

Photoreactivity of Vinyl Ether/Oxirane-Based Resin Systems

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ABSTRACT: We evaluated the reactivity in homopolymerization and as comonomers in dioxirane/polyol visible-light curable systems the following vinyl ethers (VEs): mono-, di-, and tri(ethylene glycol) divinyl ethers (EGDVE, DEGDVE, and TEGDVE, respectively); 1,6-hexanediol divinyl ether (HDDVE); cyclohexanedimethanol divinyl ether (CHDMDVE); glycidyl vinyl ether (GVE); 4-(1-propenyloxymethyl)-1,3-dioxolan-2-one (POMDO); and 1,4-butanediol vinyl ether (BDVE). The dioxirane/polyols (80/20) were Cyracure UVR 6105 or ERL 4206 dioxiranes with polytetrahydrofuran [PTHF; number-average molecular weight (M_n) = 250]. Reactivities were evaluated by photodifferential scanning calorimetry with visible light. For VE homopolymerization, the relative reactivity ranking (based on exotherm peak maximum time) was TEGDVE > EGDVE > DEGDVE > HDDVE > CHDMDVE > BDVE > GVE \gg POMDO. For VEs in UVR 6105/PTHF, the ranking was GVE

> TEGDVE > CHDMDVE > BDVE > EGDVE \gg DEGDVE = HDDVE = POMDO. In ERL 4206/PTHF, the ranking was: GVE > TEGDVE > BDVE > DEGDVE \gg HDDVE > EDGDVE \gg CHDMDVE = POMDO. The incorporation of an electron-donating reaction promoter, ethyl-4-dimethylaminobenzoate, generally shortened induction times and exotherm peak maximum times and increased rate constants for homopolymerizations and ternary polymerizations. Experimentally determined polymerization reactivities were compared with previously reported semiempirical quantum mechanical calculations of activation energies and heats of reaction. The results of laboratory and computational studies for selected compounds were in general agreement. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 314–326, 2002

Key words: poly(vinyl ethers); dioxiranes; cationic polymerization; photoreaction energetics; molecular modeling

INTRODUCTION

In an effort to develop photocationic dental adhesives and composites, we explored cationically curable vinyl ether (VE)/oxirane-based systems. Both VEs and oxiranes are known to be curable by photochemically generated acids. In an excellent review article,¹ Crivello discussed the mechanisms for photocationic initiation, described the use of photosensitizers to extend the absorption range of common photoacid systems, and provided schemes for photosensitization by both energy transfer and electron transfer processes. Photoacid initiator systems containing electron donor compounds have been developed for cationic resin systems and have been found to enhance reaction rate and efficiency.^{2,3}

Solaro et al.⁴ used both chemical and ultraviolet (UV) initiation and reported enhanced cure and phys-

ical properties when VEs were combined with bisphenol A diglycidyl ether. Koleske⁵ studied formulations containing VEs with epoxides and polyols and reported polymerizates with good heat and impact resistance. Dougherty and Crivello⁶ found that interpenetrating polymer networks resulted from UV-initiated VE/epoxy mixtures. Rajaraman et al.^{7,8} reported that epoxide polymerization was enhanced and vinyl polymerization suppressed during photocationically induced reactions of mixed epoxy/VE systems and of hybrid monomers containing cycloaliphatic epoxy and 1-propenyl ether functionalities.

Photodifferential scanning calorimetry (PDSC) has been used to study the photopolymerization of VEs,⁹ epoxides,¹⁰ and mixed free radical/cationic monomer systems.¹¹ Semiempirical quantum mechanical methods have been applied in modeling polymerization pathways and computing heats of reaction and activation energies (E_a 's) for a series of VE homopolymerizations and copolymerizations with a model epoxide.¹²

This investigation of the visible-light-initiated photoreactivity of VE/oxirane-based polymeric materials was focused in three principal areas: (a) the homopolymerization of selected monovinyl and divinyl

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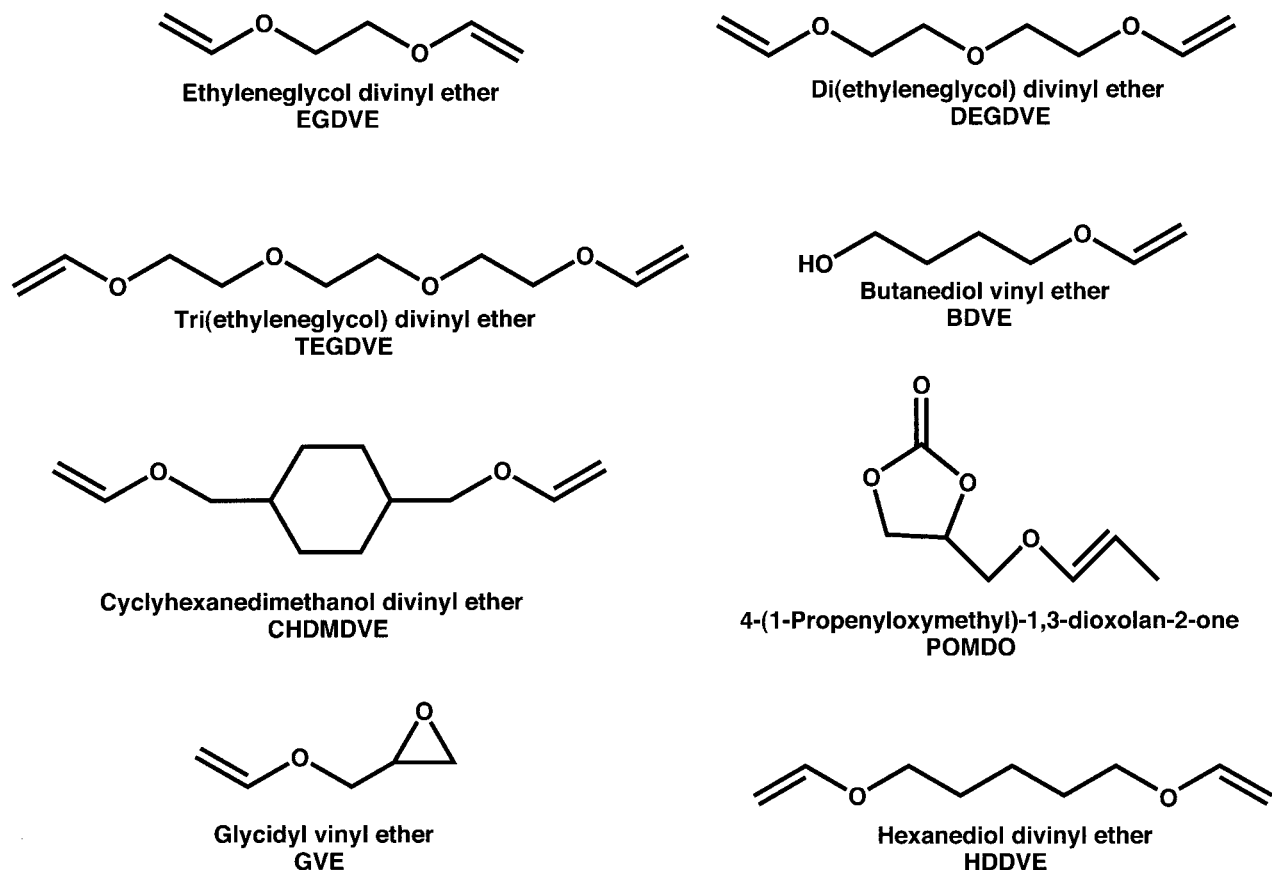


Figure 1 VE structures, chemical names, and acronyms.

ethers, (b) the polymerization of selected VE/dioxirane/polyol mixtures, and (c) the computational polymerization reaction energetics for selected VE and VE/oxirane systems and comparison with experimental findings.

