Cross-Linked Poly(orthocarbonate)s as Organic Solvent Sorbents

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ABSTRACT: A simple method for the synthesis of a series of cross-linked poly(orthocarbonate)s (CPOC), based on tetraethyl orthocarbonate, is reported. Structural evidence for CPOCs was obtained from ^{13}C solid-state NMR, FT-IR, and thermal analysis. All polymers have high and fast uptake of organic fluids such as tetrahydrofuran, dichloromethane, dichloroethane, and the dry-cleaning fluid blend "trichlor".

Introduction

Polymer gels are fascinating materials which differ in many respects from ordinary solids.[1] Although they possess all the normal characteristics of solids such as shape-retention and resistance to shear, they can absorb solvent and swell to dimensions much larger than their dry size.[2] They have important industrial and analytical applications as absorbent materials and separation agents in various industries.[3] Their uses are likely to continue expanding as gels with novel chemical and structural characteristics are developed. They are found in industrial and domestic applications such as ion exchangers,[4] diapers,[5] etc. and in analytical equipment (i.e., in high performance liquid chromatography).[6] They are also being tested for novel medical applications such as drug delivery devices.[7,8]

Orthocarbonates are thermally stable and generally inert to alkali but quite susceptible toward electrophilic agents such as protonic and Lewis acids. Aromatic poly(carbonates) have been prepared by reaction of dichlorodiphenoxymethane with aromatic diols.[9] As expected from their structure, they are resistant to alkali but decompose under acidic conditions at elevated temperatures.[10,11] On the other hand, aromatic polymonocyclic orthocarbonates have been synthesized by reaction of 2,2-dichloro-1,3-benzodioxole with various aromatic diphenols.[12] No gelation was observed in these cases. Poly(orthocarbonate)s were synthesized by condensation of dichlorodiphenoxymethane with diphenols, resulting in an extremely thick gel.[10] In this paper, we present a simple method for the synthesis of cross-linked polymers using tetraethyl orthocarbonate[13] and different diol and triol monomers.

Results and Discussion

The reactions between tetraethyl orthocarbonate and different hydroxyl functional monomers to give CPOCs are summarized in Scheme 1. CPOCs were synthesized by condensation of the neat monomers in the proper stoichiometric ratio at moderately high temperatures. All polymers were insoluble in organic solvents such as tetrahydrofuran, dichloromethane, dichloroethane, acetone, benzene, and other common solvents, but they swelled in these solvents.

By using 1,3,5-tris(hydroxymethyl)benzene as a cross-linker monomer, two more cross-linked polymers were also synthesized from the reaction of 1,3- and 1,4-benzenedimethanol with tetraethyl orthocarbonate (Scheme 2).

A polymerization attempted with 1,4-benzenedimethanol and tetraethyl orthocarbonate did not give a cross-linked polymer. However, addition of 1,3,5-tris(hydroxymethyl)benzene to the same polymerization mixture afforded the desired material.

Structural evidence for the CPOCs was obtained from FTIR, ^{13}C CPMAS NMR, and thermal analysis. The strong ν_{C-O} stretching bands at 1183 and 1005 cm^{-1} indicated the presence of C−O bonds (CO_4) and (CH_2−O), respectively. An intense peak at 3350 cm^{-1} also due to hydroxyl end groups and a carbonyl peak at 1747 cm^{-1} demand that at least one of the end groups is an ester, including the possibility of a carbonate. Except for **Poly 1**, aromatic absorptions were observed in the FTIR spectrum for all other polymers.

More concrete evidence about the structure of the poly(orthocarbonate)s was obtained from solid-state ^{13}C CPMAS NMR. The ^{13}C NMR spectrum of **Poly 1**, for example, is presented in Figure 1. From six major peaks at δ 120, 68, 59, 38.9, 29.9 and 15.8, the second two resonances (120 and 68 ppm) prove the presence of CO_4 and CH_2−O, respectively. The weak resonance at 156 ppm demonstrates the presence of carbonyl groups. The signals at 68 and 15.8 ppm are an indication of ester end groups, specifically the methylene and methyl of the ethyl ester end group. The elemental analyses were consistently off by a few percent in carbon and hydrogen, relative to $(RO_n)_4(CO_4)_n$ in accord with the interpretation of NMR and FTIR results of terminal ethyl groups.

The thermal stability of the polymers was evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under nitrogen. All polymers were thermally stable up to ca. 200 °C with a 3% weight loss; except **Poly 1**, which was slightly unstable compared to the others with a weight loss of 7% up to the same temperature. No glass transition temperature (T_g) and melting point were observed.

