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Polymer 42 (2001) 7589–7594

polymer

www.elsevier.nl/locate/polymer

A sol–gel reaction of vinyl polymers based on thermally reversible urea linkages

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Received 9 January 2001; received in revised form 8 March 2001; accepted 27 March 2001

Abstract

A thermally reversible cross-linking reaction of vinyl polymers was investigated. Poly(4-vinylimidazole-*co*-methyl methacrylate) (**2**) and poly(3-isopropenyl-α,α-dimethylbenzyl isocyanate-*co*-methyl methacrylate) (**6**) were prepared by radical copolymerization. Gelation was observed in a few minutes by mixing polymer solutions of **2** and **6** in DMF at room temperature. A clear solution was produced at high temperatures. Reversible formation of urea bonds in the reaction was confirmed by IR spectroscopy. No significant side reaction was observed under argon when the reaction was run repeatedly. In the model reaction of 4-vinylimidazole with 3-isopropenyl-α,α-dimethylbenzyl isocyanate in DMF-d_7, equilibrium constants were calculated at various temperatures by ^{1}H NMR spectroscopy. ΔH^0 of -56 kJ mol^{-1} and ΔS^0 of -152 J mol^{-1} K were determined.

Keywords: Sol–gel reaction; Imidazole; Isocyanate

1. Introduction

Thermally reversible reactions are of great interest in polymer chemistry [1]. The reversibility of cross-linking reactions between polymer chains results in processable thermosetting polymers. If polymer chains were extended by such step-growth reactions, polymerization and depolymerization could be thermally controlled. Adequate reversible reaction should not involve the loss of small molecules. In addition, the forward and reverse processes should be temperature-dependent. In the case of an exothermic reaction, covalent bonds form at lower temperatures, whereas the reverse reaction is favored at elevated temperatures [1]. So far two types of thermally reversible reactions have been employed successfully in polymer synthesis. Kennedy and coworkers used cyclopentadienes as pendent or terminal groups of polyisobutylene [2–4]. Diels–Alder and retro-Diels–Alder reactions between cyclopentadienes were found to yield thermally reversible networks. But chain extension by Diels–Alder reaction was unsuccessful due to the incompleteness of the reaction. Later Salamone et al. carried out the same reactions with polyphosphazenes containing cyclopentadienyl pendent groups and observed thermally reversible cross-linking [5]. Diels–Alder and retro-Diels–Alder reactions of the polymers having furan or maleimide moieties were also reported [6,7].

Another interesting thermally reversible reaction is the one between azlactone ring and nucleophiles. Ring opening by a nucleophile does not evolve any leaving molecules and ring closure returns the reaction product to the starting materials. Nucleophiles should have balanced leaving ability with nucleophilicity for practical reversibility. This system was studied by Wagener et al. in detail [8–10]. They prepared thermally reversible cross-linking networks from the reaction of polyvinylazlactone and bisphenols.

In an effort to seek more facile and reliable reversible reaction systems, we have studied the nucleophilic addition reaction of an isocyanate. Isocyanates are very reactive against various nucleophiles such as alcohols, amines, and water [11–13]. Their reaction with alcohols has been employed in synthesizing polyurethane. Because of their high reactivity, isocyanate groups are often protected for storage through the reaction with phenols, which transforms them in urethanes [12]. The protective phenols are usually removed by heating to regenerate isocyanates. The thermally reversible properties of a series of aromatic urethanes were investigated by Wagener and Murla [14]. However, reversible chain extension via urethane linkages was unsuccessful, probably because of the low reactivity of phenolic

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0032-3861/01/$ - see front matter
PII: S0032-3861(01)00270-1

OH groups to isocyanates in the absence of catalysts, and because of the occurrence of side reactions such as self-addition between aromatic isocyanates.

In this paper, we describe a sol–gel reaction of vinyl polymers by thermally reversible covalent urea linkages. The reaction occurs between the polymers containing α,α-dimethylbenzyl isocyanate groups and imidazole groups. Imidazole is interesting because of its good leaving ability in addition to excellent nucleophilicity. Owing to these properties, imidazole has been used as a nucleophile catalyst in organic synthesis and a blocking group of isocynates [15–19]. The isocyanate groups of the polymer have been sterically crowded with methyl groups, and thus the undesired self-addition reaction was effectively suppressed.

