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Photopolymerization without Light. Polymerization of Acrylates Using Oxalate Esters and Hydrogen Peroxide[†]

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ABSTRACT: We define the photopolymerization of acrylates *without light* as a process wherein the radical chain polymerization produced by photoinitiators are produced by nonphotochemical means. We use the chemical reactions of the chemiluminescent *lightstick* to accomplish this. An important potential application is in producing "photopolymers" in areas that are not light accessible as in the inside of a tube or behind a pipe. Polymerizable acrylate mixtures containing dissolved oxalate esters undergo radical chain polymerization when exposed to a flow of nitrogen gas saturated with hydrogen peroxide vapors. We propose aryloxyoxalyl hydroperoxides to be the reactive species.

Introduction

Few chemical processes seem to generate so much amusement as do those involving *chemiluminescence*—chemical reactions that generate light. The reaction of oxalyl chloride with hydrogen peroxide in the presence of a fluorophore[1a] (originally the inventor's blue shirt[1b]) led to an entire cottage industry—that of the so-called *lightsticks*.[2] Sold as self-contained two-part systems, lightsticks provide light of various colors for long periods following an initial breaking of a tube of peroxide into a surrounding tube containing oxalate ester plus luminophore. Another such oxidation, the *luminol* reaction,[3] has been a standard for chemistry demonstrations and science museums for years.

A parallel path in the history of photochemistry involves a concept originally called by Turro "Photochemistry Without Light".[4] As conceived, highly energetic reaction intermediates behaving like those generally resulting from the absorption of a light quantum by the ground state of the formed intermediate were generated in situ by the spontaneous decomposition of high energy content small molecules. These energetic reaction intermediates were similar and react as though they were excited states formed from a light absorption process.

Like many we have been intrigued with these various processes, and we began searching for polymerization routes in which photopolymers[5] were formed without use of light and/or heat. Among the many applications of photopolymers is their use as clear coatings, paints or varnishes, sealants and adhesives, or a protection layer for nascent surfaces like optical fibers. Polymerization without light and/or heat (which also could be named *Remote Cure*) has several potential uses[6]—for example in causing formation of photopolymer in an enclosed environment where light cannot reach as in the inside of a tube or container. Another utilization of the remote cure might be to cause the formation of a coating behind a pipe or in a room that could not be entered by humans because of contamination.

The lightstick reaction involves peroxide, oxalate ester, and an appropriate acceptor of chemical energy that can luminesce. The "chemical energy donor" formed from the reaction of oxalate with peroxide has to be (1) relatively long-lived and (2) able to be transported through the gas phase. This is markedly demonstrated, for instance, by generation of the reactive, energy carrying intermediate in one location and transporting it in a stream of argon or nitrogen to a second, remote location containing the luminophore where the luminescence is observed. In original publications from the Cyanamid group, the dimer of carbon dioxide, 1,2-dioxacyclobutane-3,4-dione (1,2-dioxetanedione),[7] was suggested as this energy rich intermediate. This postulate was modified later in Givens' laboratory,[8] with several alternatives suggested. None of the suggested intermediates had been definitively confirmed or spectroscopically observed at that time though the ^{13}C NMR spectrum of 1,2-dioxetanedione has been reported recently.[9]

Our research sought to gain further insight into these processes and to cause the genesis of the high energy content intermediate by delivering a stream of a carrier gas saturated with hydrogen peroxide vapors to a system that contained monomer(s), oxalate, and co-initiators (if necessary). The curing gas containing hydrogen peroxide vapors is *shapeless*, and the liquid to be cured can reach its own level on any surface. Therefore, bathing a wet monomeric system that has the potential to be polymerized with gaseous H_2O_2 could enable the curing of the liquid, forming a polymerized coating identical with, or at least similar to, analogous photopolymers.

What follows is a report on one of our studies of such a process—the remote polymerization of functionalized acrylate esters wherein the initiator is the prechemiluminescent intermediate formed as a result of interaction between an oxalate ester and hydrogen peroxide. Conceptually we considered Turro's clever idea of producing electronically excited molecules by thermal processes, and using the excited states so produced in subsequent radical chain reactions.[10] To test the idea, we utilized intermediates generated from the reaction of bis(2,4-dinitrophenyl) oxalate (DNPO) or bis(2,4,6-trichlorophenyl) oxalate (TCPO) and the active component of the curing gas (H_2O_2 vapor).

