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^{13}C NMR Structural Studies of a Soluble Polydiacetylene Poly(4BCMU)

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ABSTRACT: The chromism of a soluble polydiacetylene, poly(4BCMU), whose side chain substituents are $(CH_2)_4OOCNHCH_2COO(CH_2)_3CH_3$, was studied by use of high-resolution, solid-state ^{13}C NMR spectroscopy. The solid-state thermochromic transition (104 °C; DSC at 10 °C/min) resulted in a more localized electronic state for the backbone, extended side chains with more trans bond character, and retention of the hydrogen-bonding network between side chains, results similar to those observed for the thermochromic transition of poly(ETCD), whose side chains are $(CH_2)_4OOCNHCH_2CH_3$. Unlike poly(ETCD), the thermochromic transition observed in poly(4BCMU) was irreversible, and poly(4BCMU) cooled from the red phase or molten state to room temperature displayed two distinct backbone structures. Melting poly(4BCMU) (132 °C; DSC at 10 °C/min) caused a weakening of the hydrogen bonds or possibly the formation of intermolecular hydrogen bonds. A solid, red gel of poly(4BCMU) in toluene-d_8 and a liquid, yellow–orange solution of poly(4BCMU) in $CDCl_3$ were found to have backbone electronic states observable by solid-state ^{13}C NMR. The absence of both the butatrienic form of backbone conjugation and a trans to cis isomerization of the backbone double bonds was demonstrated. Backbone electronic and motional states and the conformations, motions, and hydrogen bonding of the side chains of poly(4BCMU) in the solid state and in solvents were found to be consistent with a model that suggests the thermochromic phase transition in polydiacetylenes may result from the strain placed on the backbone by its side chains.

Introduction

Polydiacetylenes are an unusual class of polymers because their solid-state polymerization from crystallized monomers can produce macroscopic single crystals of polymer.[1] The polymerization proceeds by 1,4-addition and results in polymers with conjugated backbones as illustrated in Figure 1a. Extensive delocalization of π-electrons along the backbone gives polydiacetylenes interesting optical properties[1–4] and is also responsible for their absorption of light in the visible range. External influences, such as mechanical or thermal stress, can alter the amount of π-electron delocalization, thereby changing the absorption properties of polydiacetylenes, which are well-known for their characteristic chromism.

Though most polydiacetylenes are insoluble, several form solutions in common organic solvents. One such soluble polydiacetylene was first synthesized[5,6] in 1978 from 5,7-dodecadiyne-1,12-diol bis[((butoxycarbonyl)methyl)urethane] and is commonly called poly(4BCMU) (see Figure 1b). The initial portion of the poly(4BCMU) side chain is identical with the side chains of other insoluble polydiacetylenes, such as poly(ETCD) (R = $(CH_2)_4OOCNHCH_2CH_3$) and poly(TCDU) (R = $(CH_2)_4OOCNHC_6H_5$). Apparently the longer side chains of poly(4BCMU) contribute enough conformational entropy to allow solubility in solvents like chloroform, nitromethane, and toluene.[1]

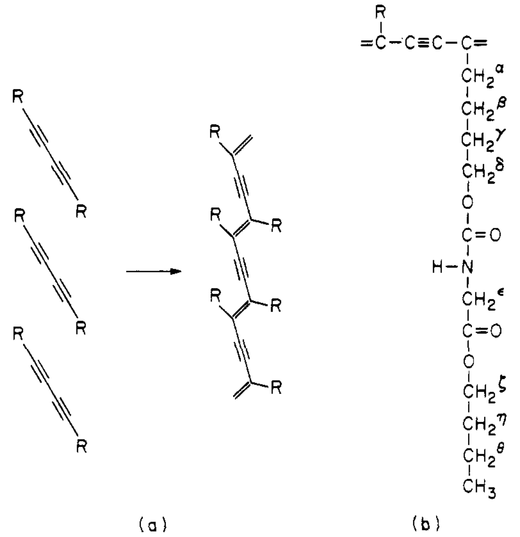

Figure 1. (a) Schematic representation of the solid-state synthesis of polydiacetylenes. (b) Chemical structure of poly(4BCMU).

Poly(4BCMU) displays chromic transitions in its crystalline and solution-cast film solid states and also in solu-

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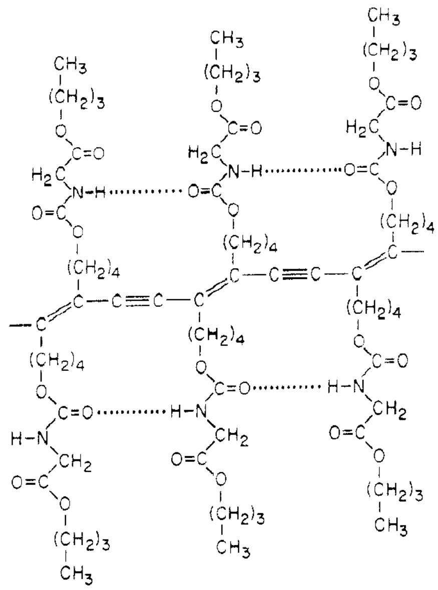

Figure 2. Hydrogen-bonded network of side chains in poly(4BCMU).

tion in organic solvents. The absorption spectrum and color of the as-polymerized polymer change (blue to red) at ca. 110 °C. Heating to ca. 120 °C melts the red crystals, producing a yellow isotropic liquid. A solution of poly(4BCMU) in a thermodynamically good solvent, like chloroform, changes color[5] from yellow to red upon addition of a nonsolvent like hexane. Solutions, or gels, of poly(4BCMU) in poor solvents can be induced[7] to change color from red to yellow by heating. In this regard, poly(4BCMU) and other polydiacetylenes are uncommon polymers. The molecular mechanisms responsible for the chromism observed in poly(4BCMU) are not well understood, though several models have been suggested.

The urethane groups in the side chains of poly(4BCMU) may form hydrogen bonds between neighboring side chains, resulting in a hydrogen-bonded network for each poly(4BCMU) molecule (see Figure 2). Patel and Miller[8] believed that melting or dissolution of poly(4BCMU) disrupted the hydrogen-bonded network, permitting nonplanar backbone conformations to be achieved via rotation about backbone single C–C bonds. Nonplanar conformations would affect the electronic distribution along the backbone, causing the observed color changes.

