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# Synthesis of thermosensitive gel by living free radical polymerization mediated by an alkoxyamine inimer

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ABSTRACT

Thermosensitive gel is synthesized through controlled/"living" free radical copolymerization of styrene and DVB mediated by an alkoxyamine inimer, 2,2,6,6-tetramethyl-1-(1′-phenylethoxy)-4-(4′-vinylbenzyloxy)-piperidine (V-ET). The inimer plays the role of both incorporating "T-shaped" inter-chain linkages and mediating the polymerization. First order kinetics is observed for crosslinking polymerizations before gel point, indicating a constant concentration of propagating radicals. Monomer conversion at the gel point depends on the feed ratio of DVB to V-ET. Higher amount of V-ET results in later gel point due to smaller molecular weight of the primary chains that depends inversely on the concentration of nitroxide. The resulting gel contains permanent and labile crosslinking points formed by DVB units and alkoxyamine moieties, respectively. Therefore, the gels exhibit gel–sol transition within a narrow temperature range. The gel properties, such as the swelling ratio and gel–sol transition temperature, can be controlled by changing the feed ratio of DVB to V-ET. The microenvironments in different gels, or at different temperatures, are investigated by ESR spectroscopy.



## 1. Introduction

Polymer gels possessing dynamic crosslinking points attract much attention for the potential application in controlled drug delivery, tissue engineering, and electronics industry, etc. [1–3] One of the approaches to synthesize dynamic polymer gels is to incorporate thermally reversible covalent bonds [4], such as those based on Diels–Alder reaction [5,6], aromatic urethane formation [7–9], ionene formation [10,11], and reversible coupling between carbon-centered and nitroxyl radicals (*vide infra*). In addition, specific spiro orthoester undergoing reversible cationic ring opening polymerization and depolymerization by cyclization has been used in the synthesis of dynamic network [12,13]. Very recently, Matyjaszewski and coworkers design and synthesize polymer gels with self-healing property achieved by reshuffling of dynamic covalent bonds in trithiocarbonate moieties [14].

Specifically, the chemistry of radical trapping by nitroxyl persistent radical to form alkoxyamine has been extensively studied [15–17] and the reversibility of the reaction has been applied to mediate the controlled/"living" radical polymerizations [18–20]. A number of dynamic polymers of linear block [21–23], cyclic [24], graft [25–29], star-like [30,31] and hyperbranched [32–34] architecture, possessing labile covalent C–ON bonds at the junction, have been synthesized. Otsuka and Takahara are the first to introduce the labile alkoxyamine covalent bonds into the preparation of thermodynamic gels by heating pre-synthesized poly(meth)acrylates bearing alkoxyamine pendent groups [35]. The crosslinking and decrosslinking reactions occur through radical crossover between alkoxyamine moieties. The alkoxyamine crosslinkages can be used to initiate the polymerization of styrene to increase the mesh size of the network, which has been proved by the chain extension reaction of a precursor gel synthesized from radical copolymerization of styrene and an asymmetric alkoxyamine crosslinkers [36].

Alkoxyamines or nitroxyl persistent radicals bearing a polymerizable double bond have been used as inimers to prepare hyperbranched [32] or highly branched [33,34] polymers. The branch points in the product are formed by labile –C–ON bond, which can be cleaved by reducing agent such as phenylhydrazine to obtain linear products. It is found by cleavage analysis that the chain propagates in a controlled manner to yield narrow disperse primary chains and homogenous distribution of branch points along the main chain [34]. Being aware that the branch points are dynamic, we have synthesized a bifunctional symmetric alkoxyamine and used it as the crosslinking agent in atom transfer radical polymerization (ATRP) of *tert*-butyl methacrylate (*t*-BMA), followed by chain extension using styrene as monomer to obtain a conetwork. After hydrolysis of poly(*t*-BMA) segment at mild condition, an amphiphilic conetwork has been obtained [37]. In the present

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work, we use a new approach to synthesize thermosensitive polymer gels containing two kinds of crosslinking points, i.e., permanent and dynamic. The former comes from divinyl benzene and the latter from alkoxyamine. Therefore, styrene and DVB are copolymerized with the mediation of an alkoxyamine inimer, *2,2,6,6-tetramethyl-1-(1′-phenylethoxy)-4-(4′-vinylbenzyloxy) -piperidine* (V-ET) (Fig. 1). It is interesting to find that the polymerization in the presence of V-ET reaches the critical gel point later than the conventional copolymerization of styrene and DVB. The crosslinking polymerization kinetics depends not only on the feed composition of DVB, but also on that of nitroxide V-ET, indicating a controlled manner of the radical polymerization. Furthermore, the gel properties, such as the swelling ratio and gel–sol transition temperature, are also determined by the feed ratio of DVB to V-ET.

