

# Synthesis and Swelling Properties of New Crosslinked Polyorthocarbonates

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**ABSTRACT:** Crosslinked polyorthocarbonates were synthesized by the condensation of tetraethyl orthocarbonate and hydroxyl functional monomers. The main goal of this study was to produce a solvent-absorbent polymer with a high absorption capacity and to use these polymers for the removal of organic solvents from the environment and the recovery of these solvents. The synthesized polymers were characterized by Fourier transform infrared spectroscopy,

solid-state  $^{13}\text{C}$ -NMR spectroscopy, thermogravimetric analysis, and differential scanning calorimetry. All of the polymers (except **Poly 1** and **Poly 2**) had a high and fast uptake ability for organic solvents, such as tetrahydrofuran, dichloromethane, benzene, and acetone. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 3300–3305, 2011

**Key words:** crosslinking; gels; polycondensation; swelling

## INTRODUCTION

Gels are crosslinked polymer networks that store large amounts of solvent. They are wet and soft and look like a solid material but are capable of undergoing large deformation. Gels can be variously classified, such as natural gels or synthetic gels, hydrogels or organogels, and chemical or physical gels, according to the source, liquid medium in the polymer network, and their crosslinkage.<sup>1</sup> Depending on their chemical structure, polymer gels can absorb solvents up to several times their original dry weight. They have important industrial and analytical applications as absorbent materials and separation agents in various industries.<sup>2–11</sup>

Absorbent materials are attractive for oil and organic solvent removal. There are several reports in the literature describing the synthesis and swelling properties of polymers for oil or organic solvent cleanup.<sup>12–19</sup> To be a good absorbing material, a sorbent should have hydrophobicity and oleophilicity, a high and fast uptake capacity, and reusability.

Recently, we showed that crosslinked polyorthocarbonates based on tetraethyl orthocarbonate can be used as absorbents for organic solvents.<sup>20</sup> These synthesized polymers had rapid and good sorption abil-

ities for organic solvents, such as dichloromethane, tetrahydrofuran (THF), dichloroethane, acetone, and a dry-cleaning fluid blend. Orthocarbonates are thermally stable and generally inert to alkali but susceptible to electrophilic agents. In studies reported in the literature, several polycarbonates have been prepared, and as expected, they were resistant to alkali but decomposed under acidic conditions.<sup>21–23</sup>

In our previous studies, we synthesized crosslinked polyorthosilicates using tetraethyl orthosilicate and hydroxyl functional monomers and used them as absorbents, also.<sup>24,25</sup> These polymers were thermally stable and had good organic-solvent-uptake abilities.

In our previous study,<sup>20</sup> in the synthesis of Crosslinked Polyorthocarbonates (CPOCs) aromatic hydroxyl functional monomers were used as multihydroxyl monomers, except **Poly 1**, which was synthesized from the condensation of 1,4-cyclohexanedimethanol and tetraethyl orthocarbonate (TEOC). In this study, using the same strategy, we synthesized new crosslinked polyorthocarbonates, which were different from the other studies from linear to aromatic various multihydroxyl monomers (linear, tetrakis functional, aromatic, cycloaliphaticglycol, and also trifunctional aliphatic diols) were used, and the effects of the use of different diols on the polymer properties were examined.

## EXPERIMENTAL

### Reagents and equipment

A mixture of 1,3-cyclohexanedimethanol and 1,4-cyclohexanedimethanol (Unoxol) was obtained from Dow Chemical Co. All other chemicals were purchased from Aldrich (Taufkirchen bei München, Germany) and were used without further purification.

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Fourier transform infrared (FTIR) spectra were recorded on a Bio-Rad; Hercules, CA, USA FTS 175C FTIR spectrophotometer with KBr pellets. Solid-state  $^{13}\text{C}$ -NMR spectra were recorded on a 500-MHz Varian; Palo Alto, CA, USA in a magic angle spinning probe (75.476 MHz). Thermogravimetric analysis (TGA) was performed under a nitrogen atmosphere at  $10^\circ\text{C}/\text{min}$  with a Mettler Toledo model TGA/SDTA 851. Differential scanning calorimetry (DSC) was performed with a Mettler Toledo; Greifensee, Switzerland. DSC 822 at a heating rate of  $10^\circ\text{C}/\text{min}$  under a nitrogen atmosphere.

