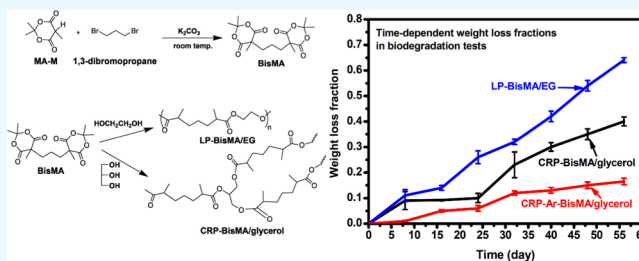


# Effective Synthesis Route for Linear and Cross-Linked Biodegradable Polyesters Using Aliphatic Meldrum's Acid Derivatives as Monomers

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**ABSTRACT:** On the basis of the reaction between ketene and alcohol groups to result in an ester linkage and Meldrum's acid as an effective precursor of ketene group, a bifunctional aliphatic Meldrum's acid compound (BisMA) is synthesized and used as a monomer to react with ethylene glycol and glycerol for the preparation of linear and cross-linked aliphatic polyesters, respectively. A 62 and 35 wt % of biodegradation fraction have been recorded on the linear and cross-linked aliphatic polyesters after an 8 week biodegradation test, respectively, to demonstrate the good biodegradability of the synthesized polyesters. In addition to conventional linear biodegradable polyesters, this synthetic route also provides a new and convenient method for preparation of cross-linked biodegradable polyesters. The types of the required monomers and reaction methods for preparation of the cross-linked biodegradable polyesters are similar to those used for conventional thermosetting resins. An integration of biodegradable polymers and thermosetting resins in polymer chemistry has been demonstrated.



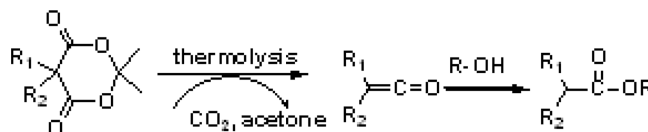
## 1. INTRODUCTION

In contrast to common polymers, biodegradable polymers are attractive for practical applications and environmental issues.<sup>1–3</sup> Biodegradable polymers possessing nontoxic and biocompatible characteristics are attractive biomaterials suitable for biomedical and bioengineering application.<sup>4,5</sup> Introduction of hydrolytic linkages, such as esters, anhydrides, carbonates, amides, urethanes, ureas, etc., to the polymer chains could be the basis of molecular designs of synthetic biodegradable polymers.<sup>1,6</sup> Nevertheless, this requirement pretty limits the monomers and polymerization routes required for preparation of synthetic polymers possessing biodegradability.

Biodegradable polyesters could be the most studied biodegradable polymers.<sup>6</sup> Synthesis of biodegradable polyesters could be achieved with two general approaches.<sup>7</sup> One is ring-opening polymerization using cyclic lactones as monomers. Lactides and the corresponding poly(lactide)s have been widely utilized in the commercial markets. This family of biodegradable polyesters has some drawbacks, including limited source of monomers, poor molecular design flexibility of monomers and polymers, and relatively poor thermal stability of polymers. The other approach to prepare biodegradable polyesters is polycondensation using aliphatic diacids and diols as monomers,<sup>8</sup> which provides a relatively wide window of structure designs to the biodegradable polyesters. Nevertheless, the low reactivity between aliphatic acids and diols limits the development of biodegradable polyesters prepared with this reaction route. As the diversity of biodegradable polymer structures plays a key factor to their properties, development of new synthesis routes with high molecular design flexibility is attractive for biodegradable polyesters.

Ketene is a highly reactive group toward nucleophiles.<sup>9</sup> Reaction between a ketene with a hydroxyl group (as the

nucleophile) forms an ester linkage. This reaction potentially provides an alternative synthetic route for ester compounds and polyesters. Nevertheless, ketene compounds could not be directly utilized in the synthetic method due to their high reactivity and less controllability. As Meldrum's acid (MA) group is an effective precursor of ketene,<sup>10–14</sup> Hawker et al.<sup>15</sup> reported a facile synthesis route of high-molecular-weight aromatic polyesters using MA derivatives as monomers based on the abovementioned ketene chemistry.



