partial support of this work through the EPSCOR program.

Registry No. TBAB, 1643-19-2.

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Solid-State Cross Polarization/Magic Angle Spinning ^{13}C NMR Study of Thermotropic Aromatic Polyester Containing a Flexible Spacer in the Main Chain

Toshiyuki Uryu* and Takashi Kato

Institute of Industrial Science, University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan. *Received May 5, 1987*

ABSTRACT: The solid-state structure of a thermotropic aromatic polyester containing an aliphatic flexible spacer based on terephthalic acid and 4,4′-dihydoxy-1,6-diphenoxyhexane has been investigated by high-resolution solid-state CP/MAS (cross polarization/magic angle spinning) ^{13}C NMR. Samples of the polymer with different thermal histories, i.e., an original sample as obtained by low-temperature solution polymerization and once-melted samples with different cooling conditions, have been prepared in order to study the effect of the thermal history on the solid-state structure of the polymer. For the original sample, the solid-state spectrum shows that a conformation of the hexamethylene spacer is all-trans in the plane of the phenoxy group and that the ester linkage is nearly perpendicular to the plane of the aromatic ring. For the once-melted sample, it has been found that the conformations of the hexamethylene spacer and the ether linkage are a function of thermal history but that no appreciable change takes place about the ester linkage. The thermotropic aromatic ester compound bis(4-butoxyphenyl) terephthalate has also been characterized by solid-state and solution NMR. The conformation of the model compound is similar to that of the original sample of the polyester.

Introduction

Thermotropic polyesters have attacted much attention[1-3] because of their high potential as materials with excellent mechanical properties. It is very important to obtain information about their solid-state structures since thermotropic polyesters are utilized in the solid state. Moreover, many useful thermotropic polyesters show too low a solubility to allow measurements of the chemical structure in solution.

Recently, high-resolution CP/MAS (cross polarization/magic angle spinning) NMR has become a powerful tool for characterizing polymers in the solid state.[4-6] A thermotropic polyester is one of the best subjects for solid-state NMR study since there is great interest in the relationship between the solid-state structure and properties. Such information as chemical structure, molecular packing, molecular order, molecular motion, and conformation of a polymer can be obtained by means of solid-state NMR. However, very little work has been reported on solid-state NMR studies of thermotropic polyesters.[7,8]

In the present work, solid-state structures of thermotropic polyester 1 containing a flexible spacer[9] are inves-

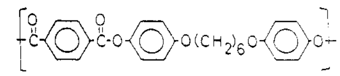

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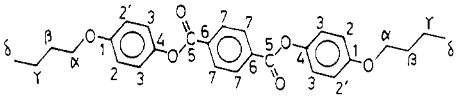
Table I
^{13}C Chemical Shifts[a] of Thermotropic Ester Model Compound 2 in the Solid State and Solution



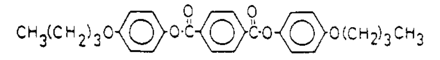
2

nematic
187°C–233°C

	aromatic ring carbons								alkyl carbons			
	1	2	2′	3	4	6	7	CO carbon 5	α	β	γ	δ
solid	155.8	111.0	117.1	124.7	145.3	133.7	130.3	163.9	68.5	33.7	21.8	16.9
soln[b]	156.8	115.5		122.3	144.2	133.8	130.0	164.1	68.2	30.9	18.7	13.4

[a] Chemical shifts (ppm) from tetramethylsilane. [b] In dimethyl-d_6 sulfoxide at 100 °C.

tigated by CP/MAS NMR. Effects of thermal histories on solid-state structures and thermal properties are examined for samples of polyester 1. NMR spectra of low molecular weight thermotropic model compound 2[10] are also measured in the solid state and solution to help to interpret the solid-state CP/MAS spectra of polyester 1.



2

Experimental Section

Thermotropic Ester Model Compound 2, Bis(4-butoxyphenyl) Terephthalate.[10] A solution of *p*-butoxyphenol (4.8 × 10^{-2} mol) and terephthaloyl chloride (2.4 × 10^{-2} mol) in 30 mL of dry pyridine was stirred for 24 h at room temperature. The reaction mixture was poured into dilute hydrochloric acid. The precipitate was filtered off and washed with sodium bicarbonate solution and then with water. The product was recrystallized from ethyl acetate: yield 55%; crystal-nematic 187 °C (lit.[10] 184 °C); nematic-isotropic 233 °C (lit.[10] 230 °C); 270-MHz ^{1}H NMR (DMSO-d_6, 100 °C) δ 8.29 (4 H, s), 7.22 (4 H, d), 7.00 (4 H, d), 4.03 (4 H, t), 1.73 (4 H, m), 1.48 (4 H, m), 0.96 (6 H, t).

