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Optically active cyclic poly(ether sulfone)s based on chiral 1,1′-bi-2-naphthol

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Abstract

Optically active cyclic poly(ether sulfone)s are prepared from 4-fluorophenyl sulfone and (*R*)- or (*S*)-1,1′-bi-2-naphthol. The measurement of MALDI-TOF MS shows that the product is composed of a series of cyclic and linear oligomers where the repeating unit number (*n*) is from 2 to 12, from which the cyclic dimers (*n*=2), and cyclic trimer (*n*=3) have been separated from their homologous compounds by TLC successfully. Specific optical rotation $[\alpha]_D^{25}$ is −583.0 for (*R*)-cyclic dimer, +588.0 for (*S*)-cyclic dimer, +22.7 for (*R*)-cyclic trimer, and −20.3 for (*S*)-cyclic trimer. Their properties are also determined by other methods, such as ^{1}H NMR and CD etc. © 1998 Elsevier Science Ltd. All rights reserved.

1. Introduction

Since the resolution of binaphthol has been carried out more conveniently,[1] it has been attracting attention for use as a chiral building block,[2] chiral catalyst[3] or chiral auxiliary[4] in asymmetric synthesis, molecular recognition and enantioselective chromatographic separation.[5] However, most of above compounds were linear and there are few literature reports regarding cyclic polymers based on binaphthol.

Recently, Nozaki[6] reported the preparation of optically active cyclic polyamides from glycine and 1,1′-binaphthyls, in which Boc-Gly was attached to (*R*)- or (*S*)-2,2′-amino-1,1′-binaphthalene and then cyclized with (*R*)- or (*S*)-1,1′-binaphthalene-2,2′-dicarboxylic chloride. In the paper the conformations of the two cyclic polyamides had been revealed. In order to establish a transesterification insertion concept, and to use this reactive processing route to effectively incorporate a functionalized cyclic carbonate into an aromatic polycarbonate via the transesterification insertion mechanism, Priddy Jr.[7] synthesized a cyclic oligomer of the carbonate which formed from racemic 1,1′-bi-2-naphthol. Takata[8] reported the

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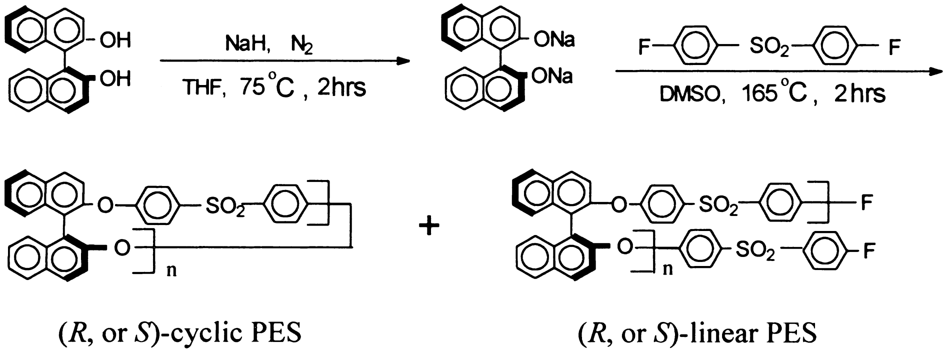
synthesis of optically active poly(aryl carbonates) consisting of axially chiral binaphthyl groups as the main chain units, which would take a stable helix in solution.

We report here the preparation and characterization of optically active cyclic poly(ether sulfone)s based on the chiral 1,1′-bi-2-naphthol.

2. Results and discussions

Optically active poly(ether sulfone)s have been synthesized from 4-fluorophenyl-sulfone and (*R*)- or (*S*)-1,1′-bi-2-naphthol (Scheme 1), and the characterization of the off-white poly(ether sulfone)s (PES) are shown in Table 1. The molecular weights of the poly(ether sulfone)s were measured by GPC analysis based on standard polystyrene. The weight-average molecular (M_w) and polydispersity (M_w/M_n) are 6060 and 3.37 for (*R*)-poly(ether sulfone), and 4470 and 2.72 for (*S*)-poly(ether sulfone), respectively. Of particular note is that both of the two enantiomers show a shoulder peak in their GPC spectra which might imply that there are two systems with different molecule structures in the product mixtures.



Scheme 1.

