Thermal sequence randomization of a wholly aromatic copolyester having an ordered sequence

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A wholly aromatic copolyester having an ordered comonomer sequence was prepared from 2,7-naphthalenediyl bis(4-hydroxybenzoate) and terephthalic acid following a method reported previously. This polymer was subjected to thermal treatment at 305°C under nitrogen atmosphere and the sequence randomization process was quantitatively analysed by ^{13}C n.m.r. spectroscopy. The melting temperature of the original polymer was 290°C. According to the results of analysis for various triad formation, the ester bonds in the triad of terephthaloyl-*p*-oxybenzoyl-oxynaphthyleneoxy (TPN) sequence were found to undergo very fast exchange reactions at the treatment temperature. The formation of PPP triad was evident after 30 min at 305°C, whereas PP dyad was formed after only 10 min. Although the sequence changes occurred rather rapidly, complete randomization was not attained even after 1 h.

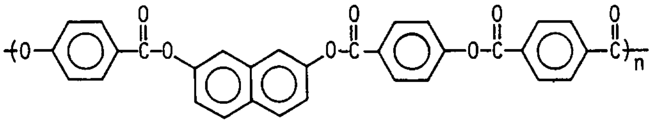
(Keywords: sequence randomization; aromatic copolyesters; liquid crystalline copolymers; transesterification; sequence distribution; ^{13}C n.m.r.)

INTRODUCTION

The properties of aromatic copolyesters depend not only on the composition, but also on the comonomer sequence[1-8]. However, unlike vinyl copolymers, where the C–C bonds along the main chain are not labile and thus the preset comonomer sequence order is maintained even at elevated temperatures, the ester bonds and terminal functional groups in copolyesters can undergo various types of transesterification reactions. Consequently, preservation of the comonomer sequence of a copolyester set by a particular preparation condition or method is not guaranteed during characterization or processing at a high temperature.

Such problems have been studied mainly for blend systems consisting of a pair of different homopolyesters[9-12], but there has been very little work concerning copolyesters having well designed sequence orders[3,13]. For incompatible blend systems, phase separation can cause erroneous kinetic results for exchange reactions. This artifact can be avoided by studying the sequence randomization of a copolyester having an ordered sequence.

We have prepared a copolyester having an ordered comonomer sequence, as shown in the following formula.



sO-2,7-2

The changes in sequence order at 305°C in the absence of any external catalyst were studied by ^{13}C n.m.r. spectroscopy. The melting temperature of this polymer is 290°C. The preparation and properties of this polymer have been reported previously[2]. The repeat unit of this copolyester contains two *p*-oxybenzoyl units all of which exist in the isolated form. Since the unit can form dimeric and longer blocks of itself through transesterification reactions, this copolyester was taken as one of the ideal copolyesters whose sequence changes could be readily followed by ^{13}C n.m.r. spectroscopy.

In order to make a comparison, the corresponding random copolyester was prepared in melt and subjected to the same thermal treatment at 305°C. ^{13}C n.m.r. spectra of the original and the treated copolyesters were analysed. The preparation and properties of the random copolymer have been reported previously[14]. The subscripts 1 and 2 in the following formula represent composition, and not the sequence length of each unit.

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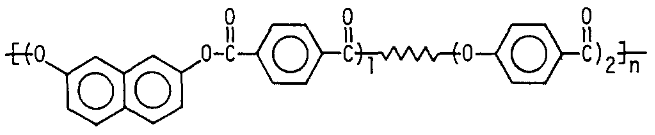


R-2,7-2

EXPERIMENTAL

Synthesis and thermal treatment of polymers

The sequentially ordered copolyester sO-2,7-2 was prepared in solution via a multistep route as previously described[2]. 2,7-Bis(4-hydroxybenzoyloxy)naphthalene was first synthesized and then polymerized with terephthalic acid at 80°C in the presence of the condensing agent $SOCl_2$/pyridine[15]. The polymer was subjected to Soxhlet extraction with ethanol for 24 h and dried at 60°C *in vacuo*. The random copolyester[10] R-2,7-2 prepared in melt from *p*-acetoxybenzoic acid, 2,7-diacetoxynaphthalene and terephthalic acid was also Soxhlet extracted with ethanol. Dry powdered polymer samples were placed in the sample compartment of a differential scanning calorimeter (Du Pont 910) at 305°C for varying periods of time under nitrogen atmosphere.

