# Photopolymerization of 1,2-epoxypropane and 1,2-epoxybutane by arenediazonium salts: evidence for anion dependence of the extent of polymerization

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The rates and extents of polymerization of 1,2-epoxypropane and 1,2-epoxybutane, induced by photolysis of dilute concentrations of salts of 2,5-diethoxy-4-tolylthiobenzenediazonium ion with various Lewis acids ($SbF_6^-$, $PF_6^-$, $BF_4^-$ etc.) have been determined by viscosity, $^1H$ n.m.r. and polymer isolation methods. A clear dependence exists of the degree of conversion on the anion: thus $SbF_6^-$ salt yields up to 100% high polymer, $PF_6^-$ salt yields c. 20% high polymer, while $BF_4^-$ salt yields small conversions (2%, but increasing to 15–18% at high initiator concentrations) which consists almost entirely of oligomers, mainly the cyclic tetramer.

## INTRODUCTION

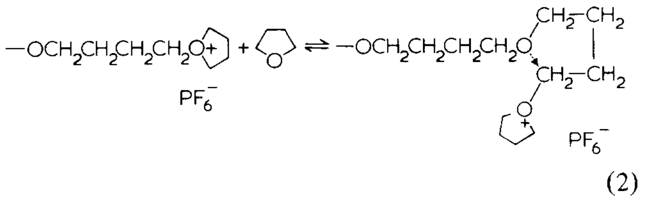
Interest in the mechanism of (ionic) polymerization of cyclic ethers by a variety of initiators[1–9] has extended recently to photopolymerization[10], particularly for improving photo-imaging systems based on the curing of epoxy monomers and oligomers[11–23]. In the latter field, studies have centred on two photocatalysts: (i) arenediazonium salts[10,17–20,22,23] and (ii) aryliodonium[10–14,21] or analogous 'onium' salts[10,15,16] For arenediazonium salts, the original mechanism[17] for the photoinitiation of epoxy polymerization depends on release of a Lewis acid, e.g.:

$$ArN_2^+BF_4^- \xrightarrow{h\nu} ArF + N_2 + BF_3 \qquad (1)$$

followed successively by complexing of $BF_3$ to the oxirane ring and cleavage of the latter to yield a propagating species of the type:

$$F_3\overset{-}{B}-O-CR_1R_2-CHR_3-O-CR_1R_2-\overset{+}{C}HR_3$$

The (thermal) cationic polymerization of tetrahydrofuran by *p*-chlorobenzenediazonium hexafluorophosphate is regarded as proceeding *reversibly* through tertiary oxonium ions[24] (after the suggestion of Bawn, Bell and Ledwith[25]), *viz.*:



(2)

The reversibility is clearly indicated by the limited conversion to polymer, with good adherence of the equilibrium concentration, $[THF]_{eq}$, to the Dainton–Ivin relation[26].

Other possible mechanisms include (i) the formation of the protonic acid, e.g. $H^+BF_4^-$ or $H^+PF_6^-$, as in the diaryliodonium salt photoinitiation[10], or $H^+[BF_3OH]^-$ or $H^+[PF_5OH]^-$; (ii) the intermediacy of aryl radicals, which are known to be formed in the photolysis[27], *viz.*:

$$ArN_2^+BF_4^- \xrightarrow{h\nu} Ar\cdot + N_2 + \cdot BF_4 \qquad (3)$$

These have been suggested to function by attacking the alpha C–H bond to yield an ether radical, which further reduces $ArN_2^+$, becoming an active 2-oxocarbonium ion[3].

Attention has been drawn to the extremely reactive carbonium ion, $Ar^+$, also formed in the photolysis, which has been matrix-isolated at 77K and characterized by e.s.r. spectroscopy as a ground triplet state[28]. This could function by direct attack on the ring to yield propagating species of the type described in equation (2).

In this study, we have examined the photopolymerization kinetics and products of 1,2-epoxypropane and 1,2-epoxybutane by a number of arenediazonium salts in order to discriminate between the possible mechanisms outlined above.

## EXPERIMENTAL

### *Materials*

Arenediazonium salts were prepared by standard methods[29] and were purified by dissolution in Analar-grade acetone followed by precipitation with diethyl ether and drying *in vacuo*. They gave satisfactory analyses by both microanalysis and nitrometer determination of available $N_2$.

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Epoxyalkanes were stirred under a nitrogen atmosphere with calcium hydride for 8 h and then refluxed overnight[30]. The resulting material was fractionally distilled, collected over molecular sieves (3Å) and stored in brown bottles under $N_2$ in a dry-box. Epikote 828, an almost monomeric form of the diglycidyl ether of bis-phenol A, was used without purification: it was the gift of Shell Chemicals Ltd.