### Synthesis of the monomers

#### 2,2,6,6-Tetrakis(hydroxymethyl) cyclohexanol (TMCOL)

This monomer was synthesized according to the literature.<sup>26</sup>

mp =  $127\text{--}132^\circ\text{C}$ . FTIR ( $\text{cm}^{-1}$ ): 3497, 3267, 2954, 1400, 1016, 776.  $^1\text{H}$ -NMR [hexadeuterated dimethylsulfoxide ( $\text{DMSO-}d_6$ ), ppm]: 4.66, 4.48, 3.71, 3.55, 3.45, 1.5, 1.  $^{13}\text{C}$ -NMR ( $\text{DMSO-}d_6$ , ppm): 76, 67, 62, 43, 27, 16.

#### 2,2,5,5-Tetrakis(hydroxymethyl) cyclopentanone (TMCP)

This monomer was synthesized according to the literature.<sup>27</sup>

mp =  $146\text{--}147.5^\circ\text{C}$ . FTIR ( $\text{cm}^{-1}$ ): 3200–3450, 2960, 1725, 1045. H-NMR ( $\text{DMSO-}d_6$ , ppm): 4.59, 3.43–3.24, 1.97.  $^{13}\text{C}$ -NMR ( $\text{DMSO-}d_6$ , ppm): 222, 62, 59, 24.

### Preparation of the crosslinked polymers

Different crosslinked polymers were synthesized with tetraethyl orthocarbonate and hydroxyl functional containing monomers TMCOL, TMCP, UNOXOL: 1,3-1,4 cyclohexanedimethanol (Unoxol<sup>TM</sup>), 1,6-hexanediol, 2(hydroxymethyl)-1,3-propanediol, 1,3-1,4 benzenedimethanol as explained later (Scheme 1).

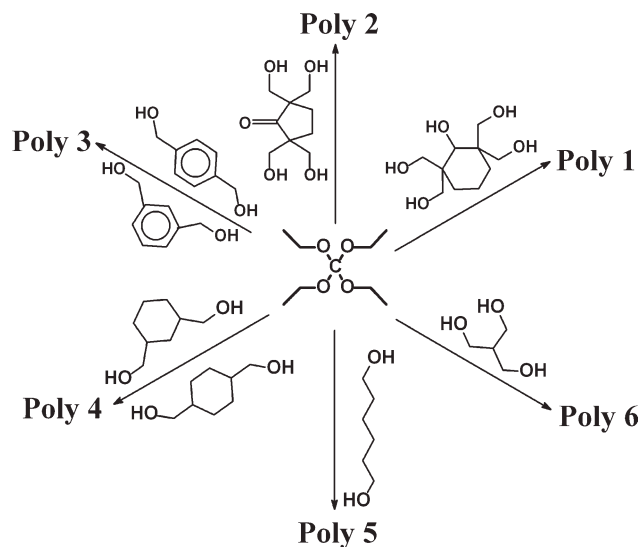
#### Synthesis of Poly 1

In a Pyrex (75 mL) pressure vessel at  $180^\circ\text{C}$  in a oil bath, TMCOL (1 g, 4.5 mmol) and tetraethyl orthocarbonate (0.95 mL, 4.5 mmol) were allowed to react for 2 days. The resulting product was washed with water and ether and dried *in vacuo* to give 0.86 g of a yellow, glassy solid polymer.

FTIR ( $\text{cm}^{-1}$ ): 3400, 2900, 1740, 1280, 1054.  $^1\text{H}$ -NMR ( $\text{DMSO-}d_6$ , ppm): 4.3–4.6, 3.6, 1–2.  $^{13}\text{C}$ -NMR ( $\text{DMSO-}d_6$ , ppm): 80–60, 20.

#### Synthesis of Poly 2

The reaction of TMCP (1 g, 4.9 mmol) and tetraethyl orthocarbonate (0.76 mL, 3.62 mmol) at  $180^\circ\text{C}$  for 3



**Scheme 1** Synthesis of the crosslinked polyorthocarbonates.

days in a pressure vessel gave a slightly red-brown crosslinked polymer. After being washed with water, ethanol, and ether, the polymer was dried *in vacuo* (0.67 g).

FTIR ( $\text{cm}^{-1}$ ): 3400, 2940, 2860, 1725, 1125, 1030.  $^{13}\text{C}$ -NMR cross-polarization/magic angle spinning (CP-MAS; ppm): 221.6, 155.6, 146.3, 65.6, 52.2, 28.7.

