Synthesis and Wide-Line NMR Studies of α-Deuterated Polyacrylates and Polyacrylonitrile

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ABSTRACT: By use of a simple, direct hydrogen-exchange reaction, deuterated vinyl compounds have been synthesized. Acrylate esters, acrylonitrile, and methyl vinyl ketone were found to undergo rapid exchange at room temperature to give easily isolated, pure, and readily polymerizable α-deuterated derivatives. Selected monomers were polymerized and the obtained polymers examined by solid-state deuterium nuclear magnetic resonance spectroscopy. The NMR data show that the acrylate polymers are rigid below T_g and move quickly and randomly at temperatures ca. 20–40 °C above T_g. The same type of motion is seen for cross-linked acrylates labeled either on the main chain or at the cross-link, but at different temperatures. That is, ^{2}H-labeled cross-link sites become mobile at ca. 10 °C lower than ^{2}H-labeled segments between cross-links. In contrast, polyacrylonitrile displays unusual deuterium line shapes due to a well-defined motion above its glass transition. T_2 values determined at various temperatures show a minimum at ca. 30 °C above the T_g for all polyacrylates while their T_1 minima were at approximately the same values as the DSC T_g's. For polyacrylonitrile, the wide-line spectra did not show large-scale motional averaging even up to 435 K, 60–65 °C above the DSC T_g value, and T_2 and T_1 plots did not show behavior similar to the acrylates.

Deuterium labeling offers numerous opportunities for the spectroscopic study of monomers and polymers. Deuterium functions as a molecular and mechanistic probe observable by infrared, ^{13}C and ^{1}H NMR, neutron scattering, mass spectroscopy, and coupled pyrolysis–GC–MS. Synthesis of a single deuterated sample can thus provide a wealth of information on polymerization mechanisms, rates, stereochemistry, and reactivity ratios; polymer relaxation and motion in solution and in solids; and the mechanisms of degradation and depolymerization of obtained polymers and copolymers.

There is an additional advantage that results directly from the use of deuterated reactants in monomer and polymer synthesis. ^{2}H NMR can be used directly to follow conversion, monitor intermediate formation and disappearance, and examine side reactions and byproducts. The synthesis of deuterated acrylates examined here stems from the use of ^{2}H NMR solution (combined with ^{1}H and ^{13}C spectroscopy) to monitor the synthesis of a deuterated α-hydroxymethylacrylate monomer (from ^2H_2CO) needed for another project.[1] Unexpected incorporation of deuterium at the α-position of the starting acrylate ester was observed.[2] Extension of this process to other monomers leads to selectively deuterated acrylates and activated vinyl species capable of conversion to polymers with deuterium on every other carbon of the backbone. This mild deuteration method was also applied to diacrylates to produce selectively labeled cross-linking agents.

Solid-state ^{2}H NMR is a well-established technique for studying the dynamics of polymer systems.[3] Molecular relaxation times available using variable-temperature wide-line techniques span the range of characteristic frequencies from ca. 10 MHz to 1 Hz. Deuterium incorporation at specific sites in monomers (and therefore in their polymers) allows separate determination of backbone and side-chain behavior. Information obtained with this method is enormously valuable in relating molecular structure and motion to the physical properties of a polymer.

The polymers prepared and examined here by solid-state deuterium NMR include poly(methyl acrylate-d_α), poly(ethyl acrylate-d_α), poly(butyl acrylate-d_α), polyacrylonitrile-d_α, and the cross-linked polymers poly(ethyl acrylate-d_α-*cross*-hexanediol diacrylate), poly(ethyl acrylate-*cross*-hexanediol diacrylate-$d_{\alpha,\alpha}$), and poly(ethyl acrylate-*cross*-ethylene diacrylate-$d_{\alpha,\alpha}$). In all cases, the vinyl position next to the ester or nitrile group is the position of deuteration.

Experimental Section

All monomers and 1,4-diazabicyclo[2.2.2]octane (DABCO) were purchased from Aldrich Chemical Co. and used as obtained. D_2O (99%) and CH_3OD (99%) were obtained from Aldrich or Isotec, Inc. 2,2′-Azobis(isobutyronitrile) (AIBN) was purchased from Polysciences, Inc., and recrystallized from methanol before use.

Monomer purities were determined by GC on a Hewlett-Packard 5880 or 5890. Polymer glass transition temperatures were measured on a Du Pont 9900 thermal analysis system equipped with a Du Pont 910 DSC unit with a heating rate of 10 °C/min. IR spectra were obtained on a Perkin-Elmer 1600 FT-IR.

Monomer Deuteration and Polymerization. Acrylonitrile-d_α (General Example Using D_2O). Acrylonitrile (8.85 g, 0.161 mol), deuterium oxide (58.73 g, 2.932 mol), and DABCO (2.39 g, 0.0213 mol) were stirred in a 100-mL round-bottom flask for 2 h. The solution was transferred to a separatory funnel, and the deuterium oxide layer was removed. The remaining deuterated acrylonitrile was dried with sodium sulfate to give 7.69 g (0.142 mol, 88.4% yield). ^{1}H NMR indicated approximately 85% deuteration.

Methyl acrylate-d_α and *n*-butyl acrylate-d_α were similarly obtained with 90% and 80% deuterium incorporation, respectively.

***n*-Butyl Acrylate-d_α (General Example Using CH_3OD).** Butyl acrylate (7.30 g, 0.057 mol), methanol-*d* (32.33 g, 0.98 mol), and DABCO (2.24 g, 0.0200 mol) were stirred in a 100-mL round-bottom flask for 1 h. The methanol was then evaporated under reduced pressure, and the remaining solution was dissolved in ether. The ether solution was extracted three times with 5% HCl and the ether fraction dried over sodium sulfate for 12 h. The sodium sulfate was removed by filtration and the ether evaporated under reduced pressure to give *n*-butyl acrylate-d_α (6.42 g, 87% yield). ^{1}H NMR indicated 80% deuteration in the α-position.

Hexanediol diacrylate-d_α and ethylene glycol diacrylate-d_α were obtained in yields and percent deuterations of 87% at 85% and 42% at 60%, respectively.

