

# Kinetics of UV-Initiated RAFT Crosslinking Polymerization of Dimethacrylates

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**ABSTRACT:** The UV-initiated RAFT polymerizations of a series of poly(ethylene glycol) dimethacrylates (PEGDMA) were investigated using differential scanning photocalorimetry (DPC) at room temperature. The rate of the RAFT system was much lower than that of a conventional free radical polymerization. A mild autoacceleration occurred as the addition reaction became diffusion controlled. The influence of the spacer length  $(\text{CH}_2\text{CH}_2\text{O})_x$  between the vinyl moieties of the dimethacrylates on the polymerization kinetics was examined. The polymerization rate of PEGDMA decreased with an increased  $x$  value from 4 to 9, but it increased with a further increased  $x$  value from 9 to 14. Mechanical proper-

ties of the resulting polymers were also examined by dynamic mechanical analysis (DMA). It was concluded that the presence of the RAFT agent during polymerization of multifunctional monomers did not have an effect on the heterogeneity of the polymer network. In comparison with three different PEGDMAs, the PEGDMA with the longest spacer formed the most homogeneous networks with a lower crosslinking density. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 660–665, 2011

**Key words:** RAFT polymerization; photopolymerization; polymerization kinetics; crosslinking structure

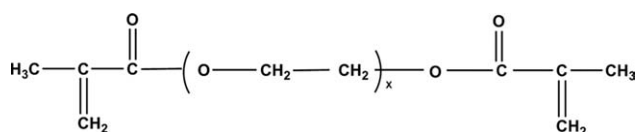
## INTRODUCTION

Photo-initiated polymerization of multifunctional vinyl monomers leads to highly crosslinked polymer networks. High crosslink densities increase dimensional stability, mechanical strength, thermal resistance, and decrease solvent penetration for the networks. These high strength polymer networks are used in a wide variety of applications such as dental restorative materials, optical discs, contact lenses, and optical communication devices.<sup>1,2</sup> The photopolymerization of di(meth)acrylate monomers proceeds via a free-radical chain growth mechanism. Free-radical polymerization (FRP) has extremely fast chain growth rates. It takes only seconds for an individual chain to fully grow from initiation to termination. Therefore, the photopolymerization of multifunctional monomers can exhibit a unique reaction behavior. This behavior includes unequal functional group reactivity, prominent autoacceleration and autodeceleration, a reaction diffusion controlled termination, limited functional group conversion due to the hindered mobility of vinyl groups and conversion dependence of kinetic parameters.<sup>3</sup> In addition, one of the most important characteristics of such a polymerization is the forma-

tion of heterogeneous polymer networks, which deteriorates the physical properties of the final crosslinked materials.<sup>4–6</sup>

Recently, several groups have reported on the synthesis of crosslinked polymers with homogeneous networks by controlled/living radical polymerization (CLRP).<sup>7</sup> CLRP has been developed to control radical polymerization for the synthesis of new materials with tailored compositions, functionalities, and architectures. Reversible addition-fragmentation chain transfer (RAFT) polymerization was considered as one of the most promising CLRPs due to its compatibility with a wide range of monomers and its versatility. RAFT and the other types of CLRPs have advantages over FRP in preparing homogeneous polymer networks. Because of the fast exchange of propagating radicals with the dormant species, the chain growth through propagation is temporarily and frequently interrupted and slowed down, giving rise to sufficient time for chain relaxation and diffusion of reaction species. The chain relaxation and the uniform distribution of reaction species minimize microgel formation by facilitating intermolecular reactions, thus generating homogeneous polymer networks. Recently, Yu et al.<sup>7–9</sup> have reported on the synthesis of crosslinked polymers with homogeneous networks by RAFT technology. In this article, we aim to expand upon the work of Yu Qiang et al. to examine the reaction behavior and the evolution of the network microstructure in the photo-initiated polymerization of dimethacrylates in

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**Figure 1** Structures of polyethylene glycol dimethacrylate.

the presence of trithiocarbonate (TTC) at room temperature. Specifically, we have compared the RAFT system and its FRP counterpart to understand the relationship between the kinetics and network structural development. The effects of various parameters, including the spacer length between methacrylate groups and concentration of TTC on the reaction behavior were examined to provide an insight into the network forming RAFT system.

