A delocalized carbanion monomer preparation: 4,5-dimethylene-1,8-octanediol for use as both functional condensation and diene monomers

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Summary

   The 2,3-dimethylene-1,3-butadiene dianion (2), prepared from 2,3-dimethyl-1,3-butadiene (1) using Lochmann's base, has been reacted with ethylene oxide to give 4,5-dimethylene-1,8-octanediol (3). This monomer has been incorporated into a polyester via low temperature solution polymerization, and the resultant copolyester has been characterized by ^{1}H NMR, intrinsic viscosity, and DSC. Also, the free radically formed diene polymer of 3 has been investigated.

Introduction

   Lochmann's base (n-butyllithium/potassium t-butoxide in pentane) (1) has been shown to cause allylic metalation of a number of conjugated dienes (2-4), including 2,3-dimethyl-1,3-butadiene (1) (5). These reactions are convenient because they are quick, clean, high yield (usually >80%), and the product precipitates out of solution as a salt, making isolation facile. Reaction of the 2,3-dimethylene-1,3-butadiene dianion (2) with ethylene oxide to form 4,5-di-methylene-1,8-octanediol (3), as shown in Figure 1, has previously been reported (6,7). This study investigates both polyesterification reactions and free radical diene polymerizations of compound 3.

   Historically, unsaturated units are incorporated into a polyester (specifically, poly(ethylene terephthalate) (PET)) through copolymerization with maleic anhydride (8). This results in a copolyester which contains isolated carbon-carbon double bonds in the backbone of the polymer itself, which are then reacted free radically with a vinyl-type monomer such as styrene to crosslink the material. Incorporation of diol 3 would lead to a copolyester which contains conjugated carbon-carbon double bonds as pendant groups. In addition to the traditional methods of crosslinking, this copolyester would have the potential to undergo a whole host of different reactions, such as Diels-Alder cycloadditions, not only to crosslink the polymer but also to form new polyester adducts.

   Previous attempts to incorporate 10 mole % of diol 3 into PET using melt condensation polymerization were unsuccessful (9). The diol did get incorporated into the polyester but the

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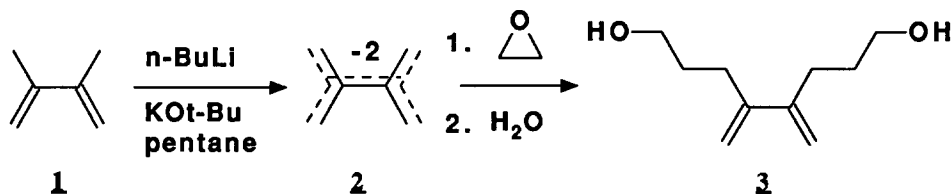
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high heat needed to carry out the transesterification also caused thermally initiated free radical polymerization of the diene moieties. It was shown that reaction conditions during the first step of the polycondensation (i.e., 195 °C under N2 for 2 1/2 hr) were severe enough to cause this effect. Thus, with two different types of polymerization occurring simultaneously, the resultant polymer was assumed to have a very complicated structure - probably being a crosslinked network.

In this study, low temperature solution polymerization was used to successfully incorporate diol **3** into PET and to keep the diene moieties intact. This copolyester has been characterized by ^{1}H NMR, intrinsic viscosity, and DSC and these results are included. Also, the diene polymer of diol **3** has been synthesized and attempts have been made to characterize it, since its structure could lead to a material with unusual properties.

Experimental

Ethylene glycol was distilled under vacuum over molecular sieves, dried for 24-48 hr over molecular sieves, redistilled under vacuum, and stored over molecular sieves in the dark. Terephthaloyl chloride was distilled under reduced pressure and used immediately after purification. Triethylamine (NEt3) was purified by refluxing with benzoyl chloride (4 ml benzoyl chloride to 100 ml NEt3) for 2 hr, filtering off insoluble material, distilling from sodium under nitrogen, refiltering, and redistilling from sodium under nitrogen; it was stored in the dark. Tetrahydrofuran (THF) was freshly distilled from sodium/potassium metal alloy with benzophenone as an indicator (blue anion radical). All other solvents and reagents were purified by standard methods.

