Polym. Bull. (2011) 67:915–926
DOI 10.1007/s00289-011-0514-z

ORIGINAL PAPER

Thermal response and recyclability of poly(stearylacrylate-*co*-ethylene glycol dimethacrylate) gel as a VOCs absorbent

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Received: 10 February 2011 / Revised: 19 May 2011 / Accepted: 20 May 2011 /

Abstract The development of absorbent materials for volatile organic compounds (VOCs) is in demand for a variety of environmental applications including protective barriers for VOCs point sources. One of the challenges for the currently available VOCs absorbents is their recyclability. In this study, we synthesized poly(stearylacrylate-*co*-ethylene glycol dimethacrylate) (NG-18) gels, and after rigorous characterization, investigated the absorption properties for VOCs. The synthesized gel could be recycled by immersing in ether and other chlorinated, aromatic, and aliphatic solvents and by cooling them at 0 °C. These recycling processes resulted in approximately 25% weight loss compared to the fully swollen state, due to the crystallization of long-alkyl chain component of the gel. This property shows the possibility of recycling absorbed solvents easily and its usefulness as VOCs absorbent material.

Keywords Stearylacrylate (Octadecylacrylate) · Volatile organic compounds (VOCs) · Swelling behavior · Absorbent matrix · Volume phase transition

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Introduction

Volatile organic compounds (VOCs) possess high vapor pressures and uniquely affect human health by vapor intrusion [1] and other exposure pathways. Accidental petroleum spills [2] such as Exxon Valdez in 1989 and Deepwater Horizon in 2010 are examples of VOCs exposures with catastrophic impacts on sea life and the environment in general. It takes several generations for complete recovery of the damage caused by the VOCs pollution. The VOCs absorbents are a promising clean-up strategy for the contaminated sites. Ideal properties for the absorbent materials are: (1) high absorbencies and convenience for shipping and storage, (2) environmentally friendly material that does not contain endocrine disruptors, and chemically stable, (3) selectivity for the absorbates and solvents, (4) recyclability of the absorbents, and (5) low production and supply costs.

The conventional VOCs absorbent materials are the polymer network gels consisting of a lipophilic polymer chain such as polystyrene [3], polybutadiene [4], polyurethane [5], poly(orthocarbonate)s [6], polyisobutylene [7], poly(ethylene-co-propylene-diene) (EPDM) [8], and their combination [9–11]. When dry gels are soaked in VOCs, the solvents can penetrate to the gel matrix due to the high compatibility between the polymers and solvents, and become entrapped within the matrix. Particular limitations of the conventional VOCs absorbent materials are the absorption capacity, environmental friendliness, and recyclability. On the other hand, some promising materials were recently developed with higher absorbent properties. For example, Gui et al. [12] reported the carbon nanotube (CNT) sponge having high swelling ability (up to 180 times their own weight) prepared by chemical vapor deposition with ferrocene as the precursor. This CNT sponge can absorb a wide range of solvents including oil with selectivity and recyclability, and withstands strains and can be compressed without collapsing. Also, Sada and co-workers [13] previously showed that “lipophilic” polyelectrolyte gels bearing tetraalkylammonium tetraphenylborate as a lipophilic and bulky ionic group can absorb a variety of organic solvents up to 500 times their dry size. The high swelling ability results from dissociation of the ionic groups in low polar media. The system is expected to provide new strategies for the design of high-swelling gels.

Herein, we focused on the recyclability of the absorbent gels, which means the ability to be able to separate solvent from swollen gels and reuse them. Such property enables us to decrease the amount of the waste of used gels. In this study, we synthesized and evaluated the properties of poly(stearylacrylate-*co*-ethylene glycol dimethacrylate) gels to realize this system. The polymers including long alkyl groups in the side chain have upper critical solution temperature (UCST) behavior in several low- or non-polar solvents, which is attributed to crystallization among long alkyl chains [14]. Also, Jang et al. [15] demonstrated the gels composed of stearylacrylate have the highest absorbency of oil than the other alkylacrylate monomers. Therefore, our stearylacrylate gels are expected to have both high swelling property and recyclability.