Thermotropic Polyester 1.[9] Diphenol monomer, 4,4′-dihydroxy-1,6-diphenoxyhexane, was prepared according to the method of Griffin and Havens.[11] An original sample of polyester 1 was prepared as follows. Terephthaloyl chloride (5.6 × 10^{-3} mol) dissolved in 10 mL of 1,1,2,2-tetrachloroethane (TCE) was added dropwise to a solution of the diphenol monomer (5.6 × 10^{-3} mol) in a mixture of 10 mL of TCE and 5 mL of pyridine under a nitrogen atmosphere. The reaction mixture was stirred at 70 °C for 3 h and then at room temperature for 48 h. Then, 300 mL of acetone was added and stirred for 2 h. It was filtered and washed successively with acetone, a mixture of acetone and water, water, and finally acetone. The precipitated polymer was dried at 70 °C under vacuum for 24 h: yield 93%; inherent viscosity, 0.23 dL/g.

Characterization of the Polyer. Thermal properties of samples of the polymer were examined on a Perkin-Elmer DSC-2 at a heating rate of 20 °C/min under a nitrogen atmosphere. The visual observation was performed on a polarizing microscope equipped with a Mettler FP85 hot stage. Inherent viscosity was measured for a 0.2 g/dL solution of the original sample of the polymer in *p*-chlorophenol with an Ubbelohde type viscometer at 45 °C.

Thermal Treatments of Polyester 1 Samples. The original sample of about 300 mg was placed in a glass vessel having nitrogen gas inlet and outlet, and the vessel was placed in oil baths at 280 and 360 °C. After the sample melted thoroughly, they were cooled and quenched under various conditions. (a) Slow cooling: the sample melted that at 280 °C was cooled in the oil bath, the temperature of which was slowly decreasing. After the sample crystallized, it was taken out of the oil bath. (b) Rapid cooling: the sample that melted at 280 °C was immediately taken out of the oil bath in order to cool it rapidly to room temperature. (c) Quenching from 280 and 360 °C: the samples that melted at 280 and 360 °C were immediately taken out of the oil bath and placed in liquid nitrogen. All thermal treatments were conducted in a nitrogen stream.

NMR Measurements. The ^{13}C solid-state NMR spectra were recorded on a JEOL JNM-GX270 spectrometer (6.34 T magnetic field, ^{13}C frequency 67.8 MHz) with a CP/MAS unit. The solid-state NMR measurements were performed at room temperature. The spinning rates were about 3.8 kHz. Contact time was 2 ms. A bullet-type Kel-F rotor contained about 300 mg of sample. Recycle time of pulse was 5 s. The Hartmann–Hahn condition[12] and the magic angle were adjusted by using the aromatic signal of hexamethylbenzene. Conventional[13] and TOSS[14] pulse sequences were used for measurements. Spectra were accumulated 300–700 times. The signal of the CH of adamantane was used as an external reference for the chemical shift (29.5 ppm downfield from tetramethylsilane).

The solution spectra of polyester 1 and model compound 2 were recorded on the same spectrometer. The spectrum of polyester 1 was recorded at 80 °C as 1% (w/v) solution in a mixture of 40 wt % of 1,1,2,2-tetrachloroethane-d_2 (TCE-d_2) and 60 wt % of pentafluorophenol (PFP). The peak of TCE-d_2 was used as an internal standard (74.5 ppm downfield from tetramethylsilane at 80 °C). The sample of model compound 2 was observed at 100 °C as 4% (w/v) solution in dimethyl-d_6 sulfoxide (DMSO-d_6). The peak of DMSO-d_6 was used as an internal standard (40.1 ppm downfield from tetramethylsilane at 100 °C).

Results and Discussion

Solid-State and Solution NMR Spectra of Model Compound 2. The low molecular weight model compound 2, that is, bis(4-butoxyphenyl) terephthalate, shows a nematic phase from 187 to 233 °C on heating (lit.[10] 183–229 °C).

^{13}C NMR spectra of model compound 2 were obtained both on the solid state and in solution. The sample recrystallized from ethyl acetate was used for NMR measurements.

The solid-state CP/MAS spectrum of 2 obtained by conventional pulse sequence[13] for single contact and spin lock CP experiments is shown in Figure 1A, and the spectrum free of spinning sidebands by using the TOSS pulse sequence[14] is shown in Figure 1B. Solid-state NMR measurements were performed at room temperature. Although highly resolved spectra can be obtained in the high magnetic field strength, quite large spinning sidebands of aromatic carbons appear due to the anisotropy of the aromatic ring.[15] The TOSS pulse sequence is useful technique to eliminate such spinning sidebands. The solution spectrum of 2 in DMSO-d_6 at 100 °C is shown in Figure 1C. The chemical shifts and assignments are given in Table I. Comparison of the solid-state spectra with the solution spectrum gives the information concerning the crystalline structure of 2.

On the basis of these results, it is proposed that model compound 2 has a conformation in the solid state depicted in Figure 2.

