

SYNTHESIS, CHARACTERIZATION AND RING-OPENING POLYMERIZATION OF CYCLIC (ARYLENE PHOSPHONATE) OLIGOMERS*

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Abstract A series of cyclic (arylene phosphonate) oligomers were prepared by reaction of phenylphosphonic dichloride (PPD) with various bisphenols under pseudo-high dilution conditions via interfacial polycondensation. The yield of cyclic (arylene phosphonate) oligomers is over 85% by using hexadecyltrimethylammonium bromide as phase transfer catalyst (PTC) at 0 °C. The structures of the cyclic oligomers were confirmed by a combination of matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) and IR analysis. These cyclic oligomers undergo facile ring-opening polymerization in the melt by using potassium 4,4'-biphenoxide as the initiator to give linear polyphosphonate. Free-radical ring-opening polymerization of cyclic(arylene phosphonate) oligomers containing sulfur linkages was also performed in the melt using 2,2'-dithiobis(benzothiazole) (DTB) as the initiator at 270 °C and the resulting polymer had a M_w of 8×10^3 with a molecular weight distribution of 4. Ring-opening copolymerization of these cyclic oligomers with cyclic carbonate oligomers was also achieved. The average molecular weight of the resulting copolymer is higher than the corresponding homopolymer and the thermal stability of the copolymer is better than the corresponding homopolymer.

Keywords Cyclic(arylene phosphonate) oligomer, Ring-opening polymerization, Copolymer

INTRODUCTION

The use of cyclic oligomers as macrocyclic precursors for the preparation of high performance polymers by ring-opening polymerization (ROP) has sparked much interest in recent years. It could produce a revolutionary change in the preparation of advanced composite materials, and is of great importance in the polymerization process yielding polymers such as the reinforced reactive injection model (RRIM) and the resin transfer model (RTM) etc. Within the last 10 years, the synthesis of cyclic (arylene ether) oligomers^[1–3], cyclic(arylene ester) oligomers^[4, 5], cyclic(arylene imide) oligomers^[6] and cyclic(arylene sulfide) oligomers^[7] have been reported continuously since the G.E company announced the synthesis of cyclic carbonate oligomers and the technique of ROP. It is obvious that most of the publications aimed for the preparation of novel structural aromatic cyclic precursors. However, ROP and the study of its relevant novel products were scarcely reported.

Polyphosphonates have been synthesized via interfacial polycondensation and received considerable attention due to their flame-retardant properties^[8, 9]. However, there was no report about the synthesis of cyclic (arylene phosphonate) oligomers and the preparation of polyphosphonate via the ROP of the cyclic precursors. Herein, we introduce the study of cyclic (arylene phosphonate) oligomers, aiming at the cyclization reaction of phenylphosphonic dichloride (PPD) with various bisphenols and developing a series of novel cyclic oligomers. A very important point was that the cyclic (arylene phosphonate) oligomers, used as additive agents based on the flame-retardant property, would undergo ring-opening polymerization with other aromatic cyclic oligomers,

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which would exert a considerable influence on turning the novel process of ROP of aromatic macrocyclic oligomers into reality.

EXPERIMENT

Materials

Phenylphosphonic dichloride, 4,4'-dihydroxybenzophenone, 4,4'-sulfonyldiphenol, 4,4'-cyclohexylidene-bisphenol, 4,4'-thiodiphenol and Adogen [methyltrialkyl (C_8 – C_{10}) ammonium chloride] were purchased from Aldrich and used as received. Bisphenol A (BPA) was also purchased from Aldrich and recrystallized in toluene before use. Other reagents and solvents were obtained commercially and used without further purification.

