Kinetic Study of Free-Radical Polymerization of Multifunctional Acrylates and Methacrylates

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Abstract

The conversion profiles of ultraviolet-induced polymerization of di-, tri-, and tetraacrylate and of di- and trimethacrylate monomers were measured by in-situ Fourier Transform Infrared (FTIR) spectroscopy. The effects on final conversion of functionality, monomer type (acrylate vs. methacrylate), photoinitiator concentration, light intensity, radiation wavelength, and film thickness were investigated. The trends in final conversion correlate with three features of the conversion profiles: (1) nominal reaction rate, (2) conversion before the onset of deceleration, (3) conversion after the onset of deceleration. The results suggests three important strategies to optimize reaction kinetics. The first, as proposed by Kloosterboer,[1] is to raise reaction rate. The second is to postpone onset of deceleration. The third is to provide conditions so that the growing network is as open and flexible as possible.

Introduction

Radiation curing of acrylates and methacrylates is used more and more in applications ranging from decorative and protective coatings to magnetic and optical disks and to dental fillings.[1-4] The primary advantages are that (1) solvent emission is eliminated, (2) curing can be done at ambient temperature. Multifunctional monomers can produce highly crosslinked polymer networks that are tough and highly solvent resistant. However, incomplete conversion is a serious problem with such systems. It is desirable to under-stand the kinetic behavior of polymerization generally, but particularly regarding factors that govern the final conversion.

In this work we characterize the UV-induced polymerization of multiacrylates (with two to four acrylate per monomer) and multimethacrylates in terms of nominal reaction rate, conversion before the onset of deceleration, conversion after the onset of deceleration, and the final conversion.

Previous Theories

Polymerization of multifunctional monomers often behaves anomalously, notably autoacceleration, autodeceleration,[1,5-8] and retarded volume shrinkage.[1,9]

Autoacceleration is thought to be caused by the decreased mobility of polymer radicals; this can occur very early in the polymerization. The decreased mobility of radicals leads to diffusion-controlled termination; this increa-ses the radical concentration and thus the propagation rate. Autodeceleration follows autoacceleration and is thought to result from the onset of diffusion control of the propagation reaction. As the mobility of the reactive functional groups is further reduced, they become less and less reactive until finally the reaction becomes immeasurably slow. At some point the material vitrifies after which all further propagation is limited by very slow segmental diffusion.

For multifunctional monomers, the proportionality between shrinkage and conversion that is commonly observed in monoacrylates breaks down.[1] Moreover, volume shrinkage can influence the kinetics. Kloosterboer[1] proposed that as the rate of reaction rises, the shrinkage of the polymer system can not attain the equilibrium volume (at a given conversion); so excess free volume is produced. This excess free volume preserves segmental mobility; so higher final conversion is reached. Other papers also indicated that faster polymerization certainly leads to higher final conversion.[10,11]

Monomer functionality also has a marked effect on the final conversion.[5,12] Anseth *et al.*[5] show a dramatic rise in the final conversion as the polymerization rate is increased by lowering functionality. However, instead of using the excess free volume reasoning, they propose that monomers with higher functionality have both lower propagation and termination rate constants.

Both acrylates and methacrylates are commonly used in radiation curing. When monomer types are changed, further considerations are required. It has been found that methacrylates exhibit a lower volume shrinkage[13,14] but they have

a lower final conversion. Anseth *et al.* attribute this to larger steric hindrance associated with the methyl group on the methacrylates.[5]

Methods

Fourier Transform Infrared (FTIR) spectroscopy has been used to follow the reaction *in situ*.[12,15] Its advantages over other techniques (such as differential photocalorimetry (DPC) and dilatometry) include a shorter induction time (*cf.* DPC, which can introduce a heat transfer delay[15]), independence of the functional group conversion from any theoretical parameters (*cf.* DPC, which requires the heat of reaction) and from artifacts of delayed volume shrinkage (*cf.* dilatometry[15,16]).

