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The significance of chain length dependent termination in cross-linking polymerizations

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Abstract

Evidence is presented in support of the existence of chain length dependent termination in cross-linking free radical polymerizations. Photopolymerizations of multifunctional methacrylates and acrylates were examined, and the difference in the inherent chain transfer characteristics of these systems provided a means for studying the effect of kinetic chain length on the polymerization behavior. The kinetic chain length was varied in each system by changing the initiation rate (R_i) and via the addition of a chain transfer agent (1-dodecanethiol). Changing R_i in the methacrylate systems led to a non-classical dependence of the rate of polymerization on R_i similar to that observed in linear polymerizations that exhibit chain length dependent termination. Additionally, incorporation of a chain transfer agent into the polymerization system, even at very low concentrations (0.1 wt%), had a dramatic effect on the methacrylate polymerization kinetics. As expected, because of their predisposition to chain transfer, the acrylate systems were minimally affected by changes in R_i and the addition of chain transfer agent. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Chain length dependent termination; Photopolymerization kinetics; Di(meth)acrylates

1. Introduction

The photopolymerization of multifunctional (meth)acrylate monomers provides an excellent method for the rapid curing of liquid monomers at room temperature into cross-linked polymer networks. These polymer systems are widely used in the coatings and biomaterials industries and are the subject of much research. Due to the cross-linking nature of these polymers, the kinetics exhibit diffusion limitations even during the initial stages of the reaction [1–8]. Initially, the rate increases dramatically due to the diffusion controlled termination process, which leads to autoacceleration. As the reaction progresses, the propagation reaction also becomes diffusion limited and the polymerization rate decreases substantially in a phenomenon typically referred to as autodeceleration. In addition, termination by segmental movement of the macroradicals eventually becomes suppressed, and the termination process then frequently becomes reaction diffusion controlled. When reaction diffusion controlled termination dominates, the free radicals come together via propagation through unreacted double bonds (either monomer or pendent vinyl groups) to facilitate termination. This mode of termination is quite significant in multifunctional (meth)acrylate polymerizations beginning at very low conversions [1,2]. Though the termination kinetics strongly depend on the mobility of the reaction environment, little research has been done in cross-linking polymerizations to determine if the termination rate constant is also dependent on the length of the macroradical undergoing termination.

Numerous publications discuss the importance of chain length dependent termination kinetics in linear free radical polymerizations. One review thoroughly details both the historical and current theory of the effects of diffusion-controlled reactions in linear free radical polymerizations and interested readers are referred to that article [9]. In brief summary, linear chains of various lengths that have different mobility restrictions are formed during free radical polymerizations. This distribution results in a termination kinetic parameter that is not constant and is affected by the lengths of macroradicals undergoing termination. The most facile termination reaction occurs between two relatively short chains whereas two longer entangled chains exhibit the slowest termination rate. Several researchers have performed experimental work utilizing pulsed laser

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polymerizations to calculate the termination kinetic parameters of linear polymerizations as a function of chain length [10,11] and others have developed kinetic models that include chain length dependent termination in the governing equations [12–14].

Despite these efforts to understand chain length dependent termination in linear systems, only one modeling study exists that addresses the issue of chain length dependent termination as a possible influence on the kinetics of cross-linking systems [15]. The lack of research in this area is most likely due to the nature of the network formation. During the cure of multifunctional systems, oligomeric chains are rapidly incorporated into the growing networks. For example, in a homogeneous cross-linked system at 10% conversion, the probability that a 10-mer chain is not incorporated into the network is only 35%. As either the conversion or the kinetic chain length increase, this percentage decreases dramatically. Based on these arguments, it seems unlikely that chain length dependent termination is occurring in multifunctional systems that quickly form gels of infinite molecular weight.

2. Experimental

2.1. Materials

The monomers used in this study were poly(ethylene glycol 600)dimethacrylate (PEG(600)DMA, Sartomer Co., Exton, PA), poly(ethylene glycol 600)diacrylate (PEG(600)DA, Sartomer Co., Exton, PA), 1,6-hexanediol diamethacrylate (HDDMA, Aldrich, Milwaukee, WI), and 1,6-hexanediol diacrylate (HDDA, Aldrich, Milwaukee, WI). Polymerizations were performed using 0.1 wt.% of the ultraviolet initiator 2,2-dimethoxy-2-phenylacetophenone (DMPA, Ciba Geigy, Hawthorne, NY). The chain transfer agent, 1-dodecanethiol (ACROS, NJ), was used. All materials were used as received.