^{13}C n.m.r. spectroscopic analysis

^{13}C n.m.r. spectra of the polymers were obtained on a Jeol JNM-GX500 spectrometer at 125.65 MHz and 55°C. A mixture of trifluoroacetic acid-*d* and chloroform-*d* (1:1 v/v) was used as a solvent. The concentration of the sample solutions were 5% w/v. The conditions of ^{13}C n.m.r. data acquisition were as follows: flip angle 90° (11.0 μs); pulse repetition time 5.0 s; frequency range 25000 Hz; 65536 data points; 7000–10000 scans; line broadening factor 0.38 Hz.

RESULTS AND DISCUSSION

The ^{13}C n.m.r. spectrum of the liquid crystalline polyester with ordered sequence (sO-2,7-2) was measured in a mixture of trifluoroacetic acid-*d* and chloroform-*d* (1:1 v/v) at 55°C and is shown in *Figure 1*. The peak assignment for aromatic carbons was made using the additivity rule reported by Lauterbur[16]. The chemical shifts of benzene and naphthalene measured in a mixture of trifluoroacetic acid-*d* and chloroform-*d* (1:1 v/v) at 55°C and the shifts induced by substitution[17,18] are listed in *Table 1*. By the use of these shift data, the chemical shifts for the aromatic carbons of the ordered sequence polyester were calculated as follows:

$$\delta = \delta_{\mathrm{ref}} + \Sigma\Delta\delta_{\mathrm{s}}$$

C-1 $134.5 + (+0.4) + (+0.4) = 135.3$

C-2 $128.6 + (-9.2) + (-0.1) = 119.3$

C-3 $126.5 + (+22.8) + (+0.9) = 150.2$

C-4 $126.5 + (-4.5) + (0.0) = 122.0$

C-5 $128.6 + (+1.6) + (-0.1) = 130.1$

C-6 $134.5 + (-1.9) + (-1.9) = 130.7$

C-8 $129.1 + (+2.0) + (-3.2) = 127.9$

C-9 $129.1 + (+1.2) + (+0.4) = 130.7$

C-10 $129.1 + (-0.1) + (-7.1) = 121.9$

C-11 $129.1 + (+4.3) + (+22.4) = 155.8$

C-13 $129.1 + (+2.0) + (+4.3) = 135.4$

C-14 $129.1 + (+1.2) + (-0.1) = 130.2$.

The calculated chemical shifts are shown in *Table 2* together with the chemical shifts observed for the sample

