Unraveling the Effect of PEG Chain Length on the Physical Properties and Toxicant Removal Capacities of Cross-Linked Network Synthesized by Thiol–Norbornene Photoclick Chemistry

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ABSTRACT: With the aim to develop chemical adsorbents that are inherently nontoxic to living beings and the environment, a gel system based on thiol–norbornene photoclick chemistry was developed. Norbornene was strategically functionalized with different poly(ethylene glycol) (PEG) chains to produce PEG-functionalized macromonomers. The influence of incorporating PEG in the cross-linked network was evaluated on the basis of its physical properties and dye-removing efficiency from aqueous solutions. The excellent swelling ability of the gels in organic solvents was found to improve with the PEG chain length. The rheological measurements of the as-synthesized materials also exhibited the presence of elasticity in the network, and a decrease in storage and loss moduli was observed with an increase in PEG molecular weight. The materials possess excellent thermal stability, which enhanced with an increase in PEG chain length, as revealed from thermogravimetric analysis (TGA). Differential scanning calorimetry (DSC) studies revealed the tendency of higher-molecular-weight PEG to form a crystalline phase in the network. Kinetic studies of dye removal from aqueous solutions by the as-prepared cross-linked networks indicate that the dye removal proceeds via pseudo-second-order kinetics. The study of adsorption isotherm of the removal process indicates that the adsorption follows the Langmuir isotherm model. In this present work, we have thoroughly evaluated the influence of PEG chain length on several physical properties and toxic cationic dye removal efficiencies of thiol–norbornene photo-cross-linked networks.

INTRODUCTION

Contamination of water with toxicants is a major threat to life. Untreated industrial discharges comprising water-soluble organic dyes can directly impair human life due to their carcinogenicity and acute toxicity. Over 50 000 tons of dyes that are commercially used in various textile, painting, paper, and cosmetics industries are annually discharged into the environment. Dye-tainted water is associated with several risk factors for both marine and human lives, as dyes are recalcitrant in nature, stable to oxidizing agents, and resistant to aerobic digestion. Thus, removing dyes from wastewater is essential and demands the attention of researchers. Several approaches, such as membrane separation, biodegradation, coagulation–flocculation, photocatalysis, adsorption, etc., have been reported for the treatment of wastewater. But most of the techniques are restricted from practical applications due to their exorbitant price, lack of flexibility, and harsh synthetic routes. In this regard, the adsorption process is a promising alternative due to its ease of operation, high efficiency, as well as economic viability. The necessary properties that an ideal adsorbent must possess are low cost, high adsorption capacity, selectivity, etc. Additionally, it is also essential to check the toxicity of the adsorbent itself to avoid any secondary pollution. Therefore, designing of an appropriate adsorbent system is of prime importance. Though there are plenty of literature examples regarding toxicant removal from wastewater, very less attention has been paid toward its environmental toxicity. Moreover, some adsorbents have been reported to show an efficient activity only at a high temperature and a low pH, which are barely the conditions in practical situations.

In our previous work, we have reported that a thiol–norbornene photo-cross-linked network is efficient to remove toxic cationic dyes from wastewater. In this work, we wanted to investigate the impact of incorporating poly(ethylene glycol) (PEG) of different chain lengths in the network structure. For the synthesis of the cross-linked network, a similar fascinating UV-light-mediated click chemistry between thiol and norbornene was performed. The thiol–norbornene photoclick reaction is a step-growth polymerization technique that yields uniform porous networks. This click reaction is particularly advantageous as it is simple, versatile, insensitive...
toward ambient water and oxygen, and can be carried out in environmentally benign solvents.16 Norbornene was strategically functionalized with different PEG chains to produce PEG-functionalized macromonomers. The influence of incorporating PEG in the cross-linked network was evaluated on the basis of its physical properties and dye-removing efficiency. The characterization of the cross-linker and macromonomers was carried out by standard spectroscopic and analytical techniques. The materials were found to show excellent swelling in organic solvents, and the swelling ratio improved with an increase of PEG chain length. Rheological measurements of the as-synthesized materials also exhibit the presence of elasticity in the network, and a decrease in storage and loss moduli was observed with an increase in the PEG molecular weight. Further, thermogravimetric analysis (TGA) revealed that the materials possess excellent thermal stability, which enhanced with an increase in the PEG chain length. The kinetics of the dye removal by as-synthesized materials from aqueous solutions was studied, and the results indicate that the dye removal proceeds via pseudo-second-order kinetics. The adsorption process was found to follow the Langmuir isotherm model. To the best of our knowledge, this is the first ever report describing the influence of PEG chain length on the physical properties and toxic cationic dye removal efficiency of norbornene-based cross-linked networks.

