# *tert*-Butyl α-(Hydroxymethyl)acrylate and Its Ether Dimer: Multifunctional Monomers Giving Polymers with Easily Cleaved Ester Groups

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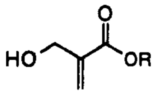
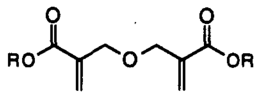
ABSTRACT: Two new members of the readily available family of α-functionalized acrylates have been synthesized, characterized, and polymerized. Reaction of *tert*-butyl acrylate with paraformaldehyde in the presence of catalytic 1,4-diazabicyclo[2.2.2]octane and *tert*-butyl alcohol at elevated temperatures leads to ca. 25% yields of *tert*-butyl α-(hydroxymethyl)acrylate. Continued reaction leads to ca. 80% conversion to the dimer ether of this material. Radical polymerization of the hydroxymethyl monomer occurs readily to give polymer of ca. $4.5 \times 10^5$ molecular weight and intrinsic viscosity of 0.6 dL/g. Solution $^{13}C$ NMR peak multiplicities appear consistent with atactic polymer rich in syndiotactic units. Copolymerization with styrene occurs readily to give products that appear to be essentially random copolymers based on their physical and spectral properties. Cyclopolymerization of the ether dimer occurs spontaneously in bulk at >120 °C or with azobisisobutyronitrile (AIBN) in solution to give soluble polymer with an intrinsic viscosity in $CHCl_3$ of 0.8 dL/g and a molecular weight of $7.5 \times 10^5$. Thermolysis of the hydroxymethyl polymer removes the *tert*-butyl group but generates lactone and ester groups as indicated by FTIR and especially solid-state $^{13}C$ NMR data. Mild, quantitative cleavage of the *tert*-butyl ester moieties of both the hydroxymethyl polymer and the cyclopolymer was achieved with neat trifluoroacetic acid. The obtained free-acid polymers exhibit polyelectrolyte behavior during viscosity measurements in dilute base but give normal straight-line plots in 1 N aqueous salt.

## Introduction

We have recently been exploring the synthesis and rich chemistry of the family of ester derivatives of α-(hydroxymethyl)acrylic acid (HMA). Initial work involved the facile synthesis of the methyl ester derivative (**1a**, MHMA)[1] and



**1**

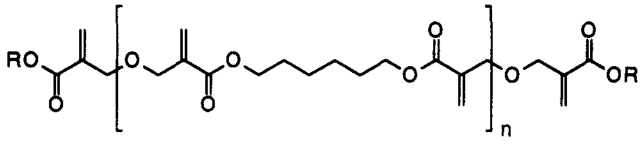


**2**

a: R = $CH_3$
b: R = $CH_2CH_3$
c: R = $CH_2CH_2CH_2CH_3$
d: R = $C(CH_3)_3$

isolation and identification of the unexpected ether dimer (**2a**) formed under base catalysis.[2,3] Also synthesized were the ethyl (**1b**) and *n*-butyl esters (**1c**), with the former finding application in wood composites[4] and both examined for use in contact lenses.[5] Ready cyclopolymerization of the ether dimers of these materials (**2a–c**) led to the formation of novel polymers containing tetrahydrofuran or tetrahydropyran units in the polymer backbone and pendent ester groups.[6] These dimers can also serve as cross-linking agents,[7] as can dimers obtained from reaction of **1a–c** or their α-(chloromethyl)acrylate derivatives with diepoxides, diacrylates, and biphenols.[8–11]

Others have begun to explore these materials as evidenced by two recent reports. The first deals with use of the hydroxymethyl- and ether-forming reaction on bisacrylates of fluorinated alcohols to give poly(ether–esters) containing pendent vinylidene groups.[12] This approach parallels our effects with 1,6-hexanediol diacrylate to generate reactive oligomers of structure 3 capable of readily cross-linking vinyl monomers and giving clear, tough, and insoluble homopolymers.[10] A second report involves extension of the ether dimer synthesis[2] and cyclopolymerization[3,6] to additional acrylates with evaluation of their cyclopolymerizability.[13] This complements our earlier description of the synthesis and spontaneous cyclopolymerization of the ether **2d** of *tert*-butyl α-(hydroxymethyl)acrylate (TBHMA, **1d**).[14]



**3**

The advantages offered by these materials include ready availability from the DABCO (1,4-diazabicyclo[2.2.2]-octane) catalyzed reaction of commercial acrylates with formaldehyde, rapid homo- and copolymerization,[1,5,11,15] higher $T_g$'s than the corresponding methacrylate polymers, and capability for functionalization before[5,8,9,11] or after polymer formation[9,11] through either the alcohol or ester group.

The only drawbacks we have encountered are the following: conversions (but not necessarily overall yields) of the acrylate ester starting materials must be kept low since, at higher than 25–30% conversion to the alkyl α-(hydroxymethyl)acrylates (RHMA), ether formation competes with further buildup of the hydroxymethyl monomers, limiting alcohol yield in a single-batch process; the methyl ester monomer (MHMA) or some unknown contaminant unique to the synthesis of MHMA causes severe poison ivy like skin irritancy and blistering in most people who handle it; however, no adverse response to the other derivatives has been observed under typical safe handling conditions for acrylate monomers.