2. Experimental procedures

2.1. Materials and instrumentation

All chemicals were purchased from Aldrich. Urocanic acid, 1-vinylimidazole, 3-isopropenyl-α,α-dimethylbenzyl isocyanate (IPDMBI), sodium methoxide (25 wt% solution in methanol) were used as received. Azobisisobutyronitrile (AIBN) was recrystallized from acetone. Methyl methacrylate (MMA) was washed twice with aq. 5% NaOH and twice with water, dried over CaH_2, and then distilled at reduced pressure. Reagent grade solvents were dried and purified as follows. *N*,*N*-Dimethylformamide (DMF) was dried over anhydrous P_2O_5 and purified by distillation. Acetone was distilled over potassium carbonate. Tetrahydrofuran (THF), *n*-hexane, and diethyl ether were dried over sodium metal and distilled. Pyridine was distilled over KOH. ^{1}H and ^{13}C NMR spectra were recorded on a Varian-Gemini 200 and a Bruker AMX-500 spectrometer. IR spectra were obtained with the use of a Nicolet Magna-IR 550 spectrometer. The spectra were collected over the range 4000–400 cm^{-1} by averaging 40 scans at a resolution of 4 cm^{-1}. Gel permeation chromatography (GPC) was carried out with a Waters 150C GPC fitted with a M410 refractive index detector and Waters Styragel HT3 and HT4 columns. DMF with LiBr (0.05 M) was used as the eluent. Elemental analyses were performed at Korea Research Institute of Chemical Technology and Korea Basic Research Center.

2.2. 4-Vinylimidazole (*1*)

This compound was prepared according to the literature [20]. Urocanic acid (2.1 g, 15.2 mmol) was heated at 220°C under high vacuum and 4-vinylimidazole (0.46 g, 33% yield) was collected.

^{1}H NMR (DMSO-d_6): δ 12.2 (s, 1H, NH), 7.1, 7.6 (s, 2H, imidazole ring protons), 6.6 (q, 1H, C═CH), 5.0, 5.6 (d, 2H, C═CH_2).

2.3. Poly(4-vinylimidazole-co-MMA) (*2*)

Monomer **1** (0.402 g, 4.3 mmol) and MMA (0.91 ml, 8.6 mmol) were charged into a polymerization tube (10 ml) and a solution of AIBN (0.033 g) in DMF (6 ml) was added. After three freeze–thaw cycles, the tube was sealed under vacuum. The solution was stirred at 70°C for 24 h. The polymer was isolated by precipitation in diethyl ether and purified by reprecipitation twice from the polymer solution in DMF into diethyl ether (yield 85%).

^{1}H NMR (DMSO-d_6): δ 6.4, 7.4 (m, imidazole ring protons), 3.0–3.5 (m, O–CH_3), 0.5–2.0 (m, backbone protons).

IR (KBr, cm^{-1}): 3337, 2990, 2951, 1726, 1448, 1148.

Number average molecular weight (M_n) and weight average molecular weight (M_w) when measured by GPC were 59,000 and 69,000, respectively.

2.4. Poly(1-vinylimidazole-co-MMA) (*4*)

This polymer was obtained from 1-vinylimidazole (4.4 mmol) and MMA (8.8 mmol) in DMF (10 ml) by following the procedure for preparation of polymer **2** in 89% yield. M_n and M_w were measured by GPC to be 31,000 and 36,000, respectively.

^{1}H NMR ($CDCl_3$): δ 7.0–7.8 (m, imidazole ring protons), 3.0–3.8 (m, O–CH_3), 0.5–2.0 (m, backbone protons).

IR (KBr, cm^{-1}): 2993, 2951, 1728, 1498, 1436, 1148.

2.5. Poly(IPDMBI-co-MMA) (*6*)

IPDMBI (2 ml, 10.0 mmol) and MMA (4.16 ml, 39 mmol) were charged into a polymerization tube (25 ml) and a solution of AIBN (0.06 g) in acetone (5 ml) was added. After three freeze–thaw cycles, the tube was sealed under vacuum. The solution was stirred at 60°C for 48 h. The polymer was isolated by precipitation in *n*-hexane and purified by reprecipitation from the polymer solution in acetone into *n*-hexane twice (yield 44%).