2.2. Methods

2.2.1. Differential scanning calorimetry

The rate of polymerization was monitored on a photo differential scanning calorimeter (Perkin–Elmer, PDSC, Norwalk, CT) with a refrigerated recirculating chiller to facilitate isothermal reactions near room temperature (NESLAB, RTE-111, Newington, NH) [1,16]. A photocalorimetric accessory capable of producing 365 nm monochromatic light (Perkin–Elmer, DPA 7, Norwalk, CT) was employed as a light source for these experiments. Neutral density filters (Melles Griot, Irvine, CA) were used to control the intensity of the incident light. All of the PDSC experiments were performed at 25°C in a nitrogen atmosphere. To ensure that the thin-film approximation for uniform light intensity throughout the sample was valid, the mass of the samples was kept small (1–2 mg), and thus, the corresponding sample thickness was also minimized (~0.1–0.6 mm). The molar absorptivity for DMPA at the peak initiating wavelength (365 nm) is 150 L/mol/cm.

2.2.2. Fourier transform infrared spectroscopy

We have used Fourier transform infrared (FTIR) spectroscopy to obtain data analogous to that obtained using differential scanning calorimetry (DSC). A horizontal transmission accessory has been designed to enable mounting of samples in a horizontal orientation for FTIR measurements [17,18]. A FTIR spectrophotometer (Nicolet Model 750 Magna Series II FTIR, Nicolet, Madison, WI) equipped with MTC/B-KBr detector-beamsplitter combination was used to monitor the polymerization kinetics. A temporal resolution of ~30 ms is obtainable using the Rapid Scan feature of the spectrometer. All experiments [18] and analyses [2,18] were conducted as previously described.

A UV light source (Ultracure 100SS 100 W Hg short-arc lamp, EFOS, Mississaugua, Ontario, Canada) equipped with a liquid light guide was used to irradiate the monomer/initiator mixtures. The incident light intensity was controlled using neutral density filters (Melles Griot, Irvine, CA) and the internal aperture of the UV light source. Initiation rate was calculated assuming an efficiency of one. An exponential decay of initiator and correspondingly R_i during irradiation was incorporated. It is important to note that it is the scaling of the polymerization behavior with initiation rate that is of primary importance in these studies, not the absolute value of R_i. The assumption of unity for the efficiency will, thus, not impact the scaling.

3. Results and discussion

Studies have been performed within our group [1,2,16,19] and by other researchers [20] to examine the effect of initiation rate, R_i, on the rate of polymerization, R_p, in cross-linking polymerizations. For classical bimolecular termination behavior, one would expect R_p to scale with R_i to the 1/2 power, i.e. $\alpha = 1/2$ in Eq. (1):

$$R_\mathrm{P} = \frac{k_\mathrm{p}}{k_\mathrm{t}^{1/2}}[\mathrm{M}]\left(\frac{R_\mathrm{i}}{2}\right)^{\alpha} \qquad (1)$$

The adherence of several multivinyl monomers to the classical behavior was tested. The methacrylate systems studied do not conform to the classical square root dependence. Their polymerization behavior was consistently explained more effectively by a dependence significantly lower than the classical value of 0.5. This behavior is illustrated in Fig. 1 for the PEG(600)DMA polymerization over a fifty-fold increase in rate of initiation. From this analysis, it is clear that the data is better fit by a power lower than 0.5. For the methacrylates examined, the dependence was in general on the order of $R_\mathrm{i}^{0.3}$. The less than $R_\mathrm{i}^{0.5}$ dependence has previously been observed for the polymerization of other multifunctional methacrylate monomers [2,21].