This MA-based synthesis route of polyesters<sup>15</sup> inspires our work on synthesis of biodegradable polyesters with MA derivatives as monomers. To target on preparation of aliphatic polyesters with biodegradability, a bifunctional aliphatic MA compound (BisMA) is newly synthesized in this work. BisMA has been utilized as a monomer to be reacted with an aliphatic diol (ethylene glycol (EG)) to result in the corresponding linear aliphatic polyester. We have also demonstrated the synthesis of biodegradable thermosetting resins by reacting BisMA with a triol (glycerol) through a procedure similar to the conventional processes for the preparation of thermosetting resins. On the basis of our best knowledge, this is the first example of preparation of biodegradable thermosetting resins through the conventional thermally induced curing processes. The biodegradability of the obtained polyesters has been

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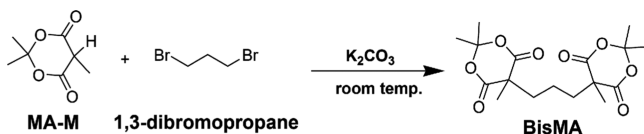
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evaluated to support the new synthesis route for biodegradable polyesters.

## 2. RESULTS AND DISCUSSION

**2.1. Preparation of Aliphatic Bifunctional MA Derivative.** To introduce biodegradability to synthetic polyesters, fully aliphatic polyesters are designed and prepared. The first step is synthesis of an aliphatic bifunctional MA derivative (BisMA) as the monomer. As shown in Scheme 1, BisMA is