Polymerization of Acrylonitrile-d_α. Acrylonitrile-d_α (2.30 g, 0.0425 mol), carbon tetrachloride (8.38 g) as solvent, and AIBN

(0.0230 g, 0.14 mmol) were added to a test tube, which was then capped with a rubber septum. The tube was purged with dry nitrogen for 5 min. The container was then placed for 4 h in a water bath heated at 65 °C. The tube was removed, and additional CCl_4 was added to assist in the removal of the insoluble polymer formed. The precipitate was collected on a Büchner funnel and washed with benzene. The pale yellow polymer was dried in a vacuum oven for 1 h at 30 mmHg to give a white product (1.23 g, 0.023 mol, 54% yield).

Polymerization of Methyl Acrylate-d_α. Methyl acrylate-d_α (3.1960 g, 0.037 mol) was polymerized in a similar manner in tetrahydrofuran (THF; 4.80 g, 0.067 mol) with AIBN (0.0635 g, 0.39 mmol) and worked up to give a viscous product (2.88 g, 0.033 mol, 89% yield).

Polymerization of Ethyl Acrylate-d_α. Ethyl acrylate-d_α was polymerized as a 30 wt % THF solution using 2 wt % AIBN as initiator. The reaction solution was degassed with the freeze–pump–thaw method three times. The solution was heated at 70 °C for 2.5 h. The solvent and unreacted monomer were then evaporated under reduced pressure, and the viscous polymer was dried in a vacuum oven.

Polymerization of Ethyl Acrylate Cross-Linked with Ethylene Diacrylate-d_α. Ethyl acrylate was placed in a test tube with ethylene glycol diacrylate-d_α at 13.7 mol % (60% deuterated). The monomer mixture was diluted to 20 wt % with THF, and 2 wt % AIBN was added. The tube was sealed with a septum and taken through the freeze–pump–thaw sequence three times. The tube was heated at 65 °C until it gelled. The insoluble product was frozen in liquid N_2, ground into small pieces, washed with THF and dried in a vacuum oven.

Polymerization of Ethyl Acrylate-d_α Cross-Linked with Hexanediol Diacrylate. Ethyl acrylate-d_α was polymerized as a 30 wt % THF solution using 2 wt % AIBN as an initiator with either 3.7 or 7.8 mol % hexanediol diacrylate as the cross-linking agent. The reaction solutions were taken through the freeze–pump–thaw method three times. The two solutions were heated at 65 °C until they gelled and were then washed with THF and dried in a vacuum oven.

Polymerization of *n*-Butyl Acrylate-d_α. *n*-Butyl acrylate-d_α (2.83 g, 0.022 mol), THF (3.33 g, 0.046 mol), and AIBN (0.052 g, 0.32 mmol) were mixed and reacted like acrylonitrile-d_α (above) to give the product as a viscous polymer (2.43 g, 0.019 mol, 86% yield).

NMR Measurements. Spectra and relaxation data were obtained on Bruker CXP-300 and MSL-200 NMR spectrometers with the ^2H resonance frequencies at 46.06 and 30.72 MHz, respectively. The solid-state ^2H spectra were acquired by using a quadrupole echo sequence for standard spectra, a saturation recovery–solid echo sequence for T_1 measurements, and a magnetization decay–solid echo sequence for T_2 measurements.[4] A 90° pulse length of 3.0 μs, a τ delay of 30 μs, and a 2-s recycle time were used with a 7.5-mm coil at 300 MHz. A 90° pulse length of 3.0 μs, a τ delay of 28 μs, and a recycle time of 3 s were used with an 8-mm coil at 200 MHz. A home-built probe was used with the CXP-300 while a Doty Scientific deuterium probe was used with the MSL-200. The solid echo was left-shifted to the top of the echo prior to Fourier transformation. During spectral acquisition, the temperature was maintained by using the Bruker temperature controllers supplied with the spectrometers. The relaxation measurements were performed by using the intensity change of the solid echo as has been demonstrated previously by Spiess and co-workers.[5,6] While reference to this type of T_2 often includes an indication of how it is obtained (T_{2SE}), we use the former throughout this paper for convenience and base it on Spiess' interpretation of its direct relationship to the actual value of T_2.[6] The intensity data were fitted using the SIMFIT program supplied by Bruker. Spin–spin relaxation data was fit satisfactorily to a single component, but the spin–lattice data gave a much better two-component fit. Apparently, the latter is able to discriminate between two different types of environments in the sample at the relaxation times being examined while the former is not. The data presented in this paper do not allow for a more detailed interpretation of this difference.

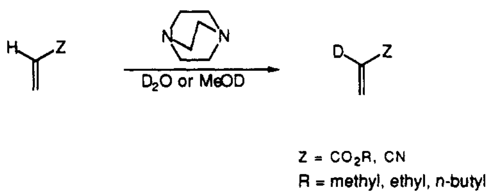

Figure 1. Deuterium-exchange reaction.

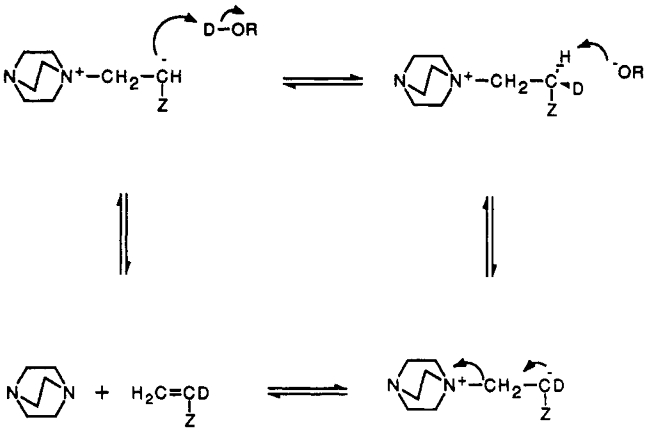

Figure 2. Equilibrium of the DABCO intermediate.