## 2. Experimental section

### 2.1. Materials

Styrene (Yonghua Special Chemicals, 99%) and DVB (Aldrich, 80%) were distilled before use. 4-(4′-vinylphenylmethoxy)-2,2,6,6-tetramethyl-1-piperidinyloxy (STEMPO) was synthesized according to the literature procedure [34]. 4-Hydroxy-2,2,6,6-tetramethyl-piperidine-1-oxy (HO-TEMPO) (BASF, 99%), 1-phenylethyl bromide (Aldrich, 97%), *N,N,N′,N′,N″*-pentamethyldiethylene triamine (PMDETA) (Aldrich, 99%) were used as received.

### 2.2. Synthesis

#### 2.2.1. Synthesis of 4-hydroxy-1-((1′-phenylethyl)oxy)-2,2,6,6-tetramethyl-piperidine (HO-ET)

The synthesis is based on an atom transfer radical addition process according to the literature [38]. As an example, a mixture of HO-TEMPO (0.86 g, 5.0 mmol), CuBr (1.32 g, 10 mmol) and Cu (0) (0.31 g, 5.0 mmol), and 1-phenylethyl bromide (1.85 g, 10 mmol) in benzene (8.0 mL) were degassed through three freeze–thaw cycles. PMDETA (4.20 g, 20 mmol) was added via a syringe and the solution was stirred until the Cu complex had formed as indicated by the appearance of a light green color. After being stirred at room temperature for 2 days, the mixture was filtered and washed with water. The organic phase was dried over anhydrous $MgSO_4$, and then purified by column chromatography (ethyl acetate/petroleum ether = 2/5). HO-ET was obtained in 65% yield as white solid. mp. 93–94 °C; $^1$H NMR ($CDCl_3$): $\delta$ (ppm) = 0.66, 1.07, 1.21 and 1.33 (each s, 3H, C***H***$_3$), 1.48 (d, 3H, C***H***$_3$), 1.20–1.73 (m, 4H), 3.94 (m, 1H, C***H***), 4.78 (q, 1H, C***H***), and 7.20–7.30 (m, 5H, Ar***H***); Anal. calcd for $C_{18}H_{26}NO_2$: C, 73.61; H, 9.81; N, 5.05. Found: C, 73.59; H, 9.62; N, 4.99. Fig. 2

#### 2.2.2. Synthesis of 2,2,6,6-tetramethyl-1-(1′-phenylethoxy)-4-(4′-vinylbenzyloxy-piperidine) (V-ET)

V-ET was prepared under similar condition as described above, using STEMPO instead of HO-TEMPO. The product was purified by column chromatography (n-Hexane/Dichloromethane = 1/1 and gradually increase to pure dichloromethane). V-ET was obtained in 55% yield as pale yellow oil. IR(KBr): 1630 (C=C), 1360 (C–ON); $^1$H NMR ($CDCl_3$) $\delta$ 0.67, 1.05, 1.20 and 1.33 (each br s, 3H, C***H***$_3$), 1.48 (d, 3H, C***H***$_3$), 1.20–1.93 (complex m 4H), 3.61 (complex m, 1H, C***H***), 4.48 (s, 2H, C***H***$_2$), 4.78 (q, 1H, C***H***), 5.20 (d, 1H, =CH***H***), 5.70 (d, 1H, =CH***H***), 6.66 (d of d, 1H, =C***H***) and 7.21–7.37 (complex m, 9H, Ar***H***) (Fig. 5); Anal. calcd for $C_{26}H_{35}NO_2$: C, 79.35; H, 8.96; N, 3.56. Found: C, 79.79; H, 8.62; N, 3.33. Fig. 3

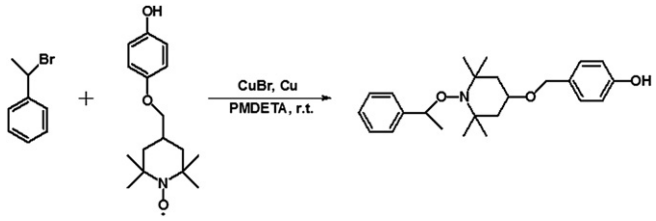


**Fig. 2.** Synthesis of HO-ET.

#### 2.2.3. Preparation of polymer networks

In a typical experiment, V-ET (0.09 g, 0.23 mmol) and DVB (0.12 g, 0.92 mmol) were dissolved in styrene (7.27 g, 0.07 mol). The mixture was degassed through three freeze–thaw cycles, and thermostated at 120 °C under a nitrogen atmosphere for a predetermined time. The gel point is determined by inversing the glass tube for 10 s without any fluidic mixture left, as shown in the Fig. 4. Five parallel experiments were carried out and listed in Table 1.