## EXPERIMENTAL

### Materials

The multifunctional monomers used in these experiments were poly(ethyleneglycol) dimethacrylate, PEG200-DMA, PEG400-DMA, and PEG600-DMA. The numbers 200, 400, and 600 refer to the molecular weight of the poly (ethyleneglycol) chain between the methacrylate groups (Fig. 1). They were supplied by Sartomer Inc., USA and used without further purification. Ethyl (2, 4, 6-trimethylbenzoyl)phenylphosphinate (TPO) (Acros Organics Co.) was used as received. *S*-1-Dodecyl-*S'*-( $\alpha,\alpha'$ -dimethyl- $\alpha''$ -acetic acid) trithiocarbonate was prepared according to reference.<sup>10</sup> After recrystallization in ethanol, the yellow product was gained (65% yield). (mp: 61–63°C). <sup>1</sup>H-NMR: 0.9 (t, 3H, —CH<sub>3</sub>), 1.25–1.50 (m, 20H, —CH<sub>2</sub>—), 1.65 (s, 6H, —CH<sub>3</sub>), 3.29 (t, 2H, —CH<sub>2</sub>—S—), 13.05 (s, 1H, —COOH).

### Reaction recipe

The molar ratio of the monomer to the RAFT agent to the initiator was set to 100: 3: 1 for the RAFT system. In a typical experiment, 2.85 g (10 mmol of monomer) of PEG200-DMA, 29.3 mg (0.1 mmol) of TPO, and 92.1 mg (0.3 mmol) of TTC were added to a dry 10 mL glass ampoule. The ampoule was then sealed with a rubber septum and degassed with ultrahigh purity nitrogen for 10 min. In the FRP system, the molar ratio of monomer to initiator was 100 : 1. 29.3 mg (0.1 mmol) of TPO was dissolved into 2.85 g (10 mmol of monomer) of PEG200-DMA in a 10 mL ampoule by stirring the solution.

### Kinetic measurements

The photopolymerizations were carried out in a differential scanning calorimeter (Shanghai Precision and Scientific Instrument Co. Ltd) equipped with a

photocalorimetric accessory, with ~ 2–6 mg of samples placed in uncovered aluminum pans. The initiation light source was a 125 W high-pressure mercury lamp with wavelength range of 200–440 nm. The light intensity measured at the sample level by a radiometer was 360  $\mu\text{W}/\text{cm}^2$ . To minimize the effect of dissolved oxygen on the polymerization, the DSC cell was purged with nitrogen gas for 10 min prior to exposing the sample pan to radiation.

Heat flow versus time (DSC thermogram) was recorded in an isothermal mode under a flow of nitrogen. The nitrogen flow rate is 50 mL/min. The heat liberated in the polymerization is directly proportional to the number of vinyl groups reacted within the system. By integrating the area under the exothermic peak in the DSC thermogram, vinyl group conversion (*C*), or the extent of reaction, can be determined according to

$$C = \frac{\int_0^t dH/dt}{\Delta H_0^{\text{theor}}} = \frac{\Delta H_t}{\Delta H_0^{\text{theor}}}$$

where  $\Delta H_t$  is the reaction heat evolved up to time *t*, and  $\Delta H_0^{\text{theor}}$  is the theoretical heat for complete conversion. For the methacrylate double bond,  $\Delta H_0^{\text{theor}} = 54.85 \text{ kJ/mol}$ .<sup>11</sup> Also, the polymerization rate (*R<sub>p</sub>*) is directly related to the heat flow (*dH/dt*):

