Studies of Allyl Alcohol Radical Polymerization by PFG-HMQC and HMBC NMR at 750 MHz

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ABSTRACT: The structures of poly(allyl alcohol) were characterized by one- and two-dimensional gradient-enhanced heteronuclear multiple quantum coherence (gHMQC) and gradient-enhanced heteronuclear multiple-bond connectivity (gHMBC) NMR spectroscopy. Main-chain structures and chain-end structures were identified from the spectra. The polymerization of allyl alcohol can be described by degradative chain transfer to allyl alcohol monomers, which results in distinctive chain ends as well as low molecular weight polymers. After the allylic hydrogen abstraction by initiator radicals, allyl radicals produce chain ends with vinyl groups and aldehyde groups. The chain-end structures were identified by the correlation peaks in gHMQC and gHMBC spectra.

Introduction

The polymerization of allyl alcohol is important because the copolymerization with other monomers is a commercial route to hydroxyl-functionalized polymers,[1] having applications in coatings, elastomers, and other thermoset polymers. The radical polymerization of allyl alcohol is distinctively different from the polymerization of vinyl monomers due to the possibility of allylic hydrogen abstraction from allyl monomers by other radicals. The radicals formed by abstraction reactions are resonance-stabilized and frequently result in termination by reaction with other propagating radicals. Therefore, the polymerization of allyl monomers produces low molecular weight products and unique chain-end structures.

A detailed knowledge of the chain-end structures of such allylic polymers would be useful for optimization of reaction conditions to produce materials with the desired properties. Two useful NMR techniques for analyzing the chemical structures of the polymers are ^{1}H-detected heteronuclear multiple quantum coherence (HMQC)[2,3] and heteronuclear multiple-bond connectivity (HMBC).[4] These techniques have been used for resonance assignments of biological and small organic molecules, because they dramatically enhance the sensitivity of NMR for detection of the spectra of nuclei other than protons. In the case of ^{13}C, the sensitivity is theoretically enhanced 32-fold relative to standard direct ^{13}C detection. This sensitivity enhancement is achieved by using J couplings to promote coherence transfer from the ^{13}C nucleus to ^{1}H followed by detection of the much more sensitive ^{1}H nucleus rather than the ^{13}C nucleus. Recently, these techniques of inverse detection have also been applied to structure determination of polymers.[5−8] In polymer NMR spectroscopy, large resonances from the backbone exist in the presence of the weaker signals from relatively small amounts of minor structure components such as defects and chain-end structures. A primary interest in polymer characterization lies in identifying these minor structural components and defects. Despite the experimental difficulties, usable spectra can be obtained with the aid of pulsed field gradient coherence selection.

^{1}H-detected gHMQC (gradient-enhanced HMQC) and gHMBC (gradient-enhanced HMBC) techniques were employed to characterize the structures of poly(allyl alcohol). The work has focused on identifying the structures formed by degradative chain transfer to allyl alcohols, as well as the chemical structures of main chain repeat units.

Experimental Section

Sample Preparation. The poly(allyl alcohol) (PAA) was prepared by radical polymerization of allyl alcohol with *tert*-butyl hydroperoxide initiator at a temperature of 165 °C. Additional initiator was added to the polymerization over the course of the 6-h reaction. The polymer contains a low concentration of polystyrene (determined to be ca. 1.4 mol % by NMR methods) as an impurity from a previous reaction. After polymerization, the sample was placed in a vacuum and heated above the boiling point of allyl alcohol. Despite vacuum annealing, it was assumed that small molecules (low molecular weight oligomers) with low vapor pressures still remain in the polymer sample.

NMR Data Collection. NMR spectra were collected on a Varian UnityPlus-750 spectrometer (^{1}H frequency 750 MHz). One-dimensional (1D) and two-dimensional (2D) NMR spectra were obtained at 50 °C using DMSO-d_6 as the solvent. The 2D gHMQC and gHMBC spectra and 1D ^{1}H spectra were obtained using a Nalorac ^{1}H/^{13}C/X/^{2}H 5 mm probe equipped with gradient coils and variable temperature capabilities (-50 to $+130$ °C). The 1D^{13}C and DEPT spectra were obtained using a Varian ^{1}H/^{13}C 5 mm broad band probe.