Although quite a few authors have described trends in the rate and/or final conversion as functionality, monomer type, and light intensity are changed, there seems to be no comprehensive FTIR study (excepting Decker's meritorious contribution[12]). Here we report and detail FTIR study that reveals how functionality, monomer type, photoinitiator concentration, light intensity, radiation wavelength, film thickness, and addition of a polymeric solvent all affect the final conversion.

Experiments

Materials

The names and abbreviations of photoinitiator (DMPA), monomers, and polymeric solvent are listed in Table 1. Their structures are shown in Table 2. All materials are from Aldrich (Milwaukee, WI), except DEGDA from Sartomer (West Chester, PA). Photoinitiator concentration, $[PI]_0$, is expressed as the ratio of moles of DMPA to total moles of double bonds presented by the monomer. The photoinitiator and monomer mixtures were prepared to the desired concentrations and were stored in dark, capped glass tubes at room temperature. In the sample containing polymeric solvent, the solvent concentration [PEG] is also expressed as the molar ratio of PEG to total double bonds of the monomer.

FTIR Measurement

A drop of liquid sample was placed between two NaCl plates separated by a $0.015 \times 25mm$ Teflon spacer (Spectra-Tech Inc., CT). (To characterize the thickness effect, a $0.050 \times 25mm$ Teflon spacer was also used.) A Nicolet 550 Fourier Transform Infrared (FTIR) spectrometer with a DTG detector was used. All kinetic measurements were performed *in situ* using a set-up shown schematically in Figure 1. A 365 nm lamp (Spectronics Corporation, Westbury, NY) was used to irradiate most of the samples, but a 254 nm lamp (Spectronics Corporation, Westbury, NY) was also used to characterize the effect of light wavelength. Light intensity was varied from 0.05 mW/cm^2 to 0.70 mW/cm^2. This relatively low intensity range was useful to slow the

reaction so that we could observe key features of the conversion profile. FTIR spectra were acquired during continuous UV irradiation. The fractional conversion of double bonds was obtained by monitoring the absorbance peak area for C = C (peaks at 1635 cm^{-1} and 1619 cm^{-1} for acrylates, peak at 1638 cm^{-1} for methacrylate).

Table 1. Materials

Name	Abbreviation
2,2-dimethoxy-2-phenylacetophenone	DMPA
Di(ethylene glycol) Diacrylate	DEGDA
Pentaerythritol Triacrylate	PETrA
Trimethylolpropane Triacrylate	TrMPTrA
Pentaerythritol Tetraacrylate	PETeA
Di(ethylene glycol) Dimethacrylate	DEGDMA
Trimethylopropane Trimethacrylate	TrMPTrMA
Poly(ethylene glycol)	PEG

Table 2. Chemical Structures of Materials

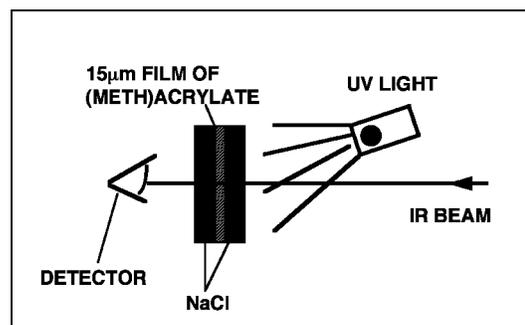| Name	Structure
DMPA	$C_6H_5COC(OCH_3)_2C_6H_5$
DEGDA	$(H_2C = CHCO_2 CH_2 CH_2)_2 O$
PETrA	$(H_2C = CHCO_2 CH_2)_3 CCH_2OH$
TrMPTrA	$(CH_2 = CHCO_2 CH_2)_3 CCH_2CH_3$
PETeA	$(H_2C = CHCO_2CH_2)_4 C$
DEGDMA	$(H_2C = C(CH_3)CO_2CH_2CH_2)_2 O$
TrMPTrMA	$(H_2C = C(CH_3)CO_2CH_2)_3 CCH_2CH_3$
PEG	$H(OCH_2CH_2)_n OH \qquad (\overline{M_n} = 200)$

Figure 1. In-situ FTIR measurement set-up, ref. 17.