In order to determine the structure of (*R*)- or (*S*)-PES, MALDI-TOF MS analyses were carried out, and the spectrum of the (*R*)-enantiomer is shown in Fig. 1. It can be seen that there is a very regular product molecular distribution which contains a series of cyclic poly(ether sulfone)s and a series of linear poly(ether sulfone)s. The lowest molecular weight of PES found is 1001 which perfectly coincides with the molecular weight of dimeric cyclic PES. The molecular weight for a repeating unit of cyclic PES is 500.5; by additions of the repeating unit molecular weight it is very easy to calculate the exact molecular weight of other cyclic PES compounds. For example, the molecular-ion peak 1524.12 (+Na^+) in the MS spectrum corresponds to a molecular weight of trimeric cyclic PES of 1501.5. In this way we also found other cyclic PES compounds in which molecular weights range from 2024.25 (+Na^+) to 5029.53 (+Na^+). The cyclic PES compounds found in the measurement range of up to 6000 in the MS spectrum exhibit the repeating unit number of n=2 to probable n=12.

Table 1
Characterization results of optically active poly(ether sulfone)s

sample	Yield (%)	$[\alpha]_D^{25\ a)}$	$M_w \times 10^{-3\ b)}$	M_w/M_n
(*R*)-PES	80	-122.8	6.06	3.37
(*S*)-PES	86	+91.5	4.47	2.72

a) specific optical rotations of the polymers measured in THF at 25°C
b) molecule weights measured by GPC analysis based on standard polystyrene.

