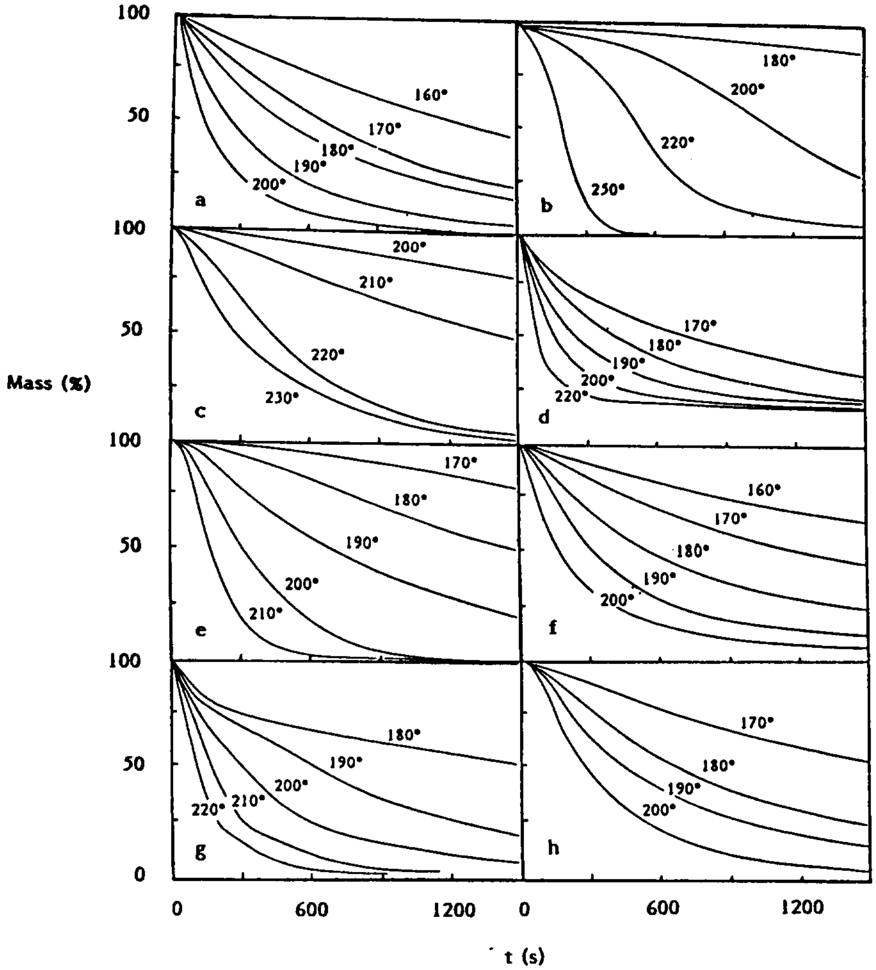


Fig. 1(a–h). Isothermal thermogravimetric analysis. a, Ph_3P initiated, M_n 1·07 × 10^6; b, Py initiated, M_n 3·6 × 10^5; c, Py initiated, HCl inhibited, M_n 4·6 × 10^5; d, Py initiated, H_2SO_4 inhibited, M_n 5·0 × 10^3; e, 4-Vinylpyridine initiated, M_n 5·3 × 10^5; f, Lutidine initiated, M_n 5·5 × 10^5; g, Pyridine initiated, solvent Et_2O, M_n 4·2 × 10^5; h, Et_3N initiated, M_n 7·0 × 10^5.

response of all polymers and is annotated with details of preparation, molecular weight and total endotherm values.

The infra-red spectrum of the volatile degradation product from a triphenylphosphine initiated polymer is compared with the spectrum of monomer vapour in Fig. 3. The result illustrated is typical of all those obtained with this technique.

Molecular weight distribution curves for original polymer and for residue after 50% mass loss are shown in Fig. 4.