The resonance of aromatic carbons ortho to the butoxy group at 115.5 ppm in the solution is separated into a doublet by 6.1 ppm in the solid state, that is, resonances of C2 and C2′ at 111.0 and 117.1 ppm, respectively. This

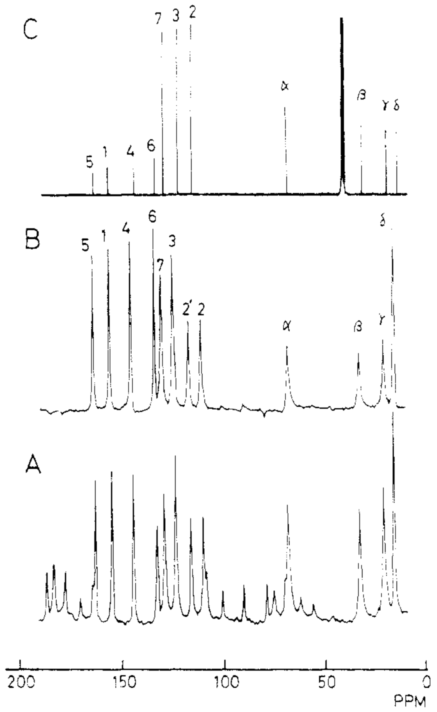


Figure 1. ^{13}C NMR spectra, 67.8 MHz, of thermotropic ester model compound **2**: (A) solid-state CP/MAS spectrum obtained by conventional pulse sequence; (B) solid-state CP/MAS spectrum which is free of spinning sidebands (SSB) obtained by TOSS pulse sequence; (C) solution spectrum in DMSO-d_6 at 100 °C.

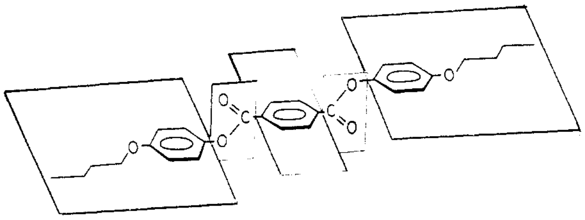


Figure 2. Proposed conformation of model compound **2** in the solid state.

splitting is caused by the fixed orientation of the butoxy group with respect to the benzene ring. Maricq and Waugh[16] studied the chemical shift values of 1,4-dimethoxybenzene in the solid state and reported that the resonance of ortho carbons shielded by a methoxy group which is fixed in one direction with respect to the benzene ring appears at 113 ppm and that of the deshielded ortho carbons at 119 ppm. This nonequivalency was also observed by Lippmaa et al.[17] Hays[18] observed the splitting of carbons ortho to alkoxy groups of p-alkoxybenzoic acids in the solid-state spectra and concluded that they are due to the fixed conformation of the alkoxy groups with respect to the benzene ring, taking into account the X-ray structure analysis.[19-21]

In the solution state, the ortho carbons are equivalent since the alkoxy groups can freely rotate about the axis of the oxygen–aromatic carbon to which the alkoxy group is attached. In the solid state, however, the motion of the substituents is frozen in one position. We[22] reported the solid-state spectrum of a thermotropic low molecular weight ester, 4′-cyanophenyl 4-pentoxybenzoate (CPPOB), the crystal structure of which was determined by X-ray analysis.[23] The pentoxy group of CPPOB is locked in one position with respect to the benzene ring, being in the coplanar position and the resonance of ortho carbons is split by 6.3 ppm.[24] The splitting of ortho carbons of **2** is also attributed to the locking effect of the butoxy group with respect to the benzene ring in the crystalline state.

The nonequivalency of the aromatic ring carbons ortho to the ester linkage is not observed in the solid-state spectrum of compound **2**. These resonances are well-resolved and narrow, revealing that the ortho carbons are completely equivalent. It is reasonable to assume that the benzene rings on both sides make an angle of nearly 90° with the plane of the ester linkage causing no splitting in the solid-state NMR spectrum. For CPPOB,[22] the pentoxyphenyl ring is coplanar and the cyanophenyl ring is perpendicular to the ester linkage. Therefore, the resonance of the pentoxyphenyl ring carbons ortho to the ester linkage is split into a doublet with a separation of 3.0 ppm, while the resonance of the ortho carbons of the cyanophenyl ring shows complete equivalency. The nonequivalency of the resonances of the carbons ortho to the carbonyloxy group was observed for 4-nitrophenyl 4-(octyloxy)benzoate.[25] The angle between the (octyloxy)phenyl ring and the ester linkage is 2°.[26] Fyfe et al.[5] reported the solid-state spectra of poly(p-hydroxybenzoate), in which the carbons ortho to carboxyl group split by 3.4 ppm and attributed the splitting to the torsional angles of the aromatic rings about the ester linkages. English[15] assigned the resonances at 127.7 and 130.3 ppm in the solid-state spectra of poly(p-phenyleneterephthalamide) to the ortho carbons of the terephthalic acid unit and ascribed the nonequivalency to the torsional angles between the aromatic rings and the amide linkages.

