Polymerization of Meldrum’s Acid and Diisocyanate: An Effective Approach for Preparation of Reactive Polyamides and Polyureethanes

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ABSTRACT: Meldrum’s acid (MA) is utilized as a monomer to polymerize with diisocyanates to result in polyamides, containing MA moieties at polymer chains. This reaction is also employed to prepare isocyanate-terminated polyamide segments which are utilized as a precursor for preparation of MA-containing polyurethanes. Based on the thermolysis reaction of MA groups, followed by ketene dimerization reaction, the reactive polyamides and polyurethanes show self-cross-linkable features. The cross-linked polyurethanes exhibit good film formability, thermal stability, and mechanical properties. A new MA-based polymerization method and a novel synthesis route for preparation of reactive polyamides and polyurethanes are demonstrated.

1. INTRODUCTION

Reactive polymers are attractive in both polymer chemistry and materials as they possess functional groups being capable of performing further chemical reactions at polymer chains for polymer modification, functionalization, and cross-linking. Preparation routes of reactive polymers could be divided into two categories. One is performing reactions on polymer chains to introduce reactive groups to the polymer chains. For example, incorporation of halomethyl groups to polyethersulfone has been carried out for further reactions and applications. The other approach is employing a monomer which contains a reactive group in polymerization. The resulting polymer chains consequently possess this reactive group. One example could be used as a dihydride containing a hydroxyl group in polymerization with a diamine compound. The resulting polyimide possesses hydroxyl groups for further chemical reactions. Although polymer reactions exhibit some convenience for commercial polymer products, the later approach has much flexibility on molecular designs and chemical diversity.

The chemically reactive groups play a key role in the chemical reactivity and diversity of reactive polymers. One of attractive groups to be incorporated to reactive polymer chains is Meldrum’s acid (MA) group. Under heating, MA could undergo thermolysis reaction to generate a ketene with evolving CO₂ and acetone molecules. Hence, the MA group is an effective precursor of the ketene group. Ketene has a high chemical reactivity toward nucleophiles such as hydroxyl, amine, and isocyanate groups to result in ester, amide, and azetidine-2,4-dione groups, respectively. Dimerization reaction of ketene could also take place at high temperatures to generate the corresponding 1,3-butandione group. Based on the ketene chemistry, reactive polymers possessing MA groups were first reported with Hawker et al. and then have received other researchers’ attention. Reactive polymers possessing pendent MA groups have been prepared through radical polymerization, ring-opening metathesis polymerization, and step polymerization with associated MA-containing monomers. Postfunctionalization and cross-linking reaction have been carried out on the polymers based on MA thermolysis reaction and ketene chemistry.

The MA derivatives used as the monomers in the abovementioned polymerization systems are synthesized through chemical reactions taking advantage of the reactivity of the acidic C–H bonds of MA, including Mitsunobu condensation, dehydrohalide reaction, and Knoevenagel condensation. For example, the MA derivative possessing two styrenic moieties could be obtained from the reaction of one MA and two chloromethylstyrene molecules. This concept inspires our interests in directly using MA as a difunctional monomer in polymerization systems and preparation of the corresponding MA-containing polymer chains. The first example is Michael-addition reaction-based MA polymerization, in which MA has been polymerized with a bismaleimide to result in poly(succinimide), possessing MA reactive groups at the main chains. In this work, we report a continuous effort on this topic—direct utilization of MA as a monomer in polymerization systems. As an isocyanate group is reactive toward chemical groups possessing active hydrogens, such as hydroxyl, amine, and carboxylic acid groups, the reactivity between isocyanate and the acidic C–H bonds of

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MA is reasonable. A polymerization system employing MA and a diisocyanate compound as the monomers has been established. The resulting polymers are reactive polyamides possessing MA reactive groups. Consequently, in addition to preparation of MA-containing reactive polymers, this polymerization system itself is a new synthetic route for polyamides.

