

Stage-Curable Free Radical/Cationic Photopolymerizations

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Abstract

Hybrid free radical/cationic photopolymerizations of acrylates and epoxides provide a convenient method for producing stage-curable systems. In these systems, stage 1 corresponds to a viscous liquid, stage 2 is a moldable putty, and stage 3 corresponds to the cured polymer. Comparison of the reaction rate profiles of the hybrid photopolymerization to those of the neat acrylate and epoxide monomers revealed that: 1) the polymerization rate of the acrylate portion of the hybrid polymerization can be attributed entirely to the dilution of the acrylate monomer by the presence of the epoxide; but 2) the rate of the epoxide polymerization is further reduced by enhanced vitrification due to the presence of the acrylate polymer.

Introduction

Photopolymerizations offer many advantages (such as temporal and spatial control, cost efficiency, and solvent-free systems) over traditional thermally-initiated polymerizations. Photopolymerizations can be classified by the type of active center used to initiate the chain reaction of polymerization. Free radical photopolymerizations are the most prevalent and offers several advantages including wide monomer and initiator availability, relatively high reaction rates, and moisture insensitivity. However, free radical photopolymerizations also have serious disadvantages, such as oxygen inhibition and relatively high polymerization shrinkage. In contrast, cationic photopolymerizations are not inhibited by oxygen and can be used for ring-opening polymerizations that exhibit low polymerization shrinkage¹ and are also practically non-terminating^{2,3} resulting in continued propagation long after the illumination has ceased. Disadvantages of cationic photopolymerizations include; inhibition by water and relatively low reaction rates for the ring-opening polymerizations of oxiranes and oxetanes and a limited number of effective photoinitiators, such as Diaryliodonium and triarylsulfonium salts.

The combination of both monomers in a one pot initiation⁴⁻⁶ yields a simultaneous polymerization in which the free radical monomer polymerizes faster than the cationic, creating a natural sequencing to the reaction and mitigating the disadvantages found in either homopolymerization⁷⁻⁹. This sequential, stage-curable hybrid photopolymerizations generally exhibit three distinct states^{10,11}, with either a free radical or a cationic polymerization accompanying the transitions between states, as illustrated in Figure 1. The first stage consists of the unreacted monomer mixture; at this time, the system is a relatively low viscosity liquid that may readily flow into small crevices or cracks. The transition from the first stage to the second stage may be driven by either a free radical polymerization (for example, many acrylate/epoxide systems) or a cationic polymerization (for example, most vinyl ether/acrylate hybrid systems). In either case, the first polymerization reaction results in a marked change in the physical properties of the system which undergoes a transition from a relatively low viscosity liquid to a high viscosity (sometimes free-standing) shapeable putty. Once the first polymerization is complete the system is now in stage 2. The second polymerization (free radical

or cationic, opposite that of the first stage) transitions the hybrid system into the third and final stage. Again this stage usually has a marked change in the physical properties of the system. The system transforms from the stage 2 high viscosity shapeable putty to a solid rigid polymer, stage 3

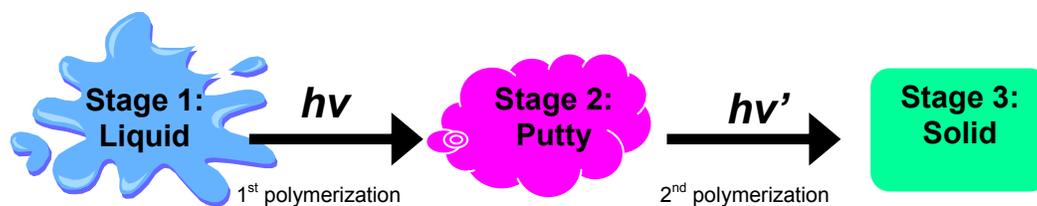


Figure 1: The development of the sequential stages of the free radical/cationic hybrid system.

Experimental Methods.