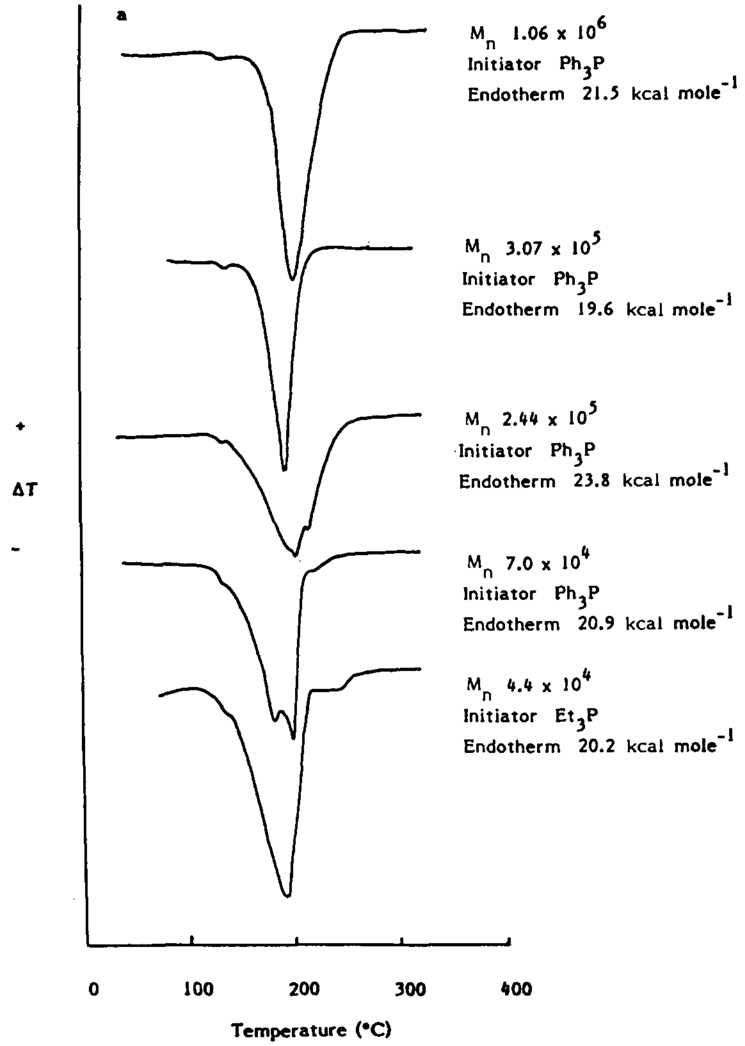


Fig. 2. (a) Calorimetric response of polymers initiated with tertiary phosphines.

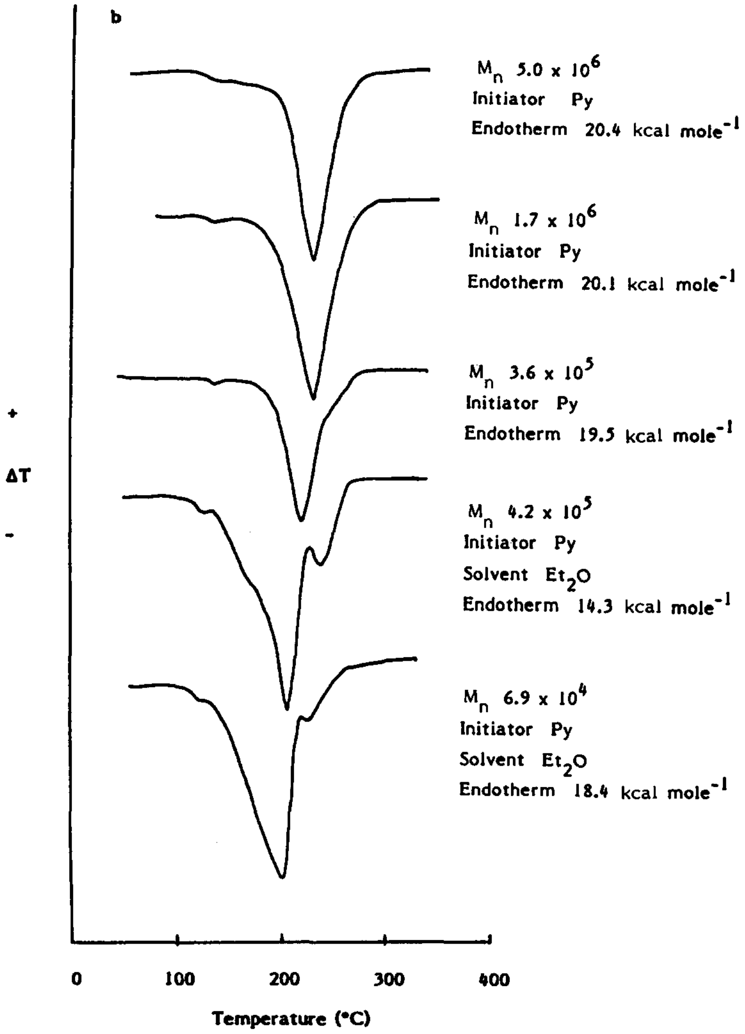


Fig. 2—*contd.* (b) Calorimetric response of polymers initiated with pyridine.

