

# Control of Free-Radical Reactivity in Photopolymerization of Acrylates

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In practical use, it is the rate of crosslinked network formation that is of most interest in the free-radical curing of acrylates. One of the simplest indicators of the vitrification point is the sharp rise in methyl ethyl ketone double rubs (MEKR) that occurs as a function of radiation dose applied. It is well known that oxygen inhibition and radical-radical recombination limit efficiency, delaying the onset of network formation to higher dose or longer exposure time.

This paper explores means to alter the reactivity of the intermediate free radicals—in one case by chain transfer to thiol and in another by complexation with stable nitroxide radicals, thereby altering the population of chain-carrying species to favor longer-lived radicals or radical precursors which, by their nature, are less affected by the normal termination processes. By chain transfer formation of thiyl radicals, a simple titration of reactive radicals is possible as observed by detection of the point of maximum MEKR as a function of dose for different starting thiol concentrations. By this means, we can demonstrate that approximately seven times more radicals are created in a typical UV-cure formula following 600 mJ/cm<sup>2</sup> exposure than are created in an EB-cure formula using the same monomer following 30 kGy exposure.

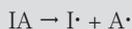
At low concentrations of organic nitroxides, a surprising decrease in radiation dose at the vitrification point

is observed, paired with an increase in ultimate rub resistance. This optimal concentration depends strongly on nitroxide structure, but in all cases it occurs at nitroxide concentrations much smaller than the estimated free-radical concentration at the point-of-cure. Both observations are consistent with a colloidal model of vitrification where first-formed cure domains are cemented together in a slower second step. Finally, we show that latent cure is accentuated by these longer-lived radicals and oxidation products formed from them, allowing a post-heat to significantly advance cure by re-initiation of free radicals.

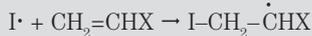
## Introduction

The ultraviolet (UV) and electron beam (EB) polymerization of acrylated materials proceeds by a radical addition mechanism. During a photocure event, a large number of highly reactive radical species are produced with a short, intense exposure to radiation.<sup>1</sup> The production and consumption of these radical species is typically organized into four major steps—initiation, propagation, chain transfer and termination, as illustrated in the following.<sup>2,3</sup>

**Initiation** depends on the formation of free-radical species. This step generally begins with the fragmentation of a photoinitiator (UV) or acrylated monomer (EB) upon exposure to radiation:

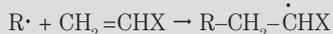
**Reaction 1**

Included in the initiation step is the addition of an initiating radical  $I\cdot$  to a monomer molecule:

**Reaction 2**

It is our convention that  $I\cdot$  is an initiating radical with correct electronic structure to efficiently add to the monomer, while  $A\cdot$  is a radical species with lower probability to initiate chain growth.<sup>2-6</sup> The group X denotes the remainder of the monomer molecule. As this paper focuses on crosslinking systems, X generally contains multiple acrylate groups.

**Propagation** occurs when the product of a previous radical addition,  $R\cdot$ , encounters and adds to an unsaturated group:

**Reaction 3**

A radical species of greater molecular weight is produced, which may continue in further addition reactions.

Alternatively, when a radical species  $R^1\cdot$  approaches a growing or terminated chain  $R^2-H$  with an accessible hydrogen, abstraction of this atom may occur:

**Reaction 4**

This **chain transfer** event results in the termination of  $R^1$ 's growth, but  $R^2\cdot$  may now act as a propagating species.

Radical species are eliminated from propagation by a number of rapid **termination reactions**. As carbon-centered radicals are highly reactive, their combination with other radicals to produce a closed-shell species is favored and this reaction is considered irreversible on the timescale of radiation curing. One form of termination

termination pathway is radical-radical recombination:

**Reaction 5**

$R^1\cdot$  and  $R^2\cdot$  are growing radical chains or initiating radicals. A second type of termination is the reaction of a propagating radical with triplet oxygen to form a peroxy radical species:

**Reaction 6**

The alkyl peroxy radical does not undergo further addition to a monomer;<sup>7</sup> oxygen inhibition, the common name for this termination reaction, is a major drawback to photopolymerizations conducted in air.<sup>8,9</sup>

The rate of double-bond conversion (Reaction 3) is of primary importance only in the early stages of cure, prior to gelation. We refer to gelation as the point at which liquid flow of the solution ceases. After gelation occurs, great differences in mechanical properties can be evident with only minor differences in overall conversion.<sup>10</sup> Thus, instead of monitoring cure kinetics in terms of conversion, we study the final network properties as a function of total exposure to radiation. The strength of a radiation-cured, acrylate-polymer film depends on the rate of vitrification, as characterized by stronger polymer network formation at lower exposure. Here vitrification refers to the formation of an infinite polymer network through crosslinking.