The monomers used in this study include a cycloaliphatic diepoxide (3,4-epoxycyclohexylmethanyl 3,4-epoxycyclohexanecarboxylate, ERL 4221, available from Dow Chemical Co.) and a hexafunctional acrylate oligomer (Ebecryl 830 available from UCB Chemicals). Polytetrahydrofuran diol (Aldrich) was added to enhance the cationic rate of the polymerization. The hybrid photopolymerizations have been initiated with a visible three-component photoinitiation system containing camphorquinone (CQ, Hampshire Chemical Corp.) or rose Bengal (RB, Aldrich) as the photosensitizer, ethyl-4-dimethylaminobenzoate (EDMAB, Aldrich) or 4-tert-butyl-N,N-dimethylaniline (TDMAB, Aldrich) as the electron donor, and diaryliodonium hexafluoroantimonate (DPI, CD1012 available from Sartomer Chemical Co.) as the iodonium salt. The photopolymerization reactions were monitored using a Perkin-Elmer DSC-7 modified in-house for photo-experiments. The light source was a 200 W Oriel hg(Xe) arc lamp. The output of the lamp was passed through a 400 nm bandpass filter and water filter to eliminate ultraviolet and infrared light from reaching the sample. The filtered light intensity was found to be $\sim 45 \text{ mW/cm}^2$ as measured by graphite disc absorption. The reaction chamber was sealed with a quartz cover and purged with nitrogen. The lamp was turned on 30 seconds after the DSC began recording the heat flow data for each sample. The heat flow data collected by the DSC was converted into the rate of polymerization and conversion using the heat of polymerization, which was estimated as 330 kJ/mol for the hexafunctional acrylate oligomer and 194 kJ/mol for the cycloaliphatic diepoxide.

Results and Discussion

The hybrid system polymerized for this study consisted of 80% cycloaliphatic diepoxide and 20% hexafunctional acrylate monomer, while the neat systems were either 100% of the cycloaliphatic diepoxide or 100% hexafunctional acrylate oligomer. Both the hybrid and neat systems were initiated with $3.0 \times 10^{-5} \text{ mol/g stock}$ of camphorquinone (stock solution contains both monomer plus polytetrahydrofuran diol), $2.5 \times 10^{-6} \text{ mol/g stock}$ of ethyl-4-dimethyl-aminobenzoate, and $2.0 \times 10^{-6} \text{ mol/g stock}$ of diaryliodonium hexafluoroantimonate. Figure 1 shows the heat flow as a function of time for the three polymerization systems described above. The large dashed line represents the neat hexafunctional acrylate monomer system, while the small dashed line represents the neat cycloaliphatic di-epoxide system. The solid line represents the hybrid photopolymerization of the monomer system containing 20% hexafunctional acrylate oligomer and 80% cycloaliphatic diepoxide. Figure 1 illustrates a number of interesting trends. For example, comparison of the reaction profiles for the neat polymerization systems reveals that the free radical acrylate polymerization reaction is more rapid than the cationic

epoxide reaction, and the reactions are essentially distinct in the hybrid reaction system. In addition, comparison of the acrylate peaks for the neat system and the hybrid system reveals that there is no change in the induction time (the reaction begins immediately upon illumination), but that the polymerization rate is reduced for the hybrid polymerization (the heat flow is directly proportional to the rate of polymerization).

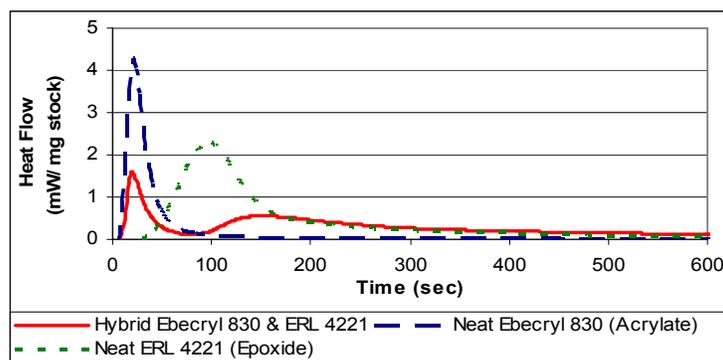


Figure 1. Heat profiles comparing the 20% acrylate / 80% epoxide hybrid photopolymerization to neat acrylate and epoxide photopolymerizations.