2. Results and Discussion

2.1. Polymerization of MA and Difunctional Isocyanate Compounds. The reaction between the acidic C–H bonds of MA and isocyanate groups is first examined with a monofunctional isocyanate compound (IPTES) and MA. The reaction is traced with 1H NMR. As the spectra shown in Figure 1, after a reaction at 25 °C for 24 h, the decreases in the peak intensities of the acidic C\(^{-}\)N of MA (peak a) and –CH\(_2\)–NCO of IPTES support the reaction taking place between these two groups. The occurrence of the reaction also transforms the isocyanate group to amide linkage so as to result in chemical shifts of the isopropyl groups toward lower frequency (peaks b\('\) and c\('\)). Based on the reaction, two diisocyanate compounds of hexamethylene diisocyanate (HDI) and methylene diphenyl diisocyanate (MDI) were employed in this study to polymerize with MA. The polymerization reaction was carried out in dried dimethylformamide (DMF) at about 30 °C for 24 h (Scheme 1). A certain amount of lithium chloride was added to enhance the solubility of the formed polyamide in the solvent. The obtained polyamides were subjected to solubility tests (3 mg mL\(^{-1}\)) in various solvents.\(^{35}\) Poly(MA-HDI) could only be dissolved in hexafluorisopropanol (6F-IPA) and formic acid, and shows poor solubility in common polar solvents such as acetone, tetrahydrofuran (THF), DMF, dimethylsulfoxide (DMSO), and 1-methyl-2-pyrrolidone (NMP). Poly(MA-MDI) shows a relatively good organosolubility as it could be readily soluble in DMF, DMSO, NMP, 6F-IPA, and formic acid. The poor solubility of the polymers could be attributed to the interchain hydrogen bonding between the amide groups. With employing NMP as the solvent, poly(MA-MDI) shows an inherent viscosity of about 0.074 dL g\(^{-1}\). Based on the Mark–Houwink–Sakurada (MHS) equation reported to polyamide in dimethylacetamide [(\([\eta]\) (mL g\(^{-1}\)) = 0.06 × \(M^0.60\))], the estimated molecular weight of poly(MA-MDI) is about 3020 g mol\(^{-1}\). The relatively small value of inherent viscosity and low-molecular weight of poly(MA-MDI) indicate the reaction rate between MA and isocyanate is not high.

Spectral characterization of poly(MA-MDI) has been carried out with Fourier transform infrared (FTIR) (Figure 2). The absorption peaks of the C–H bonds of MA at 2930 and 3004 cm\(^{-1}\) and –NHC\(_{6}\)H\(_{4}\)C=O groups of MDI at 2275 cm\(^{-1}\) were not observed in the spectrum of poly(MA-MDI), indicating the polymerization reaction taking place between these two groups. The reaction between C–H and –NHC\(_{6}\)H\(_{4}\)C=O results in amide linkages showing absorption peaks at 1650 cm\(^{-1}\) (amide I) and 1548 cm\(^{-1}\) (amide II) in the spectrum of poly(MA-MDI). These two peaks did not appear in the spectra of MA and MDI. Poly(MA-MDI) still exhibits characteristic absorption peaks of the MA ring (ester group, 1740, 1710, and 1238 cm\(^{-1}\)) and of MDI (phenyl group, 1508 cm\(^{-1}\)) supporting to its expected chemical structure. Further characterization on poly(MA-MDI) has been carried out with \(^{13}\)C NMR. As the spectra shown in Figure 1, poly(MA-MDI) exhibits resonance peaks at \(\delta = 1.65\) ppm and \(\delta = 7.05–7.45\) ppm associating to the –CH\(_{3}\) group of MA and phenyl group of MDI, respectively. The amide linkages are characterized with the resonance peak at \(\delta = 8.52\) ppm. Meanwhile, the resonance peak of acidic C–H at \(\delta = 4.08\) ppm was not observed with poly(MA-MDI), supporting that there are no MA monomers remained in the product. The result is also supported with the \(^{13}\)C NMR analysis. The formed amide linkages show resonance peaks at \(\delta = 164–170\) ppm. It is worth noting that the resonance peak at \(\delta = 123\) ppm indicates the presence of some isocyanate groups, which should be at the chain ends as the chain lengths are not high (low inherent viscosity).