**Scheme 1. Synthesis of Bifunctional Aliphatic Meldrum's Acid Compound BisMA**

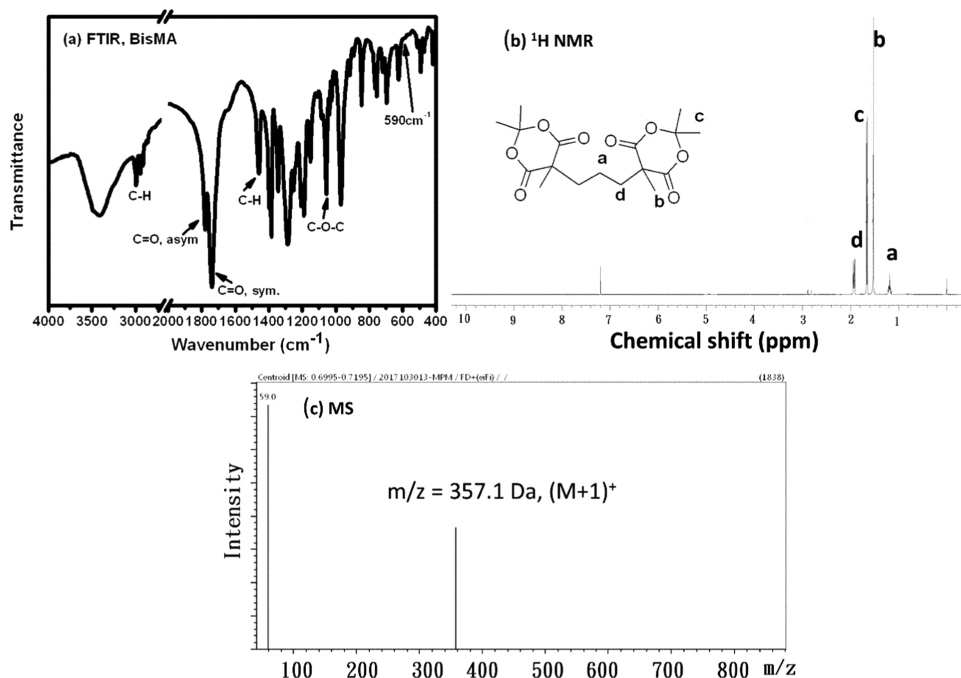


obtained from the dehydrobromide reaction between dibromopropane (DBP) and 2,2,5-trimethyl-1,3-dioxane-4,6-dione (methyl Meldrum's acid, MA-M). Spectral characterization of BisMA has been done with Fourier transform infrared (FTIR) spectroscopy,  $^1\text{H}$  nuclear magnetic resonance spectroscopy ( $^1\text{H}$  NMR), and mass spectroscopy (Figure 1). In FTIR analysis, BisMA exhibits specific absorption peaks of MA ring at  $1781\text{ cm}^{-1}$  ( $-\text{C}=\text{O}$  asymmetric stretching),  $1740\text{ cm}^{-1}$  ( $-\text{C}=\text{O}$  symmetric stretching), and  $1050\text{ cm}^{-1}$  ( $\text{C}-\text{O}-\text{C}$ ), as well as absorption peaks of  $-\text{CH}_2-$  groups at  $2970\text{ cm}^{-1}$  (stretching) and  $1445\text{ cm}^{-1}$  (bending). The  $\text{C}-\text{Br}$  absorption, which appears in the spectrum of DBP at  $590\text{ cm}^{-1}$ , is not observed with BisMA. The above results suggest occurrence of the condensation reaction between DBP and MA-M and the formation of the expected product of BisMA. The  $^1\text{H}$  NMR spectrum of BisMA provides further support to the successful synthesis of BisMA with the coincidence between the expected chemical structure of BisMA and the resonance peaks at  $\delta =$

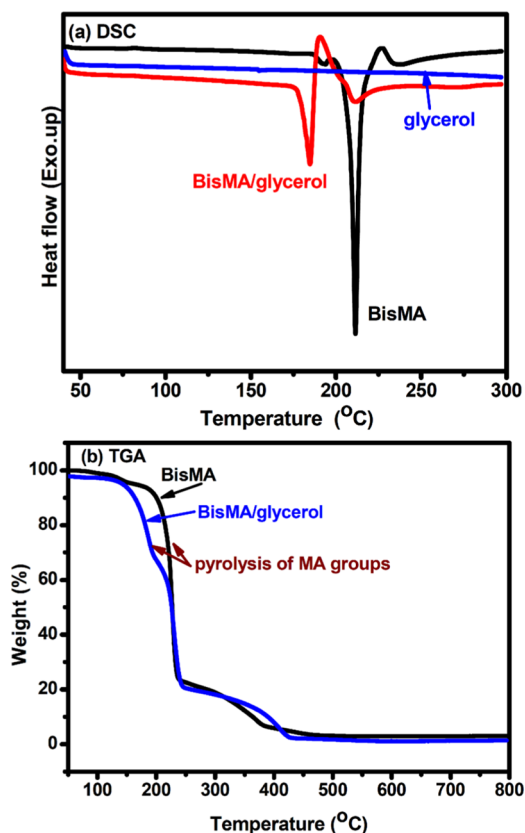
$1.18\text{ ppm}$  ( $-\text{CH}_2\text{CH}_2\text{CH}_2-$ ),  $\delta = 1.52\text{ ppm}$  ( $-\text{C}(=\text{O})\text{CCH}_3$ ),  $\delta = 1.65\text{ ppm}$  ( $-\text{OC}(\text{CH}_3)_2$ ), and  $\delta = 1.93\text{ ppm}$  ( $-\text{CH}_2\text{CH}_2\text{CH}_2-$ ). The molecular weight calculated for BisMA ( $\text{C}_{17}\text{H}_{24}\text{O}_8$ ) is  $356.37\text{ g mol}^{-1}$ , which is matched with the value ( $m/z = 357\text{ Da}$ ,  $(\text{M} + 1)^+$ ) measured with MS. Moreover, elemental analysis reveals that the obtained BisMA sample has a C and H weight fraction of 57.3 and 6.80%, respectively. Both are highly coincident to the calculated value of 57.3% for C and 6.79% for H. The results support the chemical structure and high purity of the obtained BisMA compound.

BisMA shows a sharp endothermic peak at about  $210\text{ }^\circ\text{C}$  in differential scanning calorimetry (DSC) measurement (Figure 2), which corresponds to its melting behavior. The sharp melting peak also supports the high purity of the obtained BisMA sample. Moreover, this endothermic peak somewhat overlaps with a relatively small exothermic behavior, corresponding to the thermolysis of MA groups. Generation of ketene groups with MA thermolysis and further ketene dimerization reactions takes place at such high temperatures.<sup>15</sup> The MA thermolysis reaction of BisMA evolves one acetone and one  $\text{CO}_2$  molecule, so as to exhibit a rapid weight loss at about  $220\text{ }^\circ\text{C}$  in the thermogravimetric analysis (TGA) thermogram of BisMA. The results from both DSC and TGA analysis show good coincidence and support to the proposed reactions. The thermal analysis result of BisMA indicates that this compound possesses reactive MA groups for further reactions.

