The Electron Beam-Induced Cationic Polymerization of Epoxy Resins

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SYNOPSIS

The rapid, efficient electron beam-induced cationic polymerization of multifunctional epoxy monomers has been carried out in the presence of diaryliodonium and triarylsulfonium salts. These polymerizations take place at low doses (1–3 Mrad), which make them attractive for commercial applications. The factors that contribute to the high reactivity of these monomers are discussed.

INTRODUCTION

The use of electron beam (e-beam) radiation to carry out rapid, pollution free, low energy crosslinking polymerizations of multifunctional vinyl monomers for coating applications is an established technique.[1] "E-beam curing," as it is termed, is most advantageously applied to the cure of coating materials that are either heavily pigmented or are comparatively thick in cross section. In such applications, ultraviolet radiation-induced polymerization is impractical, whereas the great depth of penetration of the e-beam radiation permits the polymerization of these substrates with relative ease. Traditionally, multifunctional acrylate and methacrylate monomers have been widely used in e-beam curing and polymerization results by means of a free radical mechanism initiated by solvated electrons and free radicals produced by bond scission in the monomers. There are also cases in which the cationic polymerization of certain monomers can take place under the influence of e-beam radiation.[2] These polymerizations are initiated by cation-radicals and free ions (cations) and require highly purified and dry monomers.[3] In one application of this technology, polymers bearing pendant glycidyl groups have been used as negative tone e-beam photoresists for photolithographic masks.[4-6] It is assumed that crosslinking in these polymers occurs as a result of free cations produced by irradiation.

Recently, the γ-ray[7] and electron beam-induced[8] cationic polymerization of vinyl ether monomers and oligomers, in the presence of reducible onium salt photoinitiators, has been reported. An abbreviated mechanism proposed by Hult and Sundell[9] involves the two major pathways shown in Scheme 1. In the first pathway, fast electrons generated by γ-rays ionize the vinyl ether monomer to produce a cation-radical, which collapses to a α-ether free radical with the ejection of a proton. The α-ether radical can reduce an onium salt such as a diaryliodonium salt or a triarylsulfonium salt indicated in eq. (2) by $Ar_nO_n^+X^-$, to generate a carbocation, which then initiates cationic polymerization.[10] Similarly, in pathway 2, solvated electrons produced by the γ-rays can directly reduce the onium salt to give radical species and an anion, X^-. The anion combines with a proton from eq. (1) to give a strong protonic acid, HX, also capable of initiating polymerization of the vinyl ether. Although the processes shown in eq. (1), (2) and (4) may be rather inefficient, vinyl ethers polymerize very well under either γ-ray or electron beam irradiation because they are so reactive and require very low levels of initiating species.

Consideration of the mechanism shown above suggested that the γ-ray and e-beam induced cationic polymerization of other related ether-containing monomers should be possible in the presence of reducible onium salts, such as triarylsulfonium and diaryliodonium salts. Of particular interest was the possible use of ionizing radiation to polymerize monomers and oligomers containing epoxide groups. Neither the e-beam nor the γ-ray polymerization of multifunctional epoxide monomers has been re-

Pathway 1:

$$\text{Scheme equations}$$
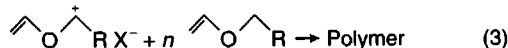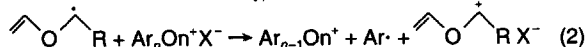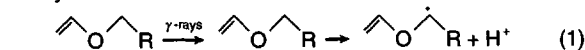
Pathway 2:
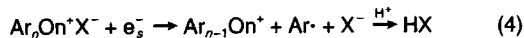
Scheme 1

ported in the literature. Initial attempts in this laboratory to use e-beam irradiation for the polymerization of commercially available bisphenol-A diglycidyl ether monomers or the difunctional cycloaliphatic epoxide monomer, 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate, were disappointing. Polymerization did occur slowly in the presence of diaryliodonium and triarylsulfonium salts, but only after massive radiation doses (100–300 Mrad) were applied. In retrospect, this is not surprising considering the relatively low order of reactivity of these monomers in the onium salt photoinitiated cationic polymerizations. Such monomers are less reactive and polymerize more slowly than either vinyl ethers or acrylates and methacrylates, even under the best conditions of photoinitiated (UV) polymerization.[11] In addition, the electron beam-induced redox decomposition of onium salts would be expected to be a less efficient method of generating protonic acids since more steps are required that involve free radical species, which can undergo a multitude of competing side reactions. In contrast, under UV irradiation, the quantum yield for the production of strong protonic acids by irradiation of the onium salts is quite high and is of the order of 0.5 to 0.7.[12] One way of compensating for both of the problems cited above would be to employ more reactive epoxide monomers than the commercially available diglycidyl ethers and biscycloaliphatic epoxides mentioned above.