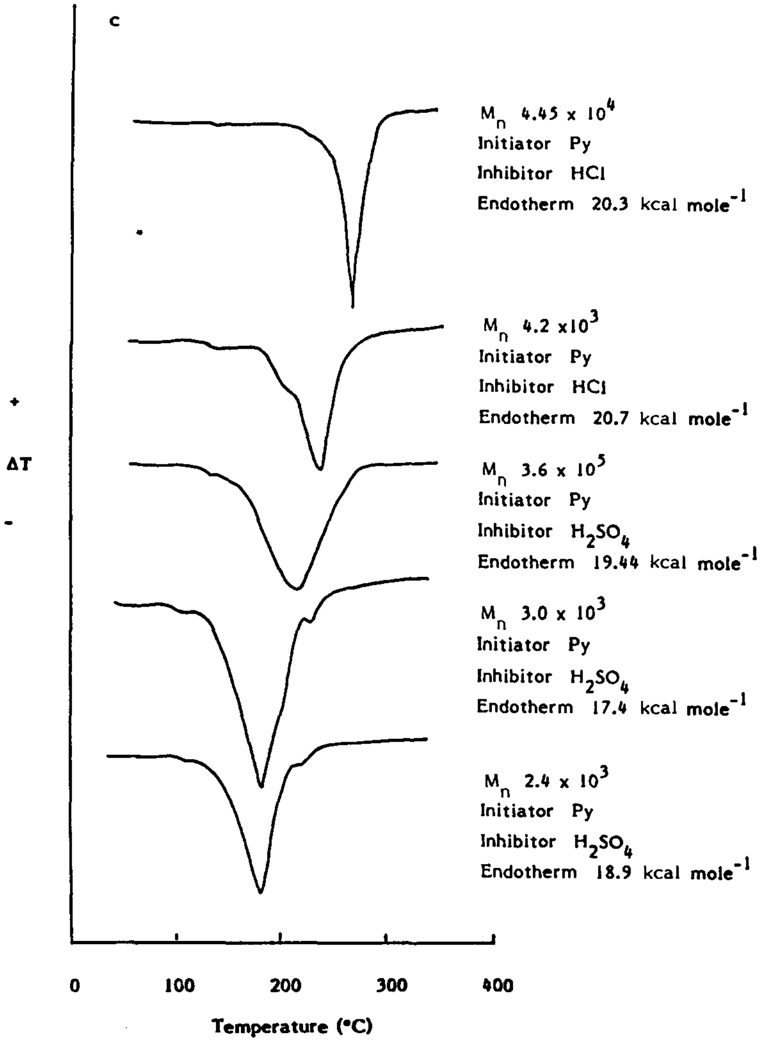


Fig. 2—*contd.* (c) Calorimetric response of polymers initiated with pyridine in the presence of strong acid inhibitors.

