

Synthesis, characterization, and cyclopolymerization of a functional non-symmetric divinyl monomer

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Received 31 December 2006; received in revised form 8 July 2007; accepted 15 July 2007

Available online 19 July 2007

Abstract

A non-symmetric divinyl monomer with terminal carboxylic acid functionality was readily synthesized from the reaction of ethyl α -hydroxymethylacrylate (EHMA) with maleic anhydride. The new monomer (EHMA–MA) was homopolymerized in both bulk and ethyl acetate using AIBN as an initiator to give cyclopolymers. The synthesis of the monomer and cyclopolymers were followed by ^{13}C NMR, ^1H NMR, and FTIR. ^1H NMR was also utilized to obtain the degree of cyclization of the polymers, which were found to be 95% or higher in all cases. The molecular weights of the cyclopolymers were around 40–60,000 g/mol as estimated by SEC. The cyclopolymers were thermally stable up to 150 °C. Although the cyclopolymers obtained were not water-soluble; they were soluble in aqueous 1 M NaOH solution. In addition to the carboxylic acid functionality present, the cyclopolymers also had an ethyl ester and a lactone moiety. These functional groups were reacted with hexylamine to obtain a polymer with imide and amide moieties.

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Keywords: Cyclopolymer; Functional polymers; Non-symmetric divinyl monomer

1. Introduction

Cyclopolymerizations of divinyl monomers have been extensively studied since the pioneering work of Butler involving diallyldimethylammonium bromide [1]. It has been shown that polymerization of 1,6-dienes proceeds through sequential intramolecular–intermolecular propagation to give soluble polymers containing cyclic structures in the main chain [2,3]. In contrast to typical vinyl polymers, more than two unique carbon atoms are included in the backbone of the cyclopolymers, allowing more variation in chemical and physical properties of polymers obtained [4]. For example, incorporation of heteroatoms and various functional moieties into the ring structure (and therefore into the backbone of the polymer) is possible through the

design and synthetic manipulation of the monomer before polymerization [4,5]. Cyclopolymers offer several general advantages over the typical vinyl polymers including increased polymer backbone rigidity and glass transition temperature as well as lower shrinkage [6,7]. Cyclopolymers have been used in a number of applications such as water treatment and purification, personal care formulations, and medical products [8].

A generally accepted assumption in this field is that equal reactivity of the two vinyl groups in the monomer is important to achieve efficient cyclization, and our group has mostly focused on the design and synthesis of symmetric monomers containing identical vinyl groups [9,10]. For instance, syntheses of various cyclopolymers from ether, malonitrile, and amine-linked acrylate dimers have been described. However, we have also cyclopolymerized non-symmetric monomers such as the cinnamate ester derivatives of α -hydroxymethylacrylates [11], ethyl α -allyloxymethylacrylate [4], and non-symmetric monomers containing *N*-vinylformamide groups in the β -position to the methacrylate double bond [12].

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In the present work, we report the synthesis and characterization of a new non-symmetric functional monomer (EHMA–MA) and its cyclopolymers. The cyclopolymers contain multiple functional sites which could be used to control solubility through pH and for further derivatization chemistry. The cyclopolymers contained carboxylic acid plus linear and cyclic ester functionalities, which were reacted with hexylamine to obtain imide and amide linkages. The different functional groups available in the cyclopolymer present opportunities for further chemistry, i.e. cleavage of functional groups under acidic or basic conditions to obtain more hydrophilic cyclopolymers with combinations of acid and hydroxyl functionalities.

2. Experimental section

2.1. Materials

Ethyl α -hydroxymethylacrylate (EHMA) was purchased from Nippon Shokubai Inc. Maleic anhydride (MA) and 4-*N,N*-dimethylaminopyridine (DMAP) were purchased from Aldrich Chemical Company. All solvents were purchased from Acros Chemical Company, Fisher Scientific, or Aldrich Chemical Company. 2,2'-Azobisisobutyronitrile (AIBN) was purchased from Aldrich and recrystallized from methanol twice before use. All other chemicals were used as-received.

