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Copolymerization of glycolic, D,L-lactic and D,L-2-hydroxybutyric acid mixtures present in kraft black liquors

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Abstract

A series of copolymers of glycolic acid (GA), D,L-lactic acid (DL-LA) and D,L-2-hydroxybutyric acid (DL-2HBA) were prepared via melt condensation polymerization. The utilized monomers represent mixtures that are present and potentially obtainable from kraft black liquor by fractionation. Polymerizations were performed in 165 ºC at nitrogen atmosphere and reduced pressure using stannous octoate as catalyst. Copolymerizations were conducted with varying DL-2HBA content in order to observe how the presence of the DL-2HBA monomer affects the properties of the polymers. Prepared copolymers were characterized with ^{1}H NMR and ^{13}C NMR, size exclusion chromatography, differential scanning calorimetry, and thermogravimetric analysis. The obtained copolymers had molecular weights between M_w = 3500 – 10 000 g/mol. DL-2HBA had a lowering effect on the glass transition temperatures and molecular weights of the copolymers. However, significant lowering of molecular weight was observed only when the amount of DL-2HBA in the feed exceeded 60%. The results indicate that DL-2HBA can be copolymerized with GA and DL-LA and therefore the corresponding kraft black liquor fractions can be utilized for polymerizations.

Keywords: polycondensation, polyester, biodegradable polymer, biobased polymer.

1 Introduction

The past decade has seen a dramatic increase in the research of bio-based materials. Diminishing fossil fuel resources and growing environmental concerns have increased the pressure to find replacing renewable alternatives for petroleum derived products. This has increased the interest towards biorefining concepts, where side streams of agriculture and forest industry offer wide variety of molecules that can be further upgraded into useful compounds.[1,2]

One major side stream in paper industry is the cooking liquor, black liquor, from kraft pulp process. Black liquor consists of numerous degradation products of different components of wood, depending on the raw material and pulping conditions.[3,4] Among other compounds, up to 30-45 wt% of black liquor dry content consists of different carboxylic acids, including hydroxy acids.[5,6] Traditionally, concentrated black liquor is combusted to produce heat that is required in the pulping process. However, majority of the black liquor hydroxy acids have a very low heat value, and therefore it might be advantageous to separate them from the black liquor to be utilized e.g. as monomers for polymeric products.[5]

Black liquor fractionation methods have been studied since 1980s, and chromatographic methods together with membrane separation have proved to be effective in the separation of high molecular weight compounds from smaller hydroxy acids.[7-9] However, separation of the three smallest α-hydroxy acids: glycolic acid (GA), D,L-lactic acid (DL-LA) and D,L-2-hydroxybutyric acid (DL-2HBA) from each other is difficult due to their similar physical properties, including boiling points and solubilities. The possibility to utilize the mixture of these three components directly, without further separation steps, as a starting material for polymerization would significantly increase the applicability of the compounds from the fractionation point of view.

GA and DL-LA are commonly used as monomers in the preparation of biodegradable polyesters, and poly(GA-*co*-DL-LA) copolymers are also well studied in the literature.[10] Their main application area is currently on the medical field, e.g. in controlled drug delivery or tissue engineering, which can be seen in the recent review articles related to the subject.[11-14] However, according to our knowledge, there are hardly any reports concerning homo- or copolymerizations of DL-2HBA. Copolymerization of black liquor hydroxy acid mixture containing these three compounds would therefore open utilization potential for DL-2HBA as a monomeric compound.

Hydroxy acid polymers can be synthesized either via ring-opening polymerization (ROP) of lactones or by direct polycondensation of hydroxy acids. Currently ROP is the more commonly utilized method, as it generally provides higher molecular weights and shorter reaction times.[12] However, direct polycondensation method is more easily applicable in the polymerization of hydroxy acid mixtures. The most common way to perform polycondensation is in bulk conditions at elevated temperature and reduced pressure.[15,16]

In this study a series of copolymers of glycolic acid (GA), D,L-lactic acid (DL-LA) and D,L-2-hydroxybutyric acid (DL-2HBA) were prepared via melt condensation polymerization. The utilized monomers represent mixtures that are obtainable from kraft black liquor by fractionation. The structures of the monomers are presented in Figure 1. The utilization of DL-2HBA as a monomer in corresponding systems has not been previously reported. Therefore, the aim of the study was to investigate how its presence affects the copolymerization reactions and the properties of the copolymer products, including their molecular weights and thermal properties. Molecular weights of the synthesized copolymers were determined with size exclusion chromatography (SEC) and the thermal properties were studied with differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