As for aliphatic carbons of the terminal butoxy group, the resonances of C_β, C_γ, and C_δ in the solid state are shifted downfield by 2.8, 3.1, and 3.5 ppm, respectively, from those in solution. These chemical shift changes can be explained by the γ-gauche effect.[27] In the solid state, the butoxy group is believed to be locked in a planar zigzag conformation, while in solution the conformation changes rapidly and some gauche conformations exist, which cause averaged upfield chemical shifts. The resonance of C_α, which is next to the oxygen, shows a very slight chemical shift change. In this case, a solvent effect on the oxygen which is next to C_α and in addition conformational changes, that is, rotation about the axis of O–C1 (which removes the shielding of C_α by C2) and rotation about the axis of C_β–C_γ (which introduces a γ-gauche effect between C_α–C_γ) can cancel one another in solution and little change occurs on the chemical shift of C_α.

Solid-State CP/MAS and Solution NMR Spectra of the Original Sample of Thermotropic Polyester 1. The original sample of thermotropic polyester **1** was prepared by low-tempterature solution polymerization in 1,1,2,2-tetrachloroethane and pyridine from terephthaloyl chloride and 4,4′-dihydroxy-1,6-diphenoxyhexane. The polymer precipitated from solution state as the polymerization proceeded. This original sample was not subjected to thermal treatment at high temperature. The inherent viscosity of the polymer was 0.23 dL/g.

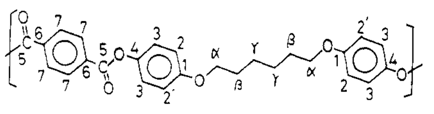
CP/MAS solid-state NMR spectra of the original sample obtained by conventional pulse sequence is shown in Figure 3A and by TOSS pulse sequence in Figure 3B. Figure 3C shows the solution spectrum obtained at 80 °C in a mixture of tetrachloroethane-d_2 (TCE-d_2) and pentafluorophenol (PFP). Chemical shifts and assignments are given in Table II.

A proposed conformation of the original sample (conformation I) is shown in Figure 4.

It is noteworthy that the nonequivalency of C2 and C2′ carbons caused by the fixed orientation of the alkoxy group of the flexible spacer is also clearly observed in the solid-state spectra of the polyester **1** original sample. Each

Table II

^{13}C Chemical Shifts[a] of the Original Sample of Thermotropic Polyester 1 in the Solid State and Solution[b] (Solution Chemical Shifts in Parentheses)



1

nematic
267°C–351°C

	aromatic ring carbons							CO	spacer alkyl carbons		
	1	2	2′	3	4	6	7	carbons 5	α	β	γ
polyester 1 original sample	156.6	111.5	117.8	124.4, 125.9[b]	145.9	134.9	131.0	163.6	68.5	33.0	27.6
	(157.9)	(116.6)		(122.8)	(145.4)	(*d*)	(131.0)	(167.5)	(70.5)	(29.7)	(26.4)
model compound 2	155.8	111.0	117.1	124.7	145.3	133.7	130.3	163.9			
1 – 2	+0.8	+0.5	+0.7	–0.3	+0.6	+1.2	+0.7	–0.3			

[a] Chemical shifts (ppm) from tetramethylsilane. [b] In a mixture of 1,1,2,2-tetrachloroethane and pentafluorophenol (PFP) at 80 °C. [c] Not clearly observed. [d] Overlapped with the peaks of PFP.

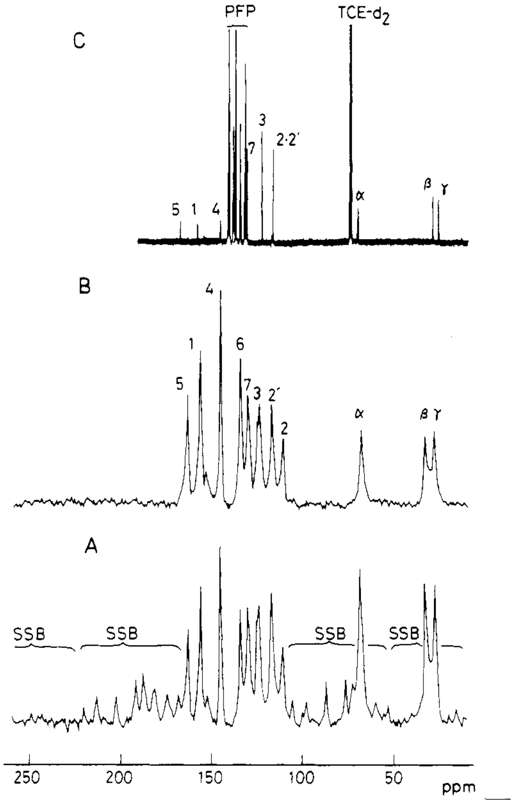


Figure 3. Solid-state CP/MAS ^{13}C NMR spectra, 67.8 MHz, of thermotropic polyester 1 original sample: (A) spectrum obtained by conventional pulse sequence; (B) spinning sidebands (SSB) free spectrum obtained by TOSS pulse sequence; (c) solution spectrum in a mixture of TCE-d_2 and PFP at 80 °C.

