Thermal characterization and crystallization kinetics of polyester polyols derived from adipic acid and bio-based succinic acid with 1,4-butanediol and 1,6-hexanediol

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ABSTRACT

Crystallization kinetics, thermodynamics, and powder XRD measurements were performed on polyester polyols (PESP) made from succinic acid, SA, or adipic acid, AA, with 1,4-butanediol, BDO, or 1,6-hexanediol, HDO, at 2000 Da M_n. The SA BDO PESP exhibited the greatest crystallization supercooling. The Avrami crystallization kinetics n values are 4 or higher, indicative of sporadic nucleation of spherulitic crystals. At similar crystallization $t_{1/2}$, SA BDO K_{eq} determined from ΔG_c is ten times greater and SA HDO is five times greater than AA BDO K_{eq}. AA BDO and AA HDO have equivalent K_{eq} at similar $t_{1/2}$. Increasing the diol chain length from four carbons to six carbons increases the ΔG_c temperature dependence for SA PESP, but has little impact on the ΔG_c temperature dependence of AA PESP. Powder XRD shows that these PESPs contain 35%—40% macrocrystals comprised of nanocrystals with average dimensions of 6—10 nm per side.

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1. Introduction

Succinic acid, 1,4-butanedicarboxylic acid (SA), derived from renewable feedstocks is an increasingly important material for the chemical industry. Large-scale manufacturing facilities have been built based on fermentation of sugar to produce succinic acid with competitive economics. Bio-based SA is competing with petroleum-based adipic acid, 1,6-hexanedicarboxylic acid (AA), in commercially important products such as polyester polyols (PESPs) useful as reactive oligomers in polyurethane applications, acrylate-functionalized coatings materials, elastomers, and adhesives [1,2].

Successful transition from adipic acid to succinic acid in these applications will depend not only on production economics, but also on competitive physical properties and processing.

The use of succinic acid-based polyester diols (SA PESPs) has increased in many applications, but comparisons of their basic properties to adipate PESPs at commercially important 2000 Da M_n has not been adequately reported. Early reports by Carothers showed the synthesis of succinate PESPs at these chain lengths [3]. Flory's report defining M_n and M_w for polymers used poly(butylene)sebacate as an example and showed that the temperature dependence of the 2000 M_n PESP viscosity temperature relationship followed an Arrhenius relationship [4]. Limited results are available showing the comparison of adipate and succinate PESPs in end-use applications [5].

The melt and crystallization behavior of the PESPs are important in their end-use applications. For example, the building of green strength for adhesion after melt processing is dependent on the amount of time required for the polyester to crystallize upon cooling [6].

Polymer crystallization kinetics are typically analyzed using

Avrami kinetics methods [7–9]. This theory allows the determination of crystallization half-life at various temperatures by following the crystallization exotherm using differential scanning calorimetry (DSC). For example, crystallization kinetics of high M_n poly(1,6-hexamethylene)succinate polyesters (SA HDO) were obtained showing that spontaneous nucleation and growth of spherulitic crystals occurs from the melt under isothermal conditions, but that non-isothermal conditions favored sporadic nucleation [10]. Single crystal analysis of SA HDO shows that the crystal structure depends on the temperature of crystal growth [11]. Avrami crystallization kinetics for high M_n poly(1,4-butylene)adipate (AA BDO) show a crystallization temperature range of 29 °C–45 °C to give half-lives for crystal growth of 0.3–19 min, respectively. The Avrami exponent was determined to be near three, suggesting a spontaneous nucleation and growth mechanism for crystallization of the AA BDO polymer [12].

The crystallization half-lives of poly(ethylene)succinate (SA EG), poly(1,3-propylene)succinate (SA PDO), and poly(1,4-butylene) succinate (SA BDO) at about M_n 7000 Da were determined by Avrami kinetics [13–15]. SA BDO was found to have the shortest half-life. SA BDO gave 210 J/g ΔH melting with percent crystallinity between 35% and 40%, similar to earlier reports [13–15]. The reports also showed by powder XRD that the SA BDO polymer crystals adopt the α polymorph as previously reported for high M_n SA PDO thermoplastics [15–18]. A recent report shows that the melting and crystallization temperatures for SA BDO are dependent on M_n from 5000 Da to 70 kDa, but that an estimate of crystallization rate seems to be independent of M_n [19].

These recent reports characterize high M_n aliphatic polyester thermoplastics, their crystal morphology, and their crystallization kinetics. Insufficient relevant data exists on the M_n 2000 Da succinic acid and adipic acid polyester diols that are useful for understanding the processing of these reactive oligomers in polyurethane and other reactive polymer systems. Our work compares the structure-property relationships of the semicrystalline homopolyester diols made from succinic acid and 1,4-butanediol (SA BDO), succinic acid and 1,6-hexanediol (SA HDO), adipic acid and 1,4-butanediol (AA BDO), and adipic acid and 1,6-hexanediol (AA HDO) at 2000 Da M_n. We obtained the crystal lattice information and crystal size from powder XRD and determined the crystallization kinetics for these materials by Avrami analysis of their crystallization exotherms. We also determined the thermodynamics of crystallization for these polyols. A comparison of the results shows that the SA BDO PESP is unlike the other three PESPs. We propose that these differences are caused by succinic acid PESPs having significantly larger negative Gibbs free energies of crystallization compared to the adipate PESPs.