^{1}H Nuclear magnetic resonance (NMR) spectra were recorded on a Varian EMS 360 spectrometer with chemical shifts reported in parts per million (ppm) downfield from tetramethylsilane (TMS). Polymer intrinsic viscosities were measured using a Cannon-Ubbelohde viscometer (size 50) suspended in a water bath at 30 °C with 3/5 v/v phenol/tetrachloroethane as the solvent. Thermal transitions were measured using a Perkin-Elmer Differential Scanning Calorimeter (DSC 7) controlled by a Perkin-Elmer 7500 Professional Data Station. Indium standard was used to calibrate the DSC 7; heating rates of 20 °C/min were used. Preparation of dianion **2** and diol **3** have been previously described (6).

Poly(ethylene terephthalate) Via Low Temperature Solution Polymerization

In a 500 ml nitrogen-filled flask equipped with a magnetic stir bar was placed 1.40 ml (1.55 g, 25 mmol) ethylene glycol, 6.94 ml (5.05 g, 50 mmol) triethylamine, and 170 ml dichloroethane. The flask was placed in an oil bath and heated to 50 °C. A solution of 5.075 g (25 mmol) freshly distilled terephthaloyl chloride in 70 ml dichloroethane was added dropwise over a period of 40 min with stirring. Upon completion of this step 10 ml dichloroethane was used to rinse in residual acid chloride from the addition funnel. The reaction was continued at 50 °C with stirring for 1 hr, during which time a white precipitate of polymer and triethylamine hydrochloride formed. After cooling, the reaction mixture was poured into 750 ml hexane with stirring. The solid material was collected via filtration, and the polymer was isolated from the triethylamine hydrochloride by a series of water washings. The polymer was dried under vacuum for 24 hr; yield of polymer was 4.50 g (94%). ^{1}H NMR (in CF3COOH): 8.2 ppm, s, 4H; 4.9 ppm, s, 4H.

Copolymer of Poly(ethylene terephthalate) and 4,5-dimethylene-1,8-octanediol (3) Via Low Temperature Solution Polymerization

The copolymer was made in the same manner as PET (above) using 0.35 ml (0.39 g, 6.3 mmol) ethylene glycol, 1.074 g (6.3 mmol) diol **3**, 3.50 ml (2.55 g, 25.2 mmol) triethylamine, 2.553 g (12.6 mmol) terephthaloyl chloride, and a total of 125 ml dichloroethane.

The polymer was isolated as before and dried under vacuum for 24 hr; yield of polymer was 1.99 g (64%). ^{1}H NMR (in CDCl$_3$): 8.2 ppm, s, 4H; 5.2 ppm, s, 2H; 5.0 ppm, s, 2H; 4.7 ppm, s, 4H; 4.3 ppm, tr, 4H; 2.4 ppm, m, 4H; 2.0 ppm, m, 4H.

Free Radical Diene Polymerization of 4,5-dimethylene-1,8-octanediol (3) in Solution - Trial 1

In a 100 ml nitrogen-filled flask equipped with a magnetic stir bar was placed 1.896 g (11.2 mmol) diol 3, 0.006 g azobisisobutyronitrile (AIBN), and 50 ml THF. The flask was heated to reflux (64 °C) and the reaction was allowed to proceed for 6 hr. After cooling, the reaction mixture was poured into 400 ml ethyl acetate whereupon a small amount of precipitate formed. The solid was isolated via filtration and dried under vacuum overnight; yield was 5.6 mg (0.3%).

Free Radical Diene Polymerization of 4,5-dimethylene-1,8-octanediol (3) in Solution - Trial 2

This polymerization was carried out in the same manner as in Trial 1, using 1.700 g (10 mmol) diol 3, 0.006 g benzoyl peroxide, and 50 ml THF. The product was isolated as before and dried under vacuum overnight; yield was 6.5 mg (0.4%).

Thermally Initiated Diene Polymerization of 4,5-dimethylene-1,8-octanediol (3) in Bulk

In a 15 ml nitrogen-filled flask equipped with a magnetic stir bar was placed 1.586 g (9.3 mmol) diol 3. The flask was placed in an oil bath and heated to 195 °C. The reaction was allowed to continue with stirring for 5 hr, during which time the reaction mass solidified. The product was collected as a solid, rubbery mass.