Experimental Section

Materials. Trifunctional (trimethylolpropane triacrylate), difunctional (dipropylene glycol diacrylate), and monofunctional (2-(2-ethoxyethoxy)ethyl acrylate) acrylates were obtained from Sartomer

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and inhibitor-free monomers were prepared using commercial inhibitor remover (Aldrich). Aqueous H_2O_2 (30%, Fisher) was used as received. 2,4-Dinitrophenol (98%) and was obtained from Matheson, Coleman & Bell and 2,4,6-trichlorophenol (98%) was obtained from Aldrich. 2,4-Dinitrophenol and 2,4,6-trichlorophenol were recrystallized and dried by azeotropic distillation with benzene prior to use. Phenol (98%) was obtained from Matheson, Coleman & Bell and used without further purification. Triethylamine (99.5%, Aldrich) and pyridine (99%, Acros) were dried before use by distillation from KOH (85%, EMD). Chloroform (99.8%, EMD, HPLC grade) was dried before use over Na_2SO_4 (99%, EMD), diethyl ether (99%, EMD, HPLC grade) and pentane (98%, Fisher, Optima Grade) were dried by refluxing over Sodium metal (99%, Aldrich) for 4 h followed by distillation. γ-Butyrolactone (99%, Aldrich) was purified by distillation. *tert*-Butyl hydroperoxide (90% in water) and di-*tert*-butyl peroxide (98%) were both obtained from Aldrich. Oxalyl chloride (98%,) was obtained from Acros and used as received. Dichloromethane (99.8%), acetonitrile (99.8%), ethyl acetate (99.8%), and hexanes (98.5%)—all HPLC grade—were obtained from EMD. *N*,*N*-Dimethylformamide (99%), methyl phenylglyoxylate (methyl benzoylformate, 98%), and benzoylformic acid (97%) were obtained from Aldrich and used without further purification. Also without further purification were used acetone-d_6 (99.5 at. % D) and chloroform-*d* (99.8 at. % D) from Acros, H_2SO_4 (98%) and $NaHCO_3$ (99.7%) from EMD, silica (230−400 mesh) from Sorbent Technologies, and argon and nitrogen (both Research Grade) from Linde Gas.

Methods. Remote Cure Experiments. For remote cure experiments, nitrogen carrier gas (430 mL/min) was passed through two reversely connected Ace Glass adjustable bubblers (diameter 1”, height 6”). The first bubbler was partially filled with a 30% aqueous solution of hydrogen peroxide. The second bubbler served as a trap to avoid physical transfer of the liquid droplets. The resulting gas containing H_2O_2/H_2O vapors was directed to the surface of a to-be-polymerized sample using a gas line (Tygon or glass tubing (i.d. $^1/_4$ in.)) equipped with a glass end extension with an aperture to fit an ATR working area. Control experiments conducted under similar conditions omitted the H_2O_2/H_2O vapors from the carrier gas. Saturation of the carrier gas with water vapor alone in the absence of H_2O_2 resulted in no polymerization of the samples. Other control experiments involved remote cure gas exposure of formulations containing diethyl oxalate or 2,4-dinitrophenol instead of DNPO. An additional control involved a monomer/lactone mixture that contained no DNPO. None of the controls evidenced significant monomer conversion. A separate gas transmission line was used for control experiments that did not involve H_2O_2. Each experiment was repeated at least three times.

NMR Spectroscopy. ^{1}H and ^{13}C NMR spectra were recorded using Bruker Avance 300 nuclear magnetic resonance spectrometer. Resonance frequencies of ^{1}H and ^{13}C were 300 and 75 MHz, respectively. The sample was dissolved in 0.9 mL of chloroform-*d* or acetone-d_6 and placed into a standard NMR sampling tube (diameter = 5 mm).

Mid-IR Spectroscopy. IR measurements of the monomer double bond (DB) conversion were obtained using a Shimadzu 8700 Series FTIR spectrometer. Mid-IR DB conversion was monitored in situ using a Pike Technology horizontal attenuated total reflectance (ATR) FTIR accessory. Typical sample contained oxalate ester (2% by weight) and monomer (90% by weight). γ-Butyrolactone (8% by weight) was added to improve the dissolution of the oxalate ester in the monomer. A constant volume liquid sample (0.3 mL) was poured onto a horizontal CdSe crystal of an ATR attachment that was placed inside the FTIR sample chamber. The mid-IR spectra were taken during continuous exposure of the surface of the formulation to the reactive curing gas.