Poly(MA-MDI) shows an endothermic peak at about 235 °C followed with an exothermic peak at about 240 °C (Figure 3), associated with the MA thermolysis reaction and ketene dimerization reaction, respectively.\(^{15}\) The MA thermolysis reaction accompanies CO\(_{2}\) evolution and acetone as byproducts,\(^{15}\) so as to exhibit a weight loss at around 200 °C in thermogravimetric analysis (TGA) measurement. The theoretical weight loss fraction calculated from the repeating unit of MA–MDI is about 25.9 wt %, which is much higher than the measured value of about 12 wt %. The result might suggest that poly(MA-MDI) chains do not contain equal molar MA and MDI units. The polymer chain ends could be MDI-capped. The result is coincident to what was observed with the NMR analysis, as poly(MA-MDI) does not show resonance peaks of the acidic C–H of the MA unit in the \(^{1}H\) NMR spectrum, and demonstrates the isocyanate signal in \(^{13}\)C NMR measurement.
Poly(MA-MDI) has been subjected to a thermally cross-linking process. The corresponding cross-linked sample [CR-poly(MA-MDI)] loses its organosolubility supporting to the formation of the cross-linked structure. Nevertheless, thermal mechanical analysis on CR-poly(MA-MDI) is a failure due to its high brittleness. Although polymerization of MA and diisocyanate has demonstrated a new approach for preparation of reactive polyamides containing MA moieties, the low-
molecular weight of the obtained poly(MA-MDI) limits needs further studies on optimizing the reaction conditions.

2.2. Reactive Poly(amide-urethane) Containing MA Moieties. With the purpose of extending the molecular weight of the MA-containing reactive polymer, the chemistry for polyurethane preparation has been utilized (Scheme 2). A mixture of MA and MDI in a molar ratio of 1:2 was charged to the polymerization system to result in a diisocyanate-terminated MA−MDI precursor. Then, equipment of a diol compound, ethylene glycol (EG), poly(ethylene glycol) (PEG, number-averaged molecular weight: 200 Da), and 1,6-hexanediol (HD), was added as a chain extender. The obtained products could be reactive poly(amide-urethane)s containing reactive MA moieties and are coded as poly(MA-MDI/EG), poly(MA-MDI/PEG), and poly(MA-MDI/HD). Spectral characterization of the poly(amide-urethane)s has been carried out with FTIR and NMR. The recorded spectra of poly(MA-MDI/EG) are shown in Figure 4 as examples. The EG segments in poly(MA-MDI/EG) are characterized with the absorption peaks at 2900−3000 cm−1 (−CH2−) and 1050 cm−1 (C−O) in the FTIR spectrum. The EG segments also exhibit the resonance peak at δ = 4.15 ppm in 1H NMR and δ = 63 ppm in 13C NMR. Moreover, poly(MA-MDI/HD) also exhibits a resonance peak of methylene groups at δ = 1.35 ppm in 1H NMR and δ = 25 and 28 ppm in 13C NMR analysis (figure not shown). The MA molar content in the feeding monomer compositions (1:2:1 for MA, MDI, and diol) is 25%. The exact content of MA in the polymer chains could be calculated from the characteristic peak area in 1H NMR spectra. The value found with poly(MA-MDI/EG), poly(MA-MDI/PEG), and poly(MA-MDI/HD) is about 24, 21, and 23%, respectively. All three samples are readily soluble in the solvents which poly(MA-MDI) is soluble in. Moreover, poly(MA-MDI/HD) is also soluble in acetone. The inherent viscosity of poly(MA-MDI/EG), poly(MA-MDI/PEG), and poly(MA-MDI/HD) is about 24, 21, and 0.19 dL g−1, respectively. The molecular weight of poly(MA-MDI/EG), poly(MA-MDI/PEG), and poly(MA-MDI/HD), which has been estimated with a MHS equation reported to polyurethane ([η] (mL g−1) = 0.101 × Mw0.59)37 is about 2400, 5400, and 7200 g mol−1, respectively. The longer molecular length of the diol compound utilized in the polymerization system is the corresponding polymer has a higher molecular weight.