1,2-dichloroethane was refluxed over calcium hydride for 24 h and fractionally distilled. The middle fraction (b.p. 62.4°C) was collected over molecular sieves (4 Å) and stored in brown bottles in a nitrogen dry-box.

### *Nitrogen dry-box*

This was made in the Engineering Workshop of the University of Warwick. It consisted of an aluminium and steel frame with a perspex window. It measured 75 cm (height) x 100 cm (width) x 69 cm (depth at the bottom) and x 62 cm (depth at the top). It featured a cylindrical air-lock chamber, 70 cm long x 30 cm diameter. An optically polished, circular (5 cm diameter) pyrex window at the side, remote from the air-lock, allowed direct irradiation of samples in cylindrical cells (5 cm long x 2.5 cm diameter) by light from a 200 W Hg–Xe point source lamp powered by a current-stabilized (±0.1%) supply. Nitrogen (containing 2–3 ppm moisture and 2 ppm $O_2$) was passed through a 1.2 m column containing heated (338K) BASF catalyst, to remove trace $O_2$, and two 0.9 m tubes of KOH pellets and silica gel to remove residual moisture before flushing the box. Circulating tubes from a Churchill chiller–thermoregulator were connected into the box to maintain constant reaction temperatures in the optical cells. A rotary piston vacuum pump (Genevac Ltd.) was also connected to the box to enable evacuation of prepolymer and solvents. An optical bench was stationed along the axis at right angles to the optical part of the box, on which was mounted the lamp housing, condensing lenses, iris and heat filter (1 cm of circulating water): a short section inside the box supported the cell mounting and the plastic tubing containing circulating water.

### *Kinetic measurements*

These were accomplished in three ways:

*(i) Viscometry of polymerizing solutions.* An Ostwaldt viscometer was modified to incorporate an irradiation cell, as previously described[23]. Degassed solutions of epoxyalkane (± cosolvent) containing arenediazonium salt were irradiated until the latter was completely photolysed. A nitrogen pressure was applied to force the solution above the capillary, and the flow time determined. This was repeated at measured time intervals until no further increase in flow time was detected. While it was impossible to convert these data into absolute polymerization rates, the 'viscometric profiles' of the reaction gave an indication of the course and duration of reaction, and enabled the gross effect of additives to be determined very easily.

*(ii) $^1H$ n.m.r spectroscopy of polymerizing solutions.* Samples were made up in the dry-box and sealed. They were irradiated directly above the n.m.r. probe and placed in the latter within seconds of the end of the irradiation period. The spectrometer was a Bruker WH-90 model with Fourier transform detection, enabling complete spectra to be taken repetitively every few seconds if necessary. The monomer-to-polymer conversion could be followed readily because of the different chemical shifts both of the $CH_3$ and $CH_2/CH$ protons in the two materials. The main drawback of this approach is that it is impossible to distinguish between low- and high-molecular weight polymer, for only an integrated polymer resonance is apparent.

*(iii) Sampling followed by $^1H$ n.m.r. and/or g.p.c. analysis.* The photolysis cell was charged with monomer-initiator solution in the dry-box and photolysed (usually 1–2 min) until the yellow colour of the initiator was discharged. 1 ml samples were then taken at measured time intervals and treated with a dilute solution of sodium phenoxide in the relevant monomer to terminate reaction. Monomer was then pumped away (for 24 h) and the presence (or absence) of residual entrained monomer proven by $^1H$ n.m.r. spectroscopy. The polymer was then weighed and analysed by g.p.c.

### *Polymer characterization*

This was by gel permeation chromatography carried out in the laboratories of RAPRA, Shawbury, UK. Two sets of Styragel® columns were used with tetrahydrofuran eluent and a differential refractometer detector. The column sets A4 and A8 consist of four (200, $10^3$, $10^4$ and $10^5$) and eight (2 x 60, 2 x 100, 200, $10^3$, $10^4$ and $10^5$ Å) columns respectively. The molecular weights quoted here are (uncorrected) polystyrene equivalents. Infra-red spectra of polymer samples were run on a Perkin–Elmer Model 457 instrument.