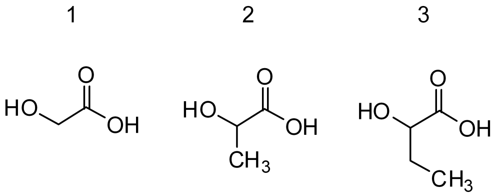

*Figure 1. Chemical structures of glycolic acid (**1**), D,L-lactic acid (**2**) and D,L-2-hydroxybutyric acid (**3**).*

2 Experimental

Materials

D,L-Lactic acid containing ~10 wt% of water (Sigma-Aldrich) was used as received. D-2-hydroxybutyric acid and L-2-hydroxybutyric acid (≥97 %, Sigma-Aldrich) were purchased separately and used as a racemic mixture prepared prior immersing into the reaction mixture. Glycolic acid (99 %, Sigma-Aldrich) and stannous octoate (Sn(II)oct, ~95 %, Sigma-Aldrich) were used as received. All the other chemicals were of analytical grade and used as received.

Melt condensation polymerizations

The poly(α-hydroxy acid)s were synthesized by melt condensation polymerization. A series of polymerizations were conducted with varying monomer unit compositions. For example, polymerization with following composition in feed: 45 mol% GA, 45 mol% DL-LA and 10 mol% DL-2HBA was conducted as follows. GA (1.901 g, 25 mmol), DL-LA (2.502 g containing 10 wt% of water, 25 mmol), D-2HBA (0.289 g, 2.8 mmol), L-2HBA (0.289 g, 2.8 mmol) and Sn(II)oct catalyst (24 mg, 0.5 wt% of monomers) were weighed into a three neck flask equipped with a magnetic stirrer and a distillation apparatus. The flask was immersed into oil bath at room temperature and the temperature was increased to 165 ºC within 1 h. After 5 h reaction time the pressure was reduced. The reduction was performed stepwise within 1.5 h to a final pressure of 250 mbar. Polymerization was performed under nitrogen atmosphere. After complete polymerization time of 10 h the obtained polymer was poured out from the reaction flask and purified by dissolving in chloroform and precipitating from methanol. Purification procedure was repeated three times. Purified polymer was dried in vacuum oven at room temperature for 24 h before further characterization.

NMR spectroscopy

^{1}H NMR and ^{13}C NMR measurements were conducted with a Bruker 500 MHz spectrometer in deuterated chloroform ($CDCl_3$). Monomer unit compositions of polymers were calculated from quantitative ^{13}C NMR spectra using chromium (III) acetylacetonate as a relaxation reagent and relaxation delay of 3 seconds. Chemical shift scale was calibrated to TMS. Distinctive peaks of each monomer unit were integrated and monomer unit composition of the polymer was calculated based on the ratios of each integral area.

Size exclusion chromatography (SEC)

Molecular weights and molecular weight distributions were determined with size exclusion chromatography (SEC) at 40 ºC. The system was equipped with Waters Styragel columns and Waters 2414 Refractive Index Detector. Tetrahydrofuran (THF) was used as an eluent and was delivered at a rate of 0.6 ml/min. The SEC was calibrated with polystyrene standards.

Thermal properties

Differential scanning calorimetry (DSC) was used to determine the glass transition temperatures (T_g) of the prepared polymers using Mettler Toledo DSC820 STAR^{e} SW 9.20 instrument under nitrogen atmosphere. Samples were heated twice from -10 °C to 200 °C at a rate of 10 °C/min. T_g was determined from the second heating scan.

Temperatures of 10 wt% decomposition ($T_{d10\%}$) were measured with thermogravimetric analysis (TGA) utilizing TG/DTA320 Seiko Instrument. Analyses were performed from 25 ºC to 550 ºC with a heating rate of 20 ºC/min under argon flow.

3 Results and discussion

A series of copolymers of GA, DL-LA and DL-2HBA were prepared via melt condensation polymerization. The polymers are presented in Table 1. The series includes a set of polymerizations, where the amount of DL-2HBA in the feed was varied from 0 % to 100 %, while the ratio between GA and DL-LA remained constant (samples PLGA, PLGHA1, PLGHA2, PLGHA3, PLGHA4 and PHBA). These samples were synthesized in order to observe how the presence of the DL-2HBA monomer affects the properties of the polymers. In addition, two samples were polymerized based on the hydroxy acid compositions in softwood (sample PLGHA-SW) and birch-hardwood (sample PLGHA-HW) kraft black liquors.[3,4]

Table 1. The conducted polymerizations and the monomer compositions, SEC results and thermal properties of the obtained polymers.