To investigate whether the acrylate polymerization rate reduction could be attributed entirely to the dilution effect due to the presence of the epoxide monomer, the data was reanalyzed by plotting the heat flow per mg of the monomer that is polymerizing (instead of the heat flow per mg of total solution in the system). In the new plot, which is shown in Figure 2, the reaction profiles for the neat monomer systems are simply obtained by dividing the heat flow by the initial monomer mass, while the reaction profile for the hybrid system is divided into two regimes. In the first regime, which corresponds to the time from 0 to 108 seconds, the heat flow is divided by the initial mass of acrylate monomer since this is the only monomer that is reacting. Similarly, in the second regime (108 to 1800 seconds) the heat flow is normalized by the initial mass of the epoxide monomer. Figure 2 shows that the acrylate portion of the hybrid system (solid line, first peak) has the same profile as its corresponding neat system (large dashed line), thereby confirming that the reduction in polymerization rate of the hybrid polymerization system can be attributed entirely to the dilution of the acrylate monomer by the presence of the epoxide (there is no evidence of any other interactions). Figure 2, also illustrates some interesting trends in the cationic portion of the hybrid polymerization (solid curve) when compared to its corresponding neat epoxide system (small dashed line). In contrast to the free radical portion, there is clearly a longer induction time before the reaction is perceptible (~ 108 seconds for the hybrid case and ~38 seconds for the neat epoxide), and a marked decrease in the heat flow per mg of epoxide monomer. The figure illustrates conclusively that these trends in the cationic portion of the hybrid system can not be entirely attributed to a dilution effect.

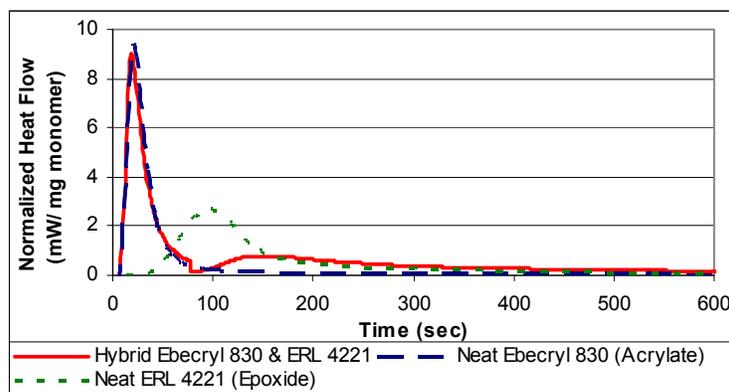


Figure 2. Normalized heat profiles comparing the 20% acrylate / 80% epoxide hybrid photopolymerization to neat acrylate and epoxide photopolymerizations.

To investigate this interference further, the normalized heat flow data was transformed into polymerization rate profiles as a function of time (Figure 3) using the equation below.

$$R_p (\text{mol} / \text{L} \cdot \text{s}) = \frac{\Delta H (W / g) * \rho (g / L)}{\Delta H_p (J / \text{mol})} \quad \text{Equation (1)}$$

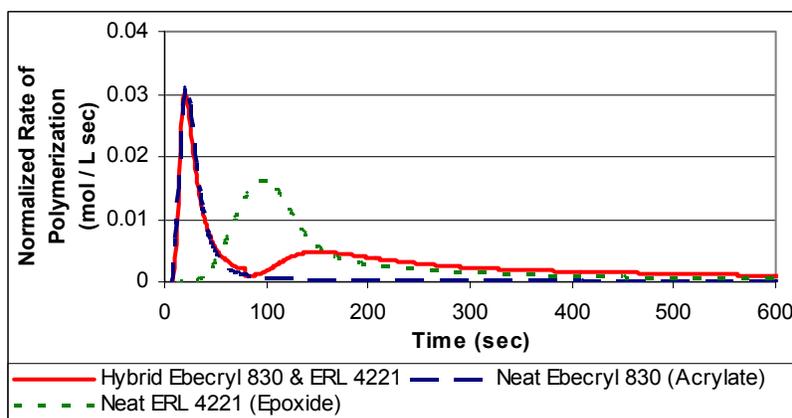


Figure 3. Rate of polymerization profiles comparing the 20% acrylate / 80% epoxide hybrid photopolymerization to neat acrylate and epoxide photopolymerizations.

