Synthesis and Swelling Properties of Crosslinked Poly(orthosilicate)s from Cyclohexanedimethanols

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ABSTRACT: Condensations of cyclohexanedimethanol derivatives with tetraethyl orthosilicate in the proper stoichiometric ratio produce crosslinked poly(orthosilicate)s. Synthesized crosslinked polymers have swelling abilities in common organic solvents such as tetrahydrofuran (THF), dichloromethane, benzene and acetone. All these polymers are moderately thermally stable and possess solvent uptake abilities that are not only good and fast but are also regenerable. FTIR, solid-state ^{13}C, ^{29}Si-NMR and thermal methods were used to characterize these synthesized polymers. The effects of different cyclohexanedimethanol derivatives on the properties of polymers were also examined. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 1182–1189, 2011

Key words: crosslinking; gels; swelling; poly(orthosilicate)s; cyclohexanedimethanol; desorption

INTRODUCTION

Crosslinked polymers have become an important class of polymers because of their wide range of applications such as in solvent ion separation, chromatography, solid phase organic synthesis, biomedical applications etc.[1–7] Depending on its chemical structure, a polymer gel can absorb solvents up to several thousand times its original weight. There is considerable interest and activity in the applications of synthetic—and biological polymer gels in analytical—and industrial applications[8–11]

There are several ways to classify gels; based on their origin-"synthetic or natural gel"; their crosslinkage-"physical or chemical gel"; and their swelling media; "hydrogel or organogel".[12] A hydrogel can swell in water but not dissolve in it. In the literature, there are many studies of hydrogels and their applications.[13–21] Organogels differ from hydrogels in their swelling media, because they can absorb organic solvents instead of water and then can subdivide based on the nature of the gelling molecule; that is into polymeric- or low molecular weight organogelators. Oil or organic solvent absorption behavior is process in which an organic molecule penetrates into a network and expands it to cause swelling, which is affected by three factors: rubber elasticity, affinity to the solution and crosslinking density.[22] In swelling, crosslinked density of the polymers and the compatibility of polymer chains with the organic solvents play an important role. When crosslink density is reduced, it causes an increase in swelling but if the crosslink density is too low, a stable network does not form. There are several studies in the literature describing improvement of swelling and deswelling properties and others on swelling percentages of the polymers.[23–28]
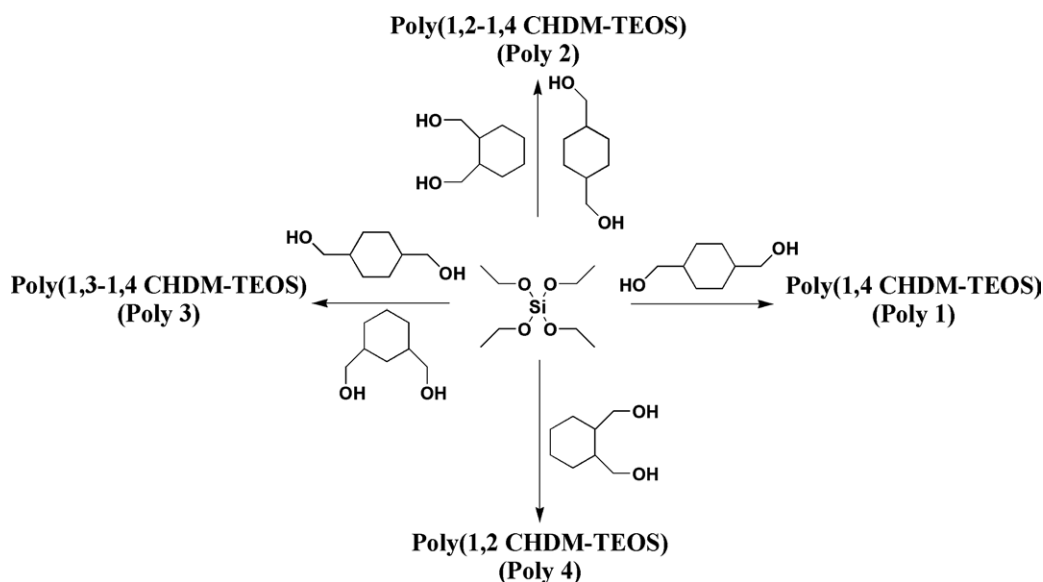
As environmental pollution caused by oil- and organic solvent spills increases, oil or organic solvent sorbents attract much more interest.[29] For cleanups of organic solvents or oil, an ideal sorbent material should have some properties such as hydrophobicity or oleophilicity, high absorption capacity, high rate of uptake, reusability, and good absorption selectivity over water. The literature contains reports of several absorbents that exhibit at least some of this properties.[30–34]

