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NOVEL (METH)ACRYLATE MONOMERS FOR ULTRARAPID POLYMERIZATION AND ENHANCED POLYMER PROPERTIES

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Introduction

Ultraviolet light is known to be one of the most efficient methods to initiate polymeric reactions in the presence of a photoinitiator. Photopolymerizations are advantageous because the chemistry of the materials can be tailored to design liquid monomers for ultrarapid polymerization into a solid polymer material. One way to achieve rapid photopolymerizations is to utilize multifunctional (meth)acrylate monomers, which form highly crosslinked polymers; however, these monomers typically do not achieve complete functional group conversion.¹⁻³ Recently, Decker *et al.* developed novel monovinyl acrylate monomers that display polymerization kinetics that rival those of multifunctional acrylate monomers. These novel acrylate monomers incorporate secondary functionalities and end groups such as carbonates,⁴⁻⁷ carbamates,^{1,5,6} cyclic carbonates,^{4,8-10} and oxazolidones,⁵⁻⁷ which promote the increased polymerization kinetics of these monomers. In addition to the polymerization kinetics, these novel monovinyl monomers form crosslinked polymers, which are characterized by having high strength and high flexibility. Unfortunately, the exact mechanism or mechanisms responsible for the polymerization kinetics and crosslinking are not well understood.

Several mechanistic theories have been proposed in an attempt to explain the enhanced reactivities of these novel monomers. Decker *et al.* proposed a possible hydrogen abstraction reaction due to labile hydrogens associated with the secondary functionalities and end groups.^{7,11} These labile hydrogens undergo a chain transfer reaction, creating branches and thus, radical sites for crosslinking. Recently, Jansen *et al.* proposed a theory attributing increases in polymerization rate to increases in monomer dipole moment.¹² Although such mechanisms may contribute to the enhanced reactivity and unique material properties achieved in these polymers, they do not provide a complete explanation.

This work expands on Decker's novel monomer systems to try to gain an understanding of the mechanism or mechanisms for the polymerization kinetics and ability to crosslink. The specific goal is to elucidate the relationship between monomer functionality and monomer structure in relationship to polymerization kinetics and polymer network structure. A better understanding of the mechanism(s) through which these materials polymerize will allow monomer design to be tailored such that specific properties will be attained.

Experimental

Instrumentation. Molecular weight between crosslinks (M_c) was obtained from mechanical property data obtained from a Perkin-Elmer DMA 7e Dynamic Mechanical Analyzer. M_c was calculated from the following equation:

$$M_c = \frac{3RT\rho}{E'}$$

where R is the gas constant, ρ is the polymer density, E' is the storage modulus in the rubbery plateau, and T is the absolute temperature where the storage modulus was evaluated.¹³

Steady state and unsteady state kinetic data was obtained from a Nicolet Magna 760 FTIR spectrometer equipped with a horizontal transmittance apparatus. All systems were polymerized with 5mW/cm² of ultraviolet light, using a filtered (peak irradiation wavelength: 365 nm) EXFO Ultracure 100ss light source and 0.1 wt% 2,2-dimethoxyphenylacetophenone (DMPA) as the photoinitiator.

Results and Discussion

This work proposes and evaluates several mechanistic theories for the enhanced reactivities and material properties exhibited by these novel monomers. Specifically, hydrogen bonding, hydrogen abstraction, and electronic and resonance effects are explored. Each of these mechanisms is interrelated; thus, it is difficult to isolate their individual contribution to the polymerization reaction. Nonetheless, experiments can be developed to emphasize each of the above mechanisms individually to test its validity.

To examine the possibility of hydrogen abstraction, the material properties of acrylate monomers were examined with experiments designed to look specifically at the molecular weight between crosslinks. Table 1 summarizes these material properties and compares the properties to those of conventional acrylate polymers.

Table 1. Material properties of monomers polymerized at 25°C.

