Photoreactivity of Expanding Monomers and Epoxy-Based Matrix Resin Systems

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ABSTRACT: The relative photoreactivity of five expanding monomers (EMs) in homopolymerization, and as comonomers in a candidate low shrinkage dental matrix resin, were evaluated. The EMs were 2,8-dimethyl-1,5,7,11-tetraoxaspiro[5.5]undecane (DM-TOSU); 3,9-diethyl-3,9-dipropionyloxymethyl-1,5,7,11-tetraoxaspiro[5.5]undecane (DEDPM-TOSU); 1,3-dioxane-2-one (DOO); 4-methyl-1,3-dioxane-2-one (M-DOO); and 5,5-diethyl-1,3-dioxane-2-thione (DE-DOT). The candidate low shrinkage resin system was an 80/20 mixture of UVR-6105 epoxide/polytetrahydrofuran ($M_n \approx 250$). All reaction mixtures contained a diaryliodonium salt as a photoinitiator and camphorquinone as photosensitizer. Reactivities were evaluated using photodifferential scanning calorimetry. For homopolymerizations, the reactivity ranking (based on time to exotherm peak and total enthalpy) was DE-DOT $\gg$ DM-TOSU $>$ DOO $>$ M-DOO $\geq$ DEDPM-TOSU. In the comonomer system, the reactivity ranking was M-DOO $>$ DEDPM-TOSU $>$ DM-TOSU $>$ DOO $\geq$ DE-DOT. This experimental work was substantiated and extended by molecular modeling studies employing the AM1 semiempirical method. Heats of formation of protonated EM structures, and heats of formation and potential energies of possible polymerization pathways were estimated. The relative reactivities of EM-based polymerization systems are related to chemical structure and the dominance of the most favored reaction mechanism. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 1715–1724, 2000

Key words: photopolymerization; expanding monomers; matrix resin systems; polymerization mechanisms, semiempirical calculations; reaction energetics

INTRODUCTION

Polymeric composite restorative dental materials have been the subject of considerable research and development during the past 45 years. Many innovative matrix resins, synthetic fillers, and cure systems have been developed for use in restorative composites.[1] Conventional restorative systems[2,3] have some major performance deficiencies related to polymerization shrinkage.[4,5] Considerable research to solve this problem has focused on the development of expanding matrix resin systems. The principal elements of a prototype photoinitiated expanding matrix resin system are an expandable monomer, an epoxy comonomer system, and a photoinitiator/sensitizer system.
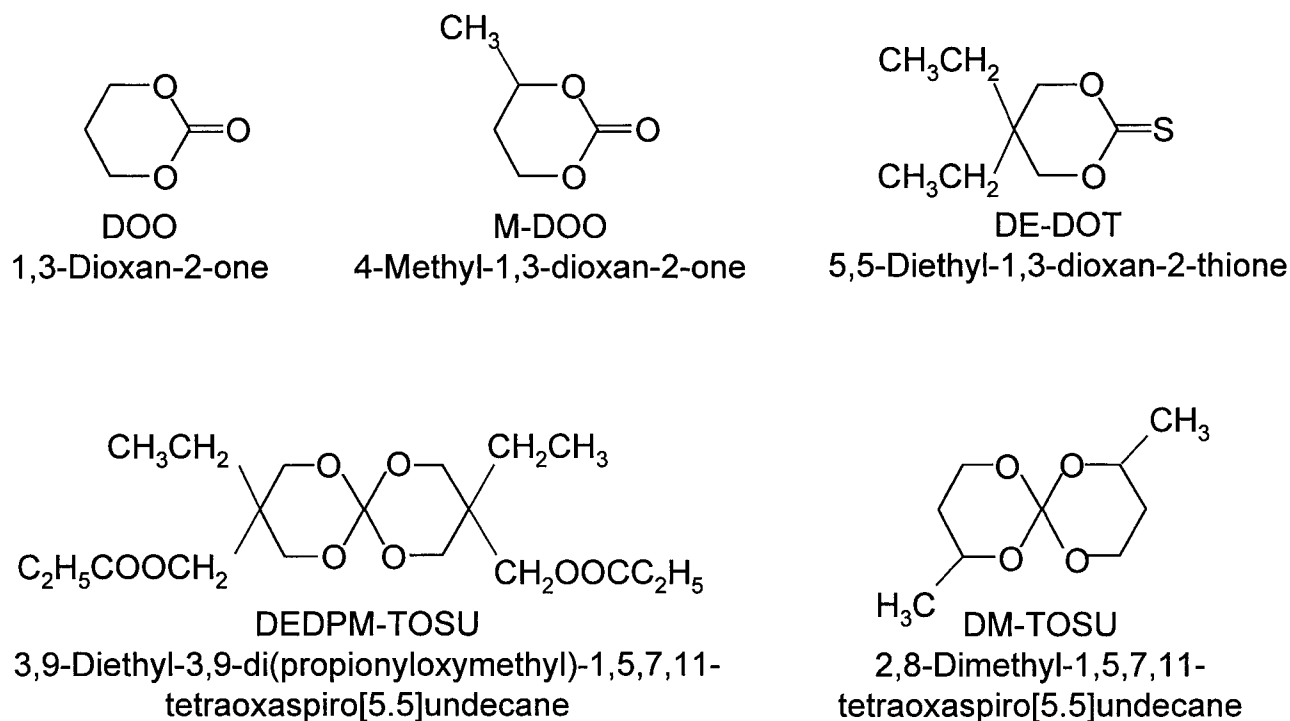
**Figure 1** Structures of potential expanding monomers.