Among them, hydrophobic network polymers-for example, aromatic polymers and alkyl acrylate polymers used as absorbents of oil or some organic solvents-have been gaining increasing attention from researchers.[27,35–38,39,40]

In one of our previous studies we had synthesized crosslinked poly(orthocarbonate)s using tetraethyl orthocarbonate and multihydroxyl monomers for organic solvent absorption.[41] All synthesized crosslinked poly(orthocarbonate)s are thermally stable, have rapid and good solvent uptake abilities. Using the methodology as in our previous paper, we show that crosslinked poly(orthosilicate) could be synthesized by the condensation of tetraethyl orthosilicate (TEOS) and *cis*-trans 1,4 cyclohexanedimethanol.

Poly(1,2-1,4 CHDM-TEOS)
(Poly 2)

Poly(1,3-1,4 CHDM-TEOS)   **Poly(1,4 CHDM-TEOS)**
(Poly 3)   **(Poly 1)**

Poly(1,2 CHDM-TEOS)
(Poly 4)

Scheme 1   Polymerization reactions of cyclohexanedimethanol derivatives with tetraethyl orthosilicate.

Further, based on this preliminary experiment we see that this polymer is thermally stable and possesses the same abilities of rapid and good organic solvent uptake.[42] In the literature, TEOS are used for hybrid polymer synthesis. Hybrid organic/inorganic materials have been successfully prepared by sol-gel processes and these materials are synthesized by chemically incorporating organic polymers into inorganic networks.[43–46] Hydrolysis and condensation of tetramethoxy or tetraethoxy silanes are used for in the synthesis of porous hybrid materials and they are attractive for development of new materials.[47–50]

Recently using TEOS together with cyclohexanediols, we have prepared the crosslinked poly(orthosilicate)s.[51] These polymers also have good solvent absorbing abilities and they can be used several times with same efficiency. As these results are very promising, in that the crosslinked poly(orthosilicate)s could be used as absorbent materials for organic solvents, in this paper, we report the synthesis and characterization of new crosslinked poly(orthosilicate)s using tetraethyl orthosilicate and cyclohexanedimethanols. Different from previous work; cyclohexanedimethanol derivatives are chosen as multihydroxy monomers instead of cyclohexanediols and show the effect of using different cyclohexanedimethanol monomers on polymer properties. We also investigate their swelling properties, swelling kinetics, and reusability and compare these properties with previous studies.

EXPERIMENTAL

Materials

The mixture of 1,3-1,4 cyclohexanedimethanol (UNOXOL™) was obtained from Dow Chemical Company, USA. All other chemicals were purchased from Sigma-Aldrich and used without further purification.

Synthesis of crosslinked polymers

Different crosslinked polymers were synthesized by using tetraethyl orthosilicate (TEOS) and cyclohexanedimethanol derivatives as explained below.

Poly(1,4 CHDM-TEOS) (Poly 1)

Mixture of *cis*-trans 1,4 cyclohexanedimethanol (CHDM) (3.0 g, 20.8 mmol) and tetraethyl orthosilicate (TEOS) (2.32 mL, 10.4 mmol) were allowed to react for three days in a Pyrex (75 mL) pressure vessel placed in an oil bath at 180°C. After washing the resulting product, **Poly(1,4 CHDM-TEOS)** with water and ether, it was dried under vacuum. **Poly(1,4 CHDM-TEOS)** was a colorless, glassy, crosslinked polymer. The relevant data are as follows: Yield: 3.0 g; FTIR: 3400, 2923, 2856, 1456, 1392, 1079, 966, and 856 cm^{-1}; ^{13}C CPMAS NMR: 70.29, 60.44, 41.08, 30.83, and 19.14 ppm; and ^{29}Si CPMAS NMR: -58.98 and -65.48 ppm.

