

Preparation of biphenyl-bridged, crosslinked polyalkoxysilanes: Determination of oil/organic solvent absorption features

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ABSTRACT: A novel type of biphenyl-bridged alkoxy-silane-based crosslinked polyalkoxysilane was prepared by the condensation of 4,4'-bis(triethoxysilyl)-1,1'-biphenyl and different lengths of linear aliphatic diols. Fourier transform infrared spectroscopy, solid-state ^{13}C and ^{29}Si cross-polarization magic angle spinning nuclear magnetic resonance, and thermogravimetric analysis were used to characterize the biphenyl-bridged, crosslinked polyalkoxysilanes. The crosslinked polymers were found to have very quick and high swelling capabilities in organic solvents and oils. The absorption-desorption kinetics and reusability features of the crosslinked polymers were also studied, and we found that the synthesized polymers reached their maximum absorption capacity during a variety of tests without losing capacity. We also tested the absorption performance of the sorbents from water surfaces. All of these results confirm that biphenyl-bridged, crosslinked polyalkoxysilanes could be good candidates as sorbent materials for the cleaning of water from organic contaminants. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 44193.

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INTRODUCTION

Polymer gels have three-dimensional networks that are capable of absorbing a large volume of liquids. They can be classified into two main groups that are divided according to the liquid they absorb: hydrogels and organogels. Hydrogels are hydrophilic polymeric networks that can swell in water but cannot dissolve in it.^{1–3} Unlike hydrogels, organogels are hydrophobic polymeric networks; therefore, they can swell in oils or organic solvents. Because of oil spills at sea,^{4–7} oil and organic solvent absorbents have garnered remarkable interest over the years.⁸ When oil leaks into water or other parts of the environment, it spreads quickly, negatively affecting living creatures and our habitat.^{9,10} To clean such oil and organic solvent pollutions from water surfaces and the environment, a wide range of synthetic and inorganic materials are used, including perlite,¹¹ clay,¹² diatomite,¹³ calcium carbonate powder,¹⁴ and zeolite for inorganic materials and polydimethylsiloxane (PDMS)-coated cotton,¹⁵ carbon nanotube sponges¹⁶; polyester sorbents;¹⁷ poly(propylene glycol)-based sorbents; poly(ethylene glycol) gels;¹⁸ cyclodextrin-based polymers;¹⁹ silica aerogels;²⁰ polypropylene sorbents;²¹ tetraethyl orthosilicate (TEOS)-based sorbents;^{22–25} crosslinked methacrylate materials;²⁶ tetraethylorthocarbonate-based crosslinked polymers;^{27–29} alkoxy-silane-based organogels;^{30–32} polytetrahydrofuran (PTHF) sorbents;³³ and alkyl and aromatic bridged polysilsesquioxanes.³⁴

Aliphatic and aromatic alkoxy-silanes are well-known molecules because of their simple hydrolysis and condensation properties, and they are used for making heat-storage devices, battery electrodes, oxygen sensors, and absorbents.^{35,36} Among these, bridged bistralkoxy-silanes $[(\text{XO})_3\text{—Si—R—}(\text{OX})_3]$ (where X = Me or Et) have attracted interest for many applications, such as catalysts, active compound release systems, biomedical applications, adsorbents, and environmental purity systems.^{34,37–41}

The existing literature contains several reports of the sol-gel polymerization of bridged trialkoxy-silane.^{35,42–44} In contrast to the sol-gel reaction, which involves a series of steps of hydrolysis and condensation that are generally acid or base catalyzed, we used only the condensation reaction without any activator, solvent, or a catalyst but simply used condensation of alkoxy-silanes with diol monomers to produce crosslinked polymers that are able to swell.

In our earlier study, we synthesized phenylene-bridged crosslinked polyalkoxy-silanes through the condensation of 1,4-bis(-triethoxysilyl) benzene (BTEB) with different lengths of linear aliphatic diols. The synthesized materials were thermally stable and showed swelling features in common organic solvents.