#### Synthesis of Poly 3

1,3-Benzenedimethanol (0.5 g, 3.63 mmol), 1,4-benzenedimethanol (0.5 g, 3.62 mmol), and tetraethyl orthocarbonate (0.76 mL, 3.62 mmol) were polymerized in a pressure vessel at  $160^\circ\text{C}$ . After 4 days, the polymerization was stopped, and a yellow, glassy, crosslinked polymer was obtained. It was washed with water, ethanol, and ether and after being *in vacuo*, it afforded 1.00 g of polymer.

FTIR ( $\text{cm}^{-1}$ ): 3044, 2930, 2876, 1740, 1100, 1016.  $^{13}\text{C}$ -NMR CP-MAS (ppm): 184, 175, 120, 65, 15.

#### Synthesis of Poly 4

The reaction of Unoxol (2 g, 13.8 mmol) and tetraethyl orthocarbonate (2.91 mL, 13.8 mmol) at  $160^\circ\text{C}$  for 3 days in a pressure vessel gave a colorless, glassy, transparent polymer. The resulting product was washed with water and ether and dried *in vacuo* to give 2.1 g of a crosslinked polymeric gel.

FTIR ( $\text{cm}^{-1}$ ): 3400, 2960, 2870, 1746, 1107, 1037.  $^{13}\text{C}$ -NMR CP-MAS (ppm): 59, 55, 49, 29, 21.

#### Synthesis of Poly 5

1,6-Hexanediol (4 g, 33 mmol) and tetraethyl orthocarbonate (3.5 mL, 16.5 mmol) were kept in a pressure vessel at  $160^\circ\text{C}$  for 5 days to give a colorless,

glassy, crosslinked polymer. After the polymer was washed with water and ether, it was dried *in vacuo* to give 2.5 g of a polymeric gel.

FTIR ( $\text{cm}^{-1}$ ): 3400, 2940, 2890, 1117.  $^{13}\text{C}$ -NMR CP-MAS (ppm): 110, 54, 21, 17.

### Synthesis of Poly 6

2-(Hydroxymethyl)-1,3-propanediol (2 g, 18 mmol) and tetraethyl orthocarbonate (2.97 mL, 14 mmol) were polymerized in a pressure vessel at  $180^\circ\text{C}$ . After 4 days, the polymerization was stopped, and a yellow crosslinked polymer was obtained. It was washed with water and ether and, after being dried *in vacuo*, gave 0.9 g of polymer.

FTIR ( $\text{cm}^{-1}$ ): 3400, 2970, 2920, 1750, 1100, 1038.  $^{13}\text{C}$ -NMR CP-MAS (ppm): 65–50, 20–30.

### Techniques

#### Soluble fraction (SF)

A weighed quantity of crosslinked polymer was put into a solvent, and the SF was extracted for a long time (48 or 72 h) with THF or dichloromethane. After extraction, the swollen polymers were dried *in vacuo* at  $45^\circ\text{C}$ . SF was calculated according to the following equation:<sup>28</sup>

$$\text{SF (\%)} = (W_0 - W) \times 100/W_0 \quad (1)$$

where  $W_0$  and  $W$  are the weights of the polymers before and after extraction, respectively.

#### Swelling test

The bags prepared from filter paper were used to determine the swelling properties of the crosslinked polymers.<sup>29</sup> First, the bags were immersed in the solvent and blotted quickly with an absorbent paper; this was followed by the addition of a dried polymer sample of known weight into the bags. The filled bags were immersed in the solvent. All swelling experiments were conducted at room temperature. Equilibrium was reached after 24 h, the bags were removed, their surfaces were dried gently by blotting, and they were weighed in a stoppered weighing bottle. The solvent-uptake percentages were calculated with the following formula:

$$\text{Solvent uptake (\%)} = \frac{(W_s - W_d)}{W_d} \times 100 \quad (2)$$

where  $W_d$  and  $W_s$  represent the weights of the dry and swollen crosslinked polymer samples, respectively.<sup>15</sup>

#### Swelling kinetics

Swelling kinetics measurements were conducted with the procedure described previously with dichloromethane as a solvent. After the bags were removed at various time intervals, they were blotted quickly to remove dichloromethane attached to the surface and weighed.

#### Desorption kinetics

We determined the dichloromethane retention of the polymers in air by weighing the swollen polymers in air as a function of time.