Monomer	T _g (°C)	M _c (g/mol)	# Repeat Units	[XL] (mol/L)
Benzyl Carbamate Acrylate	42	40200	160	0.03
Benzyl Carbonate Acrylate	18	50800	200	0.02
Hydroxy Ethyl Acrylate	2	12000	100	0.09
Hydroxy Propyl Acrylate	-11	2200	18	0.50
Diethylene Glycol Diacylate	100	--	--	--

The material property studies outlined show above in Table 1 all utilized a photoinitiator (DMPA) concentration of 0.1 wt% = 4×10^{-3} mol/L. Hydrogen abstraction/chain transfer generates branching and from which crosslinks can be formed via termination by combination of these branches. Thus, if the proposed hydrogen abstraction/chain transfer mechanism is solely responsible for crosslink formation in these materials, one would expect the quantification of crosslinks to be, at a maximum, of the same order as that of the initiator concentration. However, these materials exhibit crosslink formation that exceeds the initiator concentration by almost 10-fold. Thus, traditional hydrogen abstraction/chain transfer, although a viable mechanism for the crosslinking ability of these monomers, cannot be the sole mechanism responsible for crosslink formation.

Since hydrogen abstraction cannot fully account for the crosslink concentration and polymerization kinetics of these novel monomers, the possibility of electronic and resonance effects on the polymerization rate of the novel monomers was also investigated. To accomplish the electronic and resonance studies, monomers with electron withdrawing substituents on an aromatic end group substituent were synthesized. Figure 1 shows the arrangement of electron withdrawing substituents on an aryl end group.

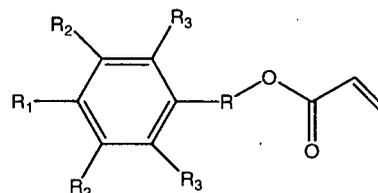


Figure 1. Monomer utilized for electronic and resonance effects studies. R₁, R₂, and R₃ can be F or H.

The electron withdrawing substituent studies revealed some very intriguing results. Figure 2 shows the steady state bulk polymerizations of the electron withdrawing (fluoro-substituted) monomers. From Figure 2, it is evident that the meta substituted monomer does not have a significant polymerization rate difference from the unsubstituted monomer. However,

the para, ortho, and penta substituted monomers decreased by approximately 2-fold in polymerization rate as compared to the meta and unsubstituted monomers. To determine the root cause of the polymerization rate difference in the differing monomers, unsteady state experiments were performed to deduce the kinetic constants for each monomer. Figures 3 and 4 show k_p and k_t versus conversion for the systems studied. k_p is the propagation kinetic constant and k_t is the termination kinetic constant.

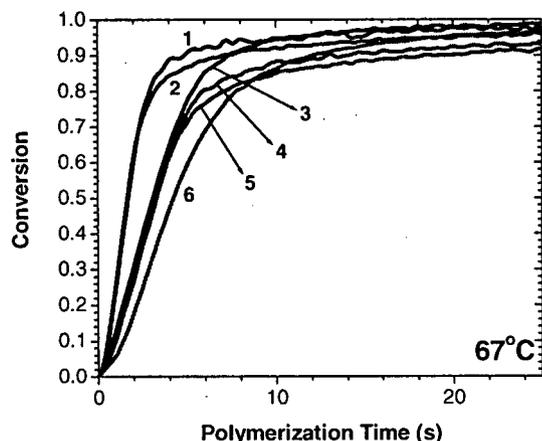


Figure 2. Effect of an electron withdrawing substituent (fluoro-substitution) on steady state kinetics. The monovinyl systems presented are: (1) unsubstituted, (2) meta, (3) ortho, (4) para, (5) penta, and (6) dimeta fluoro-substituted. Polymerizations were conducted at 67°C with 0.1 wt% DMPA at 5mW/cm².

