Carbohydrate Polymers 88 (2012) 1483–1487

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Short communication

# Synthesis and characterization of thermal-responsive chitin-based polyurethane copolymer as a smart material

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ARTICLE INFO

*Article history:*
Received 14 July 2011
Received in revised form 13 January 2012
Accepted 17 January 2012
Available online 7 February 2012

*Keywords:*
Polyurethane
Chitin
Thermo-responsive
Organogel

ABSTRACT

A chitin-based polyurethane (TRCPU) organogel composed of isophorone diisocyanate (IPDI), polyethylene glycol (PEG) and chitin is shown to undergo a temperature-dependent sol-to-gel transition in polar organic solvents. The soft segments of the prepolymer that originated from the PEG imparted elastomeric and hydrophilic characteristics to the TRCPUs. The hard segments of chitin and IPDI that contained highly polar urethane linkages acted as physical alignment sites and provided lipophilic characteristics for the TRCPUs in the polar organic solvent. The average molecular weight and the degree of acetylation of chitin were determined based on the intrinsic viscosity and solid-state $^{13}$C-CP/MAS NMR spectrum. Chitin was incorporated into polyurethane via covalent bonding; the resultant copolymer was an injectable organosol at low temperatures that transformed to a semisolid organogel at approximately 105 °C. The TRCPUs were characterized by $^{1}$H NMR, FT-IR and DSC, and the rheological behavior of the TRCPU solutions in organic solvents was studied.

## 1. Introduction

Polymers that display a physicochemical response to stimuli have been widely explored as smart materials (Behl, Razzaq, & Lendlein, 2010). Among these smart materials, thermally sensitive polymers with the ability to sense and respond to external thermal stimuli in a predetermined temperature range have been widely used in many applications, such as in artificial organs, food packaging, leather or textile finishing, and controllable gas separation (Chen et al., 2007). The typical thermally sensitive polymers based on alkyl acrylamide hydrogels, especially poly(*N*-isopropylacrylamide) (PNIPAAm), shows a sharp coil–globule transition and phase separation at the lower critical solution temperature (LCST) of the PNIPAAm in water (Schild & Tirrell, 1990). Besides, thermally sensitive polyurethanes (TSPUs) of solid phase also have been described (Ding, Hu, Tao, & Hu, 2006). These TSPUs materials have a segmented structure with soft segments that act as a thermally reversible region and hard segments that act as a fixed region. The reversible region (soft segment) can soften when it is heated above the switch temperature (the phase transition temperature, Ts) or harden when it is cooled below Ts (Zhou, Zeng, Fan, Liu, & Zhou, 2010).

To develop reasonable designs for new thermally responsive chitin-based polyurethanes (TRCPUs) including PEG segments those undergo a sol-to-gel transition in response to temperature changes. The Chitin has biocompatibility, biodegradability, antibacterial properties and nontoxicity, it has been extensively investigated for molecular separation, food packaging films, artificial skin, bone substitutes and water engineering applications (Tsao et al., 2011). Chitin has also been widely used as an adsorbent for transition metal ions and organic species. In addition to PEG also has biocompatibility and hydrophilicity, PEG-based polymers have attracted a great amount of attention in recent years (Hammouda, Ho, & Kline, 2004; Kievit et al., 2009; Smith, Bedrov, & Borodin, 2000). Herein, we report the first investigation of a TRCPU organogel composed of IPDI, PEG and chitin (degree of acetylation (DA) is approximately 75%) and its ability to undergo a temperature-dependent sol-to-gel transition in organic solvent. The preparation is illustrated in Scheme 1. The soft segments of the prepolymer that originated from the PEG imparted elastomeric and hydrophilic characteristics to the TRCPUs