Experimental section

Materials

Stearylacrylate (SA), ethylene glycol dimethacrylate (EGDMA), benzene, azobisisobutylonitrile (AIBN), methanol, ethanol, diethylether, and carbon tetrachloride were purchased from Sigma-Aldrich (Milwaukee, WI). Tetrahydrofuran (THF), isopropanol, acetonitrile, and dichloromethane were obtained from Acros Organics (Morris Plains, NJ). Dimethylsulfoxide (DMSO) and 1-octanol were supplied from Alfa Aesar (Ward Hill, MA). Chloroform and cyclohexane were distributed from VWR International (West Chester, PA). Acetone, methylisobutylketone (MIBK), toluene, and *n*-hexane were supplied from Fisher Scientific (Pittsburgh, PA). All chemical reagents were used as received.

Synthesis

SA-*co*-EGDMA with two crosslinker ratios were prepared by radical copolymerization, which are represented as NG-18-x% ($x = 1$ or 0.5; x denotes the mole ratio of crosslinker to SA). A typical synthetic protocol is as follows: 10.0 g (30.8 mmol) of SA (monomer) and 61 mg (0.31 mmol, the case of $x = 1$) of EGDMA (crosslinker) as initiator were placed in a vial tube and dissolved in 2 mL of benzene by heating at 50 °C. Oxygen in the solution was excluded by bubbling nitrogen gas for 45 min then 101 mg (0.62 mmol) of AIBN was added. The vial tube was sealed tightly and heated at 65 °C for 24 h for polymerization. Gels with low crosslinking densities were prepared in a similar way by reducing the feed ratios of EGDMA. The synthesized gels were washed by swelling in hexane repeatedly, air-dried for 2 days, and dried in vacuum overnight. Gels with lower crosslinking ratio of $x = 0.2$ and 0.1 were also prepared. However, the gels were very soft and further evaluation was carried out only with the gels with $x = 1$ and 0.5.

Characterization

The Fourier transform infrared (FTIR) spectra were performed using Jasco FT/IR-4100. Compression strength was measured with Instron 5900 electromechanical system and the compression speed was 0.25 mm/min.

Swelling studies

Swelling behavior of NG-18 gels was determined with the following solvents of various polarities at 25 ± 1 °C using 5 mL vials: water, DMSO, methanol, ethanol, isopropanol, 1-octanol, acetone, MIBK, acetonitrile, THF, diethylether, dichloromethane, chloroform, carbon tetrachloride, benzene, toluene, hexane, and cyclohexane. The mass of the empty vials was recorded and then a specified amount of dried gel was added to the vials. The vials were weighed and the amount of dried gel was noted (W_{dry}). The vials were then filled with a solvent and allowed to equilibrate for 2 days. The excess solvent was removed from the vials and they were weighed again (W_{wet}). The amount of solvent absorbed by the gels was obtained from the difference in weights. The swelling degree (Q) was defined by Eq. 1:

$$Q = \frac{W_{\mathrm{wet}} - W_{\mathrm{dry}}}{W_{\mathrm{dry}}} \tag{1}$$

Temperature dependence on swelling degree of NG-18-1% gel was measured in the above solvents at 20, 40, 60, (60→) 0, and (25→) 0 °C. Here, (60→) 0 °C indicates that the sample was heated at 60 °C to achieve the equilibrium once and then cooled to 0 °C. This was performed to investigate the record of the heating and cooling process. Due to the boiling point, dichloromethane and diethylether were not used at 40 °C, including acetone at 60 °C. Likewise, DMSO and cyclohexane were not used at 0 °C owing to the melting points. These values were indicated as $Q = 0$. To understand the kinetics of swelling behavior, also, the above procedure was followed with several vials and the amount of solvent absorbed was determined at different time intervals.