#### 2.2.4. Gel chain extension

The chain extension experiment is described as follows: gel-e (0.20 g, Table 1) and styrene (5 ml) were transferred into a flask. The mixture was subsequently degassed by three freeze-evacuate-thaw cycles. After the gel swollen at room temperature for 1 day, the flask was placed in an oil bath at 120 °C for 24 h. The resulting gel after chain extension was extracted in a Soxhlet apparatus by THF for a week to remove the unreacted monomers and linear polymers, and then dried under vacuum condition at 35 °C for three days. Yield: 3.45 g.

#### 2.2.5. Determination of gel fraction

The gel fraction ($r_{gel}$) is calculated by $W_{dry\ gel}/W_{polymer}$, in which $W_{dry\ gel}$ is the weight of the dry gel after extraction in THF for 7 days and $W_{polymer}$ is the weight of overall polymer in the sample as determined by TGA.

#### 2.2.6. Swelling ration determination

The extracted dry gel was placed in xylene at given temperatures for three days. The swelling ratio was calculated from $W_{swollen}/W_{dry\ gel}$, where $W_{swollen}$ is the weight of the swollen gel, and $W_{dry\ gel}$ is the weight of the dry gel.

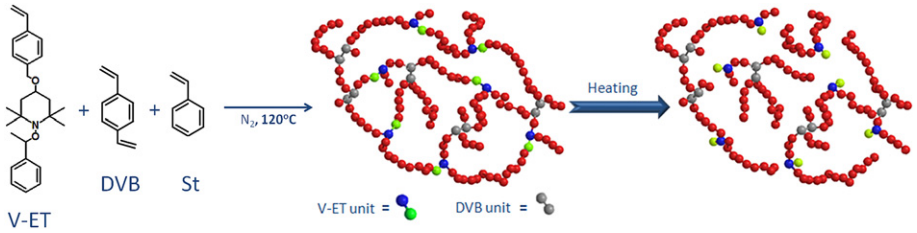


**Fig. 1.** Schematic drawing of thermosensitive gel prepared by copolymerization of DVB and styrene mediated by V-ET. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

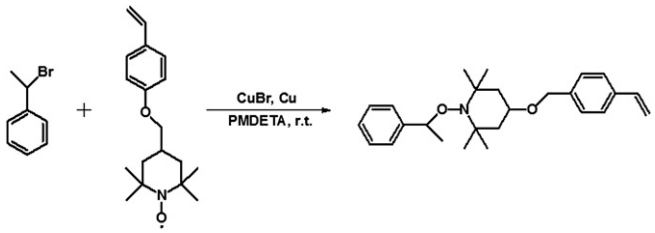


**Fig. 3.** Synthesis of V-ET.

### 2.3. Measurements

$M_n$ and $M_w/M_n$ of all the samples were measured by gel permeation chromatography (GPC) through three Waters Styragel columns (pore size: $10^2$, $10^3$, and $10^4$ Å) in a Waters 2010 system equipped with a Waters 410 RI detector, using THF as the eluent at a flow rate of 1 mL/min at 40 °C. The columns were calibrated by narrow polystyrene ($M_W$ range: 200–3 × $10^6$ g/mol) standards. Element analysis of C, H and N was carried out on an ELEMENTAR VARIO EL instrument. NMR measurement was carried out on a Bruker DMX500 instrument, using $CDCl_3$ as solvent and tetramethylsilane (TMS) as reference. Monomer conversions after gel point were determined by thermogravimetric analysis (TGA) on a NETZSCH TG209 instrument. The temperature was elevated from 25 to 550 °C at a rate of 20 °C/min. The weight loss above 275 °C gave the polymer content. ESR measurements were carried out on a Bruker ER 200D-SRC spectrometer, operating with an X-band standard cavity (~9.67 GHz) at room temperatures. The concentration of nitroxyl radical was obtained by calibration with standard solution of 4-hydroxy-TEMPO. Instrument parameters: modulation frequency = 100 kHz; modulation amplitude = 1.25 G; microwave power = 20 mW. The receiver gain was set depending on the concentration of nitroxyl radical in different samples.

