Bull. Chem. Soc. Jpn., ***68***, *791—802(1995)*

High-Resolution Solid-State ^{13}C NMR Studies on Molecular Motions and Solid-State Polymerization of Octatetraynes

Kikuko Hayamizu,* Shuji Okada,† Takanori Doi,†† Hajime Kawanami,† Naoto Kikuchi, Hiro Matsuda, and Hachiro Nakanishi†

National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305

†Institute for Chemical Reaction Science, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-77

††Toda Kogyo Corp., Ltd., 1-4 Meijishinkai, Otake, Hiroshima 739-06

(Received October 7, 1994)

The effects of monomer alignment on the solid-state polymerizations of five octatetraynes and a butadiyne to produce polydiacetylenes were studied. Structural relaxations of the resulting polymers were found to occur over long time intervals. Solid-state high-resolution ^{13}C NMR spectra were observed for six symmetrical monomers having alkyl chains ($C_{14}H_{29}$) and side chains containing either urethane or *p*-toluenesulfonate and the derived polydiacetylenes (PDA's). The spin-lattice relaxation times (T_1) of the PDA's were also measured. The alignment and mobility of the monomers, which are closely related to the solid-state polymerizability and structure of the resulting polymers, are reflected in the solid-state ^{13}C NMR spectra of the monomers.

The PDA's with urethane side chains were found to have slow structural relaxation. When the number of spacer methylenes between the acetylenic carbon and the urethane moiety is odd, a planar main-chain structure was assumed. It was found that PDA-4A's having an odd number of spacer methylenes achieved a more homogeneous structure after long-term relaxation than a PDA-4A with an even number of spacer methylenes.

Polydiacetylenes (PDA's) are known to be one of the most important materials having third-order nonlinear optical properties and have thus attracted much interest.[1)] At the same time, PDA's are especially interesting polymers because they can be synthesized by topochemical solid-state polymerization initiated by UV or γ-ray irradiation or a thermal treatment.[2—4)] Since the monomer topological structure is assumed to determine the polymerizability, the crystal structures of typical monomers and polymers have been investigated.[5—8)] The structures of the polymers have also been studied by ^{13}C NMR in both solution and solid state.[9—17)] Also, structural and conformational changes have been studied for thermal phase changes between the red and blue phases.[12—16)] However, studies concerning the molecular motions of the monomer has been rare.

We have synthesized several new classes of PDA's having conjugated side groups directly bound to the main chain. One class has aromatic rings directly bound to the main chain,[18,19)] while another class has an acetylenic moiety directly bound to the main chain system.[20—30)] To examine the roles of the conjugation of the acetylenic bonds and the long side chains on the nonlinear optical property, a butadiyne (2A), a triyne (3A), octatetraynes (4A's) or a dodecahexyne (6A) with various chains have been studied. The structures of the side chains and the length of the conjugation are important in determining the possibility of topochemical solid-state polymerization. The structural changes during the solid-state polymerization shown in Fig. 1 were determined by high-resolution solid-state ^{13}C NMR spectra.[29)]

In the present study six monomers and the derived PDA's were studied for a 2A and five 4A's symmetrically substituted by the C_{14} alkyl chain (14-2A and 14-4A), by chains with the urethane moiety (4BCMU-4A, 5BCMU-4A, and 5ECMU-4A) and by *p*-toluenesulfonate (PTS12-4A), as shown in Fig. 1. These monomers were confirmed to undergo solid-state polymerization in the scheme of 1,4-addition, as shown in Fig. 1, after either γ-ray irradiation or a thermal treatment. As already reported in our previous papers,[25,26,28,30)] the conjugated acetylenic carbons in the side chains of the polymer induce further polymerization to produce fused-ring structures at higher temperatures in 4A's and at ambient temperature in 6A. The ^{13}C NMR spectra were measured with different modes, such as cross-polarization (CP) or single pulse excitation (SE) with ^{1}H decoupling under magic-angle spinning (MAS) methods. The ^{13}C spin-lattice relaxation times (T_1) of the

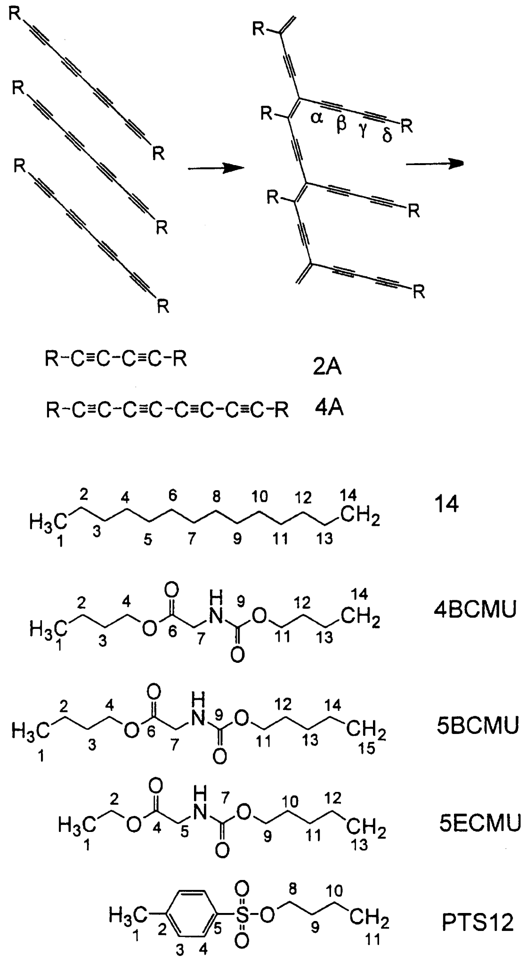

Fig. 1. The solid-state polymerization scheme of octatetrayne compounds, and the side chain structures of the compounds discussed in this paper.

polymers were also measured, and the molecular motions of the monomers and polymers studied. It was found that the alignments and molecular motions of the monomers have a close relationship with the efficiency of the solid-state polymerization. The polymer structures were found to gradually relax to more stable forms after the solid-state polymerization.

Experimental

Preparation of the Monomers and Solid-State Polymerization. The syntheses of 14-2A (15,17-dotriacontadiyne, mp 50—51 °C),[20] 14-4A (15,17,19,21-hexatriacontatetrayne, mp 78—79 °C),[21] 4BCMU-4A (5,7,9,11-hexadecatetrayne-1,16-diyl bis[*N*-(butoxycarbonylmethyl)carbamate], mp 85—87 °C),[26] 5BCMU-4A (6,8,10,12-octadecatetrayne-1,18-diyl bis[*N*-(butoxycarbonylmethyl)carbamate], mp 87—88 °C),[29] 5ECMU-4A (6,8,10,12-octadecatetrayne-1,18-diyl bis[*N*-(ethoxycarbonylmethyl)carbamate], mp 94—98 °C),[31] and PTS12-4A (5,7,9,11-hexadecatetrayne-1,16-diyl bis(*p*-toluenesulfonate), mp 93—94 °C)[27] were reported in our previous papers. Solid-state polymerization was carried out under the previously reported conditions, and completed almost quantitatively, except for 14-2A and PTS 12-4A, where the polymer yields were 57 and 70%, even after exposing to γ-ray irradiation of 0.5 and 0.3 MGy, respectively.