The key structural features offered by these monomers are the presence of two reactive functional groups in addition to the vinyl moiety available for radical polymerization. While efforts to use the alcohol group in a variety of derivatization reactions to give ether, ester,

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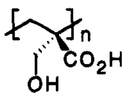
chloride, and urethane compounds have generated a number of novel derivatives, conversion of the ester groups has been less successful. For example, attempts to obtain the completely hydrolyzed free-acid polymer derivatives **4** and **5** from RHMA polymers **1a–c** and the ether cyclopolymers of **2a–c** have met with only partial success. It seemed desirable to explore the chemistry of the *tert*-butyl esters **1d** and **2d** based on the previously described use of the *tert*-butyl moiety as a readily cleavable protecting group for carboxylic acids.[16] For example, incorporation of *tert*-butyl methacrylate units at only a few percent into polystyrene followed by deprotection to give methacrylic acid groups allowed efficient blending with nylon.[17]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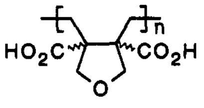
**5**

In this paper we describe the ready synthesis of TBHMA and its ether dimer; their conversion to homo-, co-, and/or cyclopolymers; mild, selective cleavage of the *tert*-butyl ester moieties with trifluoroacetic acid to give the free-acid polymers; characterization of all species using FTIR, solution and solid-state NMR, and (for the polymers) size-exclusion chromatography, light scattering, and viscosity.

## Experimental Section

**TBHMA and Ether Synthesis.** Procedures for the synthesis of α-(hydroxymethyl)acrylates and their ether dimers have been published previously.[1,2] *tert*-Butyl acrylate was used in this procedure with excellent results, although addition of ca. 5 vol % *tert*-butyl alcohol was found to be advantageous along with initial heating of the reaction to 100 °C for a few minutes followed by continued heating at 65 °C for several days.[14] Extraction to remove DABCO followed by repeated vacuum distillation gave TBHMA that was >99.5% pure by GC. The ether was obtained as the residue of the initial vacuum distillation of the crude reaction mixture and was usually pure enough for polymerization after washing several times with dilute acid and water and drying under vacuum. Yields of TBHMA were usually in the range of 25–30%, while those of the ether could be increased from ca. 50% to over 80% by prolonged heating of the reaction mixture.

$^{13}$C solution NMR of **1d** ($CDCl_3$, ppm from TMS): 27.8, $CH_3$; 61.6, $CH_2OH$; 80.7, $\mathit{O}C(CH_3)_3$; 123.9, $=CH_2$; 141.0, $\mathit{C}=CH_2$; 165.4, $CO_2R$.

$^{13}$C solution NMR of **2d** ($CDCl_3$, ppm from TMS): 26.7, $CH_3$; 67.8, $CH_2O$; 78.7, $\mathit{O}C(CH_3)_3$; 122.3, $=CH_2$; 138.0, $\mathit{C}=CH_2$; 163.0, $CO_2R$.

**TBHMA Homopolymer Synthesis.** Both bulk and solution polymerizations of TBHMA occurred successfully. Bulk polymerization was carried out by adding 0.05 g of AIBN to 5.0 g of TBHMA in a serum-stoppered 25 × 100 mm test tube, subjecting it to a freeze–thaw evacuation procedure, and then placing the test tube in a 50 °C oil bath overnight. Solution polymerization was carried out using identical ratios of monomer and initiator with a 9:1 ratio of benzene to TBHMA as solvent. The freeze–thaw method was used to remove oxygen and the mixture then heated 24 h in a 65 °C oil bath. The resulting polymers were purified by reprecipitation from $CHCl_3$ into petroleum ether. The intrinsic viscosity of one sample in $CHCl_3$ was 0.2 dL/g, and other homopolymers prepared from this batch of monomer in the same way gave values of 0.18–0.3 dL/g, perhaps due to a reactive impurity. Other bulk and solution homopolymers gave intrinsic viscosities ranging up to 0.7 dL/g in $CHCl_3$. One of the higher molecular weight samples was characterized more completely (as described below) before and after ester cleavage.

**TBHMA/Styrene Copolymer Synthesis.** In a manner similar to that above, 2 g of TBHMA, 12 g of styrene, and 0.5 g of AIBN were reacted in a 65 °C oil bath for 24 h. The polymer was purified by reprecipitation from $CHCl_3$ into petroleum ether. Other comonomer ratios were examined by using essentially the same conditions. Yields were controlled by the length of time of reaction, and all polymers were obtained as white powders from petroleum ether precipitation.

**Cyclopolymer Synthesis.** The cyclopolymer was initially obtained accidently while distilling TBHMA from a TBHMA synthesis mixture. The pot solution spontaneously polymerized after removal of TBHMA and other impurities at temperatures in excess of 120 °C even in the presence of copper chloride added as radical scavenger. The obtained polymer was essentially pure as obtained but was reprecipitated from THF into petroleum ether. Deliberate ether cyclopolymerization using AIBN occurred at 60–70 °C with neat samples over several hours (to keep conversion low) and over somewhat longer times in solvents such as benzene or THF. Lower solution concentrations favored formation of soluble material, and higher concentrations occasionally gave lightly cross-linked products. Purification again involved reprecipitation from THF or $CHCl_3$ into petroleum ether.