The mid-IR spectra were taken at the following time intervals: 5, 10, 15, 20, 25, 30, 40, 50, 60, 70, 80, and 90 min (700−4000 cm^{-1} spectral range, 30 scans, 2 cm^{-1} resolution). The percent DB conversion (% DB) was monitored from the decrease in area (A_{809}) of the acrylic peak at ca. 809 cm^{-1}.[11] To compare peak areas for the liquid and solid samples having different absolute IR intensities, the area for acrylic transition was internally referenced to either the area under the carbonyl (A_{1700}: 1650−1900 cm^{-1}) or CH stretch (A_{2900}: 2500−3200 cm^{-1}) fundamentals and the ratios obtained used to calculate the %DB using eqs 1−3. Similar values for the % DB were observed regardless of the choice of the internal reference.

$$\% \text{ DB} = \frac{I_0 - I_t}{I_0} \times 100\% \qquad (1)$$

$$I_0 = \frac{A^0_{809}}{A^0_{1700} \text{ or } A^0_{2900}} \qquad (2)$$

$$I_t = \frac{A^t_{809}}{A^t_{1700} \text{ or } A^t_{2900}} \qquad (3)$$

Near-IR Spectroscopy. At the end of each exposure period the final % DB was verified by near FTIR measurements. A clip-on FTIR cell was used to measure the near-IR spectrum in the range from 5000 to 6500 cm^{-1} with 30 scans and 2 cm^{-1} resolution of the solid polymer film resulted from an exposure to the remote cure gas. The area ratios between the peaks in the olefinic (6100−6300 cm^{-1}) and aliphatic (5500−6100 cm^{-1}) regions of the first overtone of the CH stretch were measured and compared to the ratios from the unexposed sample.[12] Double bond conversion was calculated using eq 1 with I_t and I_0 calculated as follows:

$$I_0 = A^0_{\text{ol}}/A^0_{\text{al}} \qquad (4)$$

$$I_t = A^t_{\text{ol}}/A^t_{\text{al}} \qquad (5)$$

where A_{ol} is the area under the peak in the olefinic CH region and A_{al} is the area under the peaks in the aliphatic CH region. To obtain the I_0, the near-IR spectrum was measured by placing the unexposed liquid sample into the IR cell equipped with rectangular CaF_2 windows and a 1 mm Teflon spacer.

Laser Flash Photolysis. Time-resolved experiments employed to examine the reactivity of phenoxyl radicals with the target monomers were conducted using a laser flash photolysis setup described in detail previously.[13] Phenoxyl radicals were generated using two different methodologies: by instant formation upon irradiation from phenols that were dissolved in solutions of di-*tert*-butyl peroxide,[14] and by laser flash photolysis of appropriate model peroxides.

Synthesis of Bis(2,4-dinitrophenyl) Oxalate. Bis(2,4-dinitrophenyl) oxalate (DNPO) was synthesized according to the procedure of Rauhut[15] with some modifications. Into a three-neck 5L round-bottom flask equipped with mechanical stirrer, condenser and thermometer was placed 2,4-dinitrophenol (357 g; 1.94 mol) (previously dried by azeotropic distillation of benzene) and 3 L of CH_2Cl_2. To the resulting mixture was carefully added 196.2 g (1.94 mol) of the dry triethylamine with vigorous stirring, and the solution was cooled to 8 °C. Subsequently, 123 g (0.97 mol) of the oxalyl chloride was added dropwise during 2 h while the reaction temperature was maintained between 10 and 20 °C. After the addition was complete, the reaction mixture was stirred for 3 h on an ice bath followed by addition of another 10 g (0.08 mol) of oxalyl chloride. The resulting reaction mixture was left overnight to slowly reach the ambient temperature. The precipitate formed was filtered, washed with 500 mL of the CH_2Cl_2 and dried in vacuo. The resulted product was recrystallized from acetonitrile/ethyl acetate. The product obtained was further purified by extracting the sample with $CHCl_3$ in a Soxhlet apparatus for 3 days. Crystallization of the resulting solution gave a crystalline product with mp of 191−193 °C (lit.: 189−190 °C[15]). ^{1}H NMR: (300 MHz, acetone-d_6), δ,ppm: 9.06 (d, J = 2.7 Hz, 2H, 3-Ar*H*, + 3′-Ar*H*), 8.80 (dd, J_1 = 9.0 Hz, J_2 = 2.7 Hz, 2H, 5-Ar*H* + 5′-Ar*H*), 8.02 (d, J = 9.0 Hz, 2H, 6-Ar*H* + 6′-Ar*H*). ^{13}C NMR (75 MHz, Acetone-d_6), δ (TMS, ppm): 153.4 (2C, *CO*), 147.6 (2C, *C1*-Ar + *C1′*-Ar), 147.3 (2C, *C4*-Ar + *C4′*-Ar), 142.3 (2C, *C2*-Ar + *C2′*-Ar),