## RESULTS

### *Photopolymerization of 1,2-epoxybutane by 2,5-diethoxy-4-tolylthiobenzenediazonium hexafluorophosphate ($Dz^+PF_6^-$)*

The percentage conversion to polymer, monitored by $^1H$ n.m.r. was 14.3 when determined 250 s after photolysis of a $2.0 \times 10^{-3}$ mol dm$^{-3}$ solution. This figure slowly rose to 15.0% after $10^3$ s and remained virtually unchanged for a further $3 \times 10^3$ s, rising after $10^5$ s to 16.4%. Increasing $[Dz^+PF_6^-]$ to $4.0 \times 10^{-3}$ mol dm$^{-3}$ increased the conversion slightly (16.9% at 350 s, 19.5% at $10^3$ s, 19.8% at $5 \times 10^3$ s, 21.7% at $10^5$ s). Viscometric runs indicated a similar pattern of a rapid first stage followed by only a small but definite further conversion: thus a $2 \times 10^{-3}$ mol dm$^{-3}$ solution of $Dz^+PF_6^-$ yielded $\eta_{sp}$ immediately following photolysis of 0.85 which rose to a plateau value of 1.0 after $5 \times 10^3$ s (remaining unchanged for $7.0 \times 10^4$ s). Polymer isolated after this time yielded $\bar{M}_n = 1.26 \times 10^4$, $\bar{M}_w = 2.40 \times 10^4$, $\bar{M}_w/\bar{M}_n = 1.90$.

### *Photopolymerization of 1,2-epoxypropane by $Dz^+PF_6^-$*

The main features of this system have been published [3]. New material may be summarized as follows:

(i) The attainment of the highest specific viscosities is best achieved using monomer purified as described above. Under these conditions, superior reproducibility is also obtained (*Figure 1*) over material distilled from sodium.

(ii) I.r. spectra were run on four samples as follows:

| | |
|---|---|
| sample 1: | material from polymerization terminated by addition of water; |
| sample 2: | material from polymerization allowed to go to 'completion', i.e. to reach the plateau value of conversion; |

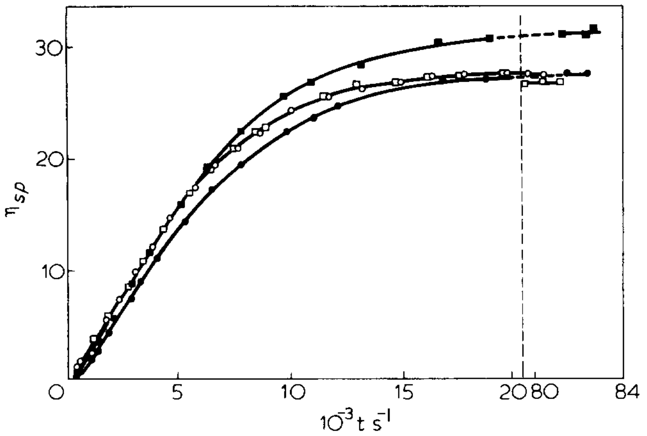


*Figure 1* Typical time-profiles of $\eta_{sp}$ in the photopolymerization of pure 1,2-epoxypropane by $Dz^+PF_6^-$ (2.0 x $10^{-3}$ mol $dm^{-3}$). Two runs carried out simultaneously on Day 1, A1, ●; B1, ○; two runs carried out simultaneously on Day 2, A2, ■; B2, □

*Table 1* Effect of addition of water to polymerizing 1,2-epoxypropane photoinitiated by $Dz^+PF_6^-$

| Time elapse from photoinitiation | $\bar{M}_n$ | $\bar{M}_w$ | $\bar{M}_w/\bar{M}_n$ |
|---|---|---|---|
| 42 h | 5800 | 11 000 | 1.90 |
| control | 8500 | 16 800 | 1.98 |
| 14d | 7800 | 15 000 | 1.92 |
| control | 8300 | 18 500 | 2.23 |

sample 3: material from polymerization allowed to go to completion and *then* treated with water;

sample 4: material from polymerization terminated with sodium phenoxide[32] and then treated with water.

Sample 1 showed a large –OH absorption which could not be removed by prolonged pumping *in vacuo*. Sample 2 showed only a small –OH band. Samples 3 and 4 showed strong –OH absorption even after pumping *in vacuo* for 2000 s, but these bands vanished after pumping for 20 000 s, indicating that they were due to entrained water.

(iii) Addition of water (0.5 ml) to polymerizing material 42 h after initiation (i.e. long after the attainment of the maximum conversion) and allowing to stand for 4 days considerably reduced the molecular weight (*Table 1*) compared with that of control material. Such an addition 14 days after initiation was, however, without comparable effect (*Table 1*).

(iv) Addition of the stable free radical, 2,2-diphenyl-1-picrylhydrazyl (DPPH) at a final concentration of 2 x $10^{-3}$ mol $dm^{-3}$ to polymerizing 1,2-epoxypropane photoinitiated by 2.0 x $10^{-3}$ mol $dm^{-3}$ $Dz^+PF_6^-$ was without effect on (i) the reaction kinetics (as indicated viscometrically), (ii) the percentage conversion and (iii) the molecular weight of recovered polymer. Oxygen saturation was also without effect.