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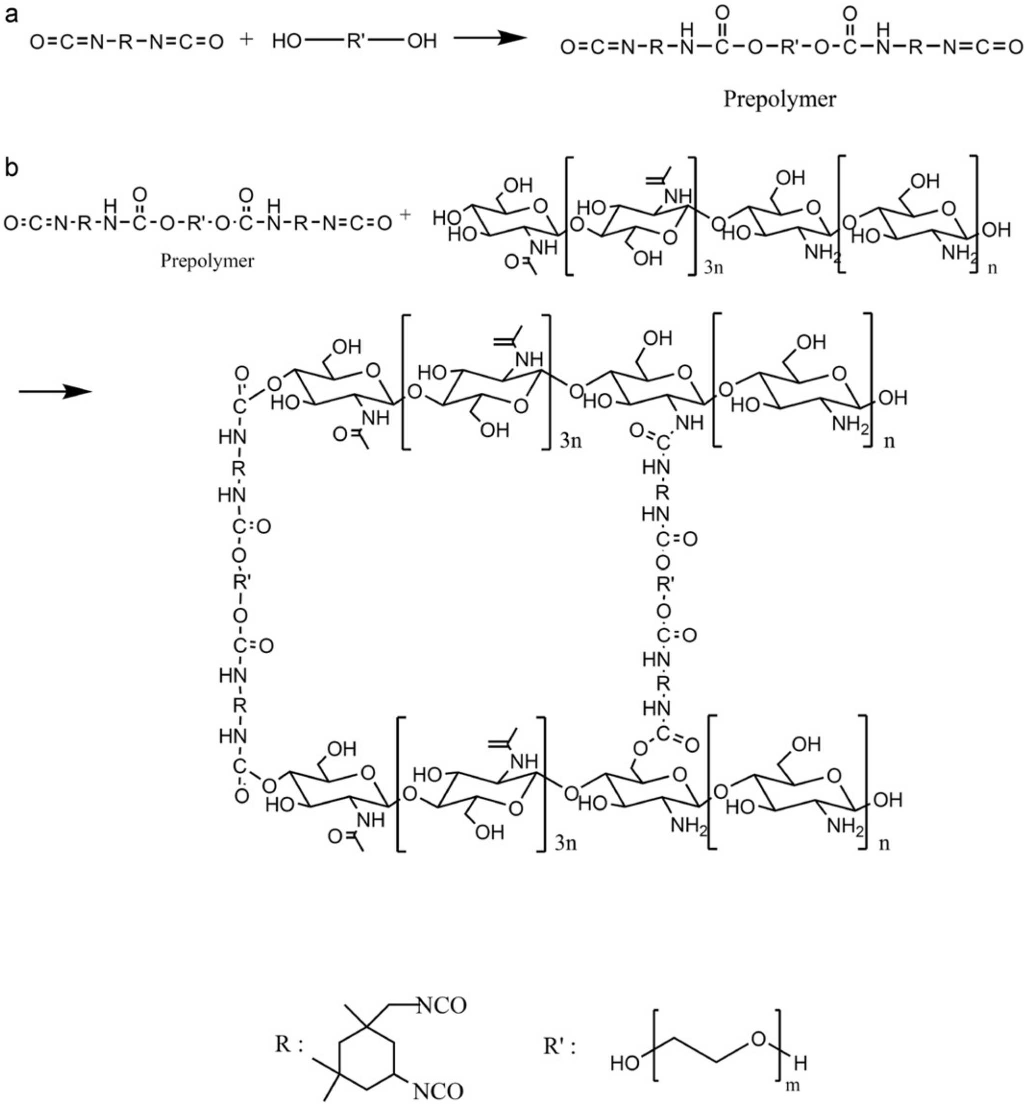
doi:10.1016/j.carbpol.2012.01.055



**Scheme 1.** Schematic representation of TRCPUs composed of IPDI, PEG and chitin.

in polar organic solvents. The hard segments of chitin and IPDI that contained highly polar urethane linkages acted as physical alignment sites and provided lipophilic characteristics for the TRCPUs in polar organic solvents. The two types of segment regions can form a hard–soft–hard-type linkage in the TRCPU matrix, resulting in alternative domains. In addition, the inclusion of chitin in the matrix provided the biodegradability and antibacterial characteristics of the material. Considering the versatile nature of the biodegradable TRCPU organogel, its use in a number of applications, such as the separation of organic substances in organic solution (Ichijo, Kishi, Hirasa, & Takiguchi, 1994) and in pharmaceuticals (Kumar & Katare, 2005), is expected.