## 3. Results and discussion

### 3.1. Synthesis of V-ET

V-ET is an alkoxyamine possessing a vinyl group at the nitroxide moiety, and is used as an inimer in the present work. The compound is prepared by atom transfer radical addition (ATRA) process [38]. The reaction is performed at room temperature so that the vinyl group does not polymerize to give polymer species at this stage. For comparison, an alkoxyamine without double bond, HO-ET, is also prepared.

Fig. 5 shows the $^1$H NMR spectrum of V-ET. The aromatic protons are observed at the chemical shift of 7.21–7.39 ppm, but overlapped with that of residual protons in the solvent. The vinylic protons appear at 6.70, 5.70 and 5.20 ppm, respectively, for =C***H***Ph and C***H***$_2$= (*cis* and *trans*). The $^3J$ coupling, $J_{bc}$ = 18.0 and $J_{bd}$ = 11.0 Hz, agree with typical values for vinylic protons, while the geminal coupling $J_{cd}$ is too small to be resolved (usually $J_{cd} \approx 1.0$ Hz). The benzylic methine **e** gives a quartet at 4.78 ppm while the methine **g** of piperdine ring gives a quintet at 3.6 ppm. The benzylic methylene gives a singlet at 4.5 ppm. The methyls of piperidine ring give four independent peaks at 1.33, 1.19, 1.05 and 0.68 ppm, while the methylene signal of the ring overlaps with that of methyl in ethylbenzene moiety at 1.48 ppm. The integration results under the peaks correlate very well with the formula of V-ET.

### 3.2. Copolymerization of styrene and DVB mediated by V-ET

The copolymerization of styrene and DVB was carried out in bulk at 120 °C in the presence of V-ET. At the early stage, the reaction mixture is fluidic, then gelation takes place in the system using V-ET. The gel point is defined as the reaction time at which the reactants are totally solidified thus no fluid is observed on inversing the glass tube for 10 s (Fig. 4).

The kinetics of polymerization before gel point with varying concentrations of DVB and V-ET are plotted in Fig. 6. All systems show linear kinetic curves, indicating a constant concentration of propagating radicals due to dynamic balance of thermal initiation and chain termination. Without thermal initiation of styrene, the polymerization will otherwise be dominated by the persistent radical effect [39,40]. The system with higher amount of V-ET exhibits lower polymerization rate (compare systems ■ and ▲). This is because higher concentration of nitroxyl moiety not only suppresses the concentration of growing radicals, but also results in more catalytic termination through hydrogen transfer reactions [41–44]. It has been reported that the rate of TEMPO-mediated styrene polymerization is independent of initial concentration of nitroxyl moieties [45–47]. The results are not contradictory to the present work because the feed amount of nitroxide is much lower in refs. [45–47] thus the suppressing effects and catalytic termination by nitroxyl radical is negligible in comparison to the thermal initiation of styrene. It is also noted in Fig. 6 that the increase of DVB accelerates the polymerization (compare system ■ and ●), which

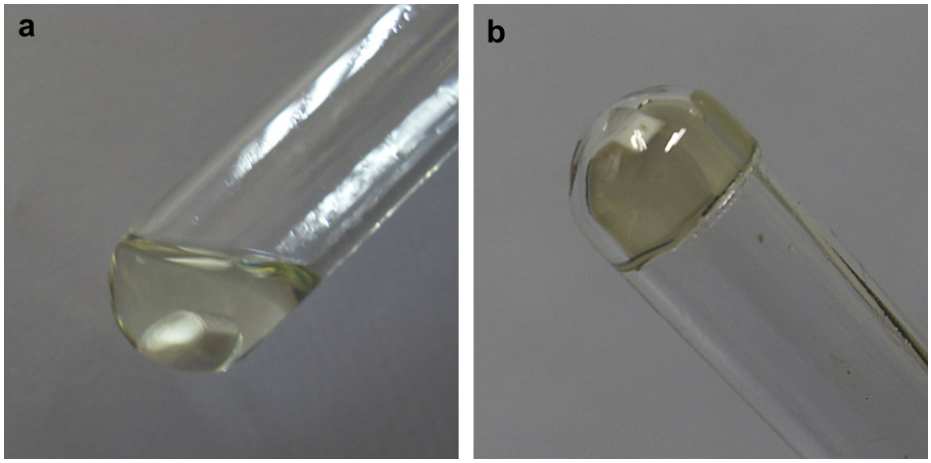


**Fig. 4.** Photographs showing the transition before (a) and after (b) the gel point. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Table 1**
Preparation and properties of thermosensitive gels.