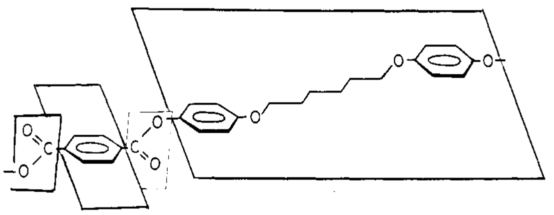


Figure 4. Proposed conformation (conformation I) of the original sample of polymester 1 in the solid state.

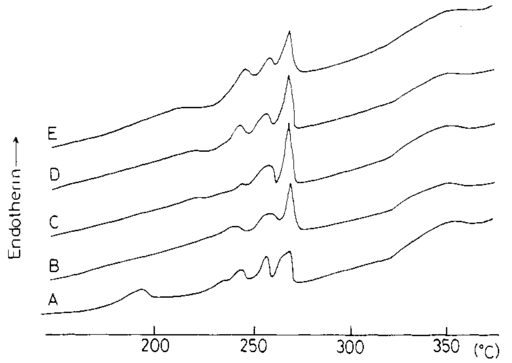


Figure 5. DSC thermograms of thermotropic polyester 1 samples with different thermal histories at heating rates of 20 °C/min: (A) original sample; (B) sample cooled slowly from 280 °C; (C) sample cooled rapidly from 280 °C; (D) sample quenched in liquid N_2 from 280 °C; (E) sample quenched in liquid N_2 from 360 °C.

aliphatic carbon of the spacer group shows distinct resonances. The resonances of C_β and C_γ show upfield shifts by 3.3 and 1.2 ppm, respectively in the solution spectrum. These chemical shifts also can be interpreted in terms of the γ-gauche effect. In solution, the conformation changes rapidly and the chemical shifts of spacer carbons are affected by γ-gauche interactions. In the solid state, the conformation that causes downfield shifts is assumed to be an all-*trans* extended conformation free of the γ-gauche effect. The resonances of C_α show a downfield shift in the solution spectrum. In addition to the deshielding effect and the γ-gauche effect, which were explained for model compound **2**, a strong solvent effect of PFP moves the resonance downfield. The resonance of the carbonyl carbon of the ester linkage shows a similar trend. The resonance of C3 carbon shows an ambiguous splitting by 1.5 ppm, which was not observed for model compound **2**. One possible explanation is that the ester linkage and the benzene ring make a slight torsional angle from 90° causing an ambiguous nonequivalency.

Chemical shifts of aromatic ring and carbonyl carbons of the original sample are similar to those found in the crystalline state of model compound **2**. The differences in chemical shifts are within 1.2 ppm. It should be pointed out that the conformation in the solid state of the original sample prepared by solution polymerization is similar to that of model compound **2** on the basis of the NMR spectra.

Thermal Properties of Thermotropic Polyester 1 Samples with Different Thermal Histories. The thermal properties of polyester 1 samples with different thermal histories were examined by differential scanning calorimetry (DSC). Samples of polyester 1 cooled or quenched from the melt state were prepared in order to investigate the effects of thermal treatments on solid-state structures and properties.

The DSC first heating curve of the original sample, which was prepared by low-temperature solution polym-

Table III
^{13}C Chemical Shifts[a] of Thermotropic Polyester 1 Samples with Different Thermal Histories in the Solid State and Solution[b] (Solution Chemical Shifts in Parentheses)

	aromatic ring carbons							CO	spacer alkyl carbons		
	1	2	2′	3	4	6	7	carbons 5	α	β	γ
original sample	156.6 (157.9)	111.5 (116.6)	117.8	124.4, 125.9[c] (122.8)	145.9 (145.4)	134.9 (*d*)	131.0 (131.0)	163.6 (167.5)	68.5 (70.5)	33.0 (29.7)	27.6 (26.4)
sample cooled slowly from 280 °C	157.4	112.3 115.6	117.8	124.9	145.5	134.6	130.8	164.6	69.0	30.9	28.0
sample cooled rapidly from 280 °C	157.0	112.2 115.3	118.2	123.3	144.7	134.4	130.2	164.5	68.7	30.6	27.9
sample quenched in liquid N_2 from 280 °C	157.2	115.0		123.6	144.6	134.2	130.7	164.5	69.0	30.4	28.0
sample quenched in liquid N_2 from 360 °C	157.5	115.0		123.2	144.4	134.6	130.5	164.1	69.0	30.4	27.9

[a] Chemical shifts (ppm) from tetramethylsilane. [b] In a mixture of 1,1,2,2-tetrachloroethane-d_2 and pentafluorophenol (PFP) at 80 °C. [c] Not clearly observed. [d] Overlapped with the peaks of PFP.

erization, is illustrated in Figure 5A. It shows multiple melting transitions. The multiple melting transitions for this polymer and its analogous series were observed by Antoun et al.[9] and Chen et al.[28] The peak temperature of the melting endotherm of the original sample is 267 °C. The enthalpy change on melting of the original sample is 2.1 kcal/mol. Under the polarizing microscope observation, this polymer shows a threaded texture characteristic of the nematic state after melting. The endothermic peak of the nematic–isotropic transition is observed by DSC. The maximum temperature of the peak for the original sample is 351 °C. The enthalpy change of the nematic–isotropic transition, ΔH_i, is 1.2 kcal/mol. An endothermic peak is observed at 191 °C for the original sample.