Poly(1,2-1,4 CHDM-TEOS) (Poly 2)

A mixture of *cis*-trans 1,4 cyclohexanedimethanol (0.5 g, 3.56 mmol), cis 1,2 cyclohexanedimethanol (0.5 g, 3.56 mmol) and tetraethyl orthosilicate (TEOS) (0.77 mL, 3.5 mmol) allowed to react at 180°C for 4 days in a pressure vessel produced a colorless, glassy, crosslinked polymer (Scheme 1). After it was washed with water and ether, the resulting polymer, **Poly(1,2-1,4 CHDM-TEOS)**, was dried under vacuum. The relevant data are as follows: Yield: 0.86 g. FTIR: 3430, 2924, 2856, 1444, 1387, 1066, and 859 cm^{-1}. ^{13}C

CPMAS NMR: 68.96, 59.70, 41.18, 29.87, and 19.78 ppm. ^{29}Si CPMAS NMR: −52.64, −58.94, −65.4, and −78.42 ppm.

Poly(1,3-1,4 CHDM-TEOS) (Poly 3)

A mixture of 1,3-1,4 cyclohexanedimethanol (UNOX-OL^{TM}) (3.3 g 22.87 mmol) and tetraethyl orthosilicate (TEOS) (5.10 mL, 22.87 mmol) were allowed to react for two days in a Pyrex (75 mL) pressure vessel placed in an oil bath at 180°C. The resulting product was washed with water and ether, and dried under vacuum. **Poly(1,3-1,4 CHDM-TEOS)** was a transparent crosslinked polymer. The relevant data are as follows: Yield: 3.8 g. FTIR: 3400, 2931, 2858, 1451, 1386, 1091, 950, and 838 cm^{-1}. ^{13}C CPMAS NMR: 60.40, 50.44, 31.82, and 19.91 ppm. ^{29}Si CPMAS NMR: −93 ppm.

Poly(1,2 CHDM-TEOS) (Poly 4)

A mixture of cis 1,2 cyclohexanedimethanol (0.57 g, 4 mmol) and tetraethyl orthosilicate (TEOS) (0.45 mL, 2 mmol) were allowed to react for two days in a Pyrex (75 mL) pressure vessel placed in an oil bath at 180°C. The resulting product, **Poly(1,2 CHDM-TEOS),** was washed with water and ether, and dried under vacuum. **Poly(1,2 CHDM-TEOS)** was a yellow glassy polymer. The relevant data are as follows: Yield: 0.20 g. FTIR: 3400, 2930, 1450, 1385, 1089, 961, and 842 cm^{-1}

Characterization

FT-IR spectra were recorded on Bio-Rad FTS 175C FT-IR spectrophotometer with KBr discs. ^{13}C and ^{29}Si solid state NMR spectra were recorded on a 500 mHz Varian Inova spectrometer in a magic angle spinning (MAS) probe 75.476 MHz. Thermal properties of polymers were investigated on Mettler Toledo TGA/SDTA 851 Thermogravimetric Analysis (TGA) and Differential Scanning Calorimeter DSC 821 (DSC) equipped with Mettler Toledo Star software at a heating rate of 10°C min^{-1} in flowing nitrogen (50 mL min^{-1}).

Techniques

Soluble fractions

A weighed quantity of crosslinked polymer was added to a solvent and the soluble fraction extracted for 48 h, using tetrahydrofuran (THF). After extraction, the swelled polymers were dried in vacuum at 40°C for 48 h. The soluble fraction was calculated using the following equation:

$$SF(\%) = (W_o - W) \times 100/W_0$$

where W_o and W are the weights of the polymers before- and after extraction, respectively.[52]

