New Free-Radical Ring-Opening Acrylate Monomers

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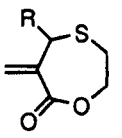
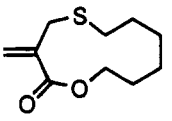
There has been a considerable and sustained interest in the study of free-radical ring-opening polymerization.[1-6] This is partly because the use of ring-opening monomers may minimize the volume shrinkage that occurs during polymerization[1] and/or allow the incorporation of functionalities such as amide, ester, or carbonate into the backbone of a polymer by chain growth rather than step growth polymerization.[6] However, the ring-opening monomers that are presently available for free-radical polymerization may suffer from one or more of the following problems among others: (1) instability to traces of water or acid,[7] (2) incomplete ring opening,[8,9] importantly (3) low reactivity toward free-radical addition, and (4) low reactivity ratios[9] with common commercial monomers such as methyl methacrylate[10] and styrene.[11] We now report a new class of acrylate-based ring-opening monomers (**1** and **2**),[12] and the homo- and copolymerization behavior of three examples is presented.



1 a: R= H
b: R= CH_3



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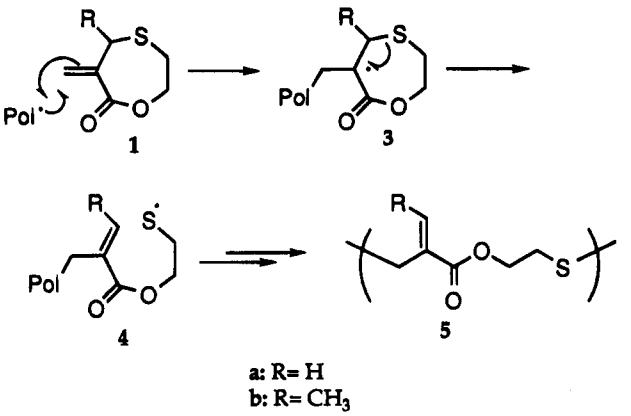
It has been established that certain allylic sulfides will readily and efficiently undergo β scission when reacted with carbon-centered radicals to produce a new carbon–carbon double bond and thiyl radical. This process is so efficient that these allylic sulfides have found use as chain transfer agents in free-radical polymerizations to regulate molecular weight.[13,14] Therefore, it was believed that cyclic allylic sulfides might undergo ring opening as depicted in Scheme 1.

The key step would be the scission of the cyclic allylic sulfide's carbon–sulfur bond (**3** → **4**). This scission must be extremely facile in order for the monomer to undergo ring-opening polymerization in preference to propagation without ring opening or depropagation. Once the ring is opened, the thiyl radical (**4**) is expected to readily react with another monomer[13,14] to give a polymer containing repeat unit **5**. Note that, for monomers like **1b**, *E*/*Z* isomerism is formally possible in the polymer repeat unit **5b**, although the *E* isomer (as shown in Scheme 1) would be expected to predominate.

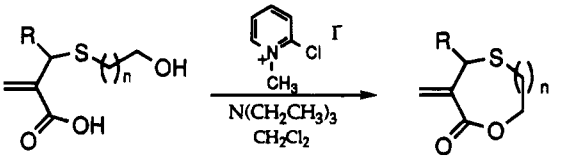
The monomers were synthesized from the appropriate α-(((ω-hydroxylalkyl)thio)methyl)acrylic acids **6** and **7** using the Mukaiyama reagent[15] under standard high dilution conditions to favor cyclization over polyesterification (Scheme 2).[16] The compounds were found to be reasonably stable and did not require the addition of an inhibitor. Monomer **2** could be kept at room temperature with no observable degradation or discoloration. Monomers **1a** and **1b** exhibited some mild discoloration after a few weeks at room temperature, but this

Scheme 1



a: R= H
b: R= CH_3

Scheme 2



6 a: R= H; n=1
b: R= CH_3; n=1
7 R= H; n=5

1 a: R= H; n=1
b: R= CH_3; n=1
2 R= H; n=5

was prevented when they were refrigerated at −15 °C. They were also stable to aqueous acid workup and required no special handling conditions. They showed excellent solubility in common organic solvents and monomers such as methyl methacrylate and styrene.

The homo- and copolymerization behavior of monomers **1** and **2** is summarized in Table 1. Typically, a solution of monomer or comonomers ($[monomer/s]_{total}$ = 3 M) in hexadeuterobenzene with AIBN ([AIBN] = 0.05 M) was prepared, freeze–thaw–degassed, and sealed in a NMR tube. The polymerization was then carried out at 70 °C and monitored periodically by ^1H NMR spectroscopy. The consumption of the monomers (**1** and **2**) and formation of the ring-opened unit in the resulting polymer was followed by observing the vinylic and $-OCH_2-$ regions of the spectrum. The signals of the monomers and polymers were readily differentiated on the basis of chemical shift and peak shape. Table 1 lists the chemical shifts of the characteristic signals of the ring-opened repeat units in the polymers.