**RESULTS AND DISCUSSION**

With the objective to develop a chemical adsorbent that is inherently nontoxic to the environment, we have synthesized three gels based on the thiol–norbornene click chemistry. Norbornene-based cross-linker 3 was synthesized using the previous report.14 Briefly, a Diels–Alder reaction between furan and maleic anhydride was carried out to yield compound 1, which was then treated with dry ethanol, N,N-dicyclohexylcarbodiimide (DCC), and 4-dimethylaminopyridine (DMAP) to produce compound 2. Compound 3 was obtained by a coupling reaction between 1,6-hexanediol and compound 2 using 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) and DMAP. Next, norbornene carboxylic acid was functionalized by PEG having three different molecular weights of 600, 1450, and 4000 by the Mitsunobu coupling reaction (Figure 1). The formation of three norbornene-functionalized macromonomers (4, 5, and 6) was characterized by 1H NMR spectra (Figures S1–S3). Then, the gelation condition was explored (Figure 2). For that purpose, compound 3 was dissolved in dichloromethane (DCM) solutions containing compound 4, 5, or 6. Pentaerythritol tetraakis(3-mercaptopropionate) (PETMP) and the photoinitiator were then added to them. Thereafter, the solutions were cured under UV light for ~30 min. The formation of the gels was initially confirmed by the vial inversion method (Figure 2e). To verify the role of
compound 3, serving as a cross-linker, gelation was carried out with compounds 4, 5, and 6 each without compound 3. The gel formation took place with only two macromonomers, one with PEG 600 and the other with PEG 1450. Photo-cross-linking did not result in gel formation with PEG 4000 under a similar experimental condition even after a prolonged irradiation time (>4 h).

The cross-linking density of all of the synthesized gels was analyzed quantitatively by measuring the gel content. Briefly, the measured amount of each gel was soaked in DCM overnight to remove any un-cross-linked reagent. Then, the swollen gels were dried in vacuum and weighed again. The gel content was calculated by the mass ratio of the gels before and after extraction. As an equal molar ratio of the thiol and total norbornene was used, the gel content suggests the amount of cross-linking. In this case, the gel content was found to be 92.1% for G1, 87.3% for G2, and 84.1% for G3 (Figure 3b). Gel contents of around 62 and 45% were observed with compounds 4 and 5, respectively (Figure S4). In general, a gel content of over 80% is considered as a sufficiently high cross-linked network when equal molar ratios of the reactive component are used. A higher cross-linking density indicates that more components are covalently attached in the cross-linked network. Hence, we have duly proceeded with the gels synthesized with compound 3, and a decrease in the cross-linking density was observed with an increase in the PEG chain length in the network.

**FT-IR Analysis.** The formation of the gels was confirmed by FT-IR analysis (Figure 3a), where the S–H stretching frequency at 2520 cm⁻¹ from the PETMP diminished after gel formation, indicating a successful thiol–norbornene click reaction.

**Rheological Measurements.** The viscoelastic properties of the as-synthesized gels were evaluated by rheological measurements at room temperature. To begin with, the storage modulus (\(G'\)) and loss modulus (\(G''\)) of the three gels were investigated by strain sweep measurement to figure out the linear viscoelastic region (Figure S5). The typical viscoelastic behavior was observed within the strain range of 28–55% at a constant angular frequency of 0.1 rad/s. Therefore, the frequency sweep experiments were carried out at a constant strain of 1%, which is much below the deformation limit of the gels. From the results (Figure 4a), it is evident that regardless of the PEG molecular weight, the storage modulus (\(G'\)) is larger than the loss modulus (\(G''\)), thereby suggesting the presence of elasticity in the networks. The absence of a crossover point in the given frequency region indicated a high cross-linking density, leading to materials with high relaxation times. It was also very fascinating to note from the results that both storage and loss moduli of the gels decreased with an increase in the PEG molecular weight. We believe that with an increase in the PEG molecular weight of the material, the entanglement degree gets significantly reduced, and as a result, it gets easier for the polymer chains to move under shear stress. This in turn gets reflected in the drop of loss modulus with an increment in the PEG chain length. Further, the incorporation of PEG into the network has led to lowering of the cross-linking density, leading to higher flexibility of the materials. Hence, there was a fall in the storage modulus with the increase in the PEG molecular weight.