^{13}C NMR Measurement. Solid-state high-resolution ^{13}C NMR spectra were recorded on a JEOL GSH-200 spectrometer operating at 50.23 MHz. The diameter of the NMR rotor was 7 mm and was made of zirconium oxide with a Vespel (a polyimide) bottom and a Kel-F (poly(chlorotrifluoroethylene)) cap. For elevated temperature measurements and keeping samples within the rotor at ambient temperature, a Vespel cap was used. The solid-state ^{13}C spectra were observed with ^{1}H decoupling under MAS. The MAS speed was about 4.5 kHz. Under the CP condition, the ^{1}H 90°pulse was 4.2 μs and the CP time was 3 ms. To obtain different motional states, three measuring methods were adopted: the usual CPMAS mode to measure the spectra of the solid state, the dipole-dephasing CPMAS (CPMAS/DD) mode to measure the quaternary and mobile carbons and the single-pulse excitation (SEMAS) mode to measure the very mobile carbons. The ^{13}C shifts were referred to the CH_2 peak of external adamantane at 29.5 ppm from TMS.[32] The spin-lattice relaxation times were measured for each carbon under the CP-condition.[33] To obtain the T_1 values, the relaxation curves were analyzed for both the monomer and polymers, except for poly(PTS12-4A), for which the null-point method was adopted.

Solution-state ^{13}C NMR spectra of the monomers in $CDCl_3$ were observed and assigned by using our spectral data-base system (SDBS-NMR),[34,35] in which the spectral patterns are available.

Results and Discussion

The initial spectral assignments of the solid-state ^{13}C NMR spectra were made based on the solution spectra. When the signals of the acetylenic carbons were overlapped by those of the CH_2O carbons, the ^{13}C shift values were obtained from the CPMAS/DD spectra, in which only quaternary and mobile carbons were observed. The assignments of the solid-state spectra were confirmed from SEMAS measurements, in which the intensities of the side-chain carbons decreased according to the distances from the terminal.

14-2A and 14-4A. The CPMAS and SEMAS ^{13}C NMR spectra of the 14-2A monomer are shown in Fig. 2. The ^{13}C chemical shift values are given in Table 1, where the differences between the solution and SEMAS spectra and those between the SEMAS and CPMAS spectra are included. The SEMAS spectrum given in Fig. 2(b) is very sharp, and the spectral pattern is almost the same as the solution spectrum (see Table 1). In the CPMAS spectrum, the acetylenic carbon signals are broad and do not include the sharp components observed in the SEMAS spectrum. However, some of the alkyl carbon signals split into two components, and the positions of the higher field peaks agree with those of the peaks in the SEMAS spectrum. Then, the alkyl carbons having two modes of molecular motions were observed in the CPMAS spectrum. The broad signal at 34 ppm can be assigned to the long alkyl chain carbons in the stack state.[36] The CPMAS spectrum includes the

Table 1. Solution- and Solid-State ^{13}C Shifts of 14-2A Monomer (ppm)

No.$^{a)}$	Carbon	Solution	SEMAS	CPMAS
16	≡C–	65.4	66.8(1.4)$^{b)}$	65.0(−1.8)$^{c)}$
15	–C≡	77.5	76.8(−0.8)	78.7(1.9)
14	CH_2	19.3	20.0(0.7)	20.0—22.1(0—2.1)
4—13	$(CH_2)_{10}$	29.7—28.5$^{d)}$	30(1.5—0.3)	30.5 34(4)
3	CH_2	32.0	31.7(−0.3)	d)
2	CH_2	22.7	23.6(0.9)	23.4(0) 25.7(2.1)
1	CH_3	14.1	14.7(0.6)	14.7(0) 15.4(0.7)

a) The numbering of the atom from the terminal methyl carbon. b) The differences from the solution spectrum. c) The differences from the SEMAS spectrum. d) Overlapped.

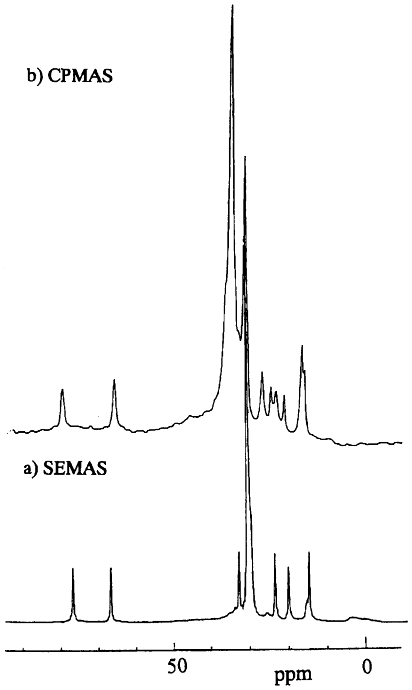

Fig. 2. The solid-state ^{13}C NMR spectra of 14-2A monomer measured by (a) CPMAS and (b) SEMAS modes. The CP time was 3 ms and the pulse repetition time was 5 s for the CPMAS measurement and the pulse width for the single excitation was about 90° and the pulse repetition time was 10 s for the SEMAS measurement.

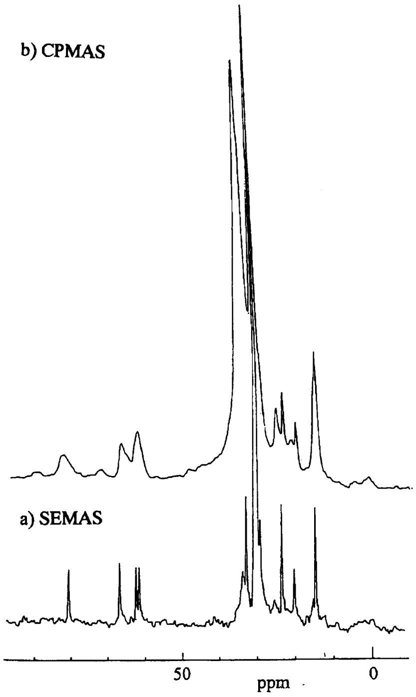

Fig. 3. The solid-stare ^{13}C NMR spectra of 14-4A monomer measured by (a) CPMAS and (b) SEMAS modes. The CP time was 5 ms and the pulse repetition time was 10 s for the CPMAS measurement and the the pulse width for the single excitation was 90° and the pulse repetition time was 30 s for the SEMAS measurement.

alkyl carbon signals in the rigid and mobile states and the immobile acetylenic carbon signals. A comparison between the CPMAS and SEMAS spectra suggests that rapidly moving molecules exist in more rigid crystal of 14-2A.

The CPMAS and SEMAS ^{13}C NMR spectra of 14-4A are shown in Fig. 3, and the ^{13}C shift values are given in Table 2. In these spectra, similar effects to those of 14-2A are noted. The number of the acetylenic conjugated bonds is twice that of 14-2A, and rapid molecular motions can be assumed for 14-4A in the solid state. Although the molecular diffusion is possible in the solid state, there is no evidence that these compounds have liquid crystalline states, as has been reported for acetylenic and diacetylenic compounds.[37—40] As previously reported,[30] 15,17,19,21,23,25-tetracontahexayne (14-6A) is very reactive at ambient temperature and undergoes rapid solid-state polymerization. Since the alkyl chains are the same for 14-2A, 14-4A, and 14-6A, the different reactivities and conversion rates for the solid-state polymerization originate from the length of the conjugated acetylenic moieties.

