Unusually Facile Cyclopolymerization of a New Allyl Ether Substituted Acrylate and Confirmation of Repeat Unit Structure by INADEQUATE NMR

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ABSTRACT: We have synthesized and polymerized ethyl α-[(allyloxy)methyl]acrylate and allyl α-(hydroxymethyl)acrylate, two diene monomers being evaluated as possible optical materials. The allyl ether showed a significant difference in polymerization behavior in comparison to the allyl ester and was found to undergo virtually complete cyclopolymerization in solution and in bulk. Ring size could not be determined directly by examination of the ^{13}C solution spectrum in the absence of suitable model compounds. The two-dimensional INADEQUATE NMR method (Incredible Natural Abundance DoublE QUAntum Transfer Experiment) was then used to determine the ring size generated in the new cyclopolymer. ^{13}C solution NMR spectral characterization gives well-defined chemical shift differences for cis and trans isomers, which can be explained by γ-gauche shielding for carbons in or next to the polymer backbone. The methylenes connected to the quaternary carbons show a γ-gauche effect of 6.8 ppm, a value which is at the high end of the γ-gauche range. Two-dimensional INADEQUATE analysis conclusively confirms monomer cyclization exclusively to five-membered rings with a ratio of trans to cis ring configurations in the polymer backbone of approximately 2.2.

Introduction

The first observed and reported cyclopolymerization was that of diallyldimethylammonium chloride to give a linear soluble polymer under free-radical polymerization conditions.[1] Subsequent work showed that a wide variety of 1,6-dienes undergo cyclopolymerization offering a simple route to polymers with backbone structures quite different from those obtained with the usual radically polymerized vinyl monomers.[2] More than two unique carbon atoms are included in the backbone, allowing more control of physical properties via functional group modification than in the typical vinyl polymers. For example, incorporation of heteroatoms into the ring structure (and therefore the backbone of the polymer) is possible through synthetic manipulation of the monomer before polymerization. Free radical, anionic, cationic, and group transfer methods have all been used for initiation of cyclopolymerization with good results.[2]

Increased awareness of cyclopolymerization has led to recognition of other monomers, expected to cross-link due to the presence of two or more alkene groups in the same molecule, as cyclomonomers. For example, soluble divinyl ether–maleic anhydride cyclocopolymer is readily obtained and has been shown to have valuable antimetastatic and antitumor properties.[3] A significant problem in characterizing cyclopolymers is determination of the size of the ring formed since most systems can cyclopolymerize to give more than one ring structure. A common characterization route involves synthesis of model compounds with the expectation that their IR and/or NMR spectra will allow determination of the polymer's chemical structure. A more straightforward and conclusive method entails the use of a two-dimensional NMR technique which allows the determination of carbon–carbon connectivity and therefore the determination of ring size.

We have synthesized poly[ethyl α-[(allyloxy)methyl]-acrylate] (referred to hereafter as the allyl ether polymer) and poly[allyl α-(hydroxymethyl)acrylate] (referred to hereafter as the allyl ester polymer), two diene monomer based polymers being evaluated as possible optical materials. The allyl ether showed a significant difference in polymerization behavior in comparison to the allyl ester and was found to undergo virtually complete cyclopolymerization in solution and in bulk. The two-dimensional INADEQUATE NMR method (Incredible Natural Abundance DoublE QUAntum Transfer Experiment)[4-6] was then used to determine the ring size generated in the new cyclopolymer.