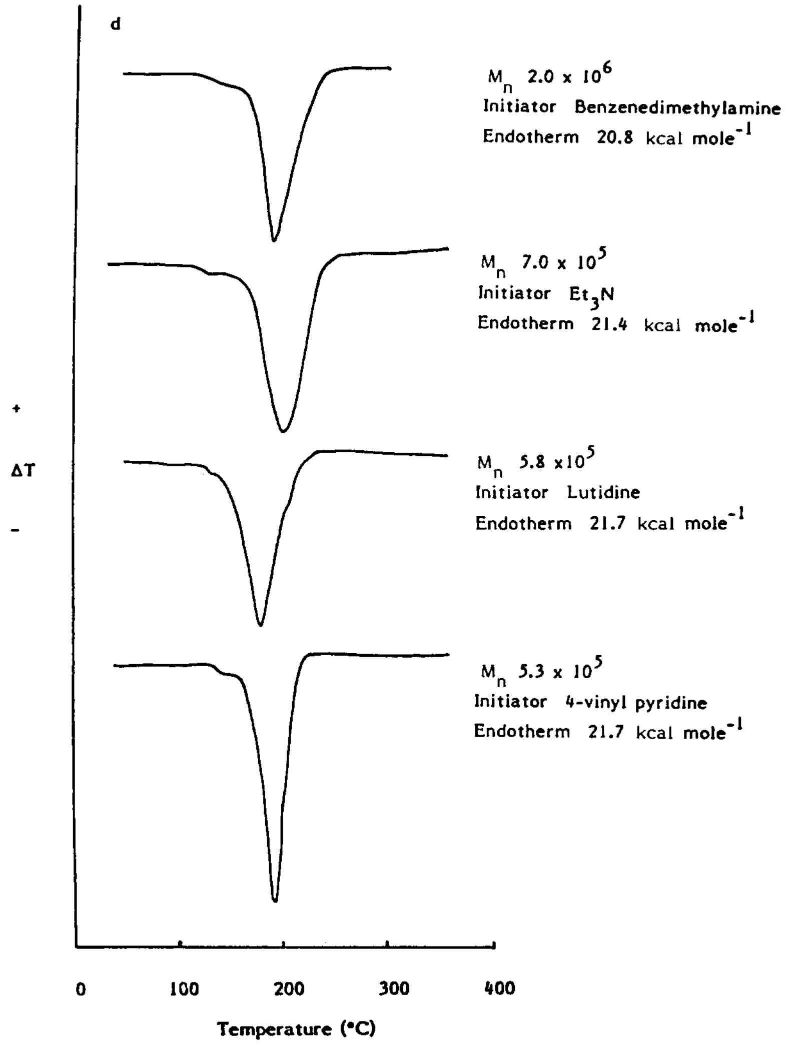


Fig. 2—*contd.* (d) Calorimetric response of polymers initiated with substituted pyridines and with other amines.

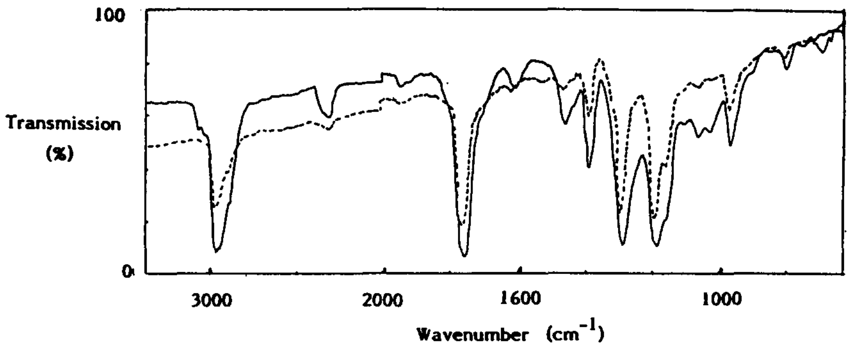


Fig. 3. Infra-red spectra of volatile degradation products. – – –, Monomer vapour. —— Degradation products of a Ph$_3$P initiated polymer at 90% mass loss and 190°C.