Table 2. Solution- and Solid-State ^{13}C Shifts of 14-4A Monomer (ppm)

No.[a]	Carbon	Solution	SEMAS	CPMAS
18	-C≡	60.7	61.5(0.8)[b]	62(0.5)[c]
17	≡C-	61.5	62.4(0.9)	62(−0.4)
16	-C≡	65.8	66.8(1.0)	67(0.2)
15	≡C-	80.5	80.5(0)	82(1.5)
14	CH_2	19.5	20.2(0.7)	20.2(0)
				22(ca.2)
13	CH_2	28.0	29.0(1.0)	d)
4—12	$(CH_2)_9$	29.7—28.9[d]	30.5(0.8—1.6)	30.6
				34
			33.4	
3	CH_2	32.0	32.7(0.7)	d)
2	CH_2	22.7	23.4(0.7)	23.5(0.1)
				25.3(1.9)
1	CH_3	14.1	14.7(0.6)	15.3(0.6)

a) The numbering of the atom from the terminal methyl carbon. b) The differences from the solution spectrum. c) The differences from the SEMAS spectrum. d) Overlapped.

The CPMAS spectra of poly(14-2A) and poly(14-4A), measured about one year after γ-ray irradiation, are shown in Fig. 4. During this period, the samples were kept in NMR rotors at ambient temperature. The spectral assignments are shown in the figure; the large displacement in the ^{13}C shifts between the two olefinic carbons in the main chain was discussed in detail in a previous paper.[23] The broad peaks between 140 and 110 ppm in poly(14- side chain 4A) indicate that the second-stage polymerization took place at ambient temperature during the long period.[24]

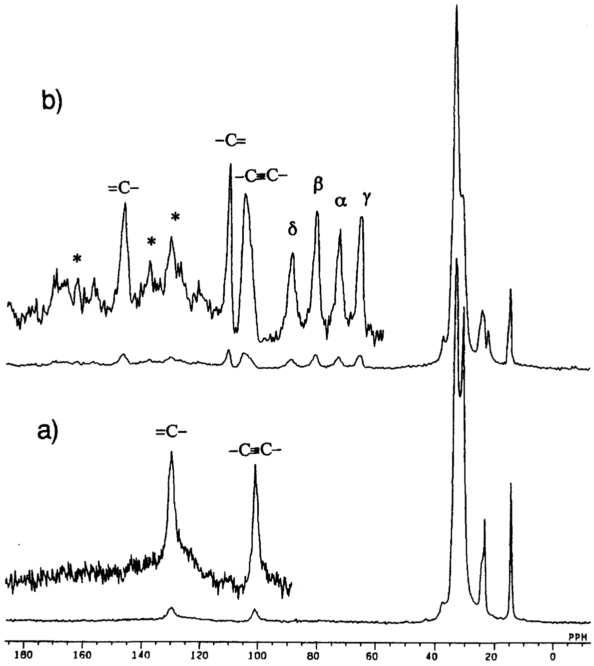

Fig. 4. CPMAS ^{13}C NMR spectra of (a) poly(14-2A) and (b) poly(14-4A) measured about one year after the γ-ray irradiation. The asterisks denote the signals of polymers due to second-stage polymerization induced by the conjugated acetylenic carbons in the side chains.

The ^{13}C shifts and T_1 values measured at the same time are summarized in Table 3. As shown in Fig. 1, poly(14-4A) has two different alkyl chains: one attached to a acetylenic carbon and the other directly attached to the main-chain olefinic carbon. Actually, there are different resonances of CH_2, depending on whether it is attached to C= and C≡ ; the other carbons of the alkyl chains, however, give no distinguishable peaks, depending on the different side chains. Both polymers give two peaks for the long alkyl chains at about 34 and 30.5 ppm, and the T_1 values of the lower field peaks for the stack carbons are much longer than those of the higher field peaks. Generally, the T_1 values in the solid-state ^{13}C NMR are proportional to correlation times of motions for the dipolar relaxing phenomena, then longer T_1 corresponds to more rigid state. In poly(14-2A), however, the T_1 values become longer approaching the terminal carbons, indicating the segmental motions of the alkyl chains satisfy the extreme narrowing limit, where $\tau_0\omega_0 \ll 1$ holds, τ_0 the correlation time of the segmental motion and $\omega_0/2\pi$ the measuring RF frequency, and $1/T_1$ is proportional to τ_0. The T_1's of poly(14-2A) fit this condition, but not poly(14-4A).[17] Thus poly(14-2A) is more flexible than poly(14-4A). The motion of the side-chain carbons accelerate the relaxation of the main chain carbons. The shorter T_1 values of poly-(14-2A) compared to poly(14-4A) can be explained by the faster motions of the pendant side chain carbons. The ^{13}C NMR spectra of the polymers were repeatedly observed over two years. Little change of the ^{13}C spectral patterns was observed for either polymer one year after γ-irradiation except for partial polymerization of the acetylenic side chains of poly(14-4A). This indicates that nearly stable structures were formed just after the solid-state polymerization.

Table 3. ^{13}C Shift and T_1 of Poly(14-2A) and Poly(14-4A)

No.[a]	Carbon type	^{13}C shift (ppm)		T_1 (s)	
		2A	4A[d]	2A	4A[d]
Main chain	=$\underline{C}$–CH$_2$	130.0	146.3	41	145
Main chain	–$\underline{C}$≡$\underline{C}$–	100.9	105 103[b]	38	131
Main chain	=$\underline{C}$–C≡	—	110.2	—	103
18	≡C– α	—	72.6	—	113
17	–C≡ β	—	80.7	—	117
16	≡C– γ	—	65.1	—	145
15	–C≡ δ	—	88.7	—	103
14	$\underline{C}$H$_2$C=	37.0	37.3	c)	c)
14	$\underline{C}$H$_2$C≡	—	22.3	—	87
3—13	CH$_2$ chain	33.4	33.7	3.5	70
		30.6	31.3[b]	0.5	7
2	CH$_2$	23.4	24.4	1.2	12
1	CH$_3$	14.4	14.8	2.8	3

a) The numbering of the atom from the terminal methyl carbon. b) Shoulder. c) The intensities are small. d) Ref. 23.

4BCMU-4A. The number of spacer methylenes between acetylenic carbon and the urethane moiety is four in 4BCMU-4A and the crystal structure of poly(4BCMU-2A) indicates intramolecular hydrogen bonds between the urethane groups in adjacent substituents.[8] Thus intermolecular hydrogen bonding between the urethane groups in the 4BCMU-4A monomer can be assumed by an analogy from poly(4BCMU-2A). The solid-state ^{13}C NMR spectra of 4BCMU-4A measured just after recrystallization by the (a) SEMAS, (b) CPMAS/DD, and (c) CPMAS modes are shown in Fig. 5. The spectral assignments are given in the spectra and the ^{13}C shift values obtained from these spectra are summarized in Table 4. The ^{13}C shift differences induced by solidification are generally not large. In the SEMAS spectrum in Fig. 5(a), signals from ten carbons were observed including the two carbonyl carbons among the eleven side-chain carbons; the relative intensities gradually decrease with the position from the terminal methyl group. In the CPMAS/DD spectrum in Fig. 5(b) for the signals of quaternary and mobile carbons, the acetylenic carbon peaks are clearly distinguishable. The splittings of the signals, especially for the peaks at 81 ppm from the α acetylenic carbon connected to a methylene, indicate that there are different conformations in the solid state, probably due to the various intermolecular hydrogen-bonded arrangements. Segmental motions of the side chains are possible in 4BCMU-4A even if an intermolecular hydrogen bonds exist as suggested in 4BCMU-2A.[8] The broadenings of the signals for CH$_2$NH (43 ppm) and HNC=O (157 ppm) in Fig. 5(c) are due to the quadrupole effect from the nitrogen atom.[41] The acetylenic carbon signals in the SEMAS spectrum were not observed, indicating little molecular diffusion in solid state, which is in contrast to 14-2A and 14-4A.