EXPERIMENTAL

Materials

4-Vinylcyclohexene dioxide, **I**, was purchased from the Union Carbide Corp. and was purified by fractional distillation prior to use. Silicone epoxides **II–V** were prepared as previously described.[13,14] The syntheses of the photoinitiators, diphenyliodonium,[15] triphenylsulfonium,[16] (4-octyloxyphenyl)-phenyliodonium[17] and diphenyl(4-thiophenoxy-

phenyl)sulfonium[18] salts were carried out as described in the indicated literature references.

E-Beam Irradiation

Samples to be irradiated were coated onto 2 mil poly(ethylene terephthalate) film using 1 and 3 mil drawknives. An Energy Sciences Inc. Electrocurtain Model CB-150 electron beam irradiator, operating at 165 KeV and equipped with a 15 cm linear cathode, was used to irradiate the samples. The wet film samples were attached to a continuous web and passed through the beam. Experiments were run under nitrogen and air at a constant web speed. The dose was varied by changing the amperage applied to the filament. Samples were tested for tackiness immediately on exiting the irradiation chamber. This qualitative test was performed by placing and twisting a thumb under moderate pressure on the cured film. If the film did not deform under these conditions, it was classified as tack-free.

Glass Transition Temperature Measurements

T_g measurements were made at 20°C/min using a Perkin-Elmer DSC-7 Differential Scanning Calorimeter.

RESULTS AND DISCUSSION

### The Design of E-Beam Curable Epoxy Monomers

A major effort in this laboratory in recent years has been the design and synthesis of novel epoxide monomers with high reactivity in photoinitiated cationic polymerization. In recent publications,[13,14] two classes of epoxide monomers were described, which undergo photoinitiated cationic polymerization at rates that exceed the photoinduced free radical polymerization of multifunctional acrylate and methacrylate monomers. The first class of these monomers includes multifunctional cycloaliphatic monomers typified by 4-vinylcyclohexene dioxide (2-epoxyethyl-7-oxabicyclo[4.1.0]heptane), **I**, which contain no heteroatoms in the molecule other than the epoxide oxygens.

I
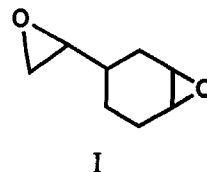
A second class of even more highly reactive epoxide-containing monomers are silicone epoxides, of which the structures shown below are typical.[13,14]

II

III

IV

V
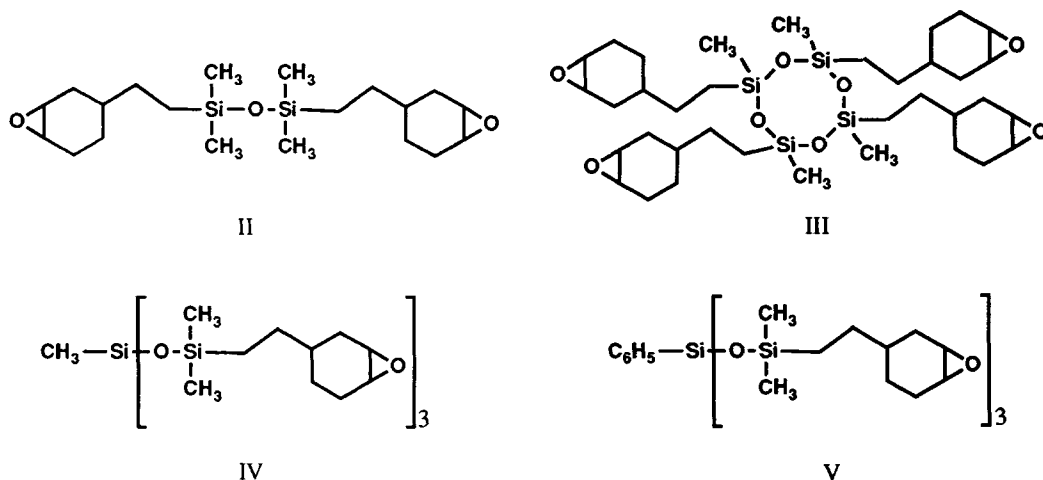
These monomers may be prepared in a straightforward manner by the direct platinum–catalyzed hydrosilylation of the appropriate vinyl-containing epoxide. For example, shown in eq. (6) is the synthesis of monomer **II**.

