is probably due to the presence of complex molecular motions which cause deviations from the predictions of simplified theories.[2] ^{15}N T_1 measurements could not be performed at higher pH due to low sensitivity resulting from broad lines (in turn due to polymer precipitation).

Conclusion

$^{15}N/^{13}C$ T_1 ratios are similar to those predicted theoretically for polymers such as poly(iminoethylene), where the motional characteristics of CH_2 and NH_2^+ are similar. In poly(vinylamine) the motional characteristics of backbone CH and CH_2 carbons are not similar to those of the NH_3^+ group. The $^{15}N/^{13}C$ NT_1 ratios at low pH indicate free rotation of the NH_3^+ group analogous to the CH_3 group rotation.

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Carbon-13 Nuclear Magnetic Resonance Studies on Soluble Poly(diacetylenes)

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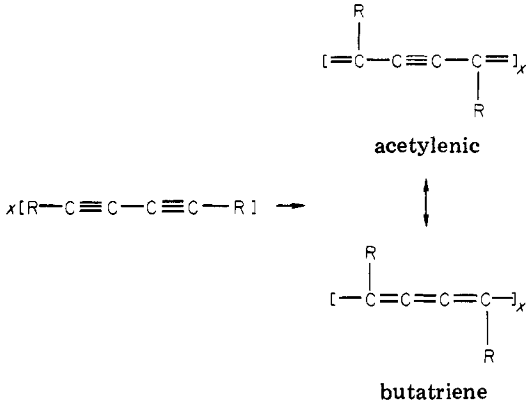
ABSTRACT: ^{13}C NMR studies on two poly(diacetylenes), $(=CR-C\equiv C-CR=)_x$, where R is $-(CH_2)_{3,4}OCONHCH_2COO(CH_2)_3CH_3$, in different solvents and at different temperatures are reported. The peaks for $-C=$ and $-C\equiv$ indicate that the backbone has the enyne structure, commonly known as the acetylenic structure, in solution. The solutions form solid gels at lower temperatures. Polymer molecules acquire a rigid planar conformation in the gels. As a result, the peaks for the backbone carbons and methylene carbons adjacent to the backbone disappear and those of carbonyl and methylene groups are broadened in the gels.

Introduction

Diacetylenes, $R-C\equiv C-C\equiv C-R$, where R is a substituent group, polymerize in the solid state either upon thermal annealing or upon exposure to high-energy radiation.[1-3] The polymerization occurs via 1,4 trans addition of the triple bonds:



The structure of the backbone is a resonance hybrid of the acetylenic and the butatriene structures. Raman spectra of a number of poly(diacetylenes) show bands for $-C\equiv C-$ and $-C=C-$ symmetrical stretching vibrations.[4] The polymers are colored because the electron density is delocalized extensively along the conjugated backbone.[4]

Since most poly(diacetylenes) are insoluble in common organic solvents, no ^{13}C NMR studies of poly(diacetylenes) have been reported. However, we recently synthesized a new class of poly(diacetylenes) which show high solubility in a number of common organic solvents, e.g., chloroform, dimethylformamide, nitromethane, dichlorobenzene, and methyl ethyl ketone.[5] The substituent groups of the soluble poly(diacetylenes) are $(CH_2)_lOCONHCH_2COO(CH_2)_mCH_3$, where $l = 3$ or 4 and $m = 1$ or 3. We used samples from this class of poly(diacetylenes) for the present ^{13}C NMR studies. We shall refer to the poly(diacetylenes) as poly*l*ACMU, where ACMU stands for [(alkoxycarbonyl)methylene]urethane and *l* represents the number of methylene groups adjacent to the backbone.

Solutions of the soluble poly(diacetylenes) undergo sharp, reversible color changes, yellow ↔ blue (or red), when the solvent/nonsolvent ratio[5] or the temperature[6] is varied. In the case of poly3BCMU the lowest energy optical transition shifts by more than 5000 cm^{-1} (21 300 to 15 900 cm^{-1}). The color changes are due to a nonplanar ↔ planar conformational transition of the backbone. On the basis of spectroscopic studies,[5,6] it is shown that the poly(diacetylenes) acquire a planar conformation in blue (or red) solution or gel while the conformation is nonplanar