All three MA-containing poly(amide-urethane)s have been applied to thermal analysis to trace the MA thermolysis/ketene dimerization reaction, as what discussed on poly(MA-MDI). Not like poly(MA-MDI), the three samples did not exhibit obvious endothermic/exothermic behaviors in heating scans up to about 300 °C. This result could be attributed to their relatively low contents of MA moieties. In TGA measurements, poly(MA-MDI/EG) shows a weight loss of about 17 wt % at about 260 °C (Figure 5), which might be associated with the MA thermolysis reaction. Nevertheless, some chain-scissoring reaction might occur at this high temperature as the weight loss fraction is higher than the theoretical value of about 14 wt %, and the weight loss behavior overlaps with the major degradation region. Moreover, this stage of weight loss is not observed with poly(MA-MDI/PEG) and poly(MA-MDI/HD), as these two samples possess relatively low fractions of MA groups. To further trace the MA thermolysis/ketene dimerization reaction, FTIR spectra of poly(MA-MDI/EG) before and after thermal treatment (200 °C for 1 h and 240 °C for 1 h) are collected in Figure 6. Performance of the MA

Figure 4. Spectral characterization of poly(MA-MDI/EG) with (a) FTIR, (b) 1H NMR, and (c) 13C NMR.

Figure 5. TGA thermograms of the 3 poly(amide-urethane)s prepared in this work.
thermolysis/ketene dimerization reaction could be characterized with the absorption peak of the 1,3-butandione group at about 1900 cm\(^{-1}\).\(^{15}\) The result supports to both poly(MA-MDI/EG)-possessing reactive MA moieties and poly(MA-MDI/EG) could undergo cross-linking reaction through MA thermolysis/ketene dimerization reaction.

### 2.3. Cross-linked Poly(amide-urethane) Films

Based on the preliminary test on cross-linking reaction of poly(MA-MDI/EG), poly(MA-MDI/EG) was fabricated into films through a solution-casting method. The sample was then thermally cross-linked with a step-heating process mentioned in the Materials and Methods section to result in the corresponding samples of CR-poly(MA-MDI/EG). The other two samples of CR-poly(MA-MDI/PEG) and CR-poly(MA-MDI/HD) were also obtained with the same manner. As the three uncross-linked samples are readily soluble in NMP, the cross-linked films loses their solubility in NMP to show a gel fraction (the insoluble fraction of the sample in NMP after a test of 24 h) of 76, 86, and 82 wt % for CR-poly(MA-MDI/EG), CR-poly(MA-MDI/PEG), and CR-poly(MA-MDI/HD), respectively. The gel fractions are high enough to support the formation of cross-linked structures in the films. Nevertheless, the cross-linking might not be as high as other thermosetting resins prepared with small molecular monomers.

The three cross-linked polymers films have been applied to dynamic thermal analysis (DMA) (Figure 7). The glass transition temperature \(T_g\) of the samples taking at the tan \(\delta\) peak is 141, 87, and 128 °C for CR-poly(MA-MDI/EG), CR-poly(MA-MDI/PEG), and CR-poly(MA-MDI/HD), respectively. The values of \(T_g\)'s could be correlated to the cross-linked densities of the films as well as to the MA contents of the corresponding precursors. It is noteworthy that CR-poly(MA-MDI/EG) and CR-poly(MA-MDI/HD) show a storage modulus of about 800 MPa at glassy states (50 °C), supporting to their high mechanical strengths. The relatively long and flexible PEG segments result in a decrease in the storage modulus of CR-poly(MA-MDI/PEG) to about 400 MPa at 20 °C.

The results demonstrate that MA could be an effective precursor for preparation of cross-linkable poly(amide-urethane)s and the corresponding cross-linked poly(amide-urethane)s with good film formability, thermal stability, and mechanical properties.

### 3. CONCLUSIONS

Based on the acidic C–H bonds, MA is reactive toward isocyanate compounds. This reaction is further extended to a new polymerization method directly employing MA as a monomer. This polymerization also provides an effective route for preparation of reactive polyamides and polyurethanes containing MA moieties as the reactive groups for further modification and cross-linking reactions. Based on the polymerization chemistry of the MA compound and the reactivity of MA rings, this work has demonstrated an effective synthesis route for reactive polyamides and polyurethanes.

