Communication

Structure of Cyclic Aryl Thioester Dimer Based on *o*-Phthaloyl Dichloride and Bis(4-mercaptophenyl) Sulfide

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A cyclic aryl thioester dimer was prepared by the reaction of *o*-phthaloyl dichloride and bis(4-mercaptophenyl) sulfide in good yield under pseudo-high dilution conditions via interfacial polycondensation. The structure of the cyclic dimer was confirmed by a combination of MALDI-TOF-MS, FTIR, gel permeation chromatography and NMR analyses. The X-ray diffraction study of the single crystal of cyclic thioester dimer obtained from two solutions reveals no severe internal strain on the cyclic structure.

Keywords cyclic aryl thioester dimer, MALDI-TOF-MS, crystal structure

Introduction

The advantage of macrocyclic oligomers as precursors for the preparation of high performance polymers via ring-opening polymerization (ROP) has sparked much interest in the area of advanced thermoplastic composites.[1-3] And a series of cyclic oligomers such as carbonates,[4] aryl esters,[5,6] ethers,[7] amides[8] and sulfides[9,10] has been successfully synthesized. Recently, Nishikubo *et al*.[11] reported a kind of novel macrocyclic oligomers containing thioester groups prepared by condensation of bis(4-mercaptophenyl) sulfide with aromatic acid dichlorides. Some of the macrocyclic thioester oligomers possessed relatively high refractive index and were useful as optical materials. The cyclic oligomers based on 5-*tert*-butyl isophthaloyl chloride could undergo solid-phase ring opening polymerization without catalysts, and Nishikubo *et al*.[12] figured out that the *S*-acyl groups were the potential propagating centers during the polymerization. This ring opening polymerization route of macrocyclic thioester oligomers without catalysts has much superiority to the anionic route, especially in processing, for its avoiding inorganic salts or alkali phenoxide in polymers caused by anionic initiators. In this paper we have determined single-crystal structure of the cyclic thioester dimer for the purpose of studying the cyclic nature and expatiating upon the relationship between cyclic nature and ROP reaction in the following work.

Experimental

Materials and instruments

Phthaloyl dichloride was distilled before use. Other reagent-grade solvents and chemicals were used without further purification. IR spectrum was recorded on a Bio-Rad FTS7 spectrometer; ^{1}H NMR and ^{13}C NMR spectra were recorded on a AV300 spectrometer (Bruker, Switzerland) at 300 MHz and 75 MHz, respectively, at room temperature. MALDI-TOF MS was recorded on a LDI-1700 instrument at a wavelength of 337 nm (N_2 laser light). The MALDI-TOF MS instrument was operated in a positive linear mode. Thermal analysis was carried out on a Perkin Elmer 7 series Thermal Analysis Systerm with a heating rate of 10 ℃/min.

Synthesis of macrocyclic thioester dimer

The cyclic dimer sample was synthesised from *o*-phthaloyl dichloride and bis(4-mercaptophenyl) sulfide according to the reported method.[9] The isolated yield was 75.6%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.866 (dd, J = 4.2, 2.4 Hz, 4H), 7.660 (dd, J = 4.2, 2.4 Hz, 4H), 7.503 (d, J = 6.3 Hz, 8H), 7.441 (d, J = 6.3 Hz, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 190.80, 137.51, 137.36, 135.60, 131.79, 129.90, 128.81, 126.74; IR (KBr) ν: 2968, 1735, 1600, 1505, 1170 cm^{-1}.

Single-crystal structure of cyclic thioester dimer

Cyclic dimer was crystallized from solution of tetrehydrofuran (THF) and methylene dichloride, respectively, and the selected crystal was sealed in silica gel for X-ray analysis. The crystal data were collected on a Siemens P4 4-Circle diffractometer with Mo Kα radiation (λ = 0.071073 nm) at 293 K. Non-hydrogen atoms were obtained from successive Fourier syntheses. H atoms were fixed at ideal positions with common isotropic displacement parameters.