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Table I
Thermochromic Properties of [(*n*-Butoxycarbonyl)methylene]urethane
[$R = (CH_2)_lOCONHCH_2COO(CH_2)_3CH_3$] Substituted Poly(diacetylenes) [$\text{-(}CR{-}C{\equiv}C{-}CR\text{)-}_x$] in Solutions

poly(diacetylene)	*l*	color transition	solvent[a]	color transition range during heating, °C	temperature during heating, °C
poly4BCMU	4	yellow ⟷ red	MEK	65-67	44-42
			NM	43-45	29-27
			$CHCl_3$	*b*	*b*
poly3BCMU	3	yellow ⟷ blue	NM	83-85	68-66
			$CHCl_3$	*b*	*b*

[a] NM = nitromethane; MEK = methyl ethyl ketone. [b] The polymers do not undergo a color change in chloroform.

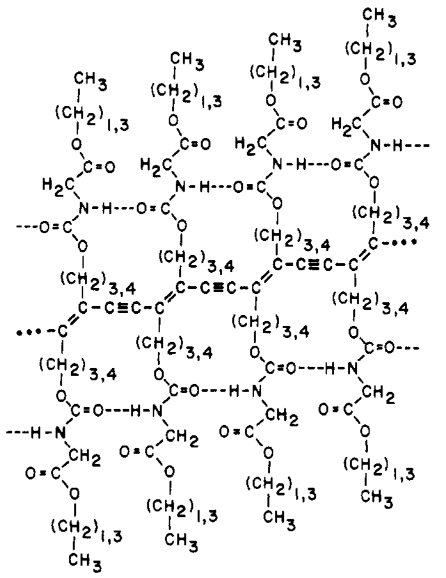

Figure 1. Hydrogen-bonded conformation of [(*n*-butoxycarbonyl)methylene]urethane-substituted poly(diacetylenes).

in yellow solution. The planar conformation is stabilized by formation of intramolecular hydrogen bonds between >C=O and >N—H functionalities of the adjacent side groups[5,6] (see Figure 1). It was thought that the chemical shifts of the carbon atoms of the backbone would be influenced significantly by the change in the conformation of the backbone. As, —C=, —C≡, and =C= have different chemical shifts,[7] we were also interested in determining the structure of the backbone of the poly(diacetylenes) in solution. In the present paper, we report ^{13}C NMR studies on yellow and blue or red solutions of poly4BCMU [$R = (CH_2)_4OCONHCH_2COO(CH_2)_3CH_3$] in $CDCl_3$, methyl ethyl ketone (MEK), and CD_3NO_2 and poly3BCMU [$R = (CH_2)_3OCONHCH_2COO(CH_2)_3CH_3$] in $CDCl_3$ and CH_3NO_2.

Experimental Section

Synthesis of the monomers has been described elsewhere.[8] Polymerization was accomplished by irradiation with 50 Mrd of ^{60}Co γ rays at room temperature. Unreacted monomer was removed by extracting with acetone. Residual unreacted monomer and oligomers were further removed by using hexane for selective precipitation of the polymers from chloroform solution. All solvents were of spectroscopic grade. ^{13}C NMR spectra were run on 10% solutions of monomeric 4BCMU and 3BCMU in $CDCl_3$ and polymeric 4BCMU in $CDCl_3$, methyl ethyl ketone, and CD_3NO_2. Poly3BCMU was run in $CDCl_3$ and CH_3NO_2. Polymer solutions were prepared directly in precision 8-mm NMR tubes by heating to a point just below the boiling point of the solvents.

A Varian CFT-20 NMR spectrometer was used to record the ^{13}C NMR spectra. A pulse width of a 10 s (60° flip angle) and acquisition time of 0.454 s were used. In MEK and CH_3NO_2 lock was attained by inserting a D_2O capillary concentrically into the 8-mm tube. All chemical shifts are relative to trimethylsilane, using the solvent as a secondary reference.

Results

Monomeric 4BCMU is colorless while its solution is pale yellow due to traces of polymer attributable to a slight thermal polymerization during the drying process. Monomer-free films of poly4BCMU are metallic green-gold in reflectance and red in transmission. In solution the polymer is yellow-orange at higher temperatures and forms red gel at lower temperatures if the solvent is *o*-dichlorobenzene, nitromethane, or methyl ethyl ketone (see Table I). The yellow ↔ red transition is associated with a hysteresis.[6] There was no drastic color change in the chloroform solution upon varying the temperature.