**Polymer Deprotection.** Poly(TBHMA) (or the cyclopolymer) was stirred overnight with 10% excess trifluoroacetic acid (TFA). Complete dissolution usually occurred within 15 min, and a white precipitate that gradually formed was isolated by evaporation of the excess acid and drying in air. Purification of these polymers involved dissolution in aqueous base and reprecipitation with aqueous acid. Final drying was done at ambient temperatures under vacuum.

All polymers obtained were characterized by FTIR and $^{13}$C solution and solid-state NMR spectroscopies. FTIR spectra were obtained on a Mattson Polaris FTIR or a Perkin-Elmer 1600 instrument. Solution NMR spectra were acquired with a Bruker AC-300 instrument, and solid-state spectra were obtained with a Bruker MSL-200 instrument. Thermal analyses were done on a Du Pont 9900 analyzer with a 910 DSC cell using a heating rate of 10 °C/min and nitrogen purge. Viscosities were run at 30 ± 0.1 °C using constant dilution Cannon-Ubbelohde semimicroviscometers. Those polymers that were soluble in THF were analyzed by size-exclusion chromatography using a $dn/dc$ detector and an in-line Wyatt Dawn multiangle laser-light-scattering molecular weight detector. A Chromatix KMX-16 differential refractometer was used to obtain $dn/dc$ values for the polymers in THF at the He–Ne laser wavelength. Values of $dn/dc$ obtained for polyTBHMA were 0.0748 in THF and 0.041 05 in $CHCl_3$. The $dn/dc$ value for the cyclopolymer was measured to be 0.0796 in THF. SEC/LLS evaluation of these and related polymers will be described in more detail in a subsequent paper.

## Results and Discussion

**Monomer Synthesis and Characterization.** The TBHMA monomer used in the polymerization of the homopolymers and styrene copolymers was obtained in reasonable yield by using *tert*-butyl alcohol and elevated temperatures of reaction, especially at the beginning to solubilize the paraformaldehyde. While others have reported use of high temperatures in a sealed tube,[13] we have not found the latter to be necessary. Excellent purity was attained through acid extraction of the crude reaction mixture dissolved in $CH_2Cl_2$ followed by multiple vacuum distillation. Use of other sources of formaldehyde (such as formalin) give lower yields and more side products, and we have found paraformaldehyde to be the best reagent for TBHMA and RHMAs in general.

Conversion of TBHMA to the ether dimer is thermodynamically favorable and merely requires continued heating of the synthesis reaction mixture in the presence of DABCO. We have found with other RHMA ethers that the presence of water liberated during ether formation can actually cleave the ether back to the RHMA. It would probably facilitate the reaction and improve the overall yield of **2** if water were removed during the later stages of

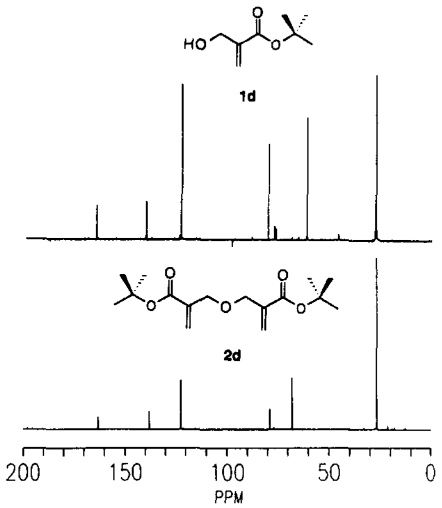

**Figure 1.** $^{13}C$ solution NMR spectra of TBHMA **1d** (lower trace) and its dimer ether **2d** (upper trace) obtained in $CDCl_3$.

the synthesis of RHMA ethers. Similarly, the formation of acetal derivatives of TBHMA (as observed for MHMA **1a** and other RHMAs[2,13]) is also reversible and is gradually driven back to the alcohol and then to the ether as the reaction is forced to completion or final equilibrium.

Figure 1 gives the $^{13}C$ solution NMR spectra of **1d** and **2d**. Typical chemical shifts are observed for the *tert*-butyl carbons and the two vinylidene carbons as listed in the Experimental Section. The $\alpha$-methylene carbon connected to the oxygen atom of the alcohol shows a characteristic downfield shift on going to the ether, i.e., from 61.6 to 67.8 ppm. A similar change in chemical shift for this carbon is observed for all of the RHMA ether derivatives that we have prepared to date.

The FTIR spectra of these two monomers show strong characteristic peaks for the ester carbonyls and C–O bonds plus weak double bond peaks at 1640 and 950 cm$^{-1}$. Key differences involve broad O–H and C–O absorptions at ca. 3300 and 1100 cm$^{-1}$ for **1d** and a strong C–O–C peak at 1140 cm$^{-1}$ for **2d**.