The results demonstrated that polymerization behavior of the monomers depended upon the nature of the substituent R. For monomer **1b** (where R = CH_3), white, soluble (chloroform, benzene, toluene, and tetrahydrofuran) polymers were obtained from its homopolymerization and its copolymerizations with methyl methacrylate or styrene. (Initially, the homopolymer was soluble in the above solvents, but it became progressively insoluble on standing in the open at room temperature for a number of weeks.) Figure 1 shows two ^1H NMR spectra from the homopolymerization experiment as an example of how ring opening was observed. Figure 1a is the spectrum of the monomer and AIBN in hexadeuterobenzene before polymerization. Figure 1b is the spectrum obtained after 205 min of heating at 70 °C with the polymerization at 82% conversion. The ring opening of the monomer is clearly demonstrated by the growth of a new single vinyl proton signal at 6.9 ppm together with other distinctive signals at 4.3 ($-OCH_2-$), 3.4 ($C{=}CCH_2S-$), 2.6 ($-OCH_2CH_2S-$),

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Table 1. Radical Polymerization of 1 and 2

monomer or comonomers (ratio of monomers)	^{1}H NMR signals due to ring-opened unit, chemical shift (ppm)[a] vinylic	$-OCH_2-$	ratio of compound: comonomer in copolymer[b]	M_w[c]	dispersity[c]	conv (%)[b] [polymn time(min)]
1a[d]	6.4, 5.6	4.2	homopol	insoluble cross-linked gel formed at ca. 20% conv [60]		
1a:MMA (1:5)	6.3, 5.3	4.1	1:5.6	25 000	2.5	90 [300]
1a:MMA (1:1)[e]	6.3, 5.7, 5.5	4.1	1:1[e]	gel formed[e]		90 [167]
1a:styrene (1:5)	insoluble cross-linked gel formed at about 50% conv [240]					
1a:MA (1:5)	insoluble cross-linked gel formed [75]					
1b	6.9 (*E*), 5.9 (*Z*)[f]	4.3	homopol	46 200	2.3	82 [203]
1b:MMA (1:5)	6.9	4.2	1:10	19 200	1.9	85 [188]
1b:styrene (1:5)	obscured by aromatics	4.0	1:8	17 100	1.8	(70+) [560]
2:MMA (1:5)	6.2, 5.3–5	4.2	1:5	19 000	1.9	80 [165]

[a] NMR spectra (200 MHz) of precipitated, freeze-dried polymer, $CDCl_3$ used as solvent. [b] Determined from the ^{1}H NMR spectrum. [c] Determined by GPC (based on polystyrene standards) on polymerization solution before precipitation and freeze drying. [d] Vinyl and $-OCH_2-$ signals clearly observed before solution gelled into an insoluble mass. [e] Sample gelled at 90% conversion. Reported vinylic and alkoxy protons are from benzene solution. Ratio 1:1. [f] Ratio of *E*:*Z* isomers in polymer 94:6.

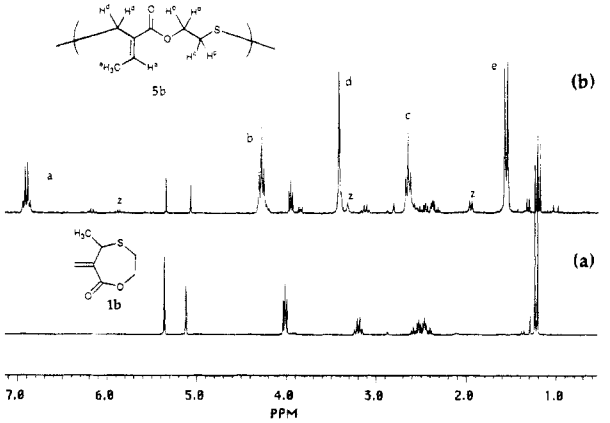

Figure 1. ^{1}H NMR spectra (solvent, benzene-d_6; 250 MHz). (a) Solution of monomer **1b** (3 M), AIBN (0.05 M), and internal reference of nondeuterated benzene. (b) Spectrum obtained after 82% conversion from 207 min of heating at 70 °C showing ring-opened polymer **5b** (*E*-isomer, R = CH_3) and residual monomer **1b** (vertical scale increased 4× for clarity). Peaks marked with "*Z*", denote identifiable signals due to the *Z* isomer of **5b**. See text for assignment. Ratio of *E*:*Z* isomers 94:6. Other minor peaks are due to a trace amount of an unreactive isomer ((*Z*)-6-ethylidene-1,4-oxathiepan-7-one) of **1b**. It played no part in the polymerization. Note the slight changes in chemical shift of the monomer due to the changing polarity of the solution.

