8872 *Macromolecules* **1995,** *28,* 8872–8874

Superfast Methacrylate Photomonomers: Ester Derivatives of Ethyl α-Hydroxymethacrylates

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Received July 13, 1995
Revised Manuscript Received October 17, 1995

Introduction. A wide variety of derivatives of α-(hydroxymethyl)acrylate have been synthesized using α-(hydroxymethyl)acrylate esters or their halide derivatives.[1–7] These monomers polymerize surprisingly well in comparison to acrylates with α-alkyl substituents greater than methyl.[8] Ester derivatives especially showed excellent polymerizability to give very high molecular weight polymers, apparently resulting from electronic effects of the ester group.[2] Although thermal solution and bulk polymerizations have been studied, the photopolymerization behavior of these ester derivatives has not been investigated. In general, most previous work in photopolymerizations has focused on multi(meth)acrylate monomers. Monoacrylates are rarely used due to their strong odor and toxicity, although monofunctional monomers as reactive as multifunctional acrylates and methacrylates that allow ca. 100% conversion are highly desirable for thin-film and coating applications. Recently, new rapid-cure, monofunctional acrylates have been examined in comparison to commonly used multifunctionals in UV curing; for example, acrylic monomers containing cyclic carbonate groups were found to be more reactive than most commonly used di- and triacrylates.[9]

The present report is part of a study to evaluate the reactivity of the new α-ester monomers in photopolymerizations using photodifferential scanning calorimetry (PDSC). Monomers used were α-ester derivatives of the ethyl ester parent (EHMA), including the formate, acetate, hexanoate, benzoate, *p*-methoxybenzoate, *p*-cyanobenzoate, and 3,4,5-trimethoxybenzoate derivatives.

Experimental Procedures. All monomers were synthesized using the general procedure given below. Photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA, Irgacure 651, Ciba-Geigy) was recrystallized from hexane before use. Acid salts were prepared from reactions of corresponding acids with $NaHCO_3$. All other solvents and starting materials were reagent grade and used as received. Ethyl α-(hydroxymethyl)-acrylate (EHMA) and ethyl α-(chloromethyl)acrylate (ECMA) were synthesized using the literature procedures.[2,10]

^{13}C-NMR solution spectra were obtained on a Bruker AC-200 spectrometer. Size exclusion chromatography (SEC) was carried out with THF solvent using American Polymer Standard columns of 500, 10^3, 10^4, and 10^6 Å packing and polystyrene calibration standards ranging from 17.5×10^3 to 3×10^6. Thermal analysis was done on a Du Pont 9900 analyzer. Photopolymerizations were done in a Du Pont 912 dual-sample DSC with a Du Pont 930 differential photocalorimeter accessory with a 200 W medium-pressure mercury lamp.

Representative Procedure for the Synthesis of Monomers. ECMA (4 g, 27 mmol), *p*-methoxybenzoic acid sodium salt (12.80 g, 73.5 mmol), and Aliquat 336 (Aldrich, 10 drops) in CH_2Cl_2 were added to a 100 mL round-bottom flask. The mixture was stirred at room temperature until all ECMA reacted as monitored by GC. The solution was filtered and the CH_2Cl_2 evaporated under reduced pressure. Vacuum distillation of most monomers gave pure products. The *p*-methoxy, *p*-cyano, and 3,4,5-trimethoxy derivatives were solids at room temperature and were purified by recrystallization from hexane. Yields were about 97% before purification. Anal. Calcd for $C_{14}H_{13}O_4N$: C, 64.86; H, 5.05; N, 5.40. Found: C, 65.00; H, 4.91; N, 5.36. Anal. Calcd for $C_{16}H_{20}O_7$: C, 59.25; H, 6.22. Found: C, 59.51; H, 6.03. Anal. Calcd for $C_{14}H_{16}O_5$: C, 63.63; H, 6.10. Found: C, 63.86; H, 5.99.

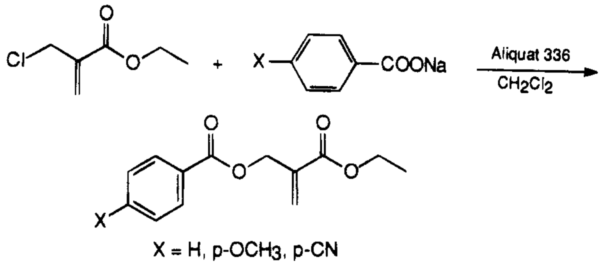

Figure 1. General synthesis scheme for benzoate ester derivatives.