Expandable spiro ortho carbonate (SOC) monomers seem to be the most promising candidates among the oxaspirocyclic monomers that have been developed as expanding monomers.[6] The incorporation of SOCs in dental matrix resins has been investigated in several different systems.[7–12] These initial studies were conducted using mixtures of unsaturated SOCs and bisphenol A glycidyl methacrylate (BISGMA)-based systems. In some cases, the resultant free-radical initiated copolymerization reduced the degree of shrinkage but not to an acceptable level for practical use. More recent studies[12–22] have focused on photoinitiated cationic polymerization of expandable SOCs with compatible epoxy resins. The results of our recent studies 11–13 are very promising.

The copolymerization of epoxy groups and SOC spirocyclic rings when mixtures of SOCs and compatible epoxy comonomers are cured with BF$_3$ complexes has been reported.[23] For example, when a mixture of 24% SOC was cured with 76% of an epoxy resin (Dow DER 332) at 100–150°C, a crosslinked copolymer was obtained with a 1.1% volume expansion.[23] However, it is not clear whether the product was a polymer blend or a copolymer. A model SOC/epoxy cationic polymerization has been studied using glycidyl phenyl ether as the model epoxy compound and BSS (a benzyl sulfonium salt) as the catalyst.[24] Studies of the volume change and polymer composition are claimed[25] to have established the copolymerization of SOCs with epoxy compounds.

A new class of photoinitiator/sensitizer systems that generate protons with high quantum yield upon irradiation are available for use as photoinitiators for cationic polymerization of cyclic ethers, cyclic acetals, lactones, and epoxies.[26] These initiators are complex aryl onium salts of metal halides that efficiently generate acid upon photolysis. The diaryliodonium salts[27,28] and the triarylsulfonium salts[29,30] are potential photoinitiators for a wide range of SOC/epoxy comonomer mixtures. In order to activate these photoinitiators with visible light sources, photosensitizers are required. Many compounds are available for this use (camphorquinone, perylene, thioxanthenones, etc.).

The ultimate goal of the research is to produce a nonshrinking, high-performance dental resin system with optimal cure characteristics, structural integrity, and biocompatibility that has the potential of long-term clinical success as a stable matrix resin for dental composites. The successful development of such a material would greatly improve the longevity of dental composite/adhe-
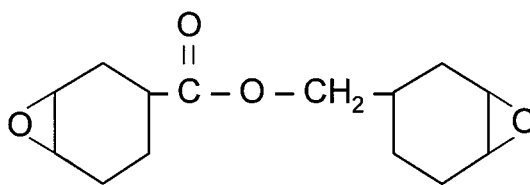
3,4-Epoxycylcohexanemethyl-3,4-epoxycyclohexane carboxylate
UCC UVR 6105
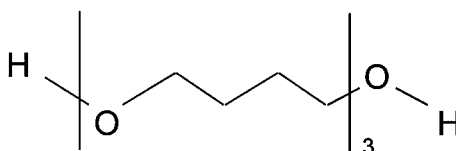
Polytetrahydrofuran ($M_n \simeq 250$)
PTHF

Figure 2 Structures of diepoxide and polyol coreactants.

sive systems and substantially improve dental patient care.

The specific objectives of this investigation were (a) to screen five expanding monomers for relative photoreactivity during UV light initiated homopolymerization, and (b) to evaluate the visible light initiated copolymerization of expanding monomer/diepoxide/polyol mixtures as potential low shrinkage dental matrix resin formulations.

MATERIALS AND METHODS

Reactants and Reagents

Included in this study were two tetraoxaspiro-[5.5]undecanes, two cyclic carbonates, one cyclic thiocarbonate, one diepoxide, one polyol, one photoinitiator, and one photosensitizer. The two substituted 1,5,7,11-tetraoxaspiro[5.5]undecanes [TOSUs] synthesized by Midwest Research Institute were: 2,8-dimethyl [DM-TOSU], and 3,9-diethyl-3,9-di(propionyloxymethyl) [DEDPM-TOSU]. The two cyclic carbonates were: 1,3-dioxan-2-one [DOO], and 4-methyl-1,3-dioxan-2-one [M-DOO]. The thiocarbonate was 5,5-diethyl-1,3-dioxan-2-thione [DE-DOT] (see Fig. 1). The cycloaliphatic diepoxide supplied by Union Carbide was UVR 6105 and the polyol supplied by Aldrich Chemical

was polytetrahydrofuran [p-THF-250] (see Fig. 2). The photoinitiators supplied by General Electric and Sartomer were diaryliodonium hexafluoroantimonates; and the photosensitizer supplied by Aldrich Chemical was camphorquinone (CQ) (see Fig. 3).

Experimental Procedures

Five homopolymerizations were conducted. Five copolymerization reaction mixtures were prepared at expanding monomer (EM)/epoxy/polyol reactant ratios of 10/70/20 (mole %). Each reaction mixture contained 0.2 mole % of photoinitiator and 0.4 mole % of CQ. The photopolymerization of each reaction mixture was evaluated by photoscanning differential calorimetry (PDSC). The photohomopolymerizations of expanding monomers were conducted using UV irradiation (285–445 nm) at selected temperature levels in the range of 80–140°C whereas the photocopolymerizations of expanding monomer/epoxy/polyol mixtures were performed using visible light (VL) irradiation (>418 nm) while the reaction temperature was maintained at 30°C.