Critical temperature studies

Critical temperatures were determined by UV–vis spectroscopy (Aquamate 100, Thermo Scientific Spectronic Products, Rochester, NY). The swollen NG-18-1% gel in THF was placed in a temperature controlled quartz cell, which was monitored with thermocouples (OMEGA DP462). The transmittance at 700 nm was measured as a function of temperature by changing temperature at 0.1 °C/min. While the swollen gel was transparent, the collapsed gel was opaque. The values of critical temperature in the heating and cooling process were obtained from a plot of transmittance versus temperature.

Cyclic temperature change test

Cyclic temperature changes of both swelling degree and transmittance were performed to ascertain the reversibility of the gel. In the swelling test, a piece of NG-18-1% gel was first placed in THF for 48 h at 25 °C. We removed the excess THF from the vial, weighed it, and calculated the swelling degree. Then the vial was filled with THF again, placed at 0 °C for 24 h, and swelling degree was measured by the same procedure. This cycle was repeated five times in total. In the transmittance study, THF swollen gels were placed in a temperature controlled quartz cell. The transmittance at 700 nm was measured at 25 and 0 °C alternatively. It took about 30 min for each step, and was repeated five cycles in total. The gels achieved equilibrium values at each step in both swelling and transmittance test.

Results and discussion

Characterization of NG-18 gels

FT-IR spectra of SA monomer and NG-18-1%, -0.5% are provided in Fig. 1. Compared to the spectrum of stearylacrylate monomer, NG-18 gels showed the disappearance of peaks in four regions. Each peak was identified as follows: 1634 cm^{-1} is C=C bond vibration, 1410 cm^{-1} is C–H of C=CH_2 in-plane scissoring, 1297 cm^{-1} is C–H of C=CH in-plane vibration, and 997 and 893 cm^{-1} are C=CH out-plane vibration. The disappearance of these peaks of the vinyl group indicates that NG-18 gels include a little non-reacted SA. Figure 2 shows the compression strength of swollen NG-18-1% gel in THF. The first breaking point is the stress of 0.371 MPa and the fracture strain of the gel is $\lambda = 67\%$. The NG-18-1% gel could withstand a similar degree of compression as reported by single network poly acrylamide gel prepared by Gong et al. [16].

Swelling behavior

The swelling behavior of NG-18 gels (NG-18-1% and -0.5%) in the solvents with various polarities from cyclohexane to water at 25 °C was investigated (Fig. 3). The swelling degree increased with increasing polarity from cyclohexane, and the maximum value was observed in chloroform. On the other hand, the gels collapsed in the more polar solvents (dielectric constant $\varepsilon > 10$). Particularly, NG-18 gels absorbed large amounts of chlorinated solvents such as chloroform ($Q = 35$ on NG-18-1%) and carbon tetrachloride ($Q = 36$). Moreover, NG-18 swelled in a moderate amount of solvents such as ether (diethylether: $Q = 12$, THF: $Q = 17$), aromatic compounds (benzene: $Q = 21$, toluene: $Q = 22$), and aliphatic reagents (hexane: $Q = 14$, cyclohexane: $Q = 20$). In more polar solvents, such as water, DMSO, alcohols (methanol, ethanol, isopropanol, and 1-octanol), ketones (acetone and