(6)
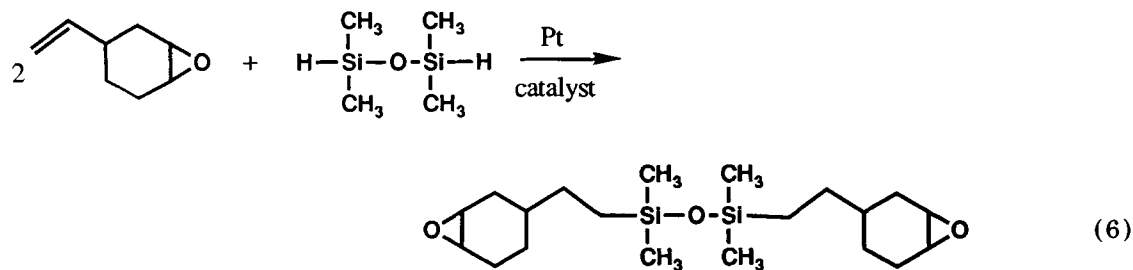
The E-Beam Cure of Monomers I–V

Based upon the observed high reactivity of monomers I–V in UV induced cationic polymerization, it was decided to attempt their polymerization using e-beam irradiation. Accordingly, a preliminary study was carried out to evaluate the polymerizability of these monomers and to establish experimental boundary conditions. Shown in Table I are the results of that study using I as the monomer.

Films of the liquid monomer containing the indicated onium salt initiator were irradiated at room temperature under a nitrogen atmosphere and then were immediately tested after irradiation for their state of cure as indicated by tackiness. In Table I and in subsequent tables, (+) indicates the film was tack-free, while (±) means that it was slightly tacky, denoting partial cure, and (−) means no cure. As Table I shows, monomer I undergoes facile e-beam induced cationic polymerization in the presence of diaryliodonium and triarylsulfonium photoinitiators bearing the SbF_6^- counterion. When these photoinitiators were omitted, no polymerization occurred. Transparent, colorless films were obtained, which

were crosslinked and completely insoluble in all solvents. In the case of Ph_2I^+ SbF_6^-, minimum dose rates as low as 1 Mrad were effective in initiating polymerization at photoinitiator concentrations of 0.5 mol %, however, 2 Mrad consistently gave completely tack-free coatings. While successful e-beam polymerizations of monomer I occurred in the presence of Ph_2I^+ SbF_6^-, $(4\text{-}C_8H_{17}OPh)PhI^+$ SbF_6^-, and Ph_3S^+ SbF_6^- salts, the corresponding photoinitiator, $(4\text{-PhSPh})Ph_2S^+$ SbF_6^-, was less effective due to its poorer solubility in the monomer. However, increasing the dose from 2 Mrad to 8 Mrad resulted in tack-free films, even with this photoinitiator.

As expected, there is a considerable effect due to the nature of the counterion present in the onium salt photoinitiators on the rate of e-beam induced cationic polymerization of this epoxy monomer. Comparing both diaryliodonium and triarylsulfonium initiators containing the SbF_6^-, AsF_6^-, and PF_6^- counterions in Table I, it can be seen that those bearing the SbF_6^- counterion are the most effective.

Silicone–epoxy monomers are more reactive than simple epoxy monomers, such as I, in photoinitiated

Table I   The E-Beam Polymerization of Monomer I[a]

Initiator	Initiator Conc. (mol %)	Dose (Mrad)	Result
None	—	2	—
Ph_2I^+ SbF_6^-	0.5	2	+
Ph_2I^+ SbF_6^-	0.25	2	+
Ph_2I^+ SbF_6^-	0.25	1	±
$(4-C_8H_{17}OPh)PhI^+$ SbF_6^-	0.5	2	+
Ph_3S^+ SbF_6^-	0.5	2	+
Ph_3S^+ AsF_6^-	0.5	2	—
Ph_3S^+ PF_6^-	0.5	2	—
Ph_3S^+ PF_6^-	0.5	3	—
$(4-PhSPh)Ph_2S^+$ SbF_6^-	0.5	2	—
$(4-PhSPh)Ph_2S^+$ SbF_6^-	0.5	4	±
$(4-PhSPh)Ph_2S^+$ SbF_6^-	0.5	8	+