**Poly(TBHMA) and TBHMA–Styrene Copolymer Synthesis and Characterization.** TBHMA homopolymerizations were carried out in bulk or in benzene. The former involved spontaneous initiation on standing in air or initiation with AIBN at 60–70 °C. Solution homo- and copolymerizations (with styrene) all involved thermal initiation with AIBN in degassed solutions. Photopolymerization in bulk, in solution, or in thin films also took place readily using various photoinitiators and a small UV lamp. All homopolymers of TBHMA were isolated in moderately high yield as white powders that were readily soluble in $CHCl_3$, $CH_2Cl_2$, $CCl_4$, THF, benzene, and toluene. Slight solubility of poly(TBHMA) was also observed in diethyl ether. Depending on relative proportions of styrene and TBHMA incorporated, the copolymers were soluble in typical solvents for each homopolymer.

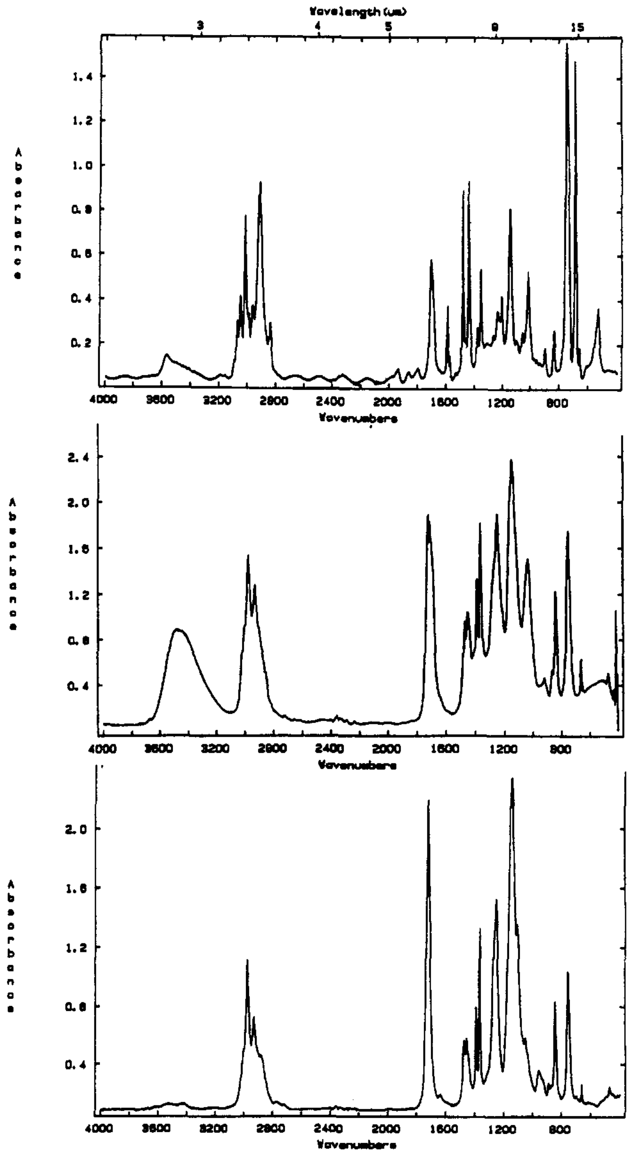

**Figure 2.** FTIR spectra of the soluble cyclopolymer of **2d** (bottom spectrum), homopolymer of **1d** (middle spectrum), and 1:9 TBHMA–styrene copolymer (upper spectrum).

The FTIR spectrum of poly(TBHMA) (middle trace in Figure 2) shows the expected symmetric and asymmetric stretching and bending absorptions characteristic of hydroxyl and ester functionality. No peaks for residual double bonds are evident, indicating the absence of unreacted monomer. Comparison of this spectrum with that of the 9:1 copolymer of styrene and TBHMA (upper trace) shows peaks for the latter characteristic of both comonomer units with the most noticeable for the TBHMA groups being the carbonyl peak at 1725 cm$^{-1}$. Only small changes in peak positions for the TBHMA functional groups indicate little effect of their incorporation into the hydrophobic polystyrene microenvironment on intra- and/or intermolecular interactions. Similar behavior is seen in the solution and solid-state NMR of this copolymer (Figure 3). This may be due to strong interactions within a TBHMA repeat unit being more important in solution and in bulk than intermolecular interactions, or it may result from blockiness in the copolymer formation resulting in several adjacent TBHMA segments behaving as an isolated environment. Copolymerization reactivity ratios for MHMA and EHMA with styrene, however, indicate essentially random incorporation with a slight tendency for alternation rather than block formation.[11,15] We expect similar behavior for TBHMA.

Figure 4 gives expanded portions of the $^{13}C$ NMR solution spectrum of the homopolymer of TBHMA and a generic repeat unit (which is not meant to indicate isotacticity). Clearly, tacticity information is evident for the carbon peaks of the backbone methylene and quaternary carbons at 40–44 and 54 ppm, respectively. While the latter is not resolved into clearly defined peaks, the former seems to display strongly resolved diad peaks with one or both of the main peaks split by tetrad (or higher) interactions. The backbone $CH_2$ groups of PMMA show