(v) We have previously shown that the effect of adding seemingly inert cosolvents to 1,2-epoxypropane prior to photoinitiation is to considerably reduce the plateau value of $\eta_{sp}$[23]. This is now seen to be due to reductions both in molecular weight and percentage conversion (*Table 2*). (The dichloroalkanes proved to be the most satisfactory cosolvents).

(vi) The effect of varying the initiator concentration was examined from two viewpoints, i.e. (i) the degree of conversion (cf. 1,2-epoxybutane above) and (ii) variation in molecular weight. Increasing initial [$Dz^+PF_6^-$] from 1.0 to 20 x $10^{-3}$ mol $dm^{-3}$ in a series of solutions caused a gradual increase in % conversion from 12.5 to 35. The molecular weights of polymer samples from these solutions showed little dependence on initial [$Dz^+PF_6^-$].

### *Photopolymerization of 1,2-epoxypropane by other salts of $Dz^+$*

A salt that appeared virtually ineffective as a photoinitiator at 2 x $10^{-3}$ mol $dm^{-3}$ concentration was $(Dz^+)_2SnF_6.H_2O$, whilst the phosphomolybdate $(Dz^+)_3\,[PO_4 \cdot 12MoO_3 \cdot xH_2O]^{3-}$ gave only c. 7 ± 2% conversion (by $^1$H n.m.r.) even after 2 h irradiation. The tetrachlorozincate salt (2 x $10^{-3}$ mol $dm^{-3}$) underwent ready photolysis in 1,2-epoxypropane, but even 12 h later only the barest trace (<1%) of polymer was formed. The tetrafluoroborate salt gave 0.4 g of polymer from 20 g of monomer on identical treatment, and when a stronger solution was employed (2 x $10^{-2}$ mol $dm^{-3}$) the polymer yield rose to 15–18% ($^1$H n.m.r.). The g.p.c. traces of the isolated polymer showed the novel feature of two large peaks at very low (polystyrene equivalent) molecular weights, i.e. 140–148 (major) and 175–185 (minor) with a long tail to $\bar{M}$c. $10^5$. In consequence, a fractional distillation at 2–8 N $m^{-2}$ was carried out: at a bath oil temperature of 353 K (still-head temperature 337 K), 50% of the material distilled as a colourless oil which gave C, H analyses of 61.67 and 10.55% respectively. (The theoretical figures for any oligomer of 1,2-epoxypropane are C, 62.04%, H, 10.41%). Other characteristics of this fraction are (i) its i.r. spectrum (strong bands at 1067, 1086, 1110, 1143 $cm^{-1}$ with *no* –OH or carbonyl bands), (ii) an $^1$H n.m.r. spectrum typical of 'polymeric 1,2-epoxypropane', (iii) a mass spectrum with *m/e* of 45, 59, 73, 87, 103, 115, 116, 117, 129, 130, 131, 143, 145, 159, 161, 175, 217 and $M^+ = 232$ (i.e. 4 x 58) and $(M + 1)^+ = 233$. No $(M-18)^+$ peak, typical of alcohols and carbonyl compounds, was evident. All of these data, especially the analytical results and the mass spectrum, and the excellent agreement of the i.r. spectrum with the literature[31,32] clearly indicate this fraction to consist of the cyclic tetramer of 1,2-epoxypropane. The other 50% of material was slightly less volatile, but did distil in a series of fractions. These showed i.r. bands in the –OH and C=O regions, but a strong peak was present in their mass spectra corresponding to $M^+ = 290$ (5 x 58), indicating the presence of some cyclic pentamer.

*Table 2* Effect of 'inert' cosolvents on the molecular weight and conversion of 1,2-epoxypropane during photopolymerization by $Dz^+PF_6^-$

| Cosolvent (50% v/v) | $\bar{M}_n$ | $\bar{M}_w$ | $\bar{M}_w/\bar{M}_n$ | % conversion |
|---|---|---|---|---|
| $CH_2Cl_2$ | 3700 | 6400 | 1.73 | 15.9 |
| $ClCH_2CH_2Cl$ | 4600 | 7400 | 1.61 | 16.4 |
| $C_6H_{12}$ | 6200 | 11 700 | 1.89 | 7.4 |
| Control | 18 000 | 38 400 | 2.13 | 23.9 |