Measurements

MALDI-TOF-MS was performed on a LDI-1700 instrument at a wavelength of 337 nm. The instrument was operated in a positive linear mode. Gel permeation chromatography (GPC) was performed on a Shimadzu LC-4A apparatus equipped with two columns (DuPont ZORBAX-PSM-60S) and a UV detector and by using tetrahydrofuran (THF) as the eluent at a flow rate of 0.5 mL/min. Differential scanning calorimetry (DSC) was carried out on a Perkin-Elmer DSC-7 analysis system at a scan rate of 10 K/min and the reported value was taken from a second heating after quick cooling (60 K/min) in a nitrogen atmosphere. Infrared spectra (KBr pellets) were obtained on a Bio-Rad FTS7 spectrometer. Thermogravimetric (T_g) analyses were performed on a Perkin-Elmer 7 series at a scan rate of 100 K/min in air. Inherent viscosities of the polymers were measured in THF (5.0 g/L) solution at $25.0 \pm 0.1^\circ\text{C}$ using an Ubbelohde viscometer.

Synthesis of Cyclic Oligomer 3a

The cyclization reaction was conducted in a 500 mL round-bottomed flask charged with 200 mL methylene dichloride, 40 mL distilled water and 0.2 g PTC (hexadecyltrimethylammonium bromide) at 0°C . A solution of disodium salt of **2a** (1.5960 g, 7.0 mmol) in 50 mL distilled water and a methylene dichloride solution of phenylphosphonic chloride (1.3649 g, 7.0 mmol) were added drop-wise to the mixture in the mechanically stirred flask in an equimolar fashion over a period of 10 h. After the addition, the mixture was stirred for another 3 h. The organic phase was separated and washed three times with 15 mL of distilled water and then evaporated to dryness. The yield of isolated cyclic oligomers was 2.11 g (86%). IR (KBr): 1132, 1272, 1170 ($\text{P}=\text{O}$), 1199 and 1016 ($\text{P}-\text{O}-\text{C}$) cm^{-1} .

Synthesis of Cyclic Oligomers 3b, 3c, 3d and 3e

Cyclic oligomers **3b**, **3c**, **3d** and **3e** were prepared according to the procedure used in the synthesis of cyclic oligomer **3a**, but the organic phase was washed with 20 mL ice water three times. Then the organic solvent was evaporated to dryness and the crude product was washed with 3 mL chloroform three times to remove part of the linear oligomers.

The yield of cyclic oligomer **3c** was 84%. IR (KBr): 1132, 1268 ($\text{P}=\text{O}$), 1193 and 1014 ($\text{P}-\text{O}-\text{C}$) cm^{-1} . The yield of cyclic oligomer **3d** was 81%. IR(KBr): 1135, 1267 ($\text{P}=\text{O}$), 1201 and 1014 ($\text{P}-\text{O}-\text{C}$) cm^{-1} . The yield of cyclic oligomer **3e** was 82%. IR (KBr): 1131, 1272, 1170 ($\text{P}=\text{O}$), 1203 and 1016 ($\text{P}-\text{O}-\text{C}$) cm^{-1} .

Ring-Opening Polymerization of 3a

The cyclic oligomer **3a** (0.4 g) was dissolved in dry methylene dichloride (10 mL) along with potassium 4,4'-biphenoxide (1 W/W%). The methylene dichloride solvent was then evaporated to provide a homogeneous mixture which was further dried at 90°C under vacuum overnight. The ring-opening polymerization was carried out in a test tube under a nitrogen atmosphere at 280°C for 15 min.

Ring-Opening Polymerization of 3c

Polymerization of cyclic oligomer **3c** was performed by a method similar to that for **3a** but the initiator was 2,2'-dithiobis(benzothiazole) (DTB) and the ROP was achieved in a test tube under nitrogen atmosphere at 270°C for 15 min.

Ring-Opening Copolymerization

The cyclic carbonate oligomers (0.5 g) and cyclic oligomer **3a** (0.057 g) were dissolved in dry methylene dichloride (12 mL) along with potassium 4,4'-biphenoxide (1 *W/W*%) and evaporated to provide a mixture which was further dried at 90°C under vacuum for 24 h. The ring-opening copolymerization was performed in a test tube under a nitrogen atmosphere at 280°C for 15 min.