Light scattering and electric birefringence measurements[9] made on yellow chloroform solutions of poly(4BCMU) suggest worm-like coil conformations for the dissolved chains, while in poorer solvents the polymers aggregate into rod-like chains. Lim et al.[10] suggested that the butatrienic form of backbone conjugation (—C(R)═C═C═C(R)—) played a role in the rod to coil conformational transition. However, no convincing experimental evidence for the presence of the butatrienic structure in solid or dissolved polydiacetylenes has been presented.[9,11-16] Berlinsky et al.[17] retracted the suggested role played by the butatrienic resonance structure and instead suggested a trans to cis isomerization of the backbone double bonds might explain the rod to coil and chromic transitions observed in poly(4BCMU) solutions. Wenz and co-workers[11] concluded that the chromism observed in poly(4BCMU) solutions was caused by aggregation and was not related to any single-chain phenomenon. Although they acknowledged that cluster growth occurs in solution, Lim and Heeger[18] maintained that aggregation was not the cause of the color changes. The roles played by aggregation, hydrogen bonding of side chains, and rod to coil conformational transitions in the chromism observed in poly(4BCMU) solutions and solids are not entirely clear. Recent studies of the thermochromism in insoluble polydiacetylenes[14,19-21] have suggested a mechanism that may be applicable to poly(4BCMU).

The structure, conformations, and dynamics of several insoluble polydiacetylenes have been studied with high-resolution, solid-state ^{13}C NMR spectroscopy.[14,19-21] The chemical shift observed for a ^{13}C nucleus reflects its electronic environment and is sensitive to the electronic structure, the surrounding bond conformations, and proximity interactions of neighboring molecules.[22] Through examination of the ^{13}C NMR spectra of poly(ETCD) at various temperatures, Tanaka et al.[19-21] observed that several changes occurred at the thermochromic phase transition. Transformation of poly(ETCD) from its crystalline blue to its crystalline red phase resulted in a 4 ppm upfield shift in the alkyne carbon resonance. This implied a decrease in the delocalization of π-electrons along the backbone,[11] causing an increase in the electron density around the alkyne carbon nuclei in the red phase of poly(ETCD).

The resonances of the side-chain β and γ carbons moved downfield (2 ppm) during the blue to red chromic transition of poly(ETCD), and this was interpreted[19-20,23,24] as an extension of the side chains from a nonplanar to a nearly planar, zigzag conformation. It was suggested that the planar side chain conformation strains the backbone, producing a nonplanar conformation via small rotations about the backbone C–C bonds. Nonplanar backbone conformations would localize the π-electrons and produce the observed upfield shift in the alkyne carbon resonances. A study[21] of melt-crystallized poly(ETCD) showed an increase in both the planarity of its side chains and the nonplanarity of its backbone compared to the single-crystal red phase. Because the alkyne carbons of several polydiacetylenes have similar chemical shifts in their blue (107 ppm) and red (103 ppm) phases, the side chain induced straining of the backbone has been suggested[14] to be generally applicable to polydiacetylenes displaying chromism.

The present investigation sought to study the mechanism responsible for the chromism of poly(4BCMU). The electronic structure of the backbone, the side chain conformations, and the hydrogen bonding of side chains associated with the solid-state thermochromic and melting transitions and the solvent-induced chromism were examined. Differential scanning calorimetry (DSC) was employed to determine the thermal characteristics of poly(4BCMU), including its thermochromic and melt temperatures. High-resolution, solid-state ^{13}C NMR spectroscopy was used to monitor the structures, conformations, and dynamics of poly(4BCMU) in its single-crystal blue and red phases, in its yellow melt and solution, and in its red gel phase as well. The data were examined and interpreted to see if the mechanism[20] suggested for the thermochromic transitions in poly(ETCD) and other polydiacetylenes[14] could also be applied to the chromism displayed by poly(4BCMU).

Experimental Section

Poly(4BCMU) was prepared by the solid-state polymerization of 4BCMU (5,7-dodecadiyne-1,12-diol bis[((butoxycarbonyl)methyl)urethane]). Monomer was synthesized by the procedures described in the literature.[25] Crystallized 4BCMU was irradiated with 50 Mrad of ^{60}Co γ-rays at room temperature, and residual monomer was extracted with acetone. The poly(4BCMU) produced was a polycrystalline powder that had a metallic, black–gold or blue appearance both before and after monomer extraction.

A Perkin-Elmer DSC-4 instrument was used to study the thermal transitions of poly(4BCMU); 5-mg samples were placed into sealed aluminum pans and heated at 10 °C/min with a He purge. Poly(4BCMU) samples were heated either from 50 to 150 °C, which exceeds the melting temperature T_m, or from 50 to 115 °C, which exceeds the thermochromic transition temperature T_c but is below T_m. Once heated to 115 °C, the samples were immediately cooled to 50 °C and reheated to 150 °C. Poly(4BCMU) samples with residual monomer extracted and samples with unextracted monomer intact were studied by DSC.

^{13}C NMR spectra were recorded on a Varian XL-200 spectrometer operating at a static magnetic field strength of 4.7 T (^{13}C resonance of 50.3 MHz). Magic angle spinning (MAS) of the samples at speeds of ca. 3 kHz was achieved with a Doty Scientific variable-temperature probe, which uses a double air bearing design. The temperature was varied from 20 to 140 °C by use of a heated N_2 flow and controlled to within ±1 °C with a standard Varian temperature-control unit. Poly(4BCMU) samples in powder form were packed in aluminum oxide rotors with end caps made of Kel-F (poly(chlorotrifluoroethylene)) for temperatures below 60 °C and of Vespel (a polyimide) for higher temperatures. Polymer samples with residual monomer extracted and with unreacted monomer intact were investigated. A 45-kHz radio-frequency field strength was used for dipolar decoupling (DD) of the ^{1}H spins, with a decoupling period of 200 ms. The optimal cross-polarization (CP) time was found to be 5 ms at room temperature, and this value was employed at all temperatures. Spectra were recorded with CP (CPMAS/DD) and without CP (MAS/DD), where the delay between decoupling pulses in the MAS/DD spectra was 3–5 s, except for the spectra obtained at 140 °C, which had a 30-s delay. All spectra were referenced[26] to the resonance of poly(oxymethylene) (POM) (89.1 ppm from TMS) that was recorded externally before and after each poly(4BCMU) spectrum.

Spin–lattice relaxation times, T_1, were measured under the CP condition by application of the pulse sequence developed by Torchia.[27] The T_1 data were analyzed by a nonlinear, least-squares method.