The evolution of this network is hindered by termination reactions such as oxygen inhibition and radical-radical recombination. If a significant number of the propagating radical species can be protected from such unproductive termination reactions, favorable network properties can develop with shorter irradiation times or with less input of energy. Through more efficient use of initiating radicals, we can produce the same or even improved

mechanical properties—all while curing at faster web speeds, with lower lamp power or less inerting.

In this work, we investigate several methods of controlling photopolymerization by changing the nature of the propagating radical. The strategies employed are chain transfer to produce thiyl radicals from carbon radicals using multifunctional thiols; reversible complexation of carbon radicals by stable nitroxide radicals; and thermal post-cure of a radiation-cured system.

We report here the results of the first strategy for control of radical reactivity—chain transfer using multifunctional thiols. The use of nitroxide radicals to reversibly complex propagating radicals and improve cure efficiency, and the possibility of thermal re-initiation in a system photocured in the presence of nitroxides or alkoxyamines is detailed in the full paper.

## Experimental

### Materials

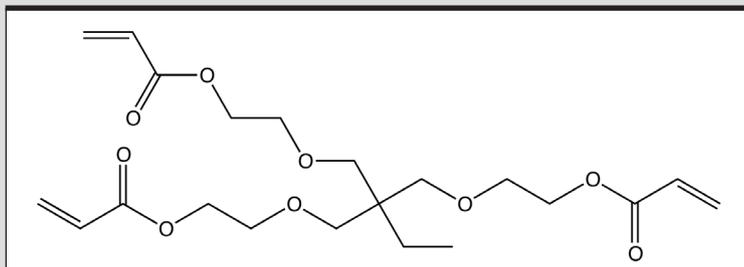
All coating solutions were based on the monomer, ethoxylated trimethylolpropane triacrylate (EOTMPTA, Photomer 4149, IGM Resins) (Figure 1). This monomer was used as received, without removal of inhibitor. The base stock solution for EB curing consisted of 0.5% (w/w) BYK-345 (BYK-Chemie), a proprietary leveling agent, in EOTMPTA.

To prepare the stock coating solution for UV application, 2% (w/w) of the photoinitiator, 1-[4-(2-hydroxyethoxy)phenyl]-2-hydroxy-2-methyl-1-propan-1-one (Irgacure 2959, Ciba, BASF), 15% (w/w) of a proprietary amine acrylate, CN373 (Sartomer Company Inc.), and 0.5% (w/w) BYK-345 were added to EOTMPTA.

Thiol-containing stock solutions for UV and EB were prepared with 4% (w/w) pentaerythritol tetra-3-mercaptopropionate (PETMP,

FIGURE 1

## Structure of monomer used in this work—EOTMPTA



Hampshire Chemical Corporation) (Figure 2) added to the respective base stock solution. An equal mass of EOTMPTA to the added PETMP is removed in the preparation of thiol stock solutions, so that the concentrations of other additives (photoinitiator, acrylated amine, leveling agent) do not differ from the base stock solutions. Samples with intermediate PETMP concentrations were prepared by blending the original stock solutions with thiol-containing stock solutions. The PETMP concentrations are reported as mmol PETMP per kilogram solution. All thiol-containing solutions were used for cure trials within one week of mixing.

### Methods

Solutions were applied to unsealed Leneta cards (form N2A, Leneta

Company) using a U.S. #3 Meyer rod for a constant coating thickness.

UV curing was conducted with a single 300 watts-per-inch, medium-pressure mercury lamp under air. Web speed was varied and the exposure was monitored by a UV Power Puck (EIT). The recorded exposure is the sum of UV-A, UV-B, and UV-C energy densities.