To observe the stability of the monomer structure and the possibility of thermal polymerization, the ^{13}C NMR spectra of the monomer were observed at ambient temperature for three days. Small main-chain carbon signals were observed at the positions of the polymer obtained by γ-ray irradiation, indicating that polymer for-

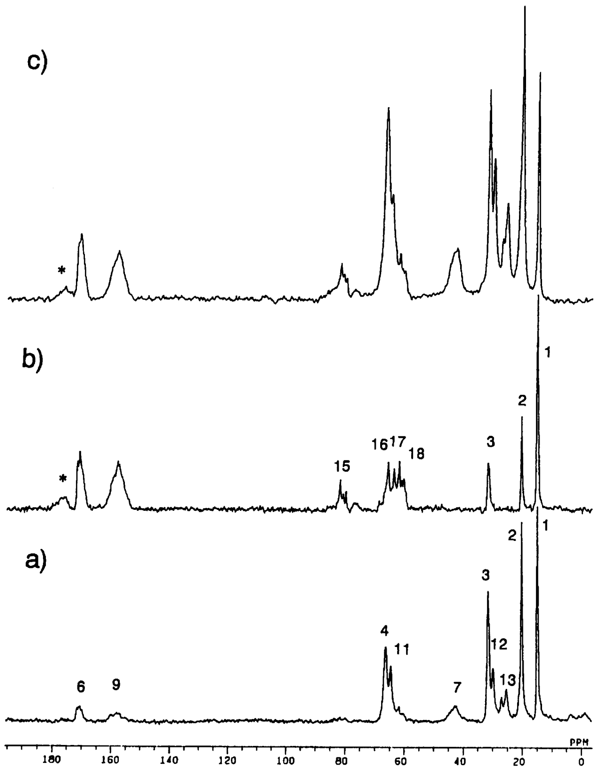

Fig. 5. The solid-state ^{13}C NMR spectra of 4BCMU-4A monomer measured by (a) SEMAS, (b) CPMAS/DD, and CPMAS modes. The numbering of the signals correspond to the carbons labelled from the terminal methyl carbon. The asterisks denote spinning side bands.

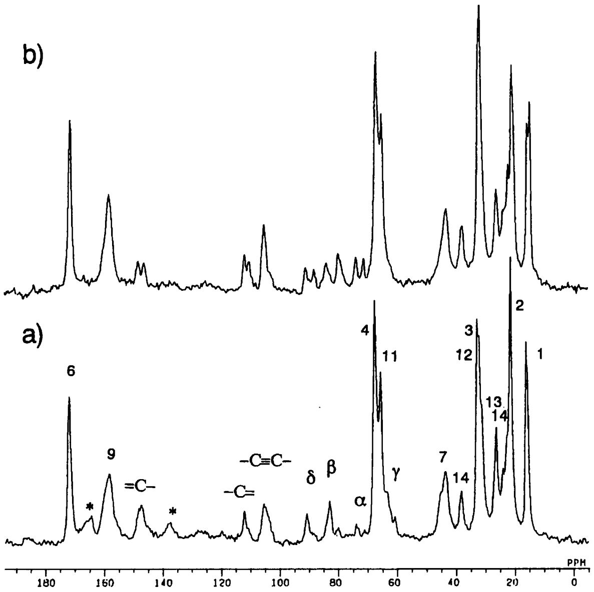

Fig. 6. The CPMAS spectra of poly(4BCMU-4A) measured (a) just after the γ-ray irradiation and (b) after one year. The asterisks denote back ground signals.

mation proceeded slowly at ambient temperature. The sample temperature was gradually increased to 50 °C and held for four days, then the intensities of the polymer signals increased, and the monomer signals still remained. However, after more than one month, no monomer signal was observed and the polymerization was completed. The ^{13}C signal positions of the polymer obtained by a thermal treatment are similar to those obtained by γ-ray irradiation. In the spectrum the signals of the mian-chain and the acetylenic carbons, two carbonyl, and CH_2NH carbons were broad, while the other side-chain methylene or methyl signals were sharp.

The CPMAS spectrum of poly(4BCMU-4A) just after γ-ray irradiation is shown in Fig. 6(a). The signals were well separated and spectral assignments were possible for each carbon. The signal of the α acetylenic carbon attached to the main chain was small. Although the side-chain methylene signals were sharp over the next several days, the signals of the main-chain and the acetylenic carbons in the side chain began to broaden and for several months they were broad, especially the signals of the side-chain acetylenic carbons spread out (not shown in Fig. 6). Gradually the acetylenic carbon resonances became sharper and resolved into doublets and the spectrum observed after fifteen months is shown in Fig. 6(b). The split signals of the main chain and the conjugated moiety indicate that there are two conformations with approximately equal populations. The ^{13}C shifts measured just after the γ-ray irradiation and the equilibrium stage are given in Table 4. Comparing each signal position, the higher field signals appeared later and are assigned to the more stable conformer. Little change of the spectral pattern was observed over the subsequent two years except for the appearance of broad signals accompanied by further polymerization of the side-chain acetylenic carbons.[26] The aged sample of the polymer obtained by the thermal treatment described above gave the ^{13}C signals at the same positions, though the relative intensities of the split signals were different and the lower side signals were larger. Thus the ratio of the two conformations changes depending on the conditions of polymerization and the process of structural relaxation. The manner of the hydrogen-bonds in the monomer remained just after the solid-state polymerization. The reformation of the hydrogen bonded structure in the polymer was necessary to approach the equilibrium form, where at least two different conformations for the main chain and the conjugated side band were produced.

It is known that poly(4BCMU- 2A) undergoes solid-state thermochromic transitions and solid-state ^{13}C NMR spectra were reported for the both phases,[15] where at higher temperatures, the higher field ^{13}C shifts and the shorter T_1's were observed for the flexible red phase. The different main-chain structures between poly(4BCMU-4A) and poly(4BCMU-2A) make a direct comparison of the ^{13}C shifts values difficult, though the ^{13}C shifts of 157.7 and 170.0 ppm for the two carbonyl carbons in poly(4BCMU-4A) correspond to those of poly(4BCMU-2A) at 140 °C in the melt state. Since poly(4BCMU-4A) is reactive at elevated temperatures, thermochromic phenomena can't be observed. From the visible absorption spectrum, poly(4BCMU-4A) was found to be in the blue phase at ambient temperature.[26] Since the electronic states mainly determine the optical properties, well-conjugated electric structures in poly(4BCMU-4A) are related to the blue phase, though the randomness of the side-chain structures have a similarity to the phase of poly(4BCMU-2A) at elevated temperature.