2.2. Measurements

^{13}C and ^1H NMR spectra were collected on a Varian 300 MHz NMR with CDCl_3 and $\text{DMSO}-d_6$ solvents containing tetramethylsilane (TMS) as internal reference. FTIR spectra were recorded on a Mattson Galaxy Series FTIR 5000 spectrometer using either pressed KBr pellets or NaCl plates. Thermal analyses were performed on a TA Instruments analyzer equipped with differential scanning calorimeter (2920 MDSC) and thermal gravimetric analyzer (2960 SDT) cells using heating rates of $10\text{ }^\circ\text{C}/\text{min}$ under nitrogen purge. Absolute molecular weights and molecular weight distributions were obtained by the Viscotek SEC with low angle light scattering using *N,N*-dimethylformamide (DMF) as eluent.

2.3. Synthesis of the functional divinyl monomer (EHMA–MA)

Ethyl α -hydroxymethylacrylate (6.5 g, 50 mmol) and DMAP (0.3 g, 2.5 mmol) were mixed in 50 mL CHCl_3 in a 100 mL three-neck round-bottom flask. An addition funnel containing maleic anhydride (5.2 g, 50 mmol) dissolved in 25 mL CHCl_3 and a condenser were attached to the flask. The flask was closed with rubber septa, purged with N_2 , and kept in an ice bath to adjust the temperature to $0\text{ }^\circ\text{C}$. Maleic anhydride was added to the flask drop-wise over 1 h with continuous stirring. The final mixture was then allowed to react for 1 h at $0\text{ }^\circ\text{C}$, 2 h at ambient temperature, and 20 h at $60\text{ }^\circ\text{C}$, respectively. After completion of the reaction, the mixture was extracted with water (100 mL) and the organic layer

was separated and extracted two more times with water to remove unreacted maleic anhydride. The organic layer was collected and treated with 1 M KHCO_3 to obtain the carboxylic acid salt of the monomer. The mixture was extracted with CHCl_3 three times. The aqueous layer containing the monomer salt was treated with 1 M HCl which formed an organic layer that was separated from the aqueous layer. The organic layer was extracted with CHCl_3 which was then evaporated using a rotary evaporator. The final product was dried in a vacuum oven at $40\text{ }^\circ\text{C}$ for 24 h to give a yellow liquid monomer (8.5 g) with 75% yield.

2.4. Synthesis of cyclopolymers

The monomer EHMA–MA was polymerized either in bulk using 1 mol% AIBN or in ethyl acetate using 5.0 and 0.5 mol% AIBN. A typical bulk polymerization was carried out as follows. The EHMA–MA monomer (0.46 g, 2 mmol) and AIBN (3.3 mg, 0.02 mmol) were mixed in a glass test tube. The tube was closed with a rubber septum and purged with N_2 using two needles for gas inlet and outlet. The tube was then placed in an oil bath adjusted to $75\text{ }^\circ\text{C}$ and the mixture was stirred for 16 h. At the end of the polymerization, the mixture had become very viscous. Upon cooling to ambient temperature, the mixture solidified. CHCl_3 was added to the tube and an insoluble white solid product was obtained. The white solid was dissolved in methanol and precipitated into CHCl_3 . The precipitation process was repeated two more times. Finally, the product was filtered and dried in a vacuum oven at $60\text{ }^\circ\text{C}$ for 24 h to give the white powdery cyclopolymer (0.24 g) with 52% yield.

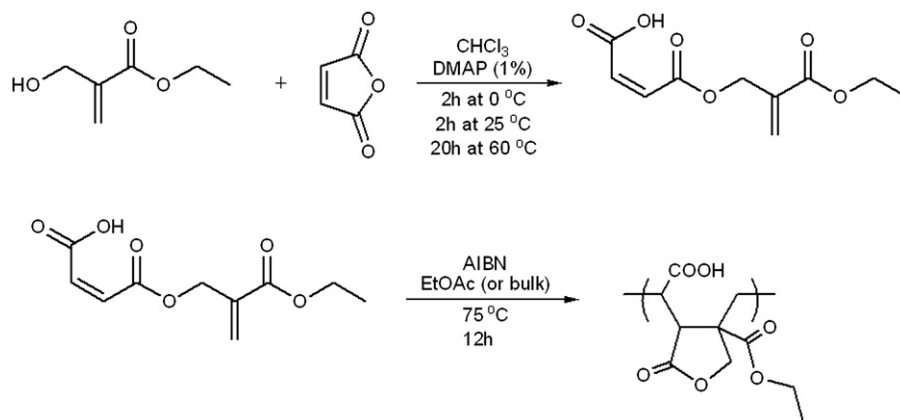
Essentially the same procedure was used for the solution polymerization of the monomer. The EHMA–MA monomer (0.46 g, 2 mmol), AIBN (1.6 mg, 0.01 mmol, 0.5 mol% or 16 mg, 0.1 mmol, 5 mol%), and ethyl acetate (1.2 mL) were mixed and polymerized under N_2 atmosphere at $75\text{ }^\circ\text{C}$ to give white powdery cyclopolymers as precipitates (0.16 g, 35% yield or 0.3 g, 65% yield, respectively).