**Analysis of Pores.** Surface visualization was carried out by scanning electron microscopy (SEM). The SEM analysis as shown in Figure S6 revealed that the materials consist of macropores (2–4 μm) as well as pores with a smaller size. For a better visualization of the pores, transmission electron microscopy (TEM) analysis of the synthesized gels was also carried out using an ultramicrotome (Figure S7). Due to the presence of larger pores in the surface as revealed by the SEM
and TEM analyses, the widely used nitrogen adsorption–desorption technique could not be applied to measure the pore size of the as-synthesized gels. For these kinds of materials, mercury intrusion porosimetry (MIP) is known to provide more accurate and precise information of the pores due to its ability to resolve pores of a wide scale of diameters ranging from few nanometers to even micrometers. Therefore, the pore size of G1 was evaluated by MIP (Figure S8) and pores of varying sizes (3–30 μm) were found to be distributed in the material. We believe that the presence of such large macropores in the network may be arising from the higher degree of intermolecular cross-linking in the material.

Swelling Ability and Correlation between Solvent Uptake and Solubility Parameter. The porous network as observed from SEM, TEM, and MIP analyses motivated us to investigate the solvent uptake ability of the synthesized gels at room temperature. For that purpose, various solvents were chosen with a broad spectrum of polarities, such as 1,4-dioxane (dielectric constant, ε = 2.25, nonpolar), tetrahydrofuran (ε = 7.58, polar aprotic), dichloromethane (ε = 8.93, polar aprotic), dimethyl formamide (ε = 36.71, polar aprotic), dimethyl sulfoxide (ε = 46.68, polar aprotic), and water (ε = 80.1, polar protic). The influence of the PEG chain length on the swelling capacity of the network was estimated, and the results are shown in Figure 4b.

To explain the swelling behavior of the as-prepared gels in different solvents, the solubility parameter of the gel (δ_g) was determined and compared to the corresponding values of different solvents. In general, the solubility parameter of gels is a fundamental thermodynamic property that directs the miscibility of the gels or polymers in various solvents. Hansen defined the solubility parameter (δ) by the following equation:

\[ \delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \]  

(1)

where \( \delta_d^2 \) is related to the dispersion interaction, \( \delta_p^2 \) is related to the dipolar interaction, and \( \delta_h^2 \) is related to the hydrogen-bonding interaction. Generally, solubility follows the rule “like dissolves like”. The gels will swell maximum in the solvent whose solubility parameter is close to that of the gel. To find the correlation between the swelling ability of the gels and the solubility parameter, we have used the Hansen solubility parameter of different solvents from the existing literature. In most of the literature reports, the % of swelling is calculated using eq S1. Haga et al. reported that the more precise approach is to include solvent densities in the measurement of the swelling ratio. Thus, the swelling ratio was computed taking the solvent densities into account (see the Experimental Section).

To determine the solubility parameter of the gels, the swelling ratio of the synthesized gels in various solvents was first plotted with respect to the solubility parameter of the solvents (Figure S9). Fitting this plot with a Gaussian function revealed that the peak maxima of G1, G2, and G3 are at 14.77, 12.58, and 12.94 (cal cm\(^{-3}\))\(^{1/2} \), respectively (Table S1). Deen et al. reported that this peak maxima value is a reasonable approximation of the solubility parameter of polymeric gels. In our case also, this was found to be true as G3 was found to swell maximum in dimethyl sulfoxide (DMSO) having a solubility parameter of 13.03 (cal cm\(^{-3}\))\(^{1/2} \) compared to the other two gels due to the maximum proximity of the corresponding solubility parameters. Further, as the solubility parameter of G2 was found to be an intermediate of the solubility parameters of DMSO [13.03 (cal cm\(^{-3}\))\(^{1/2} \)] and dimethylformamide (DMF) [12.14 (cal cm\(^{-3}\))\(^{1/2} \)], the swelling ratio of G2 in the two solvents was relatively close compared to that observed for G3. All of these clearly suggest the interpretation in terms of solubility parameter to be the superior approach for explaining the observed swelling behavior of the gels in different solvents. Besides, the swelling ability of a gel in a given solvent is often governed by polarity of the medium, cross-linking density of the gel, etc. Thus, the results (Figure 4b) can also be explained in terms of solvent polarity. The results indicated that irrespective of the PEG chain length, the gels swelled preferably in polar aprotic solvents compared to nonpolar and polar protic solvents. Moreover, for polar aprotic solvents, the swelling of the gels was found to increase with an increase in dielectric constants. Such a parallel relationship between the solvent uptake and dielectric constants of the solvent can be attributed to the stabilization via Coulombic interactions by the polar groups such as C==O and poly(ethylene glycol) present in the cross-linked network. Further, the relatively less swelling in the polar protic solvent indicates that dielectric constants of the solvents are not the only decisive aspect behind the swelling capacity. The rationale behind this can be ascribed to the absence of any exchangeable ionic groups that favor stabilization in polar protic solvents. Haga et al. reported that the swelling of polymer networks in a given solvent can follow two different mechanisms. To understand the mechanism of swelling of the as-synthesized gels in water, we plotted \( Q/Q_e \) vs time (Figure S10), where \( Q_e \) is the swelling ratio calculated from eq 8 and \( Q_e \) is the equilibrium value of \( Q \). We observed that initially there is a sharp increase in the swelling ability that thereafter reaches a plateau. This kind of behavior indicates that both “Fickian” and “case II” mechanisms govern the swelling property of the gels.
Furthermore, it is noteworthy from the results that the solvent uptake ability of the gels increased with an increase in the PEG chain length for all of the solvents. Such dependence of swelling on the length of the PEG chain can be attributed to the cross-linking density of the network. Rheological measurements have revealed that the storage modulus that reflects the stiffness of the gels decreased with an increase in the PEG chain length due to a lower cross-linking density.21 Such a decrease in the cross-linking density with an increase in the PEG chain length helps in the swelling of the corresponding gel compared to relatively stiff gels consisting of smaller PEG chains. These observations clearly indicate that by adjusting the PEG molecular weight, the swelling ability of the cross-linked networks can be fine-tuned.