| Sample | Recipe | | | Gel properties | | | |
|---|---|---|---|---|---|---|---|
| | Styrene /g,mol | DVB /g,mmol | Alkoxyamine /g,mmol | $\theta_c$ % | $r_{gel}$[b] % | SR[c] | $T_{gel}$ (°C) |
| Gel-a | 7.27,0.07 | 0.12,0.92 | 0.064,0.23(HO-ET) | 68.2 | 51.7 | 34 | – |
| Gel-b | 7.27,0.07 | 0.12,0.92 | 0.092,0.23(V-ET) | 52.5 | 66.6 | 16 | 78 |
| Gel-c | 7.27,0.07 | 0.06,0.46 | 0.092,0.23(V-ET) | 66.0 | 43.3 | 32 | 64 |
| Gel-d | 7.27,0.07 | 0.12,0.92 | 0.046,0.12(V-ET) | 38.7 | 29.8 | 38 | 70 |
| Gel-e | 7.27,0.07 | 0.12,0.92 | 0.092,0.23(V-ET) | 64.9[a] | 76.2 | 10 | 97 |
| Gel-f | Gel-e after chain extension | | | 81.5 | 84.6 | 22 | 93 |

[a] Conversion at additional 120 min after the gel point.
[b] $r_{gel}$: gel fraction determined by $r_{gel} = W_{dry\ gel}/W_{total}$, where $W_{dry\ gel}$ is the gel weight after extraction and drying, and $W_{total}$ is the total weight of crosslinked and uncrosslinked polymers measured by TGA.
[c] SR: swelling ratio calculated from $W_{swollen}/W_{dry\ gel}$, where $W_{swollen}$ is the weight of the swollen gel, and $W_{dry\ gel}$ is the weight of the dry gel.

can be ascribed to the decreased diffusibilities of both propagating radicals and pendent nitroxyl radicals.

According to Flory–Stockmayer gelation theory [48–52], the monomer conversion at the gel point is predicted as,

$$\theta_c = \frac{1}{\rho_0 \overline{M}_w}, \quad (1)$$

in which $\rho_0$ represents the fraction of vinyl groups of divinyl molecules in the initial reaction mixture, and $\overline{M}_w$ the weight-averaged degree of polymerization. Fukuda and coworkers have reported that nitroxide-mediated living free radical polymerization produces gels that are more homogenous than that prepared by conventional radical polymerization [53,54]. In the former all the living chains grow stepwise, whereas in the latter the propagating chains formed at early stage consume large part of divinyl monomer due to its larger reactivity, resulting in intramolecular loops or microgels. Therefore the critical number density of crosslinks at the gel point agrees more closely than conventional polymerization system with Flory–Stockmayer mean-field-based theory.

In order to investigate the crosslinking polymerization behavior in the presence of V-ET, three series of experiments are carried out and the results of gel point are presented in Fig. 7. In series 1, DVB content in the feed is varied while the ratio of styrene to V-ET is constant. The monomer conversion at the gel point decreases linearly with the increase of DVB content. Nevertheless, we would regard the results consistent with Eq. (1) only in trend, not quantitatively, keeping in mind that vinyl groups in V-ET also contribute to the crosslinking reaction. In series 2, V-ET content in the feed is varied while the ratio of styrene to DVB is constant. Clearly, gelation occurs at higher monomer conversion with the increasing content of V-ET. This is a consequence of smaller molecular weight of the primary chains, depending inversely on the concentration of nitroxides. In series 3, an alkoxyamine without vinyl group, HO-ET, is used instead of V-ET for comparison purpose. The relationship between conversion at gel point and nitroxide content in the feed is similar to that in series 2. Comparing series 2 and 3, the former reaches the gel point at earlier conversion than the latter due to additional linkage formed by the polymerization of vinyl group in V-ET. Thus the influence of V-ET on $\theta_c$ has double sides. On one hand, it reduces the molecular weight of primary chains and results in higher $\theta_c$. On the other hand, the polymerization of the double bond in V-ET forms additional inter-chain linkage, albeit "T-shaped" [55], leading to earlier gel point.

It is interesting to note that in series 3, where nitroxide possesses no vinyl group, $\theta_c$ increases with the increasing amount of HO-ET due to the lower molecular weight of primary chains. However, very small feed amount of HO-ET leads to deviation from the straight line and much earlier gel point (left dots in Fig. 7), indicates that the controllability of the polymerization is low and close to conventional radical polymerization. Similar trend is also observed in polymerizations using V-ET as the regulating agent.