Figure 3 illustrates some interesting trends when the reaction profile for the hybrid photopolymerization system is compared to those of the corresponding neat monomers. It is interesting to note that the reaction profile for the acrylate portion of the hybrid photopolymerization (solid line) system essentially matches that of the neat acrylate system (large dashed line). The polymerization rate when the 25% of the acrylate is converted is $0.03117 \text{ mol} / \text{L} \cdot \text{sec}$ for the neat acrylate system. This is comparable to the $0.02753 \text{ mol} / \text{L} \cdot \text{sec}$ polymerization rate for the acrylate portion of the hybrid system, within the system's 25% conversion variation of $\pm 0.0036 \text{ mol} / \text{L} \cdot \text{sec}$. The rate of polymerization at an acrylate conversion of 50% of the hybrid system was $0.01155 \text{ mol} / \text{L} \cdot \text{sec}$, which is again comparable to the neat system's polymerization rate of $0.01531 \text{ mol} / \text{L} \cdot \text{sec}$, within the system's 50% conversion standard deviation of $\pm 0.0060 \text{ mol} / \text{L} \cdot \text{sec}$. This data confirms that essentially the only effect the hybrid system has on the free radical portion of the polymerization is a dilution effect.

While the hexafunctional acrylate portion of the hybrid photopolymerization system only demonstrates a dilution effect compared to its' corresponding neat system, Figures 2 and 3 show the cycloaliphatic epoxide portion of the hybrid system is being affected by something beyond dilution. As can be seen above in Figure 3, the rate of polymerization for the cycloaliphatic epoxide portion (solid line, second peak) is greatly reduced and the polymerization time is delayed when compared to the neat epoxide system (small dashed line). The rate of polymerization at 10% epoxide conversion is reduced from $0.01605 \text{ mol/L-sec}$ for the neat system to $0.00370 \text{ mol/L-sec}$ for the cycloaliphatic epoxide portion of the hybrid photopolymerization. This is well outside the standard deviation of $0.00131 \text{ mol/L-sec}$ for the epoxide system. At 25% conversion the rate of polymerizations also dropped from $0.00493 \text{ mol/L-sec}$, for the neat system, to $0.00106 \text{ mol/L-sec}$, for the hybrid system. The induction time of the epoxide cationic reaction was delayed fifty seconds, from 53 sec. (neat system) to 108 sec. (hybrid photopolymerization system), which is greatly outside the standard deviation of 11 for the induction time of the cycloaliphatic epoxide.

This reduction of polymerization rates and induction times of the epoxide portion of the hybrid photopolymerization likely arises from the presence of the highly crosslinked acrylate network which will reduce the mobility in the system and contribute to an early vitrification of the cationic polymerization. Because the acrylate portion of the system is polymerized first, the system becomes highly viscous due to the highly crosslinked acrylate chains. This decreases the mobility of the unreacted monomer slowing their movement to the cationic active centers. Since the unreacted epoxide monomer has less mobility it will take more time to reach the cationic active centers, thus delaying the induction time and causing the epoxide portion of the hybrid system's rate of polymerization profile to reduce and become more spread out. Also, the crosslink acrylate portion of the system increases the chances for the cationic active centers to become "trapped" because the unreacted monomer can not reach them, terminating the process and decreasing the polymerization rate.