Results and Discussion

Only representative data with noted exceptions are shown here. The nominal reaction rate is defined for our purposes as the average reaction rate observed over the period after induction and before deceleration. The onset of deceleration is where instantaneous reaction rate begins to decrease. The final conversion is defined as that when the reaction rate has fallen below 0.005/min.

Functionality

Figure 2 shows the fractional conversion of double bonds with irradiation time, for acrylate monomers of different functionality at a moderate photoinitiator concentration $[PI]_0 = 0.001$ (*cf.* below). An induction period is evident at the beginning of reaction. The reaction rate then accelerates to accomplish some conversion at the nominal rate. This period is followed by rate deceleration, but significant further conversion can still be achieved. Observed trends are summarized below:

diacrylate > triacrylate > tetracrylate

⌈ nominal reaction rate
| conversion before the onset of deceleration
| conversion after the onset of deceleration (Figure 3)
⌊ final conversion

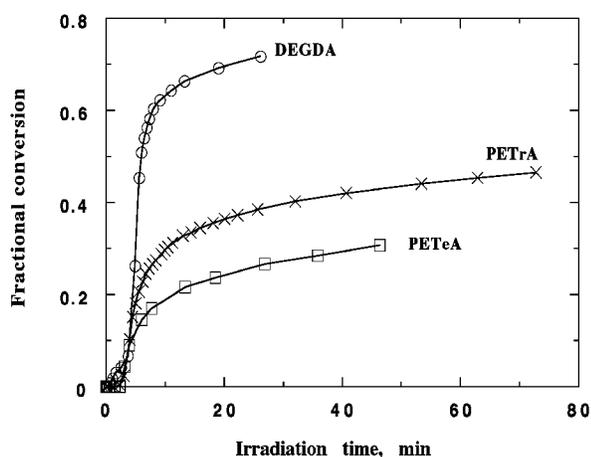*Figure 2. Conversion vs. irradiation time for different functional acrylates, $[PI]_0 = 0.001$, light intensity = 0.050 mW/cm^2*
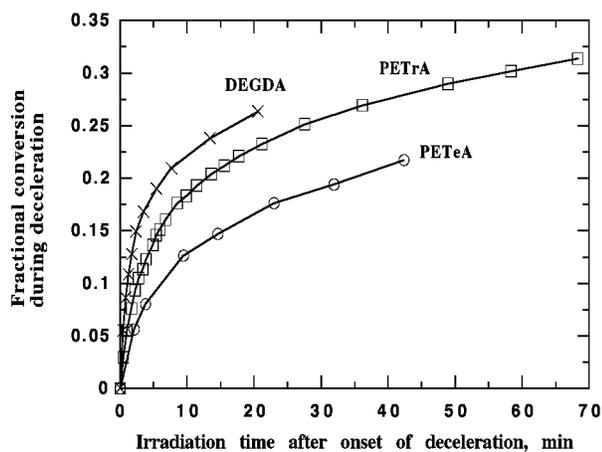

Figure 3. Conversion vs. irradiation time for different functional acrylates after the onset of deceleration, $[PI]_0 = 0.001$, light intensity = 0.050 mW/cm^2

Although many different effects are at play,[5,12] we postulate that differences in the nominal reaction rate reflect the relative magnitude of propagation rate constant (reactivity). Higher functional monomers propagate more slowly; this may result from the higher viscosity, as proposed by Anseth *et al.*[5] Furthermore, we may presume that the deceleration is associated with increasingly diffusion limited propagation. Higher functional monomers manage to achieve only a lower conversion before the onset of deceleration. Perhaps this is because increasing functionality makes it easier to form crosslinks between polymer chains (due to higher pendant group concentrations at a given conversion). Following Kloosterboer,[1] we might presume that the slow reaction rate allows the polymer structure to relax, which may act to enhance diffusion resistance to propagation. Finally, higher functional monomers achieve less conversion after the onset of deceleration. This may be due to a stiffer, more highly crosslinked network (due to reaction with pendant groups).