**Thermal Stability.** Thermal stability is one of the vital properties of gels as it dictates the practical usefulness of these systems. The material that is to be applied for toxicant removal from contaminated water must be able to withstand a high temperature to prevent degradation below the temperature of wastewater. Thermogravimetric analysis (TGA) of the three gels was carried out at a ramping rate of 10 °C/min (Figure 5a). The TGA showed a single-step degradation pattern. But the first derivative plot (DTG) revealed that the degradation temperature increased from 350 to 390 °C on going from G1 to G3. As all other components (cross-linker, photoinitiator) are similar in the three gels, different PEG chains contribute to the increase in the thermal stability. To probe this fact, we have carried out TGA of each PEG chain. The TG curve is provided in Figure S11, which displays that the degradation of PEG starts at 177, 204, and 216 °C for the molecular weights of 600, 1450, and 4000, respectively. Since the thermal stability of the PEG itself increases with an increase in the chain length, the isolated gels also follow the same trend. This observation indicates that the thermal stability of the material can be regulated by adjusting the PEG chain length.

To probe the influence of the PEG molecular weight or cross-linking density of the network on the melting and crystallization behavior, differential scanning calorimetry (DSC) analysis of the synthesized gels was carried out. The cross-linking density of the material plays a crucial role in tuning the thermal properties.33–35 The DSC curves (heating and cooling cycles) are presented in Figure 6. Analysis of the cooling curves (Figure 6b) reveals that the gel with a longer PEG chain length tends to form a crystalline phase in the network. Such crystallization behavior in the case of G3 can be credited to the favorable geometrical alignment in the network.55 The melting endotherms of the gels are displayed in Figure 6a. The results exhibited an interesting melting behavior of the gels. The melting curves of each PEG, provided in Figure S12, show that \( T_m \) increases with an increase in the PEG chain length. Now, if we compare between PEG 600 and G1, G1 showed a broad endotherm around 59 °C due to the sustained melting of the gel. This could be attributed to the efficient cross-linking (the highest gel content observed in this case, Figure 3b) and enhanced miscibility with the homogeneous phase between the norbornene cross-linker and the shorter PEG chain, which in turn reflected in the absence of any sharp \( T_c \) during the cooling cycle. On the other hand, G2 showed no such endotherm in the experimental temperature range, which might be resulting from some unusual packing of the constituents. Notably, G3 exhibited a clear and sharp melting endotherm having the maximum around 47 °C. Such reduction in \( T_m \) in the case of G3 might be due to the incorporation of a high-molecular-weight PEG moiety into the cross-linked network resulting from the increase in chain mobility due to the relatively less cross-linking density. It could also be ascribed to the crystal size reduction leading to the change in the surface free energy with the increase in the molecular weight of the PEG.35 The decrease in \( T_m \) led to the enhanced chain mobility of the gel (G3), which was corroborated with its reduced storage modulus (Figure 4a) and increased crystallinity of the same as observed in this study. Hence, the flow of the influence of the PEG chain length on the thermal property is as follows: high cross-linking density (with shorter PEG chain) → chain mobility is restricted → higher \( T_m \); reduced cross-linking density (with longer PEG chain) → increased chain mobility → lowering of \( T_m \).