The DEPT spectra were collected at 188 MHz with a 1.2-s acquisition time, a 30-kHz spectral window, a 2-s relaxation time, a 21-μs 90° ^{1}H pulse, a 12.3-μs 90° ^{13}C pulse, and 1280 transients. The data were processed using 5-Hz line broadening and zero filled to four times the original data table size before Fourier transformation.

The gradient HMQC spectrum was collected at 750 MHz with a 0.064-s acquisition time (with ^{13}C GARP decoupling), 1024 points, an 8-kHz spectral window in f_2, a 16-kHz spectral window in f_1, a 1-s relaxation delay, a 12-μs 90° ^{1}H pulse, and a 32-μs 90° ^{13}C pulse; 16 transients were averaged for each of the 640 complex fid's. The data were processed using a shifted

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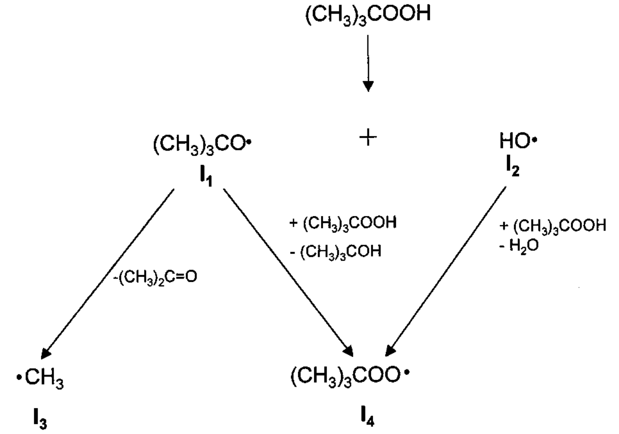
Scheme 1. Possible Initiator Fragments, I_N, Produced by Thermal Decomposition of *tert*-Butyl Hydroperoxide



sine bell weighting and zero filled (two to four times the original data table size) before Fourier transformation.

The gradient HMBC spectrum was collected at 750 MHz with a 0.17-s acquisition time, 3072 points, a 9-kHz spectral window in f_2, a 30-kHz spectral window in f_1, a 0.5-s relaxation delay, a 0.055-s fixed delay (to permit development of coherence from heteronuclear multiple-bond coupling), a 12-μs 90° ^1H pulse, and a 32-μs 90° ^{13}C pulse; 64 transients were averaged for each of the 1024 complex fid's. The data were processed using shifted sine bell weighting and zero filling (two to four times the original data table size). Three separate spectra with different decoupler offsets (corresponding to δ_{13C} = 50, 120, and 180 ppm in the f_1 dimension) were collected to achieve uniform excitation of ^{13}C nuclei for all the regions of interest.

Results and Discussion

Polymerization Mechanism of Allyl Alcohol Monomers. When the radical initiator, *tert*-butyl hydroperoxide, is thermally decomposed, *tert*-butoxy radicals and hydroxy radicals can be formed. *tert*-Butoxy radicals can abstract hydrogen from other *tert*-butyl hydroperoxide molecules to form *tert*-butyl peroxy radicals,[9] or they can further decompose into methyl radicals and acetone. Therefore, *tert*-butoxy, *tert*-butyl peroxy, methyl, and hydroxy radicals are all possible reactants for the chain initiation reaction (Scheme 1).

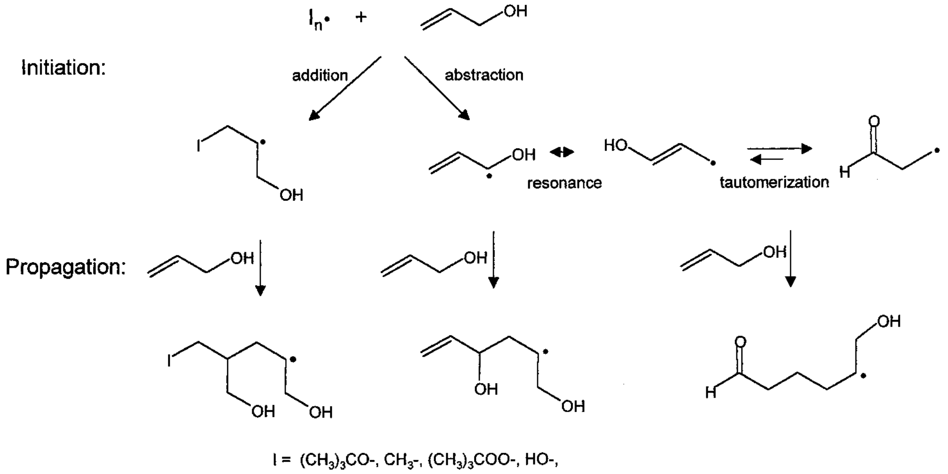
The radicals formed by peroxide decomposition can undergo one of two competitive reactions, addition or hydrogen abstraction (Scheme 2). The alkyl radicals formed in the addition reaction are very reactive to another addition or abstraction because they are not stabilized by resonance. Allyl alcohol radicals formed by allylic hydrogen abstraction have enol resonance structures, which can tautomerize to produce aldehyde. The allylic radicals formed in the abstraction reaction are relatively unreactive to other allyl monomers because of resonance stabilization. Instead, allyl radicals will undergo coupling reactions with other radicals such as initiator, allyl, and propagating radicals. However, it is also possible for a small portion of those radicals to participate in addition reactions.[10,11] Some possible propagating microstructures in poly(allyl alcohol) are also shown in Scheme 2.