### 3.3. Swelling properties and gel fraction

The above prepared polymer networks possess two kinds of crosslinkages, the permanent crosslinking point formed by the polymerization of both vinyl groups in DVB and the "T-shaped" labile –C–ON branching point formed by the polymerization of V-ET. The incoporation of the latter would endow the gel material with thermosensitivity through the dissociation of nitroxyl and carbon-centered radicals upon heating. For property study, six gel

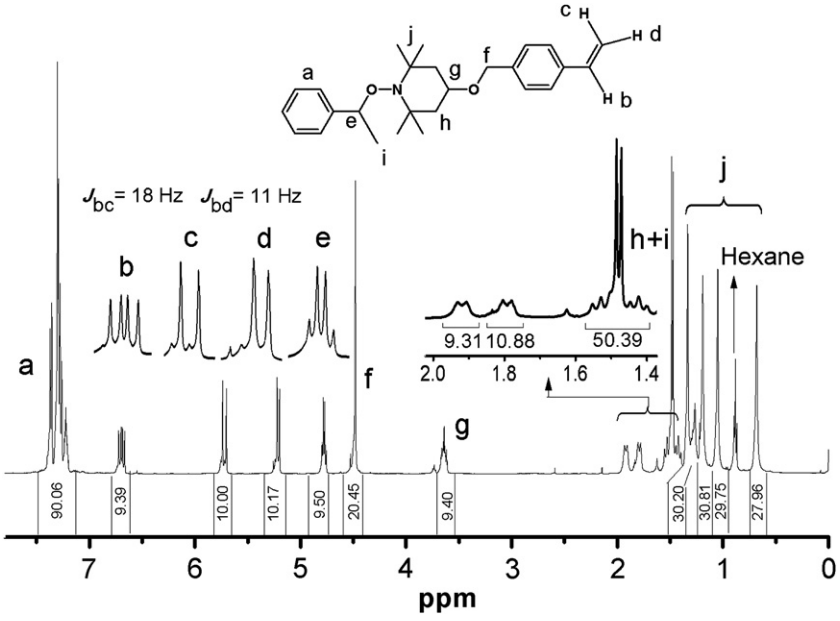


**Fig. 5.** $^1$H NMR spectrum of 2,2,6,6-tetramethyl-1-(1′-phenylethoxy)-4- (4′-vinylbenzyloxy)-piperidine (V-ET) in $CDCl_3$.

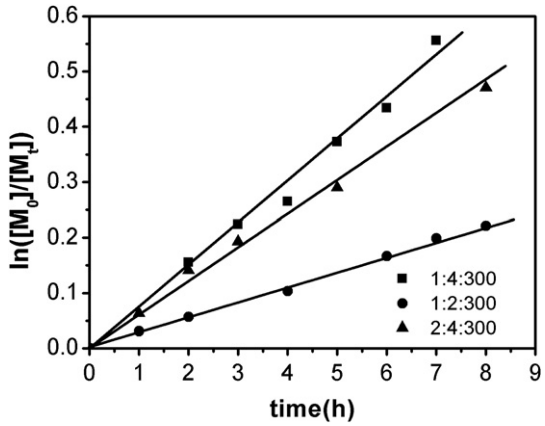


**Fig. 6.** Kinetics of living free radical copolymerization of styrene and DVB in the presence of V-ET. The feed molar ratio of V-ET:DVB:styrene are shown in the figure. Temperature = 120 °C.

samples have been prepared. The polymerization conditions, characterization and properties of the gels are listed in Table 1.

The thermal sensitivities of the gel products, as demonstrated by the dependence of the swelling ratio on temperature, are shown in Fig. 8. While the reference Gel-a, in which HO-ET is used, shows nearly constant swelling ratio at different temperatures, those gels using V-ET exhibit clear gel–sol transitions within the range of 60–100 °C. This indicates that the densities of the permanent crosslinking points are well below the critical density to hold the network after the break of "T-shaped" branching point of alkoxyamine. The break of alkoxyamine is accomplished by heating the gel in the presence of air, in which the released carbon-centered radicals are trapped immediately by oxygen, preventing the recoupling with nitroxyl radicals. In the absence of oxygen, the dissociation of alkoxyamine is reversible. The fraction of dissociative species is low, but dynamic, due to the very low equilibrium constants of dissociation. Thus the gels may display no thermoreversible ability, although dynamic exchange and chain extension go very well, as demonstrated in reference [35].