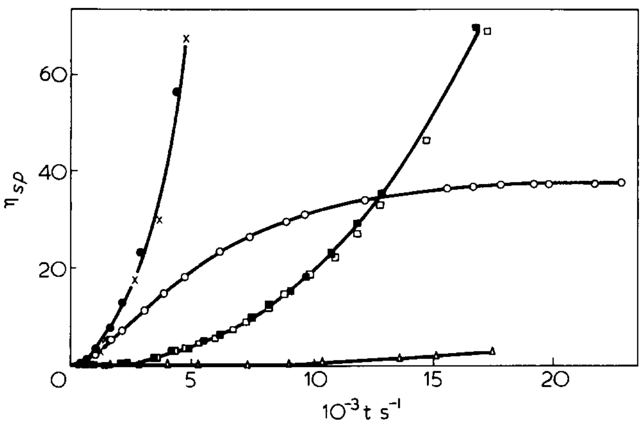


*Figure 2* Typical time-profiles of $\eta_{sp}$ in the photopolymerization of pure 1,2-epoxypropane by $Dz^+SbF_6^-$. ●, x, $[Dz^+SbF_6^-] = 2.0 \times 10^{-3}$ mol dm$^{-3}$; ■, □, $[Dz^+SbF_6^-] = 7.5 \times 10^{-4}$ mol dm$^{-3}$; △, $[Dz^+SbF_6^-] = 2.0 \times 10^{-4}$ mol dm$^{-3}$; ○, $[Dz^+PF_6^-] = 2.0 \times 10^{-3}$ mol dm$^{-3}$(for comparison)

*Table 3* Percentage conversion to polymer as a function of time for the polymerization of pure 1,2-epoxypropane initiated by $Dz^+SbF_6^-$ and determined by $^1H$ n.m.r. spectroscopy

| $2.0 \times 10^{-4}$ mol dm$^{-3}$ $Dz^+SbF_6^-$ | | $5.0 \times 10^{-4}$ mol dm$^{-3}$ $Dz^+SbF_6^-$ | | $1.0 \times 10^{-3}$ mol dm$^{-3}$ $Dz^+SbF_6^-$ | |
|---|---|---|---|---|---|
| Time(s) | % polymer | Time(s) | % polymer | Time(s) | % polymer |
| 1620 | 3.8 | 1100 | 9.3 | 565 | 14.2 |
| 2550 | 6.9 | 2230 | 15.3 | 1572 | 45.8 |
| 4560 | 11.3 | 3060 | 18.1 | 2645 | 50.9 |
| 7020 | 17.8 | 3915 | 21.1 | 3480 | 54.1 |
| 10620 | 21.2 | 4785 | 22.9 | 4350 | 57.1 |
| 13 740 | 25.9 | 5640 | 25.4 | 5232 | 60.2 |
| 16 260 | 27.4 | 7210 | 29.6 | 6060 | 61.5 |
| 19 980 | 31.3 | 9300 | 32.8 | 6800 | 62.8 |
| 22 680 | 33.3 | 10 480 | 34.9 | 7620 | 63.7 |
| 25 500 | 35.6 | 11 640 | 35.6 | 8870 | 64.7 |
| 83 250 | 52.4 | 13 180 | 37.9 | 9745 | 66.1 |
| 98 880 | 53.8 | 15 250 | 40.3 | 11 140 | 68.0 |
| 106 140 | 54.7 | 16 635 | 41.5 | 12 025 | 68.7 |
| 199 800 | 63.9 | 18 150 | 43.6 | 12 785 | 69.0 |
| 5 days | 73.6 | 58 080 | 61.9 | 14 830 | 71.5 |
| 16 days | 82.8 | 90 141 | 69.8 | 15 970 | 72.2 |
| | | 173 940 | 76.9 | 57 480 | 89.3 |
| | | | | 173 520 | 91.5 |

## *Photopolymerization of 1,2-epoxypropane and 1,2-epoxybutane by $Dz^+SbF_6^-$*

These polymerizations follow an entirely different pattern from those induced by $Dz^+PF_6^-$. *Figure 2* shows the viscometric behaviour of polymerizing 1,2-epoxypropane solutions, indicating both the greater efficiency of the $SbF_6^-$ salt and the constant increase of $\eta_{sp}$ with time (as opposed to attainment of a plateau). In conformity with these data, $^1H$ n.m.r. analysis of polymerizing mixtures (*Table 3*) indicates up to 90% conversion to polymer. Molecular weight analysis of samples (1.0 ml) taken from monomer initiated with $7.5 \times 10^{-4}$ $Dz^+SbF_6^-$ (*Table 4*) and terminated with sodium phenoxide show a steady increase in $\bar{M}_w$ with time (with considerable fluctuation in $\bar{M}_n$). The extremely rapid increase in $\eta_{sp}$ reflects increases both in $\bar{M}_w$ and in the extent of conversion. One noteworthy point is the final entry in *Table 4*, which indicates that the unterminated sample is characterized by a much lower molecular weight than the phenoxide-terminated samples: this indicates that chain-transfer takes place slowly over a long period until the most probable (thermodynamic) distribution of molecular weights is achieved. (The ideal figure of $\bar{M}_w/\bar{M}_n$ for this situation[33] is 2.0 but higher figures often appear in practice).