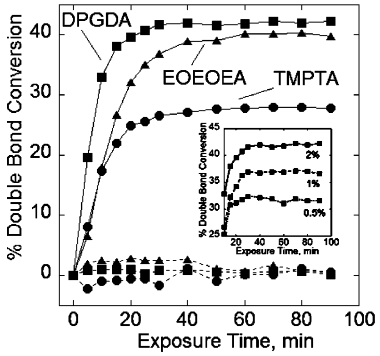


Figure 1. Double bond conversion curves for remote cure samples (solid lines) and controls (dashed lines) of trimethylolpropane triacrylate (TMPTA) (circles), dipropylene glycol diacrylate (DPGDA) (squares) and 2-(2-ethoxyethoxy)ethyl acrylate (EOEOEA) (triangles). Inset: dependence of remote polymerization rate of DPGDA on the 2,4-dinitrophenyl oxalate (DNPO) concentration (highest curve 2%, middle curve 1%, and lowest curve 0.5% of DNPO, respectively).

130.9 (2C, *C5*-Ar + *C5′*-Ar), 127.4 (2C, *C6*-Ar + *C6′*-Ar), 122.9 (2C, *C3*-Ar + *C3′*-Ar).

Synthesis of Bis(2,4,6-trichlorophenyl) Oxalate. Bis(2,4,6-trichlorophenyl) oxalate (TCPO) was synthesized using a procedure similar to the one for DNPO. The resulting crystalline product has an mp of 187−189 °C. ^{1}H NMR (300 MHz, acetone-d_6), δ, ppm: 7.81 (s, 4H, 3-Ar*H* + 3′-Ar*H* + 5-Ar*H* +5′-Ar*H*), ^{13}C NMR (75 MHz, acetone-d_6), δ, ppm: 153.19 (2C, *CO*), 142.59 (2C, *C1*-Ar + *C1′*-Ar), 134.44 (2C, *C4*-Ar + *C4′*-Ar), 130.17 (4C, *C3*-Ar + *C3′*-Ar + *C5*-Ar + *C5′*-Ar), 129.56 (4C, *C2*-Ar + *C2′*-Ar + *C6*-Ar + *C6′*-Ar).

Synthesis of Phenoxyoxalyl *tert*-Butyl and 2,4,6-Trichlorophenoxyoxalyl *tert*-Butyl Peroxides. Synthesis of the model peroxides phenoxyoxalyl *tert*-butyl and 2,4,6-trichlorophenoxyoxalyl *tert*-butyl was done according to the procedure of Lahti et al.[16] with some modifications. Synthetic details are provided in the Supporting Information.

Synthesis of 2,4-Dinitrophenyl Phenylglyoxylate. 2,4-Dinitrophenyl phenylglyoxylate (NPPG) was prepared for the first time using typical procedures for synthesis of glyoxylate esters described by Merzlikine et al.[13] with some modifications. Synthetic details are provided in the Supporting Information.