In the termination reaction shown in Scheme 3, propagating radicals can terminate in two different ways, abstraction or coupling reactions. The allylic hydrogens of allyl alcohol are easily abstracted to propagating radicals or initiator radicals. The propagating polymer radicals can also be terminated by coupling reactions with radicals. The proportion of coupling to abstraction termination will be dependent on the radical concentrations. The possible chain-end structures formed by coupling reactions contain initiator fragments (I) or allyl radical derived fragments (R). If the termination by coupling of two propagating polymer chains occurs, then a polymer molecule is formed containing a head-to-head structure and two chain ends with initiator fragments ($-I_n$). If coupling terminates chain ends with vinyl groups, then the chain ends can be further polymerized to produce branched structures.

1D NMR Analysis. The ^1H and ^{13}C 1D NMR spectra of poly(allyl alcohol) are shown in Figure 1. The aliphatic main chain CH_2 and CH peaks are found in $\delta_C = 20-40$ and $\delta_H = 1-2$ regions of the one-dimensional spectra. The $-CH_2OH$ resonances are seen in the $\delta_C = 60-70$ and $\delta_H = 3-4$ regions. The peaks near 4.2 ppm in the ^1H spectrum can be assigned to the $-OH$ resonances from allyl alcohol. Low intensity aromatic carbon and proton peaks from impurities in this sample can also be observed near $\delta_C = 128$ and $\delta_H = 7$. Small resonances found near $\delta_C = 140, 115$ and $\delta_H = 5.9, 5.2$ are attributed to olefinic carbons and protons of vinyl chain ends. The very small peaks found at $\delta_C = 203$ and $\delta_C = 9.6$ are attributed to aldehyde carbon and proton resonances.

For the identification of the CH, CH_2, and CH_3 peaks in the ^{13}C spectrum, the DEPT (distortionless enhance-

Scheme 2. Initiation and Propagation Reactions in the Polymerization of Allyl Alcohol