Experimental Section

Ethyl α-(chloromethyl)acrylate was synthesized from ethyl α-(hydroxymethyl)acrylate as described in a previous communication[7] and was used at approximately 98% purity as a reagent for the following monomer synthesis. Allyl alcohol, benzene, paraformaldehyde, 1,4-diazabicyclo[2.2.2]octane (DABCO), and methylene chloride were used as received from Aldrich Chemical Co. Triethylamine (Aldrich) was dried over calcium hydride for 24 h and then distilled into a new vessel containing fresh calcium hydride. 2,2′-Azobis[isobutyronitrile] (AIBN) was recrystallized from methanol before use. WAKO V-30 initiator [(2-[(carbamoyl)azo]isobutyronitrile] was used as received. ^{13}C solid-state cross-polarized magic angle spinning (CP/MAS) nuclear magnetic resonance spectra were acquired using a Bruker MSL-200 NMR spectrometer. The solution spectra were acquired on a Bruker AC-300 NMR spectrometer. One-dimensional spectra were processed using an in-house NMR program based on the SpectraCalc software package.[8] Viscosity measurements were taken at 30 °C in chloroform using a Cannon-Ubbelohde No. 50 microviscometer. Monomer synthesis reactions were monitored by gas chromatography using a Hewlett-Packard 5890 gas chromatograph equipped with an FID detector, 95% dimethyl/5% diphenylpolysiloxane column, and HP 3396a integrator.

The double quantum coherence experiment (INADEQUATE) was performed using the Bruker INAD45 pulse program on a Bruker MSL-400 NMR spectrometer equipped with a 10-mm probe. The data were collected on a 50 wt % concentration of polymer in $CDCl_3$ in a 10-mm glass sample tube. Data were acquired on a nonspinning sample to reduce T_1 noise. The pulse sequence [D0–90°–τ–180°–τ–90°–Δ–90°-acquire] was used. Experimental parameters were as follows: the 90° pulse width was 13.75 μs, the echo delay τ was 6.58 ms (corresponding to a ^{13}C–^{13}C coupling of 38 Hz), the incremental delay Δ was 69 μs, and the acquisition time was 70.6 ms. The number of increments in the F1 domain was 64, and the number of scans per FID was 1344. WALTZ-16 decoupling was used during data acquisition in the F2 domain. The recycle time D0 was 4.5 s, which was ~4 times

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the longest ^{13}C T_1 value. Chromium(III) acetylacetonate was added as a spin-relaxation agent. The sweep width in the F2 domain was 72 ppm, which encompassed the spectral region of interest. When the data were processed, the F1 domain was zero-filled to 1024 data points, while no zero-filling was used in the F2 domain. Gaussian line broadening was applied to both domains before application of 2-D Fourier transformation.

Monomer Syntheses

Ethyl α-[(Allyloxy)methyl]acrylate. Allyl alcohol (7.4 mL, 0.11 mol), ethyl α-(chloromethyl)acrylate (8.11 g, 0.055 mol) and a Teflon-coated magnetic stirring bar were added to 50 mL of methylene chloride in a 100-mL single-neck round-bottom flask. The vessel was placed in an ice bath, and with stirring, triethylamine (11.4 mL, 0.066 mol) was slowly added. A calcium sulfate filled drying tube was attached, and the contents were allowed to stir for approximately 10 h. The vessel was then heated to 60–65 °C and allowed to stir for approximately 2 days. The course of the reaction was monitored by gas chromatography until complete. The triethylamine/HCl salt and excess triethylamine were then extracted by rinsing with a 1 wt % aqueous HCl solution (three times with 10 mL each). The organic layer was separated and the aqueous layer back-extracted with 10 mL of methylene chloride. Organic layers were combined and dried with powdered magnesium sulfate. A pinch of copper(II) chloride was added as a free-radical inhibitor, and excess reactants and solvent were removed by rotary evaporation. Vacuum distillation gave 96% pure ethyl α-[(allyloxy)methyl]acrylate; 75% yield.

Allyl α-(Hydroxymethyl)acrylate. Allyl acrylate was synthesized by reaction of acryloyl chloride with allyl alcohol. Allyl alcohol (98.5 mL, 1.45 mol), triethylamine (202.0 mL, 1.45 mol), and 300 mL of methylene chloride were added to a 1000-mL single-neck round-bottom flask containing a Teflon-coated magnetic stir bar. The reaction vessel was placed in an ice bath and allowed to cool. Acryloyl chloride (112.1 mL, 1.38 mol) was added dropwise to the stirring vessel contents. After addition, the vessel was fitted with a drying tube and allowed to warm to room temperature. It was stirred for approximately 24 h. Vessel contents were then poured into a 4000-mL separatory funnel and washed twice with 150 mL of deionized water and once with a 150-mL 1 N HCl solution. Low-pressure distillation was used to isolate 93% pure allyl acrylate; 88% yield.