2.5. Reaction of cyclopolymer with hexylamine

The cyclopolymer (0.9 g) was mixed with excess hexylamine (5 mL) at $130\text{ }^\circ\text{C}$ in a 10 mL round-bottom flask and the mixture was stirred at this temperature for 24 h. At the end of the reaction time, the excess hexylamine was distilled off and the final yellow solid was washed with water and aqueous HCl (1 M) extensively to remove residual hexylamine. The solid product was then dissolved in diethyl ether and precipitated into hexane twice. Finally, the white solid was filtered and dried in a vacuum oven at ambient temperature overnight to give a white polymer (1.2 g) in 70% yield.

3. Results and discussion

The general route for the synthesis of the EHMA–MA monomer and its cyclopolymer is shown in Scheme 1 below.



Scheme 1. Synthesis of the EHMA–MA monomer and its cyclopolymer.

Possible structures for the repeat units in the polymer are given in Scheme 2.

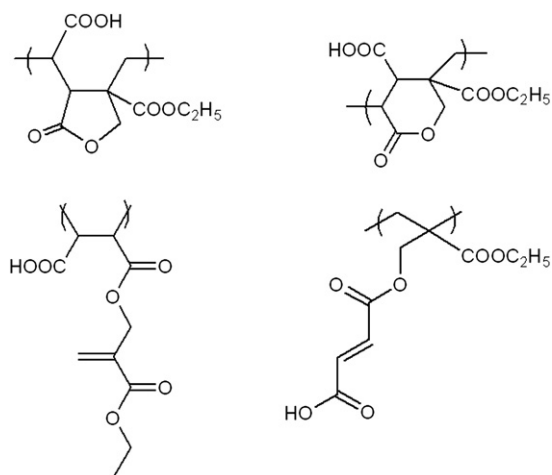
In Fig. 1 are shown the ^{13}C NMR spectra of maleic anhydride, EHMA, and EHMA–MA monomer. The carbonyl and vinylic peaks (a' and b', respectively) of the maleic anhydride (MA) are both split into two peaks upon reaction with EHMA in the EHMA–MA monomer spectrum (j, g and h, i, respectively). The peaks e and f of the EHMA starting material are shifted downfield upon reaction with MA while an upfield shift was observed for peak d. The peaks a–c of reacted EHMA appear at the same chemical shifts as in the spectrum of EHMA itself.

In Fig. 2, ^{13}C NMR spectra of the EHMA–MA monomer and its cyclopolymer (CP1) are shown. The vinylic peaks (d, e, h, i) of the monomer disappeared upon cyclopolymerization. The appearance of the lactone $-\text{CH}_2$ peak (f) at 70.0 ppm and backbone peaks (d, e, h, i) in the ^{13}C NMR spectrum of the polymer, and the fact that the polymer was soluble (not crosslinked) confirmed that the polymer obtained was a cyclopolymer rather than a homopolymer of either one of the vinyl units. The carbonyl peaks (g and j) of the monomer shifted downfield in the polymer spectrum consistent with loss of conjugation. The other peaks (a–c) of the monomer are also observed in the polymer

spectrum. The intensity of the peaks b and c decreased compared to peak a upon polymerization due to the fact that they are closer to the polymer backbone and relaxation rates are different in comparison to that of peak a. The other polymer peaks were also less intense compared to peak “a” for the same reason. The same observations were made with the other two cyclopolymer (CP2 and CP3). Although there are two possible repeat unit structures (5-membered and/or 6-membered) for the polymers, it is more likely for this monomer to form a cyclopolymer with a 5-membered repeat unit structure. It has been previously shown that monomers that are sterically and electronically similar to the monomer studied here mostly form cyclopolymer with a 5-membered ring structure [5,13–16]. Therefore, only 5-membered repeat unit structure will be shown throughout the paper.