EXPERIMENTAL

Reactants and reagents

The VEs—mono-, di-, and tri(ethylene glycol) divinyl ethers (EGDVE, DEGDVE, and TEGDVE, respectively); 1,6-hexanediol divinyl ether (HDDVE); cyclohexanedimethanol divinyl ether (CHDMDVE); glycidyl vinyl ether (GVE); 4-(1-propenyloxymethyl)-1,3-dioxolan-2-one (POMDO); and 1,4-butanediol vinyl ether (BDVE)—the photosensitizer camphorquinone (CQ), and the polyol polytetrahydrofuran (PTHF; $M_n \approx 250$) were obtained from Aldrich Chemical Co. (Milwaukee, WI) The cycloaliphatic diepoxides, 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexylcarboxylate (Cyracure UVR 6105) and vinyl cyclohexene oxide (ERL 4206), were obtained from Union Carbide (Danbury, CT). The photoacid initiator, (4-*n*-octyloxyphenyl)phenyliodonium hexafluoroantimonate (OPIA; 479-2092C), was obtained from GE Silicones (Waterford, NY). An electron-donating reaction promoter,

ethyl-4-dimethylaminobenzoate (EDMAB), was obtained from Acros Chemicals (Fairlawn, NJ). The VEs were selected to provide a variety of functionalities. Their structures are shown in Figure 1. Structures for the dioxiranes, polyol, and photoinitiator system components are given in Figure 2. BDVE contained an inhibitor (0.01% KOH), which was removed by neutralization and extraction before testing. All other chemicals were used as received.

Formulation

Formulations were prepared in the absence of light and tested on the same day as prepared. All test mixtures contained a photoacid initiator (OPIA, 0.25 mol %) and a visible-light photosensitizer (CQ, 0.50 mol %). The reaction promoter EDMAB, when used, was added at 0.1 wt %. In comonomer mixtures containing a VE, a dioxirane, and a polyol, the oxirane-to-vinyl ratio was 1:1 on a mole equivalents basis. The oxirane-to-hydroxyl ratio was 3.5:1 for formulations containing UVR 6105 and 6.5:1 for formulations containing ERL 4206 on the same basis. The oxirane group content of GVE and the hydroxyl group content of BDVE were not included in the determination of the formulation ratios when these compounds were reactants.

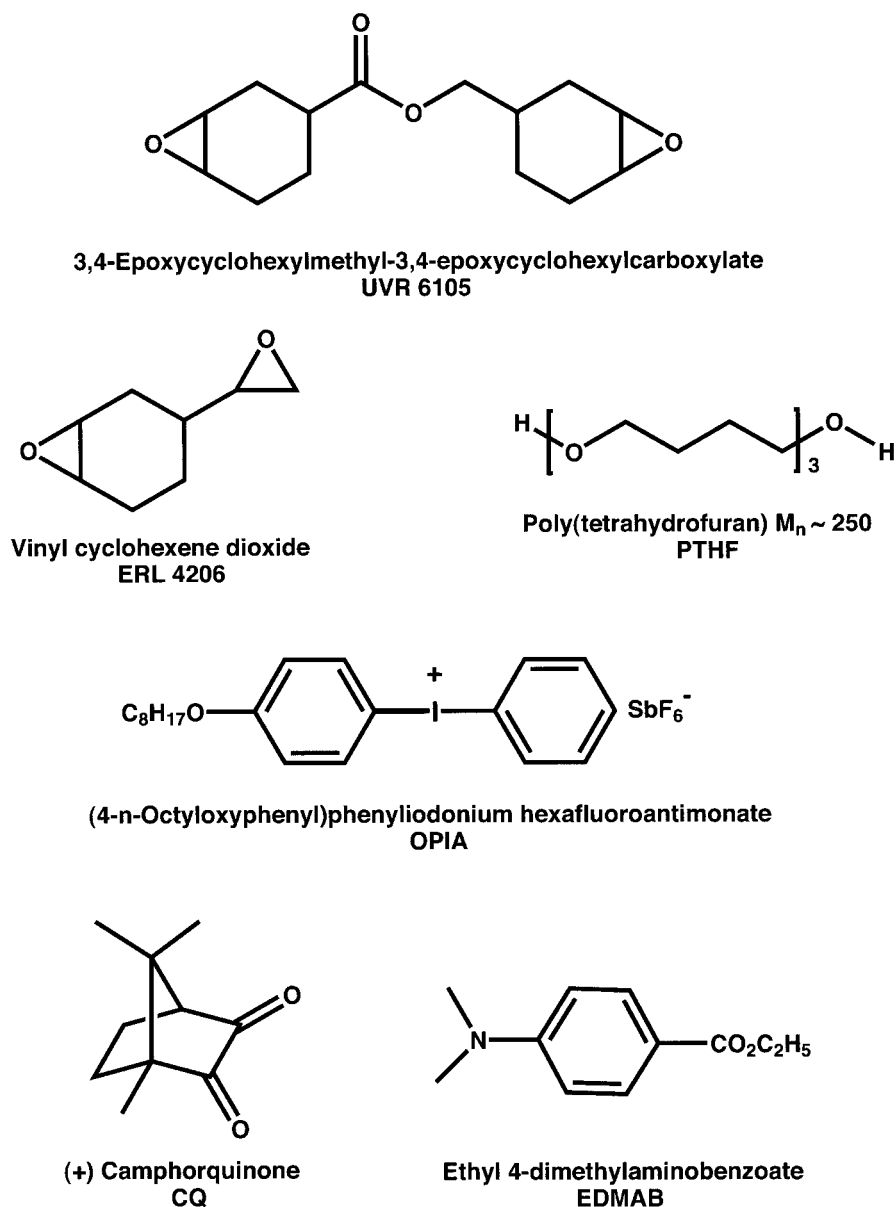


Figure 2 Dioxirane, polyol, and photoinitiator system component structures, chemical names, and acronyms.

Test methods

Polymerizations (single runs) were monitored with a DuPont/TA Instruments (New Castle, DE) photodifferential scanning calorimeter (model 910 DSC/930 DPC) at 37°C, under a continuous nitrogen purge (40 cc/min), with visible light (> 418 nm, 8.4–11.6 mW/cm²). Samples (10–11 mg) were irradiated for 20 min after 1 min equilibration at test temperature. An empty sample pan was used in the reference position in the PDSC cell. We measured the light intensity with an International Light II 1400A radiometer (Newburyport, MA) equipped with an XRL340A detector, following the photodifferential scanning calorimeter manufacturer's recommended procedure. A typical reaction exotherm profile (for the photohomopoly-

merization of EGDVE) is shown in Figure 3. Calculated PDSC parameters included the enthalpy of the observed photoreaction (ΔH_r), the time to exotherm peak maximum, and the induction time (time for 1% of the observed photoreaction to be completed). Rate constants were determined with the autocatalytic model from the data analysis program software. The typical reproducibility of PDSC parameters in this laboratory for three successive replications is usually within 5–6%.

RESULTS AND DISCUSSION

Homopolymerization of VEs

The photoreaction exotherm profiles for the visible-light-initiated homopolymerization of two monovinyl