Allyl acrylate (49.83 g, 0.44 mol), paraformaldehyde (14.35 g, 0.48 mol), and DABCO (5.055 g, 0.045 mol) were added to a 500-mL single-neck round-bottom flask fitted with a condenser and Teflon-coated magnetic stirring bar. The vessel was placed into a 50 °C oil bath. After approximately 8 h the vessel was removed from the bath and 100 mL of methylene chloride added. The solution was placed into a 500-mL separatory funnel and washed twice with 20 mL of a 1 N HCl solution. Methylene chloride was removed by rotary evaporation and allyl α-(hydroxymethyl)-acrylate isolated by low-pressure distillation to give 93% pure product; 27% yield.

Typical Polymerization Conditions

Bulk polymerizations were carried out by heating monomer samples containing 0.5–1% AIBN at 50–70 °C. Solution polymerizations were carried out as follows: ethyl α-[(allyloxy)methyl]-acrylate, WAKO V-30 azo initiator (1 mol %) and a Teflon-coated magnetic stirring bar were added to benzene (approximately 10% monomer concentration) in a 50-mL round-bottom flask with stopcock and glass stopper. The contents were purged by three successive freeze–evacuate–thaw procedures using liquid nitrogen for freezing. The vessel was then placed in a heated oil bath with temperature maintained at 70–75 °C over the course of the polymerization. After 5 days the polymer was precipitated into cold hexanes; typical yield 90%. Intrinsic viscosity for one polymer sample was 0.18 dL/g in chloroform.

Results and Discussion

One of the unique aspects of this project is the ease of incorporation of functional groups through ether formation with derivatives of α-(hydroxymethyl)acrylates such as ethyl α-(chloromethyl)acrylate (Figure 1). In addition,

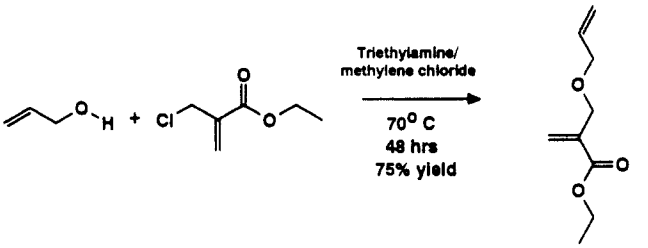


Figure 1. Synthetic scheme for ethyl α-(allyloxymethyl)acrylate.

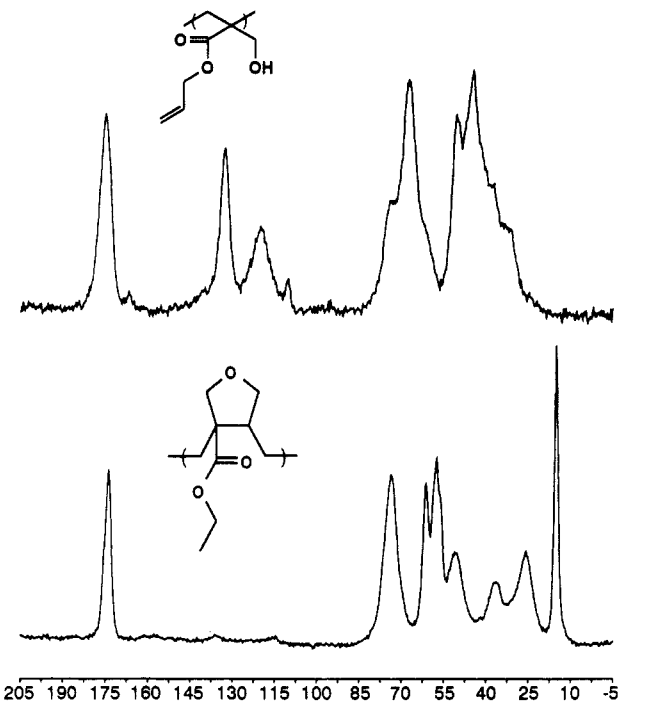


Figure 2. ^{13}C solid-state MAS NMR of poly[allyl α-(hydroxymethyl)acrylate] (top) and poly[ethyl α-[(allyloxy)methyl]acrylate] (bottom).