The effect of terminating agents upon the polymerization of 1,2-epoxypropane (induced by photolysis of $2 \times 10^{-4}$ mol dm$^{-3}$ $Dz^+SbF_6^-$) was examined. Addition of $5 \times 10^{-4}$ M sodium phenoxide immediately and completely terminated reaction, yielding somewhat higher molecular weight material than that from reaction allowed to go to completion. The addition of water gave rather unexpected behaviour: addition of a small amount ($5.6 \times 10^{-2}$ mol dm$^{-3}$) prior to photoinitiation ($1 \times 10^{-3}$ mol dm$^{-3}$ $Dz^+SbF_6^-$) produced a slightly lower conversion to polymer (88% after 3 days instead of 93%), but a much lower final $\eta_{sp}$ (3.9 at 12 400 s instead of 74.3 for the control at the same time): the molecular weight was also reduced from the control values of $\bar{M}_w = 20\,400$ ($\bar{M}_n = 5\,500$, $\bar{M}_w/\bar{M}_n = 3.71$) to $\bar{M}_w = 9\,600$ ($\bar{M}_n = 4\,400$, $\bar{M}_w/\bar{M}_n = 2.18$). Addition of 2.65 mol dm$^{-3}$ water also led to great reductions in $\eta_{sp}$ (final) and molecular weights: for a solution initiated by $6.4 \times 10^{-4}$ mol dm$^{-3}$ $Dz^+SbF_6^-$ the values are given in *Table 5*.

One general point emerging from these various data is the greater effectiveness of $Dz^+SbF_6^-$ as a photocuring agent compared with $Dz^+PF_6^-$. A systematic reduction in $[Dz^+SbF_6^-]$ leads to a significant increase in molecular weight (*Table 6*), indicating the importance of the chain-transfer process.

*Table 4* $\bar{M}$ values of polymer as a function of time for the polymerization of neat 1,2-epoxypropane initiated by $7.5 \times 10^{-4}$ mol dm$^{-3}$ $Dz^+SbF_6^-$. Aliquot samples (1.0 cm$^3$) were taken from a polymerizing mixture which had been irradiated for 120 s (complete decolouration of the solution occurred within 90 s) in a 20 cm$^3$ optical cell and terminated with 1.0 cm$^3$ $Na^+PhO^-$ ($5.0 \times 10^{-3}$ mol dm$^{-3}$) solution in pure monomer

| Time (s) | $M_n$ | $M_w$ | $M_w/M_n$ |
|---|---|---|---|
| 210 | 4336 | 11 020 | 2.54 |
| 605 | 3589 | 14 020 | 3.91 |
| 1260 | 3254 | 12 930 | 3.97 |
| 1835 | 4441 | 15 820 | 3.56 |
| 2467 | 3386 | 14 890 | 4.40 |
| 3915 | 4839 | 22 170 | 4.58 |
| 5405 | 8490 | 29 980 | 3.53 |
| 6310 | 8865 | 32 480 | 3.66 |
| 7210 | 16 730 | 35 300 | 2.11 |
| 9725 | 8890 | 36 060 | 4.05 |
| 10 805 | 5830 | 38 950 | 6.68 |
| 12 075 | 12 660 | 39 570 | 3.13 |
| * | 5076 | 14 160 | 2.79 |

* Sample *not* terminated with solution of $Na^+PhO^-$

*Table 5* Effect of adding a large quantity of water (2.65 mol dm$^{-3}$) to 1,2-epoxypropane prior to initiation by $6.4 \times 10^{-4}$ mol dm$^{-3}$ $Dz^+SbF_6^-$

| | $\eta_{sp}$[a] | % polymer[b] | $\bar{M}_n$ | $\bar{M}_w$ | $\bar{M}_w/\bar{M}_n$ |
|---|---|---|---|---|---|
| Water-doped sample | 0.2 | 100 | 275 | 295 | 1.07 |
| Control sample | 24.1 | 65 | 4500 | 9800 | 2.17 |