The rate and extent of the polymerization of each reaction mixture during irradiation with UV or VL were determined using a differential scanning calorimeter (DSC) equipped with a differen-
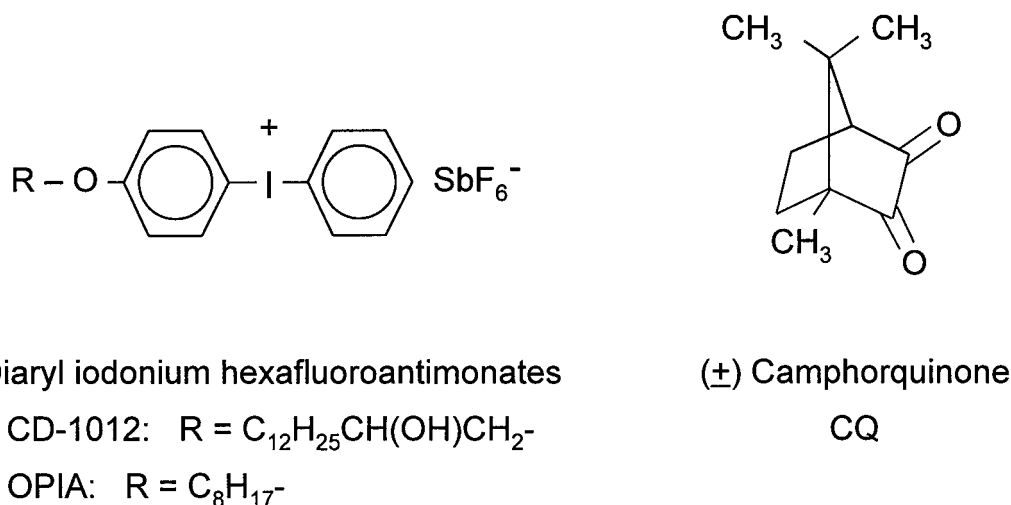
Figure 3 Structures of photoinitiators and photosensitizer.

tial photocalorimeter (PDSC), containing a 200-watt mercury lamp that was used unfiltered (285–445 nm) or filtered so as to emit light at a wavelength greater than 418 nm (Dupont Model 910 DSC with PDSC 930 unit, TA Instruments USA, Inc., New Castle, DE). A sample weighing 17–19 mg was placed in a DSC liquid sample pan equilibrated at 30°C in a nitrogen atmosphere (40 cc N_2/min) and irradiated for 20 min. The intensity of the unfiltered light was about 50 mW/cm^2 vs filtered light $\geq$ 418 nm at 5 mW/cm^2) as measured with a Demetron Model 100 Curing Radiometer 7 cm above the sample. The photopolymerization parameters measured for each example were enthalpy of reaction (ΔH), induction time, time to maximum exotherm, and percent conversion at maximum. The photopolymerizations were characterized further by generating conversion and rate plots and calculating rate constants (k). A typical PDSC thermogram of the photopolymerization of a epoxy/polyol mixture is shown in Figure 4.

Computational Procedures

The AM1 method was used for these calculations as implemented in the program *AMPAC with Graphical User Interface*.[31] Transition states (TS) for the reactions studied were located by performing reaction coordinate studies where the reactant species were forced together along a proposed reaction vector. The maximum in energy resulting from this process was fully optimized (no constraints on geometry) using a gradient minimization technique. The proposed TS was

then characterized to assure that one and only one negative eigenvector was present[32,33] and that the eigenvector corresponding to the single negative eigenvalue was a motion leading forward to products and backward to reactants. Ground state species (reactants and products) were optimized with respect to a minimum energy geometry and were then characterized in a similar manner with the requirement that there be no negative eigenvectors present. Heats of reaction (ΔH_{rxn}) were computed as the difference between the heats of formation (ΔH_f) of the reactant molecules. Enthalpies of activation (ΔH_{act}) were computed as the difference between the TS H_f and the energy of the van der Waals complex of reactant molecules. Entropies (and corresponding Gibb's free energies) were not computed for these processes since bond-breaking and bond-forming processes have large enthalpy values that dwarf the entropy effects.

RESULTS AND DISCUSSION

The investigation of the photoreactivity of the expanding monomers consisted of four interrelated studies: (a) reaction temperature and photohomopolymerization, (b) UV light initiated photohomopolymerization, (c) visible light initiated photocopolymerization, and (d) mechanistic and computational analysis of photopolymerization systems.