Swelling measurements

To determine the swelling properties of the crosslinked polymers, bags prepared from filter paper were employed.[53] The bags were first immersed in the solvent and blotted quickly with an absorbent paper; then, a dried polymer sample of known weight was added into the bags. The filled bags were immersed in the solvent. All swelling experiments were conducted at room temperature. When equilibrium was reached after 24 h, the bags were removed; their surfaces dried by blotting to remove excess solvent and weighed in a stoppered weighing bottle. Solvent uptake percentages were calculated using the following 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 crosslinked polymer samples, respectively.[36]

Swelling kinetics

The swelling kinetics measurements were recorded following the procedure described above using dichloromethane (CH$_2$Cl$_2$) as the solvent. The bags containing the swollen gels were taken out at regular time intervals, gently wiped with tissue paper, weighed on a balance in a stoppered bottle and returned to the same solvent. This procedure of swelling and weighing was continued until the sample registered a constant final weight. These experiments were conducted at 25°C.

Dichloromethane retention of crosslinked polymers retention of crosslinked polymers

After sorption, dichloromethane (CH$_2$Cl$_2$) retention of polymers in air was determined by weighing the swollen polymer in air as a function of time.

RESULTS AND DISCUSSION

Synthesis and characterization of crosslinked poly(orthosilicate)s

The reactions between tetraethyl orthosilicate (TEOS) and hydroxyl functional monomers producing crosslinked poly(orthosilicate)s are summarized in Scheme 1. The cyclohexanedimethanol derivatives based on crosslinked poly(orthosilicate)s were synthesized by condensation of the neat monomers in the proper stoichiometric ratios at high temperatures. In the synthesis of **Poly(1,4 CHDM-TEOS)**, tetraethyl orthosilicate was condensed with mixture of *cis*-trans 1,4 cyclohexanedimethanol. In the synthesis of **Poly(1,2-1,4 CHDM-TEOS)** and **Poly(1,3-1,4 CHDM-TEOS)** with *cis*-trans 1,4 cyclohexanedimethanol-cis 1,2
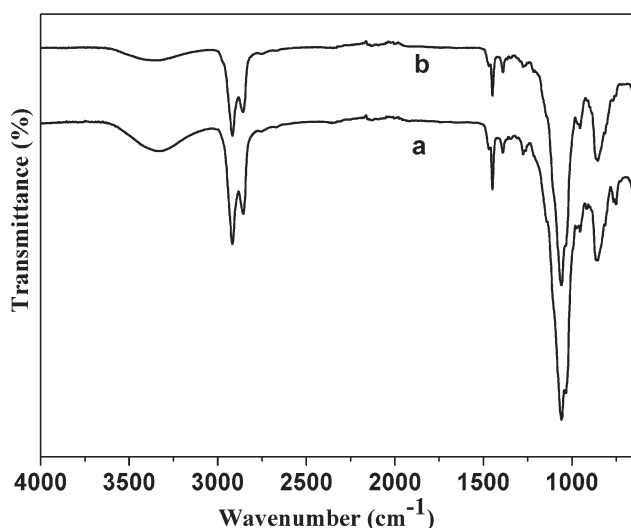
Figure 1 The FTIR spectrum of **Poly(1,2-1,4 CHDM-TEOS)** before (a) and after swelling measurements (b).

Figure 2 The CPMAS solid state ^{13}C NMR spectrum of **Poly(1,2-1,4 CHDM-TEOS)**.

cyclohexanedimethanol and UNOXOL[TM], respectively, were reacted with tetraethyl orthosilicate to produce crosslinked polymers. However to obtain a crosslinked polymer from the condensation of cis 1,2 cyclohexanedimethanol and TEOS (**Poly(1,2 CHDM-TEOS)**) is rather difficult, and only a small amount of the gel could be obtained from this polymerization reaction. All the polymers were insoluble in common organic solvents but exhibited swelling abilities in these solvents.