Figure 5, parts B–E, illustrates DSC curves of first heating runs for samples with different thermal histories: a sample cooled slowly from 280 °C (nematic state) (Figure 5B); a sample cooled rapidly from 280 °C (Figure 5C); a sample quenched in liquid nitrogen from 280 °C (Figure 5D); a sample quenched in liquid nitrogen from 360 °C (Figure 5E). Multiple melting transitions are also observed in these once-melted samples as well as the original one, though the shapes of melting transitions are different. The highest temperature endothermic peaks of the melting transitions of the once-melted samples become sharper and larger than that of the original one. The low-temperature endothermic peaks become smaller for parts B and C, of Figure 3. The enthalpy changes of the melting do not show an appreciable change. The endothermic peak at 191 °C in the heating scan of the original sample disappears for the once-melted samples. These differences of DSC curves show that the solid-state structures are changed by the thermal treatments. Griffin and Havens[11,29] studied the effects of thermal histories of the thermotropic polyesters based on 4,4′-dicarboxy-α,ω-diphenoxyalkane and 4,4′-dihydroxy-α,ω-diphenoxyalkane by DSC and observed that the thermal behavior of samples without heat treatment are different from those of the once-melted samples. These trends were observed for other aromatic polyesters containing flexible spacers.[30,31]

Solid-State CP/MAS NMR Spectra of Thermotropic Polyester 1 Samples with Different Thermal Histories. To investigate solid-state structures of thermotropic polyester 1, the solid-state CP/MAS NMR was measured on the samples with different thermal histories.

Solid-state spectra of the samples cooled or quenched from nematic melt at 280 °C are shown in Figure 6, parts B–D. The spectra are free of spinning sidebands. A conventional spectrum of the sample quenched from an almost isotropic state at 360 °C is shown in Figure 6E. The chemical shifts and assignments are given in Table III. The differences among the spectra B–E of Figure 6 indicate that the solid-state structure of polyester 1 depends on the thermal history.

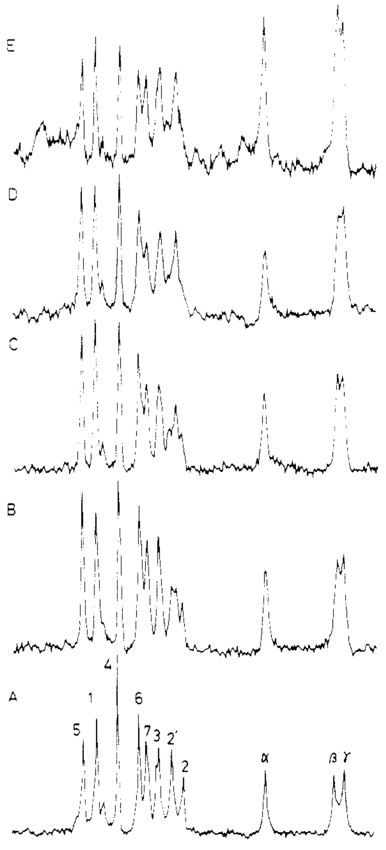


Figure 6. Solid-state CP/MAS ^{13}C NMR spectra, 67.8 MHz, of polyester 1 samples with different thermal histories: (A) original sample; (B) sample cooled slowly from 280 °C; (C) sample cooled rapidly from 280 °C; (D) sample quenched in liquid N_2 from 280 °C; (E) sample quenched in liquid N_2 from 360 °C (spectra A–D obtained by TOSS pulse sequence; spectrum E obtained by conventional pulse sequence).

The resonances of C_β shift upfield by 2.1–2.6 ppm, whereas those of C_α and C_γ show slight downfield shifts. The resonances of aliphatic carbons do not show line broadening after the thermal treatments. These results indicate that conformational changes of hexamethylene spacers occur about the C_γ–C_γ axis for once-melted samples since when rotation takes place only about the C_γ–C_γ axis and the all-trans extended conformation of the original sample is changed, γ-gauche effect causes upfield shifts only for the resonance of C_β. Belfiore et al.[32] investigated three forms of isotactic poly(1-butene) by solid-state NMR.