The spin-lattice relaxation times were measured for the sample four months after the polymerization and are given in Table 4. At that time we didn't know that the long-term structural relaxation exists for this polymer. The main-chain carbons have very long T_1's similar to that of poly(14-4A),[17] which contain no fast relaxing component. Since the side-chain acetylenic carbon signals were broad, the T_1's were difficult to determine. The relaxation curves of the side chain methylenes remote from the terminal and carbonyl carbons were not single exponential, and one component is very long and the other is rather short. This can be explained that there are two components having different mobility's, even if the ^{13}C shifts are the same. From the chemical structure of poly(4BCMU-4A), there are two different side chains: one is attached to the main-chain olefinic carbon and the other is bound to the side-chain acetylenic carbon. There is no evidence that the two side chains behave in a different manner for all of the 4A-polymers as described later. The terminal methyl and

Table 4. The ^{13}C Shift and T_1 of the Monomer and the Polymer of 4BCMU-4A

		Monomer		Polymer			
		Solution	Solid	^{13}C shift (ppm)		T_1 (s)	
No.[a]	Carbon			Just after[b]	15 months after[c]		
Main chain	$=\underline{C}-CH_2$			146.6	147.7	150	
					145.6		
Main chain	$-\underline{C}\equiv\underline{C}-$			104.5	104.7	160	
Main chain	$=\underline{C}-C\equiv$			111.4	111.2	70	
					109.5		
18	$\equiv C-$ α	60.78	60.3(−0.5)[d]	73	73.4		
			61.2(0.2)		70.8		
17	$-C\equiv$ β	61.35	61.8(0.4)	82.2	83.6		
					79.6		
16	$\equiv C-$ γ	66.17	65.6(−1.4)	65	66.0		
			63.6(−2.6)		62.6		
15	$-C\equiv$ δ	79.69	79.9(0.2)	90.0	90.4		
			80.8(1.1)		87.5		
			81.8(2.1)				
14	$CH_2C=$			37.4	37.4	45	
14	$CH_2C\equiv$	19.15	21.0(1.8)	22	21.6	e)	
13	CH_2	24.43	25.4(1.0)	25.4	25.8	70	23
			26.9(2.5)		22.8		
12	CH_2	28.07	30.0(1.9)	31.8	32.3	e)	
11	OCH_2	64.48	64.6(0.1)	64.8	64.7	90	1.1
9	C=O	156.43	157.5(1.1)	157.5	157.7	140	20
7	CH_2-NH	42.70	42.8(0)	42.8	42.7	28	12
6	C=O	170.18	170.7(0.5)	171.1	170.0	100	10
4	CH_2O	65.36	66.4(1.0)	66.7	66.7	45	2.5
3	CH_2	30.53	31.8(1.3)	31.8	31.5	—	0.7
2	CH_2	19.04	20.6(1.6)	20.7	20.6	—	0.6
1	CH_3	13.67	15.3(1.6)	15.3	15.3	—	1.3
					14.3	—	2.7

a) The numbering of the atom from the terminal methyl carbon. b) Measured just after γ-ray irradiation. c) Measured about 15 months after the solid-state polymerization kept at ambient temperature. d) The differences from the solution spectrum. e) Overlapped.

the succeeding methylene carbons have short T_1's with a single component, indicating free segmental motions in the extreme narrowing condition. A precise measurement of T_1 was not repeated thereafter, though an attempt was made one year after the polymerization to obtain T_1's of the side-chain acetylenic carbons related to poly(14-4A).[17] Although it was difficult to precisely determine the long T_1's from the split signals, they had long T_1's of similar magnitude as those of the main-chain carbons. Recently, the measurement was repeated for the sample containing a small amount of complex polymers in the second stage reported in the previous paper,[28] and found that the null points of the relaxation curves for the spacer methylene signals became slightly shorter which corresponds to shorter T_1's, though components having longer T_1 existed about three years after the polymerization. Generally, the T_1 values of poly(4BCMU-4A) are longer than those of poly(4BCMU-2A) in any phase. This may represent a general trend of poly(4A)compared to poly(2A), as seen for poly(14-4A) and poly(14-2A).

5BCMU-4A. From the chemical structures of the urethane derivatives, compounds having an odd number of the spacer methylenes between the acetylenic and the urethane group can be assumed to be more effective in maintaining the main-chain planar structure than compounds with an even number of spacers. 5BCMU-4A has five spacer methylenes and its ^{13}C CP-MAS NMR spectrum is shown in Fig. 7 and the ^{13}C shifts are given in Table 5. The fine structures of the signals of the acetylenic carbons are smaller than that of 4BCMU-4A. Thus in the solid state the monomer can be assumed to be in a more homogeneous state. The differences of the ^{13}C shifts between the solution and the solid states are larger than those of 4BCMU-4A. In particular, the spacer methylene carbons have large low field shifts of 3 ppm. Hence the monomer in the solid can be assumed to form uniform and stable intermolecular hydrogen bonds.

The CPMAS spectrum of poly(5BCMU-4A) measured about six months after γ-irradiation is shown in Fig. 7(b) and the ^{13}C shifts are given in Table 5. Although no splitting of any signal was observed in this spectrum, in the spectrum acquired just after solid-state polymerization the side-chain acetylenic carbons gave broad, split signals. The changes in the ^{13}C shifts

Table 5. The ^{13}C Shift and T_1 of the Monomer and the Polymer of 5BCMU-4A

No.[a)]	Carbon	Monomer		Polymer	
		Solution	Solid	^{13}C shift (ppm)	T_1 (s)
Main chain	$=\underline{C}-CH_2$			146.5	100
Main chain	$-\underline{C}\equiv\underline{C}-$			104.0	70
Main chain	$=\underline{C}-C\equiv$			109.8	70
19	$-C\equiv$ α	60.73	61.8(1.1)[b)]	71.6	70
18	$\equiv C-$ β	61.38	62.3(0.9)	80.3	70
17	$-C\equiv$ γ	65.98	65.2(−0.8) 66.2[c)]	62	—
16	$\equiv C-$ δ	80.01	82.0(2.0) 83.5[c)]	89	70
15	$CH_2-C=$		—	36.7	15
15	$CH_2-C\equiv$	19.40	21.5(2.1)	21.3	15
14	CH_2	27.56	30.6(3.0)	30.8	0.6
13	CH_2	25.10	26.7(1.6)	27.3	2
12	CH_2	28.39	31.7(3.3)	30.8	2
11	CH_2O	65.00	67.5(2.5)	66.9	5
9	$C=O$	156.50	157.4(0.7) 159.2(2.7)[c)]	158.7	15
7	$NH-CH_2$	42.71	43.8(1.1)	42.6	0.5
6	$C=O$	170.20	170.9(−0.7)	170.1	6
4	CH_2O	65.36	66.9(1.5)	64.9	1.5
3	CH_2	30.53	31.7(1.2)	31.5	0.6
2	CH_2	19.04	21.2(2.2)	20.0	0.8
1	CH_3	13.68	15.4(1.7)	14.3	1.0

a) The numbering of the atom from the terminal methyl carbon. b) The differences from the solution spectrum. c) Shoulder or smaller.

during the six months were as follows: 72 and 71 to 71.6 ppm for the α carbon, 83 and 80 to 80.3 ppm for the β carbon, no change for the γ carbon, and 89 and 86 ppm to 89.0 ppm for the δ carbon. These ^{13}C shifts values of the side-chain acetylenic carbons of poly(5BCMU-4A) before the structural relaxation are similar to those of poly(4BCMU-4A) after structural relaxation. For the other carbon signals, little change was observed during this time interval. The ^{13}C shifts of the carbons 1 to 6 in poly(5BCMU-4A) (see Table 5) have almost the same values as those of poly(4BCMU-2A) in the melt state, while the inner carbonyl and the adjacent OCH_2 (carbon 9 and 11) are the same as those of poly(4BCMU-2A) measured at ambient temperature. Thus the hydrogen-bonding in poly(5BCMU-4A) can be formed homogeneously rather than in poly(4BCMU-4A). More uniform polymer structures may bring wider space around the terminal carbons which accelerate faster motions similar to the melt state. 4BCMU-4A and 5BCMU-4A have two different OCH_2's and the outer one from the acetylenic moiety gave signals at the lower field side in both solution and solid states. After the polymerization, the same trend was observed for poly(4BCMU-4A), but the signal positions were interchanged in poly(5BCMU-4A).