[a] Cured as 3 mil coatings on poly(ethylene terephthalate) films under nitrogen at ambient temperature (~ 25°C).

cationic polymerization using onium salts[13] and this is also observed in their e-beam cure. The minimum dose required to cure a 1 mil liquid film of difunctional silicone–epoxy monomer II on a glass substrate in nitrogen to a tack-free state using 0.5 mol % $(4-C_8H_{17}OPh)PhI^+$ SbF_6^- was found to be 1 Mrad. This specific photoinitiator salt was chosen because of its excellent solubility in monomer II. Cured films of this polymerized monomer are transparent, colorless, hard, and brittle. Using a dose of 2 Mrad, films 10 mil in thickness were cured. Differential scanning calorimetry measurements gave a T_g of 181°C for this film, which compares very favorably with the similar value (187°C) obtained for the UV induced polymerization of II, using the same diaryliodonium salt.[13] The excellent, high T_g is characteristic of cured epoxy silicone resins and is a consequence of their unique structure and high reactivity.

In Table II is shown a study of the effects of photoinitiator structure, concentration, and dose on the e-beam cure of monomer II.

A 2 Mrad dose was sufficient to completely crosslink monomer II in the presence of as little as 0.25 mol % Ph_2I^+ SbF_6^-. Once again, polymerization was not observed when this monomer was irradiated in the absence of an onium salt initiator. Similarly, $(4-C_8H_{17}OPh)PhI^+$ SbF_6^- and $(4-PhSPh)Ph_2S^+$ SbF_6^- gave cured, crosslinked films at, respectively, doses of 2 and 3 Mrads. As was noted in the previous study involving monomer II, diaryliodonium salts

and triarylsulfonium salts bearing the SbF_6^- counterion were much more effective as initiators than their analogs bearing the AsF_6^- and PF_6^- counterions.

Results from the e-beam induced polymerization of cyclic and branched tri- and tetrafunctional silicone epoxy monomers III, IV, and V are given in Table III.

Like II, these monomers are highly reactive and underwent facile e-beam induced cationic polymerization in the presence of both diaryliodonium and triarylsulfonium SbF_6^- salt initiators. The T_g values determined for the e-beam cured monomers once again are extraordinarily high and compare well with those measured for these monomers cured with UV irradiation using the same initiator (Ph_2I^+ SbF_6^-).[13,14]

The e-beam curing of thin film coatings of multifunctional acrylate and methacrylate monomers is usually carried out in an inert atmosphere containing less than 200 ppm oxygen. This measure is necessary to counter the effects of oxygen inhibition, which is an inherent drawback in the radiation-induced free radical polymerization of these monomers. Likewise, it has been reported that oxygen has a considerable retarding effect on the γ-ray induced cationic polymerization of vinyl ether monomers in the presence of onium salt photoinitiators.[8] This effect has been explained as being due to a decrease in the efficiency of reduction the onium salt photoinitiators, caused by scavenging by oxygen

Table II   The E-Beam Polymerization of Monomer II[a]

Initiator	Initiator Conc. (mol %)	Dose (Mrad)	Result
None	—	3	—
Ph_2I^+ SbF_6^-	1.0	2	+
Ph_2I^+ SbF_6^-	0.75	2	+
Ph_2I^+ SbF_6^-	0.50	2	+
Ph_2I^+ SbF_6^-	0.50	3	+
Ph_2I^+ SbF_6^-	0.25	2	+
Ph_2I^+ PF_6^-	0.50	3	—
$(4-C_8H_{17}OPh)PhI^+$ SbF_6^-	0.5	2	+
Ph_3S^+ AsF_6^-	0.5	3	±
Ph_3S^+ PF_6^-	0.5	3	—
$(4-PhSPh)Ph_2S^+$ SbF_6^-	0.5	3	+
$(4-PhSPh)Ph_2S^+$ PF_6^-	0.5	3	—

[a] Cured as 3 mil coatings on poly(ethylene terephthalate) films under nitrogen at ambient temperature (~ 25°C).