Photopolymerization Procedure. Samples were prepared by dissolving 0.1–2 mol % initiator in the appropriate monomer. Typically, 1.5–2.0 mg of sample was placed in an uncovered aluminum DSC pan (approximately 200 μm thickness) and cured 12 min at various reaction temperatures. The chamber of the DSC was purged with nitrogen for 10 min before polymerization, and purging was continued during polymerization. The light intensity was varied between 8 and 32 μW/cm^2 and measured with an International Light radiometer. The total exotherm was taken as the area under the exotherm curve with the baseline extrapolated back from the end of the exotherm to the initial rise after the lamp was turned on. The TA Instruments-supplied analysis program was used to calculate conversion vs time plots using a theoretical heat evolved for methacrylate double bonds, $\Delta H_{\text{theor}} = 13.1$ kcal/mol.[11] Rates of polymerization were calculated from the initial slopes of the conversion–time plots. Induction time, percentage monomer reacted at the peak of the exotherm, and time to reach peak maximum were also calculated.

Results. Phase transfer catalysis was used for the synthesis of ester derivatives of EHMA (Figure 1) in which ECMA was reacted at room temperature with a variety of sodium salts of organic acids in CH_2Cl_2 in the presence of an ammonium salt phase transfer catalyst (Aliquat 336). Reaction times ranged between 2 and 15 days but could be decreased by changing solvent to $CHCl_3$ and increasing temperature to 60 °C. Although high-purity (ca. 97%) products were obtained after filtration of reaction mixtures, final purifications (distillation or recrystallization from hexane) were necessary to remove residual catalyst and to obtain more reproducible photopolymerizations. Monomers obtained were liquids except for the *p*-methoxy, *p*-cyano, and 3,4,5-trimethoxybenzoate derivatives, which were solids at room temperature melting at 35–37, 73–74, and 54–55 °C, respectively. Solution ^{13}C NMR spectra of all new monomers were consistent with expected structures.[12]

For comparison with photopolymers, monomers were also bulk and solution polymerized to moderate-to-high

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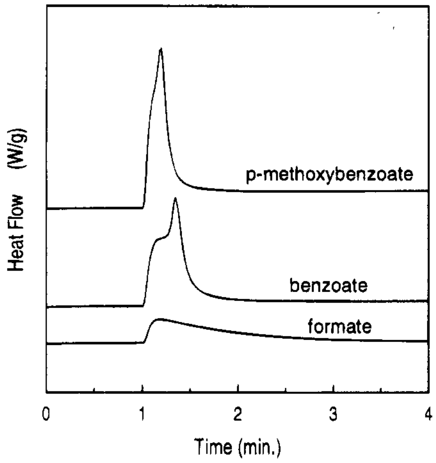

Figure 2. Exotherm curves for formate, benzoate, and *p*-methoxybenzoate derivatives at 50 °C.

molecular weight products in conversion (45–80%) when done at 60 °C using 0.5 wt % AIBN (details to be reported in a full paper). All monomers polymerized rapidly to reasonable molecular weights (from 20 000 to several hundred thousand). The ^{13}C-NMR spectra of all the polymers showed complete disappearance of the monomer double-bond carbons (at ca. 127 and 135 ppm) and appearance of the corresponding backbone peaks at 45 and 48 ppm.[12] DSC analysis showed that substitution on the aromatic ring had very little effect on the T_g's of the polymers, which were 130 °C for the parent, 134 °C for the *p*-methoxy material, 143 °C for the 3,4,5-trimethoxybenzoate, and 163 °C for the *p*-cyano polymer.