All CPOCs repoted here have good solvent uptake abilities in some organic solvents such as tetrahydrofuran, dichloromethane, dichloroethane and reasonable uptake of the dry-cleaning fluid blend "trichlor". For swelling measurements, a known amount of polymer sample was placed in a tea bag and immersed in a solvent. After 24 h, the bag was removed, blotted with an absorbent paper, and weighed. Solvent uptake

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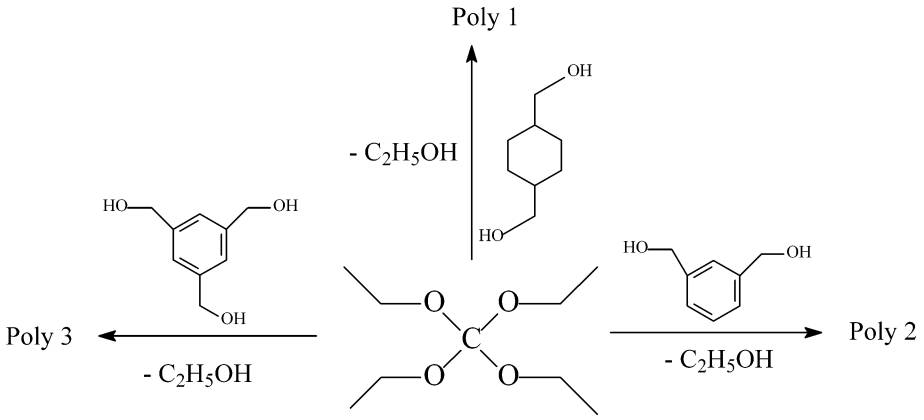
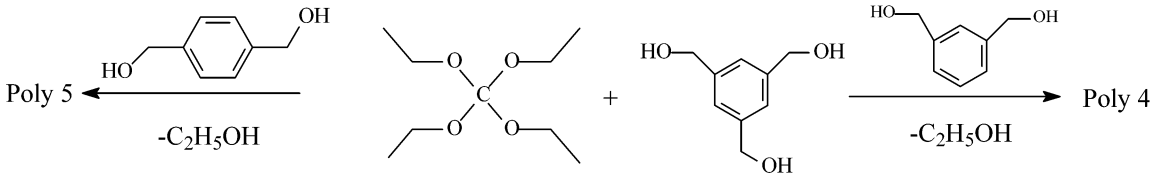
Scheme 1



Scheme 2



percentages for five different polymers in these solvents are summarized in Table 1. All polymers absorb about 200 wt % of solvents; except for **Poly 3**, which has less solvent absorption ability, very likely due to its more dense cross-linked structure. This polymer was prepared by using 1,3,5-tris(hydroxymethyl)benzene which acts as additional cross-linker. Terpolymers (**Poly 4** and **Poly 5**) contain 8% of 1,3,5-tris(hydroxymethyl)benzene as additional cross-linker. Surprisingly, these polymers absorb almost the same amount of solvent as **Poly 1**

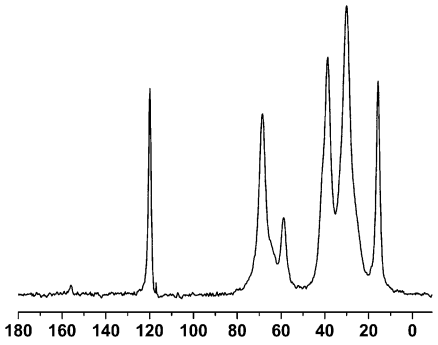


Figure 1. ^{13}C solid state NMR spectrum of **Poly 1**.

and **Poly 2**. In gasoline and kerosene CPOCs showed only weak swelling ability. The weight increase data presented in Table 1 corresponds to the solvent uptake due to the absorptive power of the gel.

Table 1. Swelling Properties of CPOCs

	swelling properties %				
solvents	**Poly 1**	**Poly 2**	**Poly 3**	**Poly 4**	**Poly 5**
dichloroethane	217.3	216	146	191	158.3
dichloromethane	227	274	148	252.7	220
THF	240	320	149	268	219.4
trichlor	41.5	80	30.3	74	78.2
gasoline	26	32	20	31	30.4
kerosene	16	38.3	18.7	26	25
acetone	70.6	108.3	72	84	78.23

Swelling properties of **Poly 1** and **Poly 2** were also examined in methyl *tert*-butyl ether (MTBE). Results showed that swelling equilibrium was achieved after 48 h. The degree of swelling in this solvent was 83.4% and 81.8% for **Poly 1** and **Poly 2**, respectively. We believe that these results are promising for the removal of MTBE from water with our cross-linked polymers.