The chemical structures of the polymers prepared were elucidated by FTIR, solid state CPMAS ^{13}C and ^{29}Si-NMR. Their thermal properties were analyzed by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). Figure 1 shows the FTIR spectrum of the **Poly(1,2-1,4 CHDM-TEOS)** before and after swelling measurements. The strong stretching vibrations detected at 1060 and 840 cm^{-1} indicated the presence of Si—O—C and Si—O—CH, respectively. Stretching vibrations of the aliphatic C—H bond were observed at 2900 cm^{-1} and scissoring vibrations of CH$_2$ at 1465 cm^{-1}. A broad peak at around 3300–3500 cm^{-1} in the FTIR spectrum of the polymers indicated hydroxyl functionality as end groups. Following swelling/deswelling measurements, examination by FTIR showed that the there was no change due to the further condensation reactions by unreacted groups and the synthesized crosslinked polyorthosilicates are quite stable for repeating measurements.

The ^{13}C CPMAS NMR spectrum of **Poly(1,2-1,4 CHDM-TEOS)** is presented in Figure 2 as an example. The resonances at 68.9 and 59.7 ppm confirm the presence of CH$_2$—O—C and CH$_2$—O—Si, respectively. The signals at 41.2 and 29.8 ppm refer to cyclohexane carbons and the peak of ~19 ppm refers to the methyl group, which appears as an end group.
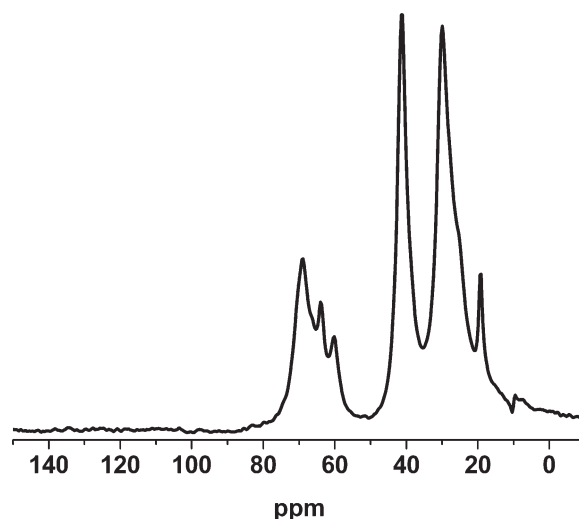
A solid-state CPMAS ^{29}Si-NMR spectrum for **Poly(1,2-1,4 CHDM-TEOS)** is shown in Figure 3. It reveals resonances indicative of the presence of trifunctional- and tetrafunctional silicon environments. From the results of solid-state spectra, the signal at around −58.2 ppm shows that the Si is bound to the hydroxyl group and at −65.5 ppm refers to CH—O—Si groups, and at −78.4 ppm refers to Si—O$_4$ groups. Besides these peaks for **Poly(1,3-1,4 CHDM-TEOS),** there is an additional peak at −93 ppm that indicates the presence of the Si—O—Si group. All these peaks support the structure of polymers and show that Si is incorporated into the polymer structure.

The thermal stability of the polymers was evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under nitrogen flow. No glass transition temperature (T_g) or melting
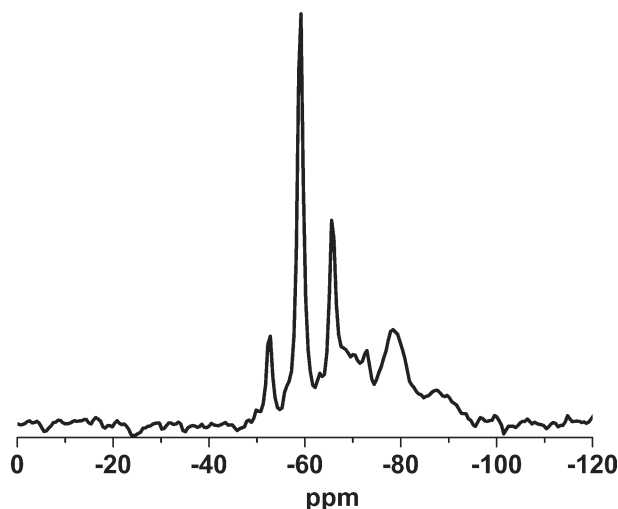