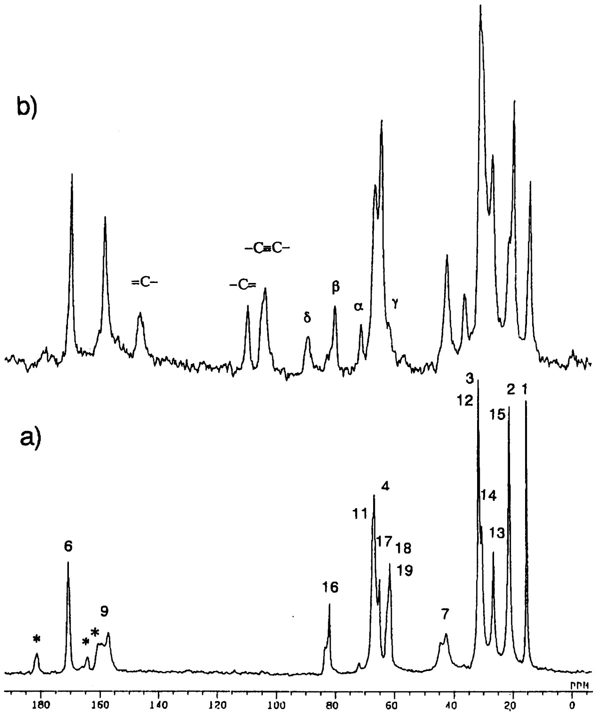

Fig. 7. The CPMAS spectra of 5BCMU-4A for (a) monomer and (b) polymer kept for one year after γ-ray irradiation. The asterisks denote spinning side bands.

The spin-lattice relaxation times were first measured about two weeks after the formation of the polymer and it was found that the T_1 values were changing during the measurement. Although precise values were difficult to determine, one example is the following: for the outer carbonyl carbon the relaxation curve was analyzed to have two components having T_1's of 27 and 11 s during the early stage of the experiment, and varied to a straight line of the T_1 being 6 s. The experiment was repeated after six months and the results are summarized in Table 5. All of the relaxation curves were analyzed as a single exponential and generally the T_1 values are shorter than that of poly(4BCMU-4A). The formation of the polymer of 5BCMU-4A occurs as follows: The monomer in the solid state is well aligned under the influence of intermolecular hydrogen bond at the inner carbonyl carbons and the spacer methylenes are rigid. The changes in the structure caused by the formation of the polymer brought alteration of the hydrogen-bond arrangements. To approach the stable structure, it took time on the order of months at ambient temperature. The relaxation curves are more sensitive to randomness of structure than the ^{13}C shift values and have multi-components with different T_1's. Since the homogeneous and planar structure of the main chain of the polymer brings some space around the side-chain carbons, the segmental motions can be accelerated in poly(5BCMU-4A). Since the ^{13}C T_1's of the PDA's are proportional to the correlation times of the molecular motions except for the terminal carbons, the faster segmental motions result in shorter T_1's of the carbonyl and the spacer methylene carbons.

5ECMU-4A. The number of spacer methylenes is five in 5ECMU-4A which is the same as 5BCMU-4A, though the terminal is an ethyl group instead of a butyl group in 5BCMU-4A. The CPMAS ^{13}C NMR spectrum of 5ECMU-4A monomer measured soon after the recrystallization is shown in Fig. 8(a). The splittings were clearly observed for signals of two carbonyl, methyl, acetylenic carbons attached to the methylene whose signal also splits. The split peaks shown almost the same intensities and imply the presence of two conformations of the 5ECMU-4A with different hydrogen-bonding arrangements in the solid state. Among five spacer methylenes except for the α-CH$_2$, four carbons gave single resonances. Upon solidification all of the spacer methylenes showed the large lower field ^{13}C shifts, suggesting a rigid alignment in the spacer part. Since the solidification shifts were larger for the 5ECMU-4A rather than for 5BCMU-4A or 4BCMU-4A, the formation of stronger hydrogen bonding can be assumed, which may be a reason for the high reactivity.

The polymerization of 5ECMU-4A proceeded at ambient temperature and completed in about one week. During the early stage of polymerization, the spectra showed overlapped patterns of the monomer and the polymer as is shown in Fig. 8. From the beginning, two carbonyl signals of the polymer were singlets and gradually the signals of the main chain carbons increased. After the polymerization was completed, the spectra were occasionally observed and slight changes in the spectral pattern were observed. The splittings of the signals of the monomer became negligible for the corresponding signals in the polymer, though new signals appeared for the side-chain β and γ acetylenic carbons split, and the spacing was smaller than that of poly(4BCMU-4A). The same ^{13}C shift values of the spacer methylenes in the monomer and the polymer suggest little change due to bonding structures. Thus the formation of the hydrogen bonds in the monomer plays an important role in the solid-state polymerization.

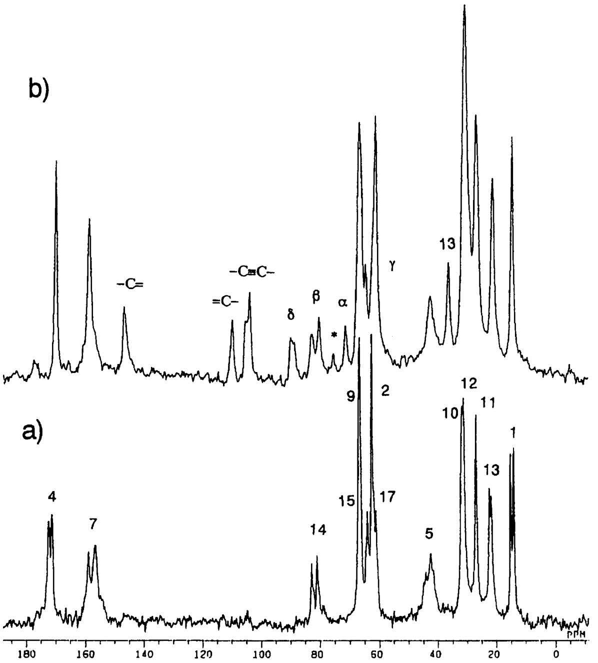

Fig. 8. The CPMAS spectra of 5ECMU-4A for (a) monomer and (b) polymer one year after the polymer formation.

The T_1's were measured about one year after the polymerization and are given in Table 6. As a general trend, the T_1's of poly(5ECMU-4A) are slightly longer than those of poly(5BCMU-4A). Since the spacer methylenes have the longer T_1's, the segmental motions are reduced, which may support the stronger formation of hydrogen bonds than in poly(5BCMU-4A). As a result the terminal carbons have longer T_1's in poly(5ECMU-4A) than poly(5BCMU-4A), while the T_1's of the main-chain carbons are of the same order.

