

Note

OPTICALLY ACTIVE COPOLYESTERS BASED ON AXIALLY DISSYMMETRIC 1,1'-BINAPHTHALENE-2,2'-DIYL UNITS*

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Abstract Optically active copolyesters based on axially dissymmetric 1,1'-binaphthalene-2,2'-diyl units have been prepared and characterized by specific rotation, ^{13}C -NMR and CD spectra. The results show that the rotation signs of tribasic copolyesters or the mixture of corresponding homopolyesters obey a three dimensional quadrant pattern. The composition of the copolyesters was determined from ^{13}C -NMR spectra to be triad sequence distributions and corresponding with the ratio by feed.

Keywords Optical activity, Copolyester, 1,1'-Binaphthalene-2,2'-diol, Diethyl tartrate

INTRODUCTION

A series of aromatic polyesters^[1], polyimides^[2], polycarbonates^[3] and polyarylenevinylenes^[4] based on axially dissymmetric 1,1'-binaphthalene-2,2'-diyl units have been prepared by solution polycondensation and widely used as engineering plastics with excellent thermal stability, insulating materials and various materials for microelectronic, electroluminescence, nonlinear optical devices^[5] having high conductivities upon doping^[6]. Fully aromatic polyesters based on 1,1'-binaphthalene-4,4'-diol are thermotropic liquid crystalline polymers and have been extensively studied and made it possible to produce films and coatings with good dielectric and mechanical properties^[1]. In previous work we reported the synthesis and characterizations of optically active polyesters derived from diethyl tartrate (DT) and benzene dicarbonyl dichloride (Tp, Ip and Op)^[7] and from 1,1'-binaphthalene-2,2'-diol (BN) and benzene dicarbonyl dichloride^[8] (Tp, Ip and Op), respectively. In order to evaluate the influence of the stereochemical composition and particular triad sequence distributions on the pattern of behavior of copolyesters, the optically active copolyesters (BN-Tp-DT) based on DT, BN and Tp have been prepared by solution polycondensation and characterized by specific rotation, ^{13}C -NMR and CD (circular dichroism) spectra. In fact, copolycondensation of mixture of enantiomers or two chiral monomers is a method frequently applied to generate stereochemical microheterogeneities in a polymer chain^[9].

EXPERIMENTAL

Polycondensation

The copolyesters, BN-Tp-DTs, were prepared by a two-step low temperature solution polycondensation method from 1,1'-binaphthalene-2,2'-diol(BN), diethyl tartrate (DT) and terephthaloyl chloride (Tp). A solution of Tp in THF was gradually added to a mixture of BN/Tp/DT with different mole ratios and triethylamine (TEA) in THF. The polycondensation reaction was carried out at 60°C for 24 h and then the product was precipitated with

* This work was supported by the State Key Laboratory of Functional Polymer Materials for Adsorption and Separation, Nankai University.

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Received October 14, 1999

methanol/water (1/1, *V/V*) and washed with methanol and dried in vacuum at 50°C.