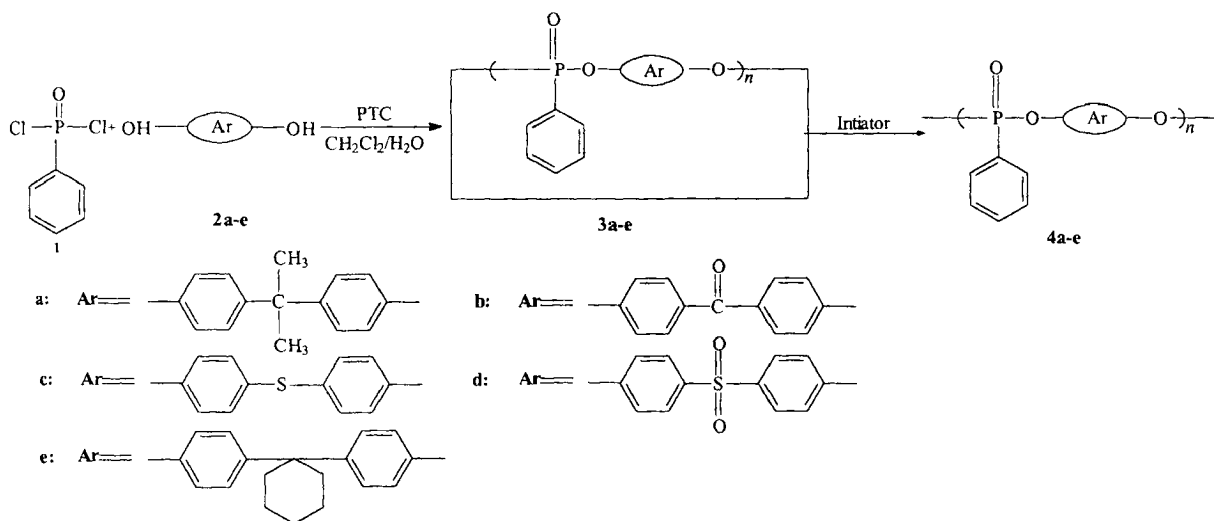
RESULTS AND DISCUSSION

Synthesis of Cyclic (Arylene Phosphonate) Oligomers

The preparation of linear polyphosphonates based on phenylphosphonic dichloride (PPD) with different bisphenols via the interfacial polycondensation was carried out at −5 to −8°C in order to avoid hydrolysis of PPD. The yield was above 90% under the reaction conditions. Thereby, an attempt was made to optimize the reaction conditions for formation of cyclic (arylene phosphonate) oligomers, a series of parallel reactions were carried out at −10°C, 0°C or 10°C in the presence of hexadecyltrimethylammonium bromide (HTAB) over 10 h and the influence of phase transfer catalysts (PTC) on the yield of cyclization was investigated, too. As shown in Table 1, high cyclic yield was obtained when the temperature is 0°C using HTAB as PTC. The result shows that the cyclization reaction of PPD with different bisphenols is strongly affected by the reaction temperature and an appropriate temperature for this cyclization reaction is 0°C. This might be caused by the mechanism of cyclization reaction and the hydrolysis of PPD. When the temperature is −10°C, the speed of cyclization is low, which is unfavorable for achieving pseudo-high dilution conditions, so the cyclic yield is low. In order to increase the speed of cyclization, the temperature must be kept high. However, at 10°C, it is difficult to obtain a high cyclic yield because of the hydrolysis of PPD. Considering both the cyclization speed and the hydrolysis of PPD, this reaction was conducted at 0°C and yielded a satisfactory result.

Table 1. The cyclic yield at different temperatures, PTCs and times

Time (h)	Temperature (°C)	PTC	Cyclic yield (%)			
			3a	3b	3c	3d
11	−10	HTAB	59	57	54	54
10	0	HTAB	86	84	84	81
12	10	HTAB	54	56	53	52
10	0	TBAC	57	58	54	48
10	0	Adogen	59	56	45	49



Scheme 1

The PTC used was tetrabutylammonium chloride (TBAC) for preparing linear aromatic polyphosphonate via interfacial polycondensation. The effect of PTC on the cyclization reaction of PPD with different bisphenols at 0°C was investigated. It can be seen from Table 1 that the cyclic yields obtained were low from the parallel reactions in the presence of TBAC or Adogen at 0°C; however, the cyclic yields can exceed 80% when HTAB was used as PTC at 0°C. This the conclusion can be drawn that HTAB as PTC is more efficient than the other two PTCs. Under optimum conditions, a series of interfacial condensation of PPD with a number of bisphenols (Scheme 1) were performed. The resulting reaction mixtures were characterized by the combination of MALDI-TOF, GPC and IR.