Table III   The E-Beam Polymerization of Monomers III, IV, and V[a]

Monomer	Initiator[b]	Dose (Mrad)	Result	T_g
II	None	3	–	–
III	Ph_2I^+ SbF_6^-	2	+	190
III	Ph_3S^+ SbF_6^-	2	+	–
III	Ph_3S^+ SbF_6^-	3	+	–
III	$(4\text{-}C_8H_{17}OPh)PhI^+$ SbF_6^-	2	+	–
III	$(4\text{-}PhSPh)Ph_2S^+$ SbF_6^-	2	+	–
IV	Ph_2I^+ SbF_6^-	2	+	176
V	Ph_2I^+ SbF_6^-	3	+	185

[a] Cured as 3 mil coatings on poly(ethylene terephthalate) films under nitrogen at ambient temperature ($\sim$ 25°C).

[b] In all cases 0.5 mol % photoinitiator was used.

of both α-ether radicals and solvated electrons. It seemed worthwhile, however, to attempt the e-beam polymerization of several of the monomers described in this article in the presence of ambient air. The results of this study are shown in Table IV.

Clearly, multifunctional epoxy monomers undergo facile Ph_2I^+ SbF_6^- assisted e-beam induced cationic polymerization in the presence of oxygen. What is even more surprising is that the dose requirements in the presence of oxygen are not substantially higher than under nitrogen. Approximately, 0.5 Mrad is the limiting dose necessary for the gelation of a 3 mil film of monomer II in the presence of 0.5 mol % of Ph_2I^+ SbF_6^-. Alternatively, the limiting dose is 1 Mrad at an initiator concentration of 0.25%. This observation is extremely interesting from a commercial point of view since the cost of maintaining an inert atmosphere over samples contributes substantially to the overall cost of an e-beam cured coating.

Table IV   The E-Beam Polymerization of Various Monomers in the Presence of Oxygen[a]

| Monomer	Initiator Conc. (mol %)[b]	Dose (Mrad)	Result
I	1.0	2	+
II	0.50	2	+
II	0.50	1	+
II	0.50	0.5	±
II	0.25	2	+
II	0.25	1	±
III	0.50	2	+

[a] Cured as 3 mil coatings on poly(ethylene terephthalate) films in air at ambient temperature ($\sim$ 25°C).

[b] Ph_2I^+ SbF_6^-.

Mechanism of the E-Beam Curing of Epoxy Monomers

Based upon the results of the e-beam polymerization studies described above, the mechanism shown in Scheme 2 is proposed for the e-beam induced polymerization of epoxy monomers. In Scheme 2, the mechanism is illustrated with diaryliodonium salts using cyclohexene oxide as a model compound for the monomers described in this article.

As in the case of vinyl ether monomers, e-beam
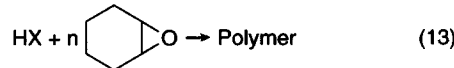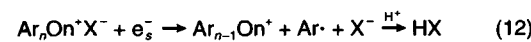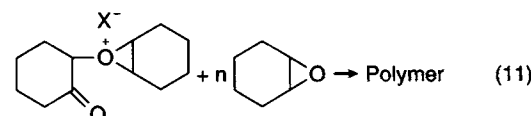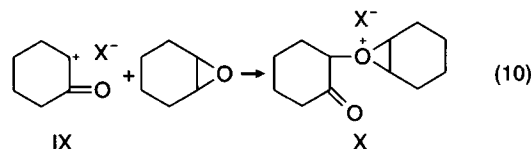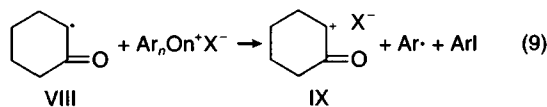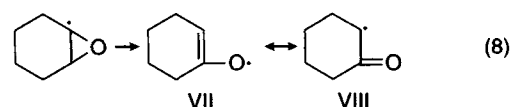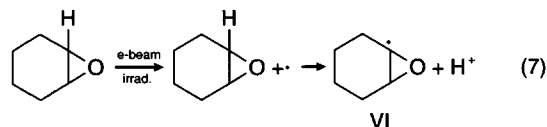
Scheme 2