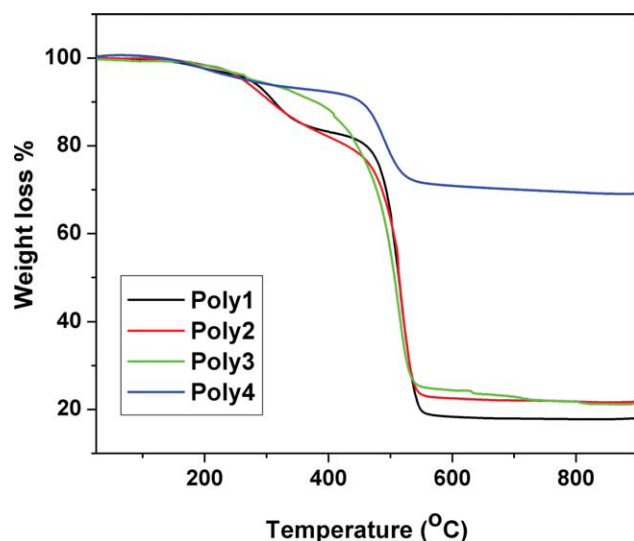**Figure 3** The CPMAS solid state ^{29}Si-NMR spectrum of **Poly(1,2-1,4 CHDM-TEOS)**.

Figure 4 TGA thermograms of crosslinked poly(orthosilicate)s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

point (T_m) were observed. The TGA thermograms (Fig. 4), together with Table I, which shows the percentages of weight loss of polymers at different temperatures, point out that cyclohexanedimethanol-based crosslinked poly(orthosilicate)s are thermally stable at temperatures lower than 200°C except **Poly(1,2 CHDM-TEOS)** which is thermally less stable than the others. In the synthesize of **Poly(1,2 CHDM-TEOS)**, cis 1,2 cyclohexanedimethanol was used and the 1,2 joint create difficulties in polymer synthesize. This polymer has weak thermal properties and also less swelling ability. The silicon content of the polymers was determined by thermogravimetric analysis and found to be 19.4% for **Poly(1,4 CHDM-TEOS)**, 23.2% for **Poly(1,2-1,4 CHDM-TEOS), 25%** for **Poly(1,3-1,4 CHDM-TEOS)** and 69.5% for **Poly(1,2 CHDM-TEOS)**.

Swelling properties of crosslinked poly(orthosilicate)s

The synthesized crosslinked poly(orthosilicate)s have swelling abilities in common organic solvents such as tetrahydrofuran (THF), dichloromethane, benzene

and acetone. Some polymer chains are not attached to the polymer network and before swelling measurements are recorded, these soluble fractions must be removed from the gel fractions. If the soluble fraction remains in the crosslinked gels, it might inhibit continuation of the swelling to some degree. To eliminate or minimize these fractions, a known amount of dried crosslinked polymers was added to a solvent and the soluble fractions were extracted and the swelled polymers were dried under vacuum. The values of the soluble fractions (SF) of the crosslinked polymers were found to be 18% for **Poly(1,4 CHDM-TEOS)**, 20% for **Poly(1,2-1,4 CHDM-TEOS)** and 2% for **Poly(1,3-1,4 CHDM-TEOS)**. The percentages of the soluble fractions extracted depend on the type and concentration of monomers and crosslinking agents.[22]

The synthesized crosslinked poly(orthosilicate)s were insoluble in tetrahydrofuran (THF), dichloromethane, acetone, benzene and other common organic solvents but they have good swelling abilities in these solvents. To determine the maximum sorption capacity of the polymers, after extraction of SF, swelling experiments have been conducted as explained in experimental part and the solvent uptake percentages of the polymers were calculated. The results are shown in Table II and **Poly(1,2-1,4 CHDM-TEOS)** which was synthesized from the condensation of the tetraethyl orthosilicate, cis-trans 1,4 cyclohexanedimethanol and cis 1,2 cyclohexanedimethanol and **Poly(1,3-1,4 CHDM-TEOS)** which was synthesized from the reaction of the TEOS and UNOXOL™ showed the best result for organic solvent absorbency. The highest solvent absorbency of about 205% was found in dichloromethane. This high swelling percentage can be explained by the use of the mixture of cis 1,2-cis-trans 1,4 cyclohexanedimethanol and 1,3- 1,4 cyclohexanedimaethanol in polymer synthesis making the polymer more flexible and facilitating the solvent's easy penetration into the chains.