Photopolymerizations were initially carried out on the alkyl esters and benzoates that were liquid at 50 °C using benzoin methyl ether (Irgacure 651) as photoinitiator. Figure 2 shows the exotherms recorded for the photopolymerizations of a typical alkyl ester monomer along with two benzoates using 0.5 mol % initiator at 50 °C. Blank runs showed that the exotherms were completely due to photopolymerization and not to thermal polymerization of the monomers. The rate of polymerization for the benzoate derivative (EBMA) was clearly greater than the alkyl ester derivatives, decreasing in the order benzoate > hexanoate > acetate > formate. This result was best shown by percent conversion versus time plots (not given): conversions of 66–90% were reached for the benzoates within 0.5 min while for the alkyl derivatives, maximum conversions were 34–60%, reached in 1.5 min. Low final conversions in photopolymerizations are usually related to the transformation of the polymer–monomer system from a viscous liquid to a glass, which greatly slows reaction. Here, however, cure temperature was higher than T_g for the hexanoate and acetate esters but much lower than T_g for the formate and benzoate polymers; i.e., the benzoates should have gone to lower conversion, not higher.

Rates and conversions for these photopolymerizations are summarized in Table 1 along with polymer T_g's. A recent comparison of EBMA with MMA in solution polymerization indicates that the former has a k_p value ($k_p = 990$, $k_t = 2.9 \times 10^{-6}$ L mol^{-1} s^{-1}) almost 2 times that of MMA while its k_t is 14 times smaller than the MMA value ($k_p = 510$, $k_t = 42 \times 10^{-6}$ L mol^{-1} s^{-1}).[13,14] Thus, not only is the benzoate inherently faster, but because the kinetic chain length is proportional to k_p/k_t, the molecular weight of the benzoate is also inherently greater. The terephthaloyl ester derivative of EHMA was also synthesized using the reaction of EHMA with terephthaloyl chloride to compare rates for a dimethacrylate with that of the benzoate monomethacrylate. Since the product was a solid ($T_m = 84$ °C), photopolymerization was done at 90 °C. The rate of the terephthaloyl ester was found to be only 2 times that of the benzoate ester.

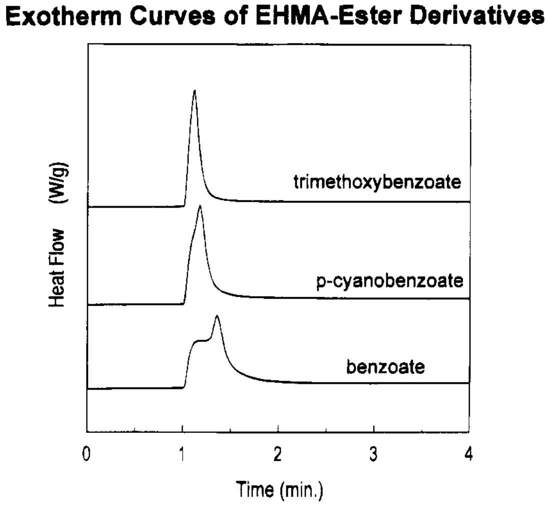

Figure 3. Exotherm curves for benzoate, cyanobenzoate, and 3,4,5-trimethoxybenzoate derivatives at 80 °C.

Table 1. Photopolymerization Results and Polymer T_g's for Alkyl and Aryl Ester Derivatives of Ethyl α-(Hydroxymethyl)acrylate

monomer	temp (°C)	R_p (kJ mol^{-1} min^{-1})	conv (%)	T_g (°C)
formate	25	14	34	77
acetate	25	15	34	49
hexanoate	25	37	60	15
benzoate	50	71	75	130
p-cyanobenzoate	80	137	80	163
p-methoxybenzoate	50	149	66	134
3,4,5-trimethoxybenzoate	80	223	90	143

Due to high reactivity of the benzoate monomer, research was directed to benzoate monomers containing electron-donating and electron-withdrawing groups at the para position to evaluate electronic effects on reactivity. Other monomers made include the *p*-cyanobenzoate and the 3,4,5-trimethoxybenzoate esters of EHMA. However, because these two monomers are solids at 50 °C, photopolymerizations were carried out at 80 °C. Figure 3 gives the DSC photopolymerization plots for these two monomers along with that of the parent benzoate, all run at 80 °C. Again, the highest peaks in the lower two traces occur after onset of polymerization, indicating autoacceleration, which is not apparent for the trimethoxy monomer. In fact, the sharpness of the peak in the top trace for the latter indicates extremely rapid polymerization. The *p*-cyano monomer was about as fast as the *p*-methoxy compound (Table 1) while the 3,4,5-trimethoxybenzoate was the fastest monomer evaluated here, displaying a rate almost 10 times greater than the alkyl ester monomers and 8 times greater than MMA. This is the fastest methacrylate-based photomonomer that we are aware of. Most important is the fact that conversions for the benzoate monomers in general were also high (ca. 70–90%) despite the fact that the polymers being formed have T_g's significantly above the cure temperature. Finally, the photopolymers were all soluble in THF, and size-exclusion analyses were carried out; number-average molecular weights ranged from 6000 to 20 000 while for solution and bulk polymerizations, values ranged from 20 000 to 610 000.

