

SYNTHESIS AND POLYMERIZATION OF BISPHENYLENE ORTHOCARBONATE

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ABSTRACT

Bisphenylene orthocarbonate (I) was synthesized by the reaction of dicopper catecholate with carbon tetrachloride, and underwent cationic ring-opening polymerization with the introduction of phenyl group into the main chain. The obtained polymer with ester and ether group was verified by IR and ^1H NMR spectra. Based on the analysis of the polymer structures, the polymerization mechanism was proposed. Its T_m and T_g are 254°C and 160°C respectively. No decomposition of the polymer was observed below 320°C. The volume expansion property of the monomer during polymerization was studied by measuring the density difference between I and its polymer at various temperatures.

INTRODUCTION

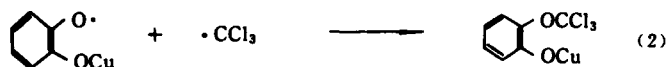
A large variety of spiro orthocarbonates were found to undergo ionic ring-opening polymerization with zero shrinkage or slight expansion^[1,2]. This interesting property is very useful in industrial applications, such as strain-free composites, potting resins and high gloss coatings; it appears to be highly desirable to have monomers that polymerize with near zero shrinkage. For other applications, such as precision castings, high strength adhesives, rock cracking materials and dental fillings, it appears highly desirable to have monomers that undergo slight positive expansion upon polymerization.

Many of the polymers that were previously reported, such as the ether-containing polycarbonates obtained from polymerization of the spiro orthocarbonate, 1,5,7,11-tetraoxaspiro (5,5) undecane with expansion in volume from 2—17%^[3], were liquid polymers. However, the polymer with higher T_g and T_m are very important for industrial applications. As we know, phenyl group on the main chain of polymer would raise its T_m and T_g since the phenyl group restricts the rotation of chain. For this reason, one monomer that appeared particularly attractive was bisphenylene orthocarbonate (I), which was first synthesized by Harrod and Gheluwe^[4]. But no description of the polymerization of this monomer occurred in the literature.

This article reports on the synthesis and polymerization of I in the presence of cationic initiators. It was found that this monomer underwent ring-opening polymerization by cationic initiators with 3% expansion in volume. Thermal properties of the polymer were measured. Based on the structures of the polymer, the polymerization mechanism is discussed.

coupling reaction produces an aryl trichloromethyl ether which is presumably the precursor to the formation of orthocarbonate (see reaction 2). The further substitution could conceivably occur to

form I with lower yield.



When the solution of I in CH_2Cl_2 was polymerized at room temperature over a period of 84 h with approximate 1 mol% of $\text{BF}_3 \cdot \text{OEt}_2$ as initiator. It was interesting to note that the monomer was very easily sublimated when the bulk polymerization proceeded. Thus, it was necessary that the whole flask had to be immersed in a oil bath for ensuring all monomers to be polymerized. After polymerization was completed, the reaction mixture was poured into n-hexane while stirring to precipitate polymer which was then purified by sublimation at 80°C – $90^\circ\text{C}/0.02\text{mmHg}$. The identification of the small amount of white solid sublimate by ^1H NMR and IR spectra, as well as elemental analysis, indicated that it was catechol. The dark-brown solid polymer in the bottom of the flask was obtained.

The IR spectrum (Fig.1b) of this polymer shows an absorption band at 1800 cm^{-1}

corresponding to the carbonyl ($\text{C}=\text{O}$) group; a band at 1160 cm^{-1} corresponding to $\text{C}-\text{O}-\text{C}$ group of ester; and another band at 1250 cm^{-1} corresponding to the diphenylene ether group. These bands indicate that 1,4,6,9-tetraoxaspiro(4,4) nonane ring does open to form polymer III according to scheme 1.