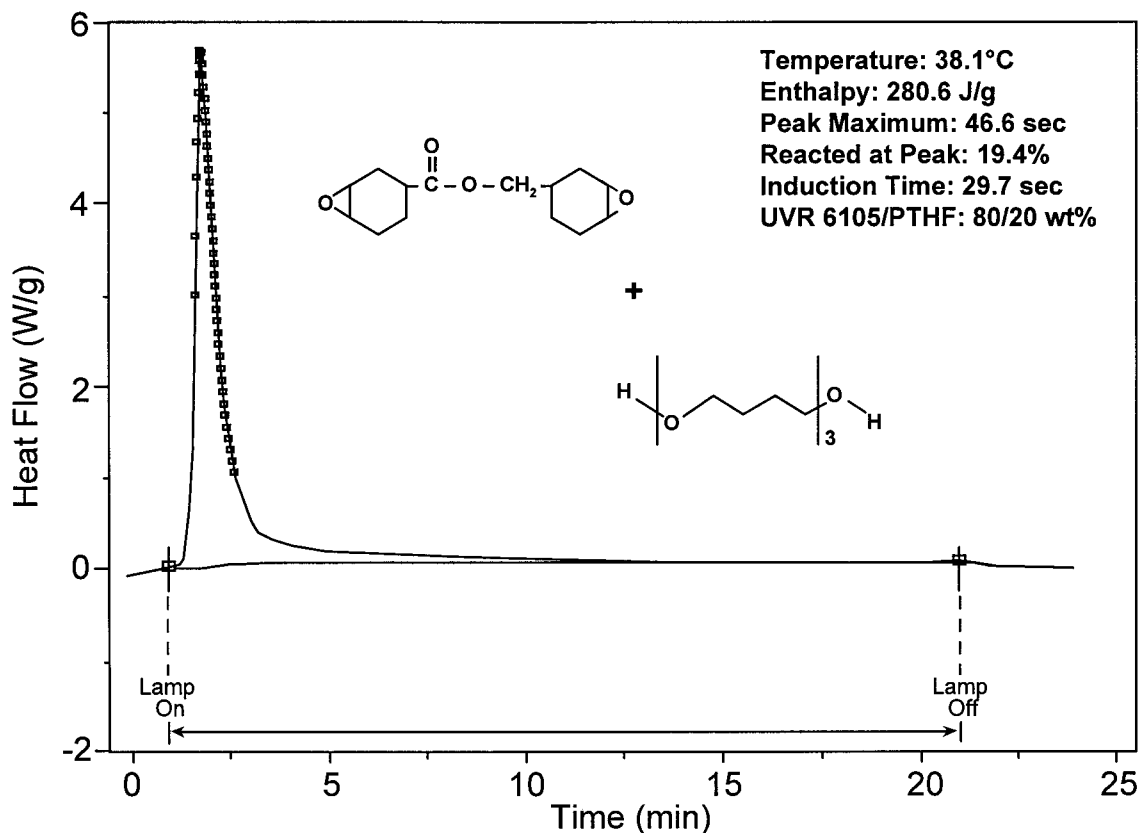The effect of temperature on the UV-initiated homopolymerization of the 2,8-dimethyl TOSU is

Figure 4 Photoreaction profile of a diepoxide/polyol mixture.

shown in Figure 5. Samples were run isothermally at temperatures ranging from 80 to 140°C. These thermal profiles clearly show that the reaction rate *increases* as the temperature is *increased* from 80 to 130°C. However, increasing the temperature to 140°C results in an apparent decrease in the enthalpy of reaction. (The apparent decrease may be related to the loss of mass due to volatilization of the compound.) Similar experiments with other expanding monomers provided the basis for selecting a temperature of 110°C for screening the relative homopolymerization rates of a series of expanding monomers. A temperature of 110°C was selected because it provided a fairly rapid reaction rate, but did not appear to change the reaction mechanism or result in volatilization and/or decomposition of the test samples. It was also well above the melting points of the solid monomers.

The UV light initiated photohomopolymerization exotherm profiles of five expanding monomers (2 dioxanones, 2 TOSUs, and 1 dioxanethione) at 110°C are shown in Figure 6. Comparison of the exotherms reveal differences in the photo-

reactivities of the five monomers: (a) the most reactive monomer was the diethyl dioxane-thione, DE-DOT (Curve A); (b) of the two spiroorthocarbonates, the disubstituted compound DM-TOSU (Curve B) was much more reactive than the tetrasubstituted monomer DEDPM-TOSU (Curve E); and (c) in the homopolymerizations of dioxanones, the methyl substituted compound M-DOO (Curve C) was slightly less reactive than the unsubstituted cyclic carbonate DOO (Curve D). The photoreactivities of these monomers were based primarily on the relative positions and magnitudes of the observed exotherms. The relative reactivities of these monomers during homopolymerization is quite different than during copolymerization with diepoxide/polyol mixtures containing them.

