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Polymer 47 (2006) 2581–2586

polymer

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Polymer Communication

Thermally reversible cross-linked polyamides and thermo-responsive gels by means of Diels–Alder reaction

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Received 10 January 2006; received in revised form 17 February 2006; accepted 20 February 2006
Available online 9 March 2006

Abstract

Cross-linked polyamides and polyamide gels were prepared from maleimide-containing polyamides and a tri-functional furan compound and showed thermal reversibility in cross-linking behavior and in gel formation through Diels–Alder (DA) and retro-DA reactions. The rate constant k of the DA cross-linking reaction were $1.25–4.83\times10^{-5}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ in the temperature range of 20–60 °C with an activation energy of $32.1\ \mathrm{kJ\ mol^{-1}}$. The cross-linking densities, thermal properties, and thermal reversibility of the polyamides/furan polymers were adjustable with the contents of maleimide groups in polyamides.

Keywords: Polyamide; Diels–Alder reaction; Thermally reversible

1. Introduction

The thermal reversibility of Diels–Alder (DA) reaction is an interesting feature. DA reaction between a dienophile and a diene formed covalent bonds, which could be easily broken down. The equilibrium of DA reaction could be displaced toward the reagents by heating through the retro-Diels–Alder (retro-DA) reaction. Utilization of DA reaction in polymer cross-linking reactions to build up the polymer networks results in a new class of thermally-reversible cross-linked polymers [1–10]. In recent years these thermally-reversible cross-linked polymers are widely studied to explore applications in encapsulants, structural materials, and coatings, etc. For example, semiconductor can be redeemed from bad encapsulation with using such polymers as encapsulants; self-repairing polymeric materials made with this kind of polymers can be used as a smart materials.

Both diene- and dienophile-containing polymers were prepared and cross-linked with small molecular cross-linkers. On the other hand, stimuli-responsive polymer gels create future technologies for the control of fluidity, viscoelasticity, solvent volatility, and material transport. Some systems, which employed small molecular aggregations switched by light, electric, and sound, showed successes on controlling gelation [11–13]. Another controlled gelation was established upon reversible cross-linking polymers in solvents. Saegusa et al. reported a thermally reversible hydrogel basing on polyoxazoline and its Diels–Alder reaction [1].

Up to our knowledge, this work reported the first investigation of thermally-reversible cross-linked polyamides and thermo-responsive polyamide gels. Polyamides possessing maleimide groups were prepared and cross-linked with a trifunctional furan compound through Diels–Alder reaction. The kinetics of DA reaction and the properties of the cross-linked polyamides were investigated. Moreover, polyamide gels in *N*,*N*-dimehylacetamide (DMAc) was also prepared and their thermally-responsive properties were studied.

2. Experimental

2.1. Materials

5-Maleimidoisophthalic acid (MIPA) was prepared from 5-aminophthalic acid and maleic anhydride according to the reported method [14]. 4,4′-Dicarboxydiphenylether (DCDPE) and 4,4′-(hexafluoroisopropylidene)dianiline (6FDA) were purchased from TCI company (Tokyo, Japan) and Aldrich Chemical company, respectively. *N*-methyl-2-pyrrolidone (NMP), triphenylphosphite (TPP), pyridine, and calcium chloride were purchased from Aldrich Chemical company and used as received. Tri-functional furan compound (TF)

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doi:10.1016/j.polymer.2006.02.057

was prepared in the laboratory according to the reported method [15].

2.2. Characterization

FTIR spectra were measured with a Perkin–Elmer Spectrum One FTIR. ^{1}H NMR spectra were recorded with a Brüker MSL-300 (300 MHz) NMR spectrometer. Differential scanning calorimetry (DSC) was performed with a thermal analysis DSC-Q10 instrument at a heating rate of 10 °C min^{-1} under nitrogen atmosphere. The gas flow rate was 40 mL min^{-1}. Thermogravimetric analysis (TGA) was performed with a Thermal Analysis TGA-2050 thermogravimetric analyzer at a heating rate of 10 °C min^{-1} under nitrogen atmosphere.