In Fig. 3, ^1H NMR spectra of the EHMA–MA monomer and its cyclopolymer (CP1) are shown. Upon polymerization, the vinylic peaks of the monomer (c, d, f, and g) disappeared and the backbone peaks of the cyclopolymer (c, d, f, and g) appeared at around 1.8–3.3 ppm. The ester methylene peaks (b and e) shifted upfield in the cyclopolymer; whereas the carboxylic acid peak (h) shifted downfield. All three peaks (b, e, and h) of the cyclopolymer were broader than the same peaks of the monomer. The methylene peak e is broadened in the cyclopolymer due to tacticity effects along the polymer backbone. The residual double bonds in the ^1H NMR spectrum of the cyclopolymer were integrated against peak e and e + b separately to calculate the degree of cyclization (DC) of the cyclopolymer. The DC values of all cyclopolymer were found to be higher than 95% in all cases and are provided in Table 1.

Fourier transform infrared spectroscopy (FTIR) was also used to follow the polymerizations (Fig. 4). The peak assignments for the EHMA–MA monomer were made as follows: 1,2-C–H out-of-plane bending in $-\text{CR}=\text{CH}_2$ (815 and 970 cm^{-1}), 3-C–O stretching of $\text{O}-\text{CH}_2$ (1025 cm^{-1}), 4-C–O–C antisymmetric stretching of $\text{O}=\text{C}-\text{O}-\text{C}$ (1175 and 1300 cm^{-1}), and C–O stretching of $\text{O}-\text{C}=\text{O}$ (1265 cm^{-1}), 5- CH_2 , CH_3 bending and stretching (1370 and 1450 cm^{-1}), 6-C=C stretching (1640 cm^{-1}), 7-C=O stretching (1740 cm^{-1}), 8-H-bonded COOH (2300 – 2850 cm^{-1}),



Scheme 2. Possible repeat units of EHMA–MA polymers.

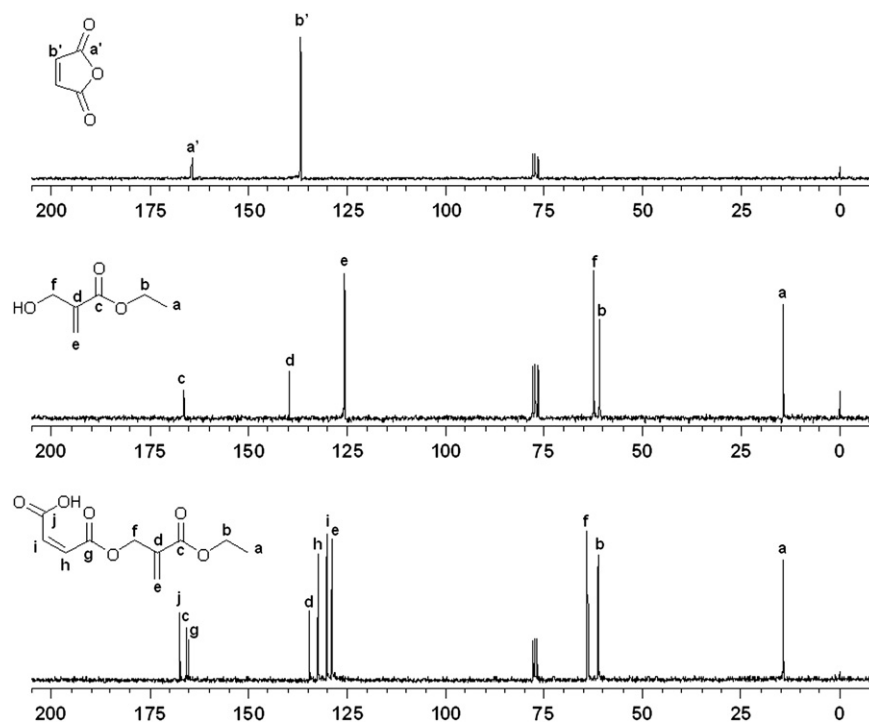


Fig. 1. ^{13}C NMR spectra of maleic anhydride, EHMA, and the monomer (EHMA-MA).