$$R_p = \frac{dC}{dt} = \frac{dH/dt}{\Delta H_0^{\text{theor}}}$$

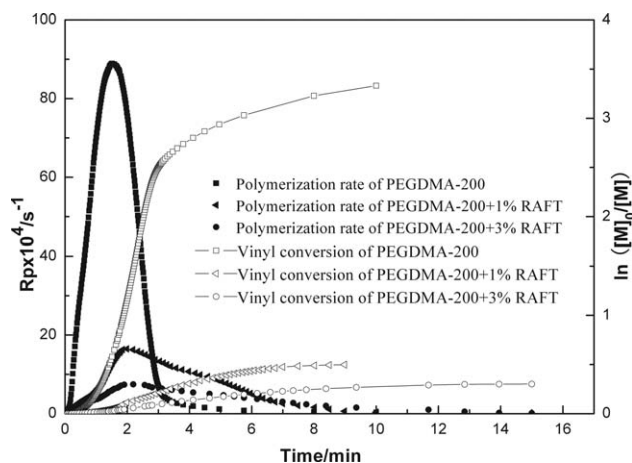
### Network characterization

The reaction mixture discussed in the kinetic study was introduced into a mold made of two quartz plates separated by a 1 mm silicone gasket. The mold was then placed under the same UV irradiation at room temperature to carry out the polymerization. The resulting products were removed for structure characterization. Dynamical mechanical measurements were performed on the samples using a dynamic mechanical analyzer (DMA, Q800, TA Instruments) in torsion model by applying a sinusoidal stress of 1 Hz frequency. The specimen was a thin rectangular sheet which was 1 mm thick and 50 × 10 mm<sup>2</sup> in area. The storage modulus and the loss tangent (tan  $\delta$ ) were recorded as a function of the temperature with a ramping rate of 5°C/min.

## RESULTS AND DISCUSSION

### Polymerization behavior in the presence of trithiocarbonate (TTC)

Figure 2 shows the evolution of the polymerization rate (*R<sub>p</sub>*) and conversion as a function of the reaction time for PEG200-DMA with different RAFT reagent



**Figure 2** Polymerization rate (filled symbol) and conversion (unfilled symbols) as a function of time for the polymerization of PEGDMA-200 with different RAFT reagent concentrations.

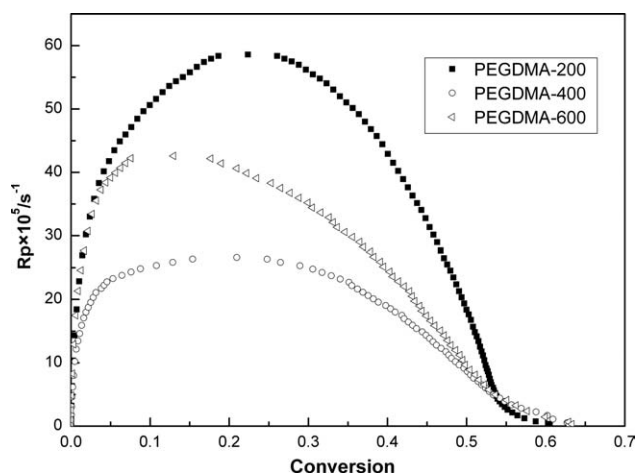
concentrations (TTC molar ratio 0%, 1%, or 3%) at room temperature. In the FRP photopolymerization of multifunctional monomers, the rate of polymerization increased dramatically at the beginning of the reaction caused by the hindered mobility of the macroradicals. The reaction became diffusion-controlled immediately upon exposure to UV radiation, resulting in a dramatic autoacceleration that gave rise to a higher polymerization rate. However, in the case of the RAFT system, the polymerization rate increased slowly from the beginning of the reaction and a mild autoacceleration appeared. The maximum rate of polymerization appeared at the beginning of the reaction, roughly one-fifth or one-tenth of the maximum rate in the FRP system. After that, the polymerization reached an apparent steady state, during which  $R_p$  almost did not change with time as vinyl groups were depleted. The increased extent of crosslinking also imposed restrictions on the diffusion of vinyl groups, leading to a further decrease in the polymerization rate. The polymerization with 1%TTC showed signs of an autoacceleration, and the polymerization with 3% TTC showed a very slight autoacceleration respectively. An increase in the TTC concentration led to a decrease in the polymerization rate. The lower polymerization rate in the RAFT of PEGDMA could be attributed to the lower propagating radical concentration determined by the addition-fragmentation equilibrium. This retardation effect has often been observed in many RAFT systems with styrenics and acrylates.<sup>12</sup> When the TTC concentration increased, the relative concentration of propagating radicals decreased because of slow fragmentation of intermediate radicals, which lead to a decreased reaction rate.