2.3. Preparation of polyamides possessing maleimide pendants

Selective reaction of amine group of 6FDA toward carboxylic acid group, rather than toward maleimide group, of MIPA was observed in the previous work [16] and was applied in preparation of maleimide-containing polyamides. 6FDA (10 mmol) and MIPA + DCDPE mixture (total 10 mmol) were dissolved in 30 mL *N*-methyl-2-pyrrolidone (NMP). The feeding molar ratios of MIPA/(DCPDE + MIPA) in this work were ca. 0.1, 0.5, and 1.0. The solution was charged into a 250 mL round-bottom flask. After adding triphenylphosphite (TPP, 32 mL), pyridine (32 mL), and calcium chloride (0.8 g), under stirring the solution was reacted at 100 °C for 3 h. After cooling to room temperature, the reaction mixture was poured into a large excess of methanol. The precipitate was filtered, washed with methanol and hot water, and then dried under vacuum at 150 °C for 24 h. The obtained polymer was continuously extracted with hot methanol for 4 h. After drying, polyamide containing maleimide pendants (PA-MI) was obtained with a yield of 93%.

2.4. Preparation of thermally-reversible cross-linked polyamides and gels

PA-MI and TF in equal equivalence ratios were dissolved in *N*,*N*-dimethylacetamide (DMAc, 25 wt%). The solutions were kept at 30 °C. The gel point was determined while the solution losing their fluidity. Polymer gel was taken out, wiped with paper, and then put into excess DMAc for retro-DA experiments. Cross-linked polyamides were obtained from drying the polymer gel at room temperature under vacuum.

2.5. Kinetic studies on DA cross-linking reaction

Time-dependent reaction conversions of DA cross-linking reaction of TMI-TF were monitored with collecting FTIR spectra with a Perkin–Elmer Spectrum One FTIR equipped a programmable heating stage and high temperature cell. The intensity changes of the absorption peak of adduct at 1057 cm^{-1} (furan ring breathing) with respective to the band of C=O group at 1715 cm^{-1}, which was taken as the internal standard for reference, was utilized to monitor the performing of the DA reaction. Let $N_0 = [I_{1057}/I_{1715}]$ at $t = 0$, and $N_t = [I_{1057}/I_{1715}]$ at $t = t$. Let $x = (N_0 - N_t)/N_0$, the reaction ratio of the adduct, thus the integrated rate expression for a second-order kinetic reactions will be Eq. (1):

$$\frac{1}{(1-x)} = kt \tag{1}$$

2.6. Measurement of swelling ratio of cross-linked polyamides

Certain amounts (about 0.1 g) of dry cross-linked polyamides (PA-MI/TF) were put in DMAc for 24 h. The swollen samples were taken out, wiped with paper, and then weighted. The swelling ratio is calculated from Eq. (2)

$$\text{Swelling ratio} = (w_s - w_d)/w_d \times 100\% \tag{2}$$

where W_d is the dry sample weight and W_s the swollen sample weight.

3. Results and discussion

3.1. Polymer preparation

Polyamides possessing different amounts of maleimide groups (PA-MI) were obtained with charging different ratios of MIPA and DCDPE in feeding monomers for polymerization. The feeding molar ratios of MIPA/(DCPDE + MIPA) in this work were ca. 0.1, 0.5, and 1.0 for PA-MI-1, PA-MI-5, and PA-MI-10, respectively. The ratios of the repeating units of MIPA/(MIPA + DCDPE) in the PA-MI copolymer chains were obtained from ^{1}H NMR analysis with the ratios of peak areas of the amide protons at $\delta = 10.54$ (MIPA unit) and at 10.84 ppm (DCDPE unit). The values were calculated to be 0.07 and 0.40 for PA-MI-1 and PA-MI-5, respectively. These two values were a little smaller than the values of the monomer feeding ratios, to imply that MIPA was less reactive than did DCDPE toward 6FDA in the polyamidation reaction.

PA-MI polymers were cross-linked with TF by means of Diels–Alder reaction (Fig. 1). The performance of the cross-linking reaction was monitored with FTIR. Time-dependent changes of absorption peak at 1057 cm^{-1} (furan ring breathing) were recorded (Fig. 2). As it was reported that the furan-maleimide DA reactions followed second order kinetics for both simple molecules and polymers [10,15,17,18], the rate constant k of the DA cross-linking reaction of PA-MI and TF was derived from the second order model and the calculated values of k were 1.25–4.83 $\times 10^{-5}$ dm^3 mol^{-1} s^{-1} in the temperature range of 20–60 °C. The activation energy calculated from the reaction constants and Arrehnius equation was 32.1 kJ mol^{-1}. All of the kinetic data were reasonable and comparable to the reported values for other furan-maleimide DA reactions [10,15,17,18].