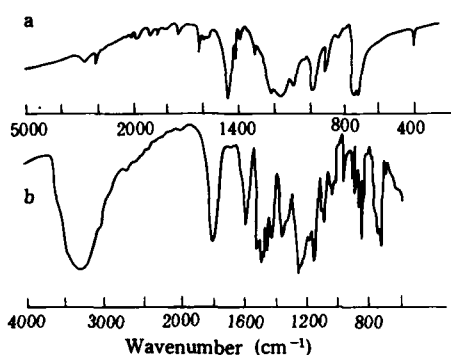
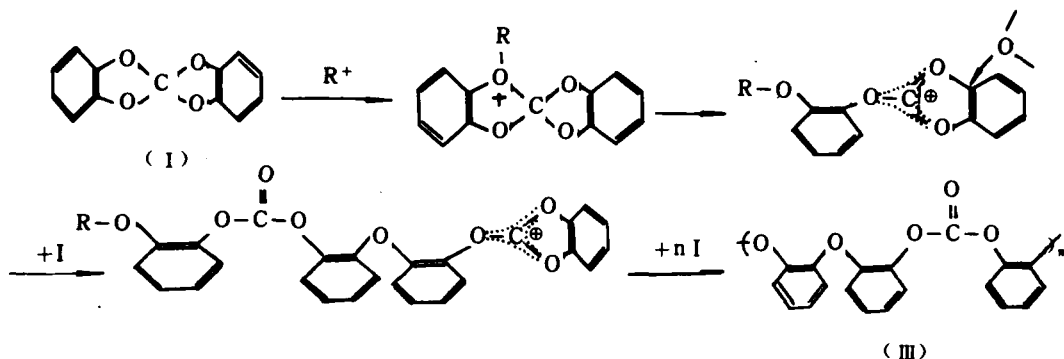


Fig.1. IR Spectra of bisphenylene orthocarbonate and its polymer

a: monomer; b: polymer

Analysis of the ^1H NMR (Fig.2b) of this polymer also confirms its structure: the multiple signals at δ 7.33 ppm and δ 6.73 ppm corresponding to phenyl protons attached to the oxygens of



ester and ether respectively.

There are two possibilities for the formation of catechol. One is:

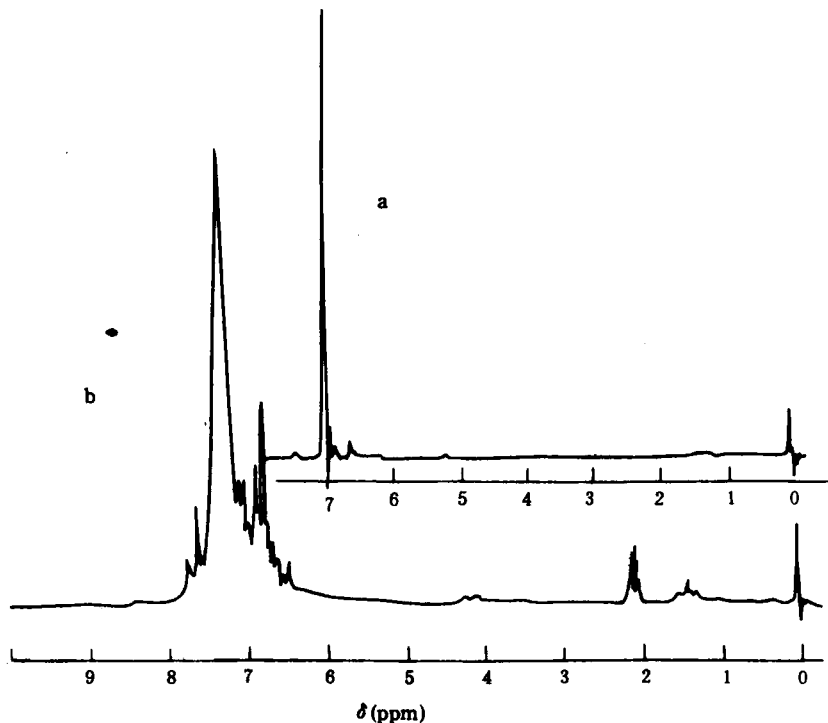
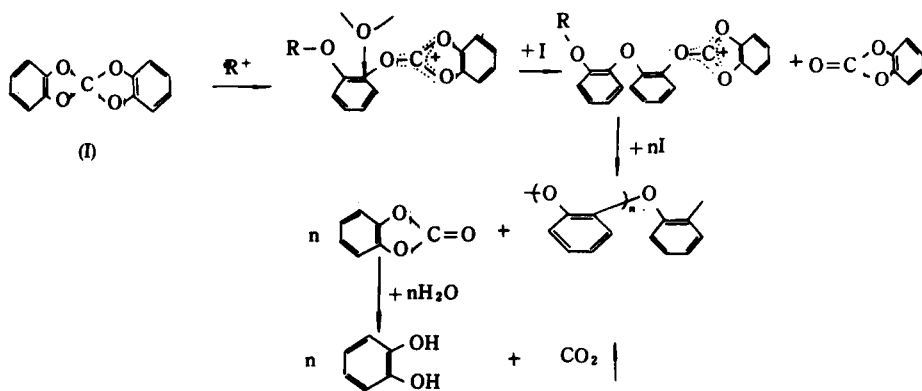