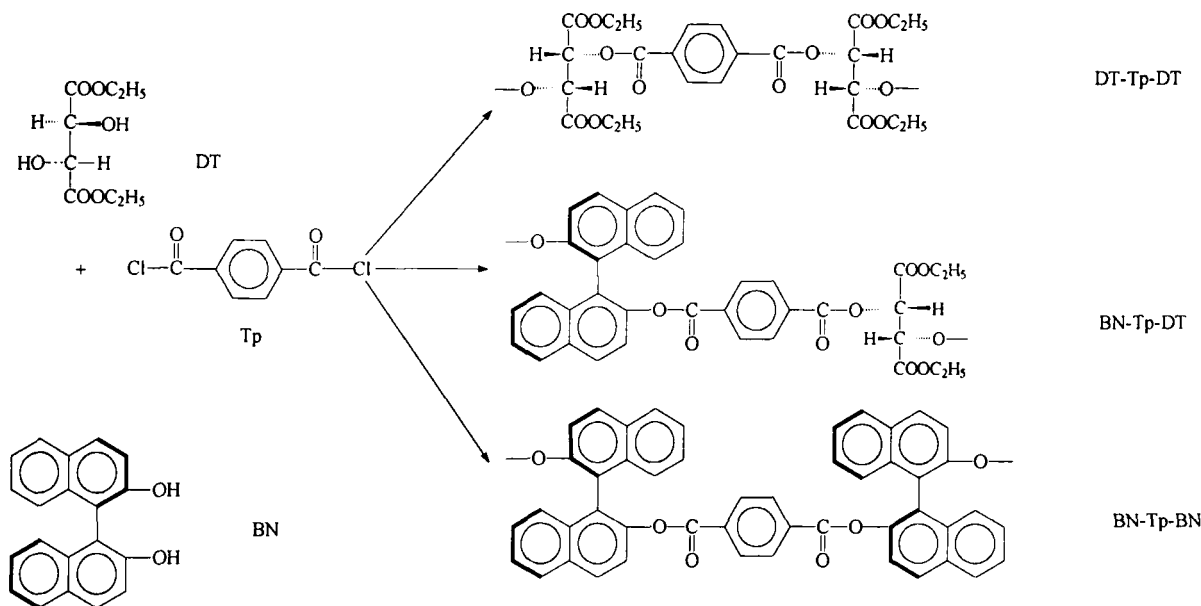
Measurement

The viscosity of the copolyesters was measured in THF ($C = 0.5$ g/dL) at $25.0 \pm 0.1^\circ\text{C}$ using an Ubbelohde dilution viscometer. Optical rotation measurements were carried out on a WZZ-15 spectropolarimeter at 20°C . CD spectrum was recorded with a 0.01 cm cell at room temperature on a JASCO-720 spectropolarimeter. ^{13}C -NMR spectra of the copolyesters in CDCl_3 were collected on a Varian XL-200 (200 MHz) spectrometer with tetramethyl silane (TMS) as the internal standard.

RESULTS AND DISCUSSION

Compositions and Sequence Structure Distributions

The three triad sequences structure of copolyesters is represented in Scheme 1. The triad sequence probabilities in this copolyester chain are identical up to the δ position in relation to the quaternary carbon of terephthalate, but an unexpected long range effect on the chemical shift is readily observed in the ^{13}C -NMR spectrum. The three triad sequences are shown in the following Scheme 1.



Scheme 1 Synthesis and three triad sequence structures of optically active copolyesters based on 1,1'-binaphthalene-2,2'-diol (BN), diethyl tartrate (DT) and terephthaloyl chloride (Tp)

It has been well known that NMR spectroscopy is a powerful technique for the qualitative and quantitative analysis of the composition of copolyester^[10]. Several investigators have studied the sequence distribution of copolyesters derived from ethylene glycol and a mixture of two dibasic acids^[11, 12] using ^1H -NMR spectra. Newmark *et al.*^[13] reported the sequence distribution of poly(ethylene/tetramethylene/terephthalate) copolyesters using ^{13}C -NMR. Jedlinski *et al.*^[14] have reported the sequence distribution of an aromatic copolyester based on 1,1'-binaphthalene-4,4'-diol, 2,2-bis(4-hydroxyphenyl) propane and terephthaloyl chloride by using ^1H -NMR spectra. The ^{13}C -NMR spectra of the homopolyesters and copolyesters based on DT, BN and Tp are shown in Fig. 1. According to the resonance difference of the terephthalate quaternary carbon atoms in symmetric homopolyesters (BN-Tp-BN and DT-Tp-DT) and asymmetric copolyesters (BN-Tp-DT), the chemical shifts of the quartet peaks appeared at $\delta = 132.3\sim 133.7$ as shown in Fig. 1. In Fig. 1 the chemical shifts of the quartet peaks are 133.63 (1 peak), 133.11 (2 peak), 132.96 (3 peak) and 132.32 (4 peak) for BN-side in BN-Tp-DT, BN-

Tp-BN, DT-Tp-DT and DT-side in BN-Tp-DT, respectively.

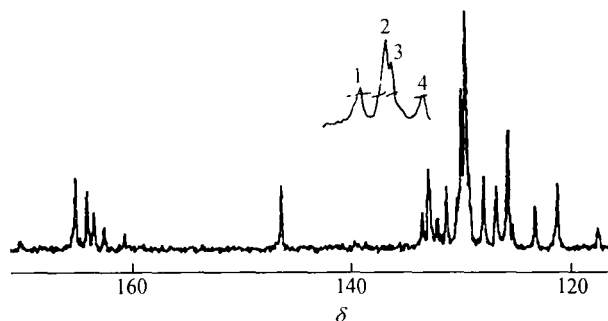


Fig. 1 ^{13}C -NMR spectra of terephthalate quaternary carbon atoms of the copolyesters

1) BN-Tp-DT (BN-side, $\delta = 133.63$)

2) BN-Tp-BN ($\delta = 133.11$)

3) DT-Tp-DT ($\delta = 132.96$)

4) BN-Tp-DT (DT-side, $\delta = 132.32$)

It is generally accepted in the analysis of ^{13}C -NMR spectra of the polymers that similar carbons (aromatic or aliphatic carbon) in different sequences can be quantitatively compared. The peak areas are determined by the cut and weigh method. Therefore, the three triad sequence distributions of copolyesters with the quartet peaks of terephthalate quaternary aromatic carbon atoms are given in Table 1.