Characterization of Cyclic (Arylene Phosphonate) Oligomers

The structure of cyclic (arylene phosphonate) oligomers was confirmed by IR spectra. The IR spectrum of cyclic oligomer **3a** shows several absorption peaks at 1132, 1272, 1170 and 1199, 1016 cm^{-1} corresponding to P=O and P—O—C stretching vibrations, respectively. The cyclic structures were confirmed by employing MALDI-TOF-MS spectrometry^[10, 11]. The MALDI spectrum of the cyclic oligomers **3a** is shown in Fig. 1(a). A relatively clean positive spectrum with reasonable signal to noise ratio was obtained without the addition of any cationization agents by using retinoic acid as the matrix. Repeating units corresponding from dimer to hexamer can be detected. The MS spectrum of **3a** cyclic oligomers shows three signals for each oligomer. For example, the signals for cyclic trimer are located at 1051.8, 1074.4 and 1090.2 Da. The signal at 1051.8 Da corresponds to the protonated molecular ion peak, that at 1074.4 Da is due to the adduct of the trimer plus a sodium cation, and the signal at 1090.2 Da is due to the adduct of trimer plus a potassium cation. Traces of linear oligomers are also present, e.g., at m/z = 899.9 Da. On the basis of MS analysis, it appears that cyclic dimer is the predominant one which constitutes over 50 wt% of the reaction mixture.

Table 2. Results of MALDI-TOF-MS analysis for cyclic oligomer **3c**, **3d** and **3e**

Cyclic oligomer	$[M_2+H]^+$	$[M_3+H]^+$	$[M_4+H]^+$	$[M_5+H]^+$	$[M_6+H]^+$	$[M_7+H]^+$	$[M_8+H]^+$	$[M_9+H]^+$
3c	Measured	681.7	1022.1	1362.7	1703.1	2043.5	2383.1	3065.7
	Calculated	681.5	1021.8	1362.1	1702.4	2042.6	2382.9	3063.5
	Intensity	100	66.7	50.1	33.3	21.7	16.7	13.3
3d	Measured	745.6	1118.2	1491.1	1863.1			
	Calculated	745.5	1117.8	1490.1	1862.4			
	Intensity	100	40.4	30.8	19.2			
3e	Measured	781.7	1172.4	1562.7	1952.8			
	Calculated	781.7	1172.1	1562.4	1952.8			
	Intensity	100	48.3	43.3	35.2			

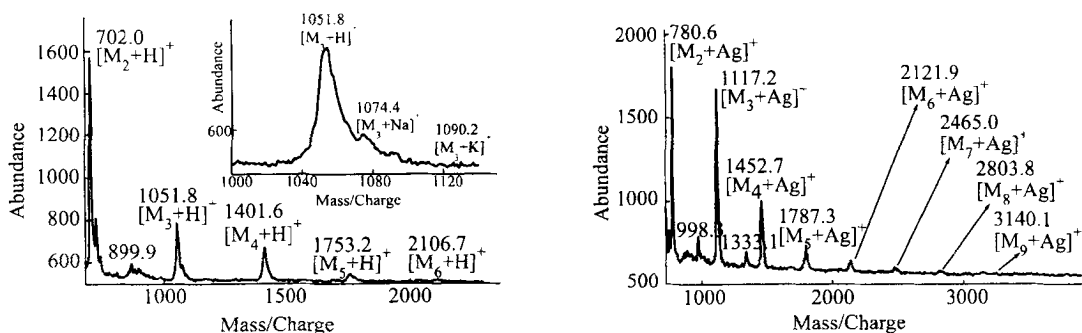


Fig. 1 MALDI-TOF-MS spectrum of (a) cyclic oligomer **3a**, retinoic acid as the matrix and (b) cyclic oligomer **3b**, 1,8,9-dithranol as matrix and silver trifluoroacetate as cationization agent