2. Experimental

SA BDO, SA HDO, and AA HDO at 2000 M_n (OH 56) were provided by BioAmber and used as received. AA BDO was synthesized at 2000 M_n (OH 56) using known methods [5]. The PESP OH numbers and M_n's were measured using ASTM E-1899 and were found to be within experimental error of OH 56 and 2000 Da M_n.

DSC measurements were made with a Mettler Toledo DSC 1 running the STARe software. Sample size was approximately 10 mg, and new samples were used for each run. Heat and cool loops were run at 10 °C/min with a 1 min hold time at 150 °C. DSC heat and cool loop data are from the second heat and second cool. Avrami kinetics data were collected by heating the sample in the DSC from −30 °C to 150 °C at 10 °C/min, holding at 150 °C for 1 min, and then cooling at 10 °C/min to −30 °C. The sample was then heated at 10 °C/minute to 150 °C, held for 1 min at 150 °C, and then cooled at 40 °C/minute to the desired crystallization temperature. DSC data was taken from the second heat and cool cycles to minimize differences in sample thermal history. Exotherm data were collected at the crystallization temperature. Fraction of crystallization, X(t), was determined by taking the ratio of the area under the second loop crystallization exotherm at time t to the total area under the second complete crystallization exotherm.

Powder XRD experiments were performed using a Rigaku MiniFlex diffractometer using a CuK α radiation (λ = 1.540 Å generated at 30 kV and 15 mA) source and equipped with a monochromator. The data were collected with a step size of 0.02°.

3. Results and discussion

3.1. Material characteristics

The four white waxy polyester diols characterized in this report are composed of repeat units of SA BDO, SA HDO, AA BDO, and AA HDO, Fig. 1. The PESPs are composed conceptually of a diol initiator with repeat units terminating in hydroxyls at each end of the chain. At 2000 Da average M_n, the SA BDO PESP has 11.2 repeat units and 44.8 carbonyls per chain, the SA HDO PESP has 9.5 repeat units and 38 carbonyls per chain, the AA BDO PESP has 10 repeat units and 40 carbonyls per chain, and the AA HDO PESP has 8.8 repeat units and 35 carbonyls per chain. The SA BDO PESP has 28% more carbonyls per chain on average compared to the AA HDO PESP, Table 1. We expect significantly more polar interchain interactions in the bulk SA BDO PESP because of its higher carbonyl functional content, especially when compared to the AA BDO PESP [5,13]. However, the physical properties of the polyols are not simply a function of the carbonyl counts in the SA and AA polyols, but they are related to the four-carbon succinate unit as shown in the following results.

3.2. Crystallization thermodynamics

The data for the PESP second heating and cooling cycles are shown in Fig. 2. SA BDO shows a crystallization exotherm just before the melting endotherm, while the other PESPs simply melt as previously reported for high M_n SA BDO polyesters [13]. The SA BDO PESP has the largest difference between melt and crystallization with 39 °C supercooling, followed by SA HDO with 22 °C supercooling. AA BDO and AA HDO have the smallest supercooling effect at 17 °C as shown in Table 2.

With the assumption that the temperature of the maximum heat flow for crystalline melting is the equilibrium melting temperature for the PESPS, the change in entropy for phase change from melt to the crystalline form of the PESP can be calculated. At the equilibrium melting/crystallization temperature the system is in phase change equilibrium, and the change in Gibbs free energy, ΔG_c, is zero. The melting endotherm provides the change in enthalpy, ΔH_c, and since $\Delta G = \Delta H - T\Delta S$, we can calculate the change in entropy, ΔS_c at the equilibrium phase change temperature. A similar approach was used previously [13]; however we convert the PESP heat of crystallization from kJ/g to kJ/mol by multiplying ΔH_c from the DSC results by the average molar mass of the PESP (2000 g/mol) and then solve for ΔS_c (in J/mol K) at the crystallization temperature, T_c. Table 2 shows the result of this analysis for the PESPs. The ΔH_c's for the four PESPs are similar while the ΔS_c's show the trend of increasing loss of disorder as the PESPs go from the 4-carbon diacid/4-carbon diol SA BDO, to the 6/4 AA/BDO, to the 4/6 SA HDO, and to the 6-carbon diacid/6-carbon diol AA HDO. The inclusion of the 6-carbon 1,6-hexane diol in the PESPS results in the greatest increase in entropy during phase change for these PESPs. These results show that the 4/6 SA HDO and the 6/4 AA BDO have similar melting and crystallization temperatures, important for practical applications, and similar carbonyl content