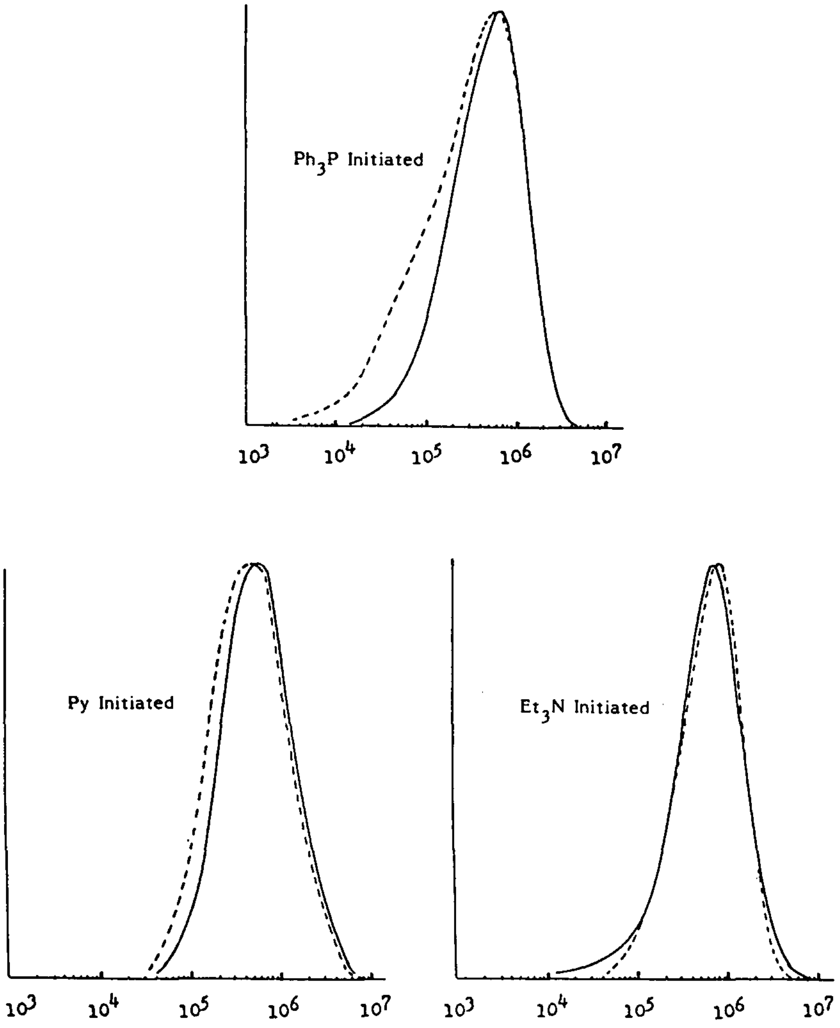
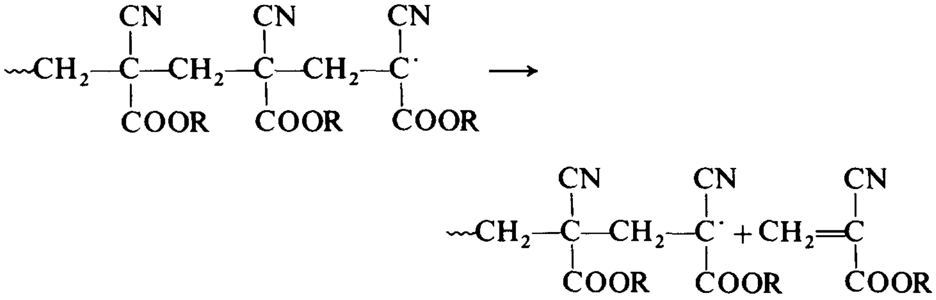


Fig. 4. Effect of degradation on molecular weight distribution. ——, Original polymer – – –, Residue at 50% mass loss.

DISCUSSION

The principal observation is that poly-*n*-butylcyanoacrylate degrades thermally between 150°C and 320°C to give volatile products, the greater part of which is monomer. The overall degradation reaction must be presumed to be a free radical unzipping of the chain:



$$\sim CH_2-\overset{CN}{\underset{COOR}{C}}-CH_2-\overset{CN}{\underset{COOR}{C}}-CH_2-\overset{CN}{\underset{COOR}{C}}{}^{\cdot} \longrightarrow \sim CH_2-\overset{CN}{\underset{COOR}{C}}-CH_2-\overset{CN}{\underset{COOR}{C}}{}^{\cdot} + CH_2=\overset{CN}{\underset{COOR}{C}}$$

Such behaviour is consistent with the structure of the polymer, the presence of the quaternary carbon conferring the radical stability normally required for an unzipping process. Additionally, the repeat unit is sterically crowded with the cyanide and ester groups severely limiting mobility, thus precluding transfer reactions.

Characterization of the partially degraded polymers indicates a process of high zip length. Table 2 summarizes the results.

To a reasonable approximation the molecular weight distribution of the residue is similar to that of the original material. Whilst some slight reduction and broadening is apparent with the triphenylphosphine initiated polymer, those initiated with pyridine and triethylamine only show the smallest of changes. Zip length must be presumed to be greater than the degree of polymerization of any of the polymers investigated; that is, 2350 repeat units. Whilst this figure is higher than that reported for most polymers, it is similar to that given[11] for poly-*p*-isopropyl-α-methyl styrene.

Two observations indicate that in the case of anionically polymerized cyanoacrylates the depolymerization is end initiated. First, choice of the

TABLE 2

Effect of Degradation to 50% Mass Loss on Molecular Weight

Initiator system	*Original*		*Degraded*	
	M_n	M_w	M_n	M_w
Triphenylphosphine	$2{\cdot}66 \times 10^5$	$6{\cdot}51 \times 10^5$	$1{\cdot}11 \times 10^5$	$5{\cdot}16 \times 10^5$
Pyridine	$3{\cdot}60 \times 10^5$	$7{\cdot}38 \times 10^5$	$2{\cdot}77 \times 10^5$	$6{\cdot}19 \times 10^5$
Triethylamine	$3{\cdot}33 \times 10^5$	$8{\cdot}81 \times 10^5$	$4{\cdot}66 \times 10^5$	$8{\cdot}63 \times 10^5$