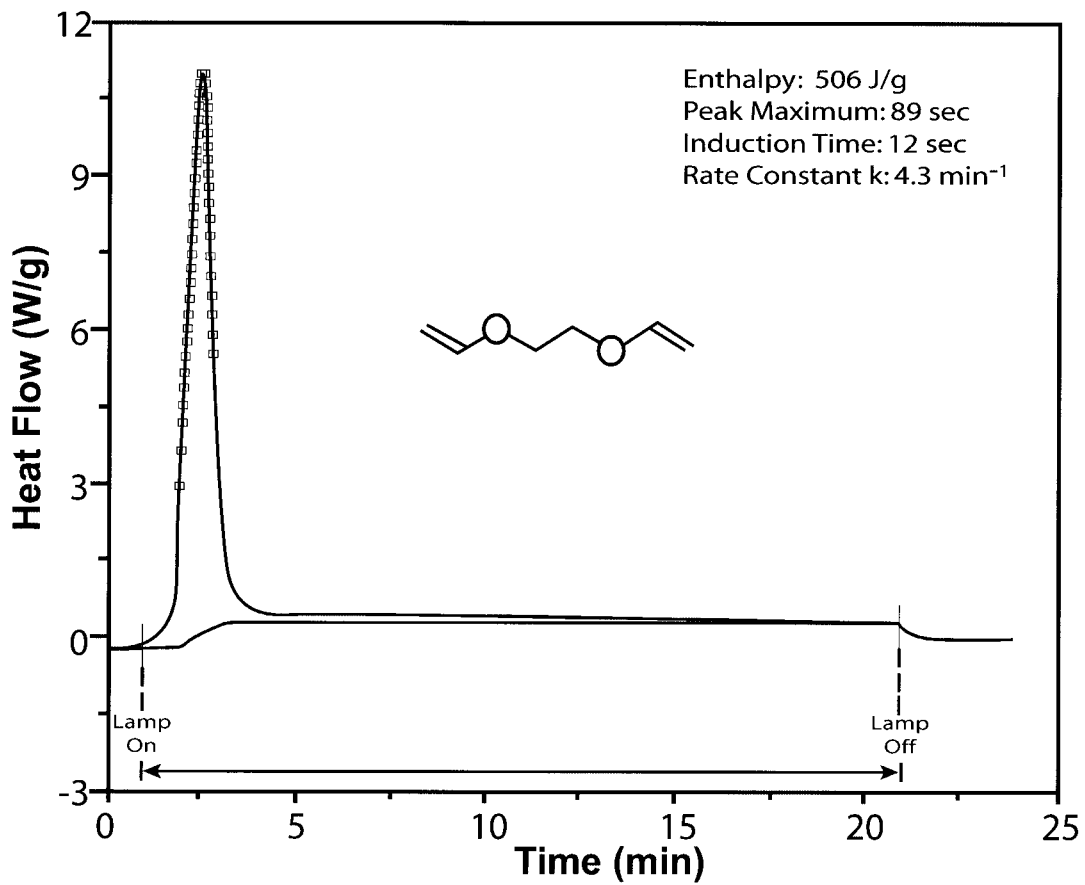


Figure 3 Typical photoreaction exotherm profile for ethylene glycol divinyl ether homopolymerization generated with PDSC.

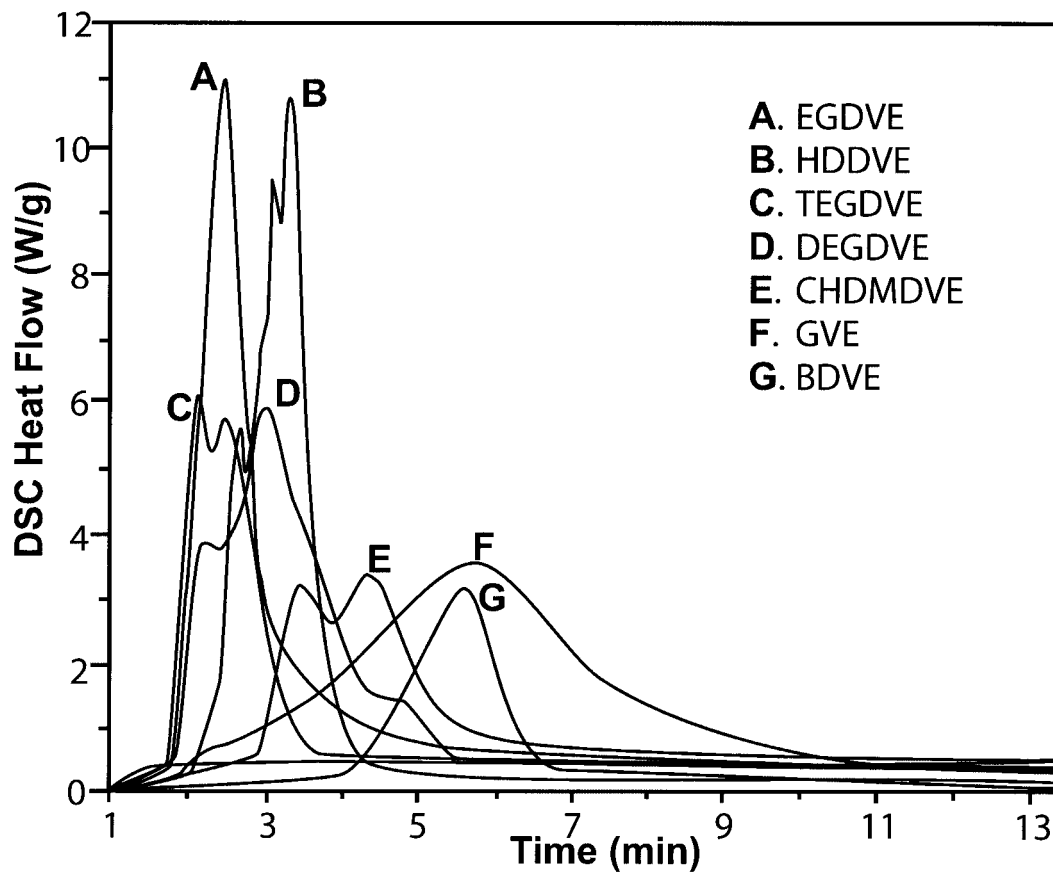


Figure 4 PDSC homopolymerization exotherm profiles for VEs formulated without the reaction promoter EDMAB.

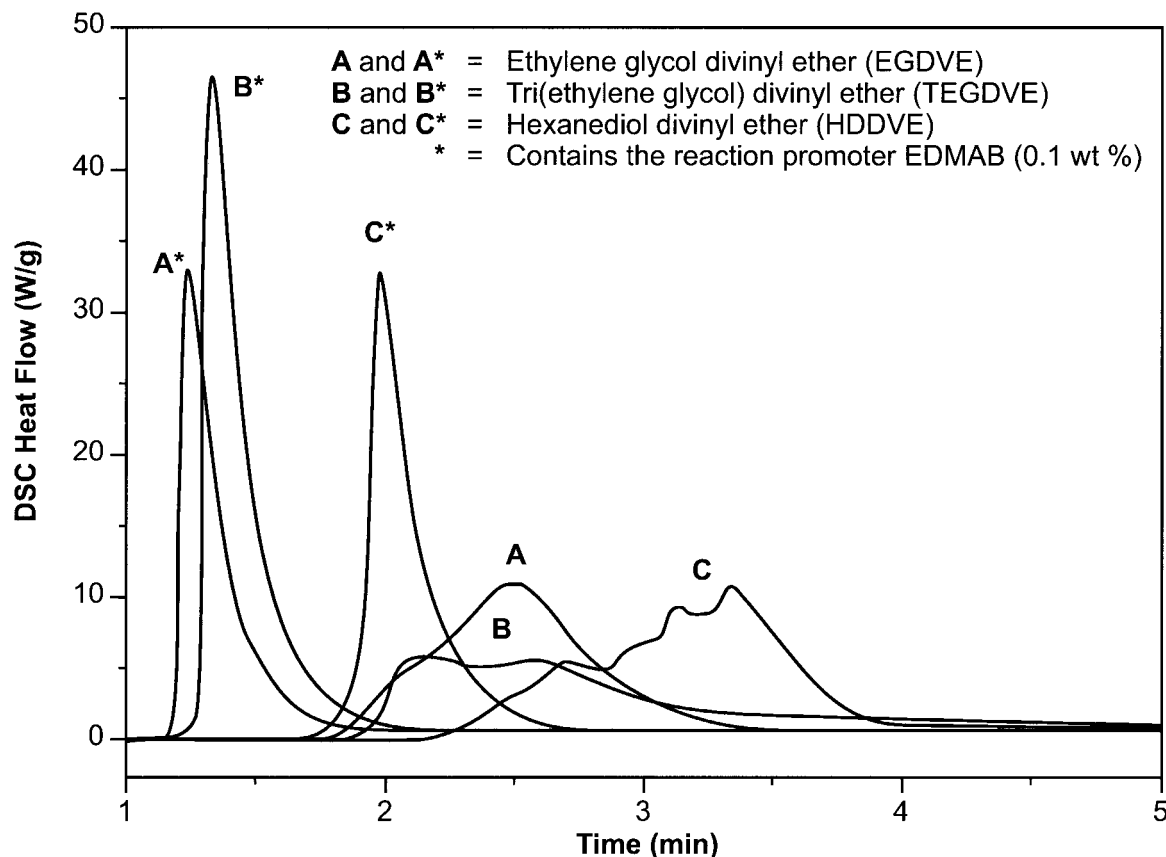


Figure 5 PDSC homopolymerization exotherm profiles for EGDVE, TEGDVE, and HDDVE formulated with or without the reaction promoter EDMAB.

ether and five divinyl ether formulations not containing the reaction promoter EDMAB are shown in Figure 4. POMDO showed no evidence of reaction under these test conditions. Exotherm profiles for EGDVE, TEGDVE, and HDDVE homopolymerizations with and without the reaction promoter EDMAB appear in Figure 5. Photoreactivity parameters for all VE homopolymerizations are summarized in Table I.