The FRP of PEGDMA was completed in minutes. However, the RAFT of PEGDMA took much longer

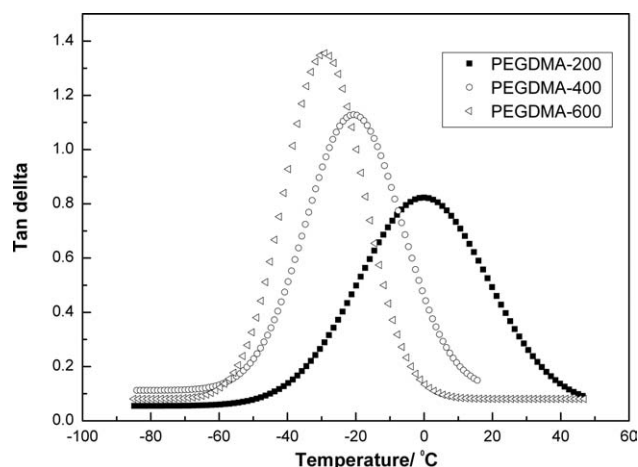
(more than an hour) to finish reacting. The final conversions were also significantly decreased in the presence of TTC. Increasing the TTC concentration from 1 to 3% resulted in a 50% decrease in  $R_p$  and almost a 66% decrease in the final conversion. Similar observations were shown for the polymerizations of other multifunctional monomers. The final conversions for the same photopolymerizations reported in Figure 2 were 96.4%, 39.2%, 26.1%, respectively. It is observed that the final conversions for the two RAFT polymerizations were much lower than those of the FRP polymerizations. In the RAFT polymerization, polymerization kinetic and vinyl group conversion depends mainly on the curing temperature and the monomer type, as well as the RAFT agent concentration. We believe that the early formation of three-dimensional networks, the hindered mobility of vinyl groups, and RAFT-capped dormant chains in the presence of TTC were responsible for the decline of the final conversion. In addition, the vitrification froze the mobility of reactive species, leaving unreacted monomer pools dispersed throughout the network. These remained monomers deteriorated the physical properties of the final crosslinked materials.

### Effect of spacer length

Three PEGDMAs (PEG200-DMA, PEG400-DMA, and PEG600-DMA) with different lengths of spacer units were selected to investigate the effect of the spacer on the RAFT polymerization behavior. The numbers 200, 400, and 600 refer to the molecular weight of the poly (ethyleneglycol) chain between the methacrylate groups. The average numbers of ethylene glycol units between the methacrylate groups were 4, 9, and 14, respectively. Figure 3 shows the relationship between the polymerization rate and vinyl conversion for these three PEGDMA, with 1% TTC



**Figure 3** Polymerization rate as a function of conversion for the polymerization of different PEGDMA with 1% RAFT reagent.



**Figure 4** Damping factor curves for RAFT polymers of different PEGDMAs.

(molar ratio) at room temperature. The maximum rate follows the order: PEGDMA-200 > PEGDMA-600 > PEGDMA-400.

There have been several reports on the influence of the length of the spacer on the rate of FRP. Cook<sup>13</sup> studied the photopolymerization kinetics of a series of bisphenol A based dimethacrylate monomers where the oxyethyl units ranged between 0 and 4. It was found that the maximum polymerization rate increased with the increase of the length of the spacer; this was attributed to the decreased mobility of the pendant double bonds and the steric shield effect by the close proximity of the bulky bisphenol A as the spacer length was reduced. In other work by Scranton et al.,<sup>14</sup> with a series of ethyleneglycol dimethacrylates, it was shown that while an increase in the ethylene glycol unit from 1 to 4 repeating units resulted in an increase in the maximum reaction rate, a decrease of the maximum rate was observed when the repeating unit was increased from 4 to 9. Peppas and coworkers<sup>15</sup> studied the photopolymerization of dimethacrylates with an iniferter; the results showed that the maximum polymerization rate and final vinyl conversion increased with decreasing the spacer length from 14 to 5, the same trend as observed in ATRP system<sup>16</sup>. They attributed this to the much slower rate of polymerization in living radical polymerizations. It was explained that since the crosslinking density increased at a much slower rate, the mobility of the pendant double bonds were not important. Instead, the location of vinyl groups in proximity to growing radicals became more crucial. Thus, the pendant double bonds with smaller spacer units were more active than those with longer spacer units, which resulted in an increase in the polymerization rate. Based on these findings and our experimental results, it seems that there is a critical spacer length for PEGDMA in the presence of TTC.