An Advanced Electron Beam laboratory processor with nitrogen inerting was used for EB curing. For typical sample exposure, the chamber was flushed with nitrogen until oxygen concentration was below 200 ppm. To investigate the sensitivity of results for the inerting level, we used short inerting times to achieve up to about 700 ppm  $O_2$  at the time of irradiation. Cures were conducted

below 200 ppm  $O_2$ , unless otherwise noted. Applied dose was varied by adjusting beam current at 100 keV, with a constant web speed of 75 fpm.

The parameter of greatest interest from a practical perspective, and the one we measured directly to characterize extent of cure, is the toughness of the final polymerized film. The technique used to ascertain cured film toughness was MEKR. A cotton-tipped swab was dipped in MEK, pressed against the film over the black (inked) portion of the Leneta card, and an up-and-down rubbing motion was performed with a standard, hard pressure against the card. The number of double rubs (one rub downward followed by another back up to the starting position) necessary to break through the film and reveal the white paper beneath the black ink, uniformly over the rubbed area, was recorded as the MEKR resistance for the film in question.

Solvent rubs, in general, test the resistance of a cured thin film to solvent swelling, as well as physical strain from the rubbing action. A film's susceptibility to these processes decreases with the extent of crosslinking. Thus, we used MEKR as a measure of the global extent of crosslinking, which develops during the final stages of cure with very small changes in double-bond conversion.<sup>10</sup>

### Cure Enhancement by Chain Transfer

Thiols are well-known chain transfer agents in radical polymerization.<sup>3,11,12</sup> The chain transfer constant, or the ratio of chain transfer rate constant to propagation rate constant, for n-butyl mercaptan in styrene (a typical thiol in a monomer analogous to acrylates) is  $C_S = 21$ .<sup>3</sup> That is, for a propagating radical, hydrogen abstraction to form thiyl radicals occurs 21 times more rapidly than addition to monomer

FIGURE 2

## Structure of tetrafunctional thiol used in this work—PETMP

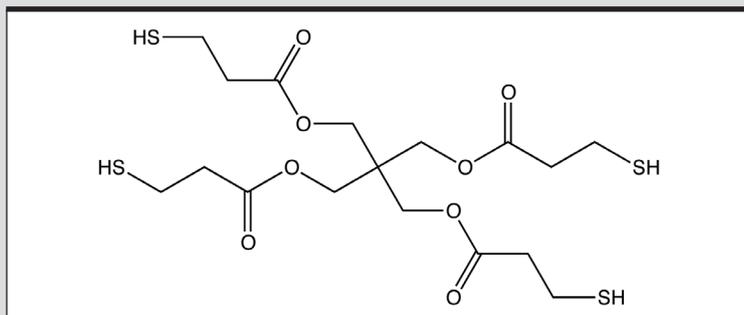
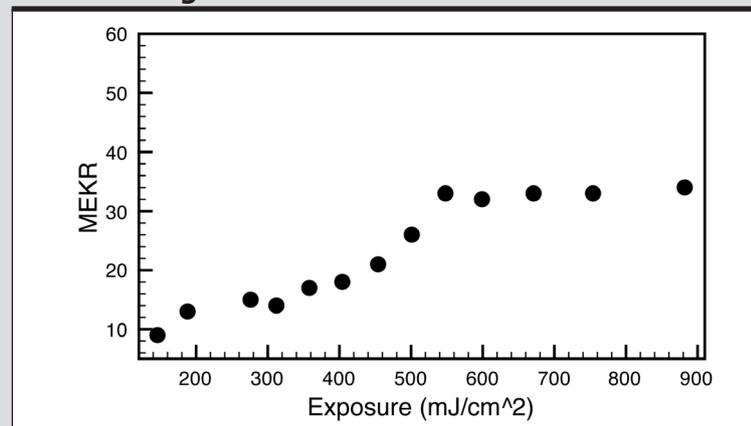


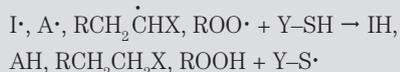
FIGURE 3

## 0.0 mmol/kg PETMP



double bonds. Such speed is necessary in radiation-cured polymerizations where consumption of the monomer is very rapid due to the high initial concentration of radicals.<sup>1</sup>

By including thiol species into a formula for radiation curing, we add several reactions to the general scheme presented earlier. Let Y-SH represent a (possibly multifunctional) thiol. Any radical that comes into contact with the thiol group is likely to abstract hydrogen:

**Reaction 7**

Thus, normally unproductive radicals such as  $A\cdot$  and  $ROO\cdot$  are replaced by thiyl radicals ( $Y-S\cdot$ ), “soft” radical species which efficiently add to acrylate double bonds.<sup>13,14</sup> Chain transfer between carbon radicals (Reaction 4) can lead to sterically hindered radical sites which cannot add to acrylate double bonds.<sup>15</sup> The conversion of these radicals to thiyl species through hydrogen abstraction can be viewed as a restoration of their propagating ability.