Comparison of the exotherms in Figure 4 for VE formulations without the reaction promoter revealed notable differences in the photoreactivities of the monomers: (a) the divinyl ethers (curves A–E) were generally more reactive than the monovinyl ethers (curves F and G); (b) the most reactive divinyl ether was EGDVE (curve A); (c) the other four divinyl ethers (curves B, C, D, and E) exhibited bimodal exotherm

TABLE I
PDSC Parameters for VE Homopolymerizations at 37°C With Visible-Light Irradiation^a

VE	ΔH_r (J/g)		Induction time (s)		Time to peak maximum (s)		Rate constant k (min^{-1})	
	Without promoter	With EDMAB ^b	Without promoter	With EDMAB ^b	Without promoter	With EDMAB ^b	Without promoter	With EDMAB ^b
EGDVE	506	381	54	12	89	14	4.34	10.6
HDDVE	576	475	78	51	139	58	1.58	16.0
TEGDVE	454	534	60	17	70	20	2.32	11.0
DEGDVE	572	343	59	37	121	112	1.39	1.26
CHDMDVE	360	136	121	50	204	77	0.78	2.13
GVE	823	445	78	55	285	241	1.10	0.83
BDVE	314	287	32	26	274	120	2.49	3.77
POMDO	—	—	—	—	—	—	—	—

A dash indicates that no reaction was observed.

^a 20 min, >418 nm, 8.4–11.6 mW/cm².

^b Formulations with reaction promoter EDMAB (0.1 wt %).

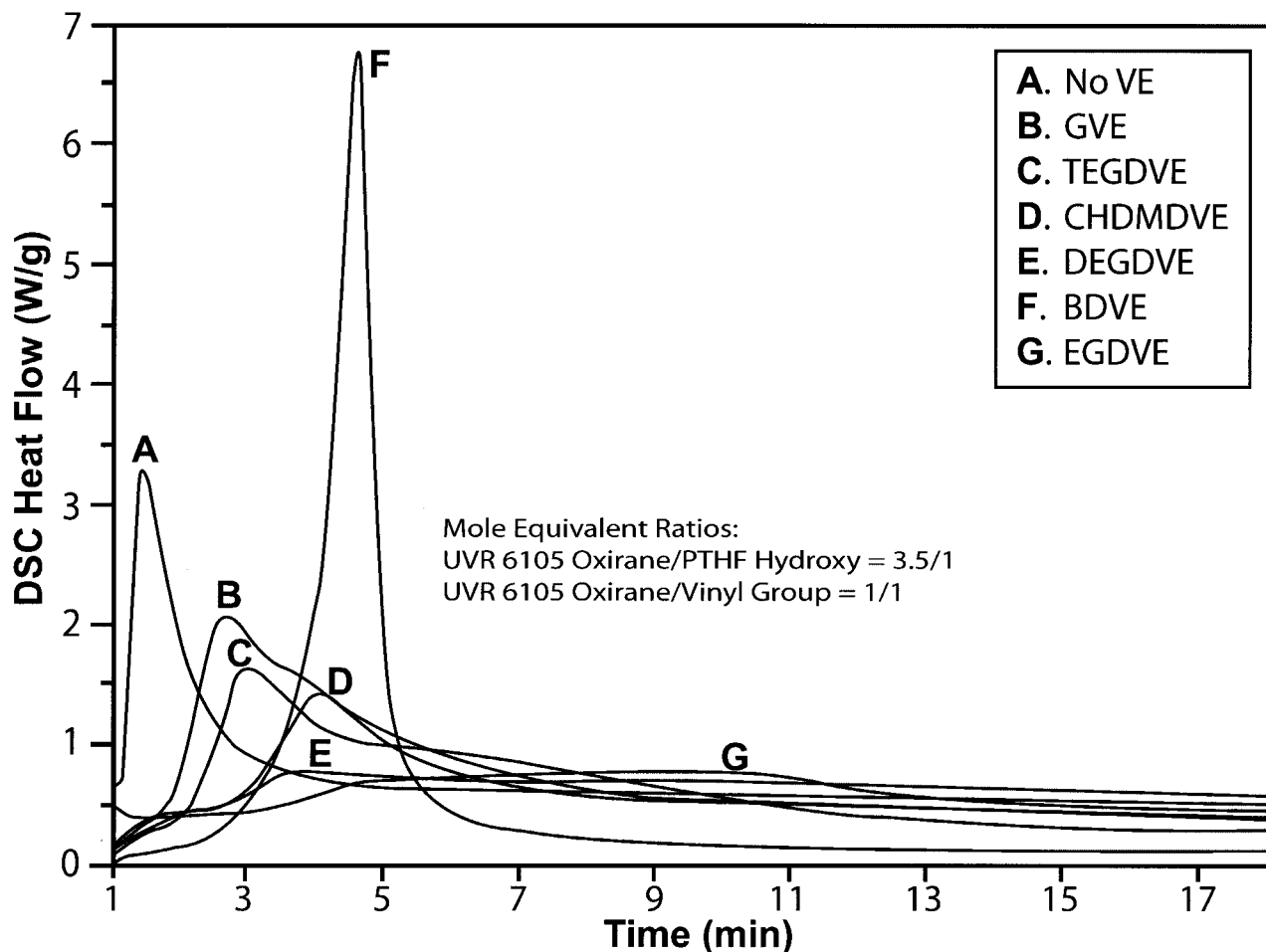


Figure 6 PDSC exotherm profiles for VE/UVR 6105/PTHF mixtures formulated without the reaction promoter EDMAB.

peaks, which were indicative of changes in the reaction mode; and (d) comparison of the relative reactivities of the two monovinyl ethers revealed that GVE, which contains oxirane functionality (curve F), had a more rapid exotherm onset but a more extended overall reaction time than BDVE, which contained a hydroxyl group (curve G). GVE, BDVE, and CHDMDVE exhibited latency (delayed onset of the polymerization reaction). Incorporation of the reaction promoter EDMAB (0.1 wt %) had the most dramatic effect on the photopolymerization exotherm profiles of EGDVE, TEGDVE, and HDDVE (Fig. 5). Examination of the PDSC parameters of EDMAB-containing formulations (Table I) showed: (a) marked reductions in induction times and peak maximum times, (b) marked increases in rate constants, and (c) generally less ΔH_r when compared to formulations without EDMAB. The latter two points would indicate that the increased initiator system efficiency due to EDMAB resulted in more rapid gelation and crosslinking and led to less monomer mobility and more trapped residual unreacted vinyl groups.

Polymerization of VE/dioxirane/PTHF mixtures. I

The photoreaction exotherm profiles for the visible-light-initiated copolymerization of VE/UVR 6105/PTHF mixtures formulated without the reaction promoter EDMAB are shown in Figure 6. Comparison of the reaction exotherms revealed notable differences in the photoreactivities of the mixtures: (a) the most rapidly reacting mixture contained the dioxirane/polyol with no VE coreactant (curve A), and (b) for mixtures containing a VE, the one with GVE as a coreactant was the most reactive (curve B). The mixture with BDVE as a coreactant exhibited latency (a longer induction period) but was very energetic (curve F), and for photoreaction mixtures containing a divinyl ether, the relative reactivity order was $C > D \gg E \gg G$. Mixtures containing HDDVE or POMDO as the VE component showed no reactivity under these conditions. The mixture containing DEGDVE was also essentially unreactive. The photopolymerization exotherm profiles for TEGDVE and UVR 6105/PTHF and TEGDVE/UVR 6105/PTHF mixtures formulated with out EDMAB are shown in Figure 7. Both TEGDVE and UVR 6105/