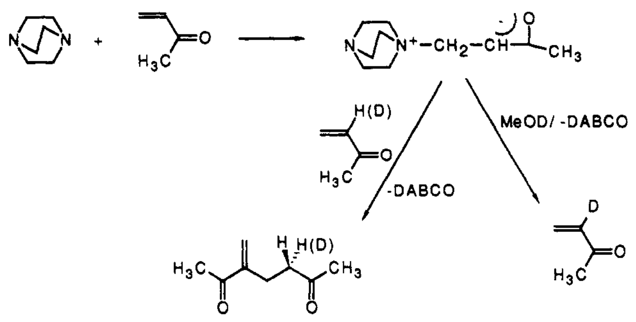

Figure 3. Michael reaction of methyl vinyl ketone to form deuterium-labeled 3-methylene-2,6-heptadione.

Results and Discussion

Monomer Deuteration and Polymerization. In the presence of a suitable exchangeable deuterium source and a catalytic amount of DABCO, rapid incorporation of deuterium at the α-position was observed for a number of activated vinyl species (Figure 1). A Michael-type addition–elimination mechanism is proposed for which deuterium incorporation is determined by equilibrium $^1H/^2H$ concentrations (Figure 2). Exchange can be driven to levels greater than 90% by use of a large excess of the deuterium donor.

While either CH_3OD or D_2O served in the exchange for acrylonitrile and acrylamides, partial hydrolysis of the intermediate species formed from acrylate esters occurred in D_2O. In addition, higher alkyl esters underwent transesterification to methyl acrylate if the exchange reaction was continued too long in CH_3OD. Reaction of methyl vinyl ketone was complete in a matter of minutes. Prolonged reaction of all these monomers led to formation of Michael addition and/or aldol condensation products. The solution ^2H NMR of methyl vinyl ketone clearly indicated that a Michael addition product was present along with the deuterium-exchanged species. Evidence exists for the reaction of methyl vinyl ketone with itself in the presence of DABCO.[7] A multiplet in the solution ^2H NMR at 2.3 ppm corresponds to the CHD β to the vinyl group and α to the carbonyl of the major impurity, 3-methylene-2,6-heptadione (Figure 3).

Table I
Coupling Constants for Vinyl Monomers

	^1H NMR[a]			^2H NMR		^{13}C NMR	% D	
compd	J_{AB}	J_{AX}	J_{BX}	J_{DA}	J_{DB}	J_{CD}	exptl	theor
methyl acrylate	1.5	17.3	10.2	2.6	1.6	25.9	93.7	91.6
butyl acrylate	1.7	17.3	10.3	2.6	1.6	25.0	81.6	93.7
acrylonitrile		17.6	11.7	2.7	1.8	27.2	91.2	90.1
acrylamide				2.7	0.8	24.5		
dimethylacrylamide[b]				2.6	1.6			
hexanediol diacrylate				2.7	1.8	25.9		
ethylene diacrylate				2.4	1.8	25.0		
methyl vinyl ketone				2.2				

[a] Determined from protonated monomer. [b] After a 12-h reaction time.

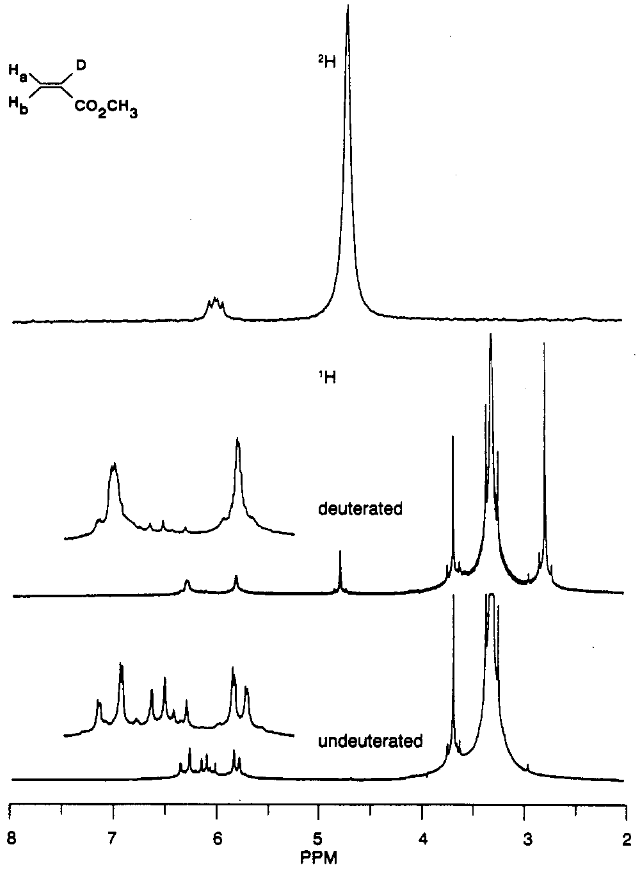

Figure 4. Representative solution ^1H and ^2H NMR spectra of methyl acrylate-d_α.

Table II
Glass Transition Temperature Comparison

	T_g, K			
polymer	ref[a]	DSC[b]	^2H NMR[c]	^2H NMR[d]
poly(methyl acrylate-d_α)	283	278	305	305
poly(ethyl acrylate-d_α)	249	247	265	
poly(butyl acrylate-d_α)	219	218	260	260
polyacrylonitrile-d_α	370	373	(400)[f]	(435)[f]
poly(ethyl acrylate-d_α-*cross*-hexanediol diacrylate), 7.8 mol %		*e*	290	290
poly(ethyl acrylate-*cross*-hexanediol diacrylate-$d_{\alpha,\alpha}$), 5.1 mol %		*e*	270	
poly(ethyl acrylate-*cross*-hexanediol diacrylate-$d_{\alpha,\alpha}$), 9.2 mol %		*e*	280	
poly(ethyl acrylate-*cross*-ethylene diacrylate-$d_{\alpha,\alpha}$), 13.7 mol %		272	290	295

[a] Values for nondeuterated polymers listed in the *Polymer Handbook*. [b] Determined by DSC at a 10 °C/min heating rate. [c] Determined from ^2H NMR line-shape changes. [d] Determined from ^2H T_2 curves. [e] Not able to be determined from the DSC trace. [f] Uncertain values due to weak or unusual transitions.

