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

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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 1.25–4.83×10^{-5} dm^3 mol^{-1} s^{-1} in the temperature range of 20–60 °C with an activation energy of 32.1 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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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)

$$\text{Swelling ratio}=(w_\mathrm{s}-w_\mathrm{d})/w_\mathrm{d}\times 100\% \tag{2}$$

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 × 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].