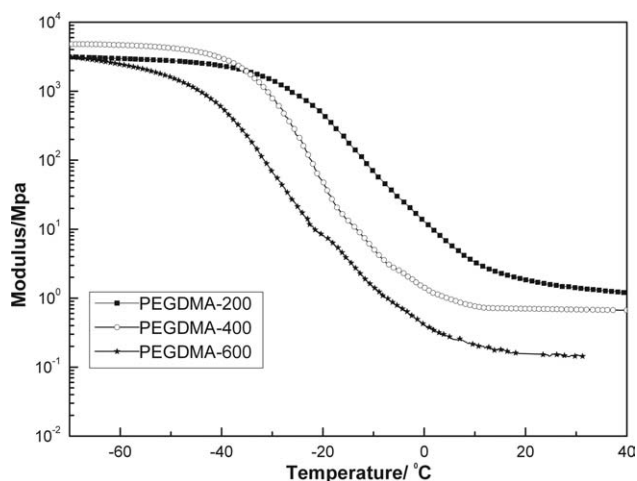
**TABLE I**  
The Structural Parameters of the Networks Resulting from the RAFT Polymerization of PEGDMA

| Sample     | Storage modulus (Pa)       | $T_g$ (°C) | Half peak width of $\tan \delta$ (°C) |
|------------|----------------------------|------------|---------------------------------------|
| PEG200-DMA | $1.568 \times 10^6$ (25°C) | 0          | 47                                    |
| PEG400-DMA | $0.787 \times 10^6$ (25°C) | -20        | 41                                    |
| PEG600-DMA | $0.147 \times 10^6$ (25°C) | -29        | 29                                    |

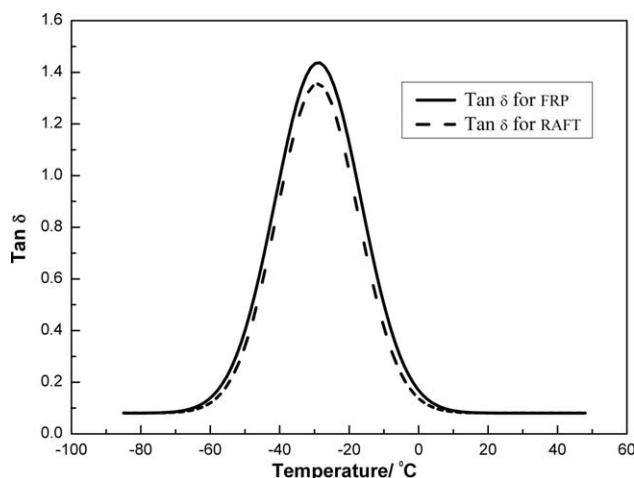
This value lies between 8 to 10 ethylene glycol units. When the length of the spacer is lower than the critical value, the mobility and accessibility of the pendant double bonds become insensitive to the number of spacer units. The increased units of ethyleneglycol chains then act as an inert "solvent" to reduce the effective concentration of the reactive species, which results in a decrease in the rate of polymerization. However, when the spacer length is over the critical value, increasing the ethylene glycol chain length provides greater activite of the pendant double bonds, leading to a faster polymerization.