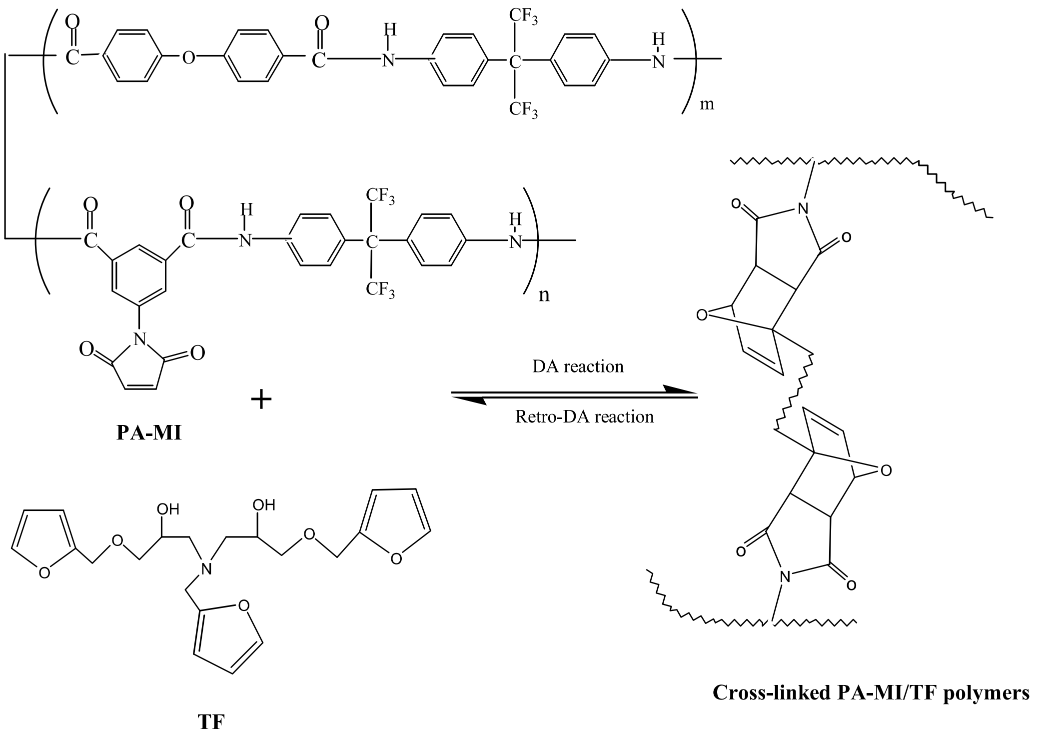

Fig. 1. Preparation of thermally-reversible polyamides.

3.2. Thermally-reversible polyamide gels

PA-MI/TF solutions in DMAc (25 wt%) formed polymer gels through Diels–Alder cross-linking reaction between maleimide (PA-MI) and furan (TF) groups at 30 °C. The observed gel time for PA-MI-1/TF, PA-MI-5/TF, and PA-MI-10/TF were 54, 18, 10 days, respectively. It is reasonable that PA-MI-10 showed short gel time as it possessed relatively high