^{1}H NMR ($CDCl_3$): δ 7.1–7.4 (m, phenyl protons), 3.0–3.7 (m, OCH_3), 0.2–2.1 (m, backbone protons and CCH_3).

IR (KBr, cm^{-1}): 2988, 2949, 2259, 1732, 1458, 1150.

To determine approximate molecular weights, the polymer was reacted with sodium methoxide in THF to give polymer **7**. Sodium methoxide (0.15 ml, 25 wt% solution in methanol) and pyridine (0.02 ml) were added to a solution of polymer **6** (0.2 g) in THF (3 ml). The solution was stirred at 60°C for 10 h. The polymer was isolated by precipitation in *n*-hexane and purified in almost quantitative yield by reprecipitation twice from the polymer solution in THF into *n*-hexane.

^{1}H NMR ($CDCl_3$): δ 7.0–7.4 (m, 4H, phenyl protons), 3.0–3.7 (m, 6H, OCH_3), 4.9 (m, 1H, NH), 0.2–2.1 (m, 13H, backbone protons and CCH_3).

IR (KBr, cm^{-1}): 3389, 2996, 2951, 1728, 1601, 1450, 1150.

M_n and M_w of polymer **7** measured by GPC were 26,000 and 28,000, respectively.

2.6. Model reaction

A solution of monomer **1** (0.0202 g, 0.215 mmol) and IPDMBI (0.0425 ml, 0.215 mmol) in DMF-d_7 (0.4 ml) was transferred to a NMR tube which was then sealed. The ^{1}H NMR spectra were recorded while the sample was heated from 30 to 80°C and then cooled from this temperature to 30°C.

2.7. Sol–gel reaction of polymers *2* and *6*

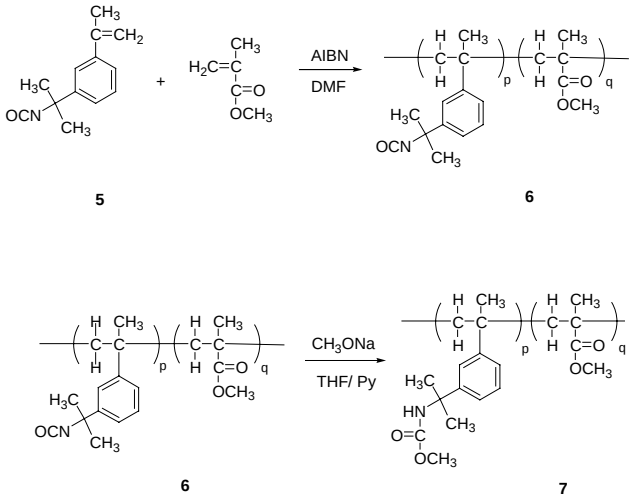
A solution of polymer **2** (0.052 g, 0.15 mmol of imidazole group) in DMF (0.5 ml) was added to a solution of **6** (0.061 g, 0.15 mmol of isocyanate group) in DMF (0.5 ml) in an ampoule (10 ml) under argon. The mixture was stirred at room temperature for 10 min to complete gelation. The ampoule was immersed in an oil bath and the sol–gel reaction was carried out by heating the bath from room temperature to 130°C at a rate of 5°C min^{-1} and then cooling. For the IR study, a gel formed by the reaction of two polymers in DMF was spread between two NaCl windows. The spectra were recorded as the cell temperature was increased from room temperature to 110°C and then decreased.

3. Results and discussion

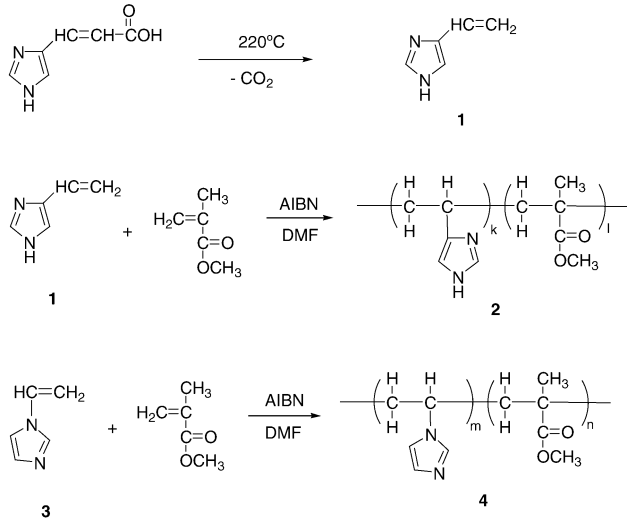
3.1. Synthesis of monomer *1* and copolymers