Samples of poly(4BCMU) (50 mg) with residual monomer unextracted were placed in 5-mm solution NMR tubes followed by the addition of 2.5 mL of either $CDCl_3$ or toluene-d_8, 0.01 mL of triethylamine (TEA), and 0.1 mL of hexamethyldisilane (HMDS). The TEA was used as a radical scavenger to help prevent thermal degradation of the poly(4BCMU) solutions.[28] NMR sample tubes were placed in heated water baths ($CDCl_3$ at 45 °C and toluene-d_8 at 95 °C) for 3 and 1 h, respectively. Small magnetic stirring bars were placed in the NMR tubes to stir the mixtures while in the water bath. After cooling to room temperature, the $CDCl_3$ and toluene-d_8 mixtures formed a clear, yellow–orange viscous liquid and a clear, dark-red gel-like solid, respectively.

Solution ^{13}C NMR spectra were recorded at 25 °C by using the Varian XL-200 spectrometer with a Zens probe. Spectra were proton-decoupled and recorded with full nuclear overhauser enhancement. The time between pulses was 5 and 30 s for the $CDCl_3$ and toluene-d_8 mixtures, respectively, and the deuterated solvents were used as signal locks. HMDS was used as an internal reference (2.0 ppm from TMS).

In addition to the spectra obtained with the Zens probe, spectra were recorded with the Doty Scientific probe normally used for solid-state NMR. About 0.2 mL of each mixture was placed in an aluminum oxide rotor whose Kel-F end caps were sealed with an epoxy glue. The CPMAS/DD spectrum of the toluene-d_8 mixture was recorded at room temperature under the same conditions as the solid-state spectra. The MAS/DD spectrum of the $CDCl_3$ mixture was also obtained at room temperature with a 5-s delay between pulses. These spectra were referenced to both internal HMDS and a POM external reference. The accuracy of both referencing methods was assessed by comparing the observed chemical shifts of adamantane with the expected chemical shifts.

Results

Thermal Analysis. When poly(4BCMU) was heated from 50 to 150 °C, a strong, sharp thermochromic transition, T_c, and a weaker, broad melting transition, T_m, were observed at 102 and 132 °C, respectively (see Figure 3a). As expected, the initial thermochromic transition observed when the polymer is heated to 115 °C (see Figure 3b) was identical with the one observed on heating to 150 °C. However, a second heating to 150 °C of the sample first heated to 115 °C revealed a thermochromic transition with a much reduced heat of transition that occurred at a slightly higher temperature (compare a and c of Figure 3). The melting transition was broad on the second heating. Table I presents the temperatures and enthalpy changes for the thermograms in Figure 3.

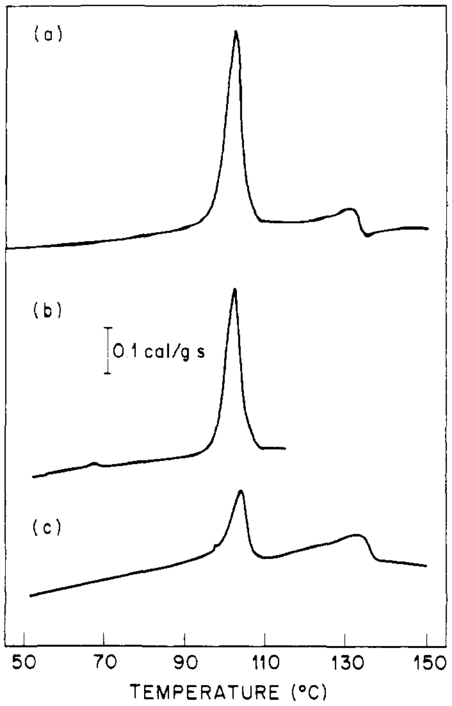

Figure 3. (a) DSC thermogram of virgin poly(4BCMU) heated from 50 to 150 °C. (b) DSC thermogram of virgin poly(4BCMU) heated from 50 to 115 °C. (c) DSC thermogram for poly(4BCMU) reheated from 50 to 150 °C after sample had been cooled from 115 °C (see b).

Table I
Temperatures and Heats of Transitions of Poly(4BCMU)

transition	temp, °C	heat of transition, J/g
thermochromic[a]	102	50
melting[a]	132	12
thermochromic[b]	104	23
melting[b]	133	17

[a] Initial heating of sample (see Figure 3a). [b] Reheating after initial heating to 115 °C (see Figure 3c).

The large, sharp thermochromic transition and the weaker, broader melting transition were similar in their shapes and temperatures to those observed by Patel and Miller.[8] The transition temperatures measured here by DSC were also close to those observed by optical absorption, while other DSC studies[29,30] found higher transition temperatures. The large thermochromic transition suggests a substantial loss of the blue-phase crystalline order for red-phase poly(4BCMU). By contrast, the melting of red-phase poly(4BCMU), with its much smaller endotherm, reflects the loss of only a modest degree of crystalline order when passing from the red to molten phase. It is apparent from Figure 3 that the thermochromic transition in poly(4BCMU) is irreversible, which may be a result[5] of the proximity and partial overlap of the thermochromic and melt transitions. Previous DSC[8,29] and X-ray diffraction measurements[29] have also noted

Table II
CPMAS/DD ^{13}C Chemical Shifts of Poly(4BCMU)[a]

carbon	blue phase (23 °C)	red phase (90 °C)	cooled from red (23 °C)	above T_m[b] (140 °C)	cooled from 140 °C (23 °C)
—C≡	107.6	102.9	104.9 101.9		104.6 101.9
>C=	132.2	131.8	132.1	131.5	132.1
α-CH_2	37.7	37.2	36.8	36.1	36.3
β-CH_2	24.9 27.9	27.3	25.8	26.1	25.5
γ-CH_2	24.9 27.9	30.9	29.5	29.8	29.5
δ-CH_2	67.3	66.5	67.1	65.9	67.1
C=O	158.6	158.5	159.1	157.5	159.0
ϵ-CH_2	44.1	44.3	44.0	44.1	43.3
C=O	171.7	171.7	172.3	170.8	172.0
ζ-CH_2	65.3	65.7	64.6	65.9	64.7
η-CH_2	32.6	32.4	33.0	31.8	32.5
θ-CH_2	20.9	20.6	21.0	20.0	20.7
CH_3	15.8	14.9	15.7	14.3	15.3

[a] ppm vs TMS. [b] MAS/DD.

this irreverisibility. Isolation of the pure red phase of poly(4BCMU) may be prevented by the proximity of T_c and T_m.

Poly(ETCD), which exhibits a completely reversible thermochromic phase transition at 123 °C, melts at 216 °C with an endotherm 4 times as large as the endotherm observed at T_c. The melting endotherm for poly(4BCMU) is only one-quarter of the thermochromic transition endotherm. This comparison makes it evident that the red phase of poly(ETCD) is much more stable than the red phase of poly(4BCMU). While poly(ETCD) is easily obtainable in both the pure blue and pure red crystalline phases, poly(4BCMU) may only be cleanly obtained in the blue phase, with the relatively unstable red phase likely contaminated with melt-crystallized material.