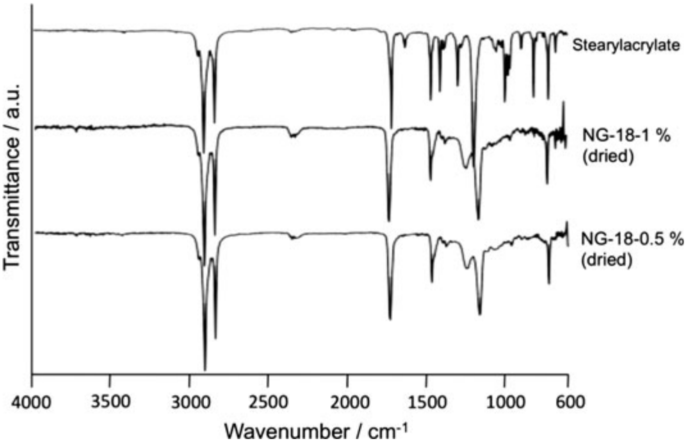


Fig. 1 FTIR spectra of stearyl acrylate and NG-18 gels

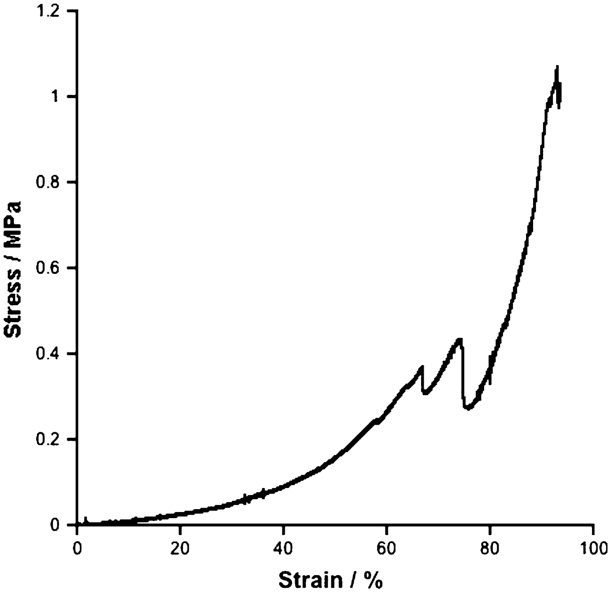


Fig. 2 Stress-strain curve of swollen NG-18-1% in THF

MIBK), and acetonitrile, NG-18 did not swell at all ($Q < 1$). Also, we attempted to enhance swelling ability by reducing the cross linker density. Reducing the feed ratio of the crosslinker to the monomer from 1 to 0.1 mol% enhanced the swelling ratio. However, the gels less than 0.2 mol% crosslinker density are too soft to separate excess solvent and we could not measure the accurate swelling degree. NG-18-0.5% indicated the same tendency as NG-18-1% and higher swelling degree than NG-18-1%. These swelling behaviors of NG-18 gels essentially depend on the compatibility of the polymer chain with the media. NG-18 did not allow penetration of the highly polar molecules into the polymer networks, while non-polar solvents were absorbed.

Subsequently, temperature dependence on the swelling degree with NG-18-1% gel was examined in Fig. 4. The temperature was changed from 20 to 40, 60, and 0 °C successively, and the variety of solvents is the same as ones used in swelling degree test at 25 °C. Also, the sample cooled from 25 to 0 °C was studied to investigate the influence of thermal record at heating process for swelling behavior, which represented as (25→) 0 °C. The comparison between (60→) 0 °C and (25→) 0 °C was summarized in Fig. 5.

The results in Fig. 4 were categorized as follows: (1) Swelling degree did not change in both heating and cooling process: water, DMSO, methanol, ethanol, isopropanol, acetone, acetonitrile, carbon tetrachloride, and cyclohexane. (2) Whereas the Q value did not change by heating, 25 wt% maximum of solvent dislodged from the gel in cooling process: THF, diethylether, dichloromethane, chloroform, benzene, toluene, and hexane. (3) The swelling degree increased, by heating, but was almost the same by