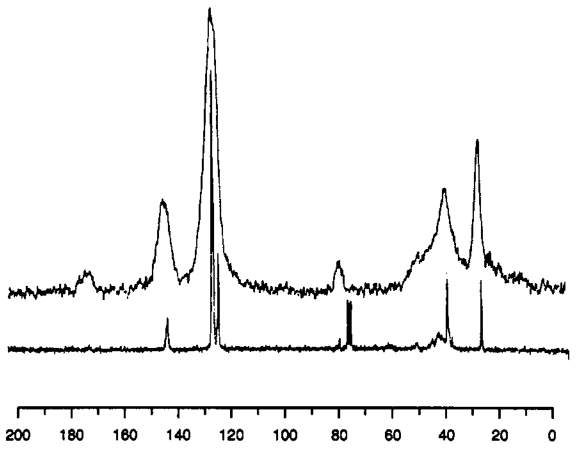

**Figure 3.** $^{13}C$ solution (lower trace) and solid-state (upper) NMR spectra of the 1:9 TBHMA–styrene copolymer.

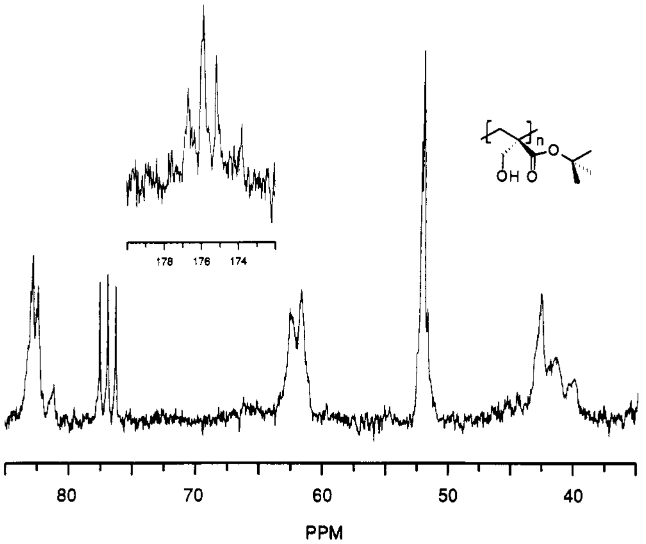

**Figure 4.** $^{13}C$ solution NMR spectrum of poly(TBHMA) from 35 to 85 ppm with carbonyl region insert above.

similar complexity with at least six resolved peaks.[18] The pendent–$CH_2OH$ peaks at 61–63 ppm seem to represent two main triad groups. This would be consistent with either a highly isotactic (unlikely) or syndiotactic polymer formed via free-radical polymerization. On the basis of the known preference of methyl methacrylate to give a radical polymer rich in syndiotactic triads[18] plus the bulkiness of the *tert*-butyl ester groups, which might be expected to increase the tendency for syndiotactic placement of incoming monomer units, we tentatively assign the upfield peak to the syndiotactic (rr) units and the downfield peak to mr and rm moieties. These relative peak positions are similar to those of PMMA α-$CH_3$ groups. The isotactic (mm) triad peak is perhaps seen here as a weak shoulder on the downfield side of the two main peaks.

Peaks for the quaternary carbon of the *tert*-butyl ester group are seen at 81–83 ppm, and also reflect stereochemical information. On the basis of the expected syndiotactic-rich structure and a reversal of triad peak order (as is seen for the ester carbonyl of PMMA but not for the ester methyl[18]), we assign the most intense and downfield peak to the rr units. The middle peak and weak upfield peak are assigned to the mr/rm and mm units, respectively. The carbonyl peaks (insert) appear to reflect greater than simple triad multiplicity that does not seem to be related in overall intensity and position to the other positions. This is similar to the behavior of the carbonyl peaks of PMMA,[18] and we make no assignments at the present time.

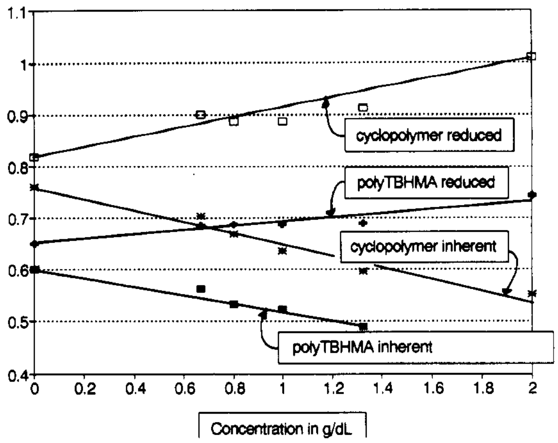

**Figure 5.** Dilute-solution viscosity plots of poly(TBHMA) (lower set) and cyclopolymer (upper) in $CHCl_3$ with extrapolated intercepts at zero concentration.

While we have tentatively assigned the aliphatic peaks as indicated above based on analogy with PMMA and intuitive arguments based on steric interactions of the bulky *tert*-butyl ester groups, strong intermolecular interactions involving hydrogen bonding of the pendent hydroxymethyl groups could play a major role in determining the stereochemistry of propagation. Interaction between hydroxyl groups and ester carbonyls could reinforce the inherent tendency for syndiotactic placement or interactions in which alcohol groups act as both hydrogen-bond donor and acceptor could lead to isotactic-rich structures. Appropriate model compounds and polymers prepared through anionic polymerization are required to confidently answer this question through comparison of peak intensities and chemical shifts.