9-aliphatic CH, CH_2 , CH_3 symmetric and asymmetric stretching ($2850\text{--}3100\text{ cm}^{-1}$), 10- H_2O and COOH ($3100\text{--}3600\text{ cm}^{-1}$). The C-H out-of-plane bending in $-\text{CR}=\text{CH}_2$ (peaks 1 and 2) and $\text{C}=\text{C}$ stretching peak (6) of the monomer disappeared upon polymerization. The COOH peak (8) decreased in apparent intensity in the polymer spectrum due to extended hydrogen bonding and the peak around $3100\text{--}3600\text{ cm}^{-1}$ also became broader.

In Table 1, the molecular weights, molecular weight distributions, and degrees of cyclization of the cyclopolymers are provided. The molecular weights of the cyclopolymers were in the range of $40\text{--}60,000\text{ g/mol}$. A decrease of the initiator concentration in the solution polymerization resulted in an increase in the molecular weight of the cyclopolymer obtained. The degrees of cyclization (DCs) calculated from the ^1H NMR results were found to be 95% or higher in all cases.

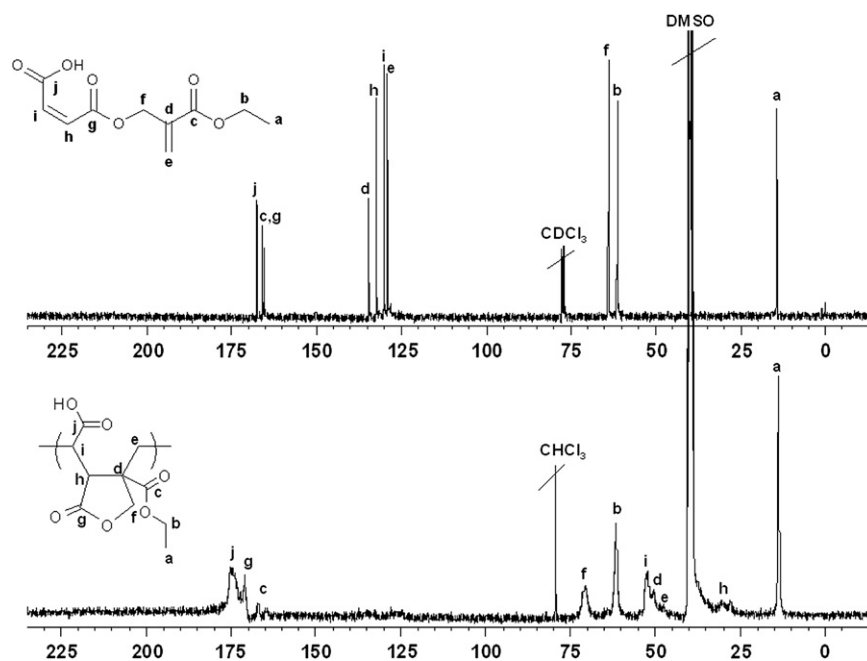


Fig. 2. ^{13}C NMR spectra of EHMA-MA monomer and its cyclopolymer (CPI).