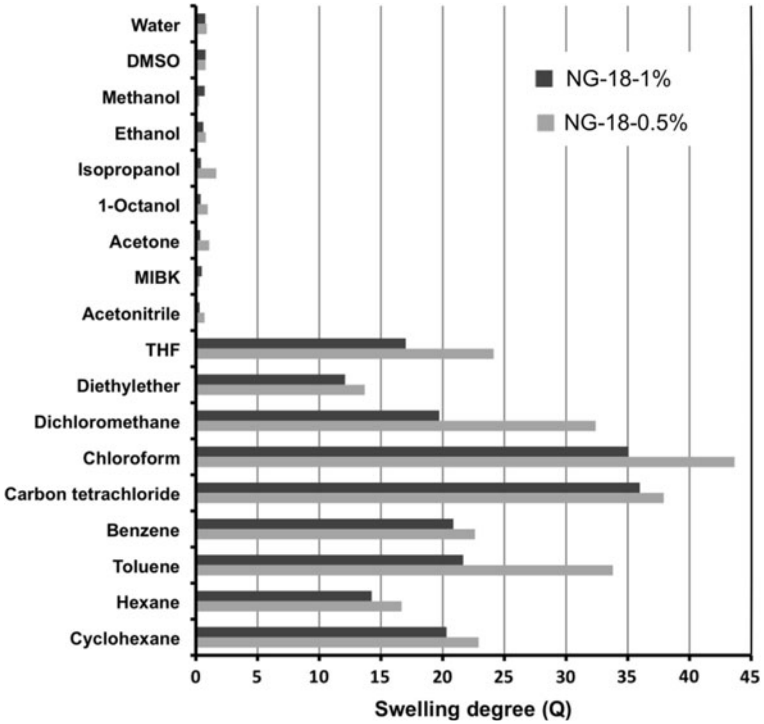


Fig. 3 Swelling degree of NG-18-1%, -0.5% in various solvents

cooling: 1-octanol and MIBK. Especially, the second category is remarkable that showed the changes of swelling degree and color to opaque by cooling to 0 °C. These transition behaviors are attributable to crystallization of long-alkyl chain among stearylacrylate. It is expected that this ability can be utilized to VOCs recycling system capable of both uptake and ejection. On the other hand, the transitions in the third category were irreversible as can be seen in Fig. 5.

Additionally, in order to determine the time dependence on the swelling degree of NG-18 gels in THF, the swelling ratio was determined as a function of time. Figure 6 shows the time required for each gel to reach the equilibrium swelling degree. A cubic dry gel (NG-18-1%, -0.5%), 5 mm on a side, was placed in a vial with excess THF at 25 °C.

The kinetics of the swelling behavior was examined by fitting the data to Lagergren pseudo-first and pseudo second-order kinetic equations [17–19]:

$$\frac{\mathrm{d}q_\mathrm{t}}{\mathrm{d}t} = k_1(q_\mathrm{e} - q_\mathrm{t}) \tag{2}$$

$$\frac{\mathrm{d}q_\mathrm{t}}{\mathrm{d}t} = k_2(q_\mathrm{e} - q_\mathrm{t})^2 \tag{3}$$