Table II provides the ^{13}C NMR chemical shifts for monomeric and polymeric 4BCMU in $CDCl_3$. Most of the chemical shift assignments are self-explanatory except perhaps for the carbonyls and acetylenic carbons. The carbonyl at 155.8 ppm was assigned to the urethane function based on the model ethyl methylcarbamate,[8] where the peak appears at 157.8 ppm. The other carbonyl at 169.5 ppm was assigned to the ester and is in good agreement with accepted values.[8] The two acetylenic carbons appear at 76.1 and 65.0 ppm. The latter is due to the interior ≡C—C≡ carbons and represents an upfield shift because of mutual anisotropic shielding by the sp bond. The outer carbons appear at a more normal shift position of 76.1 ppm. Support for this assignment is found in the literature,[9] where similar carbons in PhC≡C—C≡CPh are found near 75 ppm for the inner carbons and 82 ppm for the outer carbons, showing a shift differential of -7 ppm (vs. -11 ppm for 4BCMU). A similar trend has been noted for two oligomeric acetylenes,[10] where the inner and outer carbons appeared at 62–64 and 89 ppm, respectively.

Table II also contains the ^{13}C NMR parameters for poly4BCMU in $CDCl_3$, MEK, and CD_3NO_2 at low and high temperatures. In all solvents at higher temperatures when the polymer is in solution, the full spectrum is detected with peaks near 130 and 100 ppm due to —C= and —C≡ carbons of the backbone. When the temperature of the $CDCl_3$ solution is lowered, the spectrum and the color remain unchanged. However, when the temperature of the MEK and CD_3NO_2 solutions is lowered, a deep red solid gel forms and the ^{13}C NMR spectrum is substantially changed.

Figure 2 contains a partial ^{13}C NMR spectrum of poly4BCMU in MEK at low and high temperatures. At 10 °C the peaks for —C= and —C≡ carbons are notably absent from the spectrum and both carbonyl peaks are severely broadened. Moreover, no new replacement peaks could be found in the spectrum, including the region down to 220 ppm. The upfield methylene peaks are relatively unaffected by this temperature change except for some reduction in the $HNCH_2$ group peak near 43 ppm. Rerunning the same solution at 45 °C (when the red solid gel

Table II

^{13}C NMR Chemical Shift Assignments for Monomeric and Polymeric 4BCMU under Different Conditions

conditions	physical state and color	monomer		polymer												
		—C≡	≡C—C≡	—C=	—C≡	α CH_2	β CH_2	γ CH_2	δ CH_2	OCONH	CH_2	COO	CH_2	CH_2	CH_2	CH_3
monomer in $CDCl_3$ at 30 °C	colorless solution	76.1	65.0			18.3	24.1	27.4	64.0	155.8	42.4	169.5	64.6	29.9	18.3	13.0
polymer in $CDCl_3$ at 30 °C	orange solution			129.3	99.3	34.5	24.9	28.4	65.0	156.9	42.5	170.4	65.0	30.4	18.9	13.5
polymer in $CDCl_3$ at 6 °C	orange solution			129.4	99.5	34.9	24.9	28.4	65.0	156.8	42.6	170.3	65.0	30.4	18.9	13.5
polymer in MEK at 45 °C	orange solution			130.4	100.4			(25.9)	65.1	157.6	43.3	170.8	65.1	31.4	19.7	13.9
polymer in MEK at 10 °C	solid red gel								65.1	157.5	43.1	170.5	65.1	31.5	19.7	14.0
polymer in CD_3NO_2 at 100 °C	orange solution			130.9	100.9	36.1	26.2	29.8	66.1	158.1	43.9	171.6	66.1	31.7	19.9	13.9
polymer in CD_3NO_2 at 40 °C	solid red gel						26.2	29.6	65.9	(158)	43.5	(172)	65.9	31.5	19.9	13.9