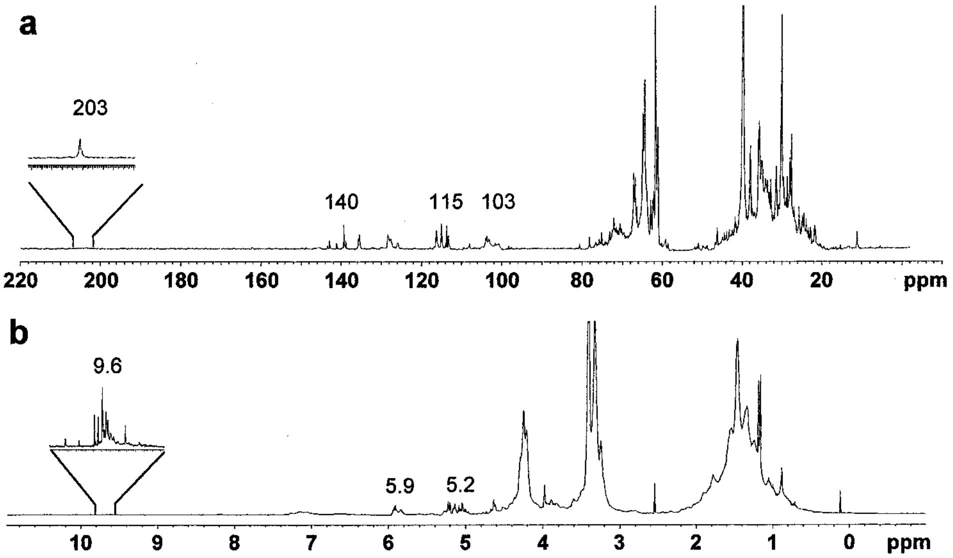
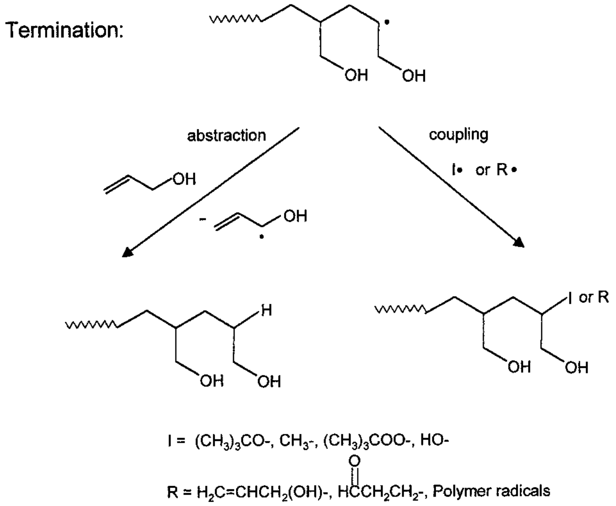


Figure 1. 188 MHz ^{13}C (a) and 750 MHz ^{1}H (b) 1D spectra of poly(allyl alcohol).

Scheme 3. Termination Reaction of Polymerization of Allyl Alcohol



ment by polarization transfer)[12] experiment was applied. The results are summarized in the expansions from the ^{13}C spectra shown in Figure 2. In Figure 2a, the CH and CH_2 peaks are from the polymer's main chain structures and CH_3 peaks are from chain ends formed by the radical initiator. The large number of CH and CH_2 peaks is due to the large variety of chemical structures present as well as stereosequence effects. In Figure 2b, the peaks at $\delta_C = 60-68$ are attributed to $-CH_2OH$ carbons and the peaks at $\delta_C = 74-81$ are attributed to $-CH(OH)-$ carbons. Figure 2c shows resonances from vinyl carbons of chain ends, including $=CH-$ resonances near $\delta_C = 140$ and $=CH_2$ resonances near $\delta_C = 115$. The methine carbon resonances found near $\delta_C = 103$ are consistent with the structures resulting from the coupling reaction between allyl alcohol radicals and initiator radicals (*tert*-butoxy, *tert*-butyl peroxy, or hydroxy). The resonances of methine carbons from these structures are found in a downfield region ($\delta_C = 95-105$) due to the attachment of two electronegative oxygen atoms; these resonances are also broadened due to restricted mobility.

2D NMR Analysis of Main-Chain Microstructures. In the aliphatic region of the gHMQC spectrum from the poly(allyl alcohol) shown in Figure 3, the

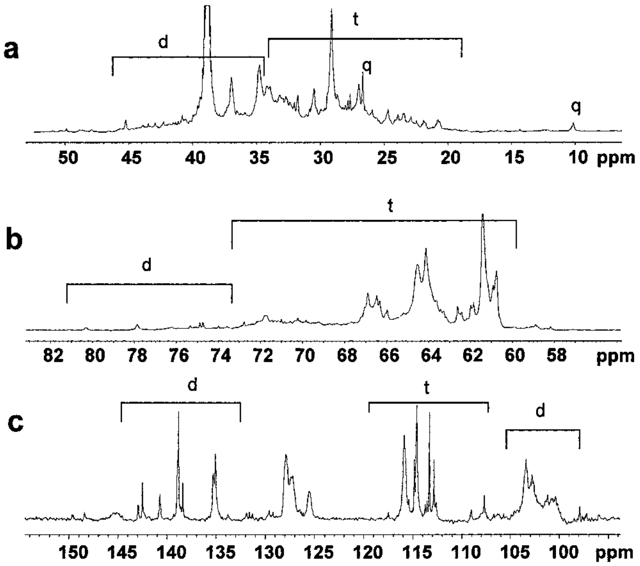


Figure 2. Expansions from the ^{13}C 1D spectrum of poly(allyl alcohol) showing CH (d), CH_2 (t), and CH_3 (q) peak assignments from DEPT analysis.

correlations of methine and methylene carbons and protons can be identified in the spectra based on the DEPT results. Many cross-peaks are observed in the spectrum due to the many possible chemical structures as well as stereosequence effects. Main chain structures of poly(allyl alcohol) can be identified by the correlations in gHMQC and gHMBC spectra. Methylene protons can have one-bond correlations (A), two-bond correlations (A_2), and three-bond correlations (A_1, A_3).