As revealed in Figure 3, no significant transition is observed for residual monomer. Also, T_c, T_m, and their endotherms were unaffected by monomer extraction. A small bump appears in Figure 3b near 68 °C, a temperature near a much stronger peak attributed to residual monomer in previous DSC studies.[29,30] The absence of a significant peak caused by monomer, even in unextracted samples, suggests a high conversion of the monomer crystal during polymerization. In previous DSC investigations, monomer extraction produced drastic changes in the morphology of the poly(4BCMU) crystals[30] and also caused the blue crystal form of poly(4BCMU) to convert to the red.[8] Similar phenomena were not observed in the present study.

Solid-State NMR. A summary of the ^{13}C chemical shifts observed for poly(4BCMU) in the solid state is presented in Table II. All values were obtained with CPMAS/DD except the chemical shifts recorded at 140 °C without CP (MAS/DD), which are listed in the fifth column.

The CPMAS/DD ^{13}C NMR spectrum of virgin (never heated) poly(4BCMU) is displayed in Figure 4a. Chemical shifts of the backbone carbons have values characteristic[14] of polydiacetylenes in the blue phase (132.2 and 107.6 ppm from TMS for the alkene and alkyne carbons). The chemical shifts of the side chain carbons observed in poly(ETCD)[20] were used to identify several of the resonances in the poly(4BCMU) spectra. The urethane carbonyl resonances in both polydiacetylenes were nearly identical. The resonance nearest the urethane peak was assigned to the ester carbonyl. The α, β, γ, and δ CH_2 carbons in poly(4BCMU) had chemical shifts very similar to the same methylene carbons in poly(ETCD).

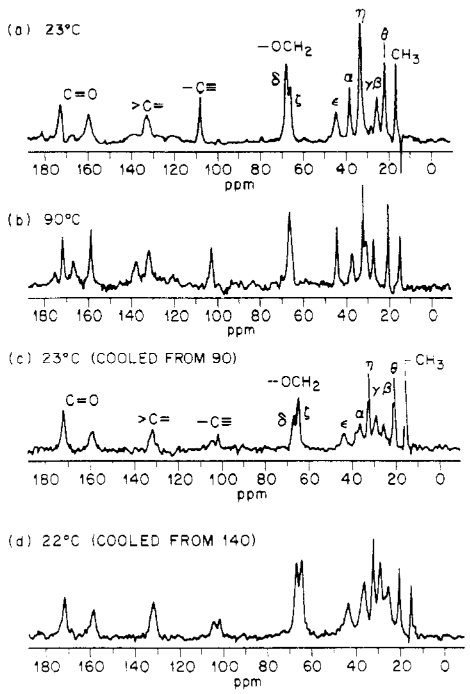

Figure 4. CPMAS/DD ^{13}C NMR spectra recorded for poly(4BCMU) at (a) 23 °C, (b) 90 °C, (c) 23 °C after cooling from 90 °C, and (d) 22 °C after cooling from 140 °C.

From the methylene carbon chemical shift (45 ppm) observed in glycine (H_2NCH_2COOH),[31] the ϵ methylene peak was identified. A resonance slightly upfield from the δ methylene peak was associated with the ζ methylene carbon. Resonances belonging to the terminal side chain carbons η, θ, and methyl were identified by comparison to the chemical shifts observed[31] in n-alkanes. Our assignment of resonances for solid poly(4BCMU) is consistent with those made previously by Babbitt and Patel[12] in solution.

When the virgin poly(4BCMU) was heated to 90 °C, some significant changes were observed in the CPMAS/DD spectrum (see Figure 4b and Table II). The alkyne backbone carbon resonance moved upfield to 102.9 ppm (from 107.6 ppm at T = 23 °C), a chemical shift characteristic[14,19,20] of polydiacetylenes in the red phase. The β and γ side chain methylene carbon resonances, which at room temperature overlapped at 24.9 ppm, separated into distinct resonances at 27.3 and 30.9 ppm, respectively, upon heating to 90 °C. Comparison with the solution[32] and solid-state[20] ^{13}C NMR spectra of poly(ϵ-caprolactone), ($-CH_2CH_2CH_2CH_2CH_2OOC-$), permitted the assignment of β and γ methylene carbon resonances at 90 °C. None of the other resonances observed in the room temperature spectrum of virgin poly(4BCMU) showed any significant changes upon heating to 90 °C. Minor resonances seen at 140 and 168 ppm belong to the Vespel end caps.

Cooling from 90 °C back to room temperature resulted in the CPMAS/DD spectrum shown in Figure 4c. Note the splitting of the alkyne carbon resonance into two peaks at 104.9 and 101.9 ppm and the upfield shift of the β and γ CH_2 resonances to 25.8 and 29.5 ppm, respectively (see Table II). Neither of these alkyne resonances is characteristic[14,19,20] of the chemical shifts observed in blue- or red-phase polydiacetylenes. Heating to 90 °C and cooling back down to room temperature had little effect on all other resonances, including the urethane carbonyl resonance whose chemical shift changed by only 0.5 ppm.

The CPMAS/DD spectrum in Figure 4d was recorded at room temperature after heating the poly(4BCMU) sam-

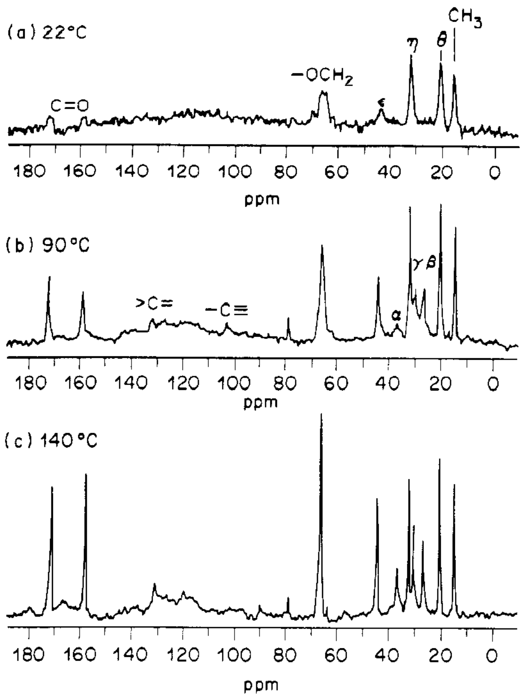

Figure 5. MAS/DD ^{13}C NMR spectra recorded for poly(4BCMU) at (a) 22 °C, (b) 90 °C, and (c) 140 °C.

ple to 140 °C, which is above the melting temperature. Aside from a slight increase in the background of the alkyl carbon region of the spectrum (20–40 ppm), this spectrum is virtually identical with that recorded at room temperature after heating to 90 °C (see Figure 4c).