Table III

^{13}C NMR Chemical Shift Assignments for Monomeric and Polymeric 3BCMU under Different Conditions

conditions	physical state and color	monomer		polymer											
		—C≡	≡C—C≡	—C=	—C≡	α CH_2	β CH_2	γ CH_2	OCONH	CH_2	COO	CH_2	CH_2	CH_2	CH_3
monomer in $CDCl_3$ at 30 °C	colorless solution	75.5	65.3			15.3	27.3	65.0	155.7	42.7	169.5	63.3	30.0	18.3	13.0
polymer in $CDCl_3$ at 60 °C	orange solution			129.2	99.8	31.9	28.1	64.9	156.9	42.8	170.2	64.9	30.6	18.9	13.5
polymer in $CDCl_3$ at 6 °C	orange solution			129.1	99.8	31.7	28.0	64.9	157.0	42.6	170.3	64.9	30.5	18.9	13.6
polymer in nitromethane at 120 °C	orange solution			129.8	100.1	32.1	28.4	65.1	147.2	43.0	168.7	65.0	30.8	19.0	12.9
polymer in nitromethane at 30 °C	solid blue gel							(62.1)		43.7		(62.1)			12.6

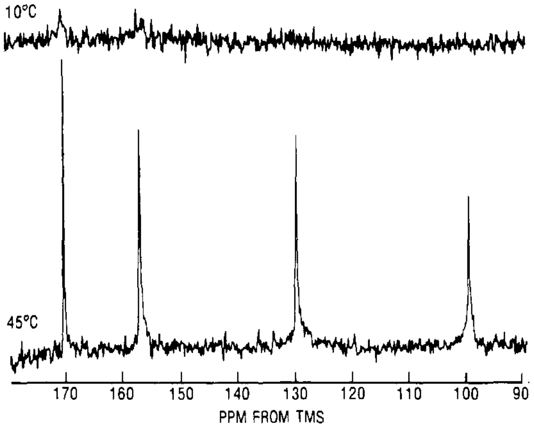

Figure 2. ^{13}C NMR spectra of the carbonyl and the backbone carbons of poly4BCMU in methyl ethyl ketone in yellow solution (45 °C) and red gel (10 °C) (also see Tables I and II).

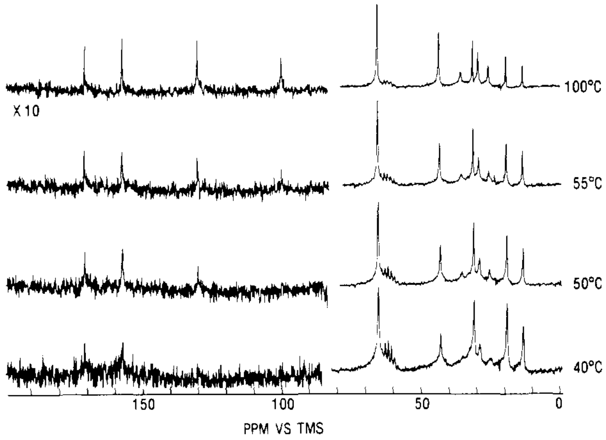

Figure 3. ^{13}C NMR spectra of poly4BCMU in CD_3NO_2 at various temperatures. Yellow solution above 50 °C; solid red gel below 40 °C (also see Tables I and II).

turns into yellow solution) produced the original spectrum, demonstrating the reversibility of the effect with respect to ^{13}C NMR.

Figure 3 shows the ^{13}C NMR spectrum of poly4BCMU in CD_3NO_2 at various temperatures through the thermochromic transition range. The region from 100 to 200 ppm is blown up 10 times relative to the aliphatic region in order to bring out the effect that temperature has on the backbone carbons and carbonyl groups. It also shows the subtle effect on the aliphatic region. At 100 °C, the peaks for carbons of the backbone are sharp whereas at 40 °C they are absent and those of carbonyls severely broadened. Moreover, the signals from the aliphatic carbons lying near the backbone and the urethane groups (e.g., 26.3, 29.6, 43.5, and, to some extent, 65.9 ppm) are broadened at 40 °C. Signals from the methylene group directly attached to the backbone are missing completely. Furthermore, the *n*-butyl group carbons are still fairly sharp in either solvent at low temperature and this denotes the higher mobility of the *n*-butyl group. It may also be noted that the solvent CD_3NO_2 produces a distinctive multiplet near 62 ppm and this also remains sharp at 40 °C, which is indicative of a higher molecular mobility of solvent relative to the polymer.

