Characterization of Copoly(*p*-hydroxybenzoate/bisphenol A terephthalate) by NMR Spectroscopy

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ABSTRACT: Copoly(*p*-hydroxybenzoate/bisphenol A terephthalate) is a new type of wholly aromatic copolyester which has an obvious character of the thermotropic liquid crystal. In this paper, we characterized the copolyester by high resolution nuclear magnetic resonance (NMR) spectroscopy (including two-dimensional technique, 2D NMR), and discussed NMR spectra of the copolyesters having various monomer compositions. The combined use of homonuclear and heteronuclear two-dimensional NMR provided unambiguous spectral assignment for the copolyester. It was found that the ¹³C NMR spectra of carbonyl group in the copolyester chain were not so simple as in the monomeric aromatic ester and they gave the useful information of the chain sequences. There are good relationships between the carboxyl group resonance peaks and the triad of the monomer residues.

KEY WORDS Copoly(*p*-hydroxybenzoate/bisphenol A terephthalate) / Nuclear Magnetic Resonance (NMR) / Wholly Aromatic Copolyester / Thermotropic Liquid Crystal / Sequence Structure /

In recent years many aromatic polyesters capable of forming anisotropic melts have been described.^{1–3} Among thermotropic copolyesters, those based on *p*-hydrobenzoic acid (PHBA) are especially attractive. However, the properties and molecular characteristics of this class of polymers have not been investigated in detail. Some of the problems associated with the study of these systems arise from their low solubility in most solvents, which greatly limits use of techniques aimed at relating microstructure to the properties. The copolyesters containing only 1,4-phenylene unit such as Xydar exhibiting unique thermal and mechanical properties are insoluble in all available solvents, and their processing temperature are about 400°C, hence, these polymers are very difficult to study. The wholly aromatic copolyester from *p*-acetoxybenzoic acid (PHBA), terephthalic acid (TPA), and acetoxybisphenol A (BPA), shortly called copoly(PHBA/BPA/TPA), is a new type of aromatic copolyester which has an obvious character of the thermotropic liquid crystal.^{4–7} Due to these three kinds of monomer forming polymers are produced on a large scale, the copolyester may have a potential to be developed into a new kind of high technique material, and its synthesis and characterization^{8,9} will have special meaning for future applications. On the other hand,

attractive property of the polyesters is also its solubility in many organic solvents, their properties and molecular characteristics can be investigated in solution. In this paper, we characterized the wholly aromatic copolyester by high resolution nuclear magnetic resonance (NMR) spectroscopy (including two dimensions technique, 2D NMR), and discussed NMR spectra of the copolyesters having various monomer compositions.

EXPERIMENTAL

Preparation of Copolyesters

The copolyesters based on three monomers, *i.e.*, terephthalic acid (TPA), *p*-acetoxy-benzoic acid (PABA) and acetoxybisphenol A (ABPA) were produced by melting polycondensation. Synthetic conditions have been reported in ref 4 and 7. The PHBA/BPA/TPA composition, transition temperatures and inherent viscosity are listed in Table I.

NMR Spectroscopy Measurements

The NMR spectra measurements were performed using Varian Unity 400 spectrometer. In the measurement, wholly aromatic copolyesters were dissolved in a mixture of CF₃COOD/CDCl₃ (vol. ratio 3:2). Their

Table I. Properties of copoly(PHBA/BPA/TPA)

Sample No.	PHBA/BPA/TPA mol ratio	PHBA% mol	<i>T</i> _g °C	<i>T</i> _m °C	<i>T</i> _d °C	[<i>η</i>] dl g ⁻¹	Opalescence
P ₁	1:3:3	14.3	166	359	440	0.485	Yes
P ₂	1:2:2	20	180	285	428	0.603	Yes
P ₃	1:1:1	33	177	280	430	0.560	Yes
P ₄	2:1:1	50	188	321	425	0.522	Yes
P ₅	3:1:1	60	181	—	480	—	No

[*η*] = inherent viscosity, measured in *p*-chlorophenol at 45°C.

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Figure 1. 400 MHz ^1H NMR spectrum of copoly(PHBA/BPA/TPA) sample P_3 .

concentrations in solution were 5–20% (w/v). The central line of tetramethylsilane (TMS) or deuterated chloroform (CDCl_3) of NMR spectra was treated as an internal reference (0 or 77.0 ppm, respectively). Instrumental conditions for ^1H NMR were as follows: observing frequency 399.952 MHz, spectral width 3.9 kHz, data point 16384, and using a single scan.

Instrumental conditions for ^{13}C NMR were as follows: observing frequency 100.577 MHz, spectral width 25 kHz, data point 26688, a total of 4500 transients were accumulated for each spectrum using a recycle time of 7.4 s, using inverse gate decoupling. When a pulse sequence of DEPT (distortionless enhancement by polarization transfer) was required, we proposed pulse repetition 5.67 s and accumulative scan 32 times.