The conversion profiles of the neat and hybrid photopolymerizations were calculated by the integration of the area under the normalized heat profiles and division by the total heat of polymerization, figure 4 below. The conversion calculated by the DSC for the epoxide system might be lower than the actual conversion of the system. This is because the cationic reaction is very long lived, non-terminating reaction, continuing over days. This slow reaction does not generate enough heat to register on the DSC. However, the DSC will pick up the bulk of the reaction and can be use to explain trends. The free radical (acrylate) and cationic (epoxide) peaks in the hybrid system were separated allowing both the acrylate and epoxide conversion to be calculated. The conversion profiles of the neat system's acrylate monomers (large dashed line) is similar to the hybrid system's acrylate monomer (solid line), Figure 4. At the point where the acrylate portion of the hybrid system becomes non-distinguishable from the epoxide portion, the conversions for the systems were shown to be 69.5% for the neat system and 67.6% for the hybrid system. These results again demonstrate that the acrylate portion of the hybrid system exhibits essentially no interference from the epoxide portion of the hybrid system and behaves like a neat acrylate system. The overall conversion of the cycloaliphatic epoxide portion of the hybrid photopolymerization was reduced from 41.9% (neat system, small dashed line) to 32.5% (mixed dashed line). This reduction is because the crosslink acrylate portion of the hybrid system increases the chances for the cationic active centers to become "trapped", which terminates the process and decreases the overall conversion.

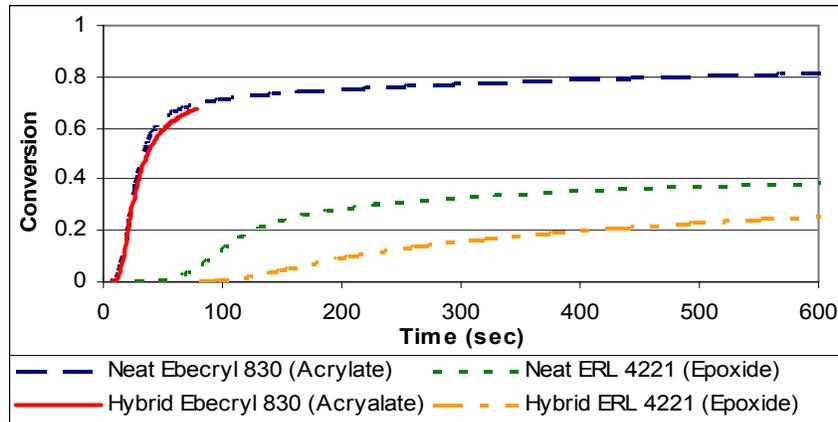


Figure 4. Conversion profiles comparing the 20% acrylate / 80% epoxide hybrid photopolymerization to the neat acrylate and neat epoxide photopolymerizations.

If the postulate that the polymerized hexafunctional acrylate is causing early vitrification of the epoxide reaction is correct, then by increasing the ratio of acrylate to epoxide in the hybrid system, the rate of polymerization for the epoxide portion of the hybrid system should continue to decrease and the induction times become more delayed. Figure 5 illustrates exactly this trend. The figure shows the normalized polymerization rate profiles as the ratio of hexafunctional acrylate oligomer to cycloaliphatic epoxide monomer is varied. The polymerization rate of the acrylate portion of the hybrid system, seen in Figure 5, remains essentially the same (within experimental error), just as in the previous study comparing the 20% acrylate / 80% epoxide hybrid photopolymerization to the neat systems. The epoxide portion of the hybrid photopolymerization system, shown in Figure 5, shows a delay in the induction time and a reduction in the polymerization rate as the amount of acrylate in the system was increased. The reduction of the normalized polymerization rate at 10% conversion is shown in Figure 6.

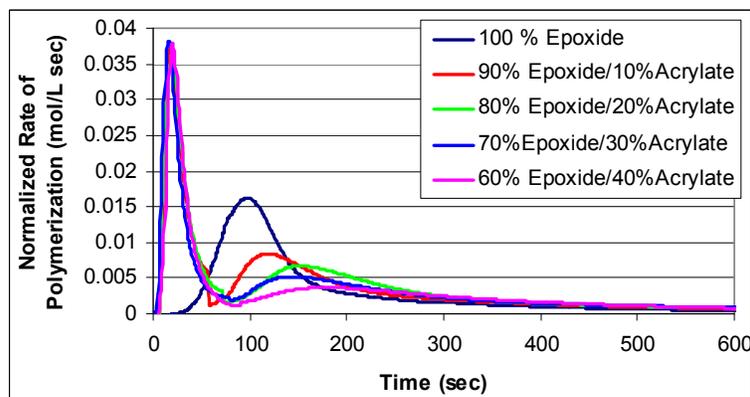


Figure 5. Rate profiles showing the effect of various ratio of epoxide/acrylate in the hybrid system's monomer mixture has on the photopolymerizations.