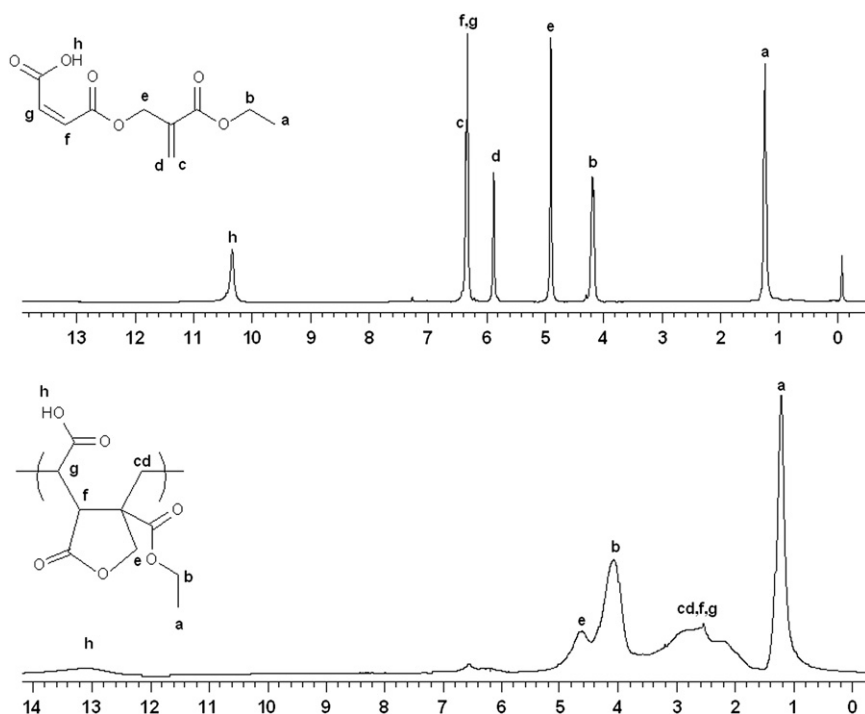


Fig. 3. ^1H NMR spectra of EHMA–MA monomer and its cyclopolymer (CP1).

TGA and DSC were used for thermal analysis of the cyclopolymer. In Fig. 5, the TGA thermograms of the cyclopolymer are shown. The initial weight loss temperatures for all cyclopolymer were around $150\text{ }^\circ\text{C}$ consistent with anhydride formation between two carboxyl groups present in the repeat unit of the polymer. The anhydride formation results in a loss of ethanol from each repeat unit. When the weight percentage of ethanol released from each repeat unit is calculated, it corresponds to the initial weight losses observed in the TGA thermograms (theoretically approximately 23%). The initial weight loss values observed in TGA for the three polymers are around 20–25%.

The DSC thermograms (not shown) did not show any glass transition temperatures in the temperature range of $25\text{--}120\text{ }^\circ\text{C}$ either because the transition is inherently broad or due to changes during analysis due to anhydride (crosslinking) reaction that occurs on heating.

The cyclopolymer were not soluble in water although they were soluble in 1 M aqueous NaOH solutions. The cyclopolymer carry a pendant carboxylic acid which can undergo acid–base reaction. In addition, the ethyl ester and lactone moiety in each repeating unit are also available for further reaction. As an example of possible derivatization chemistry, the

Table 1
Molecular weights, molecular weight distributions, and degrees of cyclization of cyclopolymer

Cyclopolymer	Solvent	AIBN (mol%)	M_n	M_w	PDI	DC (%)
CP1	Ethyl acetate	5.0	40,000	166,000	3.8	97
CP2	Ethyl acetate	0.5	61,000	186,000	3.0	95
CP3	–	1.0	38,000	69,000	1.8	97

cyclopolymer (CP1) was thermally reacted with hexylamine to obtain a polymer with pendant imide and amide moieties. This reaction was followed by NMR and FTIR spectroscopies. The solid state ^{13}C CP-MAS, and solution ^{13}C and ^1H NMR spectra of the final polymer are shown in Fig. 6 (main polymer repeat unit structure is also shown in Fig. 6). The spectral data indicate that the functional groups of the cyclopolymer reacted with hexylamine to give a final polymer with imide and amide groups. The ^{13}C solution and solid state NMR spectra are very similar to each other although it is much easier to see all the peaks of the final polymer in the CP-MAS spectrum due to higher concentration of the polymer in the rotor.

The following observations were made from the NMR data. The methylene and methyl peaks (b, f, and a, respectively) of the linear and cyclic ester groups of the cyclopolymer disappeared after reaction with hexylamine. All the methylene and methyl peaks of the hexyl group are observed around

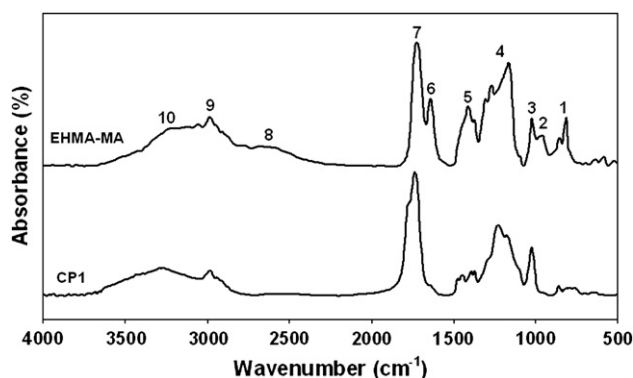


Fig. 4. FTIR spectra of EHMA–MA monomer and its cyclopolymer (CP1).