[a] Measured at 14 000 s; [b] Measured at 24 h

*Table 6* Effect of $Dz^+SbF_6^-$ concentration on the molecular weight of polymer

| $[Dz^+SbF_6^-]$ mol dm$^{-3}$ | $\bar{M}_n$ | $\bar{M}_w$ | $\bar{M}_w/\bar{M}_n$ |
|---|---|---|---|
| $1.0 \times 10^{-3}$ | 4770 | 12 300 | 2.58 |
| $5.0 \times 10^{-4}$ | 5760 | 14 600 | 2.49 |
| $1.0 \times 10^{-4}$ | 7600 | 19 600 | 2.58 |

Attempts to linearize the kinetics of the formation of polymer (e.g. *Table 3*) using the standard integrated rate equations led to the apparently absurd conclusion that the reaction orders are four and seven respectively for 1,2-epoxypropane and 1,2-epoxybutane. These are probably artefacts due to (i) the massive increase in the viscosity of the medium as reaction proceeds and (ii) the temperature jump in the early stages of polymerization (12 K over 400 s in an n.m.r. tube) which could not be moderated by the air-cooling thermostatting available in the n.m.r. cavity. The important effects of viscosity could be demonstrated another way: while pure 1,2-epoxybutane can be polymerized to a high level of conversion (70%), in the presence of 1,2-dichloroethane or water as cosolvents, the conversion reaches 100%.

*Polymerization of the diglycidyl ether of bis-phenol A*

Successful experiments with $Dz^+PF_6^-$ initiation have been described before. While $Dz^+BF_4^-$ and $(Dz^+)_2[ZnCl_4^{2-}]$ gave only tiny yields of high polymer, $Dz^+SbF_6^-$ at rather higher concentrations (1 to $2 \times 10^{-3}$ mol dm$^{-3}$) than used with the epoxyalkanes gave both a satisfactory rate and extent of polymerization. The g.p. chromatograms were rather complex, e.g. with the solution initiated with $2 \times 10^{-3}$ mol dm$^{-3}$ photocatalyst, $\bar{M}_w$ values of peaks appeared at values of 54 100, 15 600, 2 030, 840, 440 and 257: at lower photoinitiator concentrations, the highest $\bar{M}_w$ band was absent.

## DISCUSSION

The most significant result is the demonstration that both the extent of conversion and the molecular weight of the product polymer are critically dependent on the anion. The effectiveness of the salts of $Dz^+$ in polymerizing epoxyalkanes is clearly as follows:

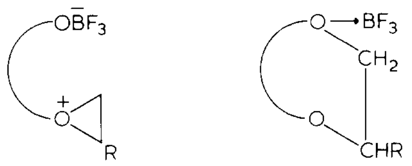
$$SbF_6^- \gg PF_6^- > \text{phosphomolybdate} > BF_4^- > SnF_6^{2-} > ZnCl_4^{2-} \sim 0$$

This implies a crucial role either for the Lewis acid released on photolysis or, possibly, its (hydrolysed) Bronsted acid form, e.g. $H^+SbF_5OH^-$ formed on reaction with trace water impurity. The sequence strongly recalls that reported by Crivello[10] for diaryliodonium salts which also photopolymerize 1,2-epoxyalkanes, *viz.*:

$$SbF_6^- > AsF_6^- > PF_6^- > BF_4^-$$

In this process, the active intermediate is regarded as the ion-pair, e.g. $H^+SbF_6^-$. The sequence strongly contrasts with that found for triphenylcarbonium salts, i.e. $PF_6^- \sim AsF_6^- \sim SbF_6^-$, in the polymerization of 1,2-epoxybutane: in this instance, $Ph_3C^+$ is the sole initiating species of any consequence[34]. Similarly, the polymerization of tetrahydrofuran in carbon tetrachloride induced by 1,3-dioxolan-2-ylium ions with $AsF_6^-$, $PF_6^-$, $SbF_6^-$ and $CF_3SO_3^-$ anions proceeds at a rate independent of anion structure[35]. Another feature indicating the essential role of the Lewis acid is our observation of large yields of cyclic tetramer in the photopolymerization of 1,2-epoxypropane by $Dz^+BF_4^-$, a circumstance noted with no other $Dz^+$ salt. The use of $BF_3$ or $BF_4^-$ salts is associated particularly with the production of cyclic oligomers, e.g. with 1,2-epoxypropane[31], 1,2-epoxybutane[32], epichlorohydrin[32], ethylene oxide[36–38], oxetane[39], in its early stages, with 1,3,6,9-tetraoxacycloundecane[40] (although, in the latter case, high polymer is produced at longer times). There are also reports of the production of sizable quantities of cyclic oligomer, however, with $PF_5$[36], $SbF_5$[36] and $SnCl_4$[41] (with ethylene oxide) and with ethyl trifluoromethylsulphonate (with oxetane[39]). In the latter study[39], it was found that no cyclic oligomer was given by triethyloxonium salts of $PF_6^-$, $SbF_6^-$ and $SbCl_6^-$.