When the swelling properties of CPOCs are compared with swelling properties of other cross-linked polymers in the literature (i.e., polycarbonate in dichloromethane, 148%;[14] carbonate polymers of dihydroxyaryl fluorine in dichloromethane, 284%;[15] arylcyclobutene-terminated polycarbonate in dichloromethane, 105%;[16] poly(ester–siloxane)urethane in NMP, 131.3%;[17] polyether based polyurethane in benzene, 181%[18]), our results for CPOCs are clearly competitive and very promising for applications of these materials.

To understand the saturation time, the swelling percentages of polymers with time was examined in THF. The corresponding results are presented in Figure 2. All polymers have very fast solvent uptake capabili-

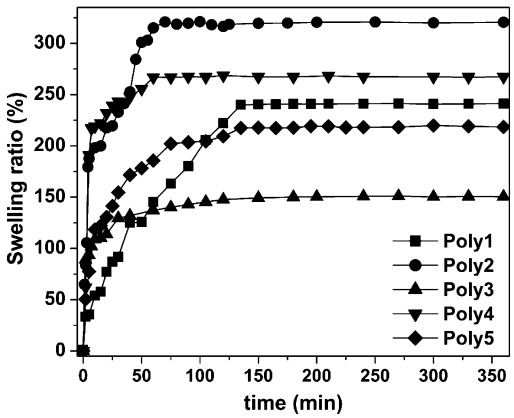


Figure 2. Swelling kinetics of polymers in THF at room temperature. Each point presented in the figure is an average of at least five different measurements. There is a maximum 8% deviation from each point.

ties. For example **Poly 2** reached 190% swelling in 4 min and saturated after 60 min. Except for **Poly 1**, all

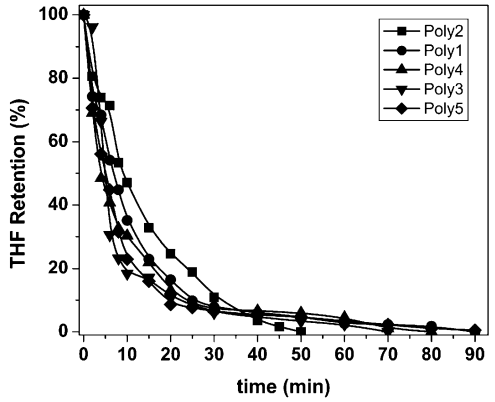


Figure 3. THF retention of CPOCs in air. Each point presented in the figure is an average of at least five different measurements. There is a maximum 8% deviation from each point.

other polymers reached their maximum capacity within 1 h. In the case of **Poly 1**, equilibrium was reached after 2 h. It is possible that this material maybe more densely cross-linked.

The THF retention of polymers was followed in time by examining the weight loss of swollen polymer in air (Figure 3). All cross-linked polymers released the absorbed THF very fast. Within 20 min almost all polymers released the absorbed THF around 80%. The rest is released almost in 1 h. These results clearly indicate that all CPOCs are easily regenerable.[19] Another experiment for the recovery of absorbed THF was as follows: **Poly 2** was first swelled in THF as explained in the Experimental Section but instead of leaving the gel in open air, ca. 90% of the swelled THF was collected from the polymer in a closed distillation system. These results show unequivocally that the CPOC polymers are useful for recovering organic solvents.

In conclusion, we report a simple synthesis of new cross-linked poly(orthocarbonate)s. All these polymers are thermally stable and have very fast and very good solvent uptake abilities.

Experimental Section

General Data. The highest purity grade chemicals available from Aldrich were used without further purification. FT-IR spectra were recorded on a Mattson Infinity IIa spectrometer with a DRIFT accessory from PIKE Technologies on a diamond frit. ^{13}C solid-state NMR spectra were recorded on a Bruker Avance 300 spectrometer in a magic angle spinning (MAS) probe operating at 75.476 MHz. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer TAC 7/DX Thermal Analysis system at a heating rate of 10 °C/min and at a nitrogen flow rate of 75 cm^3/min. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC Pyris instrument.

Synthesis of Cross-Linked Polymers. Different cross-linked polymers were synthesized by using tetraethyl orthocarbonate and different polyol monomers as explained below

Poly(1). In a Pyrex (75 mL) pressure vessel at 185 °C in a Wood's metal bath, 1,4-cyclohexanedimethanol (10 g, 69.4 mmol) and tetraethyl orthocarbonate (6.67, 34.7 mmol) were allowed to react for 4 days. The resulting product was washed with dichloromethane and dried under vacuum to give 11.5 g of a white cross-linked solid polymer. FTIR: 3350, 2943, 2849, 1745, 1443, 1382, 1270, 1183, 1150, 1011, 796, 640, and 511 cm^{-1}. ^{13}C NMR: 156, 120, 68, 59, 38.9, 29.9, and 15.8 ppm. Anal. Calcd for $C_{17}H_{28}O_4$: C, 68.92; H, 9.46. Found: C, 66.34; H, 9.77.