## 2. Materials and methods

### 2.1. TRCPUs synthesis

The TRCPUs synthesis process adopted in the current study was as follows: briefly, the purified and dehydrated PEG (MW = 1000 Da, ACROS Co., USA) reacted with IPDI (Bayer Co., Germany) in a 500 mL flask with a round bottom and four necks at 80 °C for 2 h in a dry nitrogen atmosphere. Then 0.1 wt% of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, ACROS Co., USA) was added to the above solution while stirring steadily. In the second step, a 0.5 wt% chitin (crab shells, G-HT Co., Taiwan, $M_V$: ~211.0 kDa and DA: ~75%) solution in 5 wt% lithium chloride/*N*,*N*-dimethylacetamide [LiCl/DMAc] (LiCl, DMAc, Sigma–Aldrich Co., USA) was added to the reaction mixture by drops at 60 °C for 6 h. The viscosity average molecular weight ($M_V$) of chitin was determined based on its intrinsic viscosity, obtained in DMAc containing 5% LiCl at 25 °C, according to the Mark–Houwink–Sakurada (MHS) equation (Terbojevich, Carraro, Cosani, & Marsano, 1988): $[\eta] = 0.0024 \times (M_v)^{0.69}$ and the degree of acetylation can be calculated from the solid-state $^{13}$C-CP/MAS NMR spectrum and the details of the $^{13}$C-CP/MAS NMR experiment and the spectra of the chitin (Fig. S1) are described in the supplementary data (Heux, Brugnerotto, Desbrie'res, Versali, & Rinaudo, 2000; Kasaai, 2010). The TRCPU was then formed. In addition, TRCPU containing various molar ratios of the NCO groups of IPDI, the –OH groups of PEG, and the –OH groups of chitin was prepared using a two-step polymerization process, as listed in Table 1.

### 2.2. Characterization measurements

The IPDI, PEG, prepolymer and TRCPU 1.0 were analyzed with Fourier transform infrared spectroscopy (FTIR, Perkin-Elmer

**Table 1**
Compositions of TRCPUs.

| Nomenclature | Composition (molar ratio) | | |
|---|---|---|---|
| | IPDI (NCO)[a] | PEG (OH)[b] | Chitin (OH)[c] |
| TRCPU 0.5 | 3 | 0.5 | 2 |
| TRCPU 1.0 | 3 | 1 | 2 |
| TRCPU 1.5 | 3 | 1.5 | 2 |

[a] NCO stands for the isocyanate functional group in IPDI.
[b] OH stands for the hydroxyl functional group in PEG.
[c] OH stands for the hydroxyl functional group at the C-6 position in chitin.