Results

Results of the remote cure experiments are presented in Figure 1. Noticeable double bond conversion in each of the monomers is observed when compared to control samples. The efficiency of a double bond conversion is dependent on the concentration of the oxalate initiator (Figure 1 inset). A 42% conversion for dipropylene glycol diacrylate (DPGDA) and 40% conversion for 2-(2-ethoxyethoxy)ethyl acrylate (EOEOEA) were achieved after 40 min of exposure to the remote curing gas while trimethylolpropane triacrylate (TMPTA) polymerizes more slowly and with lower (28%) conversion. This reduced reactivity may be explained by the higher viscosity of TMPTA resulting in less efficient penetration of the curing gas into the formulation. In addition, a faster increase of TMPTA viscosity during polymerization also prevents efficient adsorption of H_2O_2 thus lowering the DB conversion.

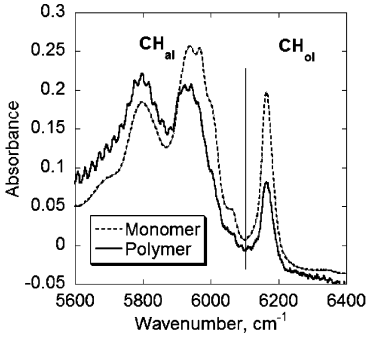


Figure 2. Near-IR spectra of dipropylene glycol diacrylate formulation before (dashed line) and after (solid line) exposure to the remote curing gas. Line at 6100 cm^{-1} divides the first overtone regions of CH aliphatic and CH olefinic stretches.

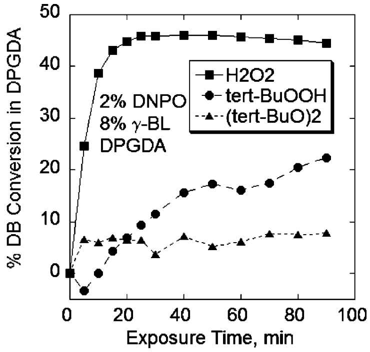


Figure 3. Double bond conversion curves for dipropylenegylcol diacrylate (DPGDA) remotely cured by different peroxides (hydrogen peroxide, squares; *tert*-butyl hydroperoxide, circles; di-*tert*-butyl peroxide, triangles). DPGDA formulation contained 2% by mass of 2,4-dinitrophenyl oxalate and 8% by mass of γ-butyrolactone.

The results obtained from mid-IR measurements could be verified by near-IR data. Figure 2 shows the near-IR spectra for the unexposed DPGDA monomer and for the polymer film obtained after 90 min of exposure to the curing gas. Reduction in the intensity of the olefinic CH signal after remote cure exposure is indicative of a partial conversion of a double bond in the monomer. The resulting 42% double bond conversion is in a good agreement with the values obtained from the mid-IR monitoring (Table 1).

The results of remote cure experiments in which peroxides other than H_2O_2 were used to trigger radical formation are presented in Figure 3. Some DB conversion was observed when *tert*-butyl hydroperoxide was used as the curing gas, although the efficiency of the process was lower than that for systems in which H_2O_2 was the curing gas. No polymerization occurred when *tert*-butyl peroxide was used, suggesting the critical role of the hydroperoxy functionality in initiating cure. The order of volatility of the peroxides examined (boiling points: H_2O_2, bp 158 °C < *tert*-BuOOH, bp 120 °C < (*tert*-BuO)$_2$, bp 110

Table 1. Comparison of the Remote Cure Response of Tested Formulations Containing DNPO[a]

monomer	% DB$_{1700ref}$	% DB$_{2900ref}$	% DB$_{nearIR}$	max % DB in the formulation[b]
dipropyleneglycol diacrylate	40 (41)	44 (46)	42 (43)	97 (100)
trimethylolpropane triacrylate	26 (28)	30 (33)	26 (29)	91 (100)
2-(2-ethoxyethoxy)ethyl acrylate	41 (41)	39 (39)	50 (50)	100 (100)

[a] Numbers in parentheses represent the percentage of double bond conversion relative to the maximum possible conversion listed in the last column. [b] Measured by near-IR. Sample containing 90% monomer, 8% γ-butyrolactone, and 2% Irgacure 819 photoinitiator was photopolymerized using an industrial mercury lamp system (Fusion H-bulb).