Herein, with a more hydrophobic bridged bistralkoxy-silane monomer source [4,4'-bis(triethoxysilyl)-1,1'-biphenyl (BTSBP)], we aimed to increase the oil/organic solvent absorption capacities of

Table I. Preparation Conditions of the Polymers

Polymer	Diol monomers (mmol)	BTSBP (mmol)	Reaction		Physical appearance	Yield (g)
			Temperature	Time		
Poly C2	1,2-Ethanediol (6.7)	2.2	160 °C	1 day	Transparent, glassy	1.00
Poly C4	1,4-Butanediol (5.1)	1.7	160 °C	3 days	White, glassy	0.60
Poly C6	1,6-Hexanediol (4.1)	1.4	160 °C	2 days	White, glassy	0.46
Poly C8	1,8-Octanediol (3.4)	1.1	160 °C	1 day	Transparent, glassy	0.42
Poly C10	1,10-Decanediol (3.0)	1.0	160 °C	8 h	Transparent, glassy	0.54
Poly C12	1,12-Dodecanediol (2.5)	0.8	160 °C	1 day	Transparent, glassy	0.54

crosslinked polymers. The synthesis procedure of the polymers was carried out by the condensation polymerization of BTSBP with different lengths of aliphatic diols monomers, without the use of any initiators, catalysts, or solvents. The prepared biphenyl-bridged, crosslinked polymers were used as sorbents for oil or organic solvents. The reaction time, effects of aliphatic diol monomers, absorption–desorption kinetics, and reusability were all studied. The results indicate that all of the prepared materials were able to swell in common organic solvents and oils. These features made the crosslinked polyalkoxysilane applicable for oil/organic solvent absorbents applications.

EXPERIMENTAL

Materials

BTSBP, 1,6-hexanediol, 1,8-octanediol, 1,10-decanediol, and 1,12-dodecanediol were purchased from Sigma-Aldrich; 1,4-butanediol and 1,2-ethanediol were purchased from Fluka and were used as received. Dichloromethane (DCM), tetrahydrofuran (THF), benzene, and toluene were obtained from Sigma-Aldrich. All organic solvents were used as received without further purification. Ninety-five octane gasoline and euro-diesel fuel were purchased from British Petroleum and used without any dilution.

Characterization

Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elmer Spectrum 100 FTIR spectrophotometer with an attenuated total reflectance objective in the range of 400–4000 cm^{-1} . ^{13}C and ^{29}Si solid-state cross-polarization (CP) nuclear magnetic resonance (NMR) spectra were recorded with a 500-MHz Varian Inova spectrometer in a magic angle spinning (MAS) probe at 75.476 MHz. The thermogravimetric analysis (TGA) was carried out with a Mettler-Toledo model TGA/SDTA 851 (Mettler-Toledo, Greifensee, Switzerland) at heating rate 10 °C/min under an argon atmosphere. For swelling measurements, a Innova 2000/platform shaker was used.

Preparation of the Polymers

BTSBP monomers were polymerized with different chain lengths of linear aliphatic diol monomers, beginning with 1,2-ethanediol to 1,12-dodecanediol in a proper stoichiometric ratio at partially high temperatures under an inert argon atmosphere with a Pyrex (75 mL) pressure vessel (Chemglas, Vineland, NJ). After completion of the polymerization, the resulting product was washed with several solvents (water, ethanol, and acetone) to remove the unreacted monomers and then vacuum-dried to

get the crosslinked polymer. The polymerization times and amounts of monomer used for the preparation of the crosslinked polymer are given in Table I.

Methods

Soluble Fractions. Before the swelling experiments with the synthesized crosslinked polymers, the soluble fractions, which were the polymer chains, oligomers, or unreacted monomers not attached to networks, had to be extracted from the gel fraction to attain reliable swelling results. For the removal of the soluble fractions, a weighed quantity of crosslinked polymer was placed in DCM, which was the most absorbable solvent, and extracted for 72 h (with the solvent refreshed every 24 h). After extraction, the crosslinked polymers were dried *in vacuo* at room temperature. The soluble fraction percentage was calculated with eq. (1):

$$\text{Soluble fraction (\%)} = [(W_0 - W)/W_0] \times 100 \quad (1)$$

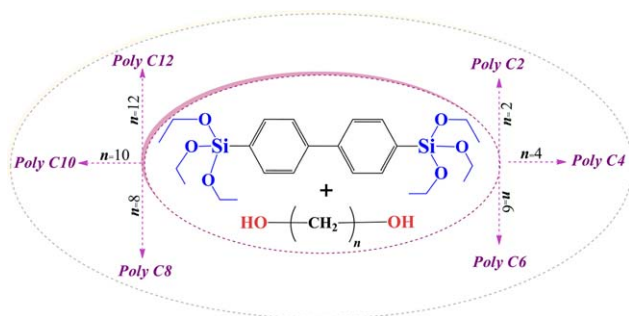
where W_0 and W represent the weights of the polymers before and after the extraction, respectively.