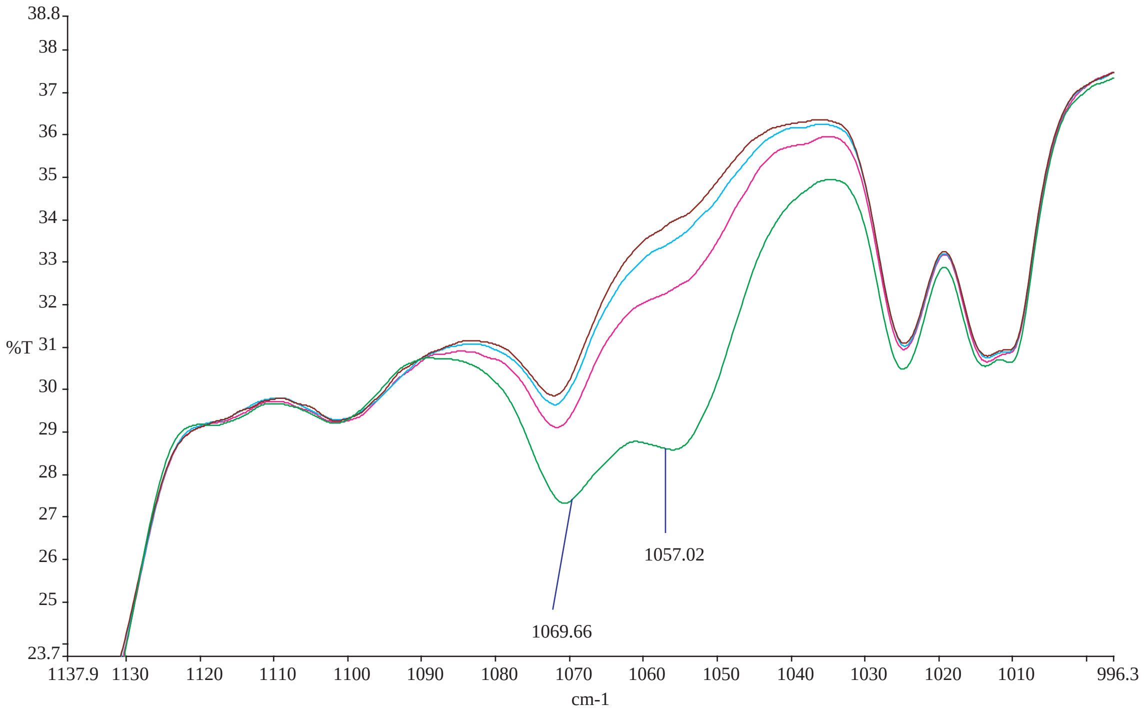

Fig. 2. Real time FTIR spectra on monitoring the DA reaction of PA-MI-5/TF polymer at 50 °C. The time-dependent absorption changes at 1057 cm^{-1} were utilized in kinetic analysis.

(a) Polymer gel based on PA-MI-1/TF in DMAc at 30 °C

(b) PA-MI-1/TF Polymer gel converting to polymer solution in DMAc at 160 °C

(c) Cross-linked PA-MI-1/TF polymer in DMAc: 30 °C, 5 h. **Unsoluble**

(d) Cross-linked PA-MI-1/TF polymer in DMAc: 120 °C, 2 h. **Soluble**

(e) Cross-linked PA-MI-10/TF polymer in DMAc: 30 °C, 5 h: **unsoluble**

(f) Cross-linked PA-MI-10/TF polymer in DMAc: 120 °C, 5 h: **partially soluble**

(g) Cross-linked PA-MI-10/TF polymer in DMAc: 160 °C, 5 h: **soluble**

Fig. 3. Photographs of observation of thermally-reversible cross-linking behavior of PA-MI/TF polymers.

content of maleimide groups. Fig. 3(a) shows the pictures of the PA-MI-1/TF gel solution. The polymer gel was thermally-responsive and could be converted to clear and fluid solution under heating (Fig. 3(b)), due to the occurrence of retro-DA reaction at the maleimide-furan adduct sites. Through retro-DA reaction the cross-linked polyamides in gels converted back to the original PA-MI and TF, which dissolved in DMAc again to form clear solutions. The retro-DA reaction obviously occurred at temperatures above 100 °C. High reaction temperatures promoted the retro-DA reaction to increase the reaction rates of retro-DA reactions and to shorten the time to transfer the polymer gels to clear polymer solutions (Table 1). In addition, the cross-linking densities of PA-MI/TF gels also significantly affect the reaction time. Among the polymer gels, PA-MI-1/TF possesses the lowest cross-linking density to show the shortest reaction time of converting gel to clear solution. On the other

Table 1
Reaction temperature and time for transformation of polyamide gels to clear solutions

	Temperature (°C)	Reaction time (min)	Solution appearance
PA-MI-1/TF gel	80	300	Gel
	100	30	Clear
	120	15	Clear
	160	10	Clear
PA-MI-5/TF gel	80	300	Gel
	100	100	Clear
	120	80	Clear
	160	50	Clear
PA-MI-10/TF gel	80	3000	Gel
	100	3000	Gel
	120	3000	Gel
	160	240	Clear

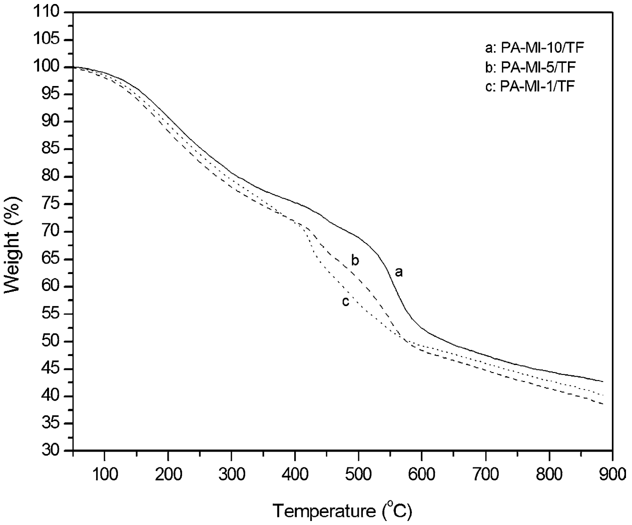

Fig. 4. TGA thermograms of PA-MI/TF gels in nitrogen.