For H–H COSY spectra, spectral width was 845 Hz, data point 512 for f_2 and 128 for f_1 , zero filling up to 512, a total of 16 transients were accumulated with a recycle time of 2 s. The window function was a form of sine bell in both dimensions. A treatment of symmetrization of spectra was used.

For C–H COSY spectra, spectral width was: 2335 Hz for f_2 and 1724 Hz for f_1 , data point 1024 for f_2 and 92 for f_1 , put zero filling up to 256, a total of 1024 transients were accumulated with a recycle time of 1.5 s. The window function was chosen the phase-shifted sine bell (for f_2) and sine bell (for f_1).

RESULTS AND DISCUSSION

^1H and ^{13}C NMR Spectra of Copoly(PHBA/BPA/TPA)

Sample P_3 in which the mole fraction of three monomers is equal to each other can be considered as a representative of these wholly aromatic copolyesters, and its ^1H NMR spectrum is shown in Figure 1. From downfield to upfield (from left to right in the figure), the peaks at chemical shift in a range 8.6–6.6 ppm are assigned to hydrogen protons of aromatic residues of TPA, PHBA, and BPA. The peak at chemical shift 1.74 ppm is assigned to two methyl protons of propane in BPA. The peak at 0.89 ppm should be assigned to the methyl proton in acetyl.

^{13}C NMR spectrum of sample P_3 is shown in Figure 2. In downfield direction the peaks belong to carboxyl (>162 ppm), quaternary carbon atoms of aromatic ring (162–133.4 ppm) and tertiary carbon atoms of aromatic ring (133.4–114 ppm), respectively. The peaks at upfield are corresponding to quaternary atoms of aliphatic series

Figure 2. 100 MHz ^{13}C NMR spectrum of copoly(PHBA/BPA/TPA) sample P_3 .

in BPA unit (~ 42 ppm) and aliphatic methyl (primary carbon atom 30.92 ppm). In addition, there are two weak peaks at upfield, one of which at 21.15 ppm is considered as methyl in acetyl group. This group of methyl also responds to a weak peak (>165 ppm) in downfield direction.

Correlated Spectroscopy (COSY) of Copoly(PHBA/BPA/TPA)

High-resolution NMR spectroscopy is a highly sensitive tool for the study of polymers. But NMR spectroscopy is of the limited because of the considerable overlap arising from the multiplicity and relative broadness of resonances. The usual methods of off-resonance and selective decoupling to determine the multiplicity of carbon bonding are not effective because of the inherent limitation of selectivity in the presence of the large number of overlapping resonances. Consequently, structure assignments to resonances are often difficult and arbitrary. In Figure 1 it seems likely that the resonance peaks of hydrogen protons of aromatic residues are complex and badly overlapped and in Figure 2 the peaks at downfield are too many. To obtain an accurate assignment for every resonance peak, two dimensional NMR experimental techniques (2D NMR) should be applied. The resolution in 2-D spectrum is better than in either the ^{13}C or ^1H spectrum alone. The homonuclear H–H COSY spectra for sample P_3 is shown in Figure 3, where the peaks correlated with themselves (*i.e.*, autocorrelated) along the diagonal are consistent with peaks of aromatic hydrogen proton in Figure 1. At the same time the off-diagonal peaks or cross-correlated peaks show a coupling interactions $^3J_{\text{HH}}$ between hydrogen protons of neighboring carbon atoms in aromatic ring. The heteronuclear C–H COSY spectra for sample P_3 was shown in Figure 4, a 2-D data matrix with the carbon chemical shifts along one axis (F_2) and the proton chemical shifts along the other (F_1) is obtained. The 2D ^{13}C – ^1H correlated spectrum maps proton signal to the carbon-13 signal of the corresponding directly attached carbon. The intensities of the (^1H , ^{13}C) cross peaks are proportional

Figure 3. H-H COSY and one-dimensional spectra of copoly(PHBA/BPA/TPA) sample P₃.

Figure 4. C-H COSY and one-dimensional spectra of copoly(PHBA/BPA/TPA) sample P₃.

to the number of protons attached to the specific carbon atom. Combining a knowledge of the chemical shifts and the nature of the coupling pattern with an analysis of the COSY spectra of Figures 3 and 4, we can obtain assignments of concerned peaks for aromatic tertiary carbon atoms and protons. The results are shown as follows:

With the exception of these above, other three series of coupling interaction $^3J_{\text{HH}}$ are found in Figure 3 and their existence is also confirmed in C-H correlation in Figure 4. They are listed as follows:

	(1)	(2)	(3)
^1H (ppm)	6.74—7.13	6.90—8.12	7.22—7.54
^{13}C (ppm)	114.73—120.72	115.31—132.38	121.48—129.53

By means of comparing ^1H and ^{13}C NMR standard spectra of similar monomeric compound with above results, it is concluded that the structure form (1) can be assigned to PHBA (PHBA-CO-CH_3) at the chain end and form (2) to BPA (BPA-CO-CH_3) at the chain end. According to the value of proton chemical shift the form (3) should be approximated to BPA, away from PHBA, but the assignments is not exactly clear.