The effects of polymerization conditions on the swelling properties of the gels are investigated. The feed amounts of DVB are decreasing from Gel-b to Gel-c with identical amount of V-ET. Clearly Gel-c exhibits larger swelling ratio and lower gel–sol transition temperature. This is easy to understand because Gel-c has smaller

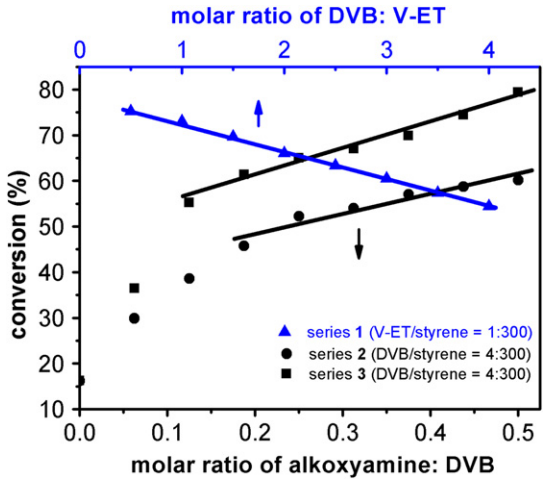


**Fig. 7.** Plots of critical monomer conversions, $\theta_c$, with different molar ratio of DVB (▲), V-ET (●) and HO-ET (■). Temperature = 120 °C (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

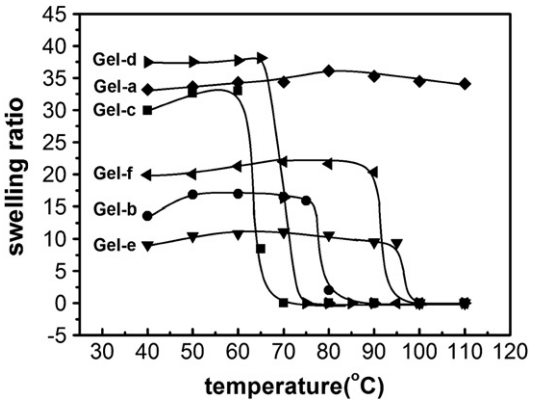


**Fig. 8.** Variation of swelling degree with temperature for gels swollen in xylene for gel-a(◆), gel-b(●), gel-c (■), gel-d (►), gel-e(▼), gel-f(◄). The lines are drawn only for guiding the eyes.

number of permanent crosslinks and consequently larger mesh size to absorb the solvent. Gel-d is prepared using half amount of V-ET as in Gel-b, much higher swelling ratio is observed for Gel-d, indicating a smaller crosslinking density due to larger molecule weight determined by smaller amount of alkoxyamine. Accordingly the transition temperature decreases in comparing with Gel-b. Gel-e is obtained after post-gel polymerization of Gel-b, e.g., by prolonging the reaction time after the gel point of a system with otherwise the same conditions for Gel-b. Both the monomer conversion and gel fraction increase with further reaction time. More interestingly, the swelling ratio of Gel-e is remarkably smaller than that of Gel-b, indicating larger crosslinking density in the gel. This is in sharp contrast with the conventional radical crosslinking polymerization using divinyl monomers, in which the swelling ratio is constant after gel point [54]. Fukuda has already pointed out that the difference between post-gel polymerizations of living and conventional systems lies in the manner of chain growth [54]. In the former all chains grow simultaneously in a macroscopic view, giving homogenous gel in which divinyl monomer units are incorporated randomly into the primary chains. In the latter, chains with full length form at the very initial stage with the formation of microgels, and the gelation is a process of "collection" of microgels, yielding a product of heterogeneous gel [54]. In the present system, additional reasons for the increase of crosslinking density during post-gel polymerization are the continuous formation of "T-shaped" branch points [55], as well as the chain propagation at the branching sites which may incorporates more crosslinking units. As a consequence, the gel–sol transition temperature increases from Gel-b to Gel-e.

Gel-e is used as a network initiator for chain extension polymerization of styrene. After 24 h immersion in styrene, the swollen gel is heated to 120 °C for another 24 h period. It is interesting to find that the gel after chain extension, Gel-f, shows remarkably larger swelling degree (Fig. 8), simply due to longer chain length of the "T-shaped" branches. Notwithstanding, the gel–sol transition temperature decreases only slightly after the chain extension, indicating small fraction breakage of the labile alkoxyamine linkages. The chain extension allows us to modify the swelling degree without much changing the transition temperature.