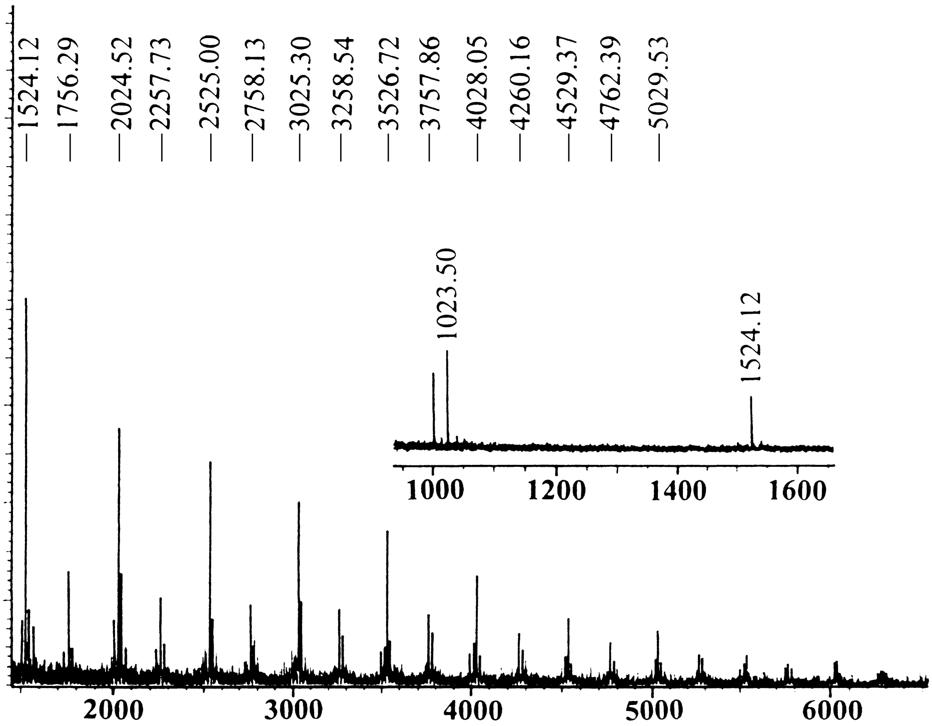


Figure 1. MALDI-TOF MS of (*R*)-PES

In an attempt to obtain the pure cyclic poly(ether sulfone) compounds from the product mixture, separation was carried out by preparative thin layer chromotograph (PTLC). It is rather difficult to separate every cyclic PES from the mixture, because the homologous cyclic PES compounds have very similar dissolution properties. Fortunately, the optically active dimers and trimers of cyclic PES are successfully separated in almost pure form by PTLC. The MALDI-TOF MS of (*S*)-dimeric and (*S*)-trimeric cyclic PES samples are shown in Fig. 2. There are three sets of molecular-ion peaks in the spectrum of (*S*)-dimeric cyclic PES, i.e. 1000.26, 1023.25, and 1039.22, in which the peak of 1000.26 accounts for the molecular-ion peak of the dimeric cyclic PES, while 1023.25 and 1039.22 represent the same molecular-ion peaks but with the addition of Na^+ and K^+, respectively. In the (*S*)-trimeric cyclic PES case, only two sets of molecular-ion peaks at 1523.38 and 1539.39 appeared in the spectrum which represents the addition of Na^+ and K^+, respectively, to the molecular ion. The MS spectra of (*R*)-dimeric and (*R*)-trimeric enantiomers are found to be the same as their (*S*)-enantiomers. (*R*)- and (*S*)-Cyclic PES have the same ^1H NMR spectra, and the ^1H NMR spectra of (*S*)-dimeric and (*S*)-trimeric PES are shown in Fig. 3.

The specific optical rotations of cyclic dimers and trimers are shown in Table 2. The (*R*)-dimeric cyclic PES exhibits a high negative specific rotation ($[\alpha]_D^{25}$ −583.0), and the (*R*)-trimeric cyclic PES has a low positive specific rotation ($[\alpha]_D^{25}$ +22.7). It is interesting that the sign of the specific rotation of the cyclic dimer is opposite to that of the cyclic trimer and the magnitudes of specific rotations show considerable differences. Similar results were also found in the (*S*)-cyclic PES system in which the (*S*)-dimeric cyclic PES exhibits a high positive specific rotation ($[\alpha]_D^{25}$ +588.0) which is opposite in sign to and higher in magnitude than that of (*S*)-trimeric cyclic PES ($[\alpha]_D^{25}$ −20.3).

According to the results obtained by the computer simulation (the software used is Alchemy 2000) of

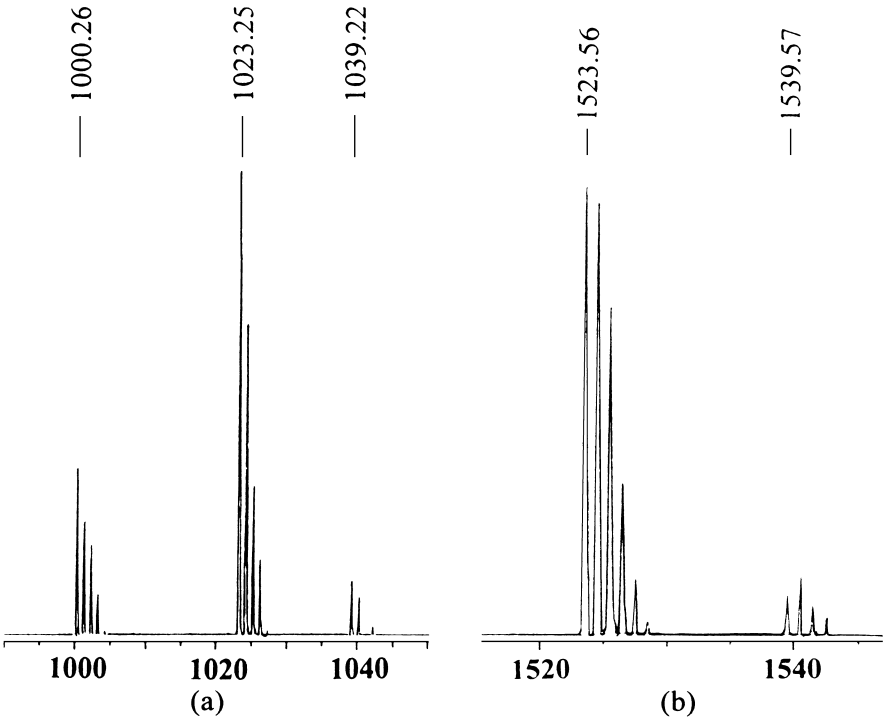


Figure 2. MALDI-TOF MS of (a) (*S*)-dimeric cyclic PES), and (b) (*S*)-trimeric cyclic PES