## RESULTS AND DISCUSSION

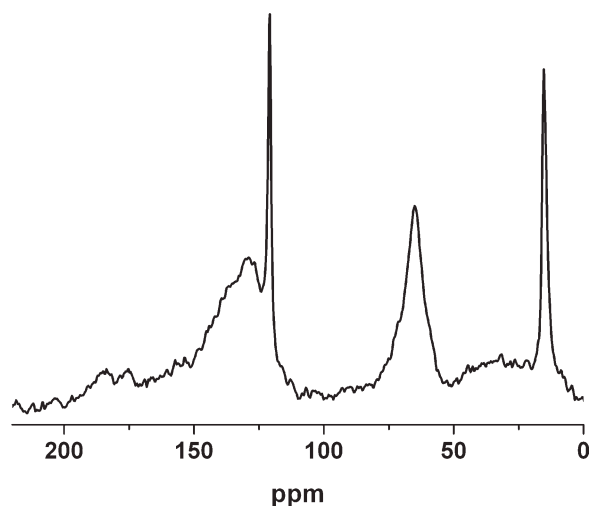
### Synthesis and characterization of the crosslinked polyorthocarbonates

The reaction between tetraethyl orthocarbonate and different hydroxyl functional monomers [TMCOL, TMCP, 1,3 and 1,4 benzodimethanol, Unoxol, 1,6-hexanediol, and 2-(hydroxymethyl)-1,3-propanediol] to give crosslinked polyorthocarbonates are summarized in Scheme 1. Different hydroxyl functional monomers based on crosslinked polyorthocarbonates were synthesized by the condensation of the neat monomers in the proper stoichiometric ratio at moderately high temperatures.

All of the synthesized polymers were insoluble in common organic solvents, including THF, dichloromethane, benzene, and acetone, although they had swelling abilities in these solvents, except **Poly 1**, which was synthesized from the reaction of TMCOL and TEOC. Because of the hydroxyl functionality, which came from the tetrakis monomer, this polymer was slightly soluble in DMSO and DMF, but it did not swell in the organic solvents.

The structure of the crosslinked polyorthocarbonates was investigated by FTIR spectroscopy, solid-state  $^{13}\text{C}$ -NMR, and thermal analysis. The strong  $\nu_{\text{C-O}}$  stretching bands at 1183 and  $1005\text{ cm}^{-1}$  indicated the presence of C—O bonds ( $\text{CO}_4$ ) and  $\text{CH}_2\text{—O}$ , respectively. An intense peak at  $3350\text{ cm}^{-1}$ , also due to hydroxyl end groups, and a carbonyl peak at  $1747\text{ cm}^{-1}$  indicated that at least one of the end groups was an ester. For **Poly 3**, aromatic absorptions were observed in the FTIR spectrum of the polymer.

Solid-state  $^{13}\text{C}$ -NMR CP-MAS of the **Poly 3** is presented, for example, in Figure 1. From the solid-state  $^{13}\text{C}$ -NMR results, the signals at 120 ppm proved the presence of  $\text{CO}_4$  and aromatic ring carbons, and the peak at 65 ppm referred to the  $\text{CH}_2\text{O}$  group. The signals at 15.8 ppm were an indication of an ester end group.



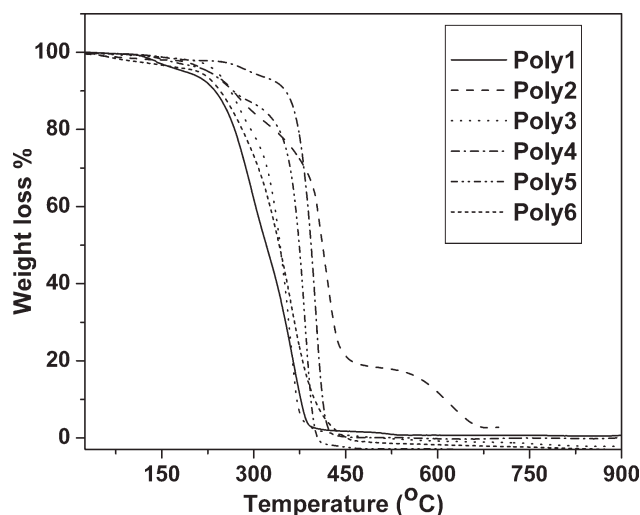
**Figure 1** Solid-state  $^{13}\text{C}$ -NMR CP-MAS spectrum of Poly 3.