Organic Solvent Absorption Experiments. After the removal of soluble fractions from polymer networks, the dried crosslinked polymers were examined to see whether or not they were suitable absorbents for organic liquids, such as DCM, THF, benzene, and toluene. The oil and organic solvent absorption capacity was calculated by a method discussed in the literature.²⁶ Bags made of filter paper were used for the purpose of defining the swelling absorbency of the crosslinked polymers. In the beginning, a polymer sample was added to the bags. All of the bags were demerged into oil and organic solvents. The oil and organic solvent absorption experiments were conducted at room temperature; at certain time points (30 min, 1 h, 2 h, 3 h, . . . , 24 h), the bags were taken out of the solvent and blotted to remove excess solvent. They were then weighed in a capped jar. The oil and organic solvent absorption capacity were calculated as shown in the following equation:

$$\text{Sorption capacity (\%)} = [(\omega_s - \omega_d)/\omega_d] \times 100 \quad (2)$$

where ω_d and ω_s represent the weights of the dry and swollen crosslinked polymer samples, respectively.

Swelling Kinetics. The swelling kinetic measurements of the crosslinked polyalkoxysilanes were applied with DCM as the solvent according to the procedure described previously. Bags made of filter paper were taken out at different time intervals



Scheme 1. Synthesis route of biphenyl-bridged, crosslinked polyalkoxysilane with aliphatic diols of different chain lengths. [Color figure can be viewed at wileyonlinelibrary.com.]

(5, 10, 15, ..., 170, and 180 min), blotted gently to remove excess DCM attached to the surface, and then measured.

The equilibrium kinetic data of absorption were then studied to understand the swelling process mechanism. The first-order kinetics (the swelling percentage) are shown in the following equation:

$$d\omega/dt = k(\omega_{\max} - \omega) \quad (3)$$

where ω is the weight of the swollen gel at time t , ω_{\max} is the swollen gel at equilibrium, and k is the swelling kinetic constant. The integration of eq. (3) gives

$$\ln[\omega_{\max}/(\omega_{\max} - \omega)] = k_1 t \quad (4)$$

When the plot of $\ln[\omega_{\max}/(\omega_{\max} - \omega)]$ versus t gives a straight line, the swelling process follows first-order kinetics (k_1 is the first order swelling kinetic constant).

The second-order rate for the swelling process was calculated by the following equation:

$$d\omega/dt = k_2(\omega_{\max} - \omega)^2 \quad (5)$$

Integration leads to the following:

$$t/\omega = [1/(k_2\omega_{\max}^2)] + (1/\omega_{\max})t \quad (6)$$

When the plot of t/ω versus time is a straight line, the swelling tends to follow second-order kinetics (k_2 is the second order swelling kinetic constant).

Desorption Kinetics. The retention feature of the crosslinked polyalkoxysilanes in air was determined by the weight losses of the swollen polymers at regular intervals of time after the swelling kinetic measurements in DCM.

RESULTS AND DISCUSSION

Synthesis of the Biphenyl-Bridged Polyalkoxysilanes

In this study, biphenyl-bridged, crosslinked polyalkoxysilanes were prepared through the reaction of BTSBP with aliphatic diol monomers at a partially high temperature under an argon atmosphere. To illustrate the effects of the chain-length differences on the polymer properties, six different aliphatic diol monomers, including 1,2-ethanediol and 1,12-dodecanediol, were used (1,2-ethanediol for Poly C2, 1,4-butanediol for Poly C4, 1,6-hexanediol for Poly C6, 1,8-octanediol for Poly C8, 1,10-ethanediol for Poly C10, and 1,12-dodecanediol for Poly

C12). The crosslinked structure occurred through the reaction of the hydroxyl groups of linear aliphatic diols and the ethoxysilane groups of biphenyl-bridged alkoxy silane by condensation polymerization without any catalysts, activators, or initiators. Scheme 1 gives a synthesis route of the biphenyl-bridged based polyalkoxysilane.

The chemical structures of the polymers were confirmed by FTIR spectroscopy and ^{13}C and ^{29}Si CP-MAS NMR. The thermal properties of the polymers were investigated via TGA.

The FTIR spectra of the synthesized crosslinked polyalkoxysilanes are shown in Figure 1. Confirmations of Si—O—C and Si—O—CH peaks were observed at approximately 1067 and 954 cm^{-1} respectively. Aliphatic C—H groups, which stemmed from the linear aliphatic diol monomers, appeared at 2842–2930 cm^{-1} . The peaks at 2930–3065 and 1600 cm^{-1} represent the aromatic C—H and —HC=CH— bonds, respectively, of the BTSBP monomer. Broad absorption peaks at 3200–3600 cm^{-1} were observed and were due to the vibrations of hydroxyl groups.