**2.2. Preparation of Polyesters with BisMA.** BisMA is utilized as a bifunctional monomer to react with multifunctional alcohol compounds for preparation of polyesters. The reaction involves generation of ketene groups through MA thermolysis reaction and formation of ester linkages by means of the addition reaction between ketene and hydroxyl groups.<sup>15</sup> As hydroxyl groups have been reported to show effective catalysis effect on MA thermolysis reaction,<sup>15,16</sup> the mixture of BisMA



**Figure 1.** Spectral characterization of BisMA with (a) FTIR, (b)  $^1\text{H}$  NMR, and (c) mass spectroscopies.

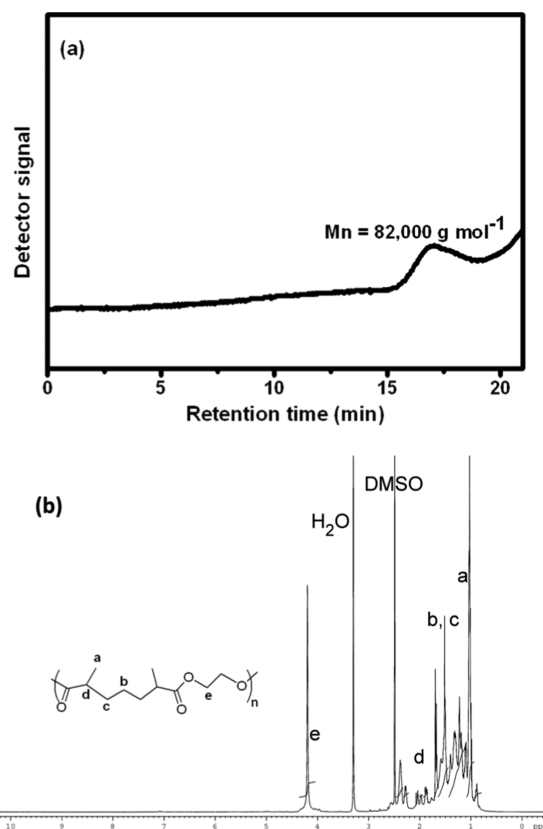


**Figure 2.** Thermal analysis on BisMA and its mixtures with glycerol using (a) DSC and (b) TGA instruments.

and glycerol might show a relatively low reaction temperature compared to the neat BisMA, as demonstrated with the DSC thermograms shown in Figure 2. BisMA/glycerol mixture shows an endothermic peak at about 160 °C and a following exothermic peak at about 184 °C in DSC analysis. A similar result is observed with TGA measurement, in which BisMA/glycerol mixture shows a rapid weight loss at about 160–180 °C, compared to the temperature of 220 °C recorded with neat BisMA. As the weight loss temperature is much lower than the boiling point of glycerol (290 °C), the weight loss is attributed to the occurrence of glycerol-catalytic MA thermolysis reaction. Once the ketene groups form with the MA thermolysis

reaction, they react with the hydroxyl groups to result in polyesters.

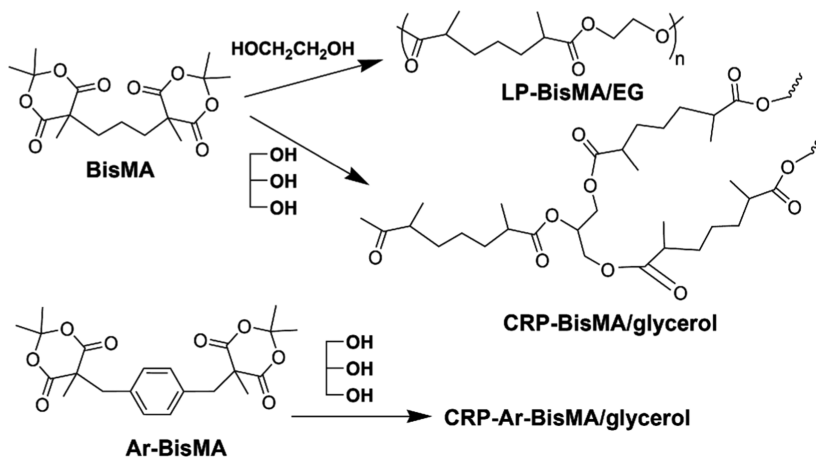
Linear and cross-linked aliphatic polyesters have been prepared through a bulk polymerization process with BisMA/EG and BisMA/glycerol as monomers, respectively (Scheme 2). LP-BisMA/EG shows good solubility in organic solvents and has a number-averaged molecular weight and polydispersity of 82 000 g mol<sup>-1</sup> and 2.2, respectively (Figure 3a). On the