The general procedure for deuteration simply involved mixing together excess deuterium donor with the activated substrate, adding DABCO, and stirring for a short period of time. The substrate was then recovered, dried, and checked with ^1H NMR for the degree of deuteration. Coupling constants (Table I) were determined directly from the splittings of the ^1H and ^{13}C NMR spectra. Figure 4 gives representative spectra for methyl acrylate before and after exchange. The small peak at 4.75 ppm and larger peak at 2.75 ppm in the middle spectrum are due to methanol present during the exchange process ($CH_3O^2H \rightarrow CH_3OH$). Additional reactions were attempted by using styrene, acrylic acid, *N*-vinylpyrrolidinone, uridine, and coumarin, but no deuteration was observed. Glass transition temperatures of the polymers were determined with no noticeable difference from those of protonated materials (Table II).

Polymerization of various monomers synthesized was carried out by using standard procedures involving three freeze–evacuate–thaw cycles and thermal initiation with low concentrations of AIBN at ca. 60 °C. With the acrylate systems examined here, high molecular weights were obtained as indicated by physical properties (DSC T_g values) and NMR analysis (no end groups). Cross-linked systems were cleaned up by extraction and were completely insoluble, confirming cross-link densities in the range expected for the ratios of mono- to difunctional acrylates employed.

NMR Measurements. For methyl, ethyl, and butyl acrylate polymers, the main-chain behavior is similar as determined by solid-state ^2H NMR using the solid-echo pulse sequence (Figures 5–7, respectively). Below T_g the spectrum is a rigid Pake pattern while at temperatures 25–50 °C above T_g, only a single sharp peak is present. On a molecular level this implies that the C–D bonds are rigid (on the solid-echo time scale) below T_g or that motion is ultraslow. Near the T_g, the signal intensity decreased and a small motionally averaged peak is superimposed on the Pake pattern. At ca. 40 °C above T_g, the polymer segments undergo large-scale motion that is almost isotropic and fast on the ^2H NMR time scale ($\tau_c \leq 10^{-7}$ s). This overall behavior is similar to that observed for other backbone-labeled polymers.[8]

The quadrupole echo deuterium spectra for 7.8 mol % cross-linked poly(ethyl acrylate-d_α-*cross*-hexanediol diacrylate), 5.1 and 9.2 mol % cross-linked poly(ethyl acrylate-*cross*-hexanediol diacrylate-$d_{\alpha,\alpha}$), and 13.7 mol % cross-linked poly(ethyl acrylate-*cross*-ethylene diacrylate-$d_{\alpha,\alpha}$) are shown in Figures 8–11, respectively. For the cross-linked systems, a ca. 20 °C increase in T_g (onset of large-scale motion) was seen for the main-chain acrylate units. However, the cross-links themselves seem to be in a less constrained environment, showing T_g's that are just

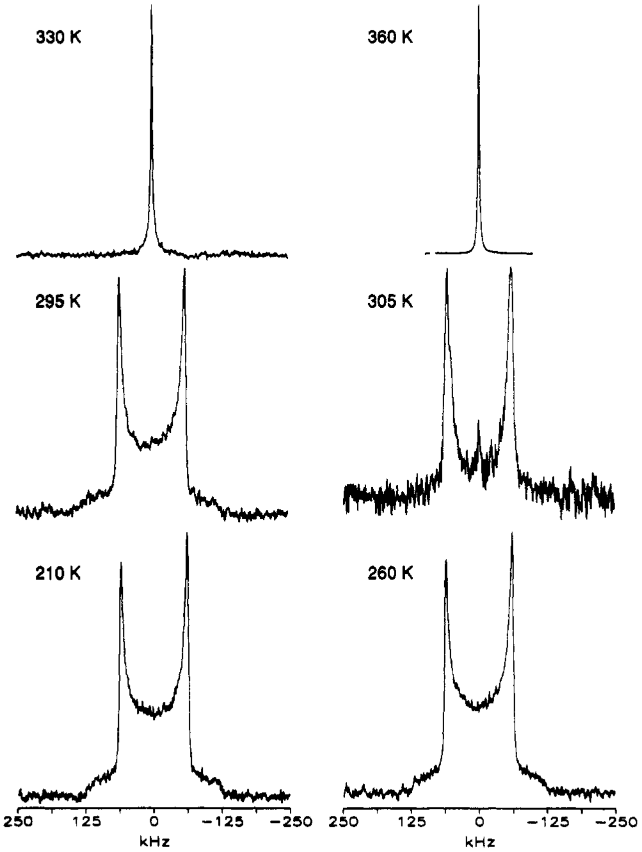

Figure 5. Solid-state ^2H NMR of poly(methyl acrylate-d_α).

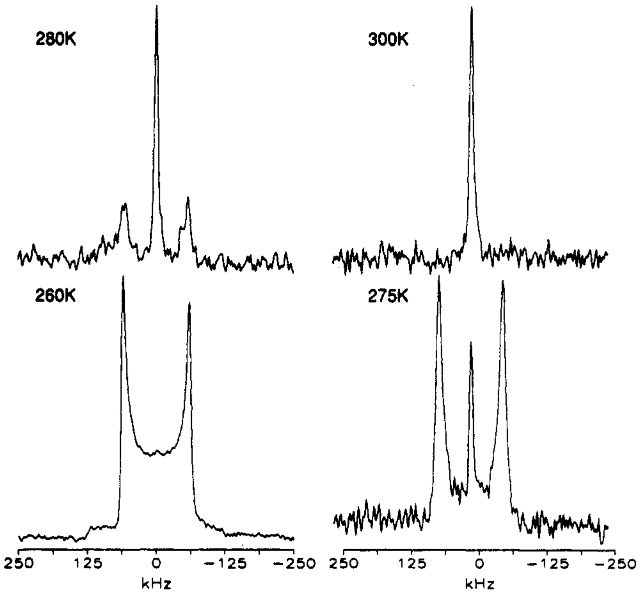

Figure 6. Solid-state ^2H NMR of poly(ethyl acrylate-d_α).

comparable to that of the un-cross-linked material at the lowest cross-link density. As the cross-link density increases, however, T_g increases (at least *at* the cross-link site), indicating increased rigidity and reduced segmental freedom. Complete insolubility of the polymers and the lack of pendent vinyl groups (solid-state ^{13}C NMR results) indicate that no unreacted acrylate groups of the cross-linking agents are present. While enhanced mobility of the cross-link site seems counterintuitive, consistency of the behavior among the three different samples and repetition of the synthesis and NMR measurements argue for the observation being correct. Further evaluation of these materials, and of the generality of the phenomenon in other systems, is certainly desirable.