Monomer **1** was prepared from urocanic acid, as indicated above [20]. It is known that 4-substituted imidazole is subjected to tautomerization and that such tautomeric pairs are inseparable [21]. Although monomer **1** was expected to be in equilibrium with 5-vinylimidazole, ^{1}H NMR spectroscopy showed singlet peaks for two imidazole ring protons at 7.1 and 7.6 ppm in DMSO-d_6 at room temperature. The signals for other protons were not separated, either.

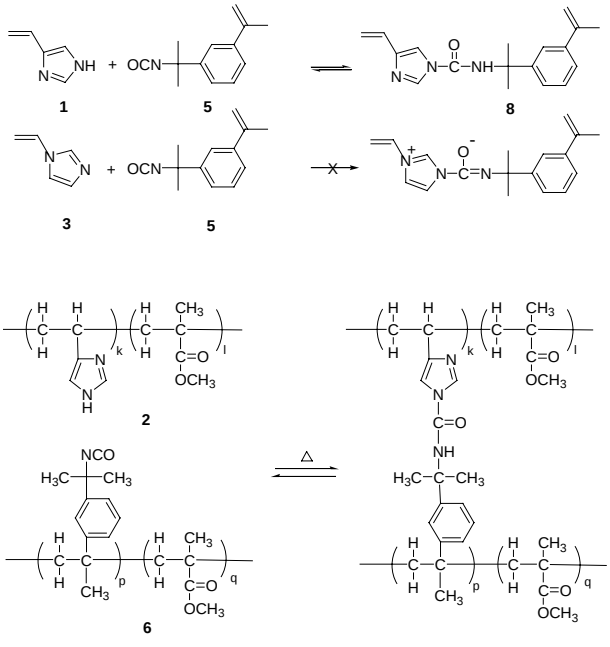
Monomer **1** was copolymerized with MMA by free radical initiation in DMF at 70°C (Scheme 1). In the ^{1}H NMR spectrum in DMSO-d_6, the peaks for imidazole ring protons showed up at 6.4 and 7.4 ppm. Based on the area ratio of the ring proton peaks to the peak for *O*-methyl protons from MMA, the copolymer composition was calculated. The composition was controlled by varying the monomer feed ratio. The copolymer with imidazole contents of 28% obtained from a monomer **1** feed ratio of 33% was used



Scheme 2.



Scheme 1.



Scheme 3.

for the polymer reaction in this work. Polymer **2** was soluble in polar aprotic solvents, such as DMF and DMSO, but was insoluble in THF, 1,4-dioxane, alcohols, and chloroform.

For comparison of the reactivities of imidazole groups, polymer **4** was also prepared from 1-vinylimidazole and MMA (Scheme 1). ^{1}H NMR spectroscopy showed the peaks for imidazole ring protons between 7.0 and 7.8 ppm. From the monomer **3** feed ratio of 33%, a copolymer with imidazole contents of 26% was obtained. In contrast to polymer **2**, polymer **4** was readily dissolved in common organic solvents including THF and chloroform.

A polymer containing isocyanate groups, designated as polymer **6**, was prepared from IPDMBI and MMA with radical initiation in acetone at 60°C (Scheme 2). The IPDMPI contents was found to be 33% by ^{1}H NMR spectroscopy in the copolymer when the feed ratio of IPDMPI was 25%. In the IR spectrum, the characteristic band for isocyanate groups appeared at 2259 cm^{-1}. To determine molecular