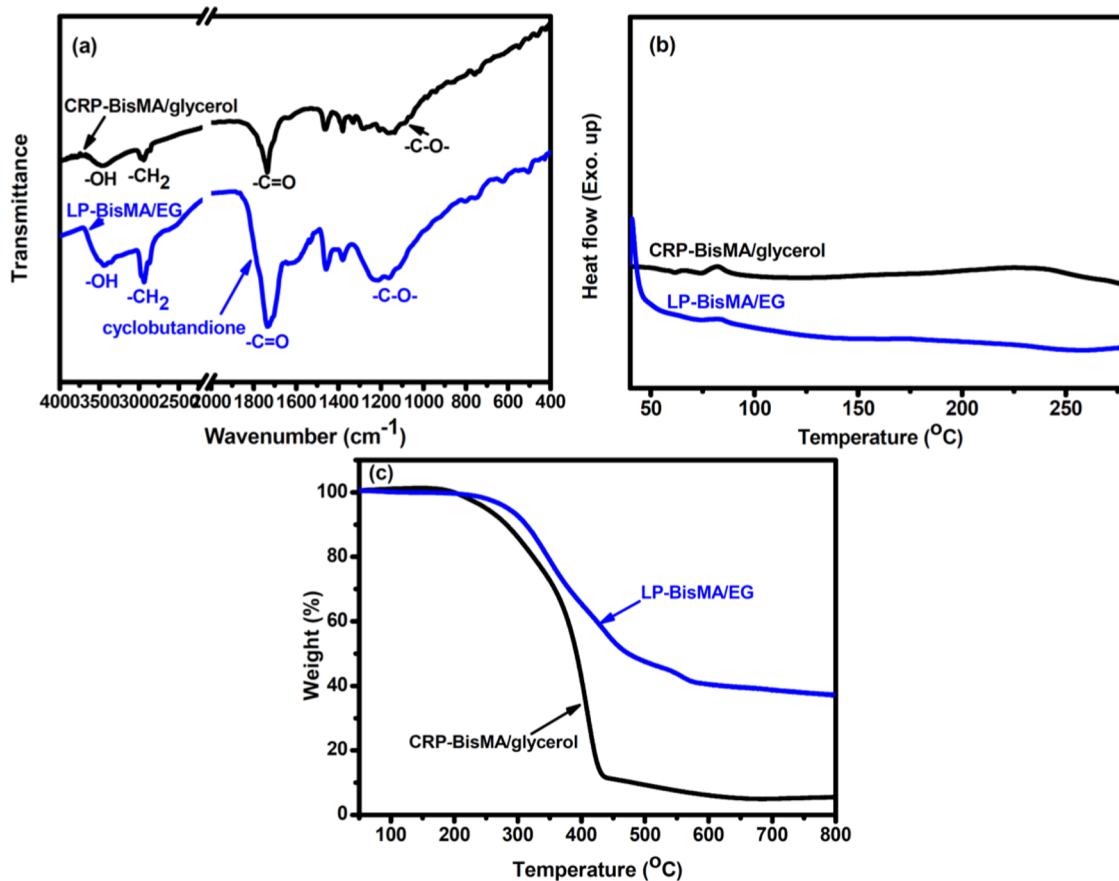


**Figure 3.** (a) Gel permeation chromatogram and (b) <sup>1</sup>H NMR spectrum of LP-BisMA/EG.

basis of its solubility in organic solvent, LP-BisMA/EG has been characterized with <sup>1</sup>H NMR (Figure 3b). The formation of EG-based ester structure is characterized with the resonance

#### Scheme 2. Polymerization of BisMA and Alcohol Compounds for Preparation of Linear and Cross-Linked Aliphatic Polyesters