synthesis of the allyl ether monomer illustrates the versatility of incorporation of the hydroxymethyl group into various acrylic esters. We have synthesized and polymerized the two diene monomers, ethyl α-[(allyloxy)-methyl]acrylate and allyl α-(hydroxymethyl)acrylate, to evaluate their use as possible optical materials. ^{13}C CP/MAS spectroscopy revealed large differences in the polymer structure of poly[ethyl α-[(allyloxy)methyl]-acrylate] and poly[allyl α-(hydroxymethyl)acrylate] samples polymerized in bulk using a low concentration of AIBN (Figure 2) even though the monomers have superficially similar 1,6-heptadiene structures. The allyl ester formed an insoluble, slightly swellable polymer which showed much residual unsaturation. The polymer was hard and had cracked into many small pieces during formation, indicating high levels of stress caused by cross-linking and volume reduction during polymerization. This material was unswellable in chloroform, and as shown in Figure 2, contained much residual unsaturation attributable to pendent allyl vinyl groups. Attempts to polymerize and copolymerize allyl acrylate by other workers also gave low levels of cyclopolymerization.[9]

The allyl ether polymer, on the other hand, showed almost no residual unsaturation and was flexible and highly swellable when polymerized under similar conditions. Subsequent solution polymerizations gave soluble polymers at high conversions and led to the conclusion that efficient cyclopolymerization was occurring. The high susceptibility of the allyl ether derivative toward cyclopolymerization in comparison to the allyl ester derivative

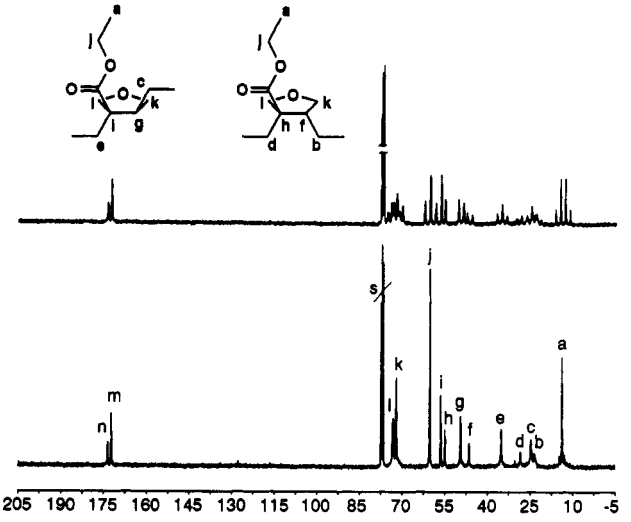
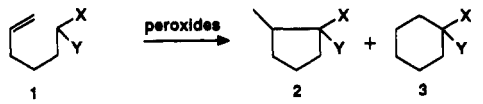


Figure 3. ^{13}C NMR spectra of poly[ethyl α-[(allyloxy)methyl]-acrylate]. The top spectrum was obtained with the decoupler off and the bottom spectrum with full WALTZ16 decoupling. Chemical shifts are listed in Table II.

Table I
Cyclization of 1-Substituted 5-Hexenyl Radicals (Table Reproduced from Reference 10)



1 2 3

X	Y	ratio, % 2	3
H	H	100	0
H	CN	100	0
H	$COCH_3$	72	28
H	$COOC_2H_5$	56	44
$COOC_2H_5$	$COOC_2H_5$	70	30
$COCH_3$	$COOC_2H_5$	50	50
CN	$COOC_2H_5$	16	84

and other unsymmetrical dienes is surprising.[2] The high conversion to polymer for the solution-polymerized allyl ether (typically ca. 90%) *without* gelation, along with the fact that ^{13}C solution NMR of the polymer showed no sign of residual unsaturation (Figure 3), confirms essentially complete intramolecular cycloaddition during propagation.