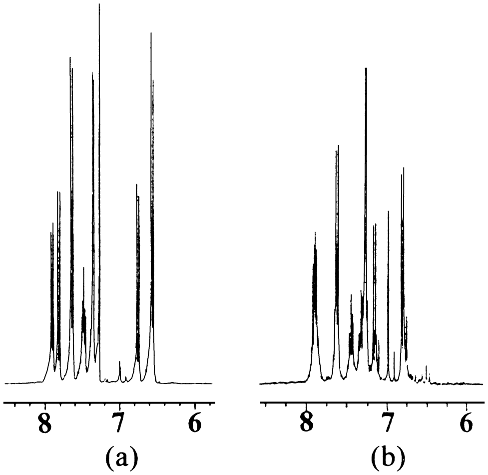


Figure 3. ^{1}H NMR of (a) (*S*)-dimeric cyclic PES, and (b) (*S*)-trimeric cyclic PES

the molecular static structure (Fig. 4), it seems that the dimer forms a turned ring and the trimer exists rather like a propeller. The exact conformations will be determined in the near future.

It was proposed that there is a regularity in the sign and the magnitude of specific rotation, i.e. the even-number cyclic homologous PES compounds possess higher specific rotations which are opposite in sign to those of the odd-number cyclic compounds. Unfortunately this could not been determined because the cyclic PES compounds with higher molecular weights have not been separated successfully.

Fig. 5 shows the CD spectra of the (*R*)- and (*S*)-dimeric cyclic PES. The two plots are very symmetrical as expected. The first absorption maximum that appears at 275 nm ($[\theta]=-5\times10^6$ deg cm^2 dmol^{-1})

Table 2
Characterization of optically active cyclic dimers and trimers

PES (cyclic)		$[\alpha]_D^{25\ a)}$	M_w $^{b)}$	m.p.(°C)
n=2	(*R*)-	-583.0	1000.10	273-274
	(*S*)-	+588.0	1000.25	287-288
n=3	(*R*)-	+22.7	1500.38	282-283
	(*S*)-	-20.3	1500.56	267-268

a) specific optical rotation measured in THF, 25°C.
b) measured by MALDI-TOF MS, Matrix : CCA.

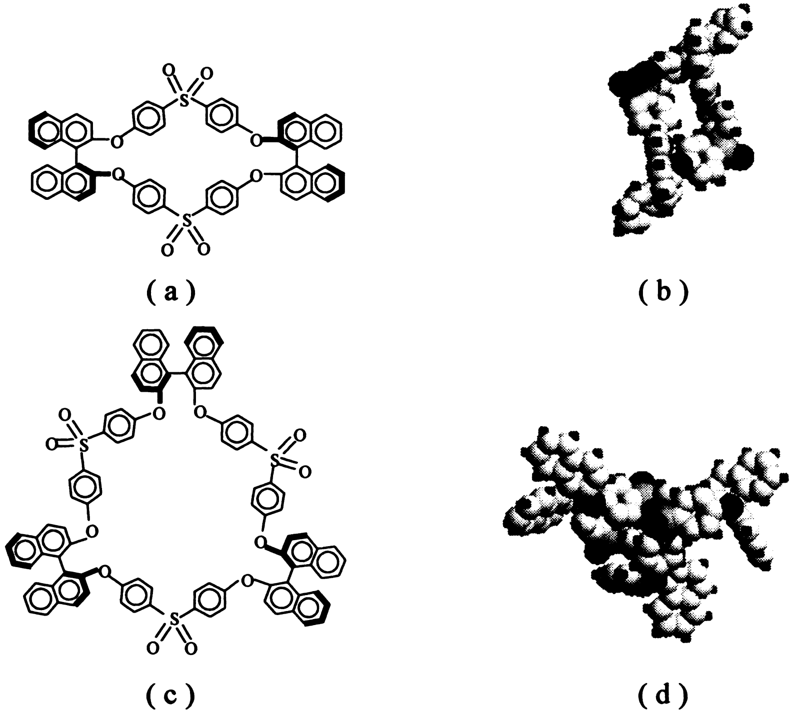

(a) (b)
(c) (d)