The sections of the gHMQC and gHMBC spectra showing cross-peaks to the hydroxymethyl ($-CH_2OH$) carbons and protons are shown in Figure 4. Four cross-peaks could be isolated in the expansion of the gHMQC spectrum (Figure 4a). Three of these peaks were assigned to C$-$H correlations of *rr*, *mr*, and *mm* triad structures. The assignments of cross-peaks from *rr* and *mm* triads were made by observing 2D patterns of adjoining backbone CH_2 groups in the gHMBC spectrum (Figure 4c). A single resonance (B_1) arises when there are two adjoining racemic triad structures, because the backbone methylene protons H_A and H_B have the same

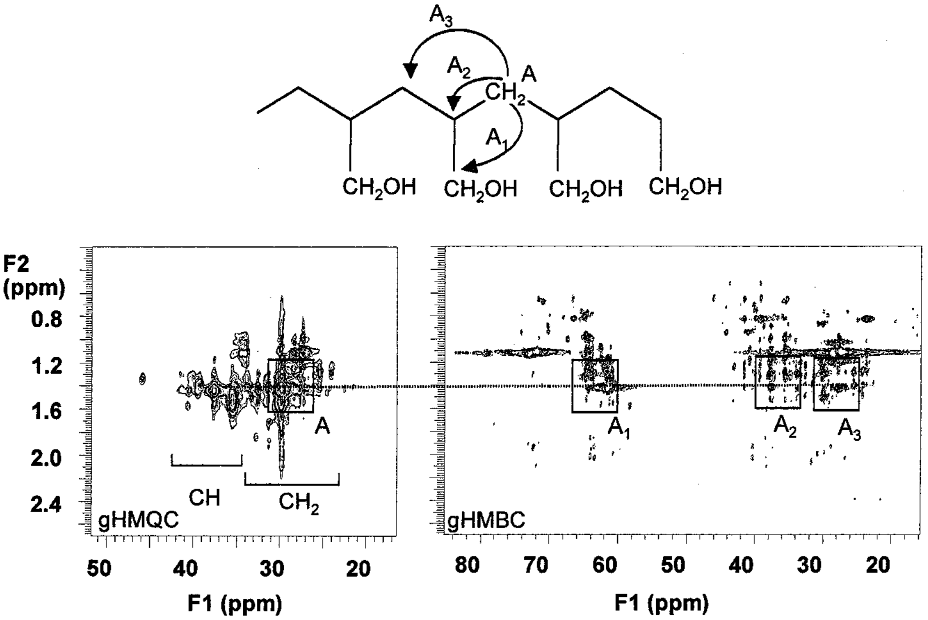


Figure 3. Main chain structures of poly(allyl alcohol) identified from gHMQC and gHMBC.