The solid-state ^{13}C and ^{29}Si CP-MAS NMR spectra of the polymers are presented in Figure 2. As shown in Figure 2, aromatic ring carbons from the BTSBP monomer signals were observed at 140–120 ppm. The resonances at 54 and 58 ppm were indicative of the presence of CH₂—OH and CH₂—O—CH, respectively. Aliphatic carbons originating from the linear diol monomers were observed at approximately 11 and 14 ppm.

The solid-state ^{29}Si CP-MAS NMR spectra of the polymers are also presented in Figure 2. The signals at −73 and −80 ppm belonged to CH—O—Si silicones, and it was evident that the polymer networks were successfully prepared by the incorporation of Si into the network.

The TGA results indicate that all of the crosslinked polymers were thermally stable at temperatures lower than 200 °C, with the exception of Poly C2, which displayed less stability than the other crosslinked polymers (Figure 3). The silicon contents of the synthesized polyalkoxysilanes were determined at 900 °C by

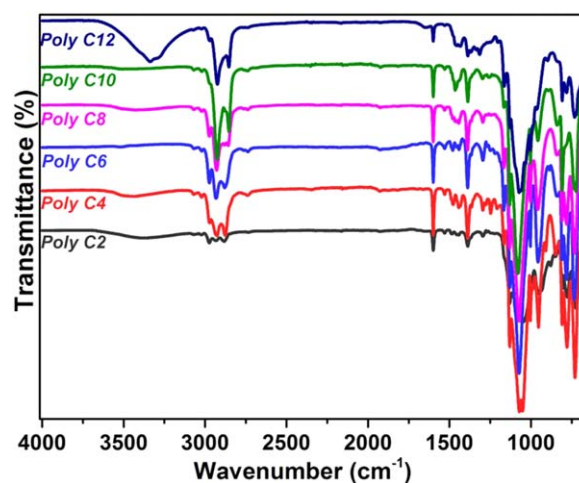


Figure 1. FTIR spectra of the crosslinked polymers. [Color figure can be viewed at wileyonlinelibrary.com.]

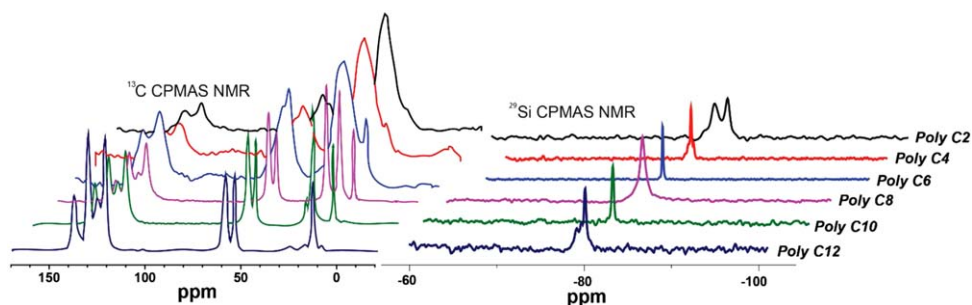


Figure 2. Solid-state ^{13}C and ^{29}Si CP-MAS NMR spectra of crosslinked polymers. [Color figure can be viewed at wileyonlinelibrary.com.]

TGA and were found to be 63% for Poly C2, 42% for Poly C4, 35.6% for Poly C6, 36.8% for Poly C8, 35% for Poly C10, and 28.5% for Poly C12.

Swelling Behavior of the Crosslinked Polymers

Organic Solvent–Oil Absorption Experiments. The synthesized crosslinked polyalkoxysilanes were examined as organic solvent sorbents. Figure 4 shows the organic solvent sorption capacities of six different crosslinked polymers for four organic solvents, DCM, THF, benzene, and toluene, and two oil derivatives, gasoline and euro-diesel.

To achieve reliable swelling results, the soluble fraction had to be removed from the gel reaction. For this purpose, the soluble fraction was extracted with DCM at room temperature until constant weights were achieved. The extracted soluble fraction percentage depended on the type and concentration of the crosslinking agents and monomers.⁴⁵ The soluble fraction values were found to be 2.8% for Poly C2, 10.8% for Poly C4, 36.8% for Poly C6, 10.6% for Poly C8, 23.1% for Poly C10, and 28.9% for Poly C12.

To calculate the solvent absorption capacity of the polymers, swelling experiments were carried out in various organic solvents by gravimetric methods. All of the reported swelling experiments were performed at room temperature and were repeated at least four times to produce reliable, reproducible

results. The swelling capacities of the crosslinked polymers are summarized in Figure 4.