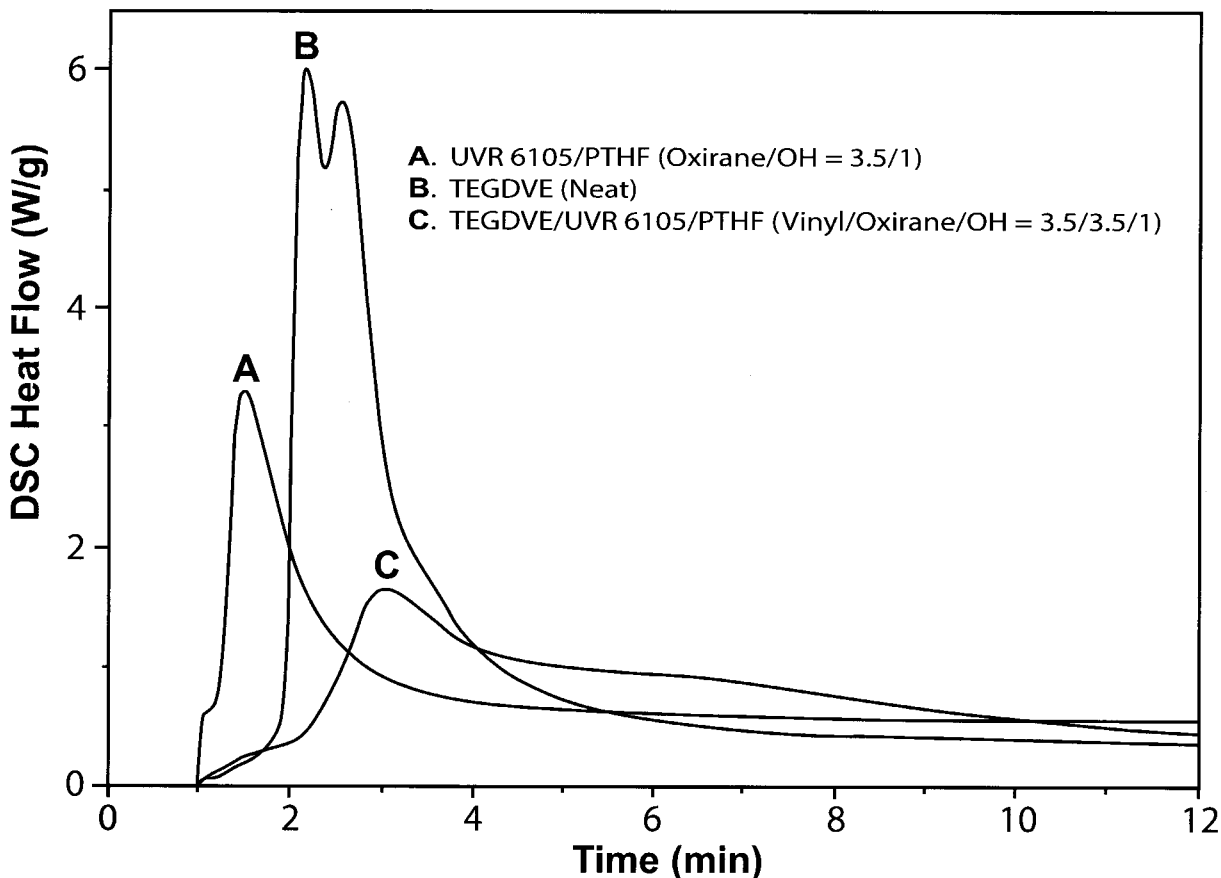


Figure 7 Comparative photoreactivity profiles for UVR 6105/PTHF, TEGDVE, and TEGDVE/UVR 6105/PTHF mixtures formulated without the reaction promoter EDMAB.

PTHF reacted more rapidly and more energetically than the combined TEGDVE/UVR 6105/PTHF mixture under these test conditions.

The effect of EDMAB incorporation on the exotherm profiles of formulations containing UVR 6105/PTHF and TEGDVE, GVE, or BDVE is shown in Figure 8. PDSC parameters for all copolymerizations of VEs with UVR 6105/PTHF are given in Table II.

As noted for VE homopolymerizations, the incorporation of EDMAB generally improved induction times, exotherm maximum times (Fig. 8), and rate constants under these conditions.

Photopolymerization of VE/dioxirane/PTHF mixtures. II

The photoreaction exotherm profiles for the polymerization of similar series of six VE/ERL 4206/polyol mixtures formulated without EDMAB are shown in Figure 9(a,b). In Figure 9(b), exotherms for mixtures containing the dioxirane/polyol with and without BDVE were not included to allow better comparison between other mixtures. The ERL 4206/PTHF 80/20 wt % mixture without VE [curve A in Fig. 9(a)] was the most rapidly reacting. Comparison of the reaction

exotherms for the six VE-containing mixtures revealed marked differences in relative reactivities: (a) the mixture containing BDVE [curve B in Fig. 9(a)] had the shortest reaction interval and fastest rate, although the onset of the reaction was latent; (b) the mixture containing TEGDVE (curve D) exhibited a bimodal exotherm peak; and (c) the mixtures containing POMDO or CHDMDVE as the VE component showed little or no reactivity under these conditions.

The photopolymerization exotherm profiles for TEGDVE and ERL 4206/PTHF and TEGDVE/ERL 4206/PTHF mixtures formulated without EDMAB are presented in Figure 10. Both TEGDVE and ERL 4206/PTHF reacted more rapidly and more energetically than the TEGDVE/UVR 6105/PTHF mixture under these test conditions.

The effect of EDMAB incorporation on the exotherm profiles of formulations containing ERL 4206/PTHF and TEGDVE, GVE, or BDVE is shown in Figure 11. PDSC parameters for all polymerizations of VEs with ERL 4206 and PTHF are given in Table III.

Induction times, exotherm peak maximum times, and rate constants were markedly improved by the incorporation of the reaction promoter EDMAB. ΔH_r ,

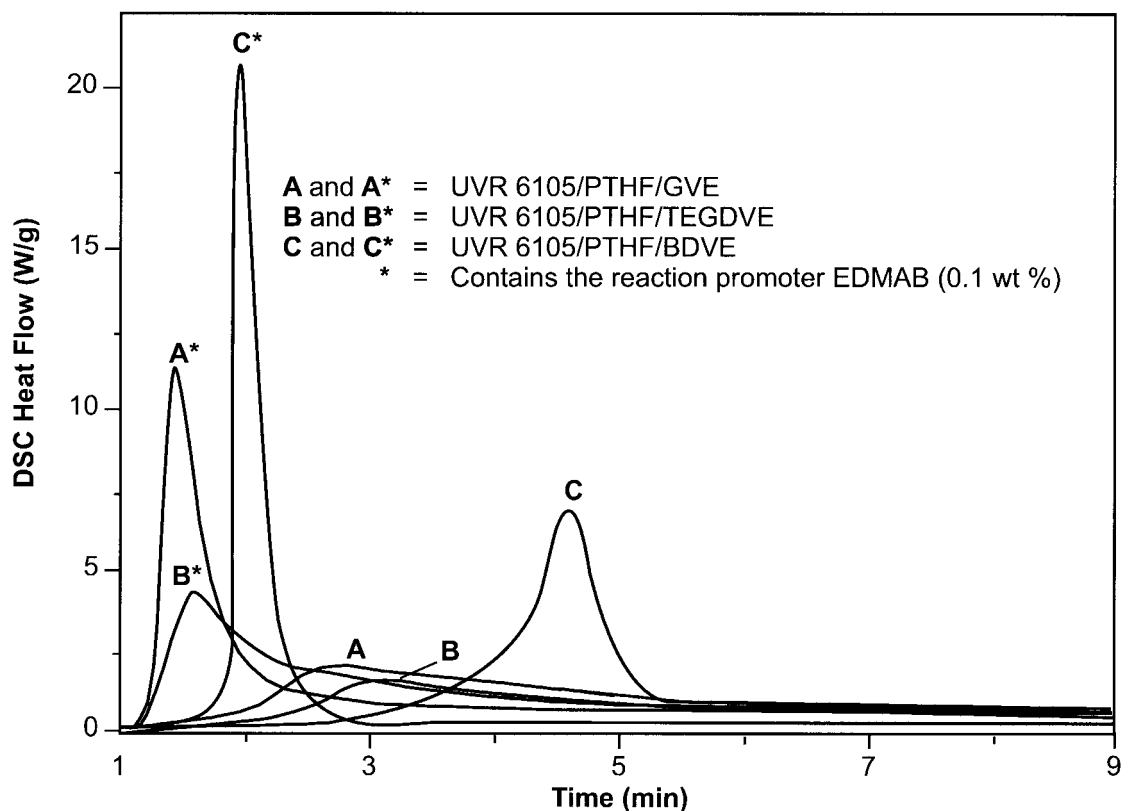


Figure 8 PDSC exotherm profiles for VE/UVR 6105/PTHF mixtures containing TEGDVE, GVE, or BDVE formulated with and without the reaction promoter EDMAB.

for the mixture containing the oxirane functional VE, GVE, was nearly doubled as a result of EDMAB incorporation.