**Dye Removal. Adsorption Kinetics.** After evaluating the outcome of varied PEG molecular weights on the physical properties of the cross-linked network, its effect toward dye removal from aqueous solutions was explored. For that, rhodamine B was chosen as the model cationic dye. Then, 20 mg of the respective gels was dipped in aqueous solutions of 0.1 mM rhodamine B and the dye removal process was probed by monitoring time-dependent UV–vis spectra of the dye solutions. To fathom the mechanism which directs the dye removal process, the data obtained from the kinetic experiments were fitted into pseudo-first-order (eq 2), pseudo-second-order (eq 3), and Weber–Morris intraparticle diffusion (eq 4) models.37,38 These models were validated by analyzing their corresponding correlation coefficients \( R^2 \).

\[
\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t
\]

(2)

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

(3)
where \( q_t \) and \( q_e \) are the amounts of the dye removed at time \( t \) and at equilibrium, respectively, \( k_1 \) (\( h^{-1} \)) is the pseudo-first-order rate constant, \( k_2 \) (\( g \text{ mg}^{-1} \text{ h}^{-1} \)) is the rate constant for the pseudo-second-order model, and \( k_i \) is the intraparticle diffusion rate constant. The slopes and intercepts of the linear plots of \( \log(q_e - q_t) \) vs \( t \) for the pseudo-first-order kinetics, \( \frac{1}{q_t} \) vs \( t \) for the pseudo-second-order kinetics, and \( q_t \) vs \( t^{1/2} \) for intraparticle diffusion model were employed to find the parameters.

The results obtained are depicted in Figures 7–9 and Table 1. The high degree of linearity in the case of pseudo-second-order kinetic models described the dye removal kinetics better than the pseudo-first-order model for all of the three gel systems. This suggested that the dye adsorption by the gel may be resulting from some kind of chemical interaction.\(^{39}\) At this initial concentration, the \( q_e \) value was found to increase on going from G1 to G3. For the intraparticle diffusion models, there were two successive linear portions. The first linear part being steeper than the later one indicated the diffusion of the dyes from the bulk solution to the boundary layer of the gel or across the boundary layer to the surface of the gel.\(^{37}\) The second linearity demonstrated intraparticle diffusion as the rate-determining step. But the lines did not pass through the origin (intercept, \( c \neq 0 \)), thereby signifying that the intraparticle diffusion mechanism, although involved in the adsorption process, is not the only rate-limiting step for dye removal.\(^{38}\)
On the other hand, when the dye removal efficiency was investigated with an anionic dye Acid Orange 7, only negligible removal took place even after 5 days (Figure S7). These results indicated that the materials are efficient toward the removal of cationic dyes but incompetent for the anionic dye removal. We believe that the presence of electron-rich groups in the cross-linked networks is responsible for such specificity toward cationic dyes over anionic ones.

**Adsorption Isotherms.** To appraise the adsorption type, the experimentally obtained data were fitted into two adsorption isotherm models, namely, Langmuir and Freundlich models. The Langmuir model that assumes monolayer adsorption of the adsorbate onto the adsorbent can be expressed as the following equation:

$$\frac{c_e}{q_e} = \frac{1}{bq_m} + \frac{c_e}{q_m}$$  \hspace{1cm} (5)

where $c_e$ is the equilibrium concentration of the dye in mg L$^{-1}$, $q_e$ is the amount of the dye removed by the gel in mg g$^{-1}$, $q_m$ is the monolayer adsorption capacity of the adsorbent in mg g$^{-1}$, and $b$ is the Langmuir constant.

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Table 1. Kinetic Parameters of Rhodamine B Removal by G1, G2, and G3

| Gel  | pseudo-first-order model | pseudo-second-order model | intraparticle diffusion model |
|------|--------------------------|---------------------------|-------------------------------|
| G1   | $R^2 = 0.94662$          | $R^2 = 0.99561$          |                               |
|      | $q_e = 5.73$ mg g$^{-1}$ | $q_e = 8.84$ mg g$^{-1}$  |                               |
|      | $k_1 = 0.125$ h$^{-1}$   | $k_2 = 0.046$ g mg h$^{-1}$ |                               |
| G2   | $R^2 = 0.97833$          | $R^2 = 0.99785$          |                               |
|      | $q_e = 8.01$ mg g$^{-1}$ | $q_e = 10.55$ mg g$^{-1}$ |                               |
|      | $k_1 = 0.096$ h$^{-1}$   | $k_2 = 0.011$ g mg h$^{-1}$ |                               |
| G3   | $R^2 = 0.98424$          | $R^2 = 0.99177$          |                               |
|      | $q_e = 8.89$ mg g$^{-1}$ | $q_e = 11.36$ mg g$^{-1}$ |                               |
|      | $k_1 = 0.0940$ h$^{-1}$  | $k_2 = 0.007$ g mg h$^{-1}$ |                               |

Figure 9. (a) Time-dependent rhodamine B absorption spectra on G3, $C_0 = 0.1$ mM at room temperature in DI water. Kinetic curves of (b) pseudo-first-order, (c) pseudo-second-order, and (d) intraparticle diffusion models.