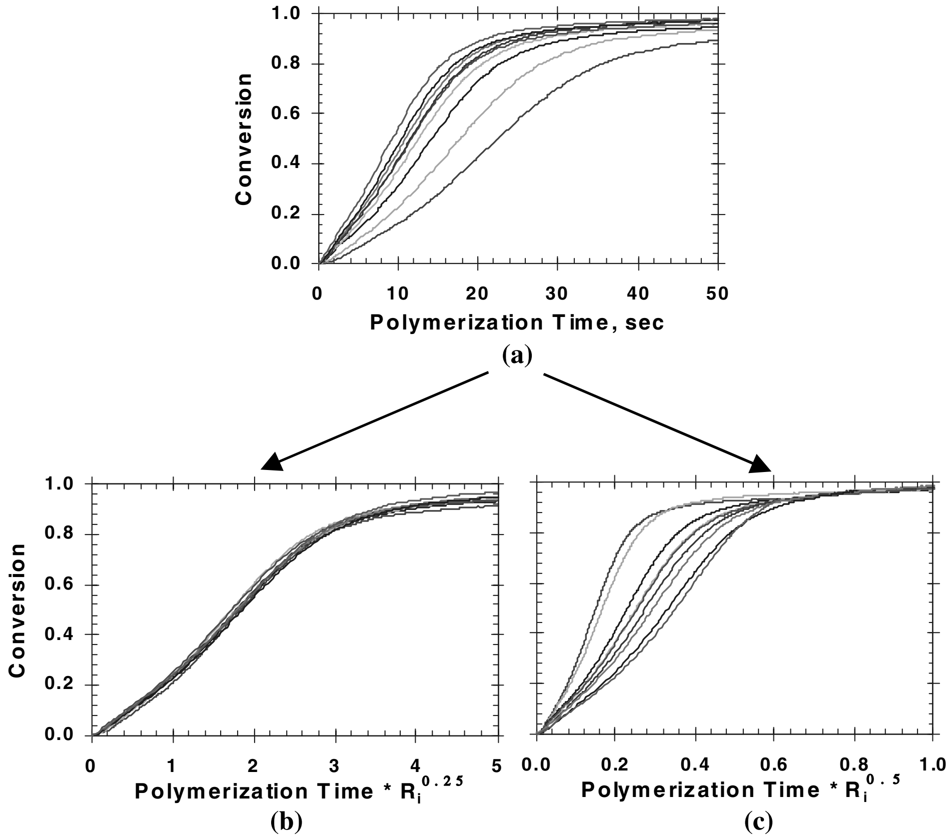

Fig. 1. Evaluation of the dependence of the rate of polymerization on the rate of initiation for the polymerization of PEG(600)DMA over a fifty-fold increase in rate of initiation (4×10^{-5}–2×10^{-3} mol/L/s). The raw conversion as a function of time data, collected using FTIR, is presented (a), as well as the raw data scaled for both $R_p \propto R_i^{0.25}$ (b) and $R_p \propto R_i^{0.5}$ (c).

This less than 0.5 dependence, ~0.3, has been observed previously in linear systems and is attributed to chain length dependent termination effects in those systems [9,22]. However, as discussed previously, an extension of this conclusion to cross-linking polymerizations is quite counter-intuitive, as the nature of the network formation seems to preclude the probability of such an observation (Fig. 2). Monomeric acrylates corresponding to the previously studied methacrylate systems were also studied. One primary difference between these two systems, for the purpose of this study, is that methacrylates do not exhibit a significant amount of inherent chain transfer whereas acrylates readily undergo chain transfer to polymer. The dominance of the chain transfer reaction in multifunctional acrylate polymerizations is clearly evidenced by EPR spectroscopy measurements [23].

It was hypothesized that the difference in the chain transfer characteristics of the two systems would be enough to impart significantly different kinetic chain lengths, ν, to these systems. Discussions of kinetic chain length are typically limited to the evaluation of linear polymerizations, however, in this discussion, kinetic chain length will be defined as the ratio of R_p to the sum of the rate of termination, R_t, and the rate of chain transfer, R_{ct}, and R_t is approximately R_i using the pseudo steady-state assumption. If the kinetic chain length does play a dominant role in the kinetics

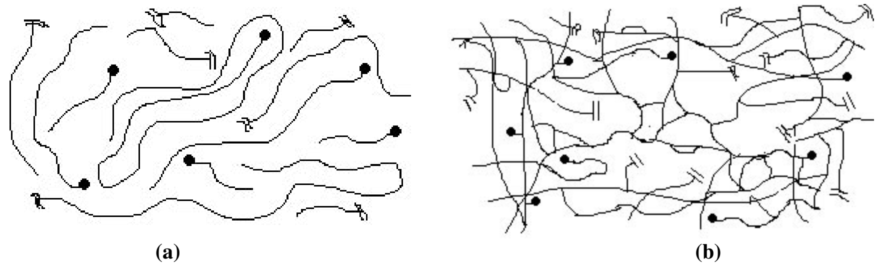

Fig. 2. A depiction of a linear polymerization: (a) the existence of chain length dependent termination effects can be rationalized via differences in mass transport rates of chains of different lengths, and of a cross-linking polymerization; and (b), where the majority of radicals are bound to the network.