irradiation of the monomers initially produces free radical species first by ionization of the epoxide, then by loss of the tertiary proton α to the epoxide oxygen. Next, cleavage of a carbon–oxygen bond is facilitated by the facile rearrangement of the initially-formed, carbon-centered radical **VI** to the resonance stabilized radicals **VII** and **VIII**. This reaction has considerable literature precedent and an analogous mechanism has been proposed by Gritter and Wallace for the free radical-induced ring opening of propylene oxide.[19] This reaction is further driven by the relief of approximately 112 kJ mol^{-1} ring strain from the opening of the epoxycyclohexane ring.[20] Radicals **VI, VII,** and **VIII** can subsequently reduce the onium salt photoinitiator as illustrated in eq. (9) for diaryliodonium salts. As depicted, the products are an aryl iodide, an aryl radical, and the cation **IX**. Initiation of polymerization takes place either by direct attack by **IX** on an epoxide oxygen to form an oxonium salt, which undergoes subsequent cationic chain propagation, or by interaction of **IX** with trace amounts of water and other hydroxylic impurities to generate protonic acids, which then initiate polymerization. Reduction of the onium salt by solvated electrons with subsequent initiation of polymerization by the protonic acid formed may also occur and this is shown in eqs. (12) and (13) of Scheme 2.

The oxidation of the free radical **VIII** to cation **IX** by an onium salt is governed by the free energy of the reaction, which depends on the difference in the oxidation potential of the free radical, E_r^{ox}, and the reduction potential of the onium salt, E_o^{red}.
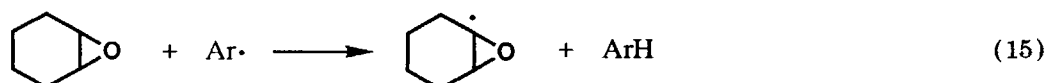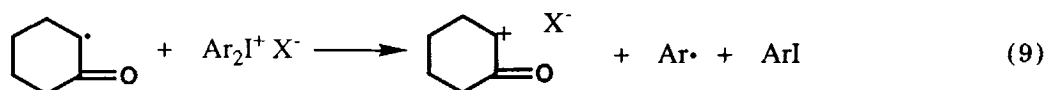
$$\Delta G = E_r^{ox} - E_o^{red} \tag{14}$$

The E_o^{red} values for diphenyliodonium and triphenylsulfonium salts have been found to be -14 and -112 kJ mol^{-1} respectively.[21] The reduction potential of diphenyl(4-thiophenoxyphenyl)sulfonium salts have been estimated to be approximately 23 kJ mol^{-1} lower than that of the corresponding triphenylsulfonium salts. For the electron transfer reduction to occur, the value of ΔG must be negative (i.e., exothermic) by at least 10 kJ mol^{-1} or more. The oxidation potential for the cyclohexanone radical, **VIII**, is estimated be of the order of 120–130

kJ mol^{-1}, which is sufficient to reduce both diaryliodonium and triarylsulfonium salts. Although it appears that the oxidation potential for **VIII** has not been determined experimentally, this value is in good agreement with the known oxidation potential of related free-radical species.[22,23]

Solvated electrons must also account for a substantial portion of the reduction of the onium salts. Hult and his coworkers[8] have shown that the γ-ray induced cationic polymerization of vinyl ethers in the presence of both diaryliodonium and triarylsulfonium salts is suppressed in the presence of oxygen, which primarily intercepts intermediate free radicals and, to a lesser extent, also intercepts solvated electrons.[8] Although no substantial increase in the gel dose was noted in e-beam cures with Ph_2I^+ SbF_6^- when nitrogen was replaced with air, it should be noted that none of the experiments reported here were carried out with rigorous exclusion of oxygen. In an Electrocurtain Irradiator with a moving web, the oxygen concentration is markedly reduced, but not completely eliminated from the reaction zone using a nitrogen purge. Doubtless, enhanced e-beam cure rates and lower minimum gel doses would be expected if those cures were carried out in the complete absence of oxygen.