Poly 2. The reaction of 1,3-benzenedimethanol (10 g, 72.4 mmol) and tetraethyl orthocarbonate (6.96 g, 36.19 mmol) at 185 °C for 4 days in a pressure vessel gave slightly yellow cross-linked polymer (Scheme 1). After being washed with water and ether, the polymer was dried under vacuum (7.8 g). FTIR: 3350, 2969, 2883, 1745, 1607, 1443, 1183, 1011, 787, 701, and 563 cm^{-1}. ^{13}C NMR: 155, 137.5, 127.8, 120, 120, 65 ppm. Anal. Calcd for $C_{17}H_{16}O_4$: C, 71.83; H, 5.63. Found: C, 70.75; H, 5.88.

Poly 3. 1,3,5-Tris(hydroxymethyl)benzene was synthesized according to the procedure reported in the literature.[20] The latter (1.5 g, 8.93 mmol) and tetraethyl orthocarbonate (1.28 g, 6.66 mmol) was kept in a pressure vessel at 185 °C for 2 days to give a polymer. After the resulting product was washed with water and ether, it was dried under vacuum to give 1.13 g of cross-linked polymer. FTIR: 3350, 2941, 2846, 1745, 1602, 1443, 1352, 1092, 851, 514 cm^{-1}. ^{13}C NMR: 139, 127, 73.3, 65, 44.7, 33, 26, 15 ppm. Anal. Calcd for $C_{39}H_{36}O_{12}$: C, 67.24; H, 5.17. Found: C, 71.35; H, 6.02.

Synthesis of Terpolymer. Poly 4. The reaction of 1,3-benzenedimethanol (5 g, 36.19 mmol) and tetraethyl orthocarbonate (4.17 g 21.69 mmol) and, as cross-linker, 1,3,5-tris(hydroxymethyl)benzene (0.85 g, 5.06 mmol) were polymerized in a pressure vessel at 185 °C for 3 days. After being washed with water and ether, the polymer was dried under vacuum (3.42 g polymer). FTIR: 3350, 2932, 1748, 1507, 1274, 1179. ^{13}C NMR: 155.9, 138.6, 127.9, 120, 66, 43.4, 25.9, 15 ppm. Anal. Calcd for $C_{18}H_{17}O_4$: C, 72.73; H, 5.72. Found: C, 70.09; H, 5.46.

Poly 5. 1,4-Benzenedimethanol (4 g, 29 mmol), tetraethyl orthocarbonate (3.34 g, 17.4 mmol), and 1,3,5-tris(hydroxymethyl)benzene (0.68 g, 4.05 mmol) were polymerized in a pressure vessel at 185 °C. After 3 days the polymerization stopped and a slightly yellow polymeric gel was obtained. It was washed with water and ether, and after being dried under vacuum, it afforded 2.57 g of polymer. FTIR: 3350, 2966, 1748, 1472, 1287, 1153, 1024, 954 cm^{-1}. ^{13}C NMR: 155.3, 138, 127.7, 121, 70.5, 65.3, 15 ppm. Anal. Calcd for $C_{18}H_{17}O_4$: C, 72.73; H, 5.72. Found: C, 71.13; H, 5.84.

Swelling Measurements. Tea bags were employed to determine swelling properties of the cross-linked polymers.[21] First, the tea bags were immersed in the solvent and blotted quickly with an absorbent paper this was followed by addition of a dried polymer sample of known weight into the tea bags. The filled tea bags were immersed in the solvent. All swelling experiments were conducted at room temperature. After 24 h, the tea bags were removed, their surfaces were dried by blotting and weighed in a stoppered weighing bottle. Solvent uptake percentages were calculated using the formula

$$\text{solvent uptake } \% = \frac{(W_s - W_d)}{W_d} \times 100$$

where, W_d and W_s represent the weight of dry and swollen cross-linked polymer samples, respectively.[22]

Swelling Kinetics. Swelling kinetics measurements were conducted using the procedure described above using tetrahydrofuran (THF) as a solvent. After tea bags were removed at various time intervals, they were blotted quickly to remove THF attached to the surface and weighed.

THF Retention of Cross-Linked Polymers. The THF retention of polymers in air was determined by weighing the swollen polymer in air as a function of time.

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