Much work has been done showing that intramolecular addition is very favorable for small molecules in comparison to intermolecular addition even in the presence of molecules containing radical stabilizing electron-withdrawing groups which might be expected to promote intermolecular reaction.[10-12] The bulk of the literature work has involved abstraction of a hydrogen or halide atom to form a radical which then reacts intramolecularly with a terminal vinyl group. Typical results are given in Table I. 5-Exo-trigonal cyclization was favored over 6-endo-trigonal cyclization when the carbon containing the radical is unsubstituted (100% five-membered ring formation). Substituted vinyl groups gave progressively more six-membered ring formation as the electron-withdrawing nature of the substituent increased. Up to 84% of the larger ring was observed for the molecule containing both a nitrile and an ethyl ester group attached at the intermediate radical carbon.[10]

Cyclopolymerization of difunctional monomers shows similar behavior. For example, diallyldimethylammonium chloride has been shown to give predominantly five-membered rings in the polymer backbone,[1] while polymerization of bis[2-(alkoxycarbonyl)-2-propenyl] ether—a symmetrical diacrylate substituted at both α positions—has

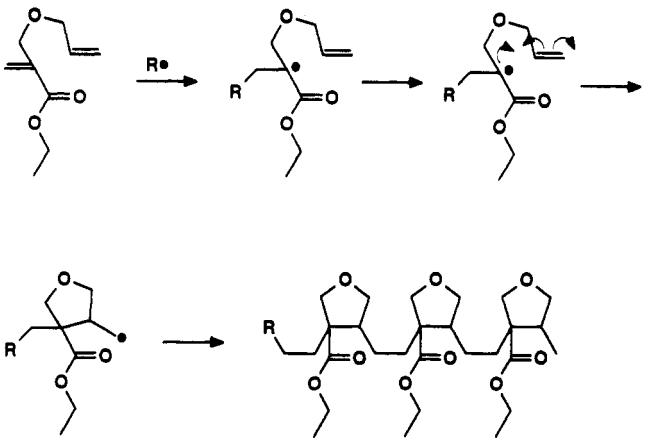


Figure 4. Initiation and propagation of ethyl α-[(allyloxy)-methyl]acrylate showing ring-forming intramolecular addition step for five-membered ring formation.

Table II
Proton-Decoupled ^{13}C NMR Chemical Shifts Referenced to $CDCl_3$ Listed by Isomer; Proton Coupling Data Included[a]

cis peak	cis chemical shift (ppm)	cis coupling	trans peak	trans chemical shift (ppm)	trans coupling
a	14.3	quartet	a	14.3	quartet
b	23.9	triplet	c	25.3	triplet
d	28.8	triplet	e	35.6	triplet
f	45.7	doublet	g	47.1	doublet
h	55.4	singlet	i	56.8	singlet
j	60.9	triplet	j	60.7	triplet
k	72.5	triplet	k	72.5	triplet
l	73.5	triplet	l	73.5	triplet
n	174.1	singlet	m	172.7	singlet

[a] Peak labels are in reference to Figures 3 and 5.

been shown to give only six-membered rings.[13] Polymerization of the allyl ether might be expected to give either five- or six-membered rings, based on the work cited above, depending on which carbon of the allyl group was attacked first during intramolecular addition (assuming that the more reactive acrylate vinyl group undergoes initial addition). Six-membered ring formation is expected to be the thermodynamic pathway since it involves the relatively stable secondary radical intermediate. On the other hand, five-membered ring formation would give an intermediate primary radical. A schematic of the latter process is shown in Figure 4.

Ring size cannot be determined directly by examination of the ^{13}C solution spectrum in the absence of suitable model compounds. However, one conclusion can be drawn on the basis of the sets of two peaks evident for all carbons except the pendent ethyl carbons at 60 and 13 ppm. This splitting is almost certainly due to cis/trans isomer formation during cyclization as polymerization occurs. Differential isomer formation has been identified in other cyclopolymerizations.[14] The ratio of peak intensities can be explained by a predominance of one isomer over the other through kinetically or conformationally determined preference during the transition from open to cyclic structure. Examination of the ^{13}C solution spectrum shows that there are only four distinct backbone carbons, each with two peaks corresponding to the cis and trans isomers (Figure 3 and Table II). A mixture of ring sizes would be expected to give more than just two peaks for each carbon, especially for the backbone tertiary (45.7 and 47.1 ppm), quaternary (55.4 and 56.8 ppm), and methylene carbons contained in the ring (28.8 and 35.6 ppm). These groups show large chemical shift effects which should be sensitive to *both* ring configuration and ring size and which would