Comparison with computational studies

A previously reported mechanistic and computational study¹² involving VEs was examined in an attempt to explain the observed difference in reactivities for ho-

mopolymerizations and ternary polymerizations. Mechanisms that may be involved during the photopolymerization of reaction mixtures containing TEGDVE (used as a representative example) and a model epoxide (cyclohexene oxide) are shown in Figure 12. The homopolymerization mechanism represented by the top equation in Figure 12 depicts nucleophilic attack by the π -electron of the double bond of one monomer at the carbocation site of an activated

TABLE II
PDSC Parameters for VE/UVR 6105/PTHF Polymerizations at 37°C With Visible-Light Irradiation^a

VE	ΔH_r (J/g)		Induction time (s)		Time to peak maximum (s)		Rate constant k (min^{-1})	
	Without promoter	With EDMAB ^b	Without promoter	With EDMAB ^b	Without promoter	With EDMAB ^b	Without promoter	With EDMAB ^b
None	199	nt	17	nt	29	nt	3.36	nt
GVE	287	384	65	15	102	25	0.75	15.00
EGDVE	209	nt	113	nt	287	nt	0.19	nt
TEGDVE	345	353	80	17	121	33	0.17	0.83
CHDMDVE	218	nt	103	nt	185	nt	1.01	nt
BDVE	422	308	39	39	215	57	4.09	48.20
DEGDVE	—	nt	—	nt	—	nt	—	nt
HDDVE	—	nt	—	nt	—	nt	—	nt
POMDO	—	nt	—	nt	—	nt	—	nt

nt = formulation not tested. A dash indicates that no reaction was observed.

^a 20 min, >418 nm, 8.4–11.6 mW/cm².

^b Formulations with reaction promoter EDMAB (0.1 wt %).

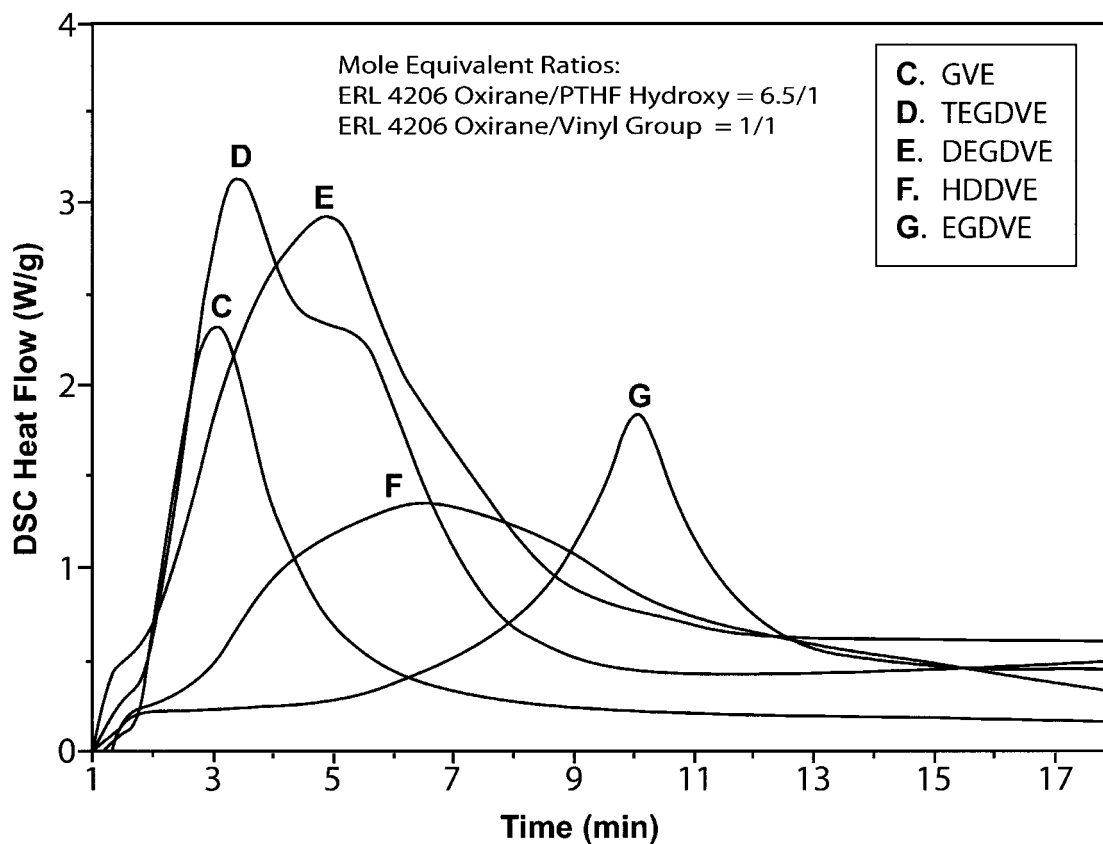
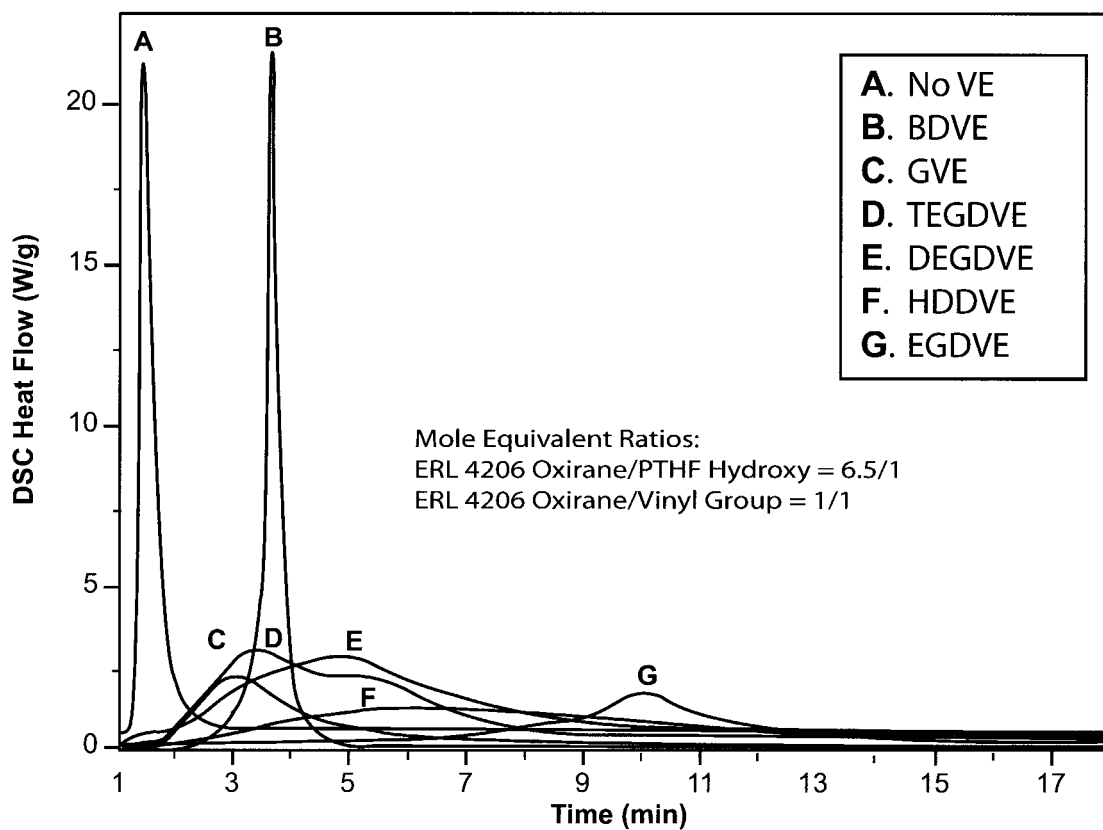


Figure 9 (a) PDSC exotherm profiles for VE/ERL 4206/PTHF mixtures formulated without the reaction promoter EDMAB. (b) Replot of Figure 9a with Curves A and B excluded.