Free Radical Diene Polymerization of 4,5-dimethylene-1,8-octanediol (3) in Bulk

In a 25 ml nitrogen-filled flask equipped with a magnetic stir bar was placed 3.42 g (20.1 mmol) diol 3 and 0.010 g AIBN. The flask was placed in an oil bath and heated to 60 °C. The reaction was allowed to continue with stirring for 3 hr, during which time the reaction mixture became very viscous. The polymer was isolated by precipitation in chloroform (CHCl$_3$) followed by repeated stirring and washing with fresh portions of CHCl$_3$ to remove any unreacted monomer. The polymer was collected via filtration and dried under vacuum for 8 hr; yield of polymer was 0.253 g (7%).

Results and Discussion

Low temperature solution polycondensation is most commonly carried out using a diacid chloride and an aromatic diol (10). Aliphatic diols do not lend themselves as readily to this procedure due to the less acidic nature of the hydroxyl group protons of aliphatic diols as compared to aromatic diols. However, the use of this procedure has led to the formation of low molecular weight polyesters from terephthaloyl chloride and both ethylene glycol and 1,6-hexanediol (11).

PET was successfully synthesized using the low temperature solution polymerization method and the results, with literature values, are given in Table 1. The yield of polymer (obtained as a white powder) was high but, as predicted, the molecular weight of the polymer was low. The polymer was also characterized by ^{1}H NMR and no peaks were seen due to chain terminal groups.

The copolymer was synthesized in the same manner as PET, using 50 mole % ethylene glycol and 50 mole % diol 3. The resultant copolyester (also obtained as a white powder), contained 57 mole % ethylene glycol and 43 mole % diol 3. The presence of the double bonds in the polymer was confirmed by ^{1}H NMR (which was the method used to determine the copolymer composition). The yield of polymer was 65%, and the intrinsic viscosity was 0.12 dl/g. DSC showed that the copolyester had a Tg of 53 °C and exhibited no melting peaks above 0 °C. It should be noted that, while the copolymer was initially soluble in CDCl$_3$, upon storage in air for a few months the polymer did not dissolve, but would only swell, in CDCl$_3$, indicating crosslinking had occurred.

Table 1: Low Temperature Solution Polymerization of PET

	Experimental	Literature[9,11]
Yield	90%	65%
Intrinsic Viscosity (dl/g)	0.08[a]	0.15[b]
Molecular Weight (g/mole)	3,000[c]	3,000
DP	15	15
Tg (°C)	61	81
Tm (°C)	237	253

a Measured at 30°C in 3/5 v/v phenol / tetrachloroethane.
b Measured at 25°C in 1/3 w/w phenol / tetrachloroethane.
c Calculated from Mark-Houwink equation.[12]

In light of the ease with which diol 3 underwent diene polymerization during melt polycondensation reactions it was decided to investigate this diene polymer more closely. For this reaction emulsion and suspension polymerization are not desirable methods to use, since it is often difficult to remove all the residual suspending and emulsifying agents and obtain pure polymer (13). Either solution or bulk polymerization is a viable method; however, one must be aware of other possible limitations. For the polymerization of other dienes such as butadiene and isoprene, the monomers do not readily polymerize in bulk or solution with free radical catalysts; the rates are slow and the polymers are either of low molecular weight or crosslinked and insoluble (14). Yet it has been shown that bulk polymerization was successful in polymerizing 2,3-dimethyl-1,3-butadiene and 2,3-dinonadecyl-1,3-butadiene (15).

Two solution polymerizations were carried out under identical conditions (refluxing THF under N_2 for 6 hr), with different free radical initiators (AIBN or benzoyl peroxide). The results were disappointing; in both cases less than 0.5% polymer formed, and ^{1}H NMR showed that virtually all of the monomer remained unreacted.

A thermally initiated bulk polymerization was attempted under conditions similar to those of the melt polycondensations (195°C under N_2 for 5 hr). The resultant product, which was a rubbery mass, was insoluble in a wide range of solvents, but did swell greatly in benzyl alcohol and N,N-dimethylformamide (DMF), which both have solubility parameters of 12.1. DSC revealed no transitions from 35-230 °C. From these results it was concluded that, under such severe reaction conditions, the polymer had become crosslinked.

A free radically initiated bulk polymerization using AIBN was carried out under milder conditions (60°C under N_2 for 3 hr). The reaction time was limited to keep the % conversion low to minimize the potential for crosslinking. Initially the reaction mixture was poured into methanol, in which no polymer precipitated. Upon removal of the methanol, chloroform was then added, which did precipitate the polymer. Repeated extractions with chloroform removed unreacted monomer, and the resultant polymer, obtained in 7% yield, was a white, slightly tacky