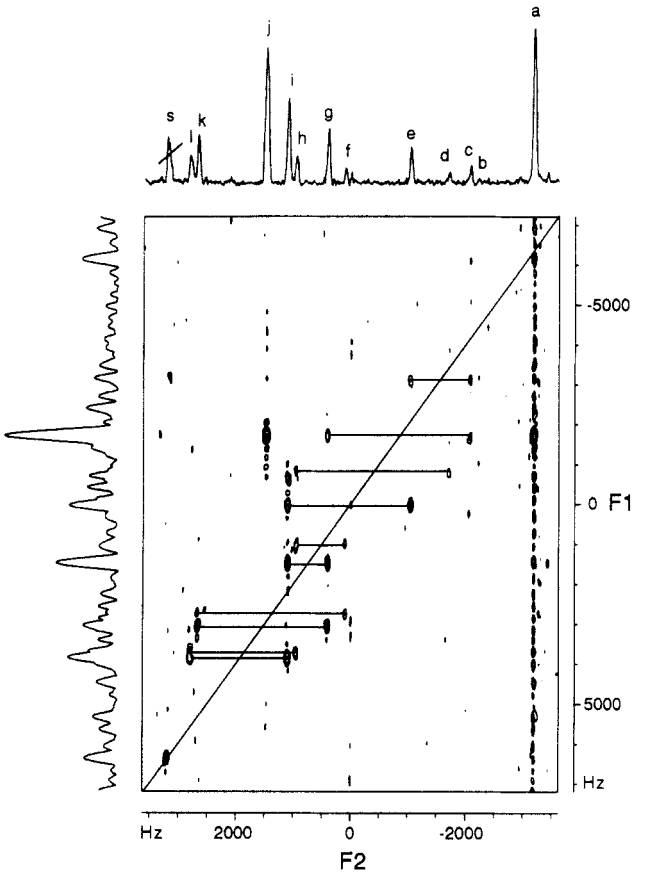


Figure 5. INADEQUATE 2D plot for poly[ethyl α-[(allyloxy)-methyl]acrylate]. The normal ^{13}C resonance spectrum from ca. 10 to 80 ppm is shown at the top, and intensities are given in the F1 domain at left. All correlated peaks should lie equidistant from the diagonal and have F1 offset frequencies equal to the sum of F2 offset frequencies. Chemical shifts are listed in Table II.

give a much more complicated spectrum if a mixture of ring sizes was present.

The INADEQUATE experiment allows determination of ring size directly through detection of double quantum coherence involving adjacent ^{13}C nuclei. The theory behind the INADEQUATE experiment is beyond the scope of this paper.[4-6] In short, however, it involves a series of free-induction decays collected using a variable evolution time during which the double-quantum coherence develops and is indirectly observed via conversion into single quantum coherence and plotting in normal 2-D fashion.

The data are plotted as the offset from the carrier frequency in the F1 domain versus offset in the F2 domain (Figure 5). Peaks for adjacent nuclei appear at their normal offset (or chemical shift) in the F2 domain and at the algebraic sum of the correlated F2 peak frequencies in F1. This allows calculation of where the cross-peaks should be seen in the F2 domain and therefore serves as a check of the authenticity of the connectivity data. The midpoint of the cross-peaks should also lie on a diagonal line with slope equal to 2, as drawn in Figure 5. Complete carbon–carbon connectivity for the entire molecule can therefore be determined unambiguously if sufficient peak resolution and sensitivity are available.

The 2-D plot shown allows straightforward determination of all carbon–carbon connectivities except those of the cis form of the methylene carbons linking the rings. However, these peaks do appear strongly at the calculated F1 frequencies at a higher noise level (plot not shown). Figure 5 is the best compromise of signal to noise.