Poly C8, which was prepared by the reaction of BTSBP and 1,8-octanediol monomers, produced the best swelling-uptake capacity. The organic solvent capacity value of Poly C8 was 1485% for DCM; this was the most highly absorbed organic solvent. The solvent uptake capacities were also studied in THF, benzene, and toluene; the values found were 1028, 786, and 761%, respectively. To understand the effects of the chain length of the diol monomer on the solvent uptake properties of the crosslinked polyalkoxysilanes, six different diol monomers (from 1,2-ethanediol to 1,12-dodecanediol) were used to produce a series of crosslinked polymers. It was evident that all of the synthesized crosslinked polyalkoxysilanes had very high swelling capacities for common organic solvents. The swelling capacities of the crosslinked polyalkoxysilanes in DCM were arranged as follows: Poly C8 > Poly C10 > Poly C4 > Poly C6 > Poly C12 > Poly C2. Although Poly C8 showed the best swelling results, Poly C2, which was prepared by the reaction of BTSBP and 1,2-ethanediol monomers, showed the lowest swelling

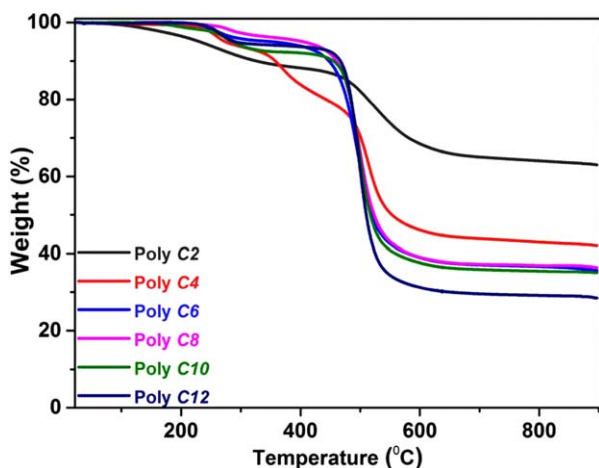


Figure 3. TGA thermograms of the synthesized crosslinked polymers. [Color figure can be viewed at wileyonlinelibrary.com.]

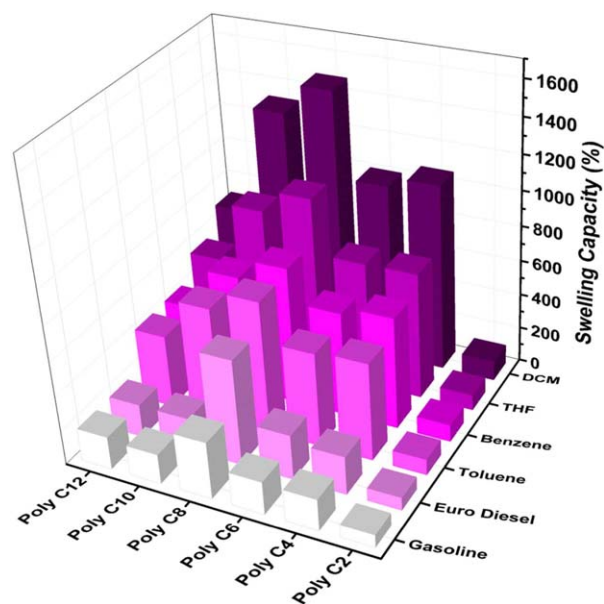


Figure 4. Swelling capacities of the crosslinked polymers in organic solvents and oils. [Color figure can be viewed at wileyonlinelibrary.com.]

results for organic solvents. The swelling values were 112% for DCM, 98% for benzene, 90% for toluene, and 88% for THF. These results likely reflected the more crosslinked structure of these substances.

The length of the crosslinker chain played an important role in the swelling properties of the crosslinked polymers. Increasing the chain length of the diol monomers from 1,2-ethanediol to 1,8-octanediol resulted in an increase in the swelling capacity of the polymers. This might have occurred because the voids between crosslinking points in the three-dimensional polymeric network grew; this allowed more solvent molecules to penetrate the three-dimensional polymeric structure. As a result, the polymer–solvent interaction and organic solvent absorption capacity increased. However, when the number of carbon atoms exceeded 10, the stretching of alkyl groups led to chain entanglement, and solvent diffusion was hindered; as a result of this, the solvent–polymer interaction and organic solvent absorption capacity decreased.

The oil absorption capacities of the synthesized crosslinked polyalkoxysilanes were also tested for two types of oils, gasoline and euro diesel. As shown in Figure 4, the oil absorption capacity values were in the following order: Poly C8 > Poly C6 > Poly C4 > Poly C12 > Poly C10 > Poly C2. As with the organic solvent swelling results, the polymers synthesized from BTSBP and 1,8-octanediol–Poly C8 had the highest swelling capacities for gasoline and diesel. The polymer synthesized from BTSBP and 1,2-ethanediol showed the lowest swelling results for oils. These results indicate that the synthesized materials could be used for absorbing organic solvents and oils from our environment and water surfaces with a high capacity; this could contribute to the cleaning of water surfaces and the environment of pollution caused by previously described events.