Dilute solution viscosity plots for a typical TBHMA homopolymer are given in Figure 5. Both reduced viscosity (positive slope) and inherent viscosity (negative slope) values are plotted, and good linearity (correlation coefficients of >0.95) with similar intercepts were obtained. The Kraemer and Huggins constants calculated from these plots summed to ca. 0.5, in excellent agreement with what is expected of well-behaved polymers.[19] The weight-average molecular weight of this polymer (by SEC plus in-line laser-light-scattering determination) was $4.5 \times 10^5$, which gives a viscosity–molecular weight relationship that appears very similar to that of PMMA; i.e., the calculated intrinsic viscosity for a PMMA sample of this molecular weight is 0.68 dL/g based on our previously determined relationship using THF as solvent.[20]

**Cyclopolymer Synthesis and Characterization.** Synthesis of the cyclopolymer was surprisingly facile, for both spontaneous and deliberate polymer formation. Spontaneous conversion of bulk monomer to soluble polymer at high temperatures gave materials with molecular weights on the order of $7.5 \times 10^6$ by SEC comparison to polystyrene standards and direct measurement of the weight-average value using the on-line laser-light-scattering spectrophotometer. Figure 5 gives the inherent and reduced viscosity plots for a typical cyclopolymer in $CHCl_3$. Correlation coefficients of >0.95 and similar intercepts give an intrinsic viscosity of 0.8 dL/g. Again, the value of intrinsic viscosity measured for this polymer is very close to that calculated with the PMMA Mark-Houwink K and a values for a PMMA sample of this molecular weight, i.e., 0.94 dL/g.[20] The smaller value of intrinsic viscosity for the cyclopolymer (vs PMMA) may indicate a somewhat more tightly coiled conformation for this material in THF. On the basis of these viscosity results, it appears that neither strong intra- and intermolecular hydrogen bonding occurs for poly(TBHMA) to disrupt random coil behavior nor does an increase in chain rigidity occur due to incorporation of the cyclic ether groups into the polymer backbone of the cyclopolymer.

Such high molecular weight for the cyclopolymer indicates an unexpectedly large preference for intramolecular over intermolecular vinyl addition. For the methyl, ethyl, and *n*-butyl ester ethers (**2a–c**), it is much more difficult to form high molecular weight polymer with no pendent (uncyclized) acrylate units that lead to cross-linking during or after polymerization. Steric interaction between the bulky *tert*-butyl ester groups may be involved in the same way as for homopolymerization of fumarate diesters.[21] While small fumarate ester groups do not allow high molecular weight polymer formation, bulky groups such as the *tert*-butyl ester do. One argument that has been put forth as explanation of this unexpected behavior is that the bulky substituents do not so much facilitate chain propagation as they inhibit chain termination, leaving propagation as the only reaction path available. For cyclopolymerization, steric interactions may inhibit intermolecular addition much more than they do intramolecular reaction. This would allow more time for the latter but would not stop intermolecular addition after cyclization since this would be the only path then available to the active chain end. Alternatively, reversible addition of the intermolecular adduct could occur at high temperatures, while cyclization would be followed by rapid intermolecular reaction with a new monomer.[22] Deliberate bulk cyclopolymerization at lower temperatures does give soluble product at lower conversions and higher initiator concentrations but not as easily as at higher reaction temperatures. This behavior is more consistent with reversible intermolecular addition.

FTIR characterization of the cyclopolymer (bottom spectrum in Figure 2) clearly shows peaks characteristic of carboxylic esters and cyclic ether groups and the absence of peaks for alcohol groups and residual double bonds (1645 cm$^{-1}$) which could result from noncyclized acrylate groups. We initially considered the possibility of five-membered ring formation based on the behavior of many 1,6-dienes in cyclopolymerization, which prefer kinetically controlled five- rather than six-membered ring generation. However, many methacrylate derivatives (such as methacrylic anhydride) do prefer six-membered ring formation, especially at elevated temperatures where entropy and reversible vinyl addition can play an important part in determining both the rate of cyclization over intermolecular addition and the ring-size preference.[22] Six-membered ring formation might be especially favorable in view of the stabilized radical intermediates that would be generated by both the inter- and intramolecular addition reactions. We have initiated a labeling and NMR study that should answer this question.

Both $^{13}$C solution and solid-state NMR spectra of the cyclopolymer show different peak positions than those of poly(TBHMA). Backbone carbons, cyclic ether versus pendent alcohol carbons, and ester carbonyls all show moderate-to-large changes. Further discussion of these spectra is given in the next section describing ester deprotection.

**Poly(TBHMA) and Cyclopolymer Deprotection.** DSC scans of poly(TBHMA) and the cyclopolymer show reproducible $T_g$ values of ca. 120 and 138 °C, respectively. Both polymers also show a large endotherm at ca. 200 °C corresponding to loss of ester *tert*-butyl groups. Such thermal elimination is typical for *tert*-butyl esters and has been used synthetically to generate free-acid groups in various polymers such as the copolymers of styrene and *tert*-butyl methacrylate.[16] For poly(TBHMA), thermal loss of the ester alkyl is accompanied by lactonization and intermolecular ester formation. Support for the latter comes from insolubility of the thermolyzed polymer even in dilute base.