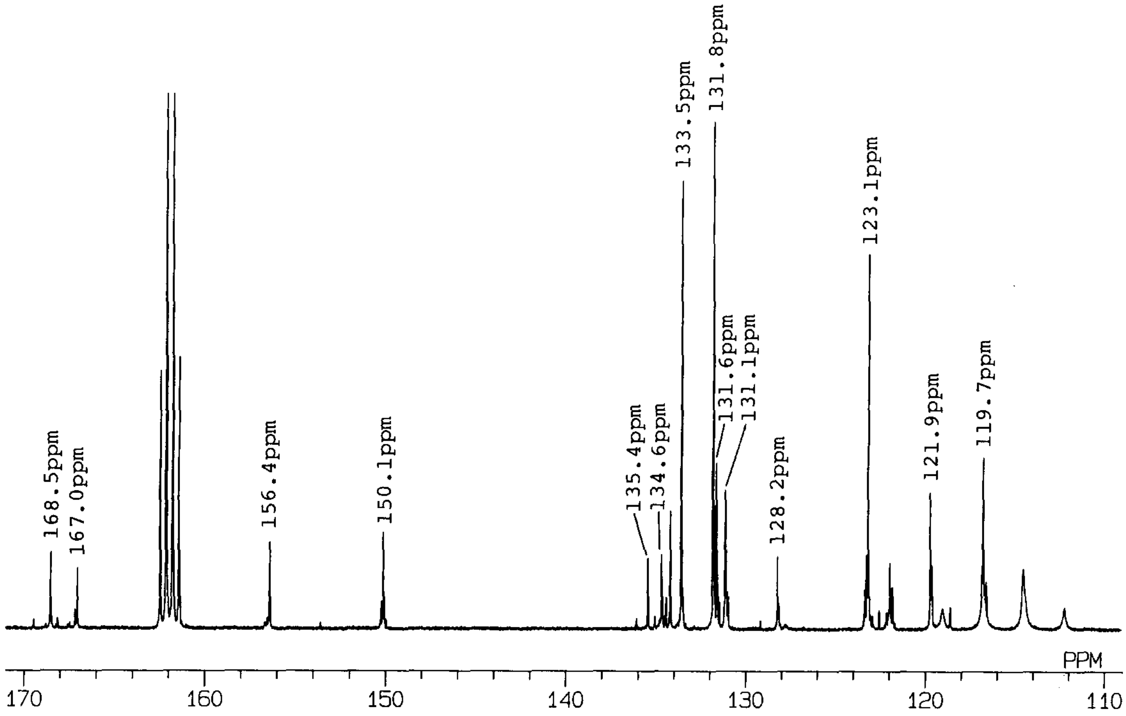


Figure 1 ^{13}C n.m.r. spectrum of the ordered sequence liquid crystalline polyester (sO-2,7-2) measured in $CF_3COOD/CDCl_3$ (1:1 v/v) at 55°C

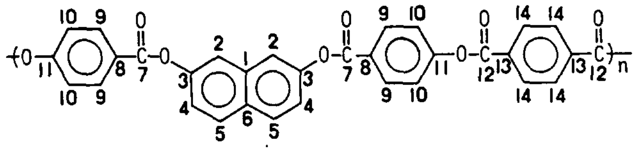
Table 1 The chemical shifts of benzene and naphthalene and values of shifts induced by substitution (SCS)[17,18]

Compounds		δ_{ref}[a] (ppm)	SCS values ($\Delta\delta_s$ (ppm)) -OCOR	SCS values ($\Delta\delta_s$ (ppm)) -COOR
Benzene	*ipso*		+22.4	+2.0
	ortho	129.1	−7.1	+1.2
	meta		+0.4	−0.1
	para		−3.2	+4.3
Naphthalene	C-1	128.6	−9.2	
	C-2	126.5	+22.8	
	C-3	126.5	−4.5	
	C-4	128.6	+1.6	
	C-5	128.6	−0.1	
	C-6	126.5	0.0	
	C-7	126.5	+0.9	
	C-8	128.6	−0.1	
	C-9	134.5	+0.4	
	C-10	134.5	−1.9	

[a] Measured in $CF_3COOD/CDCl_3$ (1:1 v/v) at 55°C

Table 2 Chemical shifts and assignments for the aromatic carbons of the sequence ordered liquid crystalline polyester (sO-2,7-2)

Number of carbon atom[a]	Observed δ (ppm)	Calculated δ (ppm)	Relative intensity
7	168.5[b]	–	2
12	167.0[b]	–	2
11	156.4	155.8	2
3	150.1	150.2	2
1	135.4	135.3	1
13	134.6	135.4	2
9	133.5	130.7	4
14	131.8	130.2	4
6	131.6	130.7	1
5	131.1	130.1	2
8	128.2	127.9	2
10	123.1	121.9	4
4	121.9	122.0	2
2	119.7	119.3	2

[a]


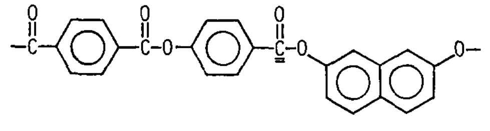
[b] Already assigned in the literature[3,19]

of sO-2,7-2. By comparing the observed chemical shifts with the calculated ones, the peaks at 156.4, 150.1, 128.2 and 119.7 ppm were definitely assigned to carbons, 11, 3, 8 and 2, respectively. The peaks at 168.5 and 167.0 ppm have already been assigned to carbons 7 and 12, respectively[3,19].

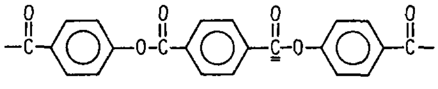
The calculated chemical shifts for carbons 1 and 13 indicate that two of the peaks at 135.4, 134.6 and 133.5 ppm can be assigned to these carbons. However, the relative peak intensities exclude the possibility for the peak at 133.5 ppm to be assigned to carbon 1 or 13. The peak at 135.4 ppm remained as a singlet during thermal randomization of the monomer sequence, while the signal at 134.6 ppm changed gradually to a multiplet. From these results, the former was assigned to carbon 1 and the latter to carbon 13.

The peaks at 123.1 and 121.9 ppm were assigned to carbons 10 and 4, respectively, from consideration of peak intensity. Assignment of the peaks at 133.5, 131.8, 131.6 and 131.1 ppm was made from the peak intensities and the calculated chemical shifts, although the assignment for carbons 9 and 14 is interchangeable.