We previously reported phenylene-bridged crosslinked polymers as both oil and organic solvent absorbents with the same linear diol monomers.⁴⁶ We also synthesized different series of crosslinked polymers by TEOS²³ and alkyltriethoxysilane monomer³¹ with linear aliphatic diols to produce sorbent materials. A comparison of the absorption capacity of the synthesized polymers with the results of our previous studies is provided in Figure 5, which shows the highest capacity polymers in each series. The maximum solvent absorbency of TEOS-based polymers was found as 310% in DCM linear alkoxyisilane-based polymers and approximately 876% in DCM. In our previous study, the phenylene-bridged alkoxyisilane polymers had a maximum solvent absorbency of 910% in the same solvent. In this study, a biphenyl-bridged crosslinking agent was used to produce more stable, high-capacity oil and organic solvent sorbent materials. The use of the biphenyl-bridged crosslinker made the polymer network more hydrophobic and increased the distance between the crosslinking point; therefore, the organic solvent uptake capacity was increased (Figure 5) by a factor of 4.79 when compared to that of TEOS-based polymers, 1.69-fold compared with alkoxyisilane-based polymers, and 1.63-fold compared with phenylene-bridged polymers. For biphenyl- and phenyl-bridged polymers, in addition to a hydrophobic effect, aromatic rings with π – π interactions may have also increased the solvent affinity.

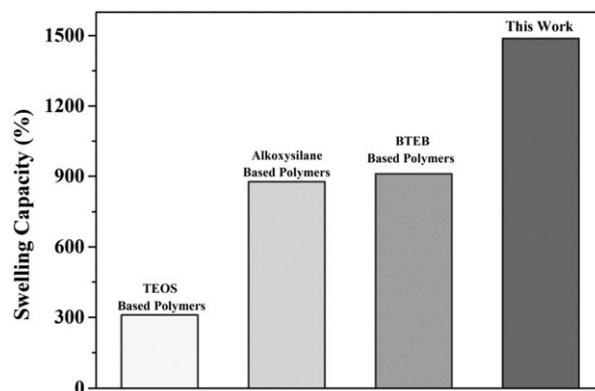


Figure 5. DCM absorption capacity of the polymers based on different crosslinking agents: TEOS,²³ linear alkoxyisilane,³¹ and BTEB.⁴⁶

When the swelling properties of the biphenyl-bridged, crosslinked polyalkoxysilanes were compared with the swelling properties of other crosslinked polymers in the literature (i.e., a semi-interpenetrating network based on polydimethylsiloxane in DCM = 120%,⁴⁷ methacrylate based crosslinked polymer in toluene = 360%,⁴⁸ crosslinked polyorthosilicates in DCM = 310%,²³ polyalkoxysilane sorbents in benzene = 520%,⁴⁹ PDMS sponges in chloroform = 1100%,⁵⁰ crosslinked polyalkoxysilanes in DCM = 876%,³¹ PTHF-based sorbents in DCM = 1800%,³³ crosslinked aminopolysiloxanes in DCM = 700%,⁵¹ conjugated microporous polymers in DCM = 1240%,⁵² crosslinked polyesters in chloroform = 800%,⁵³ and phenylene-bridged polyalkoxysilanes in THF = 670%⁴⁶). Our results for the crosslinked biphenyl based polyalkoxysilanes were clearly competitive (at this level, 1 g of biphenyl-bridged polyalkoxysilane absorbed almost 15 g of DCM), and the synthesized polymers could be used as absorbent materials for organic solvents and oils.

Swelling Kinetics. After the examination of the swelling capacity of the synthesized biphenyl-bridged, crosslinked polyalkoxysilane, the swelling kinetics were studied to determine the absorption–desorption speeds of the polymers versus time. Among all of the organic solvents, DCM was the most absorbable. Therefore, the time dependence of the swelling of the polymers was conducted in DCM. After the crosslinked polyalkoxysilanes reached their maximum capacity, retention kinetics experiments were performed in DCM through the calculation of the weight loss of the swollen polymer at regular intervals of time at room temperature. The absorption–desorption kinetic cycles of the crosslinked synthesized polymers are represented in Figure 6. As shown in the figure, the DCM absorbency increased with increasing immersion time, and almost of all polymers reached maximum capacity in only 25 min.