	Composition in feed (mol%)			**Composition in polymer (mol%) (^{13}C NMR)**			**SEC (g/mol)**			**DSC (°C)**	**TGA (°C)**
	GA	**DL-LA**	**DL-2HBA**	**GA**	**DL-LA**	**DL-2HBA**	**M_w**	**M_n**	**M_w/M_n**	**T_g**	**$T_{d(10\%)}$**
PLGA	50.0	50.0	0.0	58	42	0	9000	4200	2.12	21	224
PLGHA1	47.5	47.5	5.0	49	46	5	5900	3700	1.61	20	230
PLGHA2	45.0	45.0	10.0	47	44	9	9300	5800	1.60	23	235
PLGHA3	20.0	20.0	60.0	22	21	57	6200	4300	1.45	7	240
PLGHA4	10.0	10.0	80.0	11	10	79	3400	2700	1.26	-1	237
PHBA	0.0	0.0	100.0	0	0	100	2800	2300	1.18	-3	244
PLGHA-SW	34.6	48.6	16.8	38	46	16	10 100	6800	1.50	28	243
PLGHA-HW	24.4	30.9	44.6	29	30	41	7500	4500	1.66	22	236

The chemical structures of the prepared polymers were analyzed with ^{1}H NMR and ^{13}C NMR. The ^{1}H NMR spectrum of sample PLGHA-HW, with assigned peaks, is presented in Figure 2, and the ^{13}C NMR spectrum of PLGHA-HW, with assigned peaks, is presented in Figure 3. Quantitative ^{13}C NMR spectra were used to calculate the monomer unit compositions of the polymers. Composition calculations were based on integral areas of peaks distinctive to each monomer unit. The calculated monomer unit compositions are presented in Table 1. The results show that the monomer unit compositions in the copolymers were similar to the monomer compositions in feed. However, the amount of GA units in polymer was consistently slightly higher than in feed. Similar results have also been reported earlier and explained to be due to higher reactivity of primary hydroxyl group of GA over secondary hydroxyl groups.[15]