All these effects contribute to the final conversion trend. The same trends (not shown) were also observed for di- and trimethacrylates.

Acrylates and Methacrylates

Figure 4 shows the conversion curves of di-, and triacrylate, and di-, and trimethacrylate at $[PI]_0 = 0.001$. It shows that methacrylates have a longer induction period than acrylate. Observed trends at a given functionality are

acrylate > methacrylate

⌈ nominal reaction rate
| conversion before the onset of deceleration
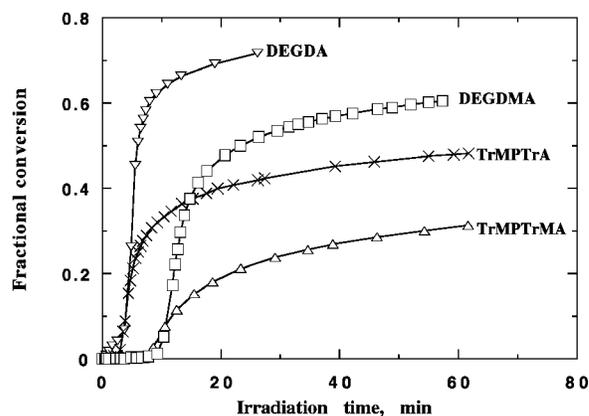| conversion after the onset of deceleration
⌊ final conversion

Figure 4. Conversion vs. irradiation time for di- and triacrylates and methacrylates, $[PI]_0 = 0.001$, light intensity = 0.050 mW/cm^2

The lower nominal reaction rate (lower reactivity) of methacrylates might be attributed to the stabilization of the free radical by adjacent methyl group in methacrylate.[18] The lower conversion of methacrylate double bonds before the onset of deceleration might be associated with slower reaction rate in the light of Kloosterboer's argument. However, it is also no doubt associated with the lower segmental mobility of methacrylate functional groups (as reflected by higher glass transition temperature of polymethacrylate than polyacrylate). In addition, Anseth[19] proposed that methacrylates might more easily form crosslinked polymer network. Finally, methacrylates accomplish less conversion after the onset of deceleration, again perhaps due to stiffer network.

Initiator Concentration

Figure 5 shows the conversion of triacrylate (PETrA) at different photoinitiator concentrations. Observed trends are

$$\text{high } [PI]_0 > \text{low } [PI]_0$$

$\left\{\begin{array}{l}\text{nominal reaction rate}\\\text{conversion before the onset of deceleration}\\\text{conversion after the onset of deceleration}\\\text{final conversion}\end{array}\right.$

As expected, the higher photoinitiator concentration, the obviously faster nominal reaction rate and the shorter induction period due to a greater radical concentration. The higher conversion before the onset of deceleration again may be associated with the higher reaction rate and/or formation of lower molecular weight polymer.
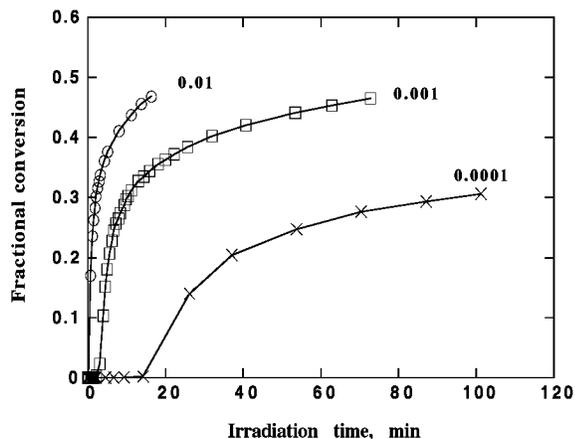

Figure 5. Photoinitiator concentration effect, PETrA, light intensity = 0.050mW/cm²

Another obvious trend, though, is a marked increase in the conversion that can be achieved after the onset of deceleration. Evidently raising the radical concentration has produced a more open and/or mobile network structure.