The thiyl radicals formed during cure are resistant to both

recombination and reaction with oxygen,<sup>16,17</sup> as compared to their carbon analogues. Thus, we can expect a higher concentration of thiyl radicals in the late stages of cure than is possible with carbon radicals ( $R\cdot$ ). Development of favorable mechanical properties is strongly linked to the extent of crosslinking, which occurs during this period. Hence, the replacement of  $R\cdot$  by  $Y-S\cdot$  will result in a more efficient use of the radical “potential” built up during initiation and, therefore, a more thoroughly cured film.

Propagation of cure by thiyl radicals results in the formation of a large number of thioether ( $R^1CH_2-S-CH_2R^2$ ) linkages in the crosslinked network. This is a flexible bond<sup>18</sup> that can increase the strain tolerated by the polymer film without breakage. Even more added structural stability can result if multifunctional thiols are used. In this case, thiol molecules can lead to additional crosslinks in the acrylate network once their functional ends connect initially separated chains.

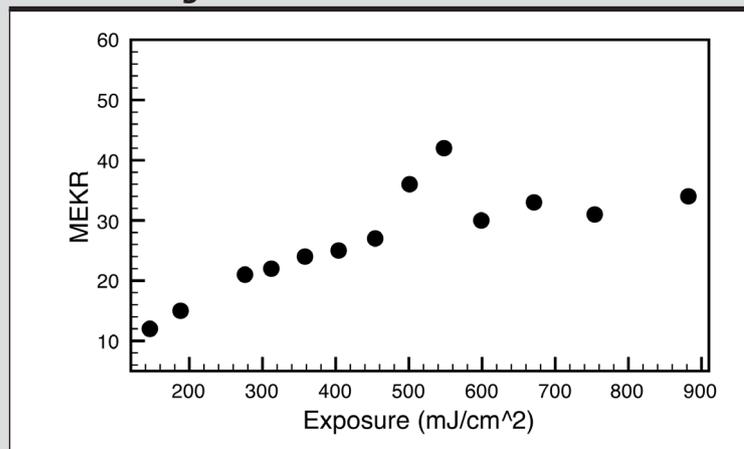
**Results**

We investigated the effects of formulating UV- and EB-curable coating solutions with small amounts of the tetrathiol PETMP. A series of UV-coating formulae with 0.0, 15.3, 20.5 and 45.8 mmol/kg PETMP was prepared, coated on Leneta and cured with UV exposure varying between 146 and 882 mJ/cm<sup>2</sup>. MEK double rubs were performed, and the results of these evaluations are shown in Figures 3-6.

In Figure 3 is the cure response of a control EOTMPTA coating with no added thiol. It conforms to the typical sigmoid shape. Following the onset of gelation (at which point MEKR can be measured), there is a “gel” plateau at