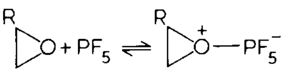
The propensity of $BF_4^-$ to be associated with cyclic oligomer formation may come about through cyclization of the propagating species[42], *viz.*:



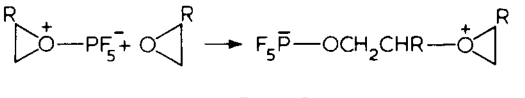
(6)

Our finding that the highly photosensitive 4-morpholinobenzenediazonium salts, e.g. of $PF_6^-$, are totally ineffective as photocatalysts indicates efficient scavenging of the photocleaved Lewis acid by morpholino residues. The cationic character of the propagation process is confirmed by the powerful termination effect of sodium phenoxide (and the lack of such an effect with added DPPH or molecular oxygen).

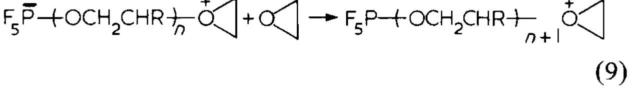
While the overall polymerizations of 1,2-epoxypropane and 1,2-epoxybutane are rather similar (as regards potency of catalyst, molecular weight of recovered polymer), there is one distinct difference, i.e. that 1,2-epoxypropane proceeds in *two* overall time domains, a fast initial stage lasting a few hundred s with $Dz^+PF_6^-$ photoinitiation (giving up to 15% conversion of high molecular weight polymer) followed by a slow stage lasting *c.* 20 000 s during which a further 5% is converted. This additional conversion is responsible for the characteristic time profile of $\eta_{sp}$. With 1,2-epoxybutane, however, the first stage is essentially the only one with negligible subsequent conversion. The mechanism for the fast stage is:



(7)

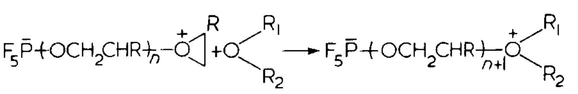


(8)

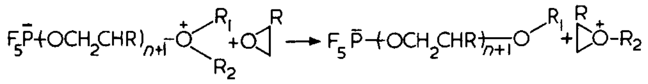


(9)

Termination may occur by transfer from the propagating species to dead polymer ($R_1OR_2$):

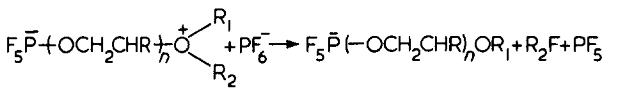


(10)



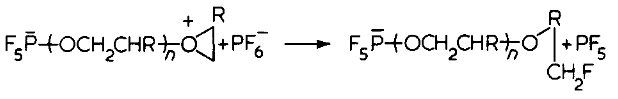
(11)

The new oxonium ion in (10) may also reaction with a $PF_6^-$ counterion:



(12)

as can the propagating species:



(13)

It appears that $SbF_6^-$ less readily engages in termination steps of type (10) or (13), and 100% conversion can be attained, provided that the viscosity of the medium is reduced by addition of a cosolvent. Two-stage processes of the type we describe for 1,2-epoxypropane with $Dz^+PF_6^-$ photoinitiation have been reported for propylene sulphide (with triethyloxonium tetrafluoroborate[45]) and 1,2-epoxybutane (with triphenylmethyl hexafluoroarsenate[46]), and reinitiation mechanisms are invoked for each system.

The final comparison we must make is with the *thermal* polymerization of tetrahydrofuran by *p*-chlorobenzenediazonium hexafluorophosphate[24]: in this case a dynamic monomer–polymer equilibrium was found. As indicated in our previous paper[23], we do not believe this situation prevails in our own system firstly because we can reinitiate a $Dz^+PF_6^-$ photopolymerized system using a fresh aliquot of $Dz^+PF_6^-$ solution and secondly, the percentage conversion can be boosted by taking higher initiator concentrations at the start of the experiment.

The most significant finding is that high molecular weight material is obtained, particularly from the $PF_6^-$ salt, for both epoxyalkanes. As recently as 1976, Dreyfuss[6] remarked: 'Nonco-ordinate cationic polymerizations of 1,2-epoxides have not been reported to give high molecular weight polymers. In fact, molecular weights of 1 000 or less seem to be the rule'. This view was influenced by the preoccupation in the literature with $BF_4^-$ salts, e.g. of triethyloxonium and triphenylcarbonium ions; and the use of $PF_6^-$ salts is to be preferred in procedures dependent on high molecular weight material such as photoimaging.

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