MALDI-TOF-MS spectrum of cyclic oligomer **3b**, using 1,8,9-dithranol as matrix and silver trifluoroacetate as cationization agent, give the correct molecular ion signals for silver adducts of the desired cyclic oligomers

(Fig. 1b) from dimer ($n = 2$, $m/z = 780.6$) up to nonamer ($n = 9$, $m/z = 3140.1$) with excellent signal to noise ratio. A few linear oligomers are also observable, *e.g.*, at $m/z = 998.3$ or 1333.1 Da. On the basis of GPC and MS analysis, cyclic dimer is the main product which makes up over 47 wt% of the reaction mixture. The data from MALDI-TOF-MS analysis of cyclic oligomers **3c**, **3d** and **3e** are given in Table 2, corresponding to details of the structure of these cyclic (arylene phosphonate) oligomers.

Ring-opening Polymerization (ROP) of Cyclic (Arylene Phosphonate) Oligomers

ROP of the cyclic oligomer **3a** can be initiated through an ether exchange reaction. Melt ring-opening polymerization of cyclic oligomer **3a** was carried out at 280°C using 1 W/W% of potassium 4,4'-biphenoxide as the anionic initiator. The polymerization reaction is depicted in Scheme 1. Figure 2(a) shows the GPC trace of resulting polymer **4a**; the result reveals that the anionic ROP of the cyclic oligomer **3a** was achieved and the resulting polymer **4a** has a M_n of 1×10^3 and a M_w of 5×10^3 with a molecular weight distribution of 5. The macrocyclic oligomers **3c** containing sulfide linkage underwent facile free-radical ROP via a transthioether reaction to give linear polymer at 270°C using 1 W/W% of DTB as the free-radical initiator. Figure 2(b) shows the GPC trace of resulting polymer **4c**; the resulting polymer **4c** has a M_n of 2×10^3 and a M_w of 8×10^3 with a molecular weight distribution of 4.

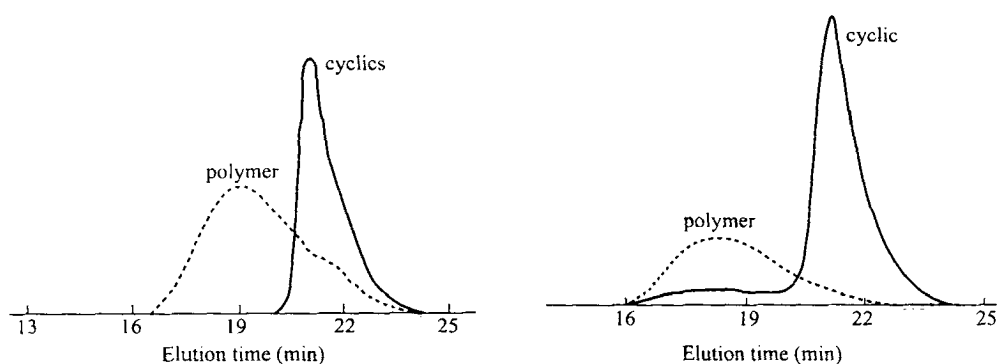


Fig. 2 The GPC trace (THF, 18°C , 0.5 mL/min) of (a) cyclic oligomer **3a** and the polymerized products in the presence of 1 W/W% potassium 4,4'-biphenoxide, (b) cyclic oligomer **3c** and the polymerized products in the presence of 1 W/W% DTB

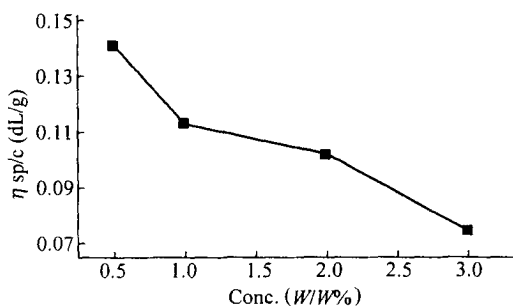


Fig. 3 Relationship between inherent viscosities and initiator concentration of the ROP of cyclic oligomer **3a**