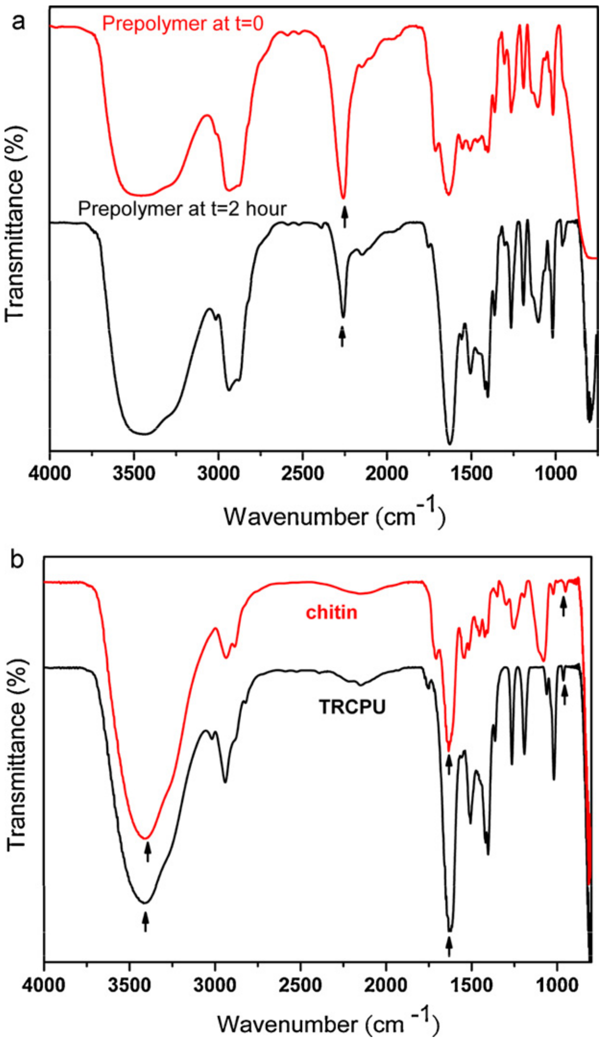


**Fig. 1.** FTIR spectra of (a) prepolymer at $t = 0$ and $t = 2$ h; (b) neat chitin and TRCPU 1.0.

Spectrum RX1 System) to examine the peak intensity variation of the hydroxyl groups, isocyanate groups and the urea linkage. The powdered organogels were mixed with dry KBr at a ratio of 1 part gel and 10 parts KBr and pressed into a transparent disk. The FTIR spectra of the TRCPU 1.0 organogel were also evaluated between 25 °C and 115 °C with a Perkin Elmer Spotlight 400N spectrometer using the salt plate (KBr) method. $^1$H NMR examination of the synthesized TRCPU were done on a Bruker AC-400 MHz using 5 mm O.D. sample tubes. $^1$H NMR spectra were collected from solutions in deuterated chloroform (chloroform-*d*, Sigma–Aldrich Co., USA) containing 1% tetramethylsilane (TMS, Sigma–Aldrich Co., USA) as an internal reference.

Rheological measurements of the TRCPU 1.0 were performed using an AR-2000ex rheometer (TA Instrument, New Castle, DE). One-milliliter size specimens were run in a parallel plate configuration using a 40 mm stainless steel plate at a gap distance of 103 μm. In a typical experiment, a constant frequency of 1 Hz and strain of 10% were used. Temperature increasing ramps at a rate of 1 °C/min were performed to obtain values for the storage and loss modules ($G'$ and $G''$, respectively) and to allow sufficient time for the sample temperature to equilibrate. A solvent trap was used to prevent the evaporation of the 5% LiCl/DMAc from the sample. Differential scanning calorimetry (DSC, Perkin-Elmer Pyris 6 Differential scanning calorimetry) thermogram for this TRCPU 1.0. The measurements were performed in the range of −50 to 160 °C at a heating rate of 10 °C/min and a cooling rate of 10 °C/min.

## 3. Results and discussion

Fig. 1a shows the FTIR spectra of the prepolymer before and after reacting for 2 h, which elucidated the extent of the reaction between IPDI and PEG. The peak of the NCO group was observed at approximately 2258 cm$^{-1}$ and gradually decreased to a constant over 2 h and the NCO group intensity area ratio was reduced near to theoretical value of 1/2 at around 2258 cm$^{-1}$, indicating the completion of the reaction between the NCO groups of IPDI and the –OH groups of PEG-diol. (Fig. S2 also shows the FTIR spectra concerning the IPDI monomer and PEG-diol molecule in the supplementary data.) Fig. 1b shows the FTIR spectra of the neat chitin and the final TRCPU 1.0. Characteristic peaks of chitin appeared at 3450, 1655, 1050 cm$^{-1}$, corresponding to the –OH groups, the carbonyl vibration from the acetylation groups, and the glycosidic linkage between the chitosan monomers, respectively (Zia, Zuber, Barikani, Jabbar, & Khosa, 2010). The FTIR spectra of the final TRCPU 1.0 featured similar characteristic absorptions with chitin. Moreover, the peak of the –OH groups around 3400 cm$^{-1}$ was observed to decrease compared with neat chitin and the half intensity of NCO group of prepolymer also disappeared at around 2258 cm$^{-1}$. Besides, the chitin we applied in this study of the degree of acetylation of 75% and the viscosity average molecular weight ($M_V$) of ∼211.0 kDa. That means, the amount of amine groups ($-NH_2$) can not to ignore and the amine groups of glucosamine (GlcN) will react with cyanate (–NCO) groups to from urea linkage. From infrared spectra Fig. 1b, the main IR bands for urea groups are observed in the range 1700–1630 cm$^{-1}$ (CO axial deformation) and 1580–1490 cm$^{-1}$ (NH angular deformation). This reaction of TRCPU may produce both urea (–NHCONH–) and urethane (–NHCOO–) groups, which form bridges between the chitin and prepolymer. The former linkage (–NHCONH–) should be preferentially formed as $NH_2$ groups react faster with isocyanates than with OH moieties (Morales, Nest, & Gandini, 1998).