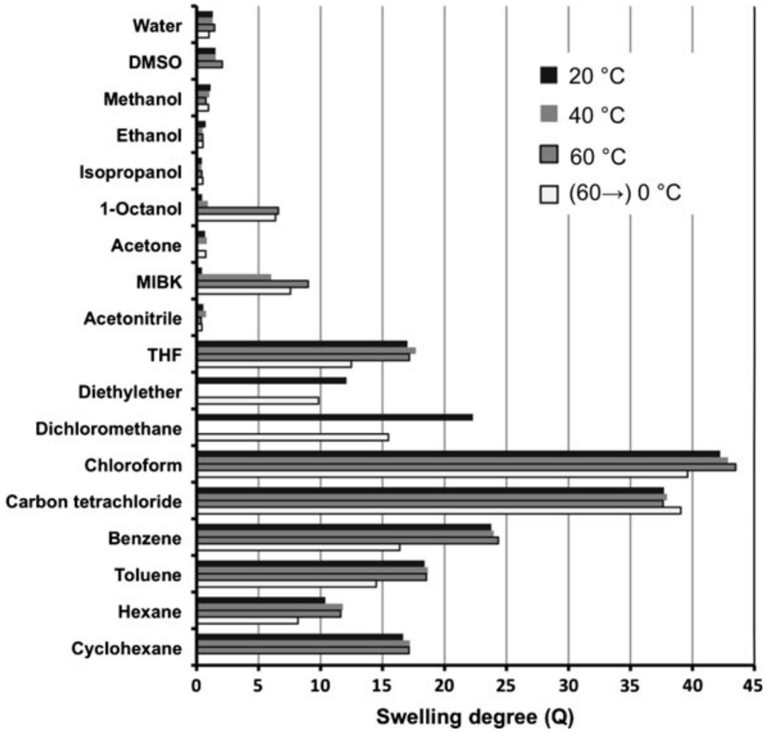


Fig. 4 Temperature dependence on swelling degree of NG-18-1%

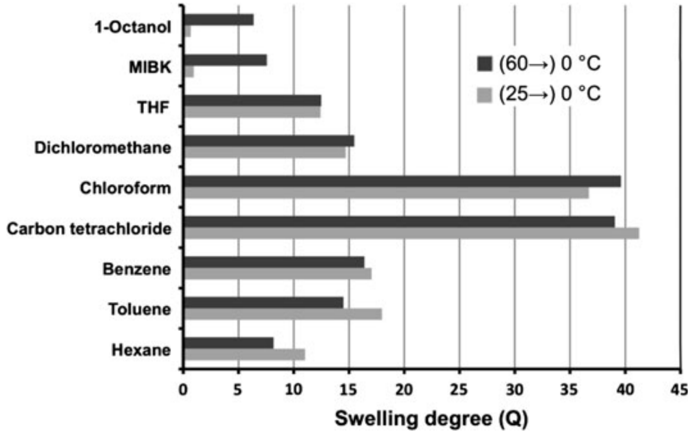


Fig. 5 Comparison of swelling degree of NG-18-1% in the different cooling process

The values of the first and second-order rate constants obtained through the linearization of Eqs. 2 and 3, are included in Table 1 along with the values of regression coefficients. A second-order kinetic equation better describes the swelling behavior of NG-18 gels.

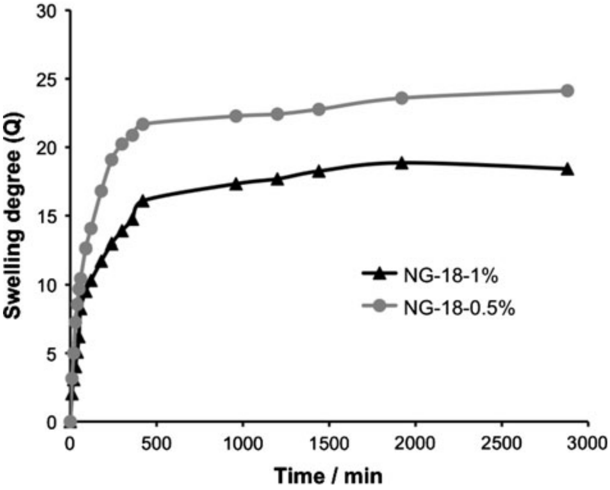


Fig. 6 Swelling degree changes of NG-18 gels with time in THF

Table 1 Lagergren first and second-order rate constants (k_1 and k_2) for swelling of the NG-18 gels in THF

Sample	First order		Second order	
	k_1 (min^{-1})	R^2	k_2 ($\mathrm{g\ g}^{-1}\ \mathrm{min}^{-1}$)	R^2
NG-18-1%	4.38×10^{-3}	0.971	5.55×10^{-4}	0.998
NG-18-0.5%	5.30×10^{-3}	0.985	5.72×10^{-4}	0.999

Critical solution temperature

Critical solution temperature was determined for swollen NG-18-1% in THF. Figure 7 shows the result obtained at 700 nm. The swollen gel is relatively transparent, while the collapsed gel is opaque. Thus, the transmittance values sharply change when the gel collapsed. The transmittance values were plotted against temperature to obtain approximate critical temperature in both the heating and cooling process. Transition temperature results in 6.6 °C in the cooling process and 12.4 °C in the heating process. This hysteresis was due to supercooling phenomenon on the cooling process. This transition process is different from NIPAM (*N*-isopropylacrylamide) in water, depending on the crystallization of long alkyl chain among stearylacrylate unit.