### 4. MATERIALS AND METHODS

#### 4.1. Materials

MA (2,2-dimethyl-1,3-dioxane-4,6-dione) and IPTES were purchased from Sigma-Aldrich Chemical Co. HDI, MDI, and 1,6-dexandiol was received from Tokyo Chemical Industry Co., Ltd. EG and PEG (200 Da) were from J. T. Baker and Alfa Aesar, respectively. Reagent grade solvents were employed after standard drying and purification processes.

#### 4.2. Instrumental Methods

FTIR analysis was conducted with a PerkinElmer Spectrum Two FTIR instrument. The spectra were collected with 16 scans at a resolution of 4 cm\(^{-1}\). The NMR instrument employed in NMR analysis \(^{\text{1}}\)H and \(^{13}\)C

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**Figure 6.** FTIR spectra of poly(MA-MDI/EG) and CR-poly(MA-MDI/EG) for tracing the cross-linking reaction based on MA thermolysis and ketene dimerization reactions.

**Figure 7.** DMA thermograms of the cross-linked poly(amide-urethane): (a) CR-poly(MA-MDI/EG), (b) CR-poly(MA-MDI/PEG), and (c) CR-poly(MA-MDI/HD).
NMR) is Varian UnityINOVA 500 NMR (500 MHz) NMR. Thermal analysis was conducted with instruments from Thermal Analysis (TA) Instruments Company. Differential scanning calorimetry (DSC) measurements were carried out with a TA DSC Q-100 instrument under a nitrogen flow at 50 mL min⁻¹ and a heating rate of 10 °C min⁻¹. TGA thermograms were recorded with a TA TGA Q-500 instrument at a heating rate of 10 °C min⁻¹ and a nitrogen flow rate of 100 mL min⁻¹. A TA DMA Q-800 instrument was employed for dynamic thermomechanical analysis. The samples were mounted with a film holder for measurements. The heating rate, applied force, frequency, and ad amplitude is 3 °C min⁻¹, 0.1 N, 1 Hz, and 10 μm, respectively.

4.3. Preparation of Polyamides. Poly(MA-MDI) was prepared with the polymerization between MA and MDI. The monomers of MA (1.0 g, 6.94 mmol) and MDI (1.76 g, 6.94 mmol) were dissolved in dried DMF (20 mL). After addition of methanol, the solution was then heated under vacuum at room temperature. Puriﬁcation was performed with the dissolution–precipitation process twice. Poly(MA-MDI) was obtained as light yellow powder (2.57 g, yield: 94%). Poly(MA-HDI) was prepared in the same manner employing MA and HDI as the monomers.

4.4. Preparation of Poly(amide-urethane). Poly(MA-MDI/EG) was prepared with two-step polymerization in an one-pot reaction. MA (0.5 g, 3.47 mmol) and MDI (7.736 g, 6.94 mmol) were dissolved in dried DMF (20 mL). The solution was reacted at room temperature for 24 h. After addition of EG (0.215 g, 3.47 mmol), the solution was then reactivated at 70 °C for another 2 h. The solution was added to excess methanol dropwise. The precipitant was collected with filtration and dried under vacuum at room temperature. Purification of the product was performed with the dissolution–precipitation process twice. Poly(MA-MDI/EG) was obtained as light yellow powder (2.24 g, yield: 91 wt %). Poly(MA-MDI/PEG) and poly(MA-MDI/HD) were obtained in the same manner.

4.5. Preparation of Cross-linked Poly(amide-urethane) Films. Taking CR-poly(MA-MDI/EG) as an example, a solution of poly(MA-MDI/EG) in NMP (25 wt %) was prepared and then degassed, with standing for 48 h. The solution was casted on a glass plate with a blade knife with a gap of 300 μm. The sample was put in an oven at 80 °C for 24 h for removal of solvent and then thermally cross-linked at 120, 160, 200, and 240 °C. The reaction time for each temperature is 1 h. After being cooled, the sample was immersed into a water/ethanol bath (v/v: 1/1) for being detached from the glass substrate. The film was then dried at 60 °C under vacuum for 3 h.

Author Contributions

Y.-C.C. and Y.-L.L. gave the original concepts of this work and designed the experiments. Y.-C.C. carried out the experiments on polymerization and material characterization. C.-H.H. contributed to the NMR traces on the model reaction between MA and isocyanates. The manuscript was written through contributions of all the authors. All the authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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