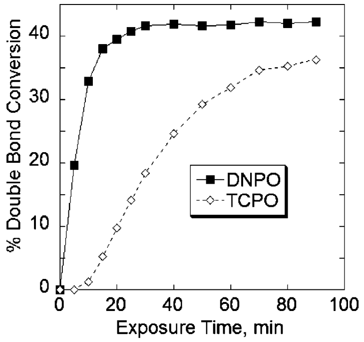
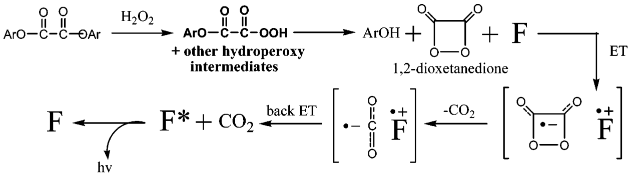


Figure 4. Double bond conversion curves for dipropylene glycol diacrylate containing 2% by mass of 2,4-dinitrophenyl oxalate (filled squares) and 2,4,6-trichlorophenyl oxalate (hollow diamonds).

Scheme 1



°C)[17] is in reverse order relative to the order of reactivity in the remote cure process presented in Figure 3.

Figure 4 compares the remote cure response of the same formulations containing DNPO and TCPO. Though the action of TCPO also results in a partial conversion of a double bond, the process is slower compared to that of DNPO.

Discussion

The results above clearly demonstrate that reaction of H_2O_2 vapor with an oxalate ester dissolved in monomer results in significant conversion of a double bond while systems constructed in a careful set of control experiments resulted in no conversion. Proposed mechanistic explanations for observed reactivity are discussed below.

Peroxyoxalate chemiluminescence (POCL) is the most efficient nonenzymatic CL reaction observed to date.[18] In addition to its use in lightsticks, POCL is widely utilized in variety of analytical methods[19] owing to its unmatched sensitivity.[20] The intermediates are postulated to interact with fluorophore (F) via chemically initiated electron exchange luminescence (CIEEL)[8,21] which involve initial electron transfer from F to the intermediate followed by annihilation of the formed charge-transfer complex accompanied by back ET (Scheme 1).

Despite the extensive mechanistic studies,[22] the exact nature of the multiple POCL intermediates remain unclear and further investigations are needed on this somewhat enigmatic process. Only recently was the intermediacy of 1,2-dioxetanedione confirmed by low-temperature ^{13}C NMR spectroscopy.[9]

The initial step in the CIEEL mechanism involves H_2O_2 attack of the oxalate carbonyl group which results in formation of hydroperoxyoxalates (Scheme 1) thought capable of producing radicals that can initiate polymerization. Studies of the thermal decomposition of phenoxyoxalyl *tert*-butyl peroxide demonstrated two-bond concerted scission producing CO_2, *tert*-butoxyl and phenoxycarbonyl radicals followed by decarbonylation of the latter with formation of the phenoxyl radical.[16] We suggest a similar process occurs in the case of phenoxyoxalyl hydroperoxide (Scheme 2) and the resulting hydroxyl and 2,4-dinitrophenoxyl radicals may add directly to the acrylic double bond.

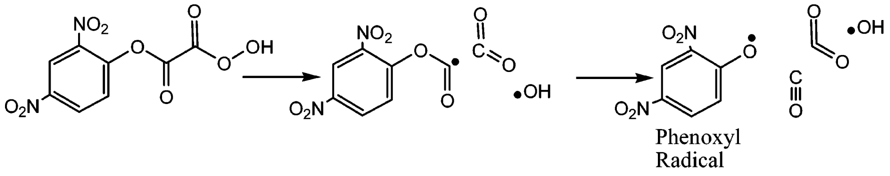
Hydroxyl radicals react rapidly with vinyl monomers with rates approaching the diffusion-controlled limit.[23] For example, the absolute rate of reaction between hydroxyl radical and methyl acrylate was estimated to be 4.7×10^9 M^{-1} s^{-1} through the use of radical clock experiments.[24]

Recent studies on the role of para-substituted phenols on acrylamide photopolymerization in aqueous solutions provide some insight on the possible role of phenoxyl radicals (Scheme 3).[25] Phenols with electron-withdrawing substituents did not significantly influence both polymerization rate and molecular weight of the resulting poly(acrylamide). This suggests that phenoxyl radicals formed are capable of the chain propagation. In contrast, the presence of electron donating para-substituents significantly decreases the rates of polymerization and results in noticeable reduction of the molecular weight of the polymer.

