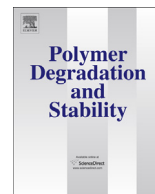




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Chemical recycling of poly(lactic acid) via controlled degradation with protic (macro)molecules

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ABSTRACT

Designing of a new method of poly(lactic acid) chemical recycling leading to potentially useful products is the purpose of this paper. Controlled chemical degradation processes of commercial poly(lactic acid) in the presence of small molecules, such as diols, dipentaerythritol, diamines and adipic acid or oligo(ethylene glycol) as well as polyesterdiols were studied. The processes were found to be efficient and in the presence of a catalytical amount of tin(II) octanoate lead to the formation of homo- or block diol type copolymers or oligomers of lactic acid. Diamines appear to be the most efficient, even without catalyst at quite low temperature, whereas adipic acid eventually at 200 °C reacts with moderate efficacy. It is demonstrated that M_w of the products is much lower with respect to that of poly(lactic acid). Degradation agents incorporate into the products' structures, however, in almost all cases some fraction of macro- α,ω -hydroxyacids is present in the samples, which seems to be unavoidable because of degradation mechanism and some residual moisture present in the polymers used. Products rich in ABA type triblock copolymers may be obtained by the degradation method presented utilizing macrodiols. The processes of poly(lactic acid) degradation with macrodiols can be carried out at temperatures of 120 °C or higher in solvent (e.g. xylene) or in bulk as well as an extruder. The reaction time depends on temperature and it is in the range from 30 min to 4 h. Aliphatic copolymers are homogeneous, whereas these containing aliphatic –aromatic macrodiols are of two-phases. The latter ones show different morphology based on composition. Triblock systems reveal multistage differential thermal analysis curves. Robust method of chemical recycling of poly(lactic acid) by controlled degradation with protic compounds is presented.

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1. Introduction

Nowadays, the total world production of polymers (thermo-plastics and thermo-/chemosets) reaches approximately 300 million metric tons per year (~9.5 Mg/s), whereas merely less than 0.5 wt.% of that (~1.16 million tons) is descended from renewable resources. A majority of the latter ones (~60%) comprises non-biodegradable materials, such as green polyethylene (PE), polyamides or poly(ethylene terephthalate) (PET), however, the remnant are biodegradable polymers, including poly(lactic acid) (PLA; 0.18 million tons) [1]. The latter one at the present times, seems to be the most popular biodegradable synthetic polymer produced from starch in several large (bio)technological installations around the World. Eco-profile (cradle-to-gate) of PLA consists of many unit operations, such as growing plants, gaining, degradation and lactate fermentation of starch, lactic acid (LAC) purification and condensation, obtaining of lactide (LA) by thermal depolymerization of LAC oligomers and finally, polymerization of

List of abbreviations: BD, 1,4-butanediol; DA, degradation agent(s); DAE, 1,2-diaminoethane; DAH, 1,6-diaminohexane; DH, dihydroxyl main product(s); DPE, dipentaerythritol; DSC, differential scanning calorimetry; DTA, differential thermal analysis; DTG, derivative thermogravimetry; GPC, gel permeation chromatography; LA, lactide; LAC, lactic acid; MD, macrodiol(s); MH, monohydroxyl byproduct(s); NMR, nuclear magnetic resonance spectroscopy; PBA, poly(1,4-butylene adipate); PBAT, poly(1,4-butylene adipate-co-terephthalate); PD, 1,3-propanediol; PE, polyethylene; PEG, poly(ethylene glycol); PET, poly(ethylene terephthalate); PLA, poly(lactic acid), polylactide; PPA, poly(1,3-propylene adipate); PPAC, poly(1,3-propylene adipate-co-carbonate); PPAT, poly(1,3-propylene adipate-co-terephthalate); PPBAC, poly(1,3-propylene-co-1,4-butylene adipate-co-carbonate-co-terephthalate); SEM, scanning electron microscopy; SnEH₂, tin (II) 2-ethylhexanoate; T_g , glass-transition temperature; TGA, thermogravimetric analysis; THF, tetrahydrofuran.

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LA leading to PLA [2]. All of these procedures are time and energy consuming and, moreover, they may cause water and air pollution. The energetic balance of early PLA technologies was worse than those for many common petroleum-based polymers [3]. The novel PLA technologies are modern and well developed, therefore, they are consuming even less energy (often from renewable resources) compared with many polyolefin installations [2,3]. Anyhow, the lifetime of goods made from PLA is rather short but after use PLA waste materials can be utilized in a few ways. First, PLA can be material recycled, however, there are the economical and environmental costs of plastic segregation, preparing and polymer degradation in every cycle [4–12]. On the other hand, waste PLA can undergo the biodegradation process affording useful bio-products [13] e.g. in anaerobic conditions or in compost plants [14,15], but compost requires appropriate conditions (temperature, oxygen and water concentration, nutrients, maximum load of PLA) and it is quite a long-term process. Another option is the recovery of the chemical bond energy by subjecting PLA to combustion in incineration plants. The two latter methods are destructive for this valuable material, thus another useful utilization way of PLA wastes was developed – chemical recycling (including monomer recovery). This kind of treatment is popular for PET wastes: the polymer is converted into bis(2-hydroxyethyl)terephthalate or higher oligomers in reaction with ethylene glycol. Monomer recovery is studied often in case of PLA and depending on the process conditions it can lead to the formation of LAc (hydrolysis of PLA) [16–21] or LA (unzipped depolymerization of PLA) [22–28]. The latter method yields the valuable monomer ready for PLA synthesis and relies usually on high temperature treatment in the presence of catalyst under diminished pressure. There are a number of papers and patents on chemical recycling of PLA by treatment with various alcohols (R–OH) leading to appropriate lactates [19,29–32] that can be used in chemical synthesis or other industries. For instance, Leibfarth et al. showed that PLA might be transformed into lactates with high yields (>95%) in the presence of triazabicyclodecene as organocatalyst during a few minutes at room temperature with a three-fold excess of appropriate primary alcohol with respect to monomeric unit (m.u.) [32]. However, it must be mentioned that sterically hindered (e.g. secondary, tertiary) or acidic alcohols (e.g. phenols) were much less reactive, so they enabled the obtaining of products under severe conditions or did not react at all. PLA blends comprising PE, polystyrene and polyesters can also undergo selective chemical recycling that leads to LAc and/or its oligomers [33,34], lactates [35] or LA [36–39].