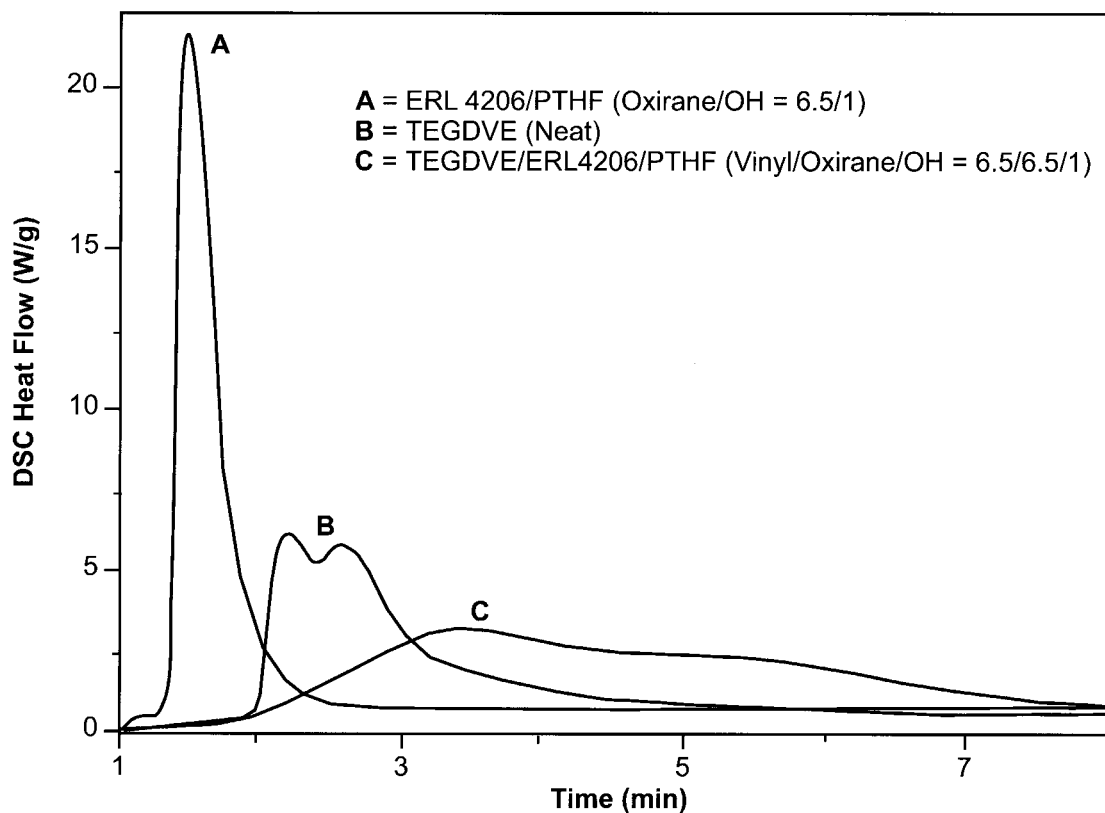


Figure 10 Comparative photoreactivity profiles for ERL 4206/PTHF, TEGDVE, and TEGDVE/ERL 4206/PTHF mixtures formulated without the reaction promoter EDMAB.

monomer initiating chain growth. The copolymerization mechanism represented by the bottom equation in Figure 12 involves nucleophilic attack by the oxirane oxygen at a carbocation site on TEGDVE, followed by epoxide ring opening to yield an intermediate with an activated cyclohexane ring.

Some agreements between the experimental findings and the reported computational study¹² are noteworthy. Computational results reported for TEGDVE are summarized in Figure 13. The homopolymerization of TEGDVE has a lower E_a (~ 0 vs. 4.0 kcal/mol) and is more exothermic ($\Delta H_r = -25.7$ vs. -14.1 kcal/mol) than the copolymerization of TEGDVE with a model epoxide (cyclohexene oxide). These findings agree with the experimental photoreaction parameters, which showed faster induction and exotherm peak maximum times (Table I) for homopolymerization than for polymerizations in dioxirane/polyol systems (Tables II and III). POMDO, which had the one of the highest activation barriers and lowest ΔH_r 's of the VEs in the computational study,¹² showed no evidence of homopolymerization photoreaction in the experimental studies. Comparison of computational and experimental values for VEs containing more than one type of functionality (GVE–vinyl and oxirane groups; BDVE–vinyl and hydroxyl groups) was problematic because of competing reaction pathways and mechanisms.

General discussion

The presence of the polyol in copolymerization reaction mixtures is problematic for precise interpretation and analysis of the experimental findings. Many alcohols are known to add to C=C bonds under acid-catalyzed conditions.^{13,14} This reaction may be competitive with polymerization through the vinyl group and may partially account for the sluggish reactivity of ternary polymerization mixtures containing dioxiranes, polyols, and VEs, as compared to VE homopolymerizations (e.g., Figs. 7 and 10).

Other researchers^{7,8,15–17} have reported extensively on the photocationic polymerization of multifunctional monomers containing both vinyl and oxirane moieties and of comonomer systems containing both VEs and oxiranes. Among their findings were the following: (1) oxirane polymerization is generally enhanced and vinyl polymerization is somewhat suppressed in these photocationic systems, (2) no appreciable oxirane–vinyl copolymerization takes place in mixed comonomer systems, and (3) free-radical-induced decomposition of the onium salt photoinitiator takes place, resulting in acceleration of the oxirane ring opening polymerization. In this study, the presence of polyol in copolymerization systems did not permit direct comparisons with these previous studies. Generally, photopolymerization induction times

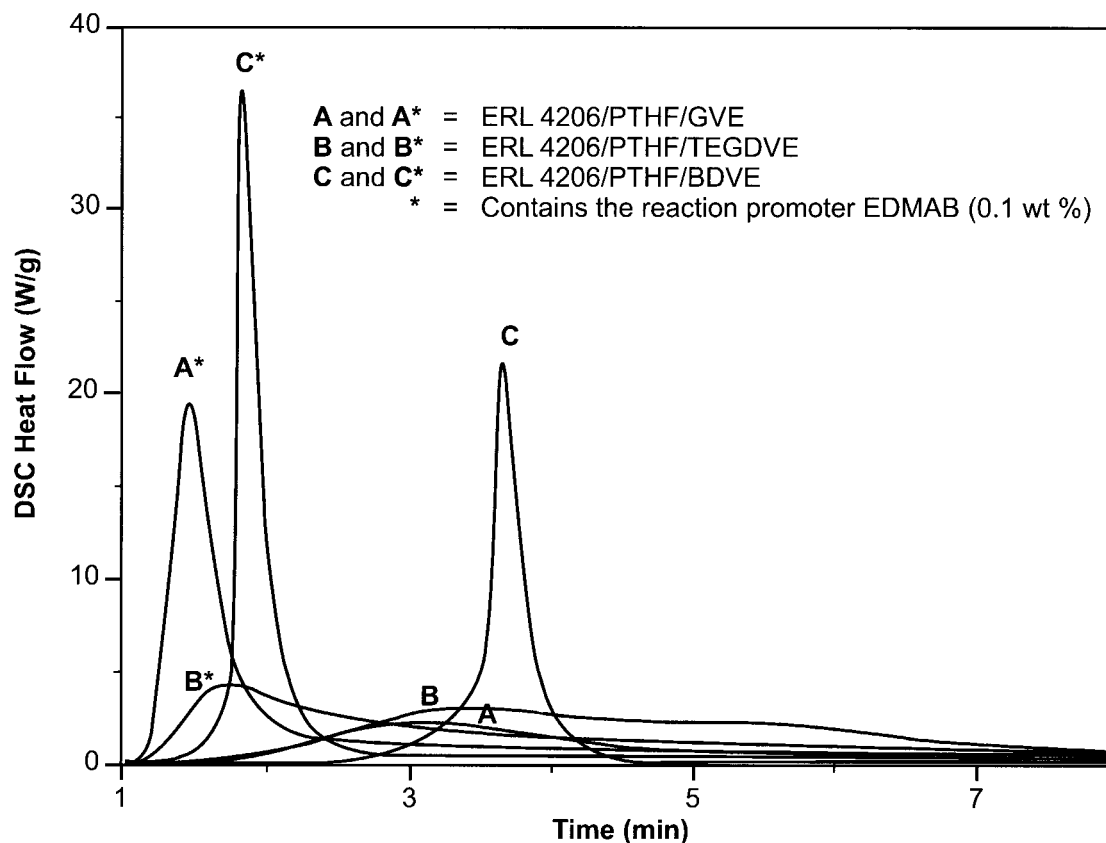


Figure 11 PDSC exotherm profiles for VE/ERL 4206/PTHF mixtures containing TEGDVE, GVE, or BDVE formulated with and without the reaction promoter EDMAB.