The MAS/DD spectrum of virgin poly(4BCMU) at room temperature seen in Figure 5a revealed resonance peaks only for the mobile portions of the polymer.[22] The terminal portion of the side chain was seen clearly and serves to confirm the peak assignments made for this portion of the molecule from the CPMAS/DD spectra. Weak resonances were also observed for both carbonyls. At 90 °C, additional resonances were observed (see Figure 5b) indicating increased mobility for all carbons. Above T_m at 140 °C, all side chain carbons showed sharp resonances (Figure 5c) suggesting a high degree of mobility, while the alkene peak was broad and the alkyne carbon was not observed at all.

Though not shown, MAS/DD spectra recorded at room temperature after heating to 90 and 140 °C indicated a decrease in the mobility compared to the spectra recorded at the higher temperatures. However, unlike the virgin polymer both backbone carbon resonances were visible, indicating an increased mobility compared to blue-phase poly(4BCMU). The only difference between the CPMAS/DD and MAS/DD spectra for samples with and without monomer extracted was that the MAS/DD spectrum for the extracted sample showed more resonances. Chemical shifts for all resonances observed by MAS/DD were very close to those obtained by CPMAS/DD (see Table II).

Spin-lattice relaxation times T_1, measured under CP[27] for solid poly(4BCMU) are listed in Table III. Accurate measurement of T_1 values requires many spectra to be recorded with an array of delays.[27] To obtain clearly resolved spectra necessary for the integration of peak intensities, at least 400 scans were required for poly(4BCMU). As a consequence, only five to eight delay times were used in the T_1 measurements. For this reason the T_1 values reported in Table III are only qualitative (short or long T_1), and their magnitudes are only suggestive. Red-phase T_1 values are shorter than the blue-phase values, and once heated to 90 °C or above they never return at room temperature to the values observed for the virgin polymer. The thermal behavior of the T_1 values measured for poly(4BCMU) seems to parallel both their CPMAS/DD and MAS/DD spectra, which reflect the irreversible change of structure and mobility occurring at 90 °C and above.

Table III
Spin–Lattice Relaxation Times of Poly(4BCMU)[a]

carbon	blue phase (23 °C)	red phase (90 °C)	cooled from red (23 °C)	cooled from 140 °C (23 °C)
—C≡	85	15	49	25 25
>C=	100	27	36	25
α-CH$_2$	27	27	19	10
β-CH$_2$	32	2	8	14
γ-CH$_2$	32	5	10	12
δ-CH$_2$	20	4	19	12
C=O	55	9[b]	53	18
ϵ-CH$_2$	3	0.5	6	10
C=O	20	11[b]	23	21
ζ-CH$_2$	2	3	2	1
η-CH$_2$	10[b]	2	2	5
θ-CH$_2$	3	3	3[b]	15
CH$_3$	3	7	5	

[a] T_1 (^{13}C), in seconds. [b] Multiple T_1 values.

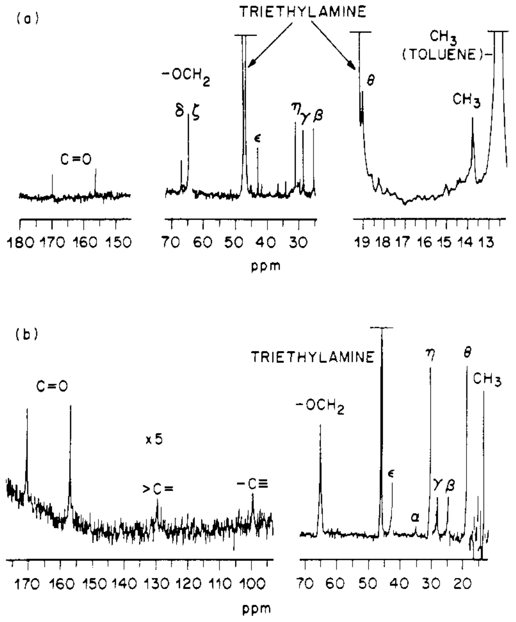

Figure 6. ^{13}C NMR solution spectra (Zens probe) of poly(4BCMU) recorded in (a) toluene-d_8 and (b) CDCl$_3$.

Solution-State NMR. The solution spectrum of the solid, red gel of poly(4BCMU) in toluene-d_8 is shown in Figure 6a. Neither backbone resonance was observed, nor was the first side chain carbon α CH$_2$. In part b of Figure 6, the solution spectrum of the CDCl$_3$ mixture, all carbon atoms exhibited resonances, though the backbone resonances were broad and the α, β, and γ methylene resonances displayed reduced intensities compared to the remaining side chain carbons, indicating a reduced mobility for the initial portion of the side chain. Both solution spectra were similar to those published by Babbitt and Patel.[12]

In the Doty solids probe, a spectrum of the toluene-d_8 gel could only be observed with CP (CPMAS/DD) as shown in Figure 7a. All carbon resonances were clearly visible, and this marks the first time the backbone carbon resonances of poly(4BCMU) have been observed by ^{13}C NMR in a poor solvent. Chemical shifts observed

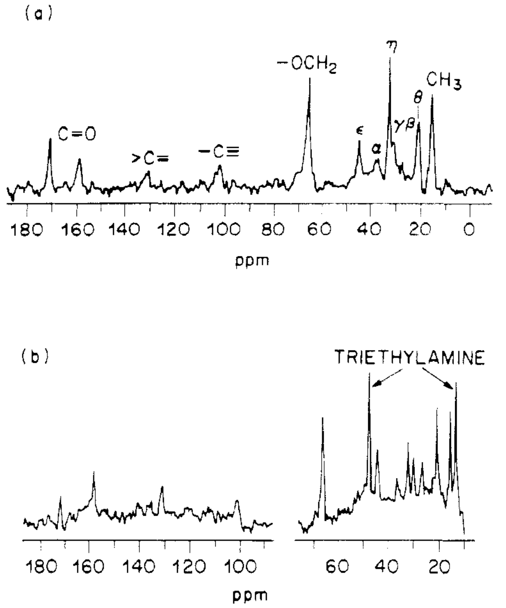

Figure 7. (a) CPMAS/DD ^{13}C NMR spectrum of poly(4BCMU) in toluene-d_8. (b) MAS/DD ^{13}C NMR spectrum of poly(4BCMU) in $CDCl_3$.