Figure 6 also illustrates the retention properties of the synthesized polyalkoxysilanes. Within 30 min, all of the absorbed solvent was released from the polymeric networks. The absorption kinetic experiments were conducted at room temperature, and the desorption kinetics experiments were also conducted at room temperature without any external effects, such as squeezing or heating. The synthesized polymers exhibited not only

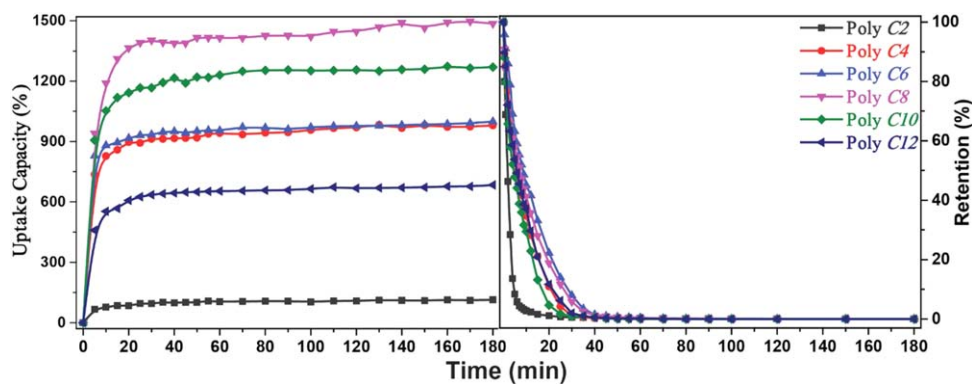


Figure 6. Absorption–desorption kinetics of the polymers in DCM. [Color figure can be viewed at wileyonlinelibrary.com.]

high absorption capabilities but also faster solvent absorption features; this indicated that all of the synthesized crosslinked polymers could be used for practical applications.

The sorption kinetics of the polymers were studied to investigate the mechanism of absorption. As evidenced in Figure 7, the plot of t/ω versus t from eq. (4) provided a perfect straight line and demonstrated that the pseudo second-order models were suitable for understanding the swelling kinetics of the synthesized crosslinked polymers.

The maximum solvent uptake ratio (ω_{\max}) and k values were acquired from the intercept of linear plots and the experimental data provided in Figure 7.

The values for all of the correlation coefficients (R^2) were extremely high (>0.998), as were the values for all of the synthesized polymers; these values are summarized in Table II. There was good agreement between the experimental and theoretical ω_{\max} values.

Effect of the Reaction Time on the Swelling Features. Poly C10, which was synthesized by the reaction of BTSBP and 1,10-decanediol, was produced to investigate the effects of different reaction times on the swelling features. For this purpose, Poly C10 was synthesized with three different reaction times (8, 16,

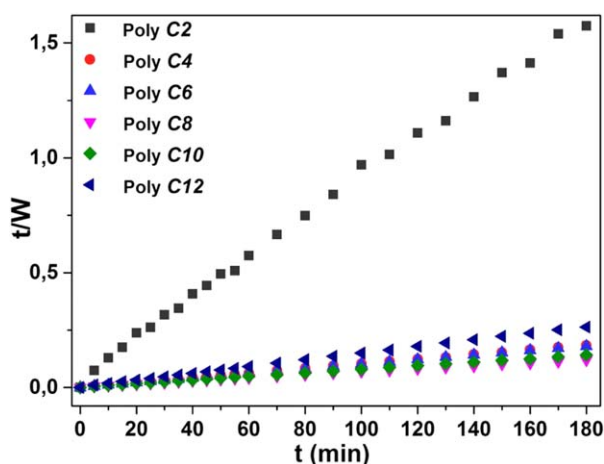


Figure 7. t/ω – t plot for all of the polymers. [Color figure can be viewed at wileyonlinelibrary.com.]

and 48 h), and the swelling capacity and soluble fractions of the polymers were calculated. These experiments were performed in DCM, which was the most highly absorbed solvent. The crosslinking density refers to the reciprocal of the molecular chain length between the two crosslink points of the polymeric network.⁵⁴ The polymer that was synthesized for 8 h showed the highest solvent absorbency, with a value of 1319%. The swelling capacity of the polymers that were synthesized for 16 and 48 h were found to be 828 and 490%, respectively. As the reaction time increased, the crosslink density of the gel increased so that the cavity in the polymeric network was reduced. As a result, the solvent molecule could not penetrate the polymeric network, and the swelling capacity decreased. The soluble fractions of the polymers synthesized for 8, 16, and 48 h were 23, 18, and 13%, respectively. Similar to the swelling results, an increase in the reaction time resulted in a decrease in the percentage of soluble fractions of Poly C10 (Figure 8).