The above mechanism does provide alternative explanations for the observed high cure rates and apparent lack of a significant oxygen inhibition effect in the e-beam cure of the epoxy monomers. Resonance stabilization, represented by radicals **VII** and **VIII**, may inherently reduce the overall reactivity of these species toward reaction with molecular oxygen. Even if oxygen did react with radical **VIII**, the resulting product, an α-peroxy ketone radical, would most likely undergo either spontaneous or acid induced fragmentation to other radical species. Further, in at least one case, indications of the existence of a free-radical-induced decomposition of an onium salt has been noted in cycloaliphatic epoxides. Ledwith[24] has obtained a quantum yield of 3 for the photolysis of diphenyl(4-thiophenoxyphenyl)sulfonium salts in cyclohexene oxide. This suggests that the catalytic cycle shown in eqs. (9) and (15) may operate, which gives rise to catalytic decomposition of the onium salt with consequent efficient initiation of polymerization.

$$\text{(cyclohexanone radical)} + Ar_2I^+ \ X^- \longrightarrow \text{(cyclohexanone cation)} \ X^- + Ar\cdot + ArI \tag{9}$$

$$\text{(epoxycyclohexane radical)} + Ar\cdot \longrightarrow \text{(epoxycyclohexyl radical)} + ArH \tag{15}$$

Similar chain reactions may occur in the e-beam irradiation of onium salt photoinitiators and may partially account for the highly efficient cationic polymerizations that have been observed.

Based on the results and the mechanism shown in Scheme 2, it can be concluded that the rate of the e-beam cationic cure of epoxide monomers depends on two major factors: the rate of the generation of the initiating species and the rate of the polymerization of the monomer. The rate and efficiency of generation of intermediate free radicals and cation radicals depends directly on the dose and the dose rate. To some degree, the magnitude of the population of free radicals present will determine the proportion of these species undergoing reduction of the onium salt as compared to those which undergo bimolecular coupling, disproportionation, and other side reactions. The actual formation of the initiating species, that is, cations and Brønsted acids, ultimately depends on the difference in the redox potentials between the intermediate free radical species (or solvated electrons) and the onium salt. The redox potentials, in turn, are related to the structures of both the starting epoxide and the onium salt. The reduction potential of the onium salt is determined only by the structure of the cation and is not influenced by the character of the anion.[12] The polymerization rate is governed primarily by the ring strain in the epoxy group and is also determined by such factors as steric hindrance and the presence of other basic functional groups in the molecule. There is also a marked effect due to the character of the counterion of the onium salt on the polymerization rate. As has been shown in this article, as well as in previous studies on photoinitiated cationic polymerization,[12] those onium salts that bear counterions of lowest nucleophilic character and highest stability give the fastest polymerization rates. Among the onium salts used in this study, those bearing the SbF_6^- were the most effective. The degree of conversion of the optimally cured monomers described in this article appears to be essentially quantitative. This conclusion is supported by the very high T_gs obtained, which were nearly identical to the values obtained from the UV induced cationic polymerization of the same monomers. In the latter case, the conversions have been shown by differential scanning calorimetry (DSC) to be essentially quantitative. In addition, further heating of the e-beam cured samples in the DSC produces no further heat of polymerization, indicating that the polymerization is complete. The T_g values obtained on 3 vs. 10 mil films of e-beam cured monomer II, using the same initiator (Ph_2I^+ SbF_6^-), were identical, indicating that the same degree of cure

was obtained for samples of both thicknesses at a dose of 2 Mrad.

An approximation for the relative reactivities of various monomers in e-beam induced polymerization can be obtained by a comparison of the minimum gel doses required to initiate polymerization. In this article it has been demonstrated that the minimum gel dose required for initiation of cationic polymerization in epoxy monomers I–V, using the optimum onium salt photoinitiators, is of the order of 1–2 Mrad. The reactivity of these systems is, therefore, somewhat greater than the e-beam induced free radical polymerization of multifunctional acrylates and methacrylates (3–4 Mrad).[25] Estimates of the minimum gel dose for vinyl ether monomers is approximately 0.2 to 0.4 Mrad or five to ten times more reactive than the epoxide monomers described in this article.[8]

CONCLUSIONS

In this preliminary study we have demonstrated for the first time, e-beam curable epoxy compositions, which undergo rapid curing at doses that are comparable with existing commercial processes for multifunctional acrylates and methacrylates. Moreover, it was also shown that the epoxy resins unexpectedly can be cured at the same doses in the presence of air and without the usual need for blanketing with an inert atmosphere. These epoxy resins have excellent mechanical and chemical properties and should find use in a number of coating, adhesive, and composite applications.

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