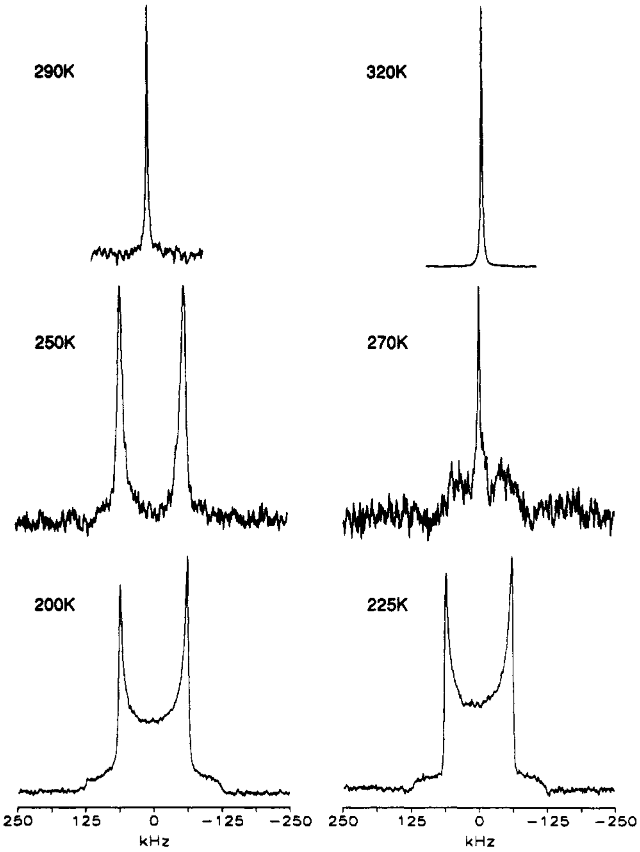

Figure 7. Solid-state ^2H NMR of poly(butyl acrylate-d_α).

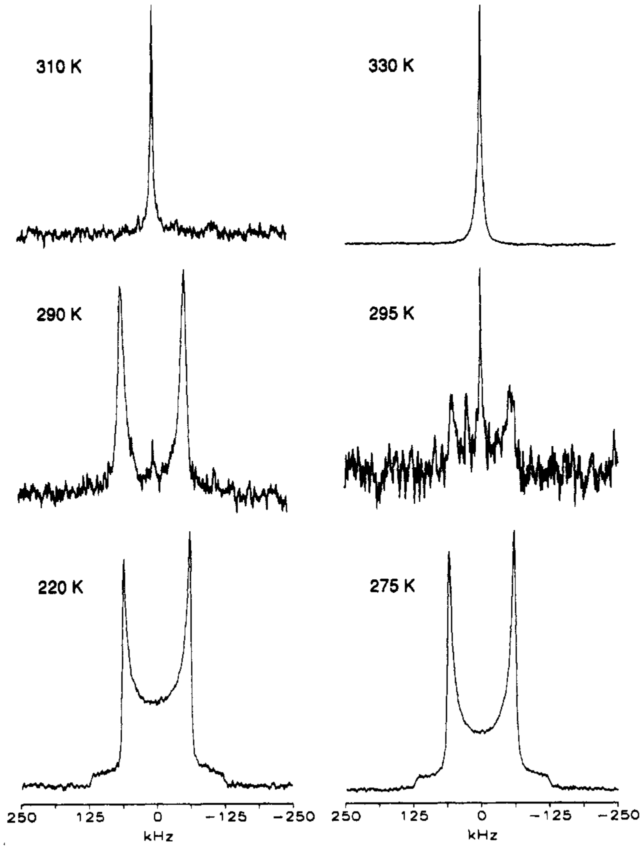

Figure 8. Solid-state ^2H NMR of poly(ethyl acrylate-d_α-*cross*-hexanediol diacrylate), 7.8 mol % cross-linking agent.

For the acrylate polymers, reaching the T_2 minimum (by temperature variation) produces lower intensity line shapes and lower signal-to-noise. This is clearly evident in the cross-linked polymers that have a lower deuterium

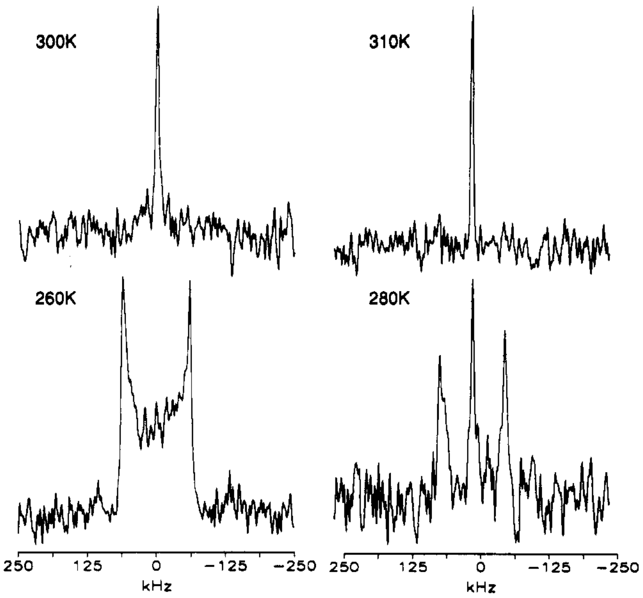

Figure 9. Solid-state ^{2}H NMR of poly(ethyl acrylate-*cross*-hexanediol diacrylate-$d_{\alpha,\alpha}$), 5.1 mol % cross-linking agent.