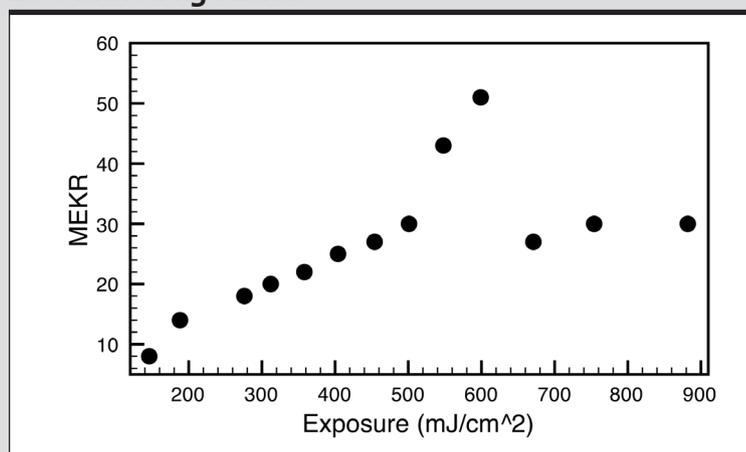
FIGURE 4

## 15.3 mmol/kg PETMP



## FIGURE 5

### 20.5 mmol/kg PETMP



low exposure with lower MEKR values. Once the critical dose is approached for the onset of vitrification, mechanical properties develop rapidly with exposure. The plot ends with the upper (or “vitrified”) plateau at high exposure. The plots at intermediate PETMP concentration in Figures 4 and 5 show a peak in MEKR values, which begins after 500 mJ/cm<sup>2</sup> UV exposure. Note that the points following the peak exposure domain belong to the unmodified upper plateau region as detected in Figure 3.

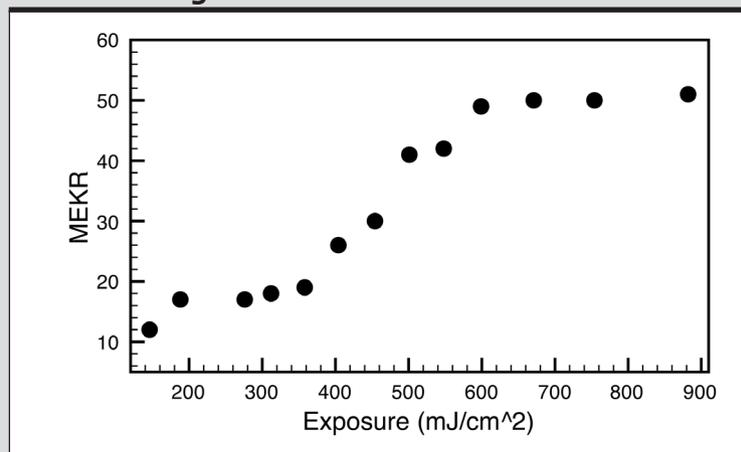
Increasing the concentration of PETMP from 15.3 mmol/kg in Figure 4 to 20.5 mmol/kg in Figure 5 results in an increase in the height of this peak, from 42 to 51 MEKR. Furthermore, the length of the peak region (range of UV exposure values corresponding to large MEKR) increases in the direction of higher irradiation with greater concentrations of PETMP. While 600 mJ/cm<sup>2</sup> gives only 30 MEKR in Figure 4, this exposure corresponds to the maximum MEKR value of 51 in Figure 5.

Finally, as shown in Figure 6, a concentration of 45.8 mmol/kg PETMP results in a cure response curve that has returned to the sigmoid shape of

Figure 3. However, while the lower plateau region is at similar MEKR values between the two, the control curve (Figure 3) provides 33 MEKR at the upper plateau but the high PETMP

## FIGURE 6

### 45.8 mmol/kg PETMP



curve (Figure 6) has an upper plateau at 50 MEKR. Thus, hugely improved mechanical properties are obtained at the vitrified plateau with a sufficient formulated level of PETMP.

An analogous experiment was conducted with EB curing. We prepared a series of EB coating formulae containing 0.0, 2.0, 4.1 and

6.1 mmol/kg PETMP. These were applied to Leneta cards and cured with EB dose varying from 10 kGy to 35 kGy. MEKR results for these cured films are presented in Figures 7-10.

These EB cure response curves mirror the ones obtained for the UV-cured system—the character of the curve and the MEKR values obtained depends on the amount of PETMP added. Figure 7 is a control sample with no PETMP. The vitrified plateau begins at a dose of about 25 kGy, and 11 MEKR are obtained in this final regime. In the cure response plots Figures 8 and 9, there are peaked upper plateau regions. The doses for this peak range from 22 to 28 kGy and 22 to 33 kGy, respectively, and about 15 MEKR are obtained. Once 6.1 mmol/kg PETMP is added, as in Figure 10, the sigmoid shape is restored. Additionally, a much greater