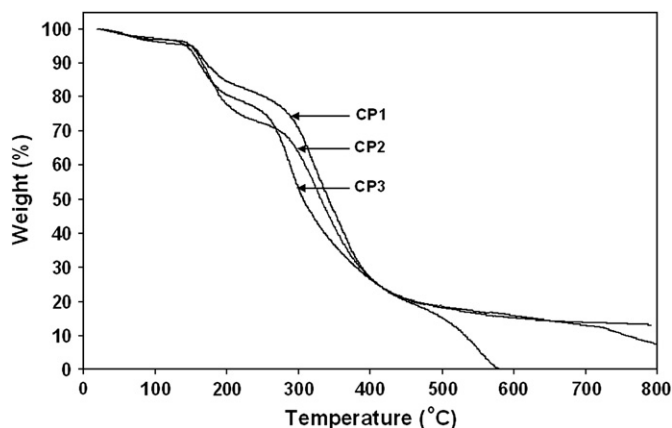


Fig. 5. TGA thermograms of the cyclopolymer (CP1, CP2 and CP3).

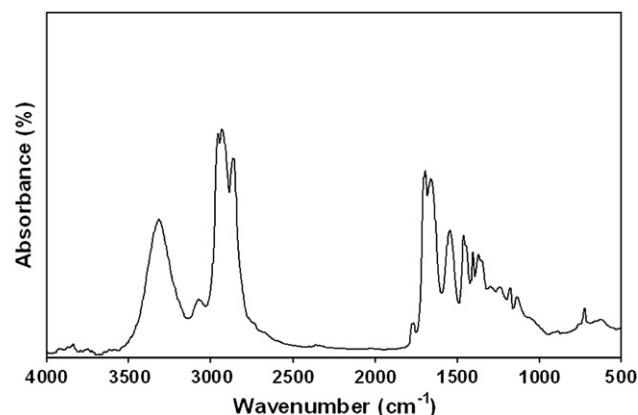


Fig. 7. The FTIR spectrum of the polymer with pendant imide and amide moieties.

15–45 ppm, and specifically the methylene peak α to the imide and amide groups showed up at 40–45 ppm in the ^{13}C solution and CP-MAS NMR spectra of the final polymer. The backbone peaks were observed at 45–55 ppm in both spectra although they are more clearly observed in the CP-MAS spectrum. The methylene peak α to the alcohol ester group at 60–70 ppm and the C=O peak of the amide group at 162 ppm are both weak in intensity, probably due to the small amount of amide groups present in the final polymer compared to the imide groups formed. The C=O peaks of the imide groups appear at 172–180 ppm and are much more intense than the amide group peak. The ^1H NMR spectrum (inset in Fig. 6) confirms reaction of the cyclopolymer with hexylamine to give both imide and amide groups. The methyl and methylene peaks (a, b and e) and carboxylic acid peak (h) of the cyclopolymer

disappeared upon reaction, and the methylene and methyl peaks of the hexyl group were observed around 0.8–1.8 ppm in the ^1H NMR spectrum of the final polymer. The backbone peaks and methylene peak α to the imide and amide groups were observed around 2.9–3.5 ppm while a small peak for the linear amide group was observed at 8.1 ppm.