Reusability. There are many sorbent materials that can be used in the removal of oil and organic solvents from the environment and water surfaces, but an important parameter in their application is their reusability. Reusability makes them applicable for the removal of oil/organic solvents from water repeatedly and without capacity loss. To illustrate the reusability of the polymers, Poly C12, which was selected as a representative example, underwent several cycles of swelling and deswelling at room temperature; the results are presented in Figure 9. From the reusability experiments, we concluded that the solvent absorption capacity of the crosslinked polymers remained unchanged and the synthesized material could be used several

Table II. Parameters from the Second-Order Kinetic Model

Polymer	k ($\text{g g}^{-1} \text{min}^{-1}$)	R^2	ω_{\max} (%)
Poly C2	1.636×10^{-3}	0.99817	114.7
Poly C4	3.840×10^{-4}	0.99966	1000
Poly C6	5.260×10^{-4}	0.99977	1000
Poly C8	2.336×10^{-4}	0.99937	1500
Poly C10	3.504×10^{-4}	0.99984	1281
Poly C12	5.298×10^{-4}	0.99977	714.3

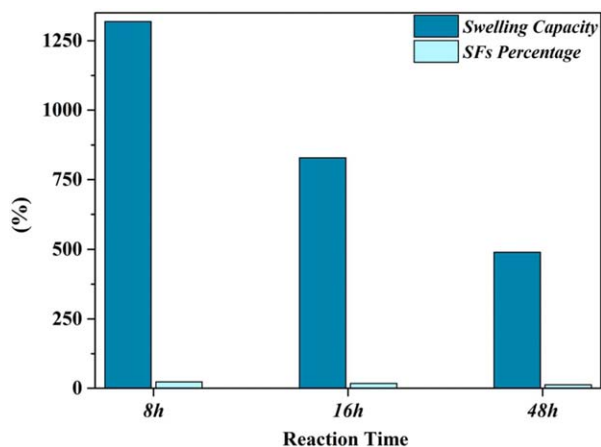


Figure 8. Effect of the reaction time on the oil absorbency and soluble fraction (SF) of Poly C10. [Color figure can be viewed at wileyonlinelibrary.com.]

times for the absorption of organic solvents without capacity loss.

Selectivity. In terms of practical applications, another important parameter to address is the buoyancy on water surfaces before and after the absorption of oil/organic solvents. To illustrate the separation of toluene from water surfaces, 1 mL of toluene dyed with methyl orange was poured into 15 mL of water. After the addition of the crosslinked polymer, toluene was absorbed within 2 s, and the polymer filled with toluene was easily separated from the water by simple filtration, as shown in Figure 10.

CONCLUSIONS

In this study, biphenyl-bridged, crosslinked polyalkoxysilanes were synthesized by the reaction of BTSBP with different length aliphatic diol monomers at partially high temperatures under an inert argon atmosphere. All of the synthesized polymers showed high sorption abilities for organic solvents, including DCM, THF, benzene, and toluene. The maximum capacity was found to be 1485% in DCM. The oil sorption properties of the

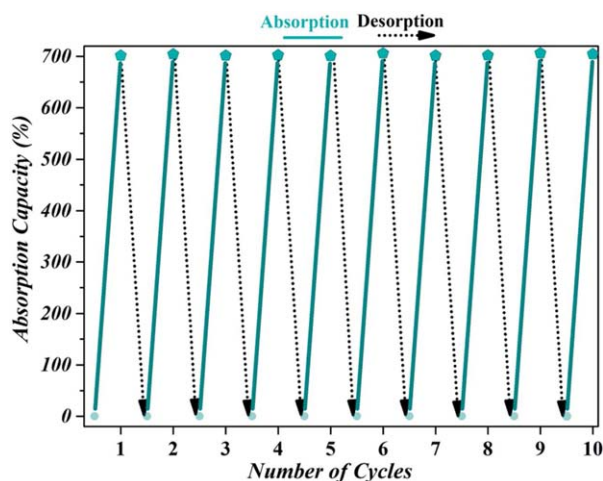


Figure 9. Reusability properties of Poly C12 in DCM. [Color figure can be viewed at wileyonlinelibrary.com.]



Figure 10. Process of separation of toluene (dyed with methyl red) from water surfaces. [Color figure can be viewed at wileyonlinelibrary.com.]

polymers were also investigated, and we found that all of the polymers also possessed swelling ability in oils such as gasoline and diesel with high values. Additionally, the synthesized polymers were found to be reusable, and the synthesized materials showed a good hydrophobicity, high sorption capacity, reusability, and low density. This translates into them being ideal absorbents for oils and organic solvent spills from water.

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