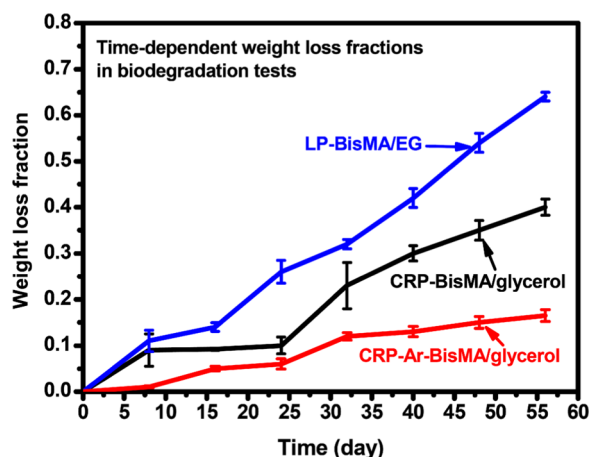
**Figure 4.** (a) FTIR, (b) DSC, and (c) TGA measurements on linear (LP-BisMA/EG) and cross-linked (CRP-BisMA/glycerol) aliphatic polyesters.

peaks at about  $\delta = 4.2$  ppm corresponding to the  $-\text{C}(=\text{O})\text{OCH}_2-$  groups. Addition reaction of  $-\text{OH}$  groups of EG to the ketene groups generated from MA-M thermolysis results in  $-\text{CH}-\text{C}(=\text{O})$  groups, which result in the resonance peaks at about  $\delta = 1.9$ – $2.0$  ppm. The resonance peaks at about  $\delta = 1.1$  and  $1.3$ – $1.6$  ppm are assigned to the  $-\text{CH}_3$  group and the methylene groups of  $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$  segments, respectively. Because of possessing a cross-linked structure, CRP-BisMA/glycerol is not soluble in organic solvents. A high gel fraction of 95% has been measured with CRP-BisMA/glycerol in toluene. Moreover, CRP-BisMA/glycerol shows a glass transition temperature of about  $-16$  °C ( $\tan \delta$ ) measured with a dynamic mechanical analyzer (DMA).

Both polyesters have been characterized with FTIR (Figure 4) and show similar characteristic absorption peaks of ester linkages at  $1730\text{ cm}^{-1}$  and  $-\text{CH}_2-$  groups at  $2970\text{ cm}^{-1}$ . The MA absorption is not observed with the polyester samples. Moreover, compared to the linear polyester (LP-BisMA/EG), the cross-linked aliphatic polyester (CRP-BisMA/glycerol) prepared with BisMA and glycerol shows a relatively strong absorption of  $-\text{OH}$  groups at about  $3450\text{ cm}^{-1}$  (compared to the ester absorption as a reference), indicating that some unreacted  $-\text{OH}$  groups of glycerol are remained in the sample. On the other hand, LP-BisMA/EG shows an absorption at about  $1810\text{ cm}^{-1}$  corresponding to the  $\text{C}=\text{O}$  groups of 1,3-butandione, which are formed from the ketene dimerization reaction. The results suggest that in the polymerization process of BisMA and EG, ketene might involve in both esterification and dimerization reactions. For the reaction between BisMA and glycerol, the dimerization of ketene becomes minor.

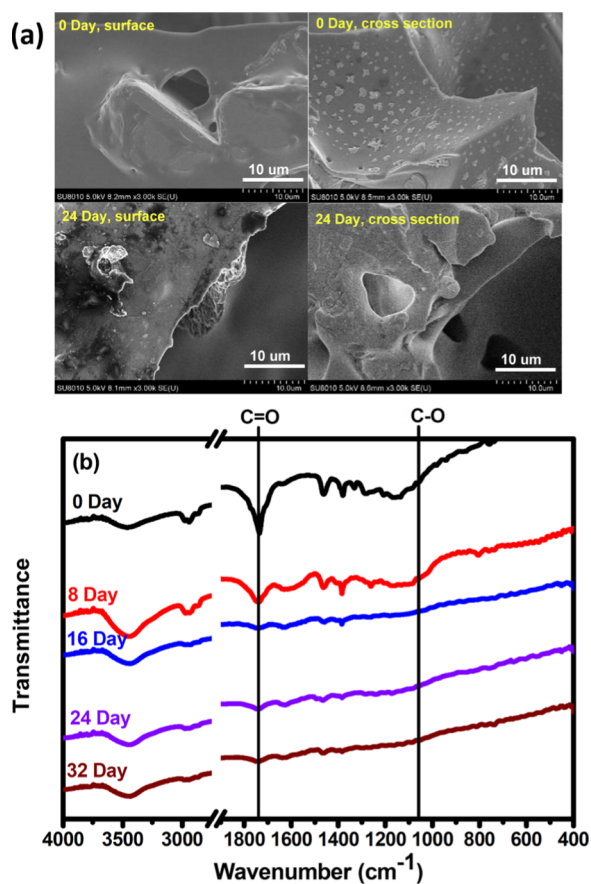
Both polyesters do not exhibit obvious endothermic and exothermic behaviors in DSC measurements (Figure 4), indicating the high conversion of MA thermolysis reaction in the polymerization processes. Moreover, no crystallization transitions were observed with these two polyesters, which are similar to some polyesters reported in literature.<sup>15</sup> In TGA measurements, the temperature of 5% weight loss ( $T_{\text{ds}}$ ) recorded on LP-BisMA/EG and CRP-BisMA/glycerol is  $247$  and  $267$  °C, respectively. The degradation patterns of the two polyesters are also different. Compared to CRP-BisMA/glycerol, LP-BisMA/EG shows a multiple weight loss behavior and better thermal stability, although CRP-BisMA/glycerol possesses some cross-linked structure. As a result, the relatively high thermal stability and retarded weight loss behavior of LP-BisMA/EG could be attributed to its cyclic 1,3-butandione structures mentioned in the discussion on FTIR analysis.