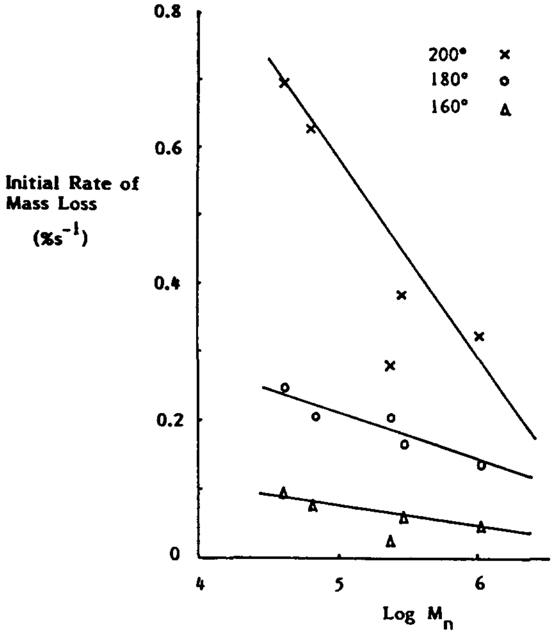


Fig. 5. Effect of molecular weight on initial rate of mass loss for polymers having the phosphonium salt end.

polymerization initiator clearly has great significance for both thermal stability and degradation kinetics. With cyanoacrylates there is no reason to believe that the initiator has any long range structural influence; structural variety is restricted to the end group and to chain length. Taking the temperature at which the sample has lost 2% mass as an indication of relative stability, Table 1 shows that the 70°C spread observed is divided into groupings associated with particular initiators. This implies that the polymerization initiator acts as the site for subsequent thermal depolymerization, and that the stability of the polymer is a function of the stability of this end group.

Secondly, within a particular initiator group the stability increases with increasing molecular weight. In general, calorimetry displays this trend more effectively than does thermogravimetry, though the mass loss rates for substituted phosphine initiated polymers show a clear dependence on the concentration of chain ends in the system. Figure 5 illustrates the relationship.

Phosphonium end group polymers give the simplest degradation behaviour. To a first approximation, isothermal mass loss curves indicate a first-order process throughout, suggesting that only one reaction, that of chain unzipping, is involved. However, on detailed analysis of rates exact correspondence to first-order kinetics only holds for the first 50% mass loss, the order increasing to slightly greater than one for the remainder of the degradation. The reason for this slight kinetic deviation in the later stages of these degradations is not obvious. Possible explanations include the onset of a termination process, some physical phenomenon associated with changing sample size, or chemical change in the degrading material. Kinetically these could be regarded as opposing reactions and would account for the slight deviation from first-order behaviour.

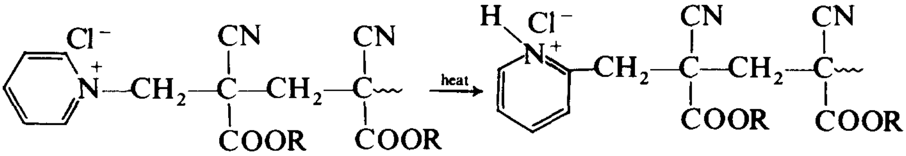
The average value of the activation energy for the phosphine initiated polymers, at 20·94 kcal $mole^{-1}$, is lower than that reported for most other polymers but is similar to that obtained[7] for low molecular weight methyl and ethyl cyanoacrylates.

Whilst the total endotherm values are relatively uniform, the shapes of the DSC plots are somewhat ambiguous. Curves obtained with the highest molecular weights are symmetrical single peaks, but those of the three lower molecular weight polymers appear to be a series of overlapped peaks. If the peaks represent separate processes, it is difficult to envisage their nature. The TG–IR technique was used to verify that in both the early and late stages of degradations of these polymers only monomer was being evolved. Pyrolysis–gas–liquid chromatography results also indicate almost quantitative conversion to monomer with both types. It is perhaps significant that the lower molecular weight polymers were prepared at a different time and using a different batch of monomer.