Figure 4. (a) Scheme of dimeric cyclic PES (*R* or *S*); (b) computer simulation of dimeric cyclic PES structure; (c) scheme of trimeric cyclic PES (*R* or *S*); (d) computer simulation of trimeric cyclic PES structure

is negative, and following it is the positive absorption maximum at 240 nm ($[\theta]=+5.25\times10^6$ deg cm^2 dmol^{-1}). The first negative Cotton effect and the second positive Cotton effect indicate a negative chirality which coincides with the sign of its actual configuration with the negative optical rotation. Besides the two absorption peaks, there is the third absorption maximum at 225 nm ($[\theta]=-4.75\times10^6$ deg cm^2 dmol^{-1}) which might be attributed to the interaction of $\pi\rightarrow\pi^*$ transition between two chromophores contained in the (*R*)-cyclic dimer. Contrary to the (*R*)-cyclic dimer, the (*S*)-cyclic dimer shows the first positive absorption maximum at 275 nm ($[\theta]=+4.75\times10^6$ deg cm^2 dmol^{-1}), the second negative at 240 nm ($[\theta]=-\ 6.20\times10^6$deg cm^2 dmol^{-1}), and the last at 225 nm ($[\theta]=+3.50\times10^6$ deg cm^2 dmol^{-1}). The first positive Cotton effect and the second negative Cotton effect of the (*S*)-cyclic dimer show a positive chirality which is consistent with the sign of the true configuration with positive optical rotation.

From Fig. 1, it can be seen that besides the cyclic homologous compounds, there is a series of linear PES oligomers which appear alternately with the peaks of cyclic compounds. By molecular weight calculation, these linear oligomers are confirmed to be terminated by the fluorophenyl sulfone residues

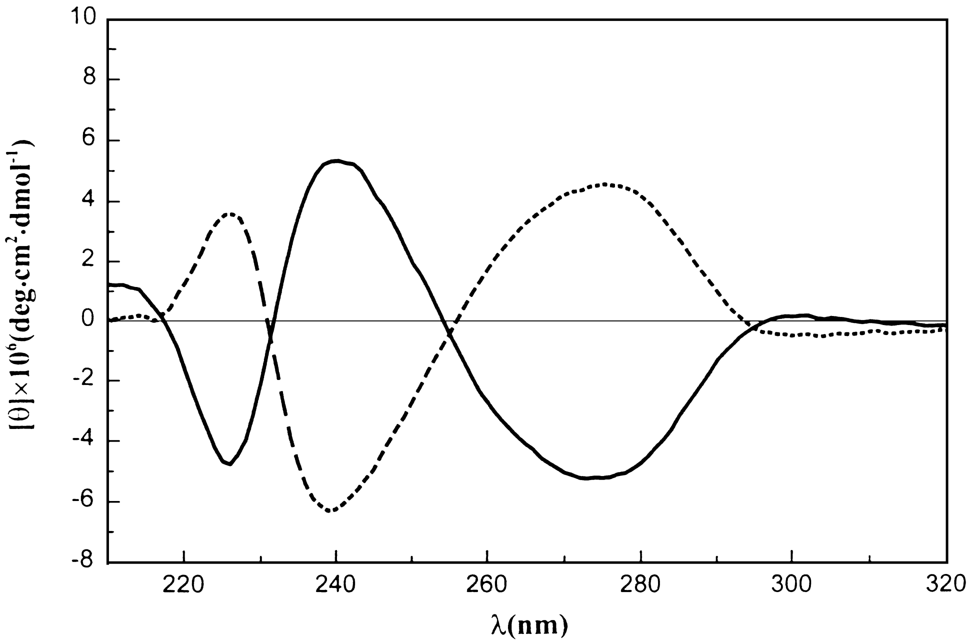


Figure 5. CD spectrum of (*R*)-dimeric cyclic PES (solid line) and (*S*)-dimeric cyclic PES (dashed line)

rather than the BINOL residues at both termini of the linear fragments. The repeating unit number (*n*) of the linear oligomer ranges from 3 to 12 in the range of MS measurement.

From the results described above, the obvious tendency of cyclization in the condensation of chiral BINOL and fluorophenyl sulfone might be considered to be mainly ascribed to the asymmetric structure of BINOL. Under the same experimental conditions, if the racemic BINOL is used in the condensation reaction, no cyclic compounds are found in its MS spectrum.

3. Experimental

3.1. Materials

4-Fluorophenyl sulfone (99%, ACROS Co.) and sodium hydride (80%, dispersion in mineral oil, Aldrich Chemical Co.) were used as commercially available. Tetrahydrofuran and dimethylsulfoxide (DMSO) were distilled and dried with 4 Å molecular sieves before use. (±)-1,1′-Bi-2-naphthol was resolved according to the literature,[1a] (*R*)-1,1′-bi-2-naphthol ($[\alpha]_D^{25}$=+34.4 deg dm^{-1} cm^3, *c*=1, THF) and (*S*)-1,1′-bi-2-naphthol ($[\alpha]_D^{25}$=−34.2 deg dm^{-1} cm^3, *c*=1, THF) were obtained.