**2.3. Biodegradation Tests.** The biodegradability of the prepared aliphatic polyesters is evaluated with a catalytic biodegradation method. For comparison, a cross-linked polyester possessing aromatic structures (CRP-Ar-BisMA/glycerol) is also prepared using Ar-BisMA and glycerol as monomers (Scheme 2). In an 8 week test, the time-dependent weight fractions of the samples have been recorded and shown in Figure 5. Compared to the semiaromatic cross-linked polyester CRP-Ar-BisMA/glycerol, both aliphatic polyesters show relatively high rate and high fractions of weight losses in the biodegradation tests. The result is reasonable and falls into the general knowledge. On the other hand, after 8 weeks, the weight losses found with LP-BisMA/EG and CRP-BisMA/glycerol are  $62$  and  $35$  wt %, respectively. Both aliphatic



**Figure 5.** Time-dependent weight loss fractions of the prepared polyesters in biodegradation tests.

polyesters prepared with BisMA demonstrate sufficient biodegradation characteristics. The biodegradability of the linear sample of LP-BisMA/EG is relatively high compared to the cross-linked CRP-BisMA/glycerol. The weight loss fractions readily increased with increasing the testing time, which is similar to poly(lactide)s<sup>17</sup> and suggests both BisMA-based polyesters perform a degradation pattern from surface to inner parts. The scanning electron micrographs (Figure 6) support the results. The smooth surface of CRP-BisMA/



**Figure 6.** (a) Scanning electron micrograms and (b) FTIR spectra tracing the morphological and chemical structural changes of CRP-BisMA/glycerol in biodegradation tests, respectively.

glycerol before biodegradation test becomes rough after a 24 day test due to the biodegradation erosion. The erosion also generates some porous structure in the inner part of the sample, indicating the catalytic medium might permeate into the sample in the biodegradation process. This result is coincident to the weight loss pattern shown in Figure 5, in which an increased weight loss rate is observed with CRP-BisMA/glycerol after 24 days. In summary, the biodegradation of CRP-BisMA/glycerol starts at the sample surface and is followed by an erosion effect inside the sample caused by the permeation of the catalytic medium.

### 3. METHODS AND MATERIALS

**3.1. Materials.** MA-M (97%), DBP (99%), ethylene glycol (EG, 99%), and glycerol (99%) were purchased from Sigma-Aldrich Chemical Co. and used as received. Potassium carbonate ( $K_2CO_3$ ) and hydrochloric acid were received from Showa Chemical Co. The bifunctional MA compound possessing aromatic group was prepared in our laboratory according to the reported method<sup>13</sup> and coded as Ar-BisMA.