The $^1$H NMR spectra of the TRCPU 1.0 confirmed that chitin was incorporated into the polymer chain because all peaks that are unique to PEG and IPDI were observed. The peaks of $^1$H NMR were registered at 2.744 ppm and 2.938 ppm due to the PEG backbone. The peak at 1.947 ppm was due to the protons from the acetamide groups of chitin. The $^1$H NMR spectra of TRCPU 1.0 also showed the 2.500 ppm peak associated with deuterated chloroform and the other two peaks (3.425 ppm, 3.498 ppm) associated with the isophorone diiocyanate. However, urea linkage will be formation and it causes the peak at 3.1–3.2 ppm represents H-2 proton of glucosamine (GlcN) residues does not become obvious. Details of the NMR experiment and the spectra of the TRCPU 1.0 are described in the supplementary data (Fig. S3). The FTIR spectra of the TRCPU 1.0 organogel were also evaluated between 25 °C and 115 °C with a Perkin Elmer Spotlight 400 N spectrometer using the salt plate (KBr) method. However, the results showed that the TRCPU 1.0 structure at 25 °C was not significantly different from the structure at 115 °C (see Fig. S4, supplementary data for detailed descriptions). This

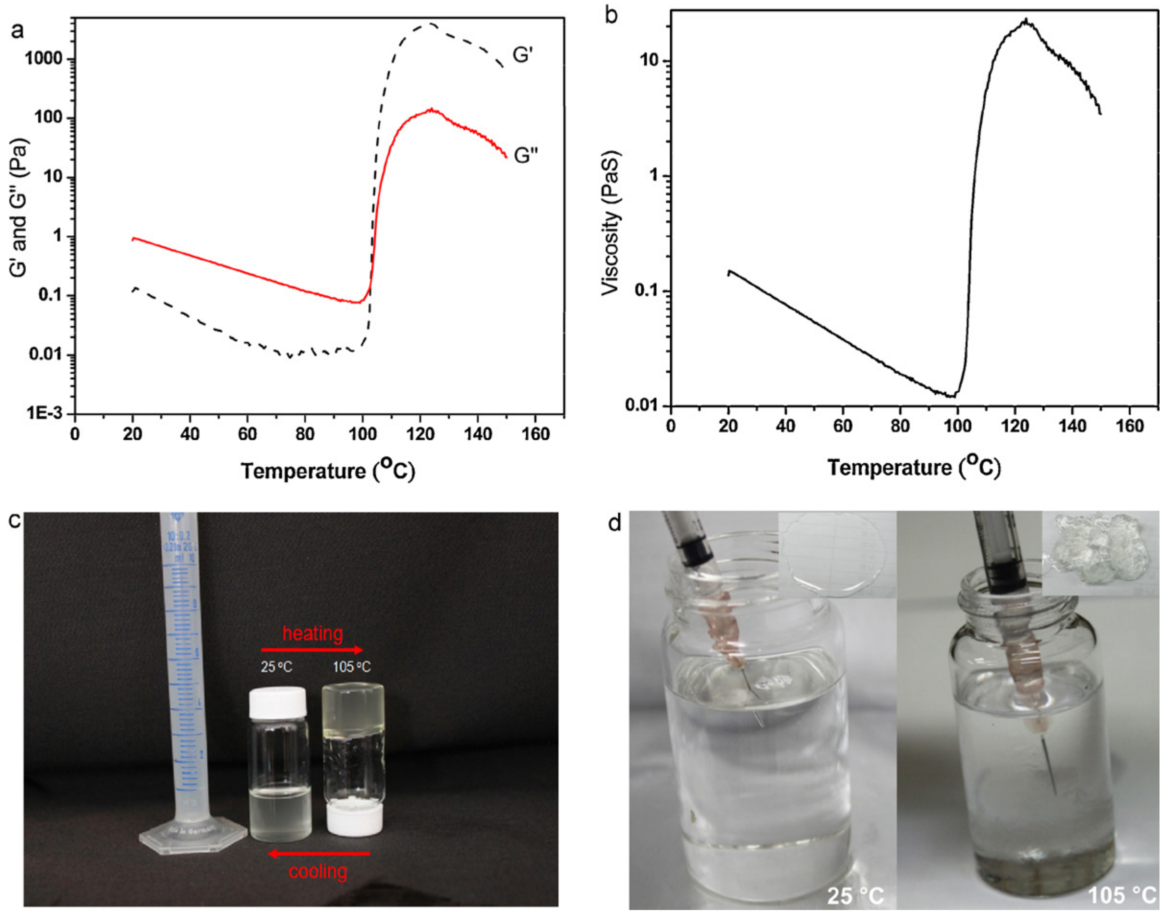


**Fig. 2.** The (a) storage modulus ($G'$) and (b) loss modulus ($G''$) of 4 wt% TRCPU 1.0 in 5 wt% LiCl/DMAc. A frequency of 1 Hz and a strain of 10 wt% were applied. The (c) digital images were shown at room temperature and at 105 °C and the (d) digital images can demonstrate injectability from placing a liquid in a syringe and injecting into a bath of 105 °C.

suggested that the covalent bonds were successfully formed between PEG and IPDI and between chitin and IPDI in the TRCPU 1.0.