As the aromatic quaternary carbon atom and the carboxyl group are not bonded with any hydrogen protons, it is easy to understand that they are not appeared in C-H COSY spectra. Considering monomeric components of samples and intensities of concerned peaks, we can decide their assignments shown as follows:

^{13}C NMR Spectra of Carbonyl Group in Wholly Aromatic Copolyester Chain

Although resonance peaks on ^{13}C NMR spectra for the carbonyl group of monomeric aromatic ester are appeared at about 160—170 ppm, the case for liquid crystal copolyesters is not so simple. The carbonyl regions of ^{13}C spectra for some poly(PHBA/BPA/TPA) samples are shown in Figure 5. From down field to up field in Figure 5a, there are four resonance peaks a, b, c, and e. Among these peaks, b is intensive (167.48 ppm), peaks a and c neighboring and weak, and peak e is further weak

(166 ppm) and slightly away from others. It is known apparently that the mole content of PHBA for sample P_1 is only 14.3%, but the amount of TPA above 40%. Therefore, according to intensity of peaks, the peak b can be assigned to carbonyl group of TPA and peak e to that of PHBA. To describe clearly the change of chain structure of liquid crystal copolyesters with increasing content of PHBA, we can use conveniently symbols B, T, and P to express the residues of BPA, TPA, and PHBA, respectively. In sample P_1 , the content of PHBA is little, its residue is isolated in the chain and exists almost only in the triad TPB of the chain sequences. But TPA has three forms of triads: BTB, BTP (including B^*TP , BT^*P) and dTP. It has to explain that because of the molecular asymmetry of PHBA residue the symbol d is designated as the inverse PHBA (*i.e.*, inverse P). Because sample P_1 is rich in both of BTB and TPB triads, the peak b in Figure 5a should be assigned to BTB, and peak e in Figure 5a to TPB. For peaks a and c in Figure 5a, their ownerships could be considered either dTP or BTP. Based on the structural dependence of chemical shifts, comparing the chemical structure of BTP with BTB, we could find the fragment PHBA in the triad BTP instead of BPA in the triad BTB. Because of an intensive electronegativity in phenol oxygen, the carbon atom bonded to oxygen atom would be directly underwent deshielding. According to the above view point, from downfield to upfield the peaks characteristic to the triad containing TPA seem to be in the order of dTP, BTP, and BTB. However, as the rearrangement direction of electronic cloud in the triad BTP is $\text{B} \rightarrow \text{T} \rightarrow \text{P}$, hence the density of electronic clouds on the carbon atom in carbonyl group of PHBA (BT^*P) is hardly decreased, but increased slightly. Due to this shielding effect, its resonance peak has to move to upfield. As the rearrangement of electronic clouds only slightly effects on the shielding, the information of both BT^*P and BTB keep in peak b. In the triad dTP, the moving direction of electronic clouds is $\text{d} \leftarrow \text{T} \rightarrow \text{P}$. In this case, there is stronger effect of deshielding on the fragment TPA. Therefore the peaks of the triad dTP move to downfield. In fact, three triads for TPA are arranged in the order of dTP, BTB (including B^*TP), and BTP. In other words the peak a should be assigned to dTP, the peak c to BTP(BT^*P).

When PHBA unit contents in molecular chains of liquid crystal copolyester are increased, triads of PPP and BTB become the primary sequence structure, and triads of TPP and PPB secondary. As regards the latter two triads mentioned above their contents in P_4 and P_5 are more than those in samples P_1 and P_2 . Observing the change in spectra from sample P_1 to sample P_4 in Figures 5a—d, it is easy to note that peaks d and e are appeared more and more obviously. The former peak is more intensive than the latter. Because there is only one carboxyl group in PHBA and the structure change in the other end of this residue PHBA has little effect, and information of triads TPP and PPP are overlapped in spectra, therefore it might be appropriate that the peak d should be assigned to the carboxyl group. As to PPB triad, the effect of BPA on it is similar to that of PHBA on BTP as discussed before. As the shielding effect increases, resonance peaks move to upfield. In this case,

Figure 5. 100 MHz ^{13}C NMR spectra of (carbonyl group) for copoly(PHBA/PA/TPA) sample P_1 – P_5 .

the triad PPB just responds to the peak f.

Summarizing assignments of carboxyl group resonance peaks, we found the following relationship: the peak a responds to the triad dTP, b to BTB (including B*TB), c to BTP(BT*P), d to PPP and TPP, e to TPB and f to PPB. The combination of several techniques proved more powerful than any one alone in assigning the ^1H and ^{13}C spectra of this complex copolyester, these results show tremendous potential for interpretation to NMR spectra of similar copolyesters.

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