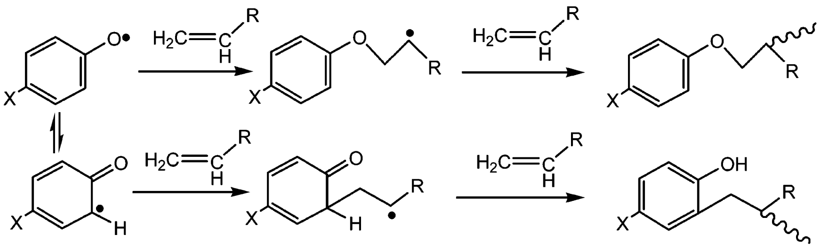
Formation of phenoxyl radicals from phenols following hydrogen abstraction is often linked to the inhibition of polymerization and of oxidation by phenols. Hindered phenols are commonly used as stabilizers of many acrylates. However, phenols may not be the most efficient inhibitors of radical polymerization with the reported $k_{\text{inhibition}}/k_{\text{polymerization}}$ ratio of 0.0012.[26] Moreover, the presence of electron withdrawing substituents further decreases radical chain inhibition by phenols. This could be attributed to the increasing polarity of the OH bond but also to the reduced ability of the resulting phenoxyl radicals to terminate the propagating carbon radicals.

Laser flash-photolysis experiments provided important evidence regarding the reactivity of phenoxyl radicals toward acrylates. We have been able to generate phenoxyl radicals by

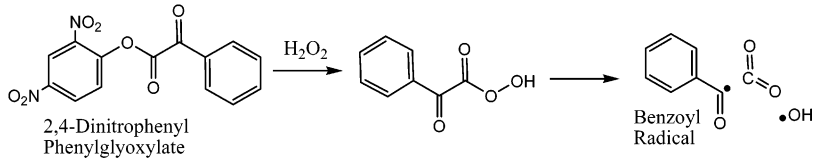
Scheme 2



Scheme 3



Scheme 4



two different methods with laser excitations at 266, 308, and 355 nm. In each case, a transient spectrum with two absorption maxima around 380−405 nm was observed. These absorptions are characteristic features of the transient spectrum of phenoxyl radical (Figure 5).[14,27] In both benzene and acetonitrile, the phenoxyl radical transient signal decays on the order of several microseconds via nonexponential kinetics consistent with the previously described bimolecular self-deactivation path.[14] Addition of up to 200 mM (25 vol %) of the acrylic monomers (DPGDA and EOEOEA) to the precursor solutions did not significantly alter the lifetime of the phenoxyl radicals (Figure 5 inset) indicating the lack of reactivity of these radicals with acrylates. The results were similar for both unsubstituted and 2,4,6-trichlorophenoxyl peroxy precursors. Since the formation of both 2,4,6-trichlorophenoxyl and hydroxyl radicals is proposed for TCPO, only the latter is responsible for the observed remote cure activity of this oxalate ester (Figure 4).

Aromatic nitro compounds terminate propagating chains from either radical attack on the nitro group or the aromatic ring.[26] While nitro-substituted aryl compounds retard styrene and inhibit vinyl acetate polymerizations, little effect was observed for polymerization of methyl acrylate and methacrylate.[26] The higher DB conversion for DNPO compared to TCPO (Figure 4) suggests no inhibition by the nitro aromatic moiety on the systems described in this paper. The lower reactivity of TCPO may be explained by the diminished ability of the 2,4,6-trichlorophenoxy moiety as a leaving group compared to the 2,4-dinitrophenoxy functionality of DNPO.

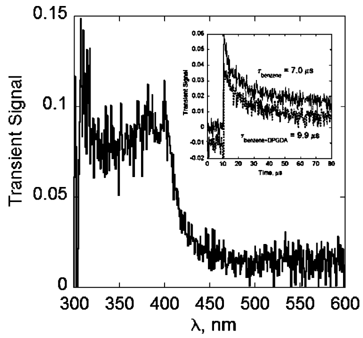


Figure 5. Transient spectrum of phenoxyl radicals obtained 100 ns after 308 nm laser excitation of 30 mM phenoxyoxalyl *tert*-butyl peroxide in benzene. Inset: kinetic traces obtained by monitoring phenoxyl radical transient signal at 400 nm without monomer added (higher solid trace, lifetime of 7.0 μs) and with 200 mM dipropylene glycol diacrylate (lower dashed trace, lifetime of 9.9 μs).