Carbon–carbon connectivity information, along with carbon–proton connectivity data from coupled ^{13}C solution spectra, allows conclusive determination of ring size and polymer structure. Examination of the two possible cyclopolymer structures shows that the tertiary and quaternary carbons are directly connected only in the five-membered ring structure. Tentative assignment of cis versus trans isomer carbon peaks can be made with knowledge of γ-gauche shielding effects. In the cis form, the methylene carbon connected to the quaternary carbon is gauche to the methylene carbon connected to the tertiary carbon and thus more shielded (upfield) relative to the trans form. The methylene carbon next to the tertiary carbon, in contrast, is always gauche to either the ester group or the methylene connected to the ring quaternary carbon and is therefore always shielded to about the same degree. There is a distinct difference in chemical shift for these two isomers with a 6.8 ppm γ-gauche effect for the methylenes connected to the quaternary carbons, a value which is at the high end of the γ-gauche range.[15]

Both the facile cyclopolymerizability of the allyl ether monomer (in contrast to the allyl ester monomer) and its exclusive preference for five-membered ring formation are difficult to rationalize in comparison to other cyclization studies.[10] This monomer resembles the fourth entry in Table I where the initially formed radical is stabilized by an ethyl ester group and then adds to the unhindered, unstabilized alkyl vinyl group leading to a mixture of five- and six-membered rings. The preferred conformations of the ether linkage may play an important role in this system. A helical conformation is preferred for ether-linked molecules such as crown ethers and poly(oxyethylene). A similar conformation in this monomer brings the allyl double bond into position for radical addition from the stabilized acrylate radical.

Many attempts have been made to identify group preassociation and/or conformational preferences favoring cyclopolymerizations, but no conclusive evidence has been found supporting these possibilities.[1] Theoretically, the probability of intramolecular addition due to the proximity of the second vinyl group of the monomer is not high enough to explain the high degree of cyclization seen for many of these monomers.[2] We have done preliminary molecular mechanics modeling studies using PCModel[16] which show an energy difference of approximately 20% lower, favoring six- over five-membered rings *after* formation, which implies that the ring-formation step is kinetically, not thermodynamically, controlled. This suggests that the cyclization step for this system is essentially irreversible or that it occurs very rapidly in comparison to intermolecular addition. There is little energy difference (from the modeling data) between the cis and trans forms of the five-membered ring structure, although the experimental data show that the trans isomer is slightly preferred over the cis isomer. More rigorous modeling efforts may further illuminate these findings. It is interesting to note that the proposed structure of this cyclopolymer is similar to that of the hydrolyzed divinyl ether–maleic anhydride cyclocopolymer mentioned earlier[3] and may have similar biological activity.

Conclusion

A new monomer has been synthesized and polymerized to give a novel cyclopolymer with reasonable molecular weight and little or no residual unsaturation. This allyl ether substituted acrylate undergoes almost exclusive intramolecular cyclization before intermolecular addition while the similar allyl ester does not. ^{13}C solution NMR

spectral characterization gives well-defined chemical shift differences for what appear to be cis and trans isomers, which can be explained by γ-gauche shielding for carbons in or next to the polymer backbone. Two-dimensional INADEQUATE analysis conclusively confirms monomer cyclization exclusively to five-membered rings with a ratio of trans to cis ring configurations in the polymer backbone of approximately 2.2.

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Registry No. $H_2C{=}CHCH_2OH$, 107-18-6; $H_2C{=}C(CO_2Et)CH_2OCH_2CH{=}CH_2$, 143970-04-1; $H_2C{=}C(CO_2Et)CH_2Cl$, 17435-77-7; $H_2C{=}C(CH_2OH)CO_2Et$, 143970-05-2; $H_2C{=}CHCOCl$, 814-68-6; $H_2C{=}CHCO_2CH_2CH{=}CH_2$, 999-55-3; H_2CO (homopolymer), 30525-89-4; $H_2C{=}C(CH_2OH)CO_2CH_2CH{=}CH_2$ (homopolymer), 143970-11-0; $H_2C{=}C(CO_2Et)CH_2OCH_2CH{=}CH_2$ (homopolymer), 143970-10-9.