Figure 10. (a) Langmuir and (b) Freundlich adsorption isotherms of rhodamine B sorption onto G1.
also be formulated in terms of the following dimensionless parameter
\[ R_L = \frac{1}{1 + b c_0} \]  
(6)
where \( c_0 \) denotes the initial dye concentration in mg L\(^{-1} \) and the \( R_L \) value defines the adsorption type. Adsorption is irreversible for \( R_L = 0 \), linear for \( R_L = 1 \), unfavorable for \( R_L > 1 \), and favorable if \( 0 < R_L < 1 \).

The Freundlich model is based on the assumption of adsorption on the heterogeneous surface and is expressed as
\[ \ln q_e = \ln k_f n + \frac{1}{n} \ln c_e \]  
(7)
where \( n \) is the Freundlich constant and \( k_f \) is the constant associated with the adsorption capacity, and they can be calculated from the plot of \( \ln q_e \) versus \( \ln c_e \).

The results of Langmuir and Freundlich isotherms are presented in Figures 10–12 and Table 2. The correlation coefficients for Langmuir isotherm models were found to be higher than those for Freundlich isotherm models for the three gels, thereby implying better applicability of the Langmuir model with the \( R_L \) value lying between 0 and 1. This suggested that though the incorporation of PEG with different molecular weights in the as-synthesized gels does not alter the adsorption type or adsorption mechanism, it has a significant effect on the maximum adsorption capacity (\( q_m = 28.9 \) mg g\(^{-1} \) for G1 to 66.7 mg g\(^{-1} \) for G3). We believe that the improvement of dye adsorption capacity with an increase in the PEG chain length is arising from the increasing swelling capacity of the gels. As higher swelling indicates the incorporation of a higher amount of solvent in the cross-linked networks, the interaction between the dye molecules and the gel gets enhanced, leading to higher adsorption.

**Effect of Initial Dye Concentration.** As depicted in Figure 13, it is evident that with an increase in the initial dye concentration from 0.479 to 479 mg/L, there is enhancement of the maximum removal capacity (\( q_m \)) of the gels. It is also noteworthy to observe that the \( q_e \) value increased with an increase in the PEG chain length.

| gel  | Langmuir model | Freundlich model |
|------|----------------|------------------|
| G1   | \( R^2 = 0.9925 \) | \( R^2 = 0.8914 \) |
|      | \( q_m = 28.9 \) mg g\(^{-1} \) | \( n = 1.84 \) |
|      | \( R_L = 0.014–0.89 \) | \[ n = 3.37 \] |
| G2   | \( R^2 = 0.9910 \) | \( R^2 = 0.9385 \) |
|      | \( q_m = 42.5 \) mg g\(^{-1} \) | \( n = 3.37 \) |
|      | \( R_L = 0.027–0.087 \) | \[ n = 2.5 \] |
| G3   | \( R^2 = 0.9926 \) | \( R^2 = 0.9014 \) |
|      | \( q_m = 66.7 \) mg g\(^{-1} \) | \( n = 2.5 \) |
|      | \( R_L = 0.007–0.08 \) | \[ n = 2.5 \] |

![Figure 11. (a) Langmuir and (b) Freundlich adsorption isotherms of rhodamine B sorption onto G2.](image)

![Figure 12. (a) Langmuir and (b) Freundlich adsorption isotherms of rhodamine B sorption onto G3.](image)

![Figure 13. Effect of initial concentration of rhodamine B on G1, G2, and G3.](image)
the initial dye concentration and the PEG chain length are two major aspects for the determination of the dye removal efficiency as long as all other parameters are constant. At low dye concentrations, the active sites provided by the gels are not saturated, resulting in lower $q_d$ values for the three gels. The $q_d$ values increased up to a certain point, and thereafter, no significant change was observed. This critical point is the saturation limit of the active adsorption sites present in the gels. The maximum adsorption capacity ($q_{bm})$ was achieved when all of the adsorption sites were saturated. With an increase in the PEG chain length in the cross-linked network, the availability of the interaction sites with the dye molecules also increased. This triggered the increment in the maximum adsorption capacity of the gel with increasing PEG chain length. This result underlines the influence of the PEG chain length on the adsorption capability of the network.