The FTIR spectrum of the polymer with pendant imide and amide groups is shown in Fig. 7. The spectrum indicates that the aliphatic and aromatic ester peaks of the cyclopolymer disappeared almost completely upon reaction with hexylamine. The ester peaks at 1710–1780, 1175–1300, and 1025 cm^{-1} decreased dramatically. The appearance of the amide N–H stretching peak at 3200–3400 cm^{-1} , the imide C=O peaks at 1780 and 1700 cm^{-1} , amide I and amide II peaks at 1660 and 1550 cm^{-1} , respectively, and the increase in the intensity

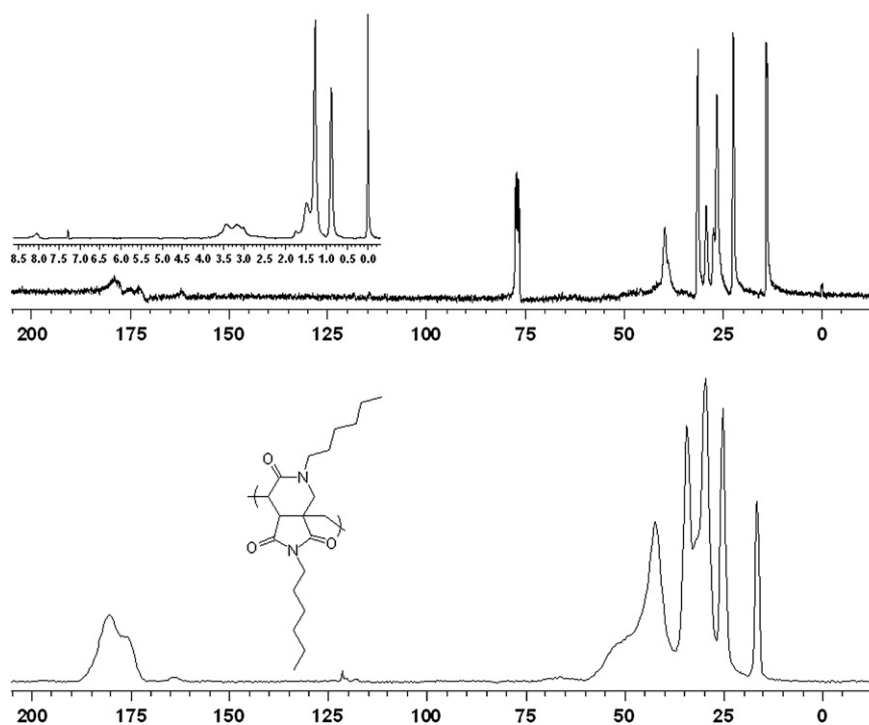


Fig. 6. ^{13}C NMR, solid state CP-MAS, and ^1H NMR (small figure) spectra of the final polymer.

of the CH₂ and CH₃ stretching peaks at around 2800–3000 cm⁻¹ and 1350–1500 cm⁻¹ also confirm the reaction of the cyclopolymer with hexylamine to form the final polymer with imide and amide groups.

The final polymer containing pendant imide and amide groups was stable up to 190 °C. The TGA thermogram of the polymer was similar in shape to those of the starting cyclopolymers and two weight losses were observed at 190 and 300 °C, respectively (TGA data not shown).

The functional moieties present on the cyclopolymer could also be utilized in other reactions. For example, the ester groups could be hydrolyzed under acidic or basic conditions to give a polymer with three carboxylic acid groups and a hydroxyl group. The functional groups could also be selectively reacted to obtain polymers with various pendant moieties.

4. Conclusions

A non-symmetric divinyl monomer with a free carboxylic acid functionality plus an ester and lactone group in each repeat unit was readily synthesized and homopolymerized in both bulk and ethyl acetate to give cyclopolymers with molecular weights around 40–60,000 g/mol. The cyclopolymers obtained were not soluble in water although they were soluble in DMF and in 1 M aqueous NaOH solution due to the carboxylic acid group present. The presence of the carboxylic acid functionality, along with the ethyl ester and lactone moieties, allows selective and sequential reaction to give a variety of derivatives. One example shown here involves the reaction with hexylamine to give a polymer with pendant imide and amide moieties. Other possibilities include hydrolysis of the diacid plus alcohol polymer, esterification, and/or transesterification to give other ester polymers and selective reaction of just the free acid group using traditional activation through

acid chloride formation. These new cyclopolymers and their various derivatives offer many applications that could be industrially important due to the low cost and ready availability of the starting materials.

Acknowledgements

This material is based upon work supported by the National Science Foundation under MRSEC (Grant No. DMR 0213883). We also thank the NSF-MRI program (Grant No. DMR-0079450) for funding to upgrade and expand the NMR capability at USM.

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