The behaviour of the pyridine initiated polymers differs in many respects from that of the substituted phosphine initiated materials; in particular, stability is significantly greater. Degradation onset temperature is, on average, 50°C higher, and initial rates of mass loss an order of magnitude lower. Additionally, the form of the isothermal curves is totally different, no longer being approximately first order throughout. The initial stage of the curve now shows an induction period during which degradation, or at least mass loss, proceeds at a very slow rate. This induction period merges smoothly into a period of accelerating rate, which is followed, in turn, by a period of deceleration. The latter stage of the degradation does show good correspondence to first-order behaviour. Calorimetry results indicate that stability increases slightly with molecular weight but this relationship is not apparent in the thermogravimetric behaviour. Total endotherm values are approximately the same as those obtained with the phosphine initiated materials and pyrolysis–gas–liquid chromatography again shows almost complete conversion to monomer.

The high stability of the polymers initiated with pyridine may be associated with an internal rearrangement of the pyridinium group similar to that reported[12] for quaternary salts such as *N*-methyl pyridinium iodide.

On heating this compound to temperatures of about 300°C the alkyl group migrates partly to the 2- and partly to the 4- position in the ring; the reaction is believed to be free radical in nature and proceeds at lower temperatures, with greater yield, in the presence of catalysts such as copper–bronze. An analogous rearrangement of the pyridinium chloride salt end would result in the polymer chain being linked directly into the highly stabilized ring:



Some support for this proposal is provided by the behaviour of the polymers initiated by the substituted pyridines, lutidine and 4-vinyl pyridine. With lutidine the most favourable positions for migration are already blocked and, consequently, degradation rates are only slightly less than those of a triphenylphosphine initiated polymer. The 4- position is theoretically available for migration but if the migrating species is polymeric steric factors almost certainly preclude the move. Whilst calorimetry only shows a slight difference in stability between the two polymers, on thermogravimetric analysis the material initiated by 4-vinyl pyridine appears significantly more stable, initial mass loss rates being exactly an order of magnitude less. Additionally, the isothermal TG curves for the 4-vinyl pyridine initiated polymer are similar in shape to those of polymers initiated by pyridine. However, the most significant variation in the pyrolysis–gas–liquid chromatography results, with only 87% monomer yield, is displayed by this material, which suggests that other unidentified processes may be involved in the degradation.

Difficulty still arises in completely reconciling the proposed mechanism of stabilization with the shape of the TG curves. The rearrangement reaction will make no direct contribution to the TG response and if the process is fast the mass loss behaviour should still be first order, albeit at a slow rate. If, as proposed, chains volatilize completely from the system once initiated, then an induction period should not be observed. The presence of the induction period suggests that the rearrangement process may control rate in the early stages of the degradation. A possible approach is to treat the system as a pair of consecutive first-order reactions represented as:

$$A \xrightarrow{k_1} X \xrightarrow{k_2} Y$$

In which case the intermediate species rises to a maximum concentration:

$$[X]_{\max} = [A]_0(k_1/k_2)^{k_2/(k_2-k_1)}$$

at a time of reaction:

$$t_{\max} = \frac{1}{k_2 - k_1} \ln (k_2/k_1)$$

Applying this to the system under consideration, boundary conditions can be established as follows. If A is the original polymer then the rate $A \rightarrow X$ can be taken as the rate measured immediately on commencement of the degradation; that is, during the induction period. The second rate can be taken as the rate of degradation of a phosphine initiated polymer of similar molecular weight. The first boundary condition is only valid if $k_2 > k_1$. The second is valid on the assumption that the overall rate of degradation of a phosphonium end group polymer is essentially the rate of depolymerization and is not a composite rate involving processes which do not occur in the degradation of pyridine initiated polymers. Accepting these conditions, the value of $t_{\max}$ calculated using the previous equations should correspond to the induction periods observed for the degradations. Because, in general, the pyridine initiated polymers have been degraded at higher temperatures than those initiated with tertiary phosphines, only a limited number of comparisons can be made without recourse to rates calculated by the Arrhenius equation, and thus introduction of further assumptions. The directly available results are compared in Table 3.

Agreement is only approximate, and whilst a possible source of error lies in the measurement of rates from the TG curves, the most probable explanation is that the assumption of consecutive first-order behaviour is simplistic. If the migratory rearrangement reaction is not significantly faster than a simple initiation from a chain end then a more complex reaction scheme may apply:

$$A \xrightarrow{k_1} X \xrightarrow{k_2} Y$$

$$A \xrightarrow{k_3} Y$$

Such a system will not be amenable to exact analysis, but may well account for the observed discrepancy in the consecutive first-order treatment.