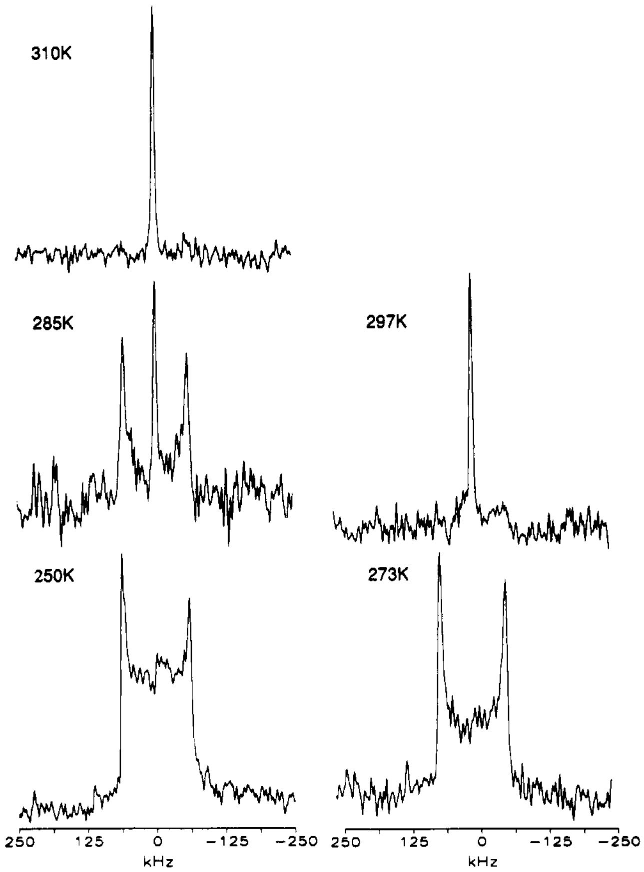

Figure 10. Solid-state ^{2}H NMR of poly(ethyl acrylate-*cross*-hexanediol diacrylate-$d_{\alpha,\alpha}$), 9.2 mol % cross-linking agent.

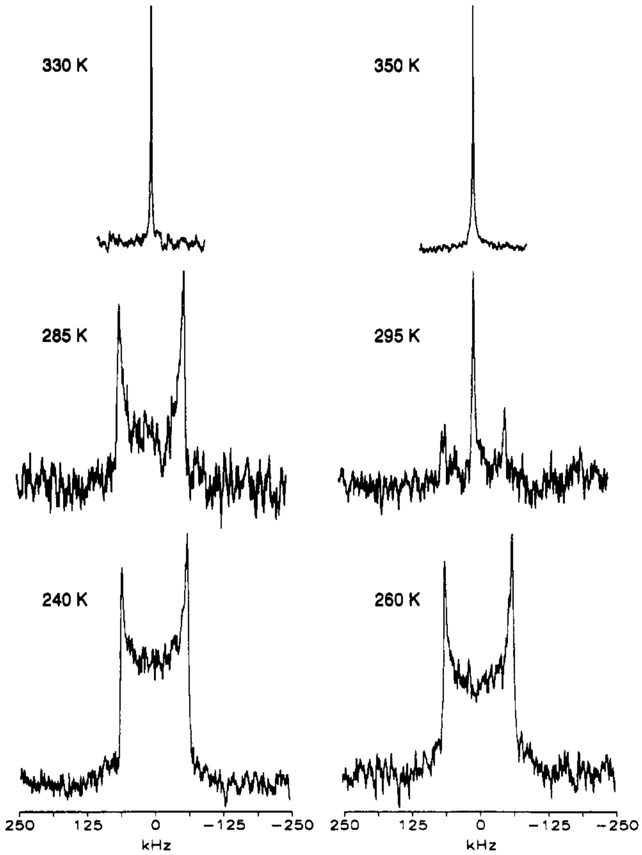

Figure 11. Solid-state ^{2}H NMR of poly(ethyl acrylate-*cross*-ethylene diacrylate-$d_{\alpha,\alpha'}$), 13.7 mol % cross-linking agent.

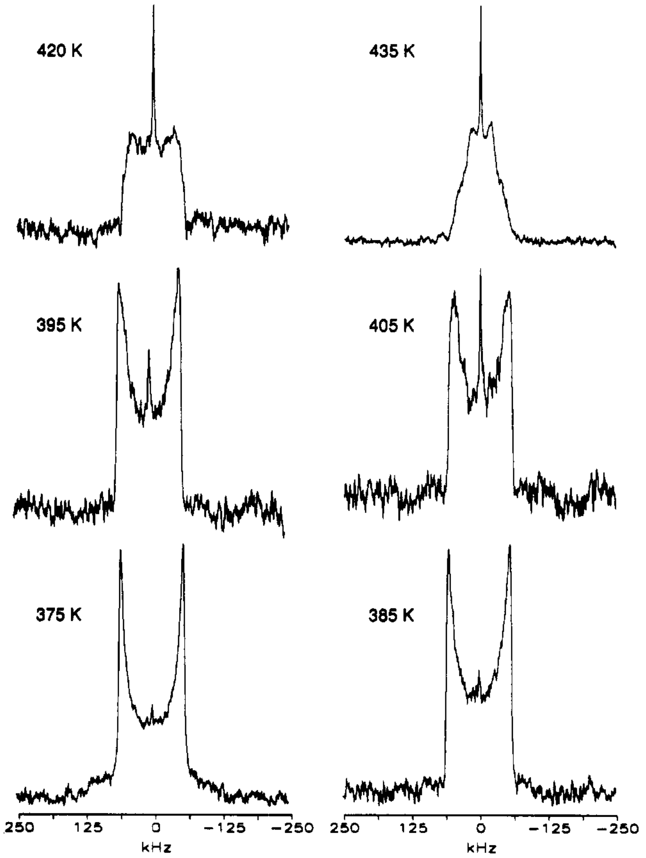

Figure 12. Solid-state ^{2}H NMR of polyacrylonitrile-d_α.

content. The result is the disappearance of the outer edges of the Pake pattern, while the horns of the pattern remain visible as two single peaks.