### 3.4. ESR measurement

In the past years, the use of nitroxyl spin labeling [56] for probing the microenvironment of large molecules has been widely used in linear [57], branched [33,34] and crosslinked [58–63] polymers. In the latter, the higher crosslinking density will cause smaller mobility of the spin label, resulting in larger line width of

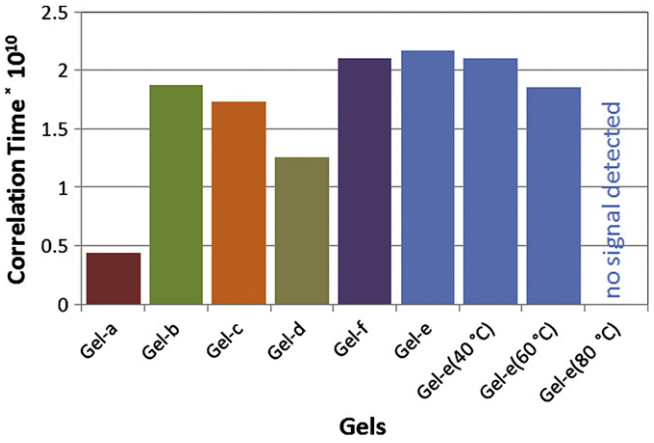


**Fig. 9.** Correlation time of various gels, and Gel-e at different temperatures. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

ESR spectrum and larger correlation time ($\tau_c$). According to Griffith, the microenvironment is expressed by rotating correlation time, $\tau_c$, which is loosely defined as the time required for the nitroxyl radical to make an arc of 40° [56],

$$\tau_c = (W_1 - W_{-1})\left(-15\pi\sqrt{3}/8b\Delta\gamma H\right) \quad (2)$$

where $W_1$ and $W_{-1}$ are the leading and trailing line widths, $b = 3.06 \times 10^8$s, $\Delta\gamma = 4.22 \times 10^4$ $s^{-1}$ $G^{-1}$, and $H$ is the laboratory field [63]. In this work, $H = 3400$ G.

The gels prepared in the present work possessing "T-shaped" alkoxyamine linkages, which are in dynamic equilibrium with dissociated state, i.e., (pendent) nitroxyl and (terminal) carbon-centered radicals. A very small fraction of nitroxyl radical will facilitate the measurement of $\tau_c$ by ESR. Fig. 9 shows the measured $\tau_c$ for gels listed in Table 1 which are swollen in xylene at room temperature. Gel-a gives the lowest $\tau_c$ in which the dissociated TEMPO undergoes free tumbling. Other gels give remarkably larger $\tau_c$ because nitroxyl radical is connected to polymer chains and thus the rotation is much slower due to conformational entropic constraints [34]. It is noted that Gel-c gives lower $\tau_c$ than Gel-b due to lower crosslinking density in the latter. Gel-e gives the largest $\tau_c$ indicating much larger crosslinking density resulted from the post-gel polymerization. The values of $\tau_c$ of corresponding gels agree with the results in swelling study.

The dependence of correlation time on heating temperature is investigated using Gel-e. Thus, Gel-e is heated in xylene at 40, 60, 80 °C, respectively for three days. The swollen gels are measured by ESR at room temperature. As shown in the Fig. 9, the correlation time decreases slightly with increase of temperature at which the gels have been heated, in line with the results of swelling study. Unexpectedly, the gel heated at 80 °C gives no signal in ESR measurement. The reason is unclear now.

The present study incorporates spin labels by copolymerization of styrene and polymerizable alkoxyamine. It gives more homogenous labeling of the networks, and is advantageous over the conventional method, in which the spin label is attached to polymer chain by post-polymerization reaction and gives heterogeneity in functionalization. Therefore, the copolymerization can be used as a new approach of spin labeling for the ESR research.

## 4. Conclusions

Thermosensitive gel is synthesized through controlled/"living" free radical copolymerization of styrene and DVB mediated by an alkoxyamine inimer. The inimer plays the role of both incorporating "T-shaped" inter-chain linkages and mediating the polymerization. The network is formed by permanent crosslinking points from DVB units and dynamic "T-shaped" inter-chain linkages from alkoxyamine moieties, the latter endowing the gel with thermosensitivity. All gels prepared by the inimer exhibit a sharp gel–sol transition within a narrow temperature range. Thus, the inimer based approach explored in the present work can be served as a new method in the preparation of thermodynamic networks.

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