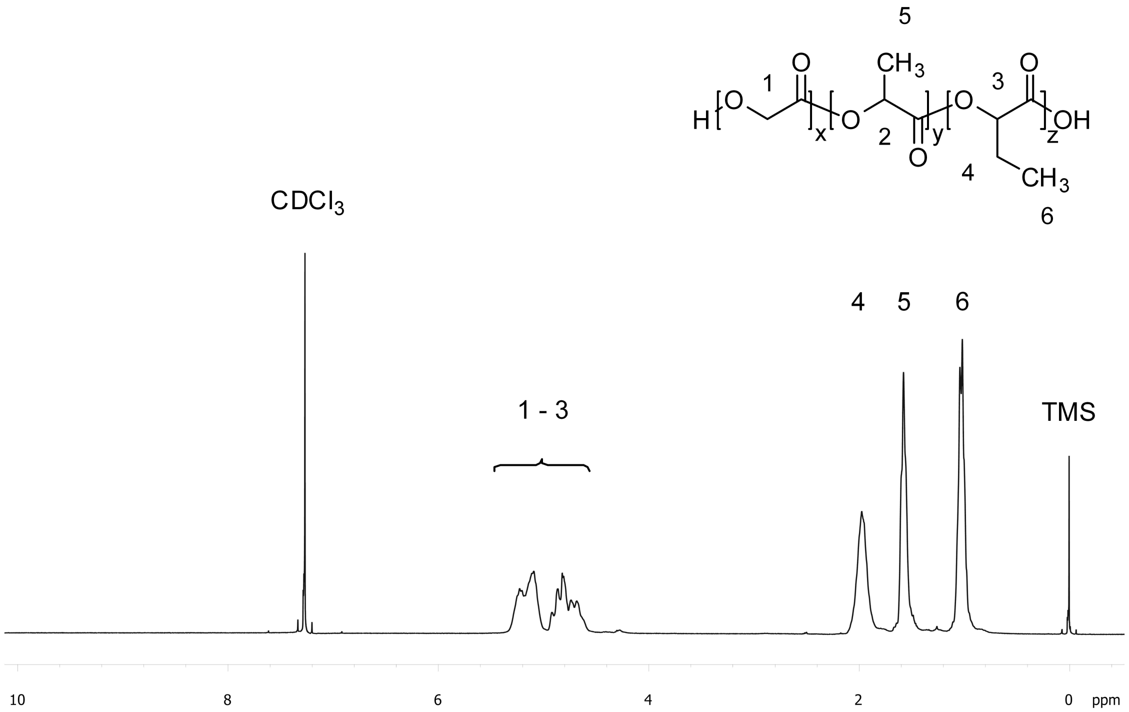

Figure 2. The ^{1}H NMR spectrum of PLGHA-HW.

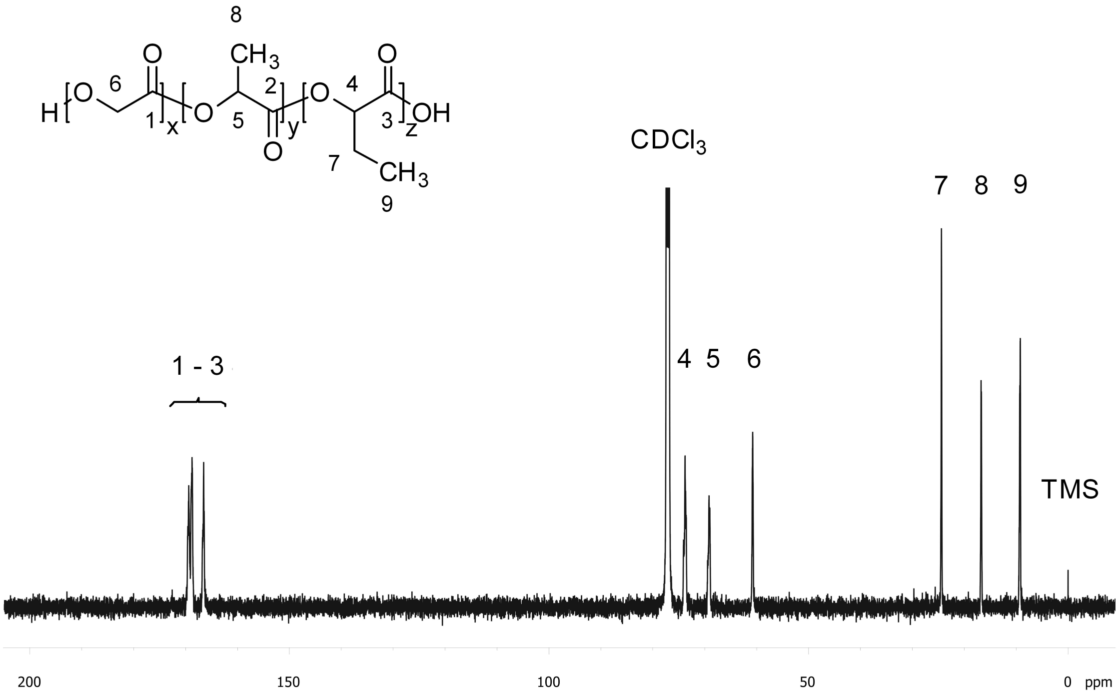

Figure 3. The ^{13}C NMR spectrum of PLGHA-HW.

Molecular weights of the synthesized copolymers were determined with size exclusion chromatography (SEC) and the results are presented in Table 1. Majority of the samples had molecular weights between M_w = 5000 – 11 000 g/mol. These values are comparable to molecular weights of previously reported GA-*co*-DL-LA copolymers prepared by similar procedures.[15,16] Molecular weights obtained by condensation polymerizations remain often below 15 000 g/mol. However, various methods have been developed to increase the molecular weights of polycondensation products.[15,17-21] Lower molecular weights were observed in samples where the amount of DL-2HBA in the feed exceeded 60%. Sample PLGHA4 (80 mol% of DL-2HBA in feed) had a M_w of 3400 g/mol and the sample PHBA, which was a DL-2HBA homopolymer, had a M_w of only 2800 g/mol. However, in these cases amount of DL-2HBA in feed exceeded significantly the amount of DL-2HBA present in actual black liquor hydroxy acid mixtures.[3,4]