The thermal stability of the polymers was evaluated by TGA and DSC under nitrogen. The thermal stability of the polymers was identified in the following order: **Poly 3 = Poly 4 > Poly 2 > Poly 5 > Poly 6 > Poly 1** (Fig. 2). No glass-transition temperature or melting point was observed.

#### Swelling properties of the crosslinked polyorthocarbonates

The synthesized crosslinked polyorthocarbonates were insoluble in THF, dichloromethane, acetone, benzene, and other common organic solvents, although they possessed swelling abilities in these solvents, except **Poly 1**, which did not absorb the solvents.

Some polymer chains are not attached to the polymer network and can, therefore, be extracted from

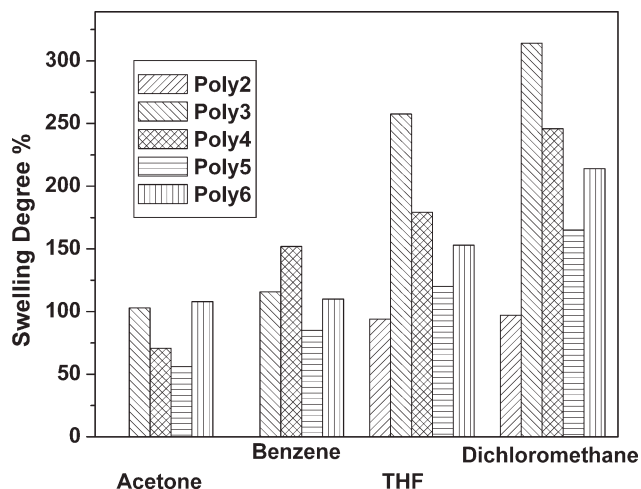


**Figure 2** TGA thermograms of the crosslinked polyorthocarbonates.

the gel fraction. These SFs can affect the swelling percentages of the polymers. Therefore, to minimize or eliminate this effect, the likely SFs in the crosslinked polyorthocarbonates were determined via an extraction technique. To achieve this, a known quantity of dried crosslinked polymers was added to the solvent, and the SFs were extracted with THF or dichloromethane for 72 h. After extraction, the swelled polymers were vacuum-dried at 45°C. The SF values determined for the crosslinked polymers ranged between 3 and 29%. The percentage of the extracted SFs depended on the type and concentration of the monomers and crosslinking agents.<sup>30</sup> **Poly 3**, which was synthesized from the reaction of 1,3-1,4 benzenedimethanol and tetraethylorthocarbonate, had an SF value of 3%.

The synthesized crosslinked polyorthocarbonates had good solvent-uptake abilities in some organic solvents. After the removal of SFs from the crosslinked polymer, the maximum solvent-absorption capacity of the polymer was determined. For this purpose, a known amount of polymer sample was placed in a bag and immersed in a solvent. All of the swelling experiments were conducted at room temperature. After 24 h, the bags were taken out, blotted quickly to remove excess solvent, and weighed in a stoppered bottle. Figure 3 shows the swelling capacities of synthesized crosslinked polyorthocarbonates for several organic liquids.

Obviously, **Poly 3**, which was synthesized from the condensation of the tetraethyl orthocarbonate 1,3-1,4 benzenedimethanol, showed the best results for organic solvent absorbency. The highest solvent absorbency, about 314%, was found in dichloromethane. In our previous study, the polymer synthesized with only 1,3-benzenedimethanol with TEOC had a swelling value of about 274% in



**Figure 3** Swelling properties of the crosslinked polyorthocarbonates.



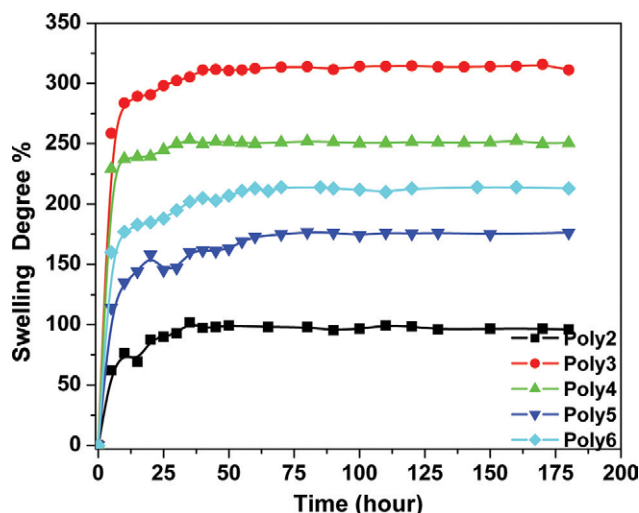
dichloromethane.<sup>20</sup> The use of a mixture of 1,3-benzenedimethanol and 1,4-benzenedimethanol together increased the swelling value by about 14.6%. This high swelling percentage could be explained by the use of the mixture of 1,3-1,4 benzenedimethanol in the polymer synthesis; this made the polymer more flexible and facilitated the solvent's easy penetration into the chains. In the same study, a polymerization attempt with 1,4-benzenedimethanol with TEOC did not give a crosslinked polymer.