If the swelling ability of **Poly(1,4 CHDM-TEOS)** which was synthesized from the reaction of cis-trans 1,4 cyclohexanedimethanol and tetraethyl orthosilicate compared with **Poly(1,2-1,4 CHDM-TEOS)** and **Poly(1,3-1,4 CHDM-TEOS)**; shows the lowest

TABLE II
Swelling Properties of Crosslinked Poly(orthosilicate)s

Solvents	Swelling ratio (%)			
	Poly 1	Poly 2	Poly 3	Poly 4
Dichloromethane	152	205	204	nd
Tetrahydrofuran	153	170	143	70
Benzene	107	135	137	nd
Acetone	65	67	62	nd

TABLE III
Comparison of Swelling Properties of Polymers

Polymer	Solvent	Swelling Ratio %	Reference
(CPOC)s	THF	250	41
Polycarbonates	Dichloromethane	148	54
Poly(ester-siloxane)urethane	NMP	131	55
Polyether-based polyurethanes	Benzene	181	56
Poly(stearylmethacrylate-co-DVB)	Toluene	360	36
Butyl rubber	THF	223	57
PDMS/PVA	Dichloromethane	120	43
(CPOSi)s (based on cyclohexanediol)	Dichloromethane	~120	51
(CPOSi)s	Dichloromethane	~200	this work

absorbing capacities. This is probably due to the reaction of *cis*-trans 1,4 cyclohexanedimethanol with tetraethyl orthosilicate, which makes the polymer structure more linear than the others and the solvent does not diffuse easily into the chains. In our previous work, we had reported that the swelling percentages of this polymer are 200% in THF, 150% in dichloromethane and in benzene, and 90% in acetone.[42] After this preliminary work, we examined the swelling properties of the polymer in detail and found that the value of the soluble fractions was higher than that we had reported (10%) earlier. After the first swelling experiment, soluble fractions remained, and as we mentioned earlier, they could affect the swelling percentages. After repeating experiments to remove the soluble fractions, the data in Table II were found to show that the actual value of swelling capacity of **Poly(1,4 CHDM-TEOS)** was lower than that obtained earlier. When the tetraethyl orthosilicate was condensed with the mixture of 1,3-1,4 cyclohexanedimethanol—UNOXOL™—**Poly(1,3-1,4 CHDM-TEOS)**- the solvent absorbing abilities and capacities of the polymer were enhanced.

A polymerization attempted with cis 1,2-cyclohexanedimethanol and tetraethyl orthosilicate produced very little amount of crosslinked polymer (**Poly(1,2 CHDM-TEOS)**) and the swelling ability of the polymer in THF was found to be about 70%. It is probable that the 1,2 joint, because of closer linkages in the polymer structure, creates difficulties for solvent diffusion, so a relatively small degree of swelling was observed. However, in the cis 1,2 cyclohexanedimethanol condensed with tetraethyl orthosilicate and *cis*-trans 1,4 cyclohexanedimethanol (**Poly(1,2-1,4 CHDM-TEOS)**) the degree of swelling was vastly greater than that of **Poly(1,2 CHDM-TEOS)**. Because this result revealed lower potential than that of other synthesized polymers of **Poly(1,2 CHDM-TEOS)**, its swelling characteristics were examined only in one solvent.

All the polymers that we report here, except **Poly(1,2 CHDM-TEOS),** exhibited good and fast solvent absorbing abilities. When the swelling properties of crosslinked poly(orthosilicate)s are compared with those of other crosslinked polymers in the literature (Table III), it is evident that our results for crosslinked poly(orthosilicate)s are competitive with the other polymers, which confirms that they can be used as efficient absorbents for organic solvents.

If we compare the swelling ability of the synthesized (CPOSi)s with our previous work, as can be seen from the Table III also, swelling ability of the polymers were increased by 66%. This is because of using cyclohexanedimethanol instead of cyclohexanediol resulted in more flexibility which is coming from dimethanol groups, between crosslinking points and much more solvents can be diffuse to the network and swelling capacity of the polymers are increased.