By analogy with PLA alcoholysis, ethylene glycol was used as well for the chemical recycling of PLA [40]. Ro et al. obtained telechelic dihydroxy-PLA with ethylene glycol molecule inserted between PLA blocks after 2 h of reaction carried out at 190 °C in bulk in the presence of 1 wt.% of tin (II) 2-ethylehxanoate (SnEH₂). Afterwards, the product was reacted with some excess of itaconic anhydride in order to convert hydroxyl end-groups into carboxyl ones, so the final product of α,ω -carboxylic acid telechelic PLA after mixing with metal acetates gave the ionomers.

In this paper we demonstrate the chemical recycling of PLA by reactions with diols, diamines, and macrodiols (such as polyesterdiols and polyetherdiols) to form oligomeric or polymeric materials comprising two terminal secondary hydroxyl groups. In case of using macrodiols, a majority of the obtained product consists of a triblock copolymer. Usually, copolymers of this kind are formed in chain extension processes of macrodiols with LA (cyclic dimer of lactic acid) via ring opening (pseudo)anionic polymerization [41–46]. The reaction requires extremely dry environment (all reagents, reactants and glassware), otherwise moisture would deactivate propagation species or cause a considerable number of kinetic chain transfers leading to homopolymer formation [47]. We

believe that our products obtained in this novel and robust method of chemical recycling of PLA can be used as additives for PLA (e.g. plasticizers, impact strength modifiers) or utilized as oligomeric segments in the synthesis of other kind of polymeric materials [48].

2. Materials and methods

2.1. Materials

PLA (NatureWorks LLC, NW2002D) of $M_w = 217$ kg/mol was used as supplied. 1,4-Butanediol (BD, 98%), dipentaerythritol (DPE, tech. grade), hexamethylenediamine (DAH, 98%), SnEH₂ (~95%), poly(ethylene glycol) (PEG) of $M_w = 320$ g/mol, poly(1,4-butylene adipate) (PBA) of $M_w = 4.1$ kg/mol (all from Aldrich) were used without further purification. 1,3-propanediol (PD, 99%, Alfa Aesar), adipic acid ($\geq 99\%$, Fluka), ethylenediamine (DAE, >99%, Merck) were used without purification. PBA of $M_w = 25.3$ kg/mol, poly(1,3-propylene adipate) (PPA) of $M_w = 11.9$ and $M_w = 7.0$ kg/mol, poly(1,3-propylene adipate-co-carbonate) (PPAC) of $M_w = 12.2$ kg/mol, poly(1,4-butylene adipate-co-terephthalate) (PBAT) of $M_w = 19.4$ kg/mol, poly(1,3-propylene adipate-co-terephthalate) (PPAT) of $M_w = 23.6$ kg/mol, poly(1,3-propylene-co-1,4-butylene adipate-co-terephthalate-co-carbonate) (PPBATIC) of $M_w = 32.6$ kg/mol were prepared in our lab according to the procedure described earlier [47] by two step polycondensation method using diacids dimethyl diesters and appropriate diols. Toluene and xylene were dried with sodium and distilled. Dichloromethane, chloroform and methanol were used without purification.

2.2. General procedure of controlled degradation of PLA carried out in a solvent

All reactions were carried out under nitrogen atmosphere in two neck round-bottom flasks with magnetic stirrer and water-cooled condenser. The three neck flask was used in the case of processes with temperature control, where the third neck was equipped with a thermometer. Toluene or xylene were added to PLA and solid state protic reagent (if any), which were placed in the flask. Then, the mixture was heated until complete dissolution of PLA. If a liquid protic reagent was used, it was introduced into the flask by a syringe and afterwards SnEH₂ was added. The reaction mixture was stirred and refluxed or heated at the adjusted temperature (in the processes with temperature control). Samples were collected during the process under nitrogen. After reaction, the mixture was cooled to room temperature and dissolved in methylene chloride (or chloroform) and then poured into excess methanol. The precipitated product was filtered off, washed with methanol and dried in a vacuum oven at 40 °C for 24 h. The products of reaction with diamines were not soluble in any popular organic solvent. In this case toluene (xylene) was vacuum distilled and the products were analyzed without any further purification.

2.3. General procedure of controlled degradation of PLA carried out in bulk

Most of the reactions were carried out under nitrogen in a two neck round-bottom flasks equipped with magnetic stirrer and water-cooled condenser. PLA and solid state protic reagent (if any) were heated until complete melting of PLA. If liquid protic reagent was used, it was introduced into the flask by a syringe and afterwards SnEH₂ was added. The reaction mixture was stirred and heated at the temperature range 180–200 °C. After reaction, the product was cooled to room temperature and dissolved in methylene chloride (or chloroform) and then poured into excess methanol. The precipitated product was filtered off, washed with methanol and dried in a

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