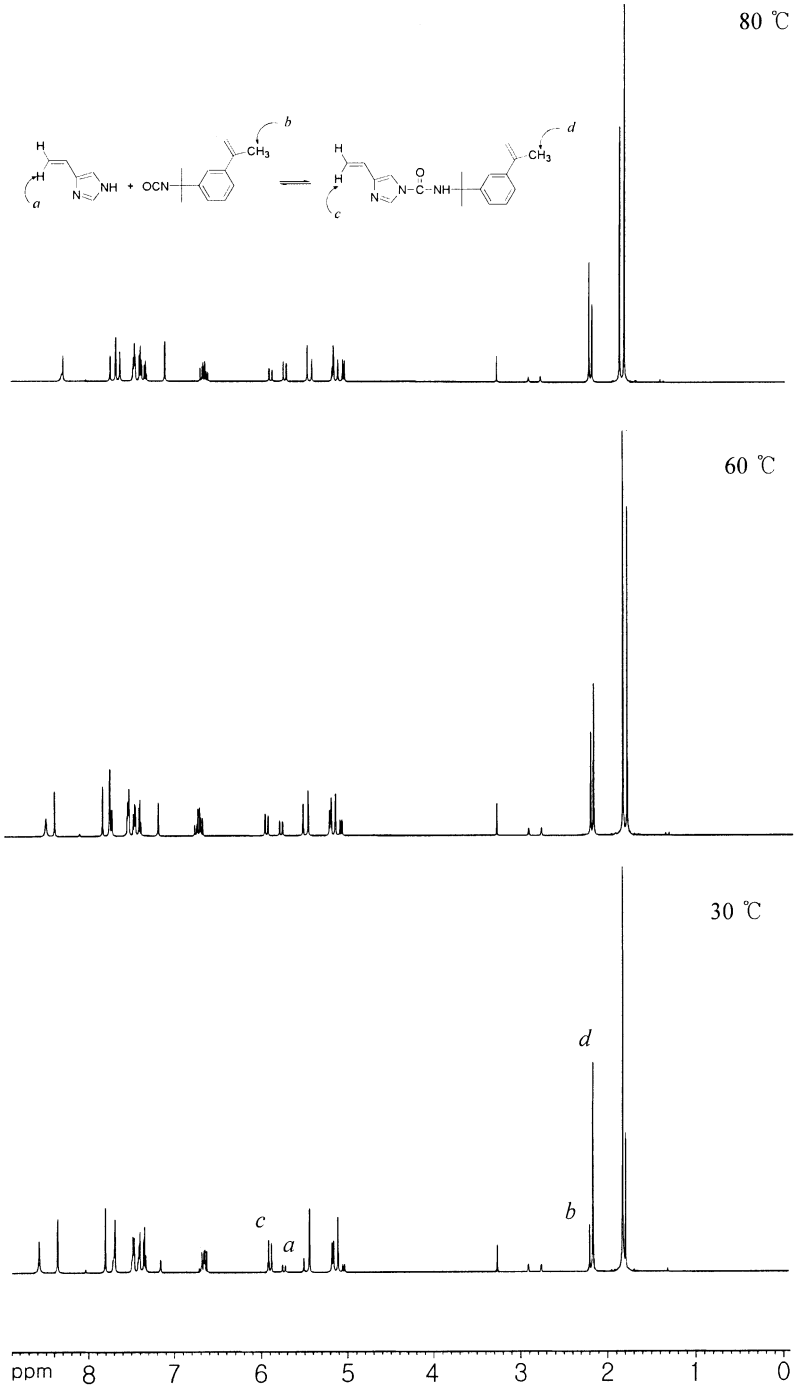


Fig. 1. ^{1}H NMR spectra of the reaction mixture of compounds **1** and **5** in DMF-d_7 obtained at various temperatures.

weights, the isocyanate groups of polymer **6** were transformed into urethane ones. Polymer **6** was thus reacted with sodium methoxide in THF to yield polymer **7**. The M_n and M_w of polymer **7** were found by GPC to be 26,000 and 28,000, respectively.

3.2. Model reaction

The thermal reversibility of the urea linkage formed by the reaction of monomer **1** with IPDMBI was investigated by ^{1}H NMR spectroscopy (Scheme 3). Equimolar amounts of monomer **1** and IPDMBI were dissolved in DMF-d_7 and subjected to NMR analysis. It has been reported that the acylation of 4-substituted imidazole gives the sterically less crowded 1-acyl-4-substituted imidazole exclusively [22]. Tautomerization to 5-substituted imidazole facilitates this reaction. The ^{1}H NMR spectrum obtained at 30°C shows the peaks for imidazole ring protons of **1** at 7.66 and 7.13 ppm along with the peaks at 8.32 and 7.77 ppm from corresponding protons of the urea formed by the reaction (Fig. 1). Since both proton peaks undergo the same downshift after completion of the reaction, it is concluded that the reaction occurs at 1-N position, yielding urea **8**.