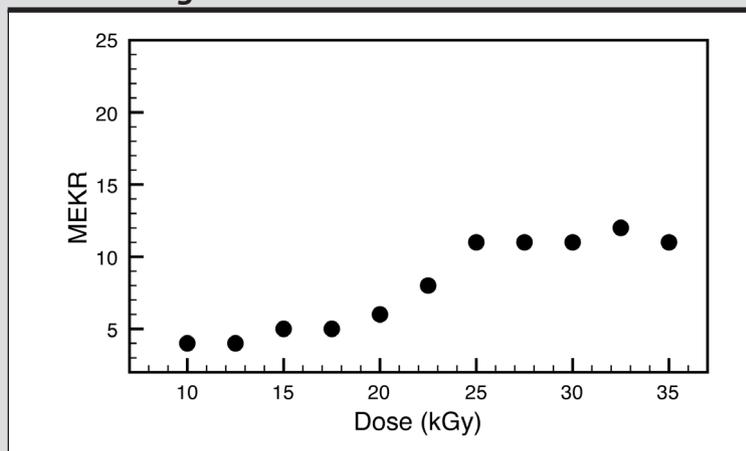
vitrified plateau MEKR value, over 20 (double that of the control), is obtained for these cure conditions.

### Colloidal Model for Acrylate Polymer Growth

To explain the shape of the cure response curves for UV- and EB-coating solutions (as the concentration

FIGURE 7

## 0.0 mmol/kg PETMP

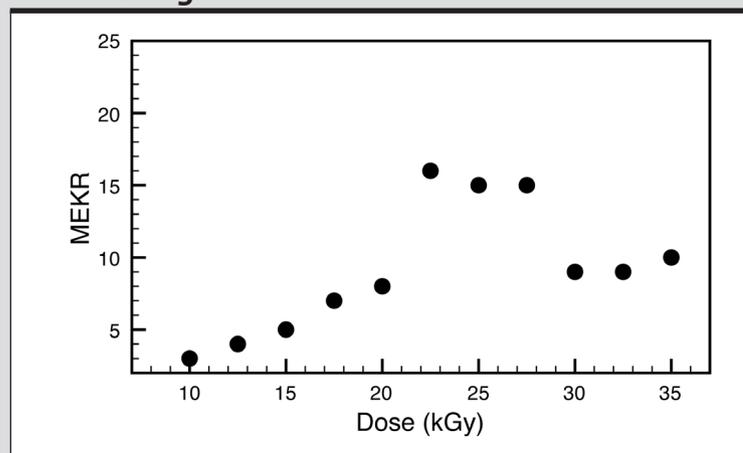


of PETMP is varied) we introduce a qualitative, two-stage colloidal model for polymer growth during radiation cure. In the first stage of curing, radicals are formed through initiation processes and begin to propagate by adding to the plentiful monomer double bonds. These growing chains are distributed stochastically throughout the liquid monomer solution. Chain addition propagates outward from these sites, radiating into the free surrounding monomer. Once most of the eventual double-bond conversion is complete, the film will contain tightly crosslinked, highly branched domains (corresponding to the beginning sites of initiation) separated by a more weakly connected polymer with fewer crosslinks.

While there are domains of dense, nearly infinite molecular weight polymer of high modulus, these are connected by a much lower modulus material. The low MEKR obtained at the early, gel plateau in a cure response curve corresponds to the material failing at the weak regions connecting the colloidal, spherical domains of high crosslink density. The transition between gel plateau

FIGURE 8

## 2.0 mmol/kg PETMP



(at low MEKR) to vitrified plateau (at high MEKR) corresponds to the fusion of colloidal domains into a more rigid global network.<sup>19</sup> We find that the propagation chemistry occurring during this transition is key to determining the polymer strength.

As evidenced by the sustained high MEKR values at the vitrified plateau in Figures 6 and 10, crosslinked polymer produced in the presence of multifunctional thiols is stronger than that produced without a thiol. Due to the extremely high chain transfer

constant of thiols, it is reasonable to assume that carbon radicals are converted to thiyl radicals as rapidly as they form. Therefore, the early stages of cure (building of colloidal domains of active propagation) always involve thiyl addition to C=C bonds. However, with greater applied doses of radiation, the number of initiating radicals increases. The final stage of cure (vitrification through the fusion of colloidal domains) will take place predominantly by the propagation mechanism corresponding to the radical species of greatest concentration.