PTS12-4A. The CPMAS ^{13}C NMR spectrum of the PTS12-4A monomer is shown in Fig. 9(a). The methylene adjacent to the oxygen gives two peaks with similar intensities. The ^{13}C shifts are given in Table 7 together with the T_1 values. One of the split signals of OCH$_2$ at the lower field gave a long T_1 of 9 s, and the other had a T_1 of 3 s. Thus there are two different conformations of PTS12-4A around the sulfonate in the solid state. This agrees with the crystal structure of PTS12-2A, where the doubling of the unit cell was observed.(7) Since the T_1's of the aromatic carbons are all long including the protonated carbons, the aro-

Table 6. The ^{13}C Shift and T_1 of the Monomer and the Polymer of 5ECMU-4A

No.[a]	Carbon	Monomer		Polymer	
		Solution	Solid	^{13}C shift (ppm)	T_1 (s)
Main chain	$=\underline{\mathrm{C}}$–CH$_2$			146.6	90
Main chain	–$\underline{\mathrm{C}}\equiv\underline{\mathrm{C}}$–			105.5[c]	85
				104.0	85
Main chain	$=\underline{\mathrm{C}}$–C≡			110.3	55
17	≡C– α	60.70	61.3(0.6)[b]	71.2	80
16	–C≡ β	61.36	64.1(2.7)	82.4[c]	80
				80.4	
15	≡C– γ	65.96	66.7(1.7)	66.0	—
				64.5	
14	–C≡ δ	80.02	82.9(2.9)	89[d]	80
			81.1(1.1)		
13	$\underline{\mathrm{C}}$H$_2$C=			36.5	25
13	$\underline{\mathrm{C}}$H$_2$C≡	19.39	22.4(3.0)	21.4	10
			21.8(2.4)		
12	CH$_2$	27.55	31.0(3.4)	31.3	10
11	CH$_2$	25.09	27.0(1.9)	27.1	10
10	CH$_2$	28.38	31.5(3.1)	31.3	10
9	OCH$_2$	64.99	66.7(1.7)	66.7	10
7	C=O	156.49	159.1(2.6)	158.6	35
			156.8(0.3)		
5	CH$_2$NH	42.72	42.5(−0.2)	42.8	1
4	C=O	170.12	172.6(2.5)	170.1	14
			171.5(1.4)		
2	CH$_2$O	61.49	62.6(1.1)	61.6	4
1	CH$_3$	14.16	15.2(1.0)	14.8	1
			14.1(0)		

a) The numbering of the atom from the terminal methyl carbon. b) The differences from the solution spectrum. c) Shoulder. d) Broad.

Table 7. The ^{13}C Shift and T_1 of the Monomer and the Polymer of PTS12-4A

No.[a]	Carbon	Monomer			Polymer	
		Solution	Solid	T_1 (s)	^{13}C shift	T_1 (s)
Main chain	$=\underline{\mathrm{C}}$–CH$_2$				150	d)
Main chain	–$\underline{\mathrm{C}}\equiv\underline{\mathrm{C}}$–				105.3	110
					104.1	110
Main chain	$=\underline{\mathrm{C}}$–C≡				109.8	70
15	≡C– α	60.86	61.9(1.0)[b]	30	72	35
14	–C≡ β	61.32	63.1(1.8)	30	81.4	70
13	≡C– γ	66.38	66.8(0.4)	30	64.9	50
12	–C≡ δ	79.19	82.8(3.6)	30	91.3	50
11	$\underline{\mathrm{C}}$H$_2$C=	—	—	—	36.7	15
11	$\underline{\mathrm{C}}$H$_2$C≡	18.82	20.8(2.0)	5	21.8	3
10	CH$_2$	23.86	24.5(0.6)	0.2	26.7	0.6
9	CH$_2$	27.81	29.0(1.2)	1	29.3	1.5
8	OCH$_2$	69.58	72.9(3.3)[c]	9	72.5	1.5
			70.8(1.2)	3		
5	C aromatic	132.94	132.7(−0.2)	70	132.6	130
4	CH aromatic	127.88	130.7(2.8)	70	128.6	15
3	CH aromatic	129.91	130.7(0.8)	70	129.6	15
2	C aromatic	144.89	143.2(−1.5)	70	143.5	130
1	CH$_3$	21.68	19.7(−20)	10	19.3	20

a) The numbering of the atom from the terminal methyl carbon. b) The differences from the solution spectrum. c) Overlapped.

matic parts are stacked and are less mobile. While four spacer methylenes have shorter T_1's, especially those of the two central methylenes are extremely short. The link part between the conjugated acetylene carbon and

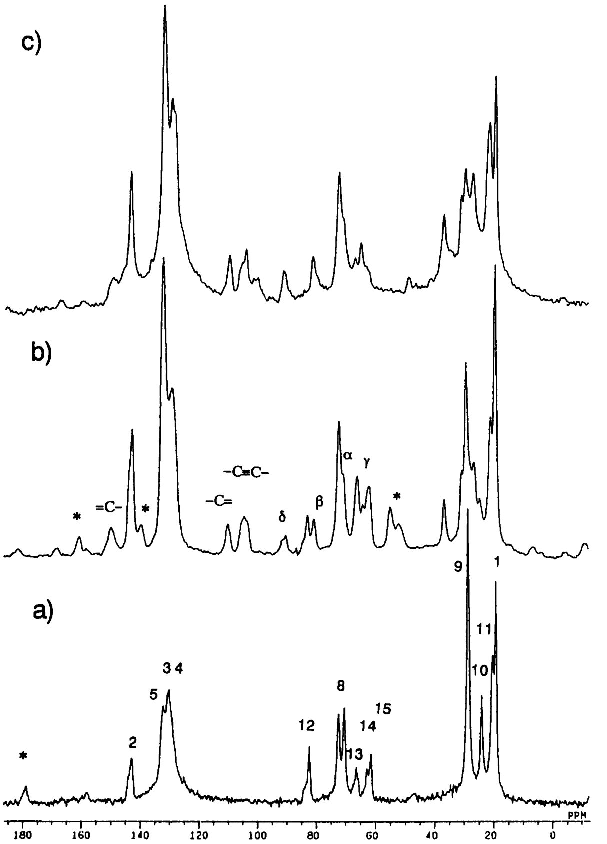

Fig. 9. The CPMAS ^{13}C NMR spectra of PTS12-4A for (a) the monomer and (b) the polymer just after γ-ray irradiation and (c) the polymer after one year. The asterisks denote spinning side bands.

the rigid sulfone are flexible in the solid state.

The CPMAS ^{13}C NMR spectrum just after polymerization is shown in Fig. 9(b), where a small amount of the monomer signals remained. No splitting of the signal was observed for the polymer, and the doublet of OCH_2 signal in the monomer became a single line. The relative intensities of the aromatic protonated and quaternary carbons became smaller, suggesting librations of the benzene plane around the para axis.[42] About one year later, the measurement of the spectra was repeated and T_1 measurement was performed. No signal from the monomer was observed, suggesting that the polymerization reaction proceeded at ambient temperature. The ^{13}C shifts and T_1 values are given in Table 7. Long T_1's were observed for the quaternary carbons including acetylenic and aromatic carbons. The aromatic protonated carbons have shorter T_1 in the polymer rather than in the monomer. Thus the stacked conformation of the aromatic rings in the monomer was released in the pendant side chains of the polymer. Fast segmental motions around the link methylenes in the polymer were also observed.