**3.2. Instrumental Methods.** FTIR spectra were recorded with a PerkinElmer Spectrum Two FTIR instrument with a resolution of  $4\text{ cm}^{-1}$  and 16 scans.  $^1H$  NMR spectra were obtained with a Varian Unity INOVA 500 NMR (500 MHz) spectrometer using  $CDCl_3$  as a solvent. Elemental analysis was conducted with a Heraeus CHN-O rapid elemental analyzer using acetanilide as a standard. Mass spectra were recorded with a JEOL AccuTOF GCX mass analyzer using a field desorption atomizer. DSC measurements were taken with a differential scanning calorimeter Q-100 instrument from Thermal Analysis (TA) Instrument Company with a nitrogen flow at  $50\text{ mL min}^{-1}$  and a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$ . TGA thermograms were recorded with a TA TGA Q-500 instrument at a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$  and a nitrogen flow rate of  $100\text{ mL min}^{-1}$ . Dynamic mechanical analysis was carried out with a TA DMA Q-800 instrument using a three-point bending mode with an applied force of 0.1 N, a frequency of 1 Hz, and an amplitude of  $10\text{ }\mu\text{m}$ .

**3.3. Preparation of BisMA.** MA-M (2.0 g, 12.66 mmol) and  $K_2CO_3$  (2.62 g, 19.0 mmol) were dissolved in dried  $N,N$ -dimethylformamide (DMF, 15 mL). The solution was charged into a 25 mL round-bottom flask. A solution of DBP (1.22 g, 6.0 mmol) in 3 mL of DMF was added dropwise. The mixture was then reacted at room temperature (about  $25\text{ }^\circ\text{C}$ ) for 20 h. After being added 2.0 mL of HCl (aq) (10 wt %), the solution was extracted with chloroform (20 mL) for three times. The collected organic phase was dried over anhydrous  $MgSO_4$ . After removal of chloroform with a rotary evaporator, the product was obtained with precipitation from excess toluene (yield: 20%).

**3.4. Preparation of Polyesters.** Polymerization of BisMA (Ar-BisMA) and alcohol compounds was carried out in a similar manner as reported in the literature.<sup>15</sup> For BisMA and EG, a stoichiometric amount of BisMA and EG was charged into an ampoule. The reaction was carried out at  $190\text{ }^\circ\text{C}$  for 20 min. The product (LP-BisMA/EG) was dissolved in 6F-isopropanol and precipitated from excess methanol. For BisMA/glycerol, a stoichiometric amount of BisMA and glycerol was mixed and poured into a Teflon-coated stainless mold. The product (CRP-BisMA/glycerol) was obtained after a reaction at  $180\text{ }^\circ\text{C}$  for 0.5 h and  $200\text{ }^\circ\text{C}$  for 0.5 h. CRP-Ar-BisMA/glycerol was prepared in the same manner using Ar-BisMA and glycerol as the monomers.

**3.5. Measurement of Gel Fraction.** A dried CRP-BisMA/glycerol sample (weight:  $W_0$ ) was immersed in toluene for 24 h. After being drawn out the wetted sample was treated with an oil-absorbing paper to remove the liquid on the sample surface and then weighed ( $W_1$ ). The gel fraction (%) of the sample was calculated from  $W_1/W_0 \times 100\%$ .

**3.6. Biodegradation Test.** Polyester thin films with a thickness of about 500  $\mu\text{m}$  were punched into disklike samples with a diameter of 7.0 mm. A solution of lipase II (from porcine pancreas) in Dulbecco's phosphate-buffered saline (10 U  $\text{mL}^{-1}$ ) was utilized as the degradation medium. Polyester samples were incubated in the degradation medium at 37  $^\circ\text{C}$  for 8 weeks. The used medium was freshly changed every 2 days. The biodegradation was evaluated with weight measurements on the samples every week. Samples (three pieces) were washed with distilled deionized (dd) water, immersed in ethanol and dd water for 24 h, and dried for weight measurement.

## 4. CONCLUSIONS

Multifunctional aliphatic Meldrum's acid compounds are effective monomers for preparation of aliphatic polyesters showing biodegradability similar to the aliphatic polyesters from other polymerization methods. The synthetic route demonstrates a high flexibility of molecular designs of biodegradable polyesters. Moreover, with multifunctional aliphatic Meldrum's acid compound and aliphatic triols as monomers, this preparation method also provides a direct synthesis of biodegradable cross-linked aliphatic polyesters.<sup>18</sup> As the reaction routes are similar to those for conventional thermosetting resins, the developed synthesis method shows a good integration between biodegradable polymers and thermosetting resins.

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### Author Contributions

L.-K.L. and Y.-L.L. gave the original concepts of this work and designed the experiments; L.-K.L. carried out the experiments on synthesis and characterization. L.-K.L. and J.W. worked on the biodegradation tests. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

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