Fig.2. ^1H NMR Spectra of bisphenylene orthocarbonate and its polymer

a: monomer; b: polymer



Scheme 2

We failed to collect phenylene carbonate. Possibly it was hydrolyzed by water to produce catechol as shown in scheme 2. Comparing with ethylene carbonate, this compound was not stable, thus it is not a strong driving force for the formation of polyphenylene ether, that is different from the polymerization of 1,4,6,9-tetraoxaspiro-(4,4)nonane (IV).

Another possibility is that a trace of water caused the decomposition of this monomer.

Table 1 Cationic polymerization of bisphenylene orthocarbonate in various conditions

No	Initiator (conc. in mol%)	Solvent	Polymerization		yield (%)	$\overline{M}_n$
			temp. (°C)	time (h)		
1	BF ₃ OEt ₂ (1.0)	Toluene ^{a)}	r.t	17	28	—
2	BF ₃ OEt ₂ (1.0)	bulk	110	17	70	2,300
3	BF ₃ OEt ₂ (2.0)	CH ₂ Cl ₂ ^{a)}	r.t	84	85	1,200
4	SnCl ₄ (1.0)	bulk	110	18	65	1,970

a) Solution polymerization, ratio of M/S(W/V) = 1/2 (M = monomer, S = solvent)

As seen in Table 1, either BF₃OEt₂ or SnCl₄ can initiate I to polymerize. Although the molecular weight of the polymer is not very high, the T_m and T_g are 254 and 160°C respectively measured on Perkin-Elmer DSC-2 Differential Scanning Calorimeter, which are higher than that of the polymer obtained from IV. The decomposition of III had not been observed below 320°C.

Volume expansion during the polymerization of I

The simple method of investigating the volume expansion property of the monomer during its polymerization is the measurement of density differences between monomer and its polymer, although it does not exactly equal to the actual volume expansion during the polymerization, because the purified polymer is used in the density measurement. Thus, the densities of I and its polymer were measured at various temperatures. The plot of their density vs. temperature is shown in Fig.3. Upon the density difference between I and its polymer at the definite temperature, the volume expansions are calculated and listed in Table 2.

Table 2 Calculation of volume expansion during polymerization at various temperatures

Temperature (°C)	Density of monomer (g/ml)	Density of polymer (g/ml)	Expansion in volume ^a
20	1.462	1.419	+3.0
40	1.444	1.400	+3.1
60	1.425	1.380	+3.3
80	1.406	1.360	+3.4
100	1.285	1.340	-4.1

a. + : expansion; - : shrinkage

An inspection of Fig.3 indicates that the densities of the monomer I and its polymer appear to across at 95°C. At that point, one would expect no change in volume during polymerization since the two materials have the same density. Below that point, the expansions are 3—3.4%. It is slightly larger than the expansion of 1,4,6-trioxaspiro (4,4) -nonane which had 0.1% expansion during the polymerization^[2]. The possible reason is the higher density of I than monomer IV (d_4^{20} 1.16).

It has been demonstrated that bisphenylene orthocarbonate was easily prepared from catechol

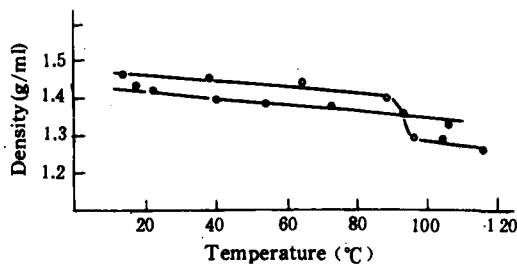


Fig.3 Density of bisphenylene orthocarbonate vs. temperature
a) monomer; b) polymer

and carbon tetrachloride and polymerized by cationic ring-opening mechanism with 3% expansion in volume. The ether-containing polycarbonate has higher T_g and T_m .

Keywords:

Volume expansion; Polycarbonate bisphenylene orthocarbonate; Cationic ring-opening polymerization;

Acknowledgement The authors gratefully acknowledge the support of this research by the National Natural Science Foundation of China.

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