For practical application, reusability of the gels is a crucial parameter. Ethanol was found to be an efficient solvent for desorption of rhodamine B from gels. The recyclability was checked by measuring the UV–vis spectra of the dye solution, and the removal efficiency was determined using eq S1. Figure 14 reveals that the removal efficiency is 73% even after the seventh cycle. Such fair recyclability of the material can be credited to the porous cross-linked network structure that enables both adsorption of dyes from aqueous solutions and the subsequent desorption in ethanolic solution.

**CONCLUSIONS**

To summarize, this work depicts the facile synthesis of chemical adsorbents based on thiol–norbornene photoclick reactions. The influence of the PEG chain length in this cross-linked network on various physical properties as well as dye removal capacities were thoroughly evaluated for the first time. The gel content of all of the synthesized gels was > 80%, which indicates a fairly high cross-linking density. The cross-linking density of the gels was found to decrease with an increase in the PEG chain length in the given condition where the molar ratios of the total norbornene and thiol were equal. All of the synthesized gels (G1, G2, and G3) exhibited excellent swelling in organic solvents, in particular polar aprotic solvents, and the swelling ability was found to improve with an increment in the PEG chain length. Rheological measurements revealed the tendency of longer PEG chains to form a more flexible network due to a decrease in the cross-linking density. The thermal stability of the network was found to improve with increasing length of PEG chains. DSC studies described the formation of the crystalline phase in the network with a higher PEG molecular weight. It also indicated the influence of the cross-linking density on the thermal properties of the material, mainly on $T_m$. SEM, TEM, as well as MIP analyses well established the presence of macropores across the cross-linked material. The gels served as efficient adsorbents to remove the toxic cationic dye rhodamine B from water. The adsorption results were in a good agreement with the pseudo-second-order kinetic models as well as the Langmuir adsorption isotherm models, and an enhancement in the adsorption capacity was observed with an increase in the PEG chain length in the network. This report yields a physical insight regarding the role of PEG behind the physical properties and the dye removal capability of the network. Conclusively, this report will pave the way for the development of a new class of robust adsorbents based on thiol–norbornene cross-linked network owing to their biocompatibility, ease of synthesis, flexibility, thermal stability, and recyclability.

**EXPERIMENTAL SECTION**

**Materials.** Furan, maleic anhydride, poly(ethylene glycol) (Mn = 600, 1450, 4000); pentacyclothexatrike(3-mercaptopropionate) (PETMP); 2-hydroxy-4-(2-hydroxyethoxy)-2-methylpropionophenone; 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) hydrochloride; ethanol; N,N-dicyclohexylcarbodiimide (DCC); 1,6-hexanediol; 4-dimethylaminopropylidine (DMPA); triphenylphosphine (PPh3); diisopropyl azodicarboxylate (DIAD); compound 2; toluene; hexane; deuterated chloroform (CDCl3); and deuterated dimethylsulfoxide (DMSO-$d_6$) were purchased from Sigma-Aldrich. Potassium bicarbonate, sodium chloride, and sodium bicarbonate were purchased from Merck and used without further purification. Dichloromethane was distilled over calcium hydride under atmospheric pressure.

**Synthesis of PEG Precursors: 4, 5, and 6.** The Mitsunobu coupling reaction was employed between norbornene carboxylic acid (mixture of exo and endo) and PEG 600, PEG 1450, and PEG 4000 individually to obtain macromonomers 4, 5, and 6, respectively. Initially, PEG 600 (5 g, 8.33 mmol) was dissolved in dry tetrahydrofuran (THF) after heating for 2 h at 120 °C. To that solution, norbornene carboxylic acid (6.97 g, 50.47 mmol) and PPh3 (13.24 g, 50.47 mmol) were added. This solution was then brought at 0 °C, followed by the dropwise addition of DIAD (10.20 g, 50.47 mmol) dissolved in anhydrous THF. The resulting mixture was then brought to room temperature and continuously stirred for 48 h under nitrogen atmosphere. Thereafter, the reaction mixture was concentrated and purified by column chromatography (ethyl acetate/hexane) to obtain a yellow viscous liquid. For 5 and 6, the concentrated solution was precipitated in cold diethyl ether three times and collected by centrifugation. $^1$H NMR of compound 4 (CDCl3, 500 MHz) $\delta$ (ppm): 6.06–6.16 (m, 2H), 5.89–5.91 (m, 2H), 4.10–4.22 (t, 4H), 3.61–3.64 (m, 5H), 3.19 (s, 2H), 2.81–2.95 (m, 4H), 2.02 (m, 2H), 1.85–1.90 (m, 2H), 1.38–1.40 (m, 4H), 1.23–1.25 (d, 2H). $^1$H NMR of compound 5, (CDCl3, 500 MHz) $\delta$ (ppm): 6.06–6.16 (m, 2H), 5.89–5.91 (m, 2H), 4.10–4.22 (t, 4H), 3.61–3.64 (m, 5H), 3.19 (s, 2H), 2.81–2.95 (m, 4H), 2.02 (m, 2H), 1.85–1.90 (m, 2H), 1.38–1.40 (m, 4H), 1.23–1.25 (d, 2H).