If the number of available thiol groups exceeds the number of

initiating radicals, the final stages of cure will also be dominated by the thioether-forming addition of Y-S• to CH<sub>2</sub>=CHX. However, if the concentration of R• (carbon centered radical) is greater than Y-S• at the end of cure, the more rigidly crosslinked all-acrylate polymer will be the material which solidifies the overall network. MEKR results show this brittle linking material to be much less rub-resistant than the flexible thioether-containing polymer produced through thiyl addition.

FIGURE 9

## 4.1 mmol/kg PETMP

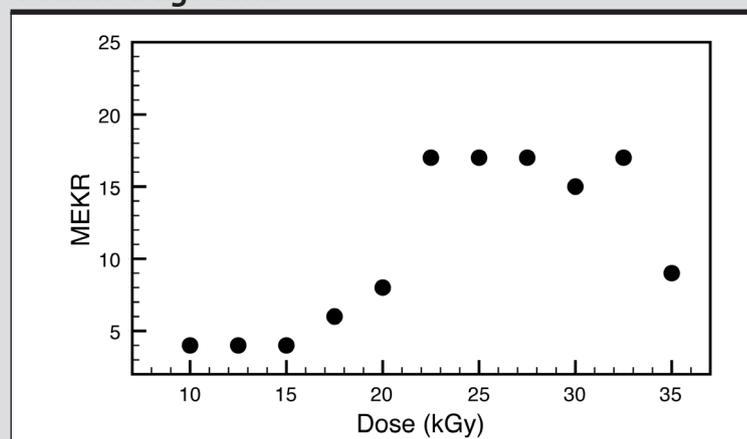
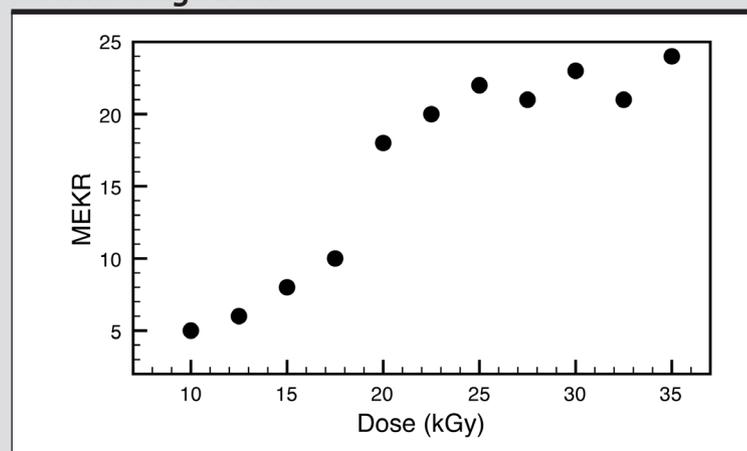


FIGURE 10

## 6.1 mmol/kg PETMP



## Thiol Groups Titrate Radicals

Based on the colloidal model of acrylate photopolymerization, we have inferred a quantitative link between the total concentration of thiol groups [SH] and the exposure at which the rate of carbon radical propagation exceeds the rate of thiyl radical propagation. For convenience, we refer to this as the crossover point for the given SH concentration. Equivalently, for each level of radiation exposure within the vitrified plateau, we can

associate a number [SH] of thiol groups such that the given exposure is the crossover point between peak and low plateau MEKR values. This concentration of thiol groups is not expected to equal the total number of radicals formed at initiation. Rather, it is the number of propagating radicals contributing to the development of mechanical properties and available for chain transfer to yield thiyl radicals.

The crossover points for the UV-cured data series in Figures 3-6 were calculated by taking the midpoint exposure between the end of the peak region and the start of the unmodified upper plateau region. These crossover exposure values are given in Table 1. We could only determine a lower bound for the crossover point with [SH] = 183.2 mmol/kg, as the (thiyl addition) peak domain extends throughout all the vitrified plateau points. That is, no crossover is observed. Analogous calculations were performed for the EB-cured series in Figures 7-10 and can be found in Table 2. Again, only a lower bound for the crossover dose with 24.4 mmol/kg thiol groups could be found in EB. By varying [SH] and determining the crossover point in this way, we titrate the number of radicals formed at each measured crossover exposure. A plot of MEKR at a fixed exposure against [SH] will have the form of a titration curve.