The percentage rates of swelling of polymers were studied to estimate the saturation times of the absorbents, for which dichloromethane was used as the solvent. It is clear from Figure 5 that the
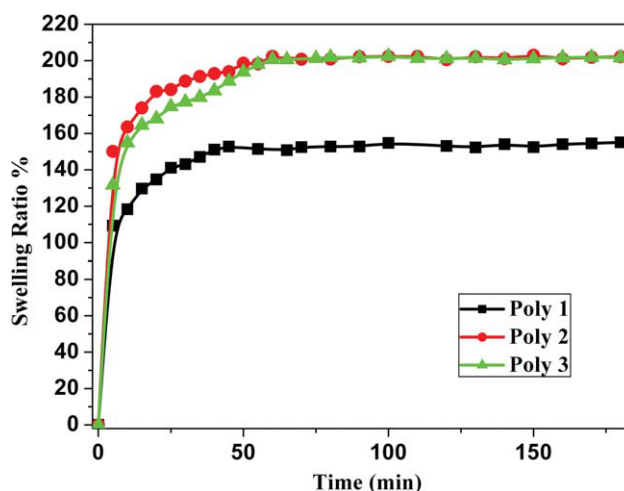

Figure 5 Swelling kinetics of the crosslinked poly(orthosilicate)s in dichloromethane at room temperature. Each point presented in the figure is an average of at least four different measurements. There is a maximum 5% deviation from each point. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
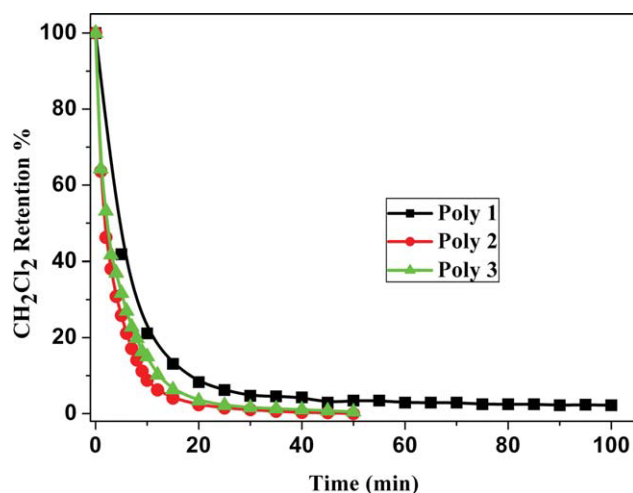
Figure 6 Dichloromethane (CH_2Cl_2) retention of crosslinked poly(orthosilicate)s. Each point presented in the figure is an average of at least four different measurements. There is a maximum 5% deviation from each point. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

synthesized crosslinked poly(orthosilicate)s have very fast solvent uptake capabilities. For example, **Poly(1,2-1,4 CHDM-TEOS)** reached 180% swelling in 10 min and saturation in 40 min.

The reusability of the sorbents and the removal of the absorbed solvents from the polymers are important especially for applications. Therefore, the retention time of the polymers by dichloromethane was obtained by determining the weight loss of swollen polymer in air (Fig. 6). The results showed that the retention behavior of all sorbents follows almost the same trend and all crosslinked polymers released the absorbed dichloromethane rapidly. Almost all absorbed dichloromethane was released within 25 min.

The ability of the swelled gels to undergo several cycles of swelling and deswelling was also investigated. All data appearing here represent the sum of at least four different measurements. As can be seen from the swelling and desorption kinetics, all synthesized crosslinked poly(orthosilicate)s based on cyclohexanedimethanol returned to their original swollen state without losing any capacity. These findings confirm that all crosslinked poly(orthosilicate)s are easily regenerable.

CONCLUSIONS

In conclusion, we report the synthesis and characterization of new crosslinked poly(orthosilicate)s. These polymers are found thermally stable and possess rapid and good organic solvent uptake abilities. These findings are very promising for the use of crosslinked poly(orthosilicate)s based on cyclohexa-

nedimethanol derivatives as absorbent material for organic solvents.

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