Polyacrylonitrile. Polyacrylonitrile-d_α gave very different results (Figure 12). Below T_g, the quadrupole echo line shape consists of a rigid Pake pattern. Above T_g, a pattern develops, with a very slight decrease in the overall width corresponding to increased motion but not of the magnitude seen for the other acrylates. That is, isotropiclike large-scale motion does *not* develop over the temperature range studied. The sample was taken through four to five heating cycles, up to 435 K (162 °C), to examine motions around and above T_g (these results will be discussed below). All experiments performed after heat

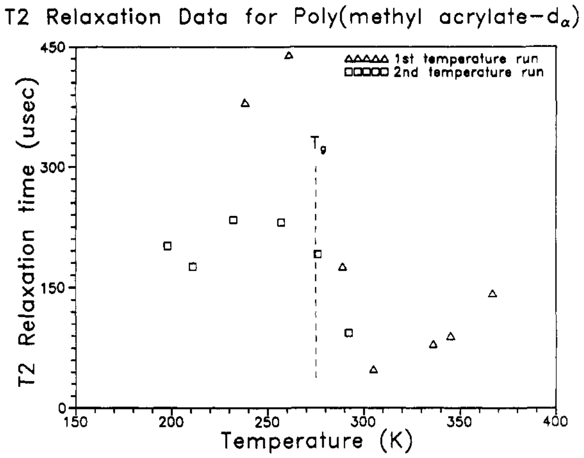

Figure 13. Spin-spin relaxation graph for poly(methyl acrylate-d_α).

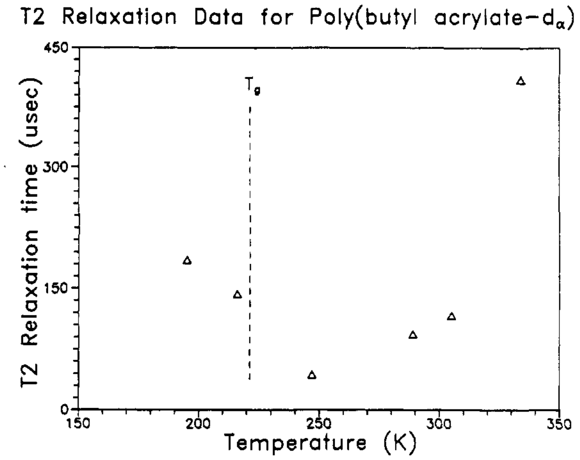

Figure 14. Spin-spin relaxation graph for poly(butyl acrylate-d_α).

treatments displayed an additional narrow peak in the center of the Pake pattern whose cause is unknown.

Deuteron spin alignment NMR was performed to examine ultraslow molecular motions.[9] For polyacrylonitrile with a T_g of 370 K (97 °C) at 300 K (27 °C), the alignment echo decay curves are dependent on τ_1, which would indicate that the polymer backbone is undergoing diffusive motions over small but ill-defined angles. Initial spin alignment line shapes also indicate that the motion is a restricted type of diffusion.

Deuterium Relaxation Experiments. Deuterium spin-spin relaxation (T_2) data for poly(methyl acrylate-d_α), poly(butyl acrylate-d_α), and the cross-linked polymer labeled on the main chain [poly(ethyl acrylate-d_α-*cross*-hexanediol diacrylate)] show a minimum at approximately 30 °C above DSC T_g values (Figures 13-15). This is expected due to the difference in frequency of observation and time scale of the ^{2}H NMR experiment compared to that of DSC. The T_2 data for the cross-linked labeled polymer poly(ethyl acrylate-*cross*-ethylene diacrylate-$d_{\alpha,\alpha'}$), with 13.7 mol % cross-linker, show a similar minimum (Figure 16). The greater scatter of data points may be due to the greater inhomogeneity associated with cross-linked systems resulting from a distribution of cross-link lengths. Overall, however, values of the T_2 minima correspond closely to the T_g's estimated from the onset of the motionally narrowed peak for all of the acrylate polymers (Table II).

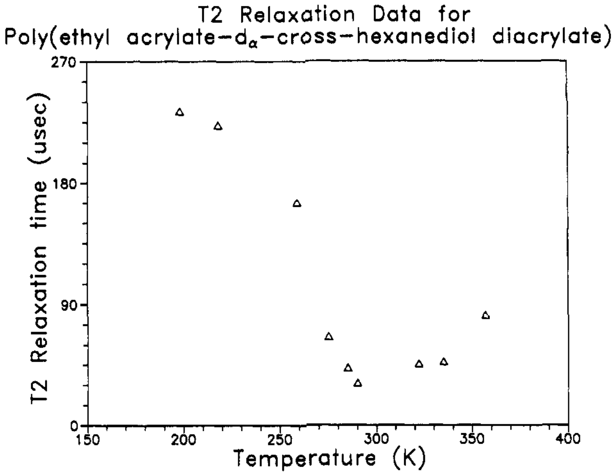

Figure 15. Spin-spin relaxation graph for poly(ethyl acrylate-d_α-*cross*-hexanediol diacrylate).

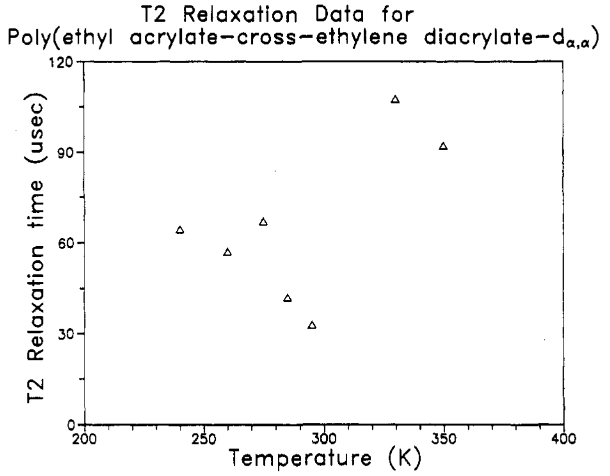

Figure 16. Spin-spin relaxation graph for poly(ethyl acrylate-*cross*-ethylene diacrylate-$d_{\alpha,\alpha'}$).