and exotherm peak maximum times for mixed systems containing VEs were found to be longer than those for corresponding oxirane/polyol systems.

Weakly basic electron-donor compounds such as EDMAB have been found to increase efficiency of visible-light photocationic initiation systems.^{2,3} The results of this study are generally consistent with these

findings. In other studies in this laboratory, we have found that for EDMAB addition levels above 0.1 wt %, the beneficial effects are diminished, and in some cases, reactivity is actually suppressed. This suppression may be due to the basicity of the amine functionality counteracting generated protons and making initiation less efficient.

TABLE III
PDSC Parameters for VE/ERL 4206/PTHF Polymerizations at 37°C With Visible-Light Irradiation^a

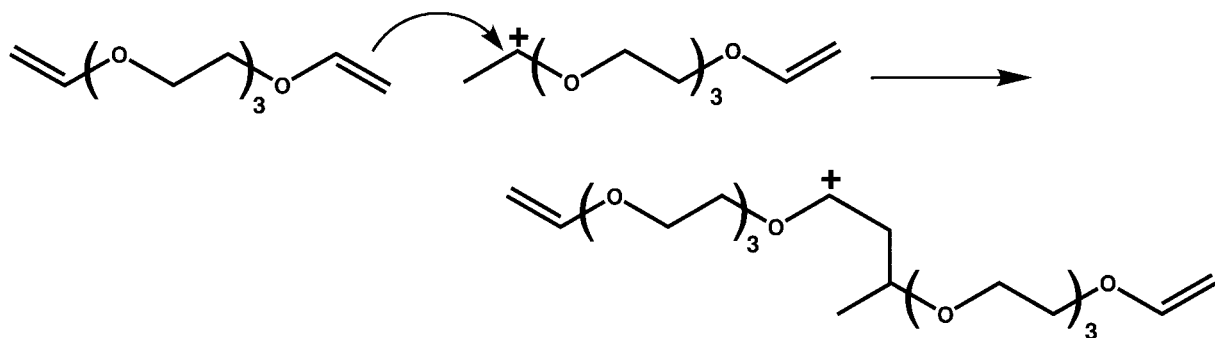
VE	ΔH_r (J/g)		Induction time (s)		Time to peak maximum (s)		Rate constant k (min^{-1})	
	Without promoter	With EDMAB ^b	Without promoter	With EDMAB ^b	Without promoter	With EDMAB ^b	Without promoter	With EDMAB ^b
None	416	nt	21	nt	27	nt	7.99	nt
GVE	304	589	60	12	123	25	1.95	23.4
EGDVE	338	nt	213	nt	542	nt	2.00	nt
TEGDVE	577	453	66	19	144	42	1.87	3.21
HDDVE	492	nt	113	nt	324	nt	0.40	nt
BDVE	487	538	88	28	158	48	41.5	61.2
DEGDVE	584	nt	72	nt	232	nt	0.72	nt
CHDMDVE	—	nt	—	nt	—	nt	—	nt
POMDO	—	nt	—	nt	—	nt	—	nt

nt = formulation not tested. A dash indicates that no reaction was observed.

^a 20 min, >418 nm, 8.4–11.6 mW/cm².

Formulations with reaction promoter EDMAB (0.1 wt %).

Homopolymerization



Copolymerization

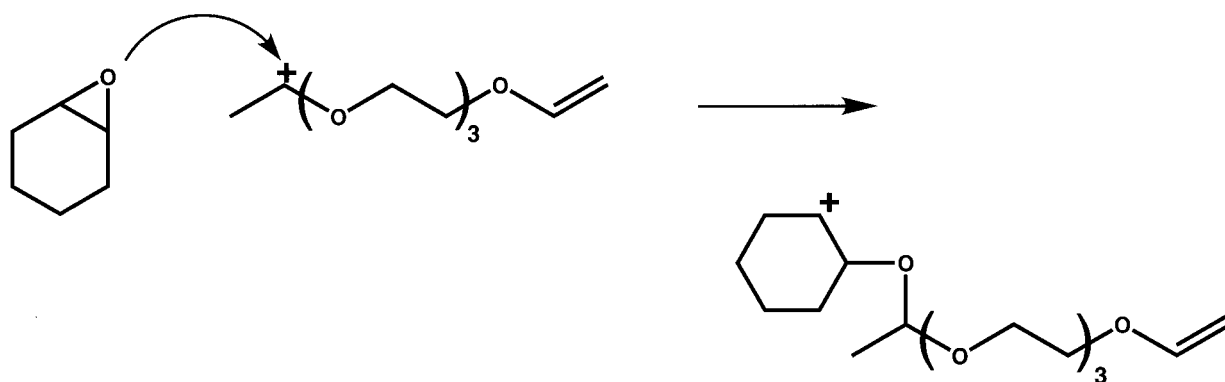


Figure 12 Reaction mechanisms that may be involved during the photopolymerization of reaction mixtures containing TEGDVE or TEGDVE and a model epoxide (cyclohexene oxide).

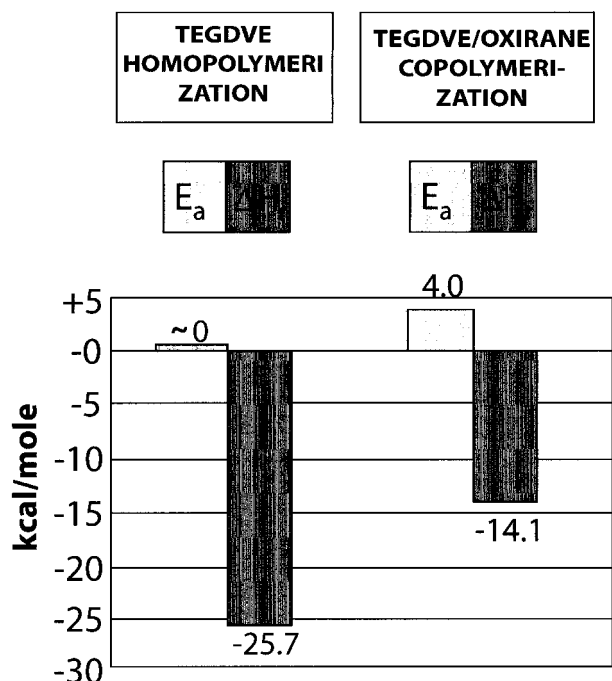


Figure 13 E_a 's (kcal/mol) and ΔH_r (kcal/mol) for the TEGDVE homopolymerization and TEGDVE/cyclohexene oxide copolymerizations.

CONCLUSIONS

The visible-light photopolymerization characteristics of VE monomers and VE/dioxirane/PTHF mixtures varied markedly and could be related to chemical composition. The relative reactivity of VE monomers during homopolymerization was different than the corresponding reactivity of VE/dioxirane/polyol mixtures. The reaction promoter EDMAB generally enhanced the photoreactivity of both homopolymerization and ternary polymerization formulations. Experimental findings with TEGDVE substantiated computational predictions with respect to the reaction energetics of TEGDVE during homopolymerization and copolymerization with a model epoxide.

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