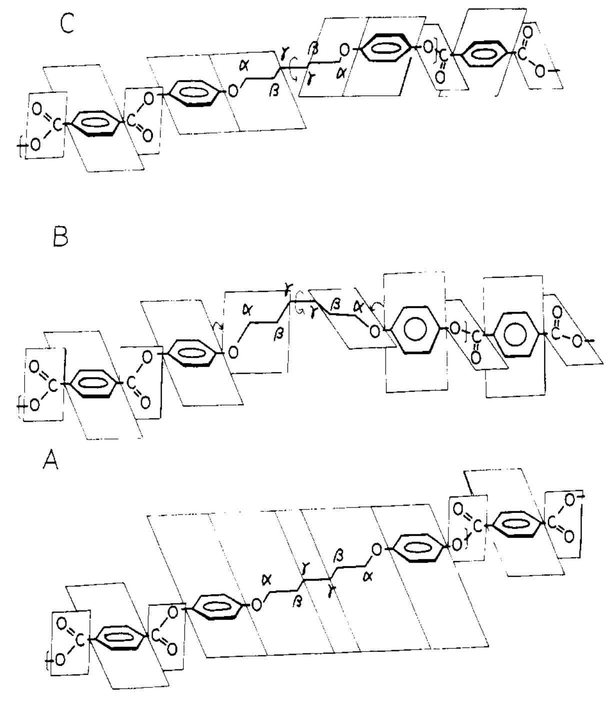


Figure 7. Proposed conformations of samples of polyester 1 with different thermal histories in the solid state: (A) conformation I (original sample); (B) conformation II (once-melted sample); (C) conformation III (once-melted sample).

It was expected that γ-gauche shielding parameters should be angle dependent. Resonances of aliphatic carbons shift upfield by about 5 ppm when the conformation changes from trans (180°) to gauche (60°).[27] It was observed that the values of the chemical shift change decrease when the gauche angle is more than 60°. The present observations that the resonances of C_β show upfield shifts by 2.1–2.6 ppm and show no broadening after the thermal treatments suggest that the angles about the C_γ–C_γ axis make torsional gauche angles of more than 60° after the thermal treatments.

Marked differences are observed for the resonances of carbons ortho to the alkoxy group of the spacer. For the once-melted samples, the spectra do not show a complete line splitting into a doublet which is observed for the original sample. This shows that the alkoxy group is not fixed at one position and is locked at various angles about the O–C1 axis with respect to the benzene ring when the polymers are cooled or quenched from the melt state in which the alkoxy group can rotate freely. In the spectrum of Figure 6D, no splitting is observed and a single peak appears at 115.0 ppm. This shows that quenching from the nematic state induces no fixed orientation of the alkoxy group of the spacer with respect to the benzene ring, resulting in the single chemical shift of the carbon ortho to the spacer group. Most of the plances of C1–O–C_α seem to be nearly perpendicular to the benzene ring. The ambiguous splitting of the C3 resonance in the spectrum of the original sample is not observed after thermal treatments. However, no appreciable changes are observed for resonances of aromatic carbons about the ester linkage. A conformation of the quenched sample from 280 °C is proposed in Figure 7B (conformation II). The spectrum of the sample quenched from 360 °C (Figure 6E) shows a trend similar to that in Figure 6D, suggesting that conformations of these two samples are almost the same.

For other once-melted samples, there are two kinds of ortho carbon resonances, that is, the single resonance appearing at a center position and the doublet resonances due to the fixed orientation (Figure 6, parts B and C; Table III). This indicates that the conformations II in Figure 7B and III in Figure 7C coexist in the solid state of these samples. The ratio of the conformation II increases as the cooling or quenched conditions become rapid.

Coesistence of two conformations corresponds to two states of C_α, that is, a deshielded one in conformation II and a shielded one in conformation III. The observation of an another model compound[33] suggested that the chemical shift of C_α is not so sensitivie to this conformational difference as those of C2 and C2′. NMR spectra of bis(4-propoxyphenyl) terephthalate, which is free of the γ-gauche effect because of the short alkyl chain, were measured in the solid state and solution. The fixed orientation of the propoxy group was also observed in the solid-state spectrum. The resonance of C_α appeared at 70.0 ppm in solution and at 69.0 ppm in the solid state. This trend was also observed for 1,4-dimethoxybenzene.[17] This insensitivity can cause difficulty in discerning the resonance of C_α in conformations II and III.

The width of resonances increases as the cooling rate becomes rapid, being the narrowest in the original sample. This suggests that slight variations in dihedral angles and molecular packing take place, and the degrees of variations are dependent on cooling or quenching conditions. Antoun et al.[9] performed wide-angle X-ray reflection study on original and quenched samples of analogous series polymers containing nonamethylene and decamethylene spacer groups. The patterns of original samples were typical for the semicrystalline polymer, and the patterns of quenched samples were typical for the nematic state. These results are in agreement with the present results.

The solid-state spectra of the once-melted samples have revealed that considerable conformational changes of polyester 1 samples mainly take place about the axes of O–C1 and C_γ–C_γ by the thermal treatments.