Table IV
Chemical Shifts of Poly(4BCMU) in Toluene-d_8[a]

carbon	solution probe[b]	CPMAS/DD[b]	CPMAS/DD[c]
—C≡		102.7	103.9
		101.0	102.3
>C=		129.4	130.6
α-CH_2		36.2	37.4
β-CH_2	25.1	25.8	27.1
γ-CH_2	28.5	28.9	30.7
δ-CH_2	64.8	61.2	65.7
C=O	156.3	158.0	159.1
ϵ-CH_2	42.8	42.9	44.3
C=O	169.8	170.0	171.7
ζ-CH_2	64.4	64.2	65.7
η-CH_2	30.9	30.2	32.3
θ-CH_2	19.0	19.7	20.9
CH_3	14.1	14.1	15.4

[a] ppm vs TMS. [b] HMDS internal reference (2.0 ppm vs TMS). [c] POM external reference (89.1 ppm vs TMS).

for the toluene gel in the Zens and Doty probe are compared in Table IV.

A spectrum of the $CDCl_3$ mixture could only be observed in the Doty probe without CP (MAS/DD) (see Figure 7b), which suggests a greater mobility for poly(4BCMU) in $CDCl_3$ compared to toluene-d_8. All carbons displayed sharp resonances, especially the side chain carbons. The alkyne carbon resonance had the most upfield chemical shift (101.0 ppm from TMS, POM reference) of all the physical states of poly(4BCMU) studied. The urethane carbonyl resonance frequency was similar to all the resonances observed for this carbon in all other physical states of poly(4BCMU). Chemical shifts observed in $CDCl_3$ using the Zens and Doty probes are compared in Table V.

Discussion

When poly(4BCMU) was heated to 90 °C, the chemical shift of the alkyne carbon nuclei changed from 107.6 to 102.9 ppm (see Table II), while the alkene carbon resonance was virtually unaffected. The chemical shifts of the alkyne backbone carbons are very close to those characteristically observed[14,19,20] for polydiacetylenes in their blue (ca. 107 ppm) and red (ca. 103 ppm) phases. The large upfield shift of the alkyne resonance reflects the increased electron density around the red-phase alkyne carbon nuclei resulting from a decrease in the delocalization[11,14] of π-electrons along the backbone. This same decrease in the delocalization of backbone π-electrons would be expected to shield the red-phase alkene carbons as well, but as we have seen the alkene carbon chemical shift is little affected by the thermochromic phase transition. We will comment further on this apparent dichotomy when we discuss the side chain conformations.

Table V
Chemical Shifts of Poly(4BCMU) in $CDCl_3$[a]

carbon	solution probe[b]	MAS/DD[b]	MAS/DD[c]
—C≡	99.6	99.4	101.0
>C=	129.6	129.3	131.0
α-CH_2	35.0	35.0	36.7
β-CH_2	25.1	25.0	26.7
γ-CH_2	28.5	28.6	30.2
δ-CH_2	65.3	65.2	66.9
C=O	157.1	156.8	158.4
ϵ-CH_2	42.7	42.8	44.4
C=O	170.6	170.2	171.9
ζ-CH_2	64.7	65.2	66.9
η-CH_2	30.6	30.6	32.3
θ-CH_2	19.1	19.1	20.7
CH_3	13.7	13.7	15.3

[a] ppm vs TMS. [b] HMDS internal reference (2.0 ppm vs TMS). [c] POM external reference (89.1 ppm vs TMS).

No evidence[33,34] was seen for a butatrienic backbone structure in any of the solid-state spectra recorded here. Nor was any indication provided by the solid-state spectra that the thermochromic transition in poly(4BCMU) is accompanied by a trans–cis isomerization of the backbone double bonds. Isomerization of the backbone double bonds would disrupt the intramolecular network of side chain hydrogen bonds (see Figure 2) and be expected[35] to lead to a significant change in the chemical shift of the urethane carbonyl resonances, which was not observed. As suggested previously,[14,19,20] we believe the solid-state thermochromic phase transitions in polydiacetylenes are accompanied by a transition in the backbone from a planar to a nonplanar conformation achieved by small counterrotations about the single C–C backbone bonds.

When poly(4BCMU) was cooled from 90 °C, the alkyne carbon split into two resonances at 104.9 and 101.9 ppm (see Table II and Figure 4), while the alkene resonance remained unaffected. This shows the irreversible nature of the thermochromic transition in poly(4BCMU), which was also observed by DSC. Cooling from above T_m also produced the same two alkyne resonances, suggesting that partial melting at 90 °C may be responsible for the irreversible thermochromic transition in poly(4BCMU).

Even though two peaks were observed for the alkyne carbon by CPMAS/DD, only a single peak was seen by MAS/DD for poly(4BCMU) cooled from 90 °C. The MAS/DD peak corresponds to the more upfield alkyne resonance observed by CPMAS/DD. The melt-crystallized form of poly(ETCD)[21] displayed a single alkyne resonance upfield from its red-phase position near the value of the most upfield resonance observed by CPMAS/DD for poly(4BCMU). An X-ray study[29] of recrystallized poly(4BCMU) concluded that the recrystallized material had an ordered phase different from the blue and red phases, plus a disordered, or amorphous, component. The two alkyne resonances observed by CPMAS/DD may be caused by the different poly(4BCMU) morphologies found in the ordered and amorphous phases by X-ray diffraction of the melt-recrystallized sample.

^{13}C NMR spectra of poly(4BCMU) in $CDCl_3$ and toluene-d_8 recorded with a Doty solids probe revealed that resonances of the backbone carbons could be detected (see Figures 6 and 7). Resonances corresponding to the butatrienic electronic structure[33,34] were not observed (see Tables IV and V). The alkene carbon resonated at 131.0 and 130.6 ppm (external POM references) in $CDCl_3$ and toluene-d_8, respectively. The single peak observed for the alkyne carbon in $CDCl_3$ (101.0 ppm) was the most upfield resonance observed for this nucleus, suggesting the highest degrees of backbone nonplanarity and π-electron localization among all the physical states of poly(4BCMU). The toluene gel displayed two resonances for the alkyne carbon at 103.9 and 102.3 ppm, which are similar to the alkyne carbon chemical shifts observed in the solid state after cooling to room temperature from the red phase (104.9 and 101.9 ppm). Thus poly(4BCMU) in the gel state has an essentially identical molecular structure as in the solid state cooled from above the transition temperature.