The carbonyl carbon n.m.r. spectra of ordered sequence polyester (sO-2,7-2) and its randomized polymers are shown in *Figure 2*. The peak assignments were made in terms of triad sequences of terephthaloyl (T), oxy-2,7-naphthyleneoxy (N) and 4-oxybenzoyl (P) units and are indicated in the figure. The peaks at 168.5 and 167.0 ppm in the spectrum of the original polyester were previously assigned to the carbonyl carbons of the central P unit in TPN triad and of the central T unit in PTP triad, respectively[3,19].



T$\underline{\text{P}}$N



P$\underline{\text{T}}$P

Small peaks were also observed at 168.6, 168.2, 168.1, 167.5 and 167.2 ppm in the spectrum of the original polyester. These peaks increased in their intensities while the randomization proceeded, indicating that the peaks were due to triads other than TPN and PTP. Therefore, we can conclude that the sO-2,7-2 sample is basically of ordered sequence, but contains various triads other than TPN and PTP, although their levels are very low. These abnormal triad structures are believed to have been derived from the impurities in the starting triad monomer, 2,7-bis(4-hydroxybenzoyloxy)naphthalene, and also from the possible transesterification reactions occurring during polymerization.

With increasing time of randomization, the intensities of the peaks at 168.6 and 168.1 ppm increased more rapidly than the peak at 168.2 ppm. Thus, the peak at 168.2 ppm was assigned to PPP triad, which can be formed only through the change of monomeric units on both sides of the central P unit of the TPN triad. The chemical shift difference between TPP and TPN triads should be larger than that between PPN and TPN triads if we consider the differences in the chemical structures for these three triads. Then the peak at 168.6 ppm can be assigned to PPN triad and the peak at 168.1 ppm to TPP triad. Similarly, the peak at 167.2 ppm was assigned to NTP triad and the triplet at 167.5 ppm to NTN and PTN triads. Both the peaks due to PTP and NTP triads split further into doublets in the case of polymers with a higher extent of randomization. The splittings may be due to the tetrad sequences of monomeric units. The triplet at 167.5 ppm may be the overlap of the two doublets due to NTN and PTN triads.

The sequence distribution for the randomized polyesters was determined from the carbonyl carbon n.m.r. spectra on the basis of the assignments mentioned above and are shown in *Table 3*. From these data, the number average sequence length of P units (L_n) was calculated by the following equation[11]:

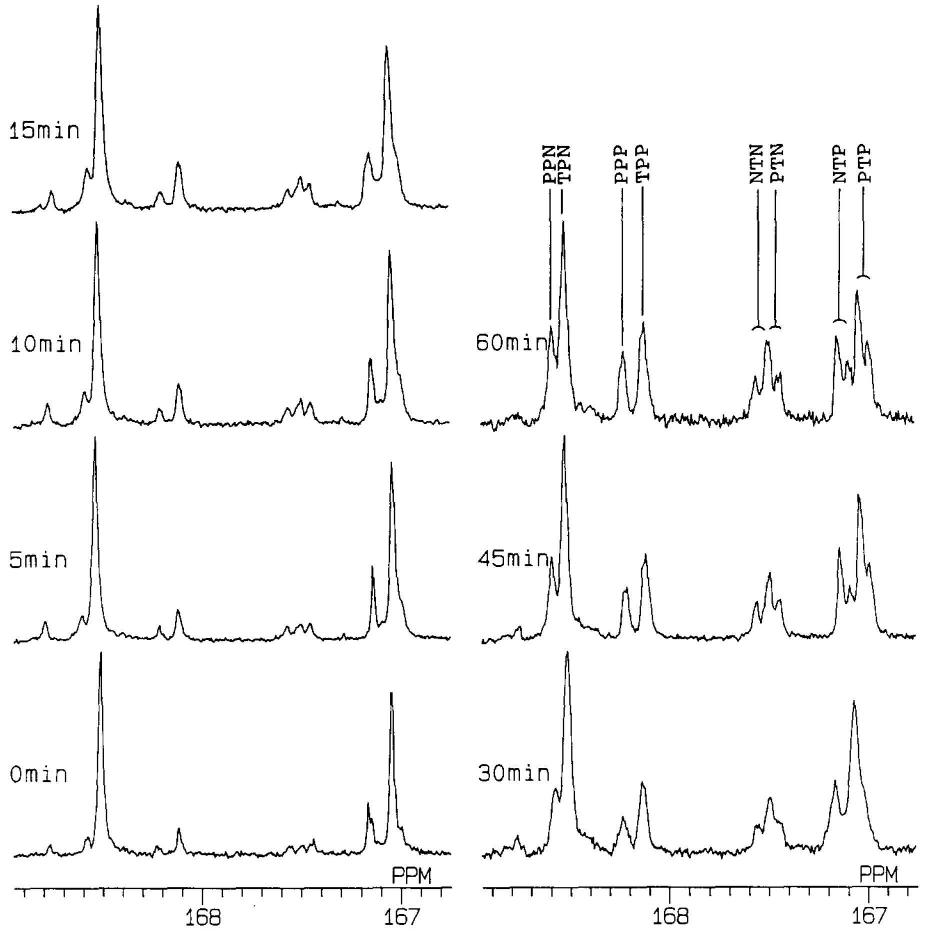


Figure 2 Carbonyl carbon n.m.r. spectra of the ordered sequence liquid crystalline polyester (sO-2,7-2) and its randomized polymers. The randomization was carried out at 305°C for various periods of time

Table 3 Sequence distributions of the liquid crystalline polyesters (sO-2,7-2 and R-2,7-2) and their randomized polymers

Polyester	Reaction time[a] (min)	Triad content[b] PPN	TPN	PPP	TPP	NTN	PTN	NTP	PTP	L_n	η_{inh}[c] ($cm^3 g^{-1}$)
sO-2,7-2	0	0.03	0.40	0.02	0.05	0.02	0.03	0.10	0.35	1.13	109
	5	0.05	0.36	0.02	0.05	0.03	0.04	0.09	0.36	1.10	110
	10	0.05	0.33	0.02	0.06	0.04	0.05	0.10	0.35	1.12	108
	15	0.06	0.32	0.02	0.07	0.04	0.06	0.10	0.33	1.16	112
	30	0.07	0.27	0.05	0.09	0.05	0.08	0.11	0.29	1.29	135
	45	0.09	0.23	0.06	0.11	0.07	0.08	0.13	0.23	1.41	136
	60	0.10	0.21	0.07	0.12	0.09	0.09	0.13	0.20	1.55	138
R-2,7-2	0	0.09	0.11	0.13	0.12	0.12	0.16	0.14	0.13	1.87	68
	15	0.10	0.10	0.13	0.11	0.13	0.16	0.14	0.13	1.86	123
	30	0.11	0.10	0.12	0.12	0.13	0.15	0.14	0.14	1.83	145
	45	0.11	0.11	0.12	0.11	0.13	0.15	0.14	0.14	1.84	142

[a] The randomization was carried out at 305°C
[b] Measured from n.m.r. peak areas
[c] Measured at 25°C for 0.1 g/100 cm^3 solutions in a mixed solvent of $CF_3COOH/CHCl_3$ (1:1 v/v)

$$L_n = \frac{2[P]}{[TP] + [PN]}$$

where [P] is the mole fraction of P unit and [TP] and [PN] are the mole fractions of TP and PN dyads, respectively. The fractions of these dyads were determined as follows:

$$[TP] = [NTP] + [PTP]$$

$$[PN] = [PPN] + [TPN]$$

In the case of the polyester with completely ordered structure, L_n should be unity (=(2 × 0.5)/(0.5 + 0.5)). The completely randomized polymer should have L_n = 2 (=(2 × 0.5)/(0.25 + 0.25)). The values of L_n given in *Table 3* clearly indicate that the ordered sequence polyester randomized rapidly with time at 305°C and that the polymer R-2,7-2 originally had a sequence very close to that for the perfectly random one. The fact that the L_n value of R-2,7-2 is not exactly 2.0 must be due to the reactivity differences between the carboxylic acid groups of T and P monomers and also between the hydroxy groups in N and P monomers.

The inherent viscosity data included in *Table 3* for the original and thermally treated polymer samples reveal that heat treatment increases molecular weight. This increase arises from the intermolecular reactions between the terminal groups, i.e. further polymerization. The terminal groups can participate not only in polymerization but also in ester exchanges. The latter causes destruction of the sequential structure. Interchange reactions between internal ester bonds also destroy the sequential order. Although the rate constants for ester–ester interchange reactions are lower compared with acidolysis and alcoholysis involving terminal carboxylic acid and hydroxy groups, their reaction rates can be significant due to the relatively high concentration of ester functional groups present in the system[12,20].

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