Table 1. Characterization of the copolyesters based on DT, BN and Tp

Copolyesters ^a	M.R. ^b (feed)	Yield (%)	$[\alpha]_D^{20c}$ degree	$[\eta]^d$ (mL/g)	Triad probabilities (normalized)			Compositions	
					$P_{(\text{DT-Tp-DT})}$	$P_{(\text{DT-Tp-BN})}$	$P_{(\text{BN-Tp-BN})}$	P_{BT}	P_{DT}
Tp-DT(D)	0/1/1	97.2	+141.3°	—	—	—	—	—	1.00
Tp-DT(L)	0/1/1	90.5	−140.2°	—	—	—	—	—	1.00
BN(R)-Tp-T(L)	1/2/1	80.1	−28.6°	4.09	0.23	0.58	0.18	0.47	0.524
BN(R)-Tp-T(D)	1/2/1	33.3	+15.9°	4.69	0.21	0.57	0.21	0.50	0.500
BN(S)-Tp-T(L)	1/2/1	38.5	−53.4°	4.52	0.25	0.39	0.35	0.54	0.452
BN(S)-Tp-T(D)	1/2/1	75.3	+44.4°	4.84	0.24	0.60	0.15	0.45	0.544
BN(S)-Tp	1/1/0	87.0	+13.0°	—	—	—	—	1.00	—
BN(R)-Tp	1/1/0	90.5	−13.1°	—	—	—	—	1.00	—

^a 1,1'-(R)-(+)-Binaphthalene-2,2'-diol: BN(R); 1,1'-(S)-(-)-Binaphthalene-2,2'-diol: BN(S); (2R, 3R)-(+)-Diethyl-L-tartrate: DT(L); (2S, 3S)-(-)-Diethyl-D-tartrate: DT(D); Terephthalate: Tp

^b Molar ratio: BN/Tp/DT

^c Specific rotation unit: $\text{deg}\cdot\text{cm}^2/\text{g}$ ($C = 0.5$ g/dL, in THF)

^d Measured in THF, $C = 0.5$ g/dL, $T = 25^\circ\text{C}$

The composition of the copolyesters was determined via three triad sequence distributions from the ^{13}C -NMR spectra which is almost in agreement with that calculated by feed (see Table 1). In addition, the composition analysis of the copolyesters has been conducted by using GPC and TLC (thin layer chromatography). The chromatograms show that the copolyesters have a single molecular weight peak and no other fractionation has occurred.

Rotation Sign

It is noteworthy that the rotation sign of the tribasic copolyesters and the mixture of two homopolyesters could be shown in Table 2 and obey a stereo-scheme having three dimensional quadrants (see Scheme 2).

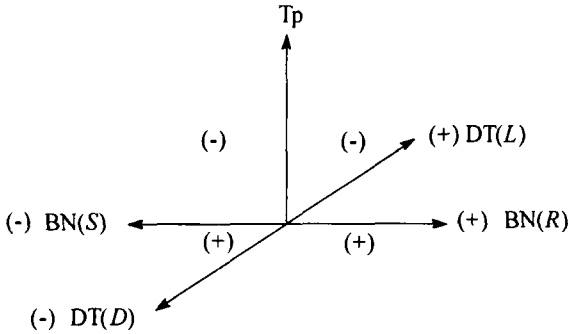
It is very clear that the rotation sign would be positive for BN(R)-Tp-DT(D) and BN(S)-Tp-DT(D) copolyesters and the corresponding mixture of homopolyesters, but negative for BN(R)-Tp-DT(L) and BN(S)-Tp-DT(L) copolyesters and the corresponding mixture of homopolyesters (Table 2 and Scheme 2). It could be attributed to the prevalence of their configuration or conformation coordination effect during the copoly-

condensation of two optically active monomers.

Table 2. The rotation signs of homopolyesters and copolyesters^a

Polyesters and copolyesters	DT(L)	DT(L)-Tp	BN(R)	BN(R)-Tp	BN(R)-Tp-DT(L)	BN(R)-Tp-DT(D)
Rotation sign	+	-	+	-	-	+
Polyesters and copolyesters	DT(D)	DT(D)-Tp	BN(S)	BN(S)-Tp	BN(S)-Tp-DT(D)	BN(S)-Tp-DT(L)
Rotation sign	-	+	-	+	+	-

^a The symbols / and -Tp indicate that they are the mixture of homopolyesters and the copolyesters, respectively.