Visible absorption measurements performed by Peiffer et al.[36] on red gels of poly(4BCMU) also indicated at least two different degrees of π-electron delocalization for the backbone. They suggested that the complex morphology of the red gel aggregates of poly(4BCMU) is the source of this difference. Higher order in the interior of an aggregate of rigid rod polymers is expected compared to the exterior of the aggregate, which is exposed to more solvent. The two alkyne carbon resonances observed in the toluene-d_8 gel of poly(4BCMU) may reflect the different morphologies or environments of the aggregated polymer chains, with the downfield peak corresponding to the more well ordered interior and the upfield resonance to the less well ordered exterior of the aggregate. The morphologies of the melt-recrystallized and red gel samples of poly(4BCMU) may be the source of the two alkyne carbon resonances observed in both phases.

For poly(4BCMU), as was observed for poly(ETCD), the alkyl portion of the side chain between the backbone and the urethane group showed the largest thermochromically induced difference in their ^{13}C resonances. As-polymerized poly(4BCMU) had a single resonance at 24.9 ppm for both the β and γ methylene carbons and a single urethane carbonyl resonance at 158.6 ppm. These chemical shifts are the same as those observed for the blue phase of poly(ETCD).[14,19,20] Comparison of the solid-state ^{13}C chemical shifts observed for the side chain carbons in blue phase poly(ETCD) with those of several model compounds with known[37] conformations revealed[30] the bonds between the α, β, γ, and δ methylene groups to be gauche (g), trans (t), and gauche of the opposite sense to the first gauche bond ($\bar{g}$). The side chains in blue-phase poly(4BCMU) likely adopt a similar conformation based on the similarity of their ^{13}C chemical shifts to those of blue-phase poly(ETCD). The urethane carbonyls in the side chains of poly(ETCD) and poly(4BCMU) are hydrogen-bonded in their blue phases,[15,19,20,38] because they have nearly identical chemical shifts. As discussed by Tanaka et al.,[20] gauche conformations for the bonds connecting the α, β and γ, δ methylene groups are higher in energy than an all-trans conformation, but this may be balanced by the hydrogen bonding and packing of side chains.

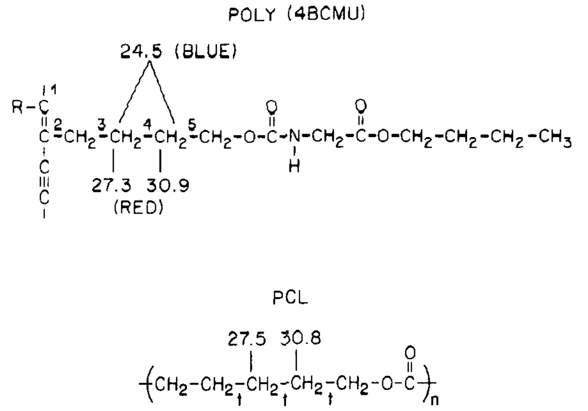

Figure 8. Comparison of the structures and ^{13}C chemical shifts of the β and γ methylene carbons in the red and blue phases of poly(4BCMU) with those of the crystalline polyester PCL.

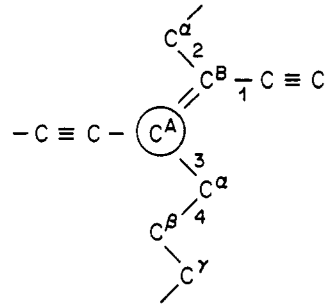

Figure 9. Possible rotations about the single C–C bonds in poly(4BCMU) which might affect the ^{13}C chemical shift of the backbone alkene carbon C^A.

Heating to 90 °C caused the β and γ methylene carbons to resonate at 27.3 and 30.9 ppm, respectively, while the chemical shift of the urethane carbonyl carbon did not change significantly (158.5 ppm). Comparison of the solid-state ^{13}C chemical shifts[20] of red-phase poly(4BCMU) with the shifts of a chemically similar portion of poly(ε-caprolactone) (PCL) indicates that they have a closely similar electronic environment (see Figure 8). Thus the conformation of PCL(ttt) also describes the conformations of bonds 3, 4, and 5 surrounding the β and γ CH_2 carbons in red-phase poly(4BCMU). The all-trans assignment to these bonds is consistent with the X-ray-observed[29] expansion of the unit cell of poly(4BCMU) in the side chain direction as it transforms from the blue to red phase. Similar X-ray observations have been reported for red-phase poly(ETCD)[20,21,40] and poly(TCDU).[15] The thermochromic and melt transitions occur at lower temperatures in poly(4BCMU) compared to poly(ETCD), probably due to the potentially greater conformational entropy of its longer side chains.

The change in the side-chain conformation from gt$\bar{g}$ to ttt, which is believed to accompany the thermochromic transition, would also be expected to affect the chemical shift of the alkene backbone carbons via the γ-gauche effect,[23] because side chain bond 4 (see Figure 9) is transformed from g to t. The downfield shift expected at the alkene carbon from this conformational change (ca. 5 ppm)[23] is probably offset by the increased localization of backbone π-electrons which should move the red-phase alkene carbon resonance upfield by a similar amount. (For the alkyne carbon, Δδ ^{13}C 102.9–107.6 = −4.7 ppm, presumably due to the same localization of backbone π-electrons in the red phase of poly(4BCMU)).

The absence of a change in the chemical shift of the urethane carbonyl resonance upon heating to 90 °C suggests that intramolecular hydrogen-bonded side chains are retained in the red phase. If a significant weakening of the hydrogen bonds were to accompany the thermochromic phase transition in poly(4BCMU), then we would have expected[35] to see a several parts per million shift in the urethane carbonyl carbon resonance and not the 0.1 ppm difference actually observed. Retention of the poly(4BCMU) side chain hydrogen bonding through the thermochromic transition is consistent with the observations[19,20,38] made on poly(ETCD) by solid-state NMR and infrared measurements but disagrees with the conclusion of an infrared study[30] performed on poly(4BCMU).

The chemical shifts of the β and γ side chain methylene carbons in toluene-d_8 and $CDCl_3$ were 27.1 and 30.7 ppm and 26.7 and 30.2 ppm, respectively. These chemical shifts are close to those observed in solid poly(4BCMU) at 90 and 140 °C, respectively. In the toluene-d_8 red gel, no resonance was observed for the α methylene carbon using the Zens solution probe suggesting greater side chain rigidity in this solvent compared to $CDCl_3$. Urethane carbonyl carbon resonances were observed at 159.1 (toluene-d_8) and 158.4 ($CDCl_3$) ppm. In $CDCl_3$, hydrogen bonds that are weaker, or partially converted to intermolecular hydrogen bonds, or rapidly breaking and reforming may explain the 0.7 ppm upfield shift observed in this solvent. Because[35] the urethane carbonyl carbon chemical shifts in both solvents are very close to those observed in the solid for virgin poly(4BCMU), it does not appear, as suggested by Babbitt and Patel,[12] that the hydrogen-bonded network of side chains is disrupted in solution. Retention of the side chain hydrogen bonds in both the red gel and yellow–orange solution states argues against a trans to cis isomerization of double bonds description[17,18] of the rod to coil transition.