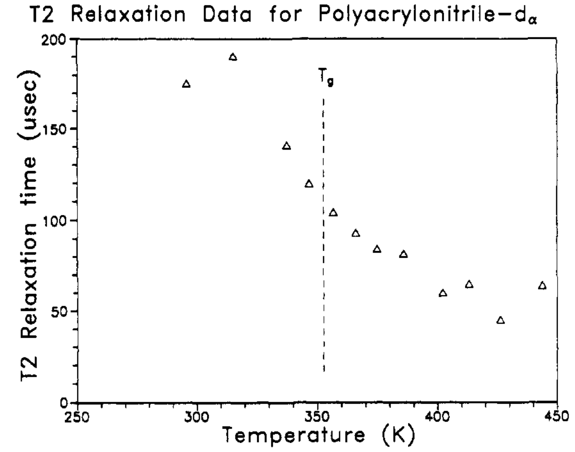

Figure 17. Spin-spin relaxation graph for polyacrylonitrile-d_α.

Polyacrylonitrile does not display a T_2 minimum for the temperature range employed (Figure 17), unless the minimum is just beginning to show up at the highest values measured. The minimum is most likely shifted to a higher temperature due to the specific jump motion, which is indicated from the spectrum for polyacrylonitrile above 400 K (127 °C).

Deuterium spin-lattice relaxation (T_1) data for poly(methyl acrylate) and polyacrylonitrile are shown in Figures 18 and 19. The data for both samples give a much better fit using a two-component analysis. Relaxation data for bulk polymers can be difficult to interpret due to the inherent heterogeneity of polymers.[10,11] For poly(methyl acrylate), the short T_1 component decreases with increasing temperature, while the long T_1 component goes through

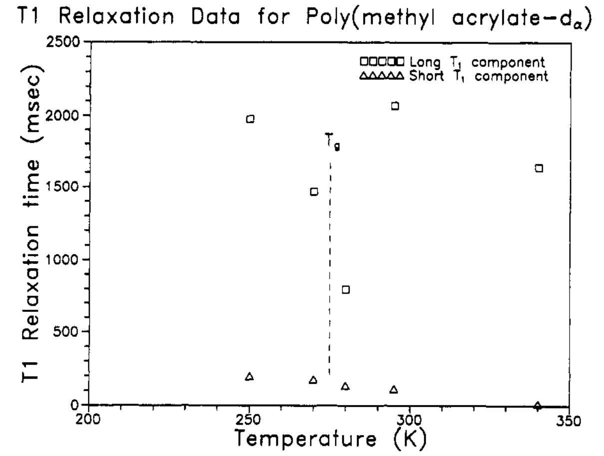

Figure 18. Spin-lattice relaxation graph for poly(methyl acrylate-$d_α$).

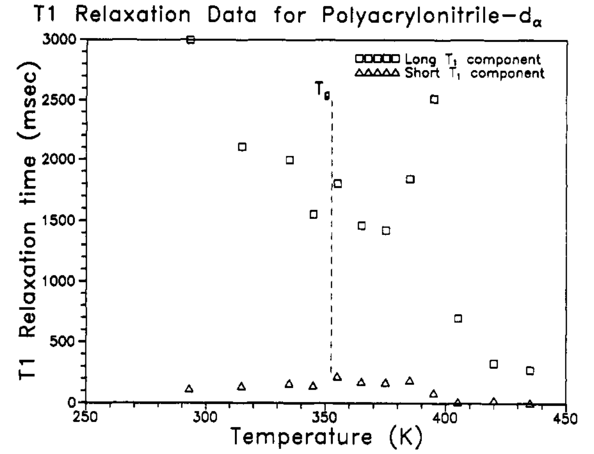

Figure 19. Spin-lattice relaxation graph for polyacrylonitrile-$d_α$.

a minimum analogous to the T_2 relaxation but at a temperature (280 K) much closer to the T_g measured by DSC. Similarly for polyacrylonitrile, the short T_1 component decreases almost linearly as the temperature is increased, and the long T_1 component goes through a minimum at almost the same value as the DSC T_g (370–380 K). For this sample, however, the T_1 increases beyond the minimum and abruptly drops again at a temperature ca. 30 °C above the T_g. Such behavior was not seen for the acrylates and may be related to the onset of restricted motion indicated by the drastic change in peak shape between 405 and 420 K (Figure 12). Torchia and Szabo have shown that there may not be a unique T_1 for each frequency associated with a specific C–^{2}H bond orientation.[12] Thus, the two-component T_1's and additional transitions may be the result of morphological heterogeneity in the amorphous components.

Summary

For polyacrylates, ^{2}H line shapes and T_2 minima both show that molecular motions go from rigid to isotropiclike at temperatures ca. 20 °C above the glass transition while polyacrylonitrile undergoes a transition to a less well-defined type of motion. T_1 data, however, show minima at about the same temperatures as the DSC T_g's. Cross-linking increases the T_g of the acrylate chains *between* cross-links although the cross-link sites themselves show *reduced* T_g's (compared to non-cross-linked material) that gradually increase with increasing cross-linker content.

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Registry No. Acrylonitrile-$d_α$, 4635-82-9; *n*-butyl acrylate-$d_α$, 112741-03-4; methyl acrylate, 96-33-3; butyl acrylate, 141-32-2; acrylonitrile, 107-13-1; acrylamide, 79-06-1; dimethylacrylamide, 2680-03-7; hexanediol diacrylate, 13048-33-4; ethylene diacrylate, 2274-11-5; methyl vinyl ketone, 78-94-4; methyl acrylate-$d_α$ (homopolymer), 9003-21-8; ethyl acrylate-$d_α$ (homopolymer), 9003-32-1; butyl acrylate-$d_α$ (homopolymer), 9003-49-0; acrylonitrile-$d_α$ (homopolymer), 25014-41-9; (ethyl acrylate-$d_α$)(hexanediol diacrylate) (copolymer), 79311-40-3; (ethyl acrylate)(ethylene diacrylate) (copolymer), 28261-25-8.