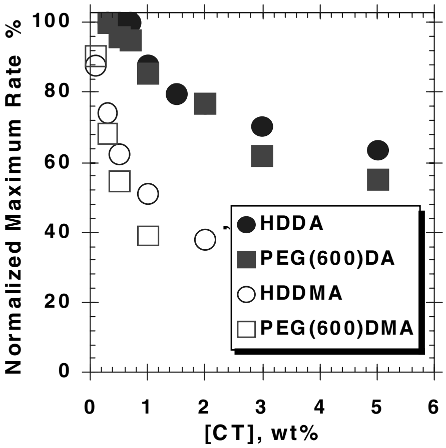

Fig. 3. The effect of the addition of chain transfer agent, 1-dodecanethiol, on the maximum polymerization rate of two different methacrylates and the corresponding acrylate systems. Polymerization conditions: initiator concentration: 0.1 wt% DMPA; light intensity: 3.5 mW/cm^2. Maximum rate data was obtained using PDSC.

Table 1
Summary of Results

	Methacrylates	Acrylates
Inherent chain transfer	No	Yes
$\nu = \frac{R_p}{R_t + R_{ct}}$	$\frac{R_p}{R_i}$	$\frac{R_p}{R_{ct}}$
$R_p \propto R_i^{\alpha}$	$\alpha < 0.5$	$\alpha \geq 0.5$
Addition of chain transfer agent	Reduces rate	Minimal effect on rate at low concentrations

of these cross-linking polymerizations, it would be apparent from the kinetic data.

The kinetic data supports the hypothesis of different kinetic chain lengths upon examination of the dependence of R_p on R_i. As mentioned previously, over a wide range of light intensity, the methacrylate dependence is less than 1/2, whereas the acrylate polymerization under the same conditions exhibits a dependence of $R_p \propto R_i^{\alpha \geq 1/2}$ throughout. Similar dependence has been demonstrated in other multifunctional acrylate polymerizations [14,24–26] where the dependence on $R_i^{\alpha > 1/2}$ has been attributed to the existence of a competing unimolecular termination mechanism, such as radical trapping [6].

The chain length dependent effect was also explored further via the addition of small amounts (0–2 wt%) of a chain transfer (CT) agent to the polymerization of both the acrylate and the methacrylate systems. These results also support the hypothesis of chain length dependent effects in these systems.

Upon addition of the CT agent at concentrations as low as 0.1 wt%, the polymerization rate of the multimethacrylates was suppressed (Fig. 3). This result was expected if the termination reaction was indeed more facile for shorter radicals in this system. The acrylate systems required CT agent concentrations greater than 1 wt% before a significant change in the polymerization rate was observed (Fig. 3). As a result of the higher reactivity of acrylates in comparison to methacrylates, a transfer constant at least as high as that present in the methacrylate polymerization would be expected. Thus, this result is not likely a result of the difference in transfer constants between the two systems. However, the need for a large concentration of CT agent in the acrylates makes sense when one considers that the chain transfer that readily occurs in the acrylates, without the addition of a CT agent, controls the chain length distribution in these networks. Until the rate of chain transfer to the chain transfer agent becomes comparable to the inherent chain transfer, the kinetic chain length will not be significantly affected. These results also support the concept that chain length has a dramatic influence on the termination kinetics in these cross-linking polymerization reactions.

In summary, since multi(meth)acrylate systems rapidly form highly cross-linked materials, little research has been conducted to determine if the termination process is affected by the kinetic chain length of the macroradicals. In contrast, much research has been done on linear (meth)acrylate systems to prove that the termination kinetic constant is often a function of the kinetic chain length. In this work, the polymerization kinetics of cross-linking systems with varying kinetic chain lengths were compared. The experimental results are summarized in Table 1 and demonstrate that, although counterintuitive, the kinetics of these systems are significantly impacted by kinetic chain length. This result is indicative of a termination environment that is dominated by the more mobile radical species present in the system.

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