TABLE 1

## Crossover exposure values for UV-cured EOTMPTA coatings with PETMP

The crossover is obtained by linear interpolation in the abscissa of the cure response curve, between the final peaked point and the first nonpeaked plateau point.

[PETMP] (mmol/kg)	[SH] (mmol/kg)	Exposure (mJ/cm <sup>2</sup> )
15.3	61.2	574
20.5	82.0	635
45.8	183.2	>882

TABLE 2

### Crossover dose values for EB-cured EOTMPTA coatings with PETMP

Crossover is defined and calculated in the same manner as for UV results in Table 1.

[PETMP] (mmol/kg)	[SH] (mmol/kg)	Dose (kGy)
2.0	8.0	28.8
4.1	16.4	33.8
6.1	24.4	> 35.0

By linear interpolation of the crossover data, we found that a 600 mJ/cm<sup>2</sup> UV exposure required a thiol group concentration of 70 mmol/kg for equivalence with propagating radicals. For an EB dose of 30 kGy, the necessary value of [SH] was 10 mmol/kg. Hence, we have measured the ratio of propagating radicals in UV curing to that in EB as 7-to-1.

The fact that far fewer radicals are produced in EB cure, as compared to UV, is not surprising as there are clearly pronounced differences in the mechanical properties of UV- and EB-cured coatings. The UV control cure response in Figure 3 has a vitrified plateau with more than 30 MEKR, while the EB control curve (Figure 7) shows only 12 MEKR at this plateau.

Formulated concentration of photoinitiator in our UV-cured samples was 2.0 % (w/w) Irgacure 2959 or [PI] = 89.17 mmol/kg. The published quantum yield for dissociation,  $\Phi$ , of Irgacure photoinitiators ranges from 0.2 to 0.6.<sup>20-22</sup> Thus, using  $\Phi = 0.6$ , the maximum concentration of radical pairs produced is:

#### Reaction 8

$$\Phi \cdot [\text{PI}] = 53.5 \text{ mmol/kg.}$$

Doubling this value, since there are two free radicals originating from each radical pair, we find the predicted maximum concentration of initiating radicals to be 107 mmol/kg. Comparison

to the 70 mmol/kg concentration of propagating radicals, as measured by titration with thiol groups, shows that fewer radicals than the theoretical maximum actually contribute to cure.

### Conclusions

The photoinitiated free-radical polymerization of acrylates in modern applications requires extremely rapid conversion using high concentrations of initiating radicals. The molecular architecture of the polymer generated is, thus, largely uncontrolled. As reported in the full paper, we have explored several distinct means of altering photopolymerization dynamics and, hence, final mechanical properties, through the intelligent control of free-radical reactivity.

Partial replacement of carbon-centered radicals with sulfur-centered thiol radicals (from chain transfer to a thiol) results in a propagating species that is resistant to radical-radical recombination and oxygen inhibition. Furthermore, the thioether bonds produced in the cured film add strength and flexibility.

Competition between this thiol addition and standard acrylate propagation provided an interesting means of probing the growth of cured domains through space and led to the development of a colloidal model for acrylate polymerization. Based on this model and the data showing

competition between thiol and acrylate addition, we were able to estimate that seven times more radicals are produced in UV cure than in the EB process.

In the full paper, we make use of the colloidal model developed here to explain the results of two additional investigations into the control of free-radical reactivity.

Within a narrow range of concentrations, stable nitroxide radicals afford benefits in cure efficiency, as measured by a lowering of the onset point or dose required for the beginning of vitrification, along with an increase in the eventual MEKR obtained. The reversible complexation of radicals (in the form of alkoxyamines) grants them an effectively longer lifetime. Radicals that would be terminated in the early stages of cure are complexed rapidly; and these complexes dissociate during late cure; when the total radical concentration has been greatly reduced and a small increase in radical concentration leads to a much greater extent of vitrification.

It was found that the presence of alkoxyamines during photocure (generated in situ from nitroxides or added at the time of formulation) leads to what can be called stored radical potential. Post-heating of a cured film that contains these materials shows a significant increase in MEKR. The apparent activation energies of post-curing; and the dependence on oxygen concentration during cure; suggests that oxidized species, rather than alkoxyamines themselves, are responsible for releasing radicals during thermal initiation. ▀

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