Despite the fact that we do not understand how the electronic nature of the substituents effects polymerizability of these new monomers, their rapid cure with high conversion to linear polymers makes them excellent candidates for extending the use of photopolymerizations to new systems with good cure kinetics and excellent physical properties.

Acknowledgment. This work was supported by grants from the National Science Foundation (DMR-9111903) and NASA (MSFC T6-12031).

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(12) ***p*-Cyanobenzoate monomer:** ^{13}C NMR (DMSO-d_6) 14.0 (CH_3), 60.7 (CH_2O), 63.3 (CH_2O), 115.7 (Ar, *C*CN), 118.0 (CN), 128.3 ($\mathit{C}H_2{=}C$), 129.9 (Ar, CH), 132.86 (Ar, CH), 133.2 (Ar, C), 134.8 ($CH_2{=}\mathit{C}$), 164.0 (C=O), 164.5 (C=O) ppm. ***p*-Cyanobenzoate polymer:** ^{13}C NMR (DMSO-d_6) 13.0 (CH_3), 44.0 (backbone CH_2), 47.4 (backbone C), 61.3 (CH_2O), 63.0 (CH_2O), 115.9 (Ar, *C*CN), 117.7 (CN), 129.7 (Ar, CH), 132.3 (Ar, CH and Ar, C), 164.0 (C=O), 171.8 (C=O) ppm. ***p*-Methoxybenzoate monomer:** ^{13}C NMR (DMSO-d_6) 13.9 (CH_3), 55.5 (OCH_3), 60.6 (CH_2O), 62.3 (CH_2O), 114.0 (Ar, CH), 121.5 (Ar, C), 127.4 ($\mathit{C}H_2{=}C$), 131.3 (Ar, CH), 135.4 ($CH_2{=}\mathit{C}$), 163.3 (Ar, $\mathit{C}OCH_3$), 164.7 (C=O), 164.8 (C=O) ppm. ***p*-Methoxybenzoate polymer:** ^{13}C NMR ($CDCl_3$) 13.2 (CH_3), 45.0 (backbone CH_2), 47.9 (backbone C), 55.2 (OCH_3), 61.2 (CH_2O), 63.0 (CH_2O), 113.4 (Ar, CH), 122.4 (Ar, C), 131.6 (Ar, CH), 163.0 (Ar, $\mathit{C}OCH_3$), 165.7 (C=O), 172.4 (C=O) ppm. **3,4,5-Trimethoxybenzoate monomer:** ^{13}C NMR (DMSO-d_6) 13.9 (CH_3), 55.9 (OCH_3), 60.1 (OCH_3), 60.7 (CH_2O), 62.6 (CH_2O), 106.5 (Ar, CH), 124.4 (Ar, C), 127.2 ($\mathit{C}H_2{=}C$), 135.3 ($CH_2{=}\mathit{C}$), 142.0 (Ar, $\mathit{C}OCH_3$), 152.8 (Ar, $\mathit{C}OCH_3$), 164.6 (C=O), 164.7 (C=O) ppm. **3,4,5-Trimethoxybenzoate polymer:** ^{13}C NMR (DMSO-d_6 and $CDCl_3$) 13.0 (CH_3), 47.0 (backbone C and backbone CH_2), 55.6 (OCH_3), 59.9 (OCH_3, CH_2O), 106.6 (Ar, CH), 123.8 (Ar, C), 141.9 (Ar, $\mathit{C}OCH_3$), 152.6 (Ar, $\mathit{C}OCH_3$), 164.9 (C=O), 172.6 (C=O) ppm.

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MA9510045