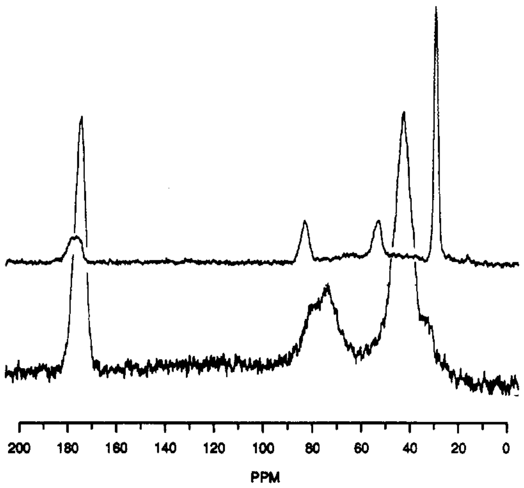

**Figure 6.** $^{13}$C CP/MAS spectra of poly(TBHMA) before (upper trace) and after (lower) heating to 200 °C.

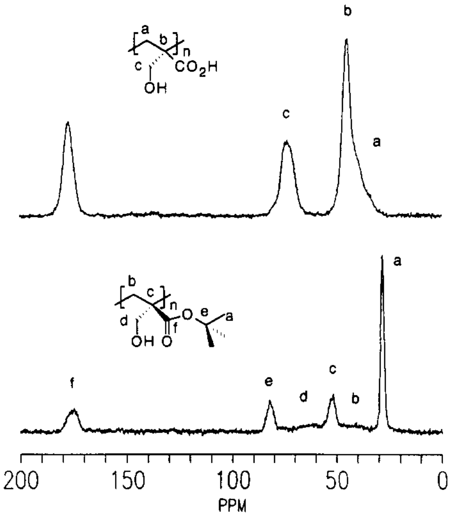

**Figure 7.** $^{13}$C CP/MAS spectra of poly(TBHMA) before (lower trace) and after (upper trace) treating with trifluoroacetic acid.

Figure 6 shows the solid-state $^{13}$C CP/MAS NMR spectra of a poly(TBHMA) sample before and after heating to just above 200 °C. The peaks at approximately 28 and 82 ppm of the *tert*-butyl methyl and quaternary carbons have cleanly disappeared in the spectrum of the thermolyzed polymer. Comparison should be made with Figure 7, which gives the deprotected free-acid polymer (poly(HMA), **4**) obtained cleanly by treatment with TFA. Also given in Figure 7 are peak assignments for poly(TBHMA) and **4** (the structures drawn are generic and not meant to indicate isotactic polymers). Two observations are important: First, the TFA-generated polymer carbonyl peak is more consistent with the free-acid structure than that of the thermolyzed material, appearing at 177 ppm (downfield from the poly(TBHMA) ester carbonyl at 175), while the thermolyzed material has a carbonyl peak at 172 ppm, more consistent with a lactone group. Second, the $-CH_2O$ peak of the thermolyzed sample shows a strong downfield shoulder compared to the TFA polymer, which is attrib-

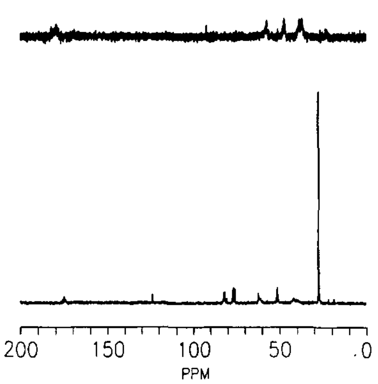

**Figure 8.** $^{13}C$ solution spectra of poly(TBHMA) before (lower trace in $CDCl_3$) and after (upper trace in dilute NaOD–$D_2O$) treating with trifluoroacetic acid.

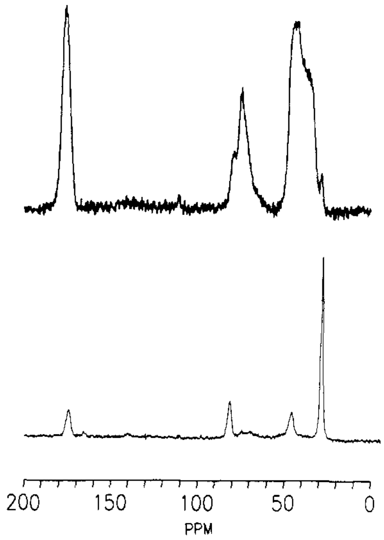

**Figure 9.** $^{13}C$ CP/MAS spectra of **2d** cyclopolymer before (lower trace) and after (upper trace) treating with trifluoroacetic acid.

utable to incorporation of some of the alcohol groups into lactone or ester moieties. This peak is surprisingly far downfield compared to its position in the solution spectrum of 4 in dilute base (Figure 8), where it appears at ca. 58 ppm. This downfield shift may reflect strong hydrogen bonding involving alcohol and acid groups with themselves and with each other in the solid state. In any event, the solubility of the TFA-deprotected polymer in dilute base and the absence of the *tert*-butyl peaks in the $^{13}C$ solution and solid-state NMR spectra substantiate the mildness and completeness of this procedure for generation of the free-acid polymer without undesired side reactions.