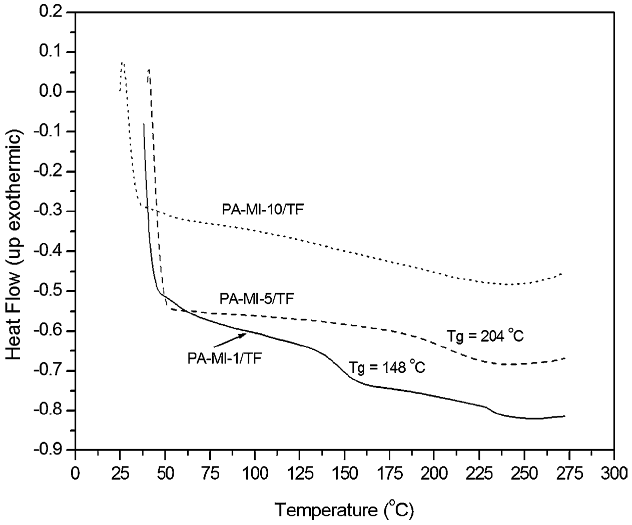

Fig. 5. DSC thermograms of cross-linked PA-MI/TF polymers.

hand, PA-MI-10/TF was highly cross-linked. A high temperature of 160 °C was necessary to convert the PA-MI-10/TF gel to clear solution in a reasonably short period of 240 min. From the above it is concluded that the polyamide gels are temperature responsive, and the responsive temperature and time are adjustable with the maleimide contents of PA-MI polymers.

Cross-linked polyamides were sampled in TGA measurements (Fig. 4). The initial weight loss could be attributed to lose of residual solvent. Weight loss at 150–400 °C came from furan compound TF, which was generated from retro-DA reaction at about 150 °C. Weight loss at high temperature regions indicates the degradation of cross-linked polyamide polymers. The relatively good thermal stability and retarded degradation rate observed with PA-MI-10/TF is due to its high maleimide contents.

3.3. Thermally reversible cross-linked polyamides

Condensed cross-linked polyamides were obtained from drying polymer gels. All of the cross-linked polymers were not soluble in DMAc at room temperature (Fig. 3(c) and (e)) and were soluble under heating. PA-MI-1/TF dissolved in DMAc at 120 °C (Fig. 3(d)). However, PA-MI-10/TF showed poor solubility in DMAc at 120 °C (Fig. 3(f)). To break the cross-linked structure of PA-MI-10/TF, a high temperature of 160 °C is needed (Fig. 3(g)). The swelling ratios of cross-linked polyamides in DMAc were measured to be 1750, 360, and 160% for PA-MI-1/TF, PA-MI-5/TF, and PA-MI-10/TF, respectively. The swelling ratio order of the three cross-linked polyamides agree with the expected cross-linking density order of the polyamides. The high swelling ratio of PA-MI-1/TF is attractive to indicate such polymers could be used as a solvent absorber. Therefore, the PA-MI/TF polymers could be utilized as a new class of thermally-reversible cross-linked polymers which reserve its properties at low temperatures and show removability and solubility at high temperatures. Meanwhile, changes of the maleimide contents in PA-MI polymers could alter and control the removalibility and solubility conditions of the cross-linked polyamides.

The thermal properties of cross-linked PA-MI/TF polymers were investigated with DSC, and the analytical thermograms are shown in Fig. 5. Glass transition behaviors were observed with PA-MI-1/TF and PA-MI-5/TF polymers at 148 and 204 °C, respectively. The relatively high glass transition temperature of PA-MI-5/TF polymer is due to its high cross-linked density. Therefore, owing to the high cross-liking density, no obvious glass transition behavior was observed for PA-MI-10/TF polymer till 280 °C.

4. Conclusions

Polymers based on maleimide-containing polyamides and a tri-functional furan compound showed thermal reversibility in cross-linking behavior and gel formation through Diels–Alder and retro Diels–Alder reactions. The thermal-responsive properties of the cross-linked polymers and polymer gels were adjustable with changes of the maleimide densities in polyamides. High glass transition temperatures above 200 °C were observed with the cross-linked polyamides to indicate their good thermal properties and potentials of using as advanced structural materials.

Acknowledgements

The authors thank the National Science Council of Taiwan for the financial support on this work (Grant No. NSC 94-2216-E-033-002). The support from the Center-of-Excellence (COE) Program on Membrane Technology from the Ministry of Education (MOE), Taiwan is also appreciated.

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