Figure 4 shows a partial ^{13}C NMR spectrum of poly3BCMU in nitromethane (CD_3NO_2) at high and low temperatures. Table III contains chemical shift data on the same polymer under various conditions of solvent and temperature. With minor exceptions its behavior follows that for poly4BCMU (Figure 2). It should be noted that

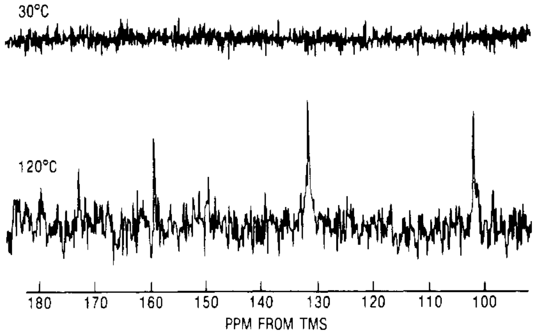

Figure 4. Partial ^{13}C NMR spectra of the carbonyl and the backbone carbons of poly3BCMU in CD_3NO_3 in yellow solution (120 °C) and blue gel (30 °C) (also see Tables I and III).

the effect of lowering temperature is more pronounced in the spectrum of poly3BCMU than in the spectrum of poly4BCMU.

Discussion

Though =C= and —C≡ carbons have the same sp hybridization, they have different chemical shifts; =C= absorbs around 220 ppm while —C≡ absorbs around 100 ppm. The ^{13}C NMR spectra were carefully searched for =C= of the butatriene structure of the backbone, beyond 200 ppm, but to no avail. The peaks for —C= and —C≡ at 130 ± 1 and 100 ± 1 ppm, respectively, suggest that the poly(diacetylene) backbone has the acetylenic structure (=C—C≡C—C=) in the yellow solutions. The peaks for —C= and —C≡ disappear when the yellow solutions form blue or red gels at lower temperatures because the backbone acquires a rigid planar conformation[5,6] (Figure 1). It is noteworthy that with either polymer the carbonyl peaks are severely broadened in the low-temperature spectra, an observation which suggests the formation of hydrogen bonds between >C=O and >N—H functionalities of the adjacent side groups, which, while not conclusive from ^{13}C NMR alone, is compatible with vibrational spectroscopic results[6] which list the urethane carbonyl at 1725 cm^{-1} in yellow solution and 1689 cm^{-1} in the red and blue gels.[6] The rigidity is reinforced by the two hydrogen bond chains: one on each side of the backbone (see Figure 1) decreases the mobility of methylene groups between the two hydrogen bond chains. That is why the signals of the methylene groups directly attached to the backbone are missing and those for the others are broadened in the low-temperature spectra. The low-temperature ^{13}C NMR spectra (Tables II and III) indicate that poly3BCMU has a more rigid conformation than poly4BCMU. The mobility of CH_2 of the *n*-butyl groups is not seriously affected by the formation of the hydrogen bonds and hence their peaks remain almost unchanged. The spectra of the polymers in chloroform are not affected by variation in temperature because the conformation of the molecules remains unchanged.[5,6] Future work utilizing solid-state ^{13}C NMR should prove beneficial for determination of the structure of the backbone in the solid gels and bulk poly(diacetylenes) through the thermochromic transitions.

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Characterization of the Catabolic Transformation of Lignin in Culture Using Magic-Angle Carbon-13 Nuclear Magnetic Resonance

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ABSTRACT: Catabolic transformation of softwood kraft lignin in culture with the white-rot fungus *Coriolus versicolor* increases lignin functionality, thereby improving its potential for incorporation into useful end products. Cross-polarization, magic-angle spinning ^{13}C NMR spectra of the total solid products from 1-, 4-, and 8-week lignin cultures show lignin is not massively transformed by *C. versicolor* in these experiments, although the spectra do reveal significant differences. Analysis of the spectrum of the solids from the 8-week fermentation shows that about 7% of the carbons have been oxygenated. Of these, almost half appear to be vinyl aldehydes and this represents a fourfold increase compared to the starting lignin.

As a major constituent of all vascular plants, lignin represents a major renewable source of reduced carbon. Over half of the photosynthetic activity in these plants is devoted to the conversion of atmospheric carbon dioxide to lignocellulosic materials. The lignin component of the lignocellulosic cell wall material presents the greatest technological barrier to utilization of this biomass resource. Progess in lignin research is hampered by the chemical and