In runs with rapid syneresis, which prevented the $G'$ and $G''$ curves from crossing (due to slippage), the phase change was defined when the $G'$ curve exhibited a rapid increase in slope. Fig. 2(a) was the changes in the storage modulus and the loss modulus for the sample TRCPU 1.0, which has 4 wt% TRCPU 1.0 in DMAc, at a frequency of 1 Hz. When the sample temperatures were below 105 °C, the $G'$ and $G''$ values remained around 1 to 0.01 Pa, indicating that the samples remained in a liquid state. When the temperatures were over 105 °C, the $G'$ and $G''$ values increased rapidly. The transition from liquid-like behavior to elastic gel-like behavior occurred at the crossover point of $G'$ and $G''$, which was observed at approximately 105 °C. Fig. 2(b) shows the complex viscosity of the sample with 4 wt% TRCPU 1.0 in DMAc. The storage modulus, loss modulus and complex viscosity quickly increased after 105 °C, indicating that the random linear structure of TRCPU 1.0 might be formed through a hydrophobic interaction between the chitin groups. The dramatic sol-to-gel transition was confirmed through the digital images shown in Fig. 2(c) and (d). When heated above 105 °C, TRCPU 1.0 underwent phase transition from a solution phase to a gel phase within 10 s. It also showed the resultant copolymer can be an injectable organosol at low temperatures that transformed to a semi-solid organogel at approximately 105 °C. The TRCPU 0.5 and TRCPU 1.5 samples also underwent phase transition when they were heated, but the phase transition temperatures were not the same as that for TRCPU 1.0.

Fig. 3 shows the differential scanning calorimetry thermogram for this TRCPU 1.0. The measurements were performed in the range of −50 to 160 °C. The thermograms from the DSC method can show the curve behavior of the sol-to-gel transition above the phase transformation temperature but prior to degradation. In this case, the thermograms showed a sharp endothermic peak between 82