In conclusion, the alignments and molecular motions of the conjugated acetylene monomers are important factors in solid-state polymerization. The ^{13}C NMR spectra of the monomer in the solid state always give evidence for the stack structure: The signal of stack methylene carbons at about 34 ppm for 14-2A, 14-4A, and 14-6A, large solidification shifts of the order 2—3 ppm around the spacer methylenes between the acetylenic carbons and the urethane moiety for 4BCMU-4A, 5BCMU-4A, and 5ECMU-4A, or the splitting of the OCH_2 signal for PTS12-4A. The solid-state alignment of the monomer affects polymer structures after solid-state polymerization; a homogeneous monomer forms the homogeneous polymer in 5BCMU-4A. When the side-chain structures are the same, the higher conjugated acetylenic carbons are more active in the solid-state polymerization. The PDA's having hydrogen bonds between the adjacent pendant side chains experience long-term structural relaxation.

References

1) J. L. Bredas, C. Adant, P. Tackx, A. Persoons, and B. M. Pierce, *Chem. Rev.*, **94**, 243 (1994), and papers cited therein.

2) G. Wegner, *Z. Naturforsch., B*, **24**, 824 (1969).

3) G. Wegner, *Makromol. Chem.*, **154**, 35 (1972).

4) G. Wegner, "Molecular Metals," ed by W. E. Hatfield, Plenum Press, New York (1979), p. 209.

5) D. Siegel, H. Sixl, V. Enkelman, and G. Wenz, *Chem. Phys.*, **72**, 201 (1982).

6) V. Enkelmann, "Polydiacetylenes," in "Advances in Polymer Science, Vol. 63," ed by H.-J. Cantow, Springer-Verlag, Tokyo (1984), and papers cited therein.

7) V. Enkelmann, G. Wenz, M. A. Muller, M. Schmidt, and G. Wegner, *Mol. Cryst. Liq. Cryst.*, **105**, 11 (1984).

8) P. C. Brouty, P. Spinat, and A. Whuler, *Acta. Crystallogr., Sect. C*, **C44**, 1070 (1988).

9) G. E. Babbitt and G. N. Patel, *Macromolecules*, **14**, 554 (1981).

10) G. Wenz, M. A. Muller, M. Schmidt, and G. Wegner, *Macromolecules*, **17**, 837 (1984).

11) H. Eckert, J. P. Yesinowski, D. J. Sandman, and C. S. Velazquez, *J. Am. Chem. Soc.*, **109**, 761 (1987).

12) H. Tanaka, M. Thakur, M. A. Gomez, and M. Tonelli, *Macromolecules*, **20**, 3094 (1987).

13) H. Tanaka, M. A. Gomez, M. Tonelli, and M. Thakur, *Macromolecules*, **20**, 1208 (1987).

14) H. Tanaka, M. A. Gomez, M. Tonelli, A. J. Lovinger, and D. D. Davis, *Macromolecules*, **22**, 2427 (1989).

15) A. D. Nava, M. Thakur, and M. Tonelli, *Macromolecules*, **23**, 3055 (1990).

16) H. Tanaka, M. Thakur, M. A. Gomez, and A. E. Tonelli, *Polymer*, **32**, 1834 (1991).

17) K. Hayamizu, S. Okada, S. Tsuzuki, H. Matsuda, A. Masaki, and H. Nakanishi, *Bull. Chem. Soc. Jpn.*, **67**, 342 (1994).

18) H. Matsuda, H. Nakanishi, T. Hosomi, and M. Kato, *Macromolecules*, **21**, 1238 (1988).

19) H. Matsuda, H. Nakanishi, N. Minami, and M. Kato, *Mol. Cryst. Liq. Cryst.*, **160**, 241 (1988).

20) H. Nakanishi, H. Matsuda, S. Okada, and M. Kato,

"Frontiers of Macromolecular Science," ed by T. Saegusa, T. Higashimura, and A. Abe, Blackwell Scientific Publications, Oxford (1989), p. 469.

21) S. Okada, H. Matsuda, H. Nakanishi, and M. Kato, *Mol. Cryst. Liq. Cryst.*, **189**, 57 (1990).

22) S. Okada, M. Ohsugi, A. Masaki, H. Matsuda, S. Takaragi, and H. Nakanishi, *Mol. Cryst. Liq. Cryst.*, **183**, 81 (1990).

23) S. Okada, K. Hayamizu, H. Matsuda, A. Masaki, and H. Nakanishi, *Bull. Chem. Soc. Jpn.*, **64**, 857 (1991).

24) S. Okada, H. Matsuda, A. Masaki, H. Nakanishi, and K. Hayamizu, *Chem. Lett.*, **1990**, 2213.

25) S. Okada, H. Matsuda, A. Masaki, H. Nakanishi, and K. Hayamizu, "Optical and Electrical Properties of Polymers," (Mat. Res. Soc. Symp. Proc., 214), ed by J. A. Emerson and J. M. Torkelson, Materials Research Society, Pittsburgh (1991), p. 29.

26) S. Okada, H. Matsuda, A. Masaki, H. Nakanishi, and K. Hayamizu, "Nonlinear Optical Properties of Organic Materials IV," (Proc. SPIE, 1560), ed by K. D. Singer, SPIE, Bellingham (1991), p.25.

27) S. Okada, H. Matsuda, A. Masaki, T. Doi, K. Hayamizu, A. Masaki, and H. Nakanishi, "Organic Materials for Non-Linear Optics III," Oxford (1992), p. 225.

28) S. Okada, K. Hayamizu, H. Matsuda, A. Masaki, N. Minami, and H. Nakanishi, *Chem. Lett.*, **1992**, 301.

29) S. Okada, T. Doi, A. Mito, K. Hayamizu, A. Ticktin, H. Matsuda, N. Kikuchi, A. Masaki, N. Minami, K.-H. Haas, and H. Nakanishi, *Nonlinear Opt. Prop. Org. Mol. Cryst.*, **8**, 121 (1994).

30) S. Okada, K. Hayamizu, H. Matsuda, A. Masaki, N. Minami, and H. Nakanishi, *Macromolecules*, **29**, 6259 (1994).

31) H. Kawanami, S. Okada, H. Matsuda, T. Doi, N. Kikuchi, K. Hayamizu, H. Oikawa, and H. Nakanishi, *Mol. Cryst. Liq. Cryst.*, **255**, 103 (1994).

32) S. Hayashi and K. Hayamizu, *Bull. Chem. Soc. Jpn.*, **64**, 685 (1991).

33) D. A. Torchia, *J. Magn. Reson.*, **30**, 613 (1978).

34) O. Yamamoto, K. Hayamizu, and M. Yanagisawa, *Anal. Sci.*, **4**, 461 (1988).

35) O. Yamamoto, K. Hayamizu, and M. Yanagisawa, *Anal. Sci.*, **5**, 645 (1989).

36) D. L. VanderHart, *J. Chem. Phys.*, **64**, 830 (1976).

37) Y. Ozcayir, J. Asrar, and A. Blumstein, *Mol. Cryst. Liq. Cryst.*, **110**, 263 (1980).

38) J. Tsibouklis, A. R. Wernink, A. J. Shand, and G. H. W. Milburn, *Liq. Cryst.*, **3**, 1393 (1988).

39) J. L. Moigne, A. Soldera, D. Guillon, and A. Skoulios, *Liq. Cryst.*, **6**, 627 (1989).

40) F. Vicentini, M. Mauzac, R. C. Laversanne, P. Pochat, and P. Parneix, *Liq. Cryst.*, **16**, 721 (1994).

41) J. G. Hexem, M. H. Frey, and S. J. Opella, *J. Chem. Phys.*, **77**, 3847 (1982).

42) W. S. Price, N. Kikuchi, H. Matsuda, S. Okada, H. Nakanishi, and K. Hayamizu, to be published.