Figures 3 and 4 reveal that the meta substituted and unsubstituted monomers have approximately equivalent k_p and k_t values over the conversion range studied. However, the para, ortho, and penta substituted monomers show drastically different kinetic values as compared to the meta and unsubstituted monomers. There is an approximate 2-fold increase in k_p and an approximate 10-fold increase in k_t for the para, ortho, and penta substituted monomers as compared to the meta and unsubstituted monomers. Unsteady state analysis of the fluoro-substituted monomer shows a significant electronic and resonance effect on the kinetics. These electronic effects will be influenced by several factors, including the dipole moment of the molecule, as the choice of substituent and position on the benzene ring will affect the overall dipole moment of the molecule. Additionally, these benzene ring substituents will influence the degree of abstraction and chain transfer attainable from these monomers. The most significant observed effect is associated with the termination kinetics, as the para and ortho substitutions significantly increase the termination of these monomers, thus decreasing the overall polymerization rate.

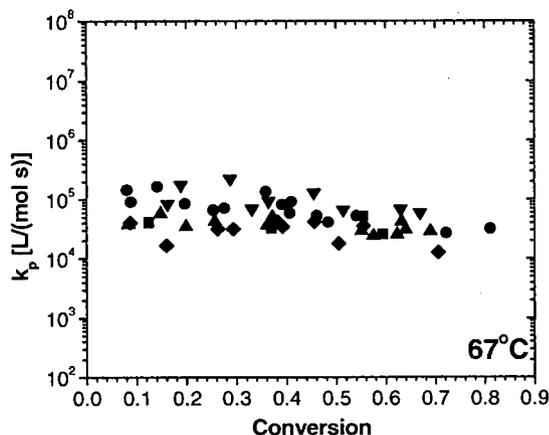


Figure 3. Propagation kinetic constant versus conversion for the fluoro-substituted monomer. The monovinyl systems presented are: (■) Unsubstituted, (●) para, (▲) meta, (▼) ortho, and (◆) penta fluoro-substituted.

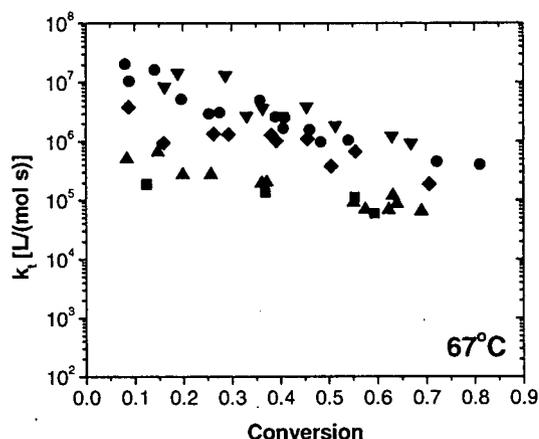


Figure 4. Termination kinetic constant versus conversion for the fluoro-substituted monomer. The monovinyl systems presented are: (■) Unsubstituted, (●) para, (▲) meta, (▼) ortho, and (◆) penta fluoro-substituted.

The fluoro-substitution results verify that the electronic and resonance effects do influence the reactivity of these novel monomers. The results show that a specific substituent can negatively impact the overall polymerization rate. However, with careful selection of an appropriate substituent, a positive influence is observed and the overall polymerization rate is increased.

Conclusions

Novel monovinyl (meth)acrylates have been developed that show ultrarapid polymerization and the ability to form crosslinked networks. The exact mechanism(s) for these enhanced polymer properties are not well understood. Hydrogen abstraction/chain transfer is a possible mechanism for the ability to crosslink, but this chain transfer cannot account for the significant crosslink concentrations measured in these materials. In addition, electronic and resonance effects show a significant influence on the polymerization kinetics of these polymers. Electron withdrawing substituents on the benzene ring alter the reactivities of the monomer and display a significant increase in termination kinetics for the para, ortho, and penta substitutions.

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