The ROP of cyclic (arylene phosphonate) oligomer was carried out successfully. However, the average molecular weights of the resulting polymers were not very high. This may be caused by traces of linear oligomers present in the cyclic oligomer, which acted as chain-transfer agents^[4] and limited the propagation of linear chains. The influence of initiator concentration on the molecular weight of the resulting polymer via ROP was studied, too. As shown in Fig. 3, the inherent viscosity of the polymer decreases as the initiator concentration is increased and the higher initiator concentration results in the lower average molecular weight.

Thermal Behavior of Polymer 4a, Polycarbonate and Copolymer

Polycarbonate was obtained via ring-opening polymerization of cyclic carbonate oligomers. Scheme 2 shows the synthesis of a copolymer via ring-opening copolymerization. DSC analysis (Table 3) shows that the copolymer has only, single T_g value a suggesting phase mixing has occurred. The relationship between T_g of homopolymers [polymer 4a and polycarbonate] and that of copolymer were in accord with the FOX equation^[12].

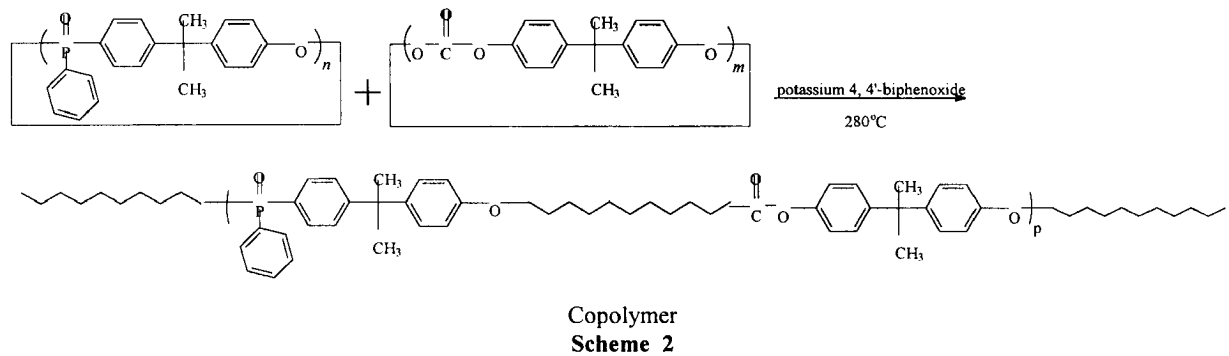


Table 3. Results of DSC (at a scan rate of 10 K/min under nitrogen atmosphere) and T_g measurements (at a scan rate of 10 K/min in air) of homopolymer (polymer 4a and polycarbonate) and copolymer

	Polycarbonate	Polymer 4a	Copolymer
T_g (°C)	146	77	125
Temperature at 5 wt% loss (°C)	377	348	391

The inherent viscosity of the copolymer ($\eta_{sp}/c = 0.38$ dL/g) was higher than that of corresponding homopolymer ($\eta_{sp}/c = 0.11$ dL/g, $\eta_{sp}/c = 0.35$ dL/g). As shown in Table 3, 5% weight loss of homopolymer (polymer 4a) in air appears at about 348 °C and that of polycarbonate and copolymer appears at about 377 °C and 391 °C, respectively. It is evident that the copolymer has higher thermal stability than the corresponding homopolymers.

CONCLUSION

A series of cyclic (arylene phosphonate) oligomers prepared by the reaction of PPD with various bisphenols via the interfacial polycondensation route were described. The cyclic structure was identified by IR and MALDI-TOF-MS. ROP of cyclic (arylene phosphonate) oligomers produced polyphosphonates. Ring-opening copolymerization of cyclic oligomer 3a and cyclic carbonate oligomers was carried out successfully and the thermal stability of the resulting copolymer is better than that of the corresponding homopolymer, which indicates that the cyclic (arylene phosphonate) oligomers used as an adduct agent of the cyclic precursor are suitable for ROP.

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