At $[PI]_0 \geq 0.1$, surface rippling appeared. Payne *et al.*[20] attributed this to the attenuation of light intensity through the reacting coating, which may result in solidification stress gradients.

Light Intensity

Figure 6 merely shows that the effect of increasing light intensity (polymerizing trimethacrylate, at $[PI]_0 = 0.01$) is similar to the above photoinitiator concentration effect. Stronger light intensity causes higher nominal reaction rate, higher conversion before the onset of deceleration, and higher conversion after the onset of deceleration—and thus higher final conversion.
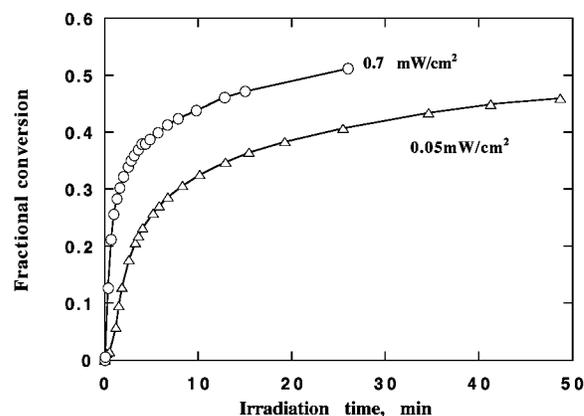

Figure 6. Conversion of TrMPTMA at different light intensities, $[PI]_0 = 0.01$

Radiation Wavelength

The effect of radiation wavelength on conversions is illustrated in Figure 7. A 254 nm lamp was used to compare with the standard (for this paper) 365 nm radiation. Other conditions were set at $[PI]_0 = 0.002$, light intensity = 0.21 mW/cm². Because the photoinitiator has an absorption coefficient two orders of magnitude greater at 254 nm than at 365 nm, the former wavelength produces the higher nominal reaction rate, higher conversion before the onset of deceleration and higher conversion after the onset of deceleration—and thus higher final conversion. This is the same effect as produced by raising initiator concentration.
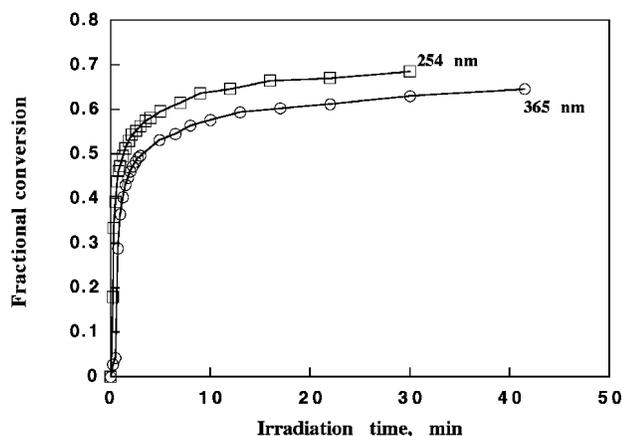
Figure 7. Wavelength effect, TrMPTrA, $[PI]_0 = 0.002$, light intensity = 0.210mW/cm²

Film Thickness

At greater thickness of curing film, the effect of attenuation of light intensity with depth can be seen. Figure 8 shows that raising the sample thickness from 15µm to 50µm decreases the final conversion by almost one-third. Thus the stronger attenuation of light intensity leads to lower nominal reaction rate, lower conversion before the onset of deceleration, and lower conversion after the onset of deceleration—the same effect as initiator concentration.