3.2. Measurements

^{1}H NMR spectra were measured with an Instrum DM×300 spectrometer in $CDCl_3$ at room temperature. MALDI-TOF MS were detected on an Instrum Biflex III spectrometer with CCA as a matrix. Optical rotations were carried out on a Perkin–Elmer 241 MC polarimeter using the 589 nm wavelength of a sodium lamp at 25°C in THF. Circular dichroism (CD) spectra were recorded in a 0.01 cm cell at room temperature on a JASCO-720 spectropolarimeter.

3.3. Condensation

A 25 ml flask, equipped with a magnetic stirring bar and a reflux condenser, was filled with (*R*)-1,1′-bi-2-naphthol (1 mmol) and sodium hydride (2 mmol). Tetrahydrofuran (15 ml) was added and the resulting solution was treated at 65°C under nitrogen for 2 h, then distilled to dryness. The residue was dissolved in DMSO (7 ml), 4-fluorophenyl sulfone (1 mmol) was added, and the reaction mixture was heated at 165°C for 2 h. After filtration, the filtrate was poured into a solution of 90 ml methanol and 10 ml 1 N hydrochloric acid. An off-white precipitate appeared immediately, and allowed to stand overnight at room temperature, then the precipitate was separated, washed with 80 ml methanol, filtered and dried in vacuo to yield a white solid product of (*R*)-PES (400 mg, 80 wt%). The (*S*)-PES (430 mg, 86 wt%) was obtained in the same way.

3.4. Separation

Separation was performed by preparative thin-layer chromatography (PTLC). The thin layer plate was coated with silica gel H(60) and the eluent was a solution of petroleum ether (60–90°C):chloroform which ratio changed gradually from 80:60 to 75:76 (V/V) in the separation process. The bands separated were collected and eluted with THF. After evaporation, the chiral cyclic dimer and trimer were obtained, respectively. Characterizations are as follows: (*R*)-dimeric cyclic PES (yield 6.8%): mp 273–274°C; $[\alpha]_D^{25}$ −583; ^{1}H NMR in $CDCl_3$ δ 6.54–6.57 (m, 8H, PhH), 6.73–6.76 (m, 4H, ArH), 7.34–7.35 (m, 8H, ArH), 7.45–7.47 (m, 4H, ArH), 7.62–7.65 (m, 8H, PhH), 7.79–7.82 (m, 4H, ArH), 7.86–7.91 (m, 4H, ArH). (*S*)-Dimeric cyclic PES (yield 7.5%): mp 287–288°C; $[\alpha]_D^{25}$ +588; ^{1}H NMR in $CDCl_3$ δ 6.54–6.57 (m, 8H, PhH), 6.73–6.76 (m, 4H, ArH), 7.3–7.38 (m, 8H, ArH), 7.43–7.50 (m, 4H, ArH), 7.62–7.64 (m, 8H, PhH), 7.79, 7.82 (m, 4H, ArH), 7.88,7.91 (m, 4H, ArH). (*R*)-Trimeric PES (yield 4.1%): mp 267–268°C; $[\alpha]_D^{25}$ +22.7; ^{1}H NMR in $CDCl_3$ δ 6.73–6.81 (m, 12H, PhH), 6.98–7.00 (m, 6H, ArH), 7.12–7.17 (m, 6H, ArH), 7.30–7.35 (m, 6H, ArH), 7.41–7.47 (m, 6H, ArH), 7.60–7.65 (m, 12H, PhH), 7.84–7.92 (m,12H, ArH). (*S*)-Trimeric chiral PES (yield 5.4%): mp 282–283°C; $[\alpha]_D^{25}$ −20.3; ^{1}H NMR in $CDCl_3$ δ 6.75–6.82 (m, 12H, PhH), 6.98–6.99 (m, 6H, ArH), 7.10–7.17 (m, 6H, ArH), 7.30–7.35 (m, 6H, ArH), 7.42–7.47 (m, 6H, ArH), 7.61–7.65 (m, 12H, PhH), 7.85–7.92 (m, 12H, ArH).

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