The photocopolymerization exotherm profiles of five expanding monomer/diepoxide/polyol mixtures are shown in Figure 7. Comparison of the five exotherms reveal differences in the photoreactivities of the mixtures: (a) the most reactive mixture was the diepoxide/polyol mixture which contained the methyl dioxane, M-DOO (Curve A);
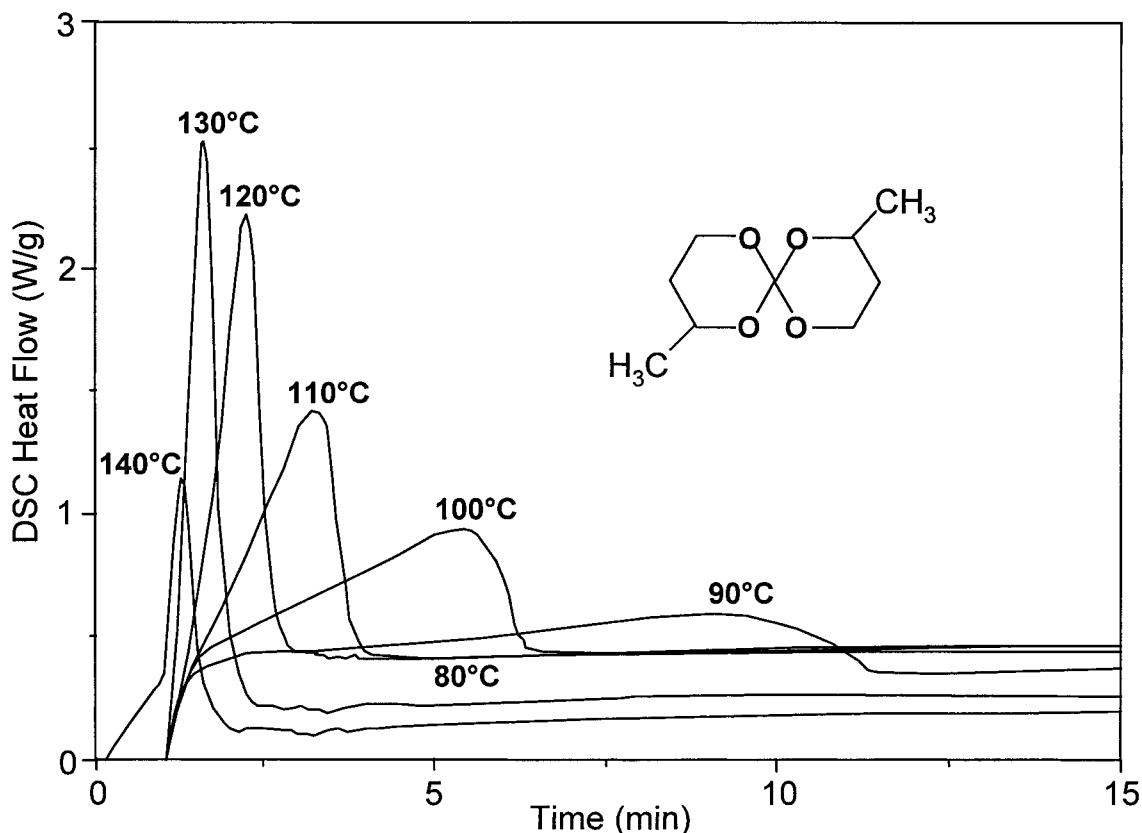
Figure 5 Photohomopolymerization reactivity profiles of 2,8-dimethyl-1,5,7,11-tetraoxaspiro[5.5]undecane at elevated temperatures.

(b) for reaction mixtures containing substituted TOSUs, the one containing DEDPM-TOSU (Curve B), was much more reactive than the mixture containing DM-TOSU (Curve D); and (c) the reaction mixture containing the cyclic carbonate, DOO (Curve C), was more reactive than the mixture containing the thiocarbonate, DE-DOT (Curve E). Generally, the observed reactivities of the expanding monomers and mixtures containing them can be elucidated by polymerization mechanisms and semiemperical calculations.

Mechanistic and computational studies were conducted on all of the expanding monomers and comonomer mixtures involved in this investigation. Two example systems were selected to illustrate the utility of this approach. Studies involving the SOC, DM-TOSU, and the thiocarbonate, DE-DOT, were undertaken in an attempt to provide a basis for interpreting the observed difference in reactivities of test mixtures containing them.

Two reaction mechanisms that may be involved in the photohomopolymerization of DM-TOSU and during the photocopolymerization of

reaction mixtures containing this monomer and a model epoxide (cyclohexene oxide) are shown in Figure 8. The homopolymerization mechanism, represented by the top equation, depicts nucleophilic attack by the TOSU oxygen (the one adjacent to the ring substituent) at the methyl-substituted carbon in a ring-opened TOSU intermediate to initiate chain growth. The copolymerization mechanism, represented by the bottom equation, involves nucleophilic attack by the oxirane oxygen at the methyl-substituted carbon in a single ring opened TOSU intermediate to yield an active site for chain growth.