Scheme 2 The rotation sign of the copolyesters or the mixture of corresponding homopolyesters having three dimensional quadrants derived from (+)DT(L), (-)DT(D), (+)BN(R), (-)BN(S) and Tp

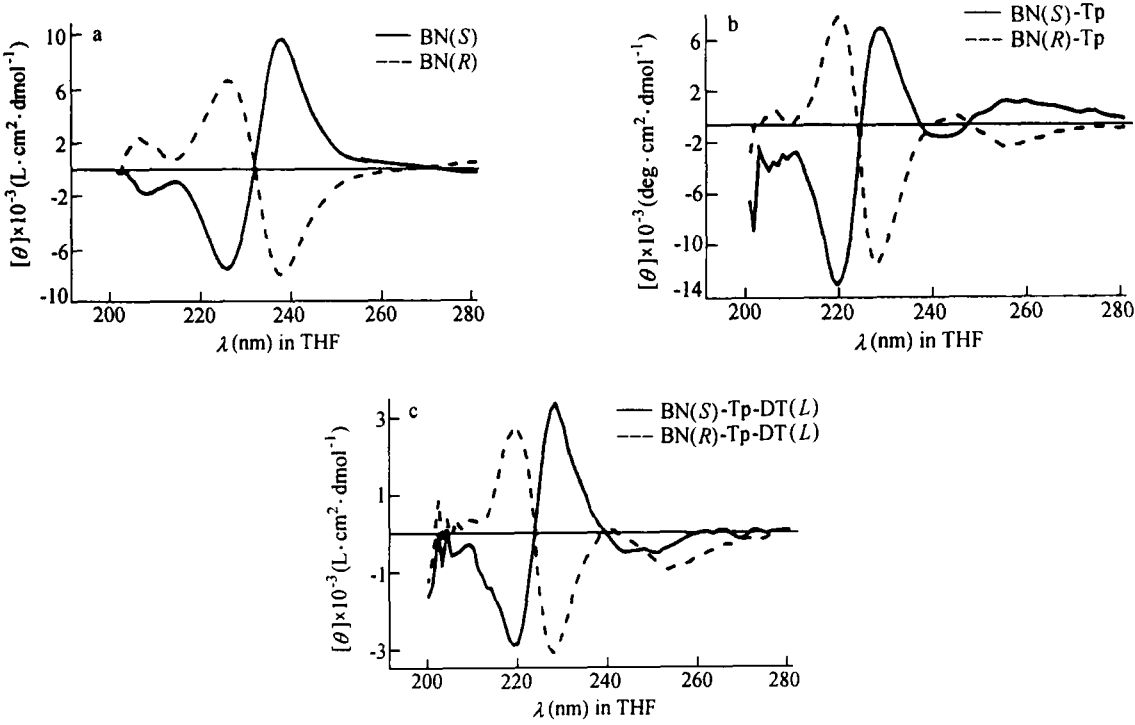


Fig. 2 The circular dichroism spectra of BN (*R* and *S*) (a), BN (*R* and *S*)-Tp (b) and BN (*R* and *S*)-Tp-DT(*L*) (c) $C = 1.2 \sim 2.0 \times 10^{-5}$ mol/L, in THF

Circular Dichroism Spectrum

The circular dichroism (CD) spectra of pairs of BN (*R* and *S*), BN (*R* and *S*)-Tp and BN (*R* and *S*)-Tp-DT(*L*) are shown in Figs. 2a, b and c, respectively.

The naphthalene chromophore in BN gives two strong Cotton effects around 227 and 238 nm derived from the ^1B_b transition^[15] in Fig. 2a, i.e. a positive first Cotton effect and a negative second Cotton effect. Their rotation signs could be decided by the sign of positive or negative first Cotton effects situated at long wavelength in the CD spectra, but Fig. 2b indicates that the rotation signs of the homopolyesters, BN(*R*)-Tp and BN(*S*)-Tp which have opposite configuration isomers^[16] are negative and positive, respectively. Because two weak negative Cotton effects at ca. 260 nm in the CD spectrum shown in Fig. 2c could be effected by a strong negative Cotton effect at ca. 260 nm in the CD spectrum of Tp-DT(*L*) homopolyester in our previous paper^[7], these could make the rotation sign of the copolyesters, BN(*R*)-Tp-DT(*L*) and BN(*S*)-Tp-DT(*L*), negative (see first negative Cotton effect situated at long wavelength in the CD spectrum of copolyesters).

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