Thermal behaviour of the synthesized polymers was studied with differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). No melting peaks were observed in the DSC results, indicating that all the synthesized polymers were amorphous. This was expected, as majority of the samples were statistical copolymers containing optically impure monomer units (DL-LA and DL-2HBA). These compositions can be expected to result in irregular structures that are not able to crystallize. The optical impurity explains also why the DL-2HBA homopolymer (sample PHBA) was amorphous. In literature, similar behaviour has been observed for poly(lactic acid) homopolymer, which has been reported to lose its crystallinity when optical purity is decreased below 66-76 %. [22,23] By contrast, the GA monomer has a regular structure. According to literature, GA-*co*-DL-LA copolymers can contain GA crystals in case the GA content is above 90 %.[15] However, the GA content did not exceed 50 % in the current copolymer series.

Glass transition temperature (T_g) values for all the prepared polymers are presented in Table 1. When the amount of DL-2HBA incorporated in the polymer was 40 mol% or lower, the measured T_g values were between 20–28 ºC. These values are comparable to previously reported values for GA-*co*-DL-LA copolymers (20 – 40 ºC).[15] When the amount of DL-2HBA incorporated in the polymer structure was higher than 40 %, the T_g values started to decrease, reaching T_g = -3 ºC in the DL-2HBA homopolymer sample. However, in the case of some of the samples (PLGHA4 and PHBA), the lowering of T_g can also be partially due to their lower molecular weights.

TGA results showed no major differences in the thermal decomposition behaviour between the samples. The $T_{d10\%}$ values of the polymers are presented in Table 1. The values were around 230 ºC for all the samples. Thermogravimetric (TG) and differential thermogravimetric (DTG) curves of PLGHA-HW are presented in Figure 4. From these curves it can be seen that thermal decomposition started after the temperature was increased over 200 °C. The relatively high decomposition temperatures indicate that the copolymer materials are well suited for melt processing.

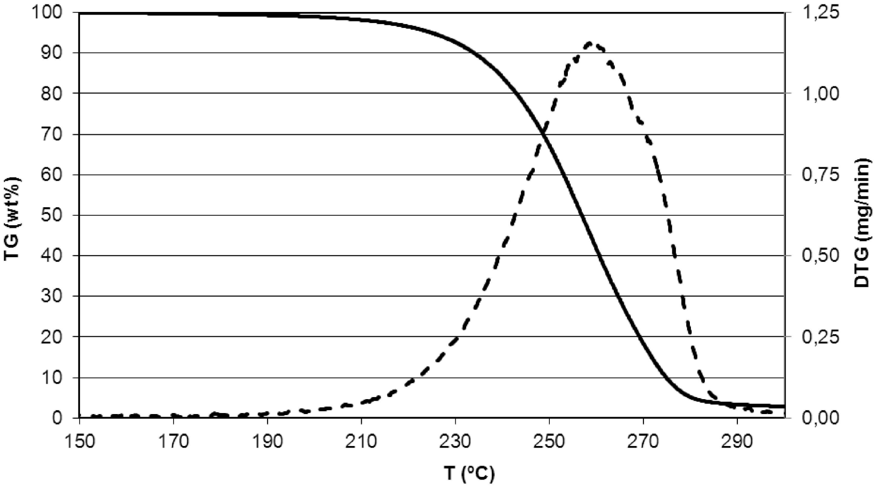

Figure 4. TG (solid line) and DTG (dashed line) curves of PLGHA-HW.

4 Conclusions

In this study, copolymerizations of GA, DL-LA and DL-2HBA were performed. The behaviour of DL-2HBA as a monomer in corresponding systems has not been previously reported. Similar polymerization procedures could be applied as in the homo- or copolymerizations of GA and DL-LA. The molar amount of DL-2HBA in feed could be increased to 60 mol% before it started to have a lowering effect on the molecular weight of the copolymers. All the obtained polymers were amorphous. Glass transition temperatures of the copolymers containing up to 60 mol% of DL-2HBA were between 20-28 °C. Higher amounts of DL-2HBA in the copolymer structure had a lowering effect on the glass transition temperature of the material. However, lowering in molecular weights and glass transition temperatures was not seen in samples polymerized with actual black liquor hydroxy acid compositions.

The monomers applied in this study are the three smallest α-hydroxy acids present in kraft black liquor. The successful polymerization of GA, DL-LA and DL-2HBA mixtures indicates that these three monomers need not be separated from each other in the fractionation process of black liquor in order to be applied as monomers for polymerization.

5 Acknowledgement

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