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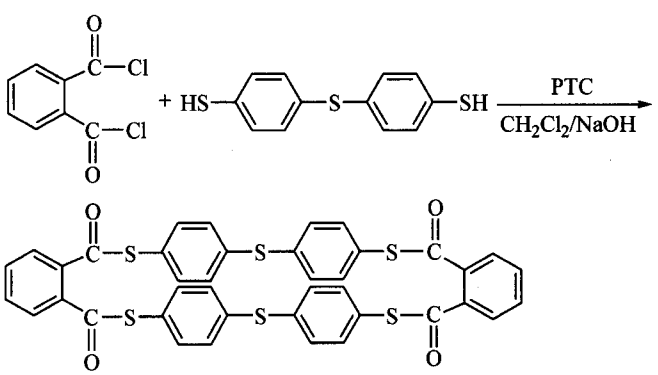
Results and discussion

Synthesis and characterization of cyclic dimer

The preparation of cyclic oligomer based on bis(4-mercaptophenyl) sulfide and *o*-phthaloyl dichloride was carried out under the pseudo-high dilution condition by interfacial polycondensation reaction (Scheme 1). It is surprising that GPC chromatography of the isolated product showed a very narrow single peak suggesting the exclusive formation of a single molecular weight product. The absence of end groups deteched by FTIR, ^{1}H NMR and ^{13}C NMR spectra supports the formation of cyclic oligomer. The most direct confirmation of the cyclic nature of the oligomer comes from matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS). The MS spectrum of the product is shown in Fig.1. By using 1,8,9-dithranol as matrix, a clean positive spectrum with reasonable signal to noise ratio was obtained for the product without the addition of any cationization agents. The spectrum is very simple and the difference from our previous work[5,9] is that the protonated molecular ion peak of cyclic oligomers correponding to polymerization degree of more than 2 is absent. The signal at 762.2 Da corresponds to the protonated molecular ion peak of cyclic dimer; that at 783.9 Da is due to the adduct of the dimer with a sodium cation. The signal at 381.7 Da may correspond to the dimer with two protons.

Scheme 1



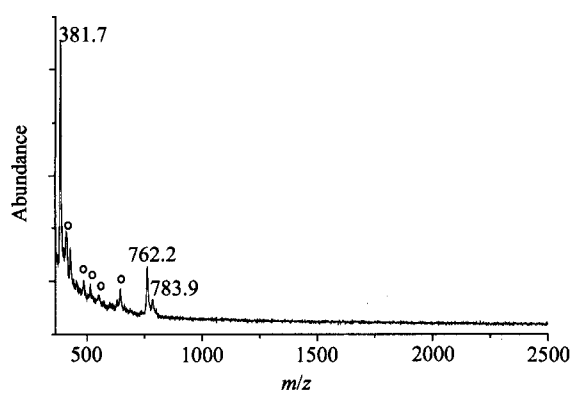


Fig. 1 MALDI-TOF MS spectrum of cyclic aryl thioester dimer. The peaks labeled with "o" result from matrix.

From the above analysis, the small ring size dimer is the main product under the pseudo-high dilution condition and other cyclic oligomer with a polymerization degree of more than 2 is not detected by MALDI-TOF MS and NMR. So the conclusion can be drawn that the cyclic thiosester dimer can be prepared selectively with high yield under the pseudo-high dilution condition. This result may be due to the following reasons: first, according to Jacobson and Stockmayer's theory, dilution beyond a critical concentration may favor the formation of small ring size cyclic oligomers.[13] Second, the structure of *o*-phthaloyl dichloride favors the formation of cyclic product, and the sulfur atom with bigger radius is advantageous for forming molecular cavity of cyclic dimer, too.[9]

The differential scanning calorimetry (DSC) curve of cyclic thioester dimer shows an intense melting endotherm (midpoint: 288.9 ℃). This indicates that the product is highly crystalline, and the cyclic product is easily crystallized from solvents.

Single-crystal structure of cyclic thioester dimer

In order to obtain decisive evidence of the structure and investigate the relationship between the cyclic nature and ROP reaction, the single crystal structure of thioester cyclic dimer was determined by X-ray diffraction analysis. The single crystals of cyclic dimer were obtained from THF solution and CH_2Cl_2 solution. Details of data collection and refinement are given in Table 1. The single crystal structure of thioester cyclic dimer obtained from THF solution shown in Fig. 2 (A) exhibits two types of conformations about thioester groups. All of the carbonyl groups stretch toward the inner cavity of the cyclic structure and the carbonyl groups in the two conformations deviate from the phenyl attached to the carbonyl groups by 36.7° and 119.9°, respectively. The interplanar dihedral angle of the phenyls attached to the thioether is 108.8°. The bond angle of 105.12° at the thioether sulfur atoms is very close to the normal open-chain values around 105°.[14] The phenyl rings in cyclic dimer have a good planarity (root mean square deviations from the planarity of the phenyl planes are 0.00049, 0.00074 and 0.00062 nm, respectively). The distance between S(2) and its symmetrical sulfur atom is 1.2147 nm, which is close to the distance of 1.2013 nm between S(3) and its symmetrical sulfur atom. The X-ray structure of single crystal from CH_2Cl_2 presents four similar conformations about the thioester group [Fig. 2 (B)]. The similarity lies in that the four carbonyl groups all stretch towards the inner cavity of the cyclic structure and the angles between the carbonyl groups and the phenyl rings attached to the carbonyl group range from 51° to 55°. The bond angles of 104.6° for C(1)-S(1)-C(38) and 105.4° for C(21)-S(4)-C(18) are very close to the idealized value of 105°, too. Overall, X-ray analysis indicated that the cyclic dimer was constructed without severe internal strain. The study on ROP reaction and the relationship between the cyclic nature and ROP is in progress.