Similar studies involving the thiocarbonate, DE-DOT, were conducted. The reaction mechanisms that may be involved in the homophotopolymerization of DE-DOT and during the photocopolymerization of mixtures containing this monomer and a model epoxide, cyclohexene oxide, are shown in Figure 9. The homopolymerization mechanism, represented by the top equation, depicts nucleophilic attack by the thiocarbonyl sulfur at available ring carbon sites to yield a ring
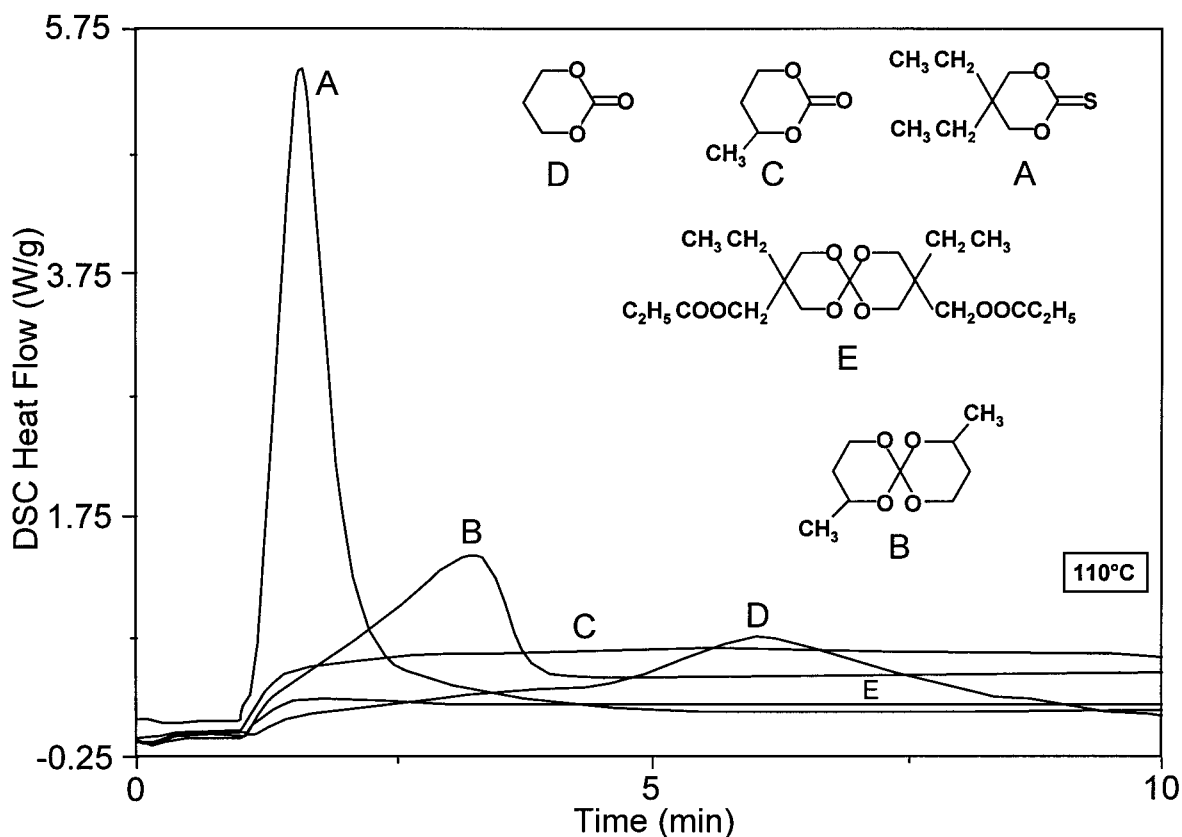
Figure 6 Photohomopolymerization reactivity profiles of five expanding monomomer structures at 110°C.

opened thiocarbonate intermediate to initiate chain growth.

The copolymerization mechanism, represented by the bottom equation, involves nucleophilic attack by the oxirane oxygen at an unsubstituted carbon site, yielding a ring-opened thiocarbonate intermediate with an active site for chain growth.

The results of the computational studies to evaluate the reaction energetics of the proposed photopolymerization mechanisms for the two expanding monomers are summarized in Figure 10. AM1 semiempirical quantum mechanical calculations were employed to evaluate the reaction energetics of the proposed homo- and copolymerizations.

Comparison of the calculated potential energy barrier (E_a) and the heats of reaction (ΔH_r) of the proposed polymerizations revealed the following: (a) Nucleophilic attack of the diethyl-DOT is favored at the 4,6-unsubstituted carbon sites, whereas attack of the dimethyl-TOSU is energetically favored at the 2,8-substituted carbons. (b) The most energetically favored reaction is the homopolymerization of the diethyl-DOT. The *lower* activation energy (13 kcal/mole) and the

greater exothermicity of the reaction (-19 kcal/ mole) indicate that this homopolymerization is favored both kinetically and thermodynamically. (c) Copolymerization of the TOSU with the model epoxide has a lower activation energy than the corresponding TOSU homopolymerization, and thus copolymerization is favored.

These computational predictions support the assumption that the more reactive EMs are more likely to participate in chain stopper reactions that retard the rate of epoxide homopolymerization than less reactive EMs.

CONCLUSIONS

Based on the results of this investigation, the following conclusions are drawn:

- The photopolymerization characteristics of EMs and EM/diepoxide/polyol mixtures vary markedly and can be related to the chemical composition of the coreactants.
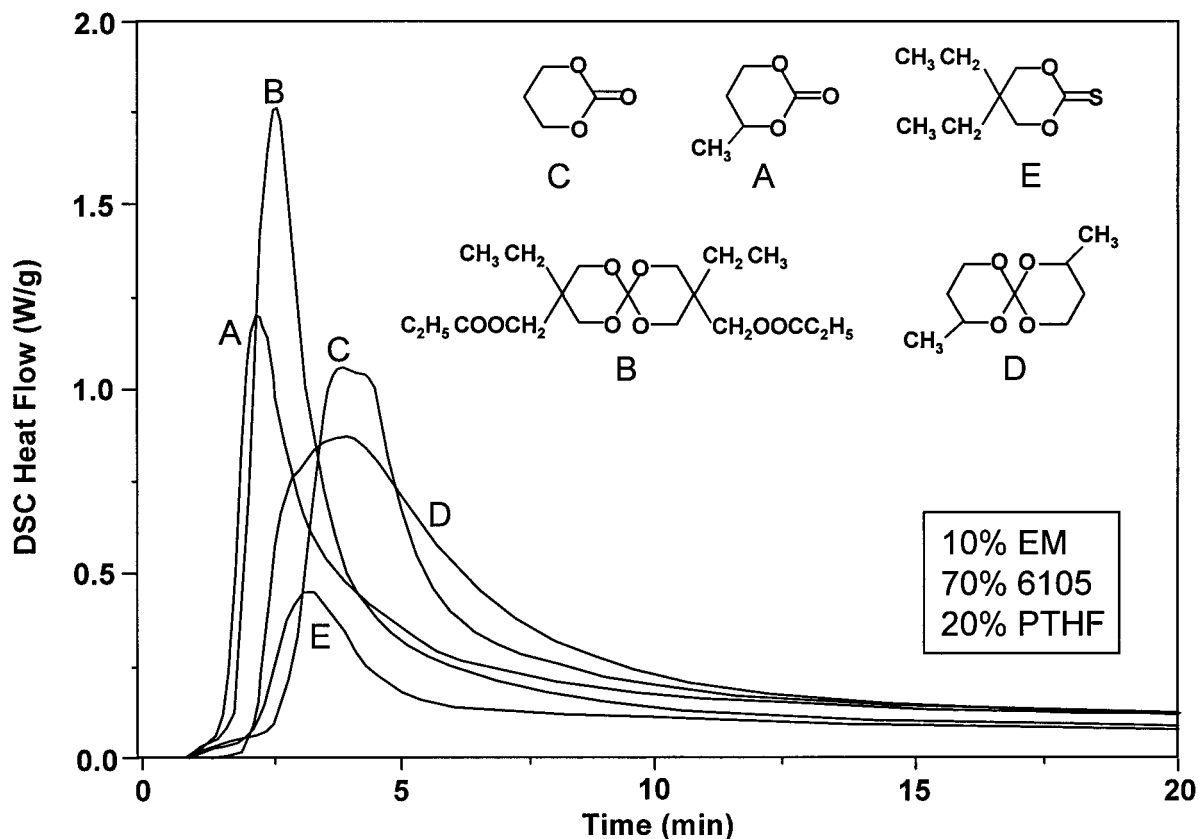
Figure 7 Photocopolymerization reactivity profiles of five expanding monomer (10%)/diepoxide (70%) polyol (20%) mixtures at 30° C.

- The relative reactivity of the EMs during UV initiated homopolymerization at 100°C was in the order shown, with the thiocarbonate, DE-DOT, being by far the most reactive, and the SOC, DEDPM-TOSU being the least reactive.
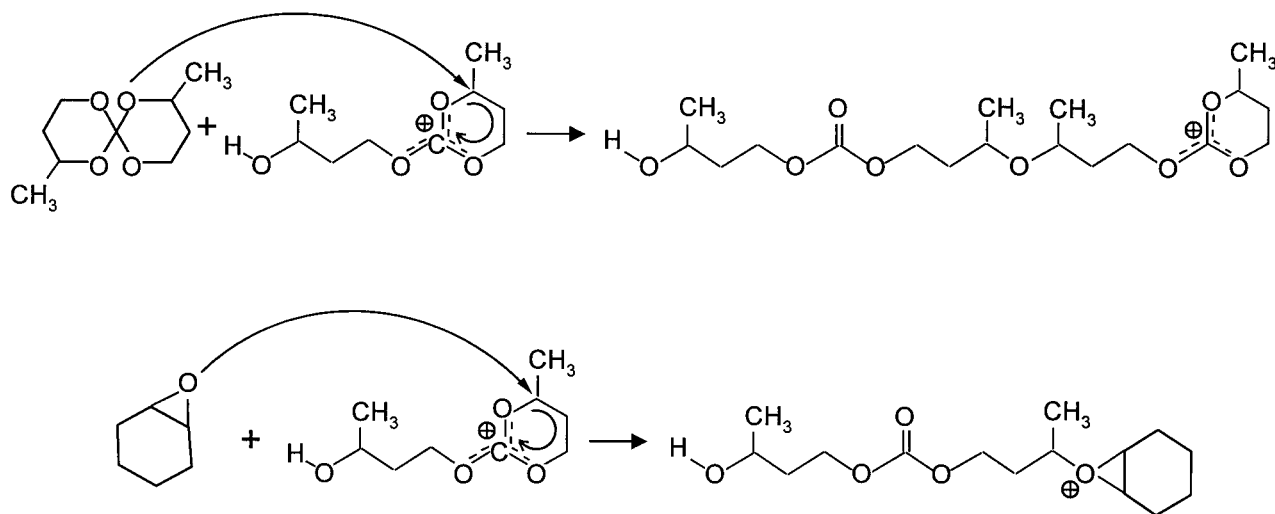