#### Material properties of polydimethacrylates

Dynamic mechanical analysis (DMA) was used to examine the properties of polymers synthesized from dimethacrylates with the RAFT agent TTC. Three types of PEGDMA monomers were used to investigate the effect of the spacer length on the structural heterogeneity in the RAFT system. All samples were polymerized for 2 h at room temperature, with [monomer]: [TTC]: [TPO] = 100: 3: 1, as in Figure 2. Figure 4 shows the loss tangent ( $\tan \delta$ ) versus temperature curves of the three polymer networks and Table I gives storage modulus, and glass transition temperature for the samples. Figure 5 was the  $E'$  (storage modulus) versus  $T$  curves for RAFT



**Figure 5** The  $E'$  (storage modulus) versus  $T$  curves for RAFT polymers of different PEGDMAs.



**Figure 6** Damping factor curves for polymers of PEG600-DMA with and without RAFT reagent.

polymers of different PEGDMAs. The final vinyl conversions in all the three RAFT polymerization runs were almost same.

The decrease in storage modulus and that in glass transition temperature with increased spacer length can be explained on the basis of oligomer composition. The smaller oligomer had a higher “methacrylate” end-group concentration relative to the “oxyethylene” content, which contributed to a higher crosslinking density and reduced flexibility of the oligo(oxyethylene) chains. Generally, the damping factor is a measure of the heterogeneity of the network. The breadth of the glass transition region is related to the degree of structural heterogeneity.<sup>17,18</sup> The wider the peak is, the more heterogeneous the crosslinked polymer is. It was also observed that the half-width of the  $\tan \delta$  peak decreased as the number of ethyleneglycol units between the methacrylate groups increased. The half-width values were 47°C for PEG200-DMA, 41°C for PEG400-DMA, and 29°C for PEG600-DMA. The networks formed by the large spacer length monomers were more homogeneous. This spacer length dependence could be attributed to the reduced probability of primary cyclization. In the PEG200-DMA system, the distance between propagating radical and the pendant double bond was short and the pendant double bond concentration in the close proximity of a propagating radical was relatively high. The system was thus prone to form primary cycles, resulting in a heterogeneous network. The high level of crosslinking density from PEGDMA with a shorter spacer length also contributed to a broader distribution of chain segmental mobilities.

Figure 6 shows the evolution of the loss  $\tan \delta$  as a function of the temperature for FRP and RAFT polymerizations of PEG600-DMA network products. The curves for the two polymers were very similar. It was observed that both networks experienced a

transition from a glassy state to a rubbery state over the temperature range of  $-60^{\circ}\text{C}$  to  $0^{\circ}\text{C}$ . The glass transitions for the two networks were almost the same. There is not a noticeable difference in the widths of the damping factors for the two polymers synthesized by the FRP or the RAFT polymerization. This was in agreement with the results of Peppas and coworkers<sup>15</sup>. In highly crosslinked polymeric networks, the living radical polymerization does not have an effect on the pendent double bond reactivity. It appears that the living radical polymerization just slows the polymerization down, as indicated by the kinetic studies.

## CONCLUSIONS

Based on experimental investigation of the kinetics and network structure of the RAFT photopolymerization of dimethacrylates, the following conclusions can be drawn. The fast exchange of propagating radicals with dormant chains made the RAFT of PEGDMA proceed at a much slower polymerization rates compared to corresponding conventional radical polymerizations. The autoacceleration effect became mild in the RAFT photopolymerizations of the PEGDMA system.

For PEGMA RAFT photopolymerizations in the presence of TTC, there is a critical spacer length determining the polymerization reactivity. This value lies between 8 and 10 oxyethyl units. When the length of the spacer is lower than the critical value, the increased units of ethyleneglycol chains result in a decrease in the rate of polymerization. However, when the spacer length is over the critical value, increasing the ethylene glycol chain length leads to a faster polymerization rate.

The polymer networks prepared by the RAFT polymerization of PEGDMA were not any different than those prepared by FRP. It was concluded that the RAFT technique did not have an effect on the network heterogeneity of the highly crosslinked polymers. The RAFT polymerization of PEGDMA with shorter spacers yielded networks with a higher crosslinking density, higher glass transition temperature, and higher degree of structural heterogeneity.

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