Table 1 Details of data collection and refinement for the cyclic dimer

Molecular formula	$C_{48}H_{40}O_6S_6$	$C_{42}H_{28}Cl_4O_4S_6$
Formular weight	905.16	930.80
Crystal system	Triclinic	Triclinic
Space group	*P*-1	*P*-1
a (nm)	0.9015(3)	0.9388(5)
b (nm)	1.1346(3)	1.2085(4)
c (nm)	1.1526(2)	2.1410(7)
α (°)	91.34(2)	74.49(3)
β (°)	95.00(7)	84.01(3)
γ (°)	107.23(7)	68.88(3)
Volume (nm^3)	1.1202(4)	2.1833(15)
Z	1	2
D_c ($g \cdot cm^{-3}$)	1.342	1.416
μ (mm^{-1})	0.354	0.599
F(000)	472	952
Crystal size (mm)	0.52×0.42×0.38	0.52×0.32×0.24
θ Range for data collection	1.78° to 26.02°	1.86° to 25.02°
Limiting indices	$-1 \leqslant h \leqslant 10$, $-13 \leqslant k \leqslant 13$, $-14 \leqslant l \leqslant 14$	$-1 \leqslant h \leqslant 11$, $-13 \leqslant k \leqslant 13$, $-25 \leqslant l \leqslant 25$
Reflections collected	5439	9353
Independent reflections	4388	7571
Absorption correction	None	Psi-scan
Final *R* indices [$I > 2\sigma(I)$]	$R = 0.0551$, $wR = 0.1497$	$R = 0.0784$, $wR = 0.1939$

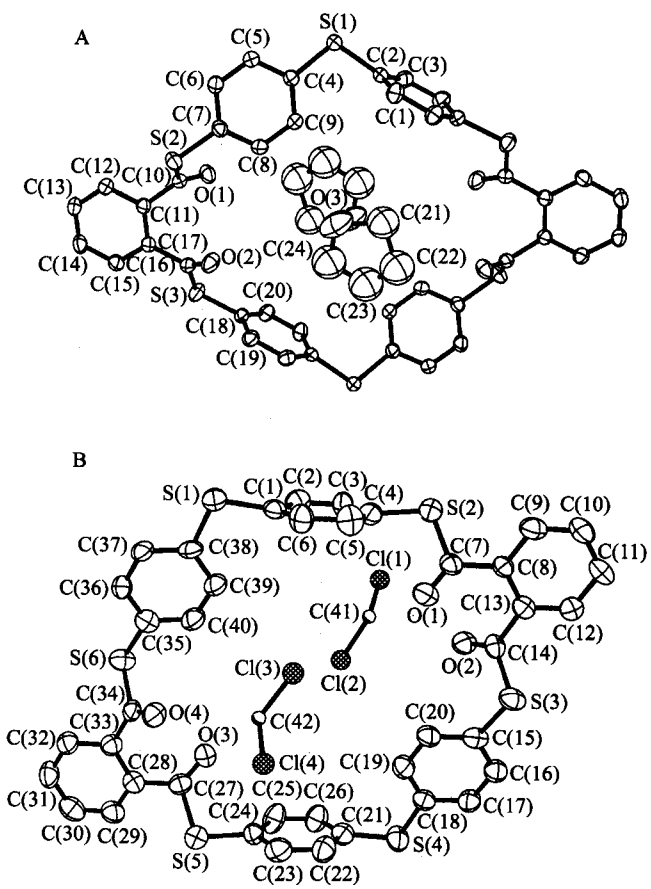


Fig. 2 Molecular structure of cyclic aryl thioester dimer. The single crystals are from the solutions of (A) THF and (B) CH_2Cl_2, respectively.

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