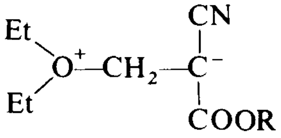
TABLE 3

Kinetic Analysis of Pyridine Initiated Polymers

M_n	T (°C)	k_1 (s^{-1})	k_2 (s^{-1})	t_{max} (s)	*Induction period* (s)
$5\cdot 00 \times 10^{6}$	200	$1\cdot 27 \times 10^{-4}$	$3\cdot 20 \times 10^{-3}$	1048	720
$1\cdot 76 \times 10^{4}$	190	$1\cdot 24 \times 10^{-4}$	$2\cdot 17 \times 10^{-3}$	1398	660
$3\cdot 60 \times 10^{5}$	180	$5\cdot 00 \times 10^{-5}$	$1\cdot 64 \times 10^{-3}$	2195	3600
$3\cdot 60 \times 10^{5}$	200	$1\cdot 50 \times 10^{-4}$	$3\cdot 81 \times 10^{-3}$	868	1020

The failure to obtain consistent and rational activation energies with the pyridine initiated polymers is explained by the composite nature of the processes occurring; that is, an internal molecular rearrangement accompanied by both simultaneous and consecutive degradation reactions.

A supposition arising from polymerization kinetics, that polymers initiated by pyridine in diethylether would show degradation behaviour similar to other pyridine initiated materials, has not been realized. Stability is much lower, and both the thermogravimetry and the calorimetry results suggest that the individual samples are not homogeneous. In all important respects, however, the behaviour of the two samples examined is identical and must be taken as typical of such systems in general. Endotherms, at 18 kcal mole^{-1}, are low, but may be influenced by the early onset of degradation being coincident with the glass transition, thus obscuring the proper position of the calorimetry base line. The shape of both TG and calorimetry curves can be interpreted as suggesting that the samples contain a relatively unstable major fraction and a more stable minor fraction, the latter perhaps identifiable with chains having the pyridinium end group. This interpretation raises the possibility that the ether group itself may be effective as an initiator, forming a zwitterion having an initial oxonium ion:



There is no kinetic evidence for this mechanism of initiation but an analogous oxonium zwitterion has been suggested to account for the activity of propylene carbonate as an initiator.[13]

An interesting contrast in the reactivity of anions is provided by the behaviour of the two sets of polymers prepared under conditions of acid inhibition. With hydrochloric acid as the inhibitor the associated anion is Cl–, and polymers of high, but somewhat irregular, stability are obtained. High stability is consistent with the presence of a pyridinium end group; the polymer–anion system being effectively the same as that of pyridine initiated polymers prepared in the absence of acid inhibitor, but killed and precipitated with methanol acidified with hydrochloric acid. With sulphuric acid inhibition, and therefore a sulphate anion, the results clearly show the formation of a thermally resistant char. The sulphate ion is presumed to be extracting the elements of water from the polymer chain with subsequent carbonization of the residue. Pyrolysis–gas–liquid chromatography results, at 97% and 94% monomer for the two sulphate polymers examined, compared with 99% for the chloride salt end polymer, also reflect this additional reaction. With all the acid inhibited polymers activation energies are inconsistent, this again being a result of more than one process occurring during degradation.

Amine terminated chains are of low stability compared with those containing the pyridinium group, thus confirming that the presence of the C—N bond in the terminal group does not, of itself, confer stability. There is some slight evidence to suggest that aromatic amine end groups are less stable than the equivalent aliphatic structure. This may be associated with the relative stabilities of the initial radical degradation products.

CONCLUSION

Poly-*n*-butylcyanoacrylates of high chain regularity degrade by an end initiated unzipping reaction giving almost quantitative conversion to monomer. At a temperature of 180°C the zip length is in excess of two thousand repeat units and may be effectively infinite. The clear influence of polymerization initiator on the subsequent stability of the chain indicates that unzipping commences at the residue of the polymerization initiator. Pyridine initiated polymers degrade at much slower rates than the other materials examined, and therefore by extension the pyridinium chloride salt end is presumed to be of greater stability. Whilst an internal rearrangement process, linking the chain directly into the ring, has been proposed to account for this higher stability, the mechanism remains unconfirmed.

The degradation behaviour of acid inhibited materials has demonstrated that the salt anion may interfere with the unzipping process if sufficiently reactive.

With the exception of the materials prepared in diethyl ether, degradation behaviour can be reconciled with the structural assumptions made on the basis of polymerization kinetics.

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