In the ^{1}H NMR spectra, the peaks from the starting compounds and the product were clearly separated, and it was possible to calculate the concentration of each component from the peak area. We have used the peaks for vinyl proton *a* of monomer **1** at 5.73 and methyl protons *b* of IPDMBI at 2.17 ppm. The peaks for corresponding protons *c* and *d* in the urea appeared at 5.89 and 2.20 ppm, respectively. The NH of the urea bond gave a signal at 8.32 ppm. At 30°C, 81% of the imidazole groups were found to be in the urea form. As the temperature of the reaction mixture was increased, the reverse reaction proceeded and the peaks for *c* and *d* became smaller. The NH peak of the urea disappeared completely at 80°C, although the other peaks from the urea were still observed. This is attributed to rapid proton exchange at high temperatures.

The reaction seemed to reach the equilibrium very quickly. The reaction mixture was heated from room temperature to 80°C and the ^{1}H NMR spectra were recorded at desired temperatures. After recording the spectrum at 80°C, the reaction was monitored by ^{1}H NMR spectroscopy, but no appreciable change of the peak area ratio was observed within an hour. Fast equilibration was also confirmed by the ^{1}H NMR spectra obtained upon cooling the reaction mixture. The spectra recorded at 10°C intervals from 80°C to room temperature showed the same results as those obtained from the heating experiment.

Equilibrium constants were calculated according to Eq. (1). Molar concentrations determined by the peak area ratio of *a* and *c* in imidazole units were the same as those calculated from *b* and *d* in IPDMBI units, indicating that no other reactions except urea formation occurred under the reaction conditions. Logarithmic values of equilibrium constants were plotted against T^{-1} to give a straight line

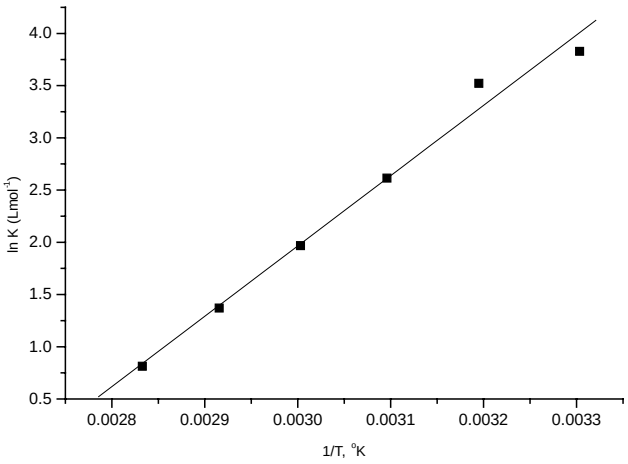


Fig. 2. Plot of ln K vs T^{-1} for the reaction of compounds **1** and **5**.

(Fig. 2). According to Eq. (2), ΔH^0 of -56 kJ mol^{-1} and ΔS^0 of -152 J mol^{-1} K were determined from the slope and the intercept, respectively [23].

$$K = \frac{[\text{molar conc. of } \mathbf{8}]}{[\text{molar conc. of } \mathbf{1}][\text{molar conc. of } \mathbf{5}]} \quad (1)$$

$$\ln K = -\Delta G^0/RT = -\Delta H^0/RT + \Delta S^0/R \quad (2)$$

At 30°C, the reaction showed a large equilibrium constant of 46 l mol^{-1}. As the temperature increased, the reverse reaction became favored owing to $T\Delta S^0$ entropy term. At 150°C, K was calculated to be 0.1 l mol^{-1}. These data suggest that this reaction could be applied to the polymer system for reversible sol–gel reaction. In contrast with 4-vinyl imidazole (**1**), 1-vinyl imidazole (**3**) did not react with IPDMBI under the same reaction conditions.

3.3. Sol–gel reaction

Polymers **2** and **6** were dissolved in DMF separately under argon. The concentrations were adjusted for the mixture to have equimolar of imidazole and isocyanate groups. The solutions were mixed in an ampoule with stirring under argon. Gelation was observed in a few minutes (Scheme 3). In a similar manner, polymer **4** was reacted with polymer **6** in DMF. However, no appreciable change occurred in a day.