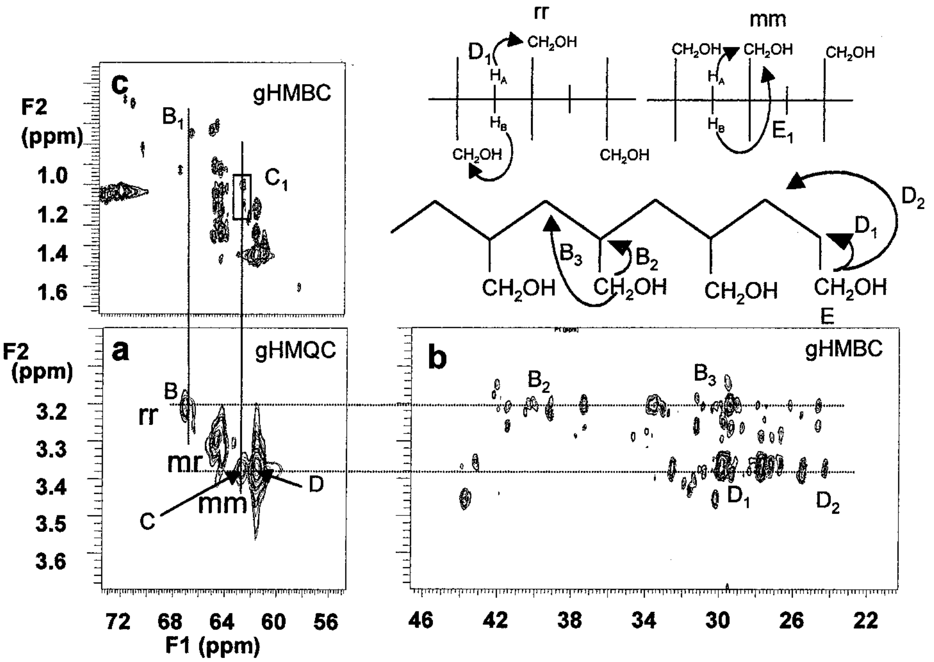


Figure 4. Assignment of hydroxymethyl group correlations in the gHMQC and gHMBC spectra of poly(allyl alcohol).

chemical environments. The two nonequivalent proton resonances (C_1) at the single carbon shift of C can be assigned to nonequivalent backbone methylene protons from adjoining methylene groups centered in meso structures, due to two different chemical environments of H_A and H_B in a meso diad.

2D NMR Analysis of Chain-End Microstructures. In Figure 4, the cross-peak at D (at $\delta_C = 61$ and $\delta_H = 3.4$) was assigned to the chain-end CH_2OH units (formed when a radical chain end abstracts a hydrogen, left half of Scheme 3), because two- or three-bond cross-peaks (D_1, D_2) at $\delta_H = 3.4$ are correlated with CH_2 carbon resonances. At $\delta_H = 3.2$, two- or three-bond correlations with methine (B_2) and methylene carbons (B_3) were found.

The resonances of *tert*-butoxy and methyl chain ends, derived from the *tert*-butyl hydroperoxide initiator fragments, were identified from portions of the 2D spectra shown in Figure 5. The one-bond methyl CH correlations (E) of the *tert*-butoxy group were found at $\delta_C = 27.0$ in gHMQC, and two- or three-bond correlations were found at $\delta_C = 71.5$ (E_1) and 27.0 (E_2) in gHMBC spectrum. An HMQC leakage of one-bond CH coupling can also be observed as a doublet along the F_2 dimension at $F_1 = 27.0$ ppm in the gHMBC spectrum. These correlations are attributed to structures produced by initiation through reaction with *tert*-butoxy radicals. The small intensity resonances found ca. 1 ppm downfield in the F_1 dimension of the spectra ($\delta_C = 28.0$ in gHMQC and $\delta_C = 28.0$, 72.5 in gHMBC) are attributed to termination by coupling reactions between *tert*-butoxy radicals and radicals at the ends of polymer chains. At least three types of *tert*-butoxy cross-peak patterns are seen in the spectra. Methyl radicals formed by the

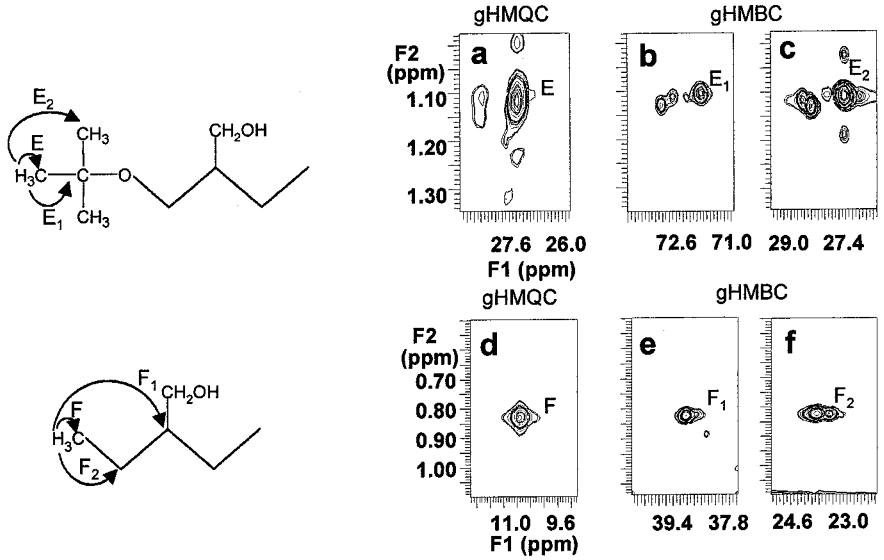


Figure 5. Initiator fragments identified from gHMQC and gHMBC spectra.