Registry No. 1 (copolymer), 78644-11-8; 1 (SRU), 78666-22-5; 2, 24707-01-5.

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^{13}C NMR Investigation of the Interactions between Amines and Ziegler–Natta Catalysts for α-Olefin Polymerization

Incoronata Tritto,* Maria Carmela Sacchi, Paolo Locatelli, and Giulio Zannoni

Instituto di Chimica delle Macromolecole del C.N.R., 20133 Milano, Italy.

Received June 10, 1987

ABSTRACT: Propylene has been polymerized in the presence of the catalyst δ-$TiCl_3/Zn(^{13}CH_2CH_3)_2$, used as a model system, at different concentrations of Et_3N and of 2,2,6,6-tetramethylpiperidine. The ^{13}C NMR analysis of the steric structure of the chain end groups of all the fractions of the polymers indicates that there are a variety of active sites, both isotactic and atactic, with different steric features, although producing polymer chains of the same tacticity. The distribution among the different types of active sites belonging to the same class changes at different concentrations of the free and/or complexed base. Moreover at concentration corresponding to the maximum of catalyst activity, the stereospecificity of the first step in the most isotactic fractions is higher than that observed in the absence of base and depends on its steric features. This fact provides evidence for the presence of the amines in the active-center environment.

Introduction

Lewis bases are widely used in Ziegler–Natta catalysis as enhancers of the stereospecificity of $MgCl_2$-supported catalysts for the polymerization of α-olefins. In propylene polymerization the stereospecificity has always been found to increase upon addition of a base as a third component, often accompanied by a loss of productivity. On the basis of these results many authors explained the increase in polymer isotacticity by the ability of the bases to poison selectively the nonstereospecific polymerization centers.[1,2] However, increase of isotactic productivity was observed by other authors in the presence of such Lewis bases as esters of aromatic acids,[3-5] 2,2,6,6-tetramethylpiperidine,[4,5] and phenyltriethoxysilane.[5] Therefore the way by which Lewis bases affect the catalyst stereospecificity is more complex than a simple poisoning, as at least a further effect has to be considered, i.e., the activation of the isotactic centers.

In a previous paper[6] we reported a study of the effects of two amines, Et_3N and 2,2,6,6-tetramethylpiperidine (TMPip), on the catalysts $MgCl_2/TiCl_4/AlEt_3$, δ-$TiCl_3/AlEt_3$, and δ-$TiCl_3/ZnEt_2$. Our findings indicated that the poisoning and the activation act at the same time and either the former or the latter effect dominates, depending on the relative strength of the complexation equilibria between the bases and the various Lewis acids present in solution. In particular, the interaction of the uncomplexed base with the active sites was shown to be responsible for the poisoning effect, the selectivity of the process depending on the steric hindrance of the base. On the other hand, the presence in solution of sufficient base–alkylmetal complex was connected to the activating effect, the extent of the activation depending also on the structure of the base.

The purpose of this report is to obtain information on the mechanism by which the base–alkylmetal complex activates the isotactic sites. A ^{13}C NMR analysis was performed on ^{13}C-enriched chain end groups of polypropylene samples obtained in the presence of the catalyst δ-$TiCl_3/Zn(^{13}CH_2CH_3)_2$, using Et_3N and TMPip as Lewis bases. In the last few years the study of the stereochemistry of the ^{13}C-enriched chain end groups has allowed one to evaluate the steric control exerted by different alkyl and halide ligands of the catalitically active titanium and their mutual interactions.[7-9] Since such an analysis is sensitive to even small variations in the titanium coordination sphere, we expected that it could give evidence for the presence, if any, of the activating complex in the neighborhood of the active titanium and therefore of the possible direct influence of Lewis bases on the active centers.

Results

Table I summarizes the conversion and fractionation results for polypropylene samples obtained in the presence of the catalyst δ-$TiCl_3/ZnEt_2$, using Et_3N and TMPip at three significant base/$ZnEt_2$ (R) ratios. As was observed by Boor,[10] increasing the base concentration produces in dialkylzinc-based catalysts first a lowering and then an increase of activity. Therefore, this catalyst, since it allows one to partially distinguish the concurrent deactivating and activating effects, could be useful as a model system to study the mechanism of the activation and deactivation observed in many conventional and supported catalytic systems. On this basis, we have examined by ^{13}C NMR polypropylene samples prepared with the catalyst δ-$TiCl_3/Zn(^{13}CH_2CH_3)_2$, at $R = 0.032$ (minimum of catalyst activity) and 0.320 (maximum of catalyst activity). In Figure 1 are shown in the ^{13}C NMR spectra of the heptane-insoluble, octane-soluble fractions[11] of the samples obtained in the absence of base (Figure 1a) and in the presence of Et_3N (Figure 1b) and TMPip (Figure 1c), at $R = 0.032$. The labeled peaks are due to the ^{13}C-enriched

0024-9297/88/2221-0384$01.50/0