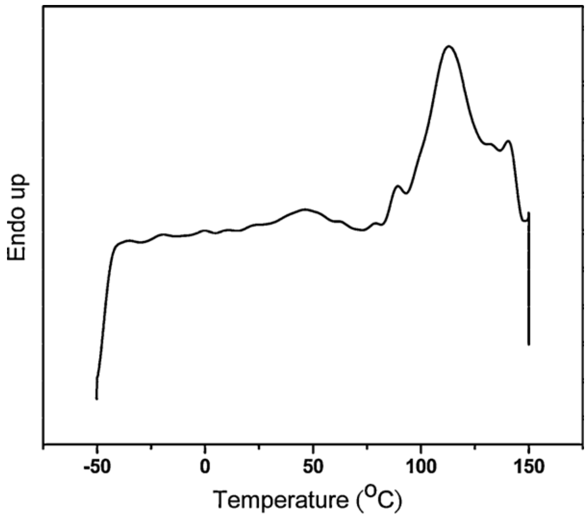


**Fig. 3.** DSC thermogram of TRCPU 1.0 in 5 wt% LiCl/DMAc between −50 and 150 °C.

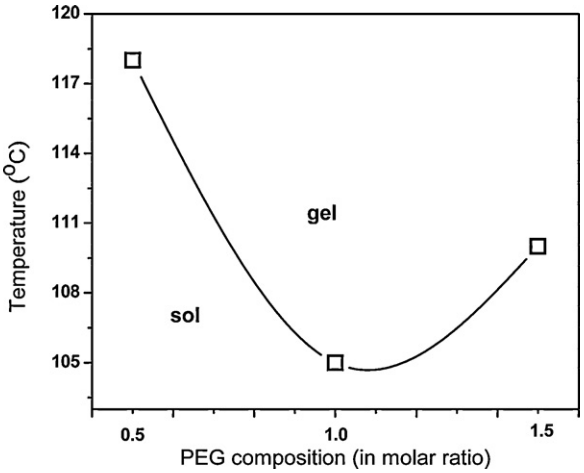


**Fig. 4.** Sol-to-gel transition curves of TRCPU with PEG/Chitin molar ratio. The sol-to-gel transition temperature was determined from the cross-over point of the storage modulus ($G'$) and loss modulus ($G''$) in the rheology analysis.

and 88 °C. The peak was likely due to the rearrangement of chitin segments as the hydrogen bonds between the hydroxyl groups of TRCPU and carbonyl, tertiary amine groups of DMAc solvent began to break. The second endothermic peak, which appeared at approximately 105 °C as a second up-shift in the curve, was the result of heat absorption during the gelling process of the partially soluble phase. Then, the phenomenon is similar to thermo-responsive hydrogel of PNIPAAm. The endothermic peak position ($\Delta H$) agreed well with the drastic changes in viscosities that were observed in the test vial when it approached the transition temperature.

Fig. 4 shows the phase diagram of the TRCPUs. Both TRCPU 0.5 and TRCPU 1.5 samples formed a gel at a higher temperature than the TRCPU 1.0 sample did. Increasing the PEG composition from 0.5 to 1.0 mole ratio compared with chitin can increase the aggregation tendency of PEG in DMAc (as seen in the TRCPU 0.5 and TRCPU 1.0 samples), resulting in a decrease of the sol-to-gel transition temperature. That is, the onset of gelation occurred sooner. However, the comparison between the TRCPU 1.0 and TRCPU 1.5 samples showed that the PEG composition have critical mole ratio compared with chitin. When PEG composition mole ratio was reached 1.0 compared with chitin, continuing to increase the PEG component tended to disturb the gelling process. This increased the phase separation temperature and caused the onset of gelation to occur later. Therefore, the sol-to-gel transition temperature is a function of the PEG composition. By changing the PEG composition, the sol-to-gel transition temperature can be easily manipulated.

## 4. Conclusion

In conclusion, TRCPUs copolymers are chitin-based polyurethanes and new negative thermally responsive organogel. TRCPU gels composed of IPDI, PEG and chitin were synthesized for the first time via a two-step polymerization technique. When chitin was incorporated into polyurethane via covalent bonding (urethane and urea), the resultant copolymer was an injectable organosol at low temperatures that transformed to a semi-solid organogel at approximately 105 °C. The incorporation of chitin is considered the cause of the thermally reversible conversion between the sol state and the gel state. There are several aspects of the phenomenon that should be studied further in the future, such as the entanglement within chitin, the possible sharp coil-globule transition effects of heating, the change in microstructure and the effect of cooling rates on the thermal transitions. Further researches on the thermal-responsive properties of TRCPUs are expected to lead to novel functional materials with applications in new areas, such as the heavy metals separation of organic substances in organic solution could be expected.

## Acknowledgements

The authors gratefully acknowledge the support for this research by the National Science Council in Taiwan under the grant numbers NSC98-2622-E-002-021-CC3 and NSC98-2221-E-037-003, respectively.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbpol.2012.01.055.

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