Among the synthesized polymers; **Poly 2** had the lowest solvent-absorbing abilities. This was mostly because the tetrakis functionality of the diol monomer made the polymer more rigid than the others, and that is why the solvent did not diffusing easily. Because of the lower swelling capacity, only two solvents were examined for this polymer.

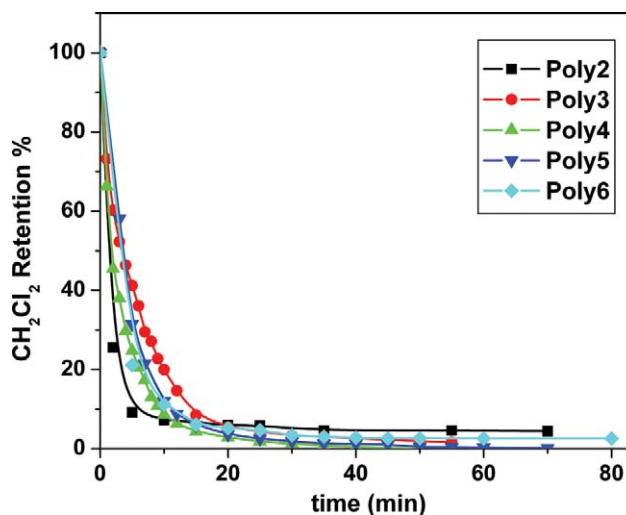
To examine the effect of linearity for the polymer properties; in the synthesize of **Poly 5**, a linear diol monomer, 1,6 hexanediol, was used, together with tetraethyl orthocarbonate. This monomer made the polymer more hydrophilic than the others, and the swelling capacity was lower compared to **Poly 3** and **Poly 4**.

For **Poly 6**, the trifunctional hydroxyl monomer 2-(hydroxymethyl)-1,3-propanediol was used to get crosslinked polyorthocarbonate. Although this monomer had more branching point than the others, the swelling properties were higher than those of **Poly 5** but lower than those of **Poly 3** and **Poly 4**.

In Figure 4, the solvent-uptake percentage is plotted against time to understand the saturation time of the polymers. For all of the synthesized polymers,



**Figure 4** Swelling kinetics of the crosslinked polyorthocarbonates. Each point presented in the figure is an average of at least four different measurements. There is a maximum 5% deviation from each point. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 5** Dichloromethane retention of crosslinked polyorthocarbonates. Each point presented in the figure is an average of at least four different measurements. There is a maximum 5% deviation from each point. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

the most absorbable solvent was dichloromethane, and in the kinetic measurements, dichloromethane was used as a solvent. The samples, after their dried weights were measured, were put into bags and placed in dichloromethane. The bags were taken out at regular intervals; the solvent adhering to the surface was rubbed off, and the samples were weighed quickly and replaced in the solvent. This procedure was repeated at least for four times for each polymer to ensure the reproducibility of the values. From the sorption curves, it was clear that all of the polymers had very fast solvent-uptake capabilities. For example, **Poly 3** reached 180% swelling in 10 min and saturation in 40 min.

All of the crosslinked polyorthocarbonates released the absorbed dichloromethane very fast (Fig. 5). The dichloromethane retention of the polymers was followed over time by examination of the weight loss of the swollen polymer in air. Within an average of 20–25 min, all of the polymers released almost all of the absorbed solvent.

## CONCLUSIONS

In conclusion, crosslinked polyorthocarbonates were synthesized by the reaction of tetraethyl orthocarbonate and various diols. As multihydroxyl monomers, linear, tetrakis functional, aromatic, cycloaliphaticglycol, and also trifunctional aliphatic diols were used. These polymers were found to be thermally stable and possessed rapid and good organic-solvent-uptake abilities. These results clearly show that crosslinked polyorthocarbonates can be used as absorbents for organic solvents.

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