Characterization of the deprotected cyclopolymer also involved FTIR, $^{13}C$ solution NMR, and $^{13}C$ CP/MAS solid-state NMR spectroscopies, although only the last will be discussed here in detail. Figure 9 gives the solid-state spectra before and after deprotection. Comparison of the cyclopolymer spectrum (lower trace) with that of poly(TBHMA) points out two key differences: the backbone quaternary carbon peak is at 52 ppm for the latter but at 45 ppm for the former, and the alcohol methylene peak for poly(TBHMA) appears as a broad peak at 52–70 ppm while the corresponding ether methylenes of the cyclopolymer are at 65–80 ppm, consistent with the behavior of these two peaks for the monomers and alcohols versus their ethers in general.

Similar to the ease of cleavage of the *tert*-butyl groups for poly(TBHMA), loss of the ester alkyls is essentially complete for the cyclopolymer as shown by disappearance of the peaks at 28 and 82 ppm. Characteristic of the formation of the free acid polymer is the shift of the ester carbonyl from ca. 174 ppm down to 176 ppm, the same magnitude of shift as seen for poly(TBHMA) going to poly(HMA).

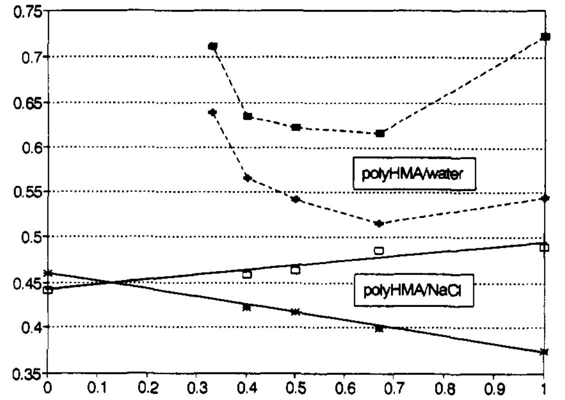

**Figure 10.** Reduced and inherent viscosity plots for poly(HMA), 4, in deionized water (upper data pair) and in 1 N aqueous NaCl (lower pair).

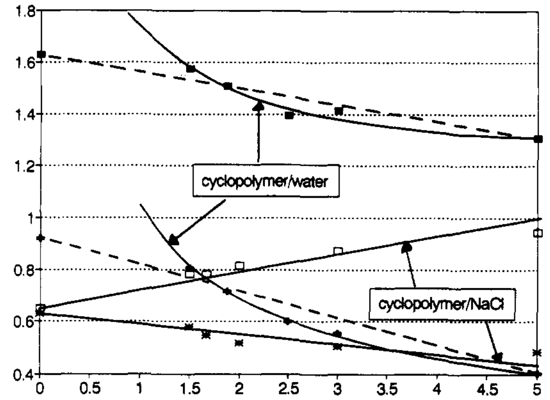

**Figure 11.** Reduced and inherent viscosity plots for cyclopolymer 5 in deionized water (upper data pair) and in 1 N aqueous NaCl (lower pair); dashed lines are linear least-squares best fits for the nonlinear data sets.

The obtained free-acid polymers were slowly soluble in DMSO and water and readily soluble in dilute aqueous base. Both types of polymers displayed typical polyelectrolyte behavior in water containing a slight molar excess of NaOH as shown in Figures 10 and 11. While the upward change in slope on going to lower concentration appears to be more dramatic for poly(HMA), in fact the concentrations for the cyclopolymer were not taken to as low a set of values, and essentially identical behavior was observed for both polymers. On going to salt solutions (lower sets of data points), both systems gave linear relationships with similar intercepts for extrapolation of the reduced and inherent plots to zero. The relative magnitudes of the intrinsic viscosities thus obtained are in the same order as found for the precursor *tert*-butyl ester polymers in $CHCl_3$ (Figure 5), with that of the cyclopolymer being larger than that of the pendent hydroxymethyl sample.

## Conclusions

A new α-hydroxymethyl monomer containing a *tert*-butyl ester group and its ether dimer are readily available from *tert*-butyl acrylate. Both alcohol and ether are capable of deliberate and spontaneous radical polymerization to give the corresponding linear homopolymer and cyclopolymer, respectively, in good yield and high molecular weights. Facile copolymerization occurs for these monomers as demonstrated for TBHMA with styrene. We suggest that steric inhibition of intermolecular addition for the 1,6-diene ether may allow, or even promote, high degrees of cyclization to give soluble polymer. Trifluoroacetic acid provides a mild, essentially quantitative method for *tert*-butyl ester cleavage to give the free-acid derivatives of both polymers. The sodium salts of both polymers exhibit polyelectrolyte behavior in water but not in salt solution. FTIR, solution, and solid-state $^{13}$C NMR data are consistent with the structures expected for all polymers obtained, confirming the synthesis and polymerization results. These materials open up new and exciting applications of the family of $\alpha$-(hydroxymethyl)acrylate polymers by providing ready access to the deprotected (free acid or salt) derivatives. The combined alcohol and acid or ester functionality of the homo- and copolymers of these new monomers should facilitate further derivatization reactions, surface interactions and modifications, adhesion, polymer blending, and reinforcement of vinyl materials, to list a few areas of potential application of these materials that we are continuing to explore.

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