The ampoule was heated in an oil bath. Above 100°C of the bath temperature, the gel began to dissolve and a clear solution was obtained at 130°C. Upon cooling, a stable gel formed again. In this way, reversible sol–gel reaction could be carried out repeatedly. The reaction also took place under atmosphere conditions. In this case, however, the gel partially became white after a few cycles, probably due to a reaction with moisture.

The reversible formation of urea bonds in a sol–gel reaction was also confirmed by IR spectroscopy (Fig. 3). A gel formed by the reaction of polymer **2** with polymer **6** in DMF was cast on a NaCl plate and subjected to IR analysis

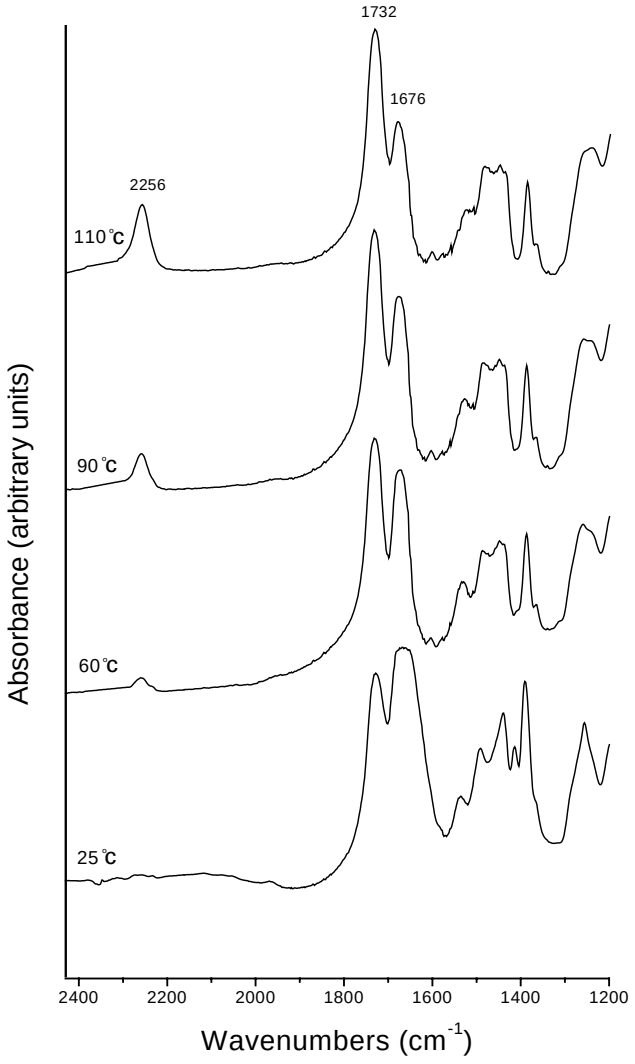


Fig. 3. Part of the IR spectra of the gel formed by the reaction of polymer **2** with polymer **6** at various temperatures.

at variable cell temperatures. A strong band for C=O stretching of urea groups showed up at 1676 cm^{-1} at room temperature [24–28]. As the cell temperature increased, its intensity decreased, while a characteristic peak for isocyanate groups began to appear at 2256 cm^{-1} from 60°C and became stronger. The band for C=O stretching of MMA units appeared at 1732 cm^{-1}, which remained relatively unchanged during heating. The reverse peak appearance in the IR spectra was observed during cooling of the cell. The same results were obtained by repetitive heating and cooling the sample until the reaction with moisture occurred to make the system irreversible.

4. Conclusion

The reaction between imidazole and isocynato groups yielded completely thermally reversible urea bonds. In the model reaction study, the forward and reverse reactions were found to reach an equilibrium state very quickly. The polymers containing these groups as pendants were successfully employed in the thermally reversible sol–gel reaction in DMF with varying the temperatures. No significant side reaction was observed under argon when the reaction was run repeatedly.

Acknowledgements

Financial support by Korea Science and Engineering Foundation through a grant (No. 95-0502-07) and Hyperstructured Organic Materials Research Center is gratefully acknowledged.

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