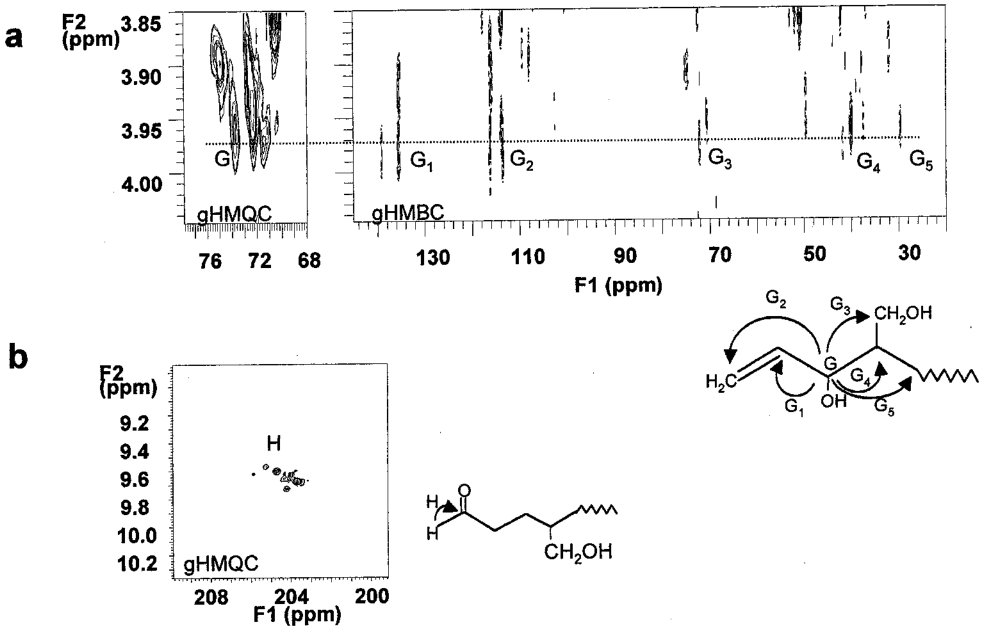


Figure 6. Vinyl (a) and aldehyde (b) chain-end cross-peak assignments by gHMQC and gHMBC.

decomposition of *tert*-butoxy radicals can also initiate polymerization of allyl alcohol. The one-bond methyl correlation was found at $\delta_C = 10.6$ (F) in gHMQC (Figure 5d) and two- or three-bond correlations were identified at $\delta_C = 38.8$ (F_1, Figure 5e) and 23.3 (F_2, Figure 5f) in the gHMBC spectrum.

Allyl radicals may couple with polymer radicals to terminate the polymerization. Some of structures containing vinyl and aldehyde chain ends produced by this coupling are shown in Figure 6. In Figure 6a, the resonances of methine protons (at $\delta_H = 3.97$) from vinyl alcohol chain ends shows a one-bond correlation (G), two- or three-bond correlations with the resonances of vinyl carbons (G_1, G_2), hydroxymethyl carbons (G_3), methine carbons (G_4), and methylene carbons (G_5). Several sets of this type of cross-peak pattern are observed in Figure 6a, possibly due to stereosequence effects. In Figure 6b, one-bond correlations (H) of aldehyde groups were found in a gHMQC spectrum. However, due to very weak resonances from these structures that are present at very low concentrations, two- or three-bond correlations were not found in the gHMBC spectrum. In general, HMBC experiments have less sensitivity than HMQC experiments due to the smaller long-range couplings used to transfer coherence between protons and carbons in the experiments.

2D NMR Analysis of Hydroxy Alkoxy Groups. When the initiator radicals couple with allyl radicals, hemiacetals can be formed. The hemiacetals from coupling of allyl radical and $RO^\bullet$ are active monomers, and can be incorporated into polymer structures. The cross-peaks from these structures can be found in one-bond correlations in a gHMQC spectrum (Figure 7, I). The incorporation of these structures into the polymer can be verified by the observed multiple-bond correlations (I_1) between the methine carbons and main-chain aliphatic protons ($\delta_H = 1.5-2$). Many peaks in this region are due to the many possible stereo and monomer sequences, as well as the possibility that these structures also exist near chain ends.