Figure 8 Reaction mechanisms for the homopolymerization of 2,8-dimethyl-1,5,7,11-tetraoxaspiro[5.5]undecane and the copolymerization with cyclohexene oxide.
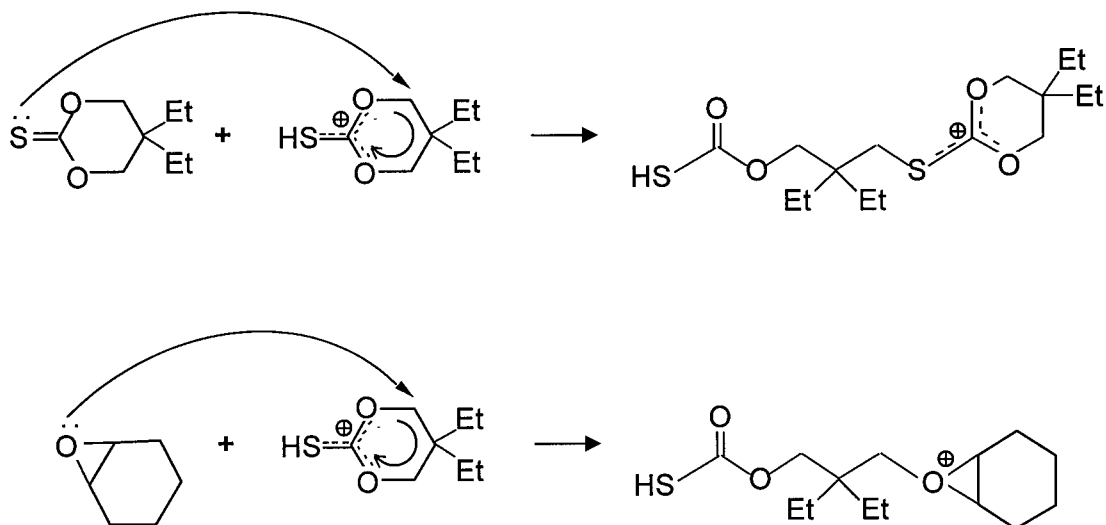
Figure 9 Reaction mechanisms for the homopolymeriization of 5.5 diethyl-1,3-diox-ane-2-thione and the copolymerization with cyclohehexene oxide.

- The relative reactivity of the EM/diepoxide/ polyol systems can be related to the EM component in the order shown, with the diepoxide/polyol mixture containing the dioxanone, M-DOO, being the most reactive, and the mixture containing the SOC, DM-TOSU, being the least reactive.

- The experimental results and the thermal and kinetic analyses of the reaction systems are consistent with the computational find-
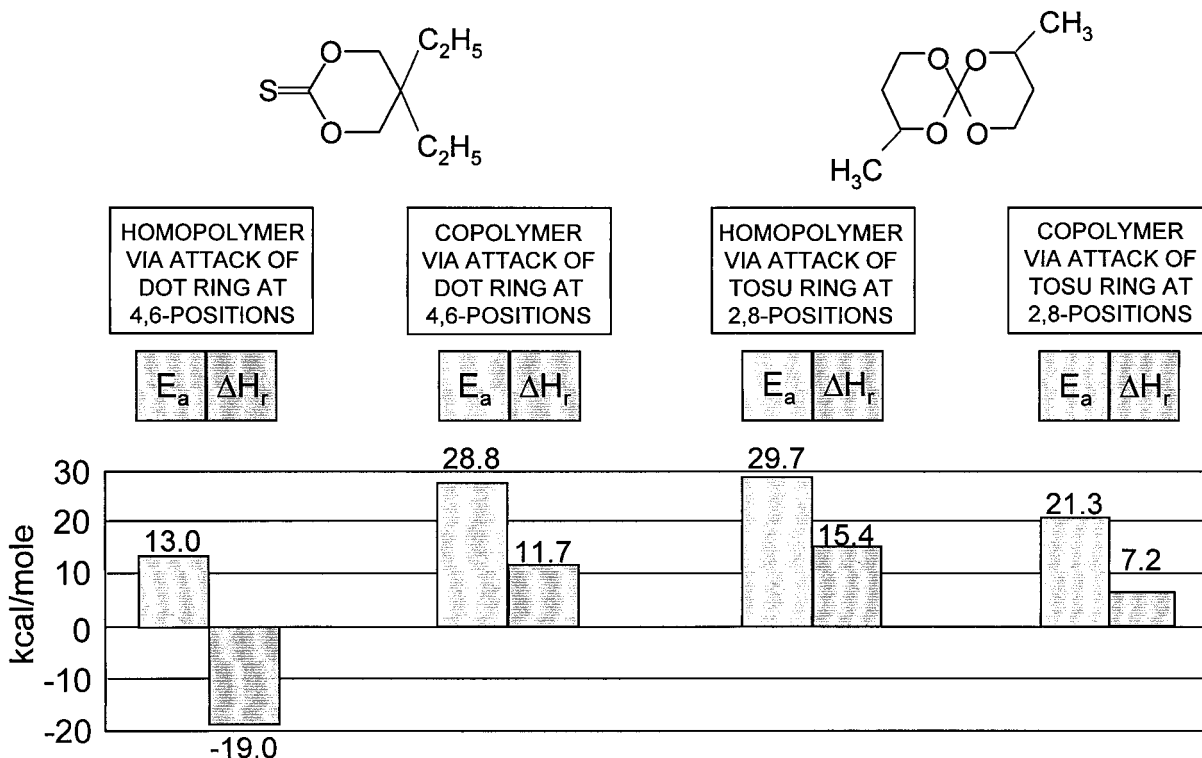

Figure 10 Calculated reaction energetics for the proposed reaction pathways for the homo- and copolymerization of two expanding monomer systems.

ings for the proposed photopolymerization mechanisms.

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