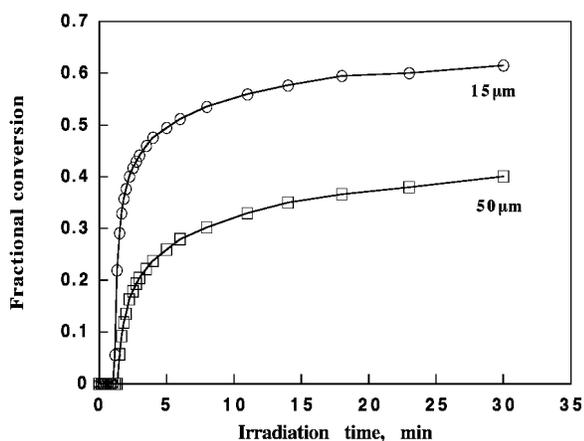Attenuation of radiation through thick films may also lead to rippling. Details are presented elsewhere.[20]

Figure 8. Film thickness effect, TrMPTrA, $[PI]_0 = 0.002$, light intensity = 0.210mW/cm²

Addition of Solvent

Even though one of the advantages of UV curing of acrylates and methacrylates is that it is generally solventless, it is worthwhile to probe the nature of diffusion limitation by adding a non-volatile solvent. Figure 9 shows the effect of adding a small amount of solvent PEG on polymerization

of PETrA at two initiator concentrations, $[PI]_0 = 0.01$, and 0.001. The addition postpones the onset of deceleration (higher conversion before the onset of deceleration) and raises the conversion after the onset of deceleration. Thus, the final conversion is enhanced even though PEG does not significantly change the nominal reaction rate.
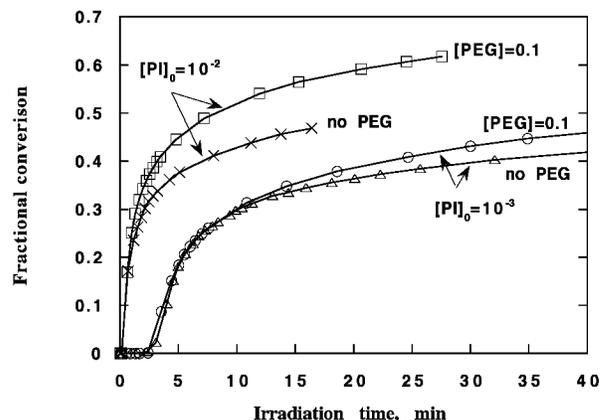

Figure 9. Effect of addition of PEG on conversion, PETrA, $[PI]_0 = 0.01$

Conclusions

This work clarifies trends in three key kinetic features, each of which affects the final conversion of polymerizing multifunctional acrylate and methacrylate monomers: (1) the nominal reaction rate; (2) the conversion before the onset of deceleration; (3) the conversion after the onset of deceleration. These three are generally coupled; an increase in any can be responsible for higher final conversion. We note several situations, though, where it is clear that one (or two) of the three is predominately responsible for increasing the final conversion.

The nominal reaction rate is mainly determined by the monomer reactivity and by the radical concentration. The apparent monomer reactivity decreases with monomer viscosity (increasing functionality) and with radical stability (higher stability for methacrylate). The radical concentration decreases with film thickness, but it increases with photoinitiator concentration, light intensity and absorptivity at the light wavelength.

The onset of deceleration is primarily caused by diffusion-controlled propagation; so it is directly related to the mobility of reacting species. The conversion before the onset of deceleration falls with crosslink density, but grows with excess free volume, and addition of solvent.

The conversion that can be achieved after the onset of deceleration is associated with the nature of the network structure formed. An open and flexible network can enhance reaction. This varies with monomer functionality, monomer type, reaction rate, and the addition of solvent.

The above trends suggest that there may be three important strategies to maximize the final conversion.

(1) Raise the nominal reaction rate by using highly reactive monomers and increasing radical concentration.

(2) Postpone the onset of deceleration by increasing the mobility of reaction species.

(3) Augment the conversion that can be achieved after network formation by forming open and flexible networks, e.g. by adding polymeric solvent, or by increasing the chain length of monomer. The last is consistent with proposal by Peppas *et al.*[21]

Aspects of these strategies have been proposed before, but this work serves to relate them to each other and to emphasize the role of the conversion before and after the onset of diffusion-controlled propagation.

Acknowledgment

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