Cyclic temperature changes test

The cyclic swelling degree and transmittance studies were performed in order to investigate the reversibility and reproducibility of the swelling behavior. The procedures were followed for five cycles for NG-18-1% gels and the results are

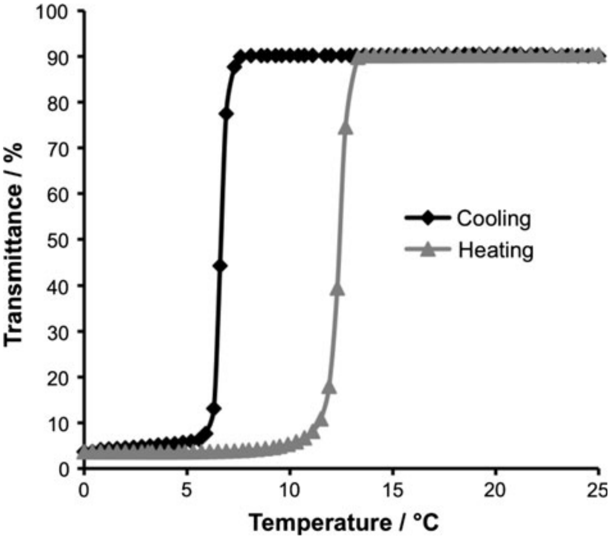


Fig. 7 Temperature dependence of transmittance at 700 nm light of NG-18-1% gel swelled in THF

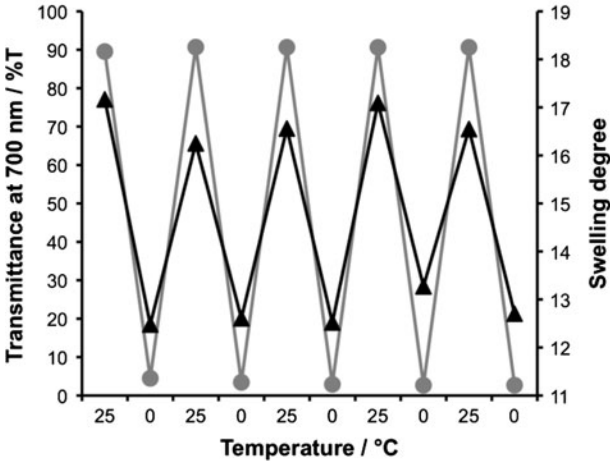
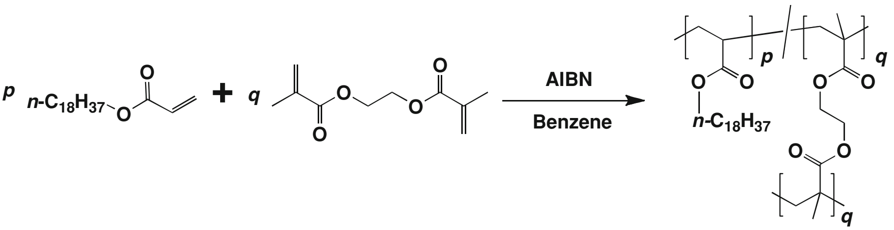


Fig. 8 Results of temperature cycle (25 and 0 °C) test: changes of (*circle*) transmittance at 700 nm (*triangle*), swelling degree in THF

shown in Fig. 8. The gel appears to be stable and retains its transition characteristics even after five cycles. In other words, this transition is reversible and non-destructive for gel network. Also, the changes of transmittance is so fast and the color changes, in fact, occur less than 30 min, but the changes of swelling degree was slow, which takes more than 24 h. This result indicates that the color change is one of the processes in swelling and not equivalent to the changes of swelling degree.



Scheme 1 Reaction scheme for NG-18 gel synthesis

Conclusion

In this study, we first demonstrated the synthesis and characterization of poly(stearylacrylate-*co*-ethylene glycol dimethacylate) (NG-18) gels. The swelling characteristics of the gels were studied as a function of the solvent polarity and temperature, and the kinetics of swelling were also examined. Volume transition via crystallization of the long alkyl chain was investigated by transmittance at 700 nm light with controlling temperature. Moreover, the reversibility and reproducibility of the transition were studied by both swelling and transmittance with cyclic temperature changed. These properties suggested the utility of NG-18 gels as a recyclable VOCs absorbent materials (Scheme 1).

Acknowledgment Funding for this research is provided by the Strategic Environmental Research and Development Program (SERDP), USA, under the project number WP-1761.

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