The overall results suggest that the mechanisms for the chromism in poly(4BCMU) in the solid and in solution are essentially similar. The backbone is transformed to an increasingly nonplanar structure, with a greater degree of π-electron localization, and leads to the color change from red to yellow. In the solid state, thermal energy drives the transition, while the solvent quality induces the transition in solution.

Summary and Conclusions

The as-polymerized blue phase of poly(4BCMU) was found to be similar to other blue-phase polydiacetylenes,[14] especially poly(ETCD).[19-21] As in poly(ETCD),[19,20] the thermochromic transition of poly(4BCMU) is characterized by an increase in π-electron localization along the backbone[11,14] and a conformational change in the side chain between the backbone and the hydrogen-bonded urethane group. The bonds between the α, β, γ, and δ methylene groups are transformed from a $gt\bar{g}$ conformation to the ttt conformation, probably aided by the increased thermal motion of the side chains.

Theoretical calculations[41] suggest that a change in side chain conformation may cause small changes in the bonding geometry of the backbone as a result of small changes in the bond lengths, bond valence angles, or bond rotation angles. Though these geometric changes may be small, the strain they may produce on the backbone can cause large changes in the distribution of π-electrons along the backbone.[41,42] Such a change in electron distribution was evidenced[11,14,19,20] by the change in the chemical shift of the alkyne carbon from 107.6 to 102.9 ppm. As suggested previously, the strain placed on the backbone by the conformational alteration of the side chain is manifested by equal and opposite small counterrotations about the backbone $\equiv$C—C$=$ single bonds.

Two alkyne carbon resonances are observed in poly(4BCMU) cooled from 90 °C. A melt-recrystallized and amorphous phase may have side chains with less and more flexibility, respectively, than those in the red phase. Compared to the red phase, this would place less and more strain on the backbone leading to two alkyne carbon resonances that are shifted downfield and upfield, respectively, from the single red-phase resonance.

The $CDCl_3$ solution of poly(4BCMU) and solid poly(4BCMU) at 140 °C are similar in several respects. They share a yellow color, suggesting similar electronic structures for their backbones. Hydrogen bonding also appeared comparable on the basis of their similar urethane carbonyl carbon chemical shifts. Thermal energy at 140 °C provided the side chains with increased mobility, and solvation of the side chains with the thermodynamically good solvent $CDCl_3$ also produced an increased mobility that permitted the observation of the poly(4BCMU) chains by solution NMR. The greater flexibility of the side chains in $CDCl_3$ solution placed greater strain on the backbone and would account for the upfield shift of the alkyne resonance compared to the red toluene-d_8 gel.

The ^{13}C NMR spectra of the toluene-d_8 red gel of poly(4BCMU) displayed similarities to spectra of the red phase after cooling down to room temperature from 90 °C. Chemical shifts of the α, β, γ, and δ methylene and urethane carbonyl carbons in the red gel were very similar to those in the solid at 90 °C. The red gel alkyne carbon showed two resonances similar to the solid-state spectrum observed after cooling from the red phase at 90 °C. Just as the two solid-state alkyne resonances were attributed to different morphologies (amorphous and ordered) produced by partial melting, different degrees of delocalization (extent of planarity) within the gel aggregates of poly(4BCMU) molecules may explain the two alkyne resonances observed there. Aggregate exteriors, with their greater exposure to solvent, may have more mobile side chains. This increased side chain flexibility would place more strain on the exterior poly(4BCMU) backbones and result in an alkyne resonance displaced from those alkyne carbons residing in the interior of the gel aggregates. The addition of a nonsolvent decreases the mobility of the polymer backbones and thus leads to increased planarity. However, this single chain effect continues only up to a point, after which some aggregation of the chains occurs. The two alkyne resonances observed in the gel state signify this process. The chromism we observe in poly(4BCMU) solutions is neither a purely single chain phenomenon nor just an aggregation effect but likely a combination of both.

It is hoped that the present study has demonstrated the utility of high-resolution, solid-state ^{13}C NMR spectroscopy in pursuit of the structures, conformations, and mobilities of the soluble polydiacetylene poly(4BCMU).

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^{13}C Solid-State NMR Study of the Interfacial Region in Glass-Filled Polyamide-6 Composites

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ABSTRACT: ^{13}C-labeled (γ-aminopropyl)triethoxysilane (γ-APS) has been used to enhance the sensitivity and selectivity of solid-state ^{13}C NMR in an investigation of the interfacial region of microcomposite samples composed of polyamide-6 (PA6), glass microspheres, and γ-APS. As the interphase is crucial in determining the properties of a composite, we have focused our attention on this region with the goal of elucidating the adhesion mechanism. From the MAS spectra, some indication has been obtained for the occurrence of amide formation between the PA6 carboxylic acid end groups and the amines of γ-APS, but the evidence is not overwhelmingly strong. Several relaxation times, i.e., T_1 (^{13}C), T_2(^{13}C), $T_{1\rho}$ (^1H), $T_{1\rho}$(^{13}C), and T_{IS}($^1H \rightarrow {}^{13}C$), of both γ-APS and PA6 have been studied as a function of sample composition, and their behavior can be explained on the basis of the presence of entanglements and interpenetration of the polysiloxane and polyamide networks. So the interpenetrating network mechanism and presumably also chemical bonding contribute to the adhesion between the PA6 matrix and γ-APS.

Introduction

The use of organosilane reagents to modify inorganic surfaces has found widespread application in reinforced polymer composites. These reagents have been reported to give a composite of better mechanical and electrical properties, to give enhanced resistance to ingress by chemicals, and also to improve rheological properties.[1-4]

Several spectroscopic techniques have been applied to study these composite systems including FT-IR, Raman, NMR, and ESCA.[1,2,5,6] However, the small relative volume of the interfacial region often results in it being obscured by the bulk of the filler and/or polymer in spectroscopic measurements. To avoid this problem, various strategies have been explored including radioisotopic labeling of the coupling agent,[7] isolation of the filler from the composite,[8] examining interdiffusion of protonated and deuterated polymers with secondary ion mass

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