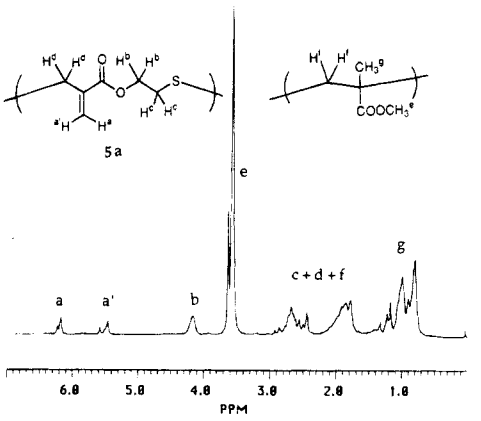

Figure 2. ^{1}H NMR spectrum (solvent, $CDCl_3$; 200 MHz) of freeze-dried copolymer of **1a**:MMA (1:5 ratio in monomer feed) with a ratio of ring-opened units **5a** (R = H) to MMA units of 1:5.6.

and 1.6 ppm ($-CH_3$) which are expected of a repeat unit of structure **5b** (*E* isomer, R = CH_3). Also observable at 5.9 (vinylic), 3.3 (C=CC**H$_2$**S–), and 1.9 ppm ($-CH_3$) are signals due to *Z* isomer repeat units of **5b** in the polymer. The ratio of *E*:*Z* isomers was 94:6. The integration ratio of the vinylic to $-OCH_2-$ protons was the required 1:2, indicating that ring opening was complete. If significant polymerization had occurred without ring opening, then this would have been apparent in the integration ratio of the vinylic to $-OCH_2-$ protons being 1:>2 (i.e., a shortage of vinylic protons).

In the copolymerizations, a similar growth of signals due to the new vinyl proton and $-OCH_2-$ protons with the disappearance of the monomer **1b** was observed. The use of the integrated form of the copolymerization equation[17,18a] on the conversion/monomer feed composition data of the methyl methacrylate–**1b** copolymerization gave values on the order $r_{MMA} = 2.1$ and $r_{1b} = 0.42$.

The presence of a methyl substituent in the ring-opened repeating unit (**5b**, R = CH_3) appears to have deactivated it toward radical attack. Thus, cross-linking or network formation via the "in-chain" acrylic carbon–carbon double bonds was not observed during the homo- and copolymerizations. The methyl group in the monomer (**1b**) also appears to slightly lower the reactivity of the monomer in copolymerizations as compared to the unsubstituted monomers (**1a** and **2**) (described below). This is presumably due to steric effects of the methyl group partially hindering radical addition.

The monomers **1a** and **2** (where R = H) gave white, soluble (chloroform, benzene, toluene, and tetrahydrofuran) copolymers when copolymerized with an excess of methyl methacrylate (**1a/2**:MMA 1:5). As in the case of **1b**, the formation of the new vinylic and $-OCH_2-$ protons (ratio 1:2) due to the monomer (**1a** and **2**) ring opening was clearly observable in the copolymerization with methyl methacrylate. Figure 2 shows the ^{1}H spectrum of the isolated, freeze-dried copolymer of the **1a**:MMA (1:5) experiment as an example. Cross-linking in a copolymerization of **1a** and methyl methacrylate was observed when the monomer (**1a**) was in a much higher concentration (**1a**:MMA 1:1), but this only occurred near the end of the polymerization. Within experimental error, the relative proportions of **1a** to methyl methacrylate in the comonomer feeds remained the same throughout the polymerizations, irrespective of the initial ratio of monomers (1:5 or 1:1). This was also observed for the copolymerization of **2** with methyl methacrylate (1:5). This implies that reactivity ratios of each **1a** and **2** with methyl methacrylate are near 1.0.[18b]

However, cross-linked, insoluble polymers were obtained from monomer **1a** when homopolymerized or

copolymerized with styrene or methyl acrylate. This is presumably due to the propagating polymer chain attacking an acrylic carbon–carbon double bond (**5a**, where R = H) in a neighboring chain. This cross-linking appeared to be somewhat suppressed in copolymerization with methyl methacrylate. This is possibly due to steric restraints making radical attack of the in-chain acrylic carbon–carbon double bond (of **5**) less favorable or more reversible[19] or due to fragmentation of the polymer chain by β scission of allylic carbon–carbon bonds.[20,21]

In conclusion, our initial experiments have shown compounds **1** and **2** to be relatively stable monomers with good solubility properties. They show high reactivity toward free-radical homo- or copolymerization and undergo essentially complete ring opening. The nature of the substituent R had a significant effect on the reactivity of the monomer and the resultant polymer or copolymer. The synthesis of more examples of these monomers is underway. This type of monomer appears to be not only commercially useful[12] but of fundamental interest in terms of structure–reactivity studies.

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References and Notes

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