$^1$H NMR of compound 6, (CDCl3, 500 MHz) $\delta$ (ppm): 6.06–6.16 (m, 2H), 5.89–5.91 (m, 2H), 4.10–4.22 (t, 4H), 3.61–3.64 (m, 5H), 3.19 (s, 2H), 2.81–2.95 (m, 4H), 2.02 (m, 2H), 1.85–1.90 (m, 2H), 1.38–1.40 (m, 4H), 1.23–1.25 (d, 2H).
Synthesis of the Gel. Compound 3 was dissolved in DCM solutions containing either compound 4, or 5, or 6. PETMP (equal molar ratio of the thiol to total norbornene component), the photoinitiator (2-hydroxy-4′-(2-hydroxyethoxy)-2-methylpropionophenone) was then added to it, and the solutions were cured under UV light for ~30 min. The formation of the gel was initially confirmed by the vial inversion method. Then, the gels were washed with DCM repetitively to remove any unreacted monomer, cross-linker, or photoinitiator, followed by drying under vacuum. For the ease of understanding, the gels synthesized with compounds 4, 5, and 6 are denoted as G1, G2, and G3, respectively, in the future discussion. The schematic representation of the thiol—norbornene photo-cross-linked reaction mechanism is illustrated in Supporting Information (Figure S14).

Determination of Gel Content. During the purification process of the gels, a specific amount of the material (mass $M_f$) was immersed in DCM and kept overnight to allow any un-cross-linked components to diffuse out to the solvent from the cross-linked network. After that, the swollen gels were dried in vacuum and weighed again to get mass $M_s$. The % of gel content was measured from the ratio of the gel before and after extraction ($M_s/M_f$).\(^{19}\) This process was carried out in triplicate for each of the gels to obtain the correct gel content value.

Solvent Uptake Analysis. The ability of the cross-linked networks to uptake different solvents was measured by the gravimetric method. For that purpose, a measured amount of the dried gel was taken in a vial, to which various solvents of different polarities were added. The vial was kept undisturbed for 24 h for the gel to reach the maximum swelling capacity. Thereafter, the gels were taken out from the solvents and wiped carefully with tissue paper before weighing. The percentage (%) of swelling ($Q_s$) or the swelling ratio was calculated using the following formula\(^{21}\)

$$\text{swelling ratio (\%)} = \left(\frac{w_f - w_d}{w_d}\right) \times \frac{d_{\text{gel}}}{d_{\text{solv}}} \times 100$$

where $w_f$ and $w_d$ are the masses of swollen and dry gels, respectively, $d_{\text{solv}}$ is the solvent density, and $d_{\text{gel}}$ is the density of the cross-linked network, which is taken as unity in all of the three cases owing to its difficulty in determination.

Dye Removal Studies. The influence of the PEG molecular weight in the cross-linked network on its dye removal capability (rhodamine B) was tested by spectroscopic methods. For the kinetic studies, 20 mg of each gel was added to 0.1 mM rhodamine B solution (4 mL, prepared in deionized water, pH = 6.89 and at room temperature) and the removal of the dye was probed by change of intensity in the UV-vis spectra as the absorbance was found to decrease with increase in time. Each experiment was carried out in triplicate. The concentration of the removed dye was measured from the appropriate calibration curve. For the isotherm studies, 20 mg of each gel was added to dye solutions of various concentrations (from 0.479 to 479 mg/mL) and the decrease in absorbance after 48 h was recorded. The amount of the dye removed by unit weight of the gel ($q_s$, mg/g) was acquired using the following formula\(^{37}\)

$$q_s = \frac{C_0 - C_e}{m} V$$

where $C_0$ and $C_e$ are the concentrations of the dye solution in mg/L at the initial stage and at equilibrium, respectively, $m$ is the mass of the gel in g, and $V$ stands for the volume of the dye solution in liters.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03554.

\(^{1}H\) NMR spectra of 4, 5, and 6; rheology data of G1, G2, and G3 for strain sweep experiments; SEM and TEM images of the gel, pore size distribution data; kinetics of swelling in water data; DSC and TGA curves of PEG 600, 1450, and PEG 4000; anionic dye (Acid Orange 7) removal by UV–vis spectra; dye absorption formula; and the mechanism of thiol–norbornene photoclick reaction (PDF)

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### Notes

The authors declare no competing financial interest.

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