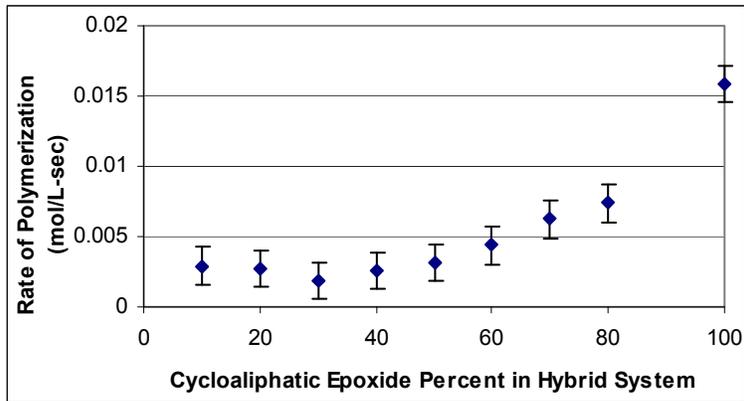


Figure 6. Rates of polymerization (at 10% epoxide conversion) showing the effect that the percent of cycloaliphatic epoxide in the monomer system has on hybrid photopolymerization kinetics.

Figure 6 shows that as the percent of epoxide in the hybrid system increases, and the percent of acrylate decreases, the rate of polymerization for the epoxide of the system increases. This further supports the postulate that the epoxide portion of the hybrid photopolymerization is being inhibited by vitrification. The delay of induction times that vitrification causes can be seen in Figure 7. Figure 7 shows that as the ratio of epoxide to acrylate decreases, the induction time of the cationic reaction in the hybrid polymerization will be more and more delayed. The influence of the monomer ratio further supports the theory that the acrylate portion in the hybrid photopolymerization is causing early vitrification of the epoxide portion.

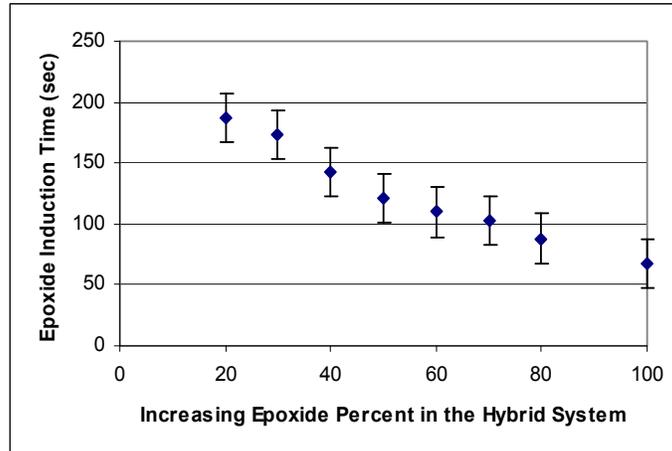


Figure 7: Cycloaliphatic epoxide induction times showing the effect that the percent of cycloaliphatic epoxide in the monomer system has on hybrid photopolymerization kinetics.

Conclusions

Hybrid free radical/cationic photopolymerizations of acrylates and epoxides provide a convenient method for producing stage-curable systems. In these systems, stage 1 corresponds to a viscous liquid, stage 2 is a moldable putty, and stage 3 corresponds to the cured polymer. Results verify the polymerization rate of the acrylate portion of the hybrid polymerization can be attributed entirely to the dilution of the acrylate monomer by the presence of the epoxide. Confirming the existence of the

epoxide as a non-reactive diluent in the second stage polymerization. With this increase in viscosity and the crosslink density of the system the reaction diffusion become the primary vehicle limiting the termination of the acrylate and the initiation of the epoxide¹²⁻¹⁴. Thereby further reducing the rate of the epoxide polymerization due to the enhanced vitrification of the acrylate network in the presence of the polymerizing epoxy monomer.

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