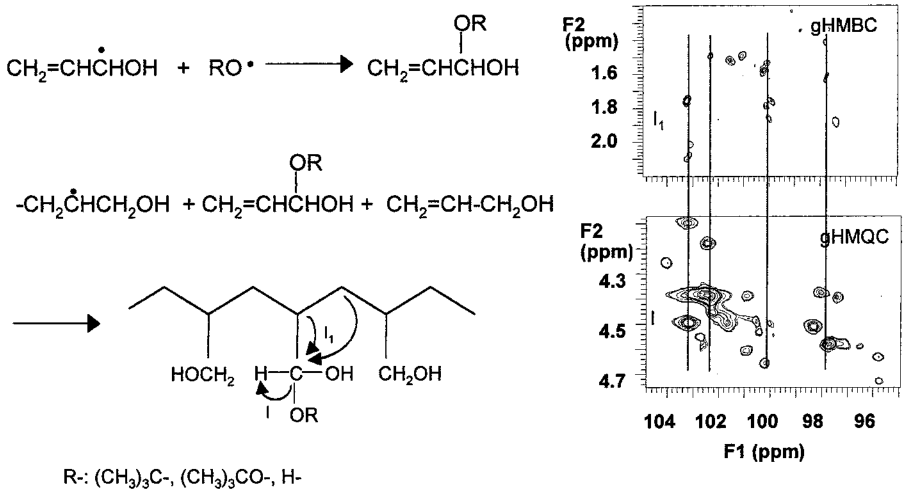


Figure 7. Assignments of −CH(OH)OR correlations by gHMQC and gHMBC.

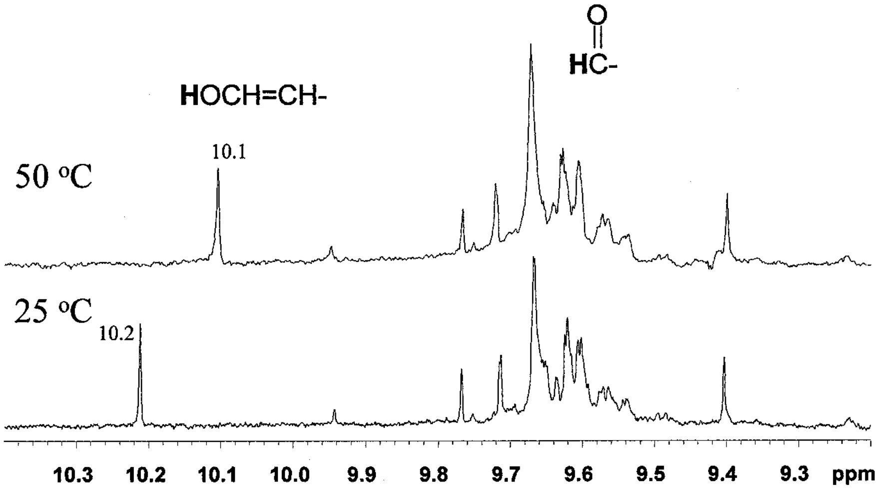


Figure 8. Assignment of enol −OH peak by variable temperature experiment. The peak at 10.2 ppm shifts to upfield by increasing temperature.

Assignments of Tautomerized Structures. Aldehyde chain ends might tautomerize with vinyl alcohol (enol) chain ends. A signal is detected near 10 ppm in the ^{1}H NMR (Figure 8) consistent with the presence of vinyl alcohol −OH groups. The chemical shift of this resonance is temperature dependent, consistent with an enol, and uncharacteristic of an aldehyde. An increase in temperature results in an upfield shift due to the change of the exchange rate, probably with other −OH groups or residual H_2O (chemical exchange correlations were also found among enol, −OH, and H_2O protons in a NOESY spectrum.). The peak shown at $\delta_H = 10.2$ at 25 °C shifts to $\delta_H = 10.1$ upon increasing the temperature to 50 °C.

Conclusions

The polymerization of poly(allyl alcohol) is controlled by a degradative chain transfer to allyl alcohol monomers during propagation steps. The driving force of chain transfer is the formation of stable delocalized radicals. The chain transfer leads to distinctive chain-end structures and low molecular weights. The chain ends can also be formed by coupling termination with allyl alcohol radicals, resulting in terminal vinyl and aldehyde structures.

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