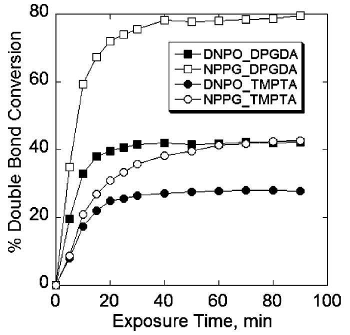


Figure 6. Double bond conversion curves for dipropylene glycol diacrylate (squares) and trimethylolpropane triacrylate (circles) containing 2,4-dinitrophenyl oxalate (solid points) and 2,4-dinitrophenyl phenylglyoxylate (hollow points).

Considering the process outlined by Scheme 2, formation of peroxyacid as a result of H_2O_2 attack from *any ester* containing both 2,4-dinitrophenoxy (or any other good leaving group) and α,β-dicarbonyl moieties followed by radical forming decomposition may produce an efficient remote cure system. Utilization of 2,4-dinitrophenyl phenylglyoxylate (NPPG) provides a good example to illustrate this point. The sequence presented by Scheme 4 results in formation of hydroxyl and benzoyl radicals which are both known as excellent radicals for polymerization initiation. Therefore, NPPG is expected to display higher efficiency in the remote cure process compared to DNPO. Direct comparison of the remote cure activity in both TMPTA and DPGDA confirms this assumption (Figure 6).

The presence of the 2,4-dinitrophenyl moiety, which is a good leaving group, is necessary to ensure the remote cure activity. Experiments involving methyl phenylglyoxylate resulted in almost no DB conversion in TMPTA (minor gelation, 4% DB conversion measured).

In summary, the remote polymerization concept has been demonstrated by exposing the oxalate containing monomers to the flow of nitrogen saturated with hydrogen peroxide vapors. The aryloxyoxalyl hydroperoxy intermediate postulated as a result of interaction between H_2O_2 and aryl oxalate is responsible for the remote cure action of this system. This intermediate, in turn, produces phenoxyl and hydroxyl radicals with the latter responsible for the initiation of polymerization. The efficiency of the remote cure process is even greater for systems containing glyoxylate esters owing to their ability to produce both hydroxyl and benzoyl radicals. Additional investigations are underway to further improve the efficiency of the process.

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Supporting Information Available: Text giving details of synthetic procedures, additional double bond conversion curves, and additional results of LFP studies and figures showing ^{1}H NMR of purified DNPO, ^{13}C NMR of purified DNPO, comparison of DB conversion profiles for TMPTA and DPGDA, combined data for TMPTA and DPGDA, control experiments investigating the effect of various factors on remote cure activity for various internal references, transient LFP spectra and kinetic traces and fits for LFP studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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(4) This term could be used only for situations where chemical reaction shares common intermediates with the corresponding photochemical process.

(5) The word “photopolymer” is generally used to mean a polymer or polymeric mixture that is generally formed by a photopolymerization process. The advantages of photopolymerization are well-known. Photopolymerizations are fast, they can be turned on and off, the systems form so-called “all-solids” polymers, and so forth. For a complete review the reader is directed to: Neckers, D. C.; Jager, W. *Chemistry & Technology of UV & EB Formulations for Coatings, Inks, and Paints. Volume VII: Photointiation for Polymerization: UV and EB at the Millenium*; Wiley/SITA Series in Surface Coatings Technology: John Wiley and Sons: Chichester, U.K., 1998.

(6) As requested by one of the reviewers, a more detailed discussion on the importance of remote cure follows. Development of the technology which enables polymerization without direct use of light and/or heat is important and represents a needed innovation in the area of coatings. We have had a strong indication from several manufacturers (through our collaborations) regarding the need for such technology. Any object having a complex 3-dimensional shape would be a challenge to cure with light as light requires direct line of sight. Painting of submarine ballast tanks and rear spoilers for cars already attached to the main body can serve as two examples of many applications where remote cure technology can be successfully used. Use of blue LED arrays and/or fiber optics will simply not work because both methodologies might lack sufficient power and the latter can only provide cure for a small spot. While curing of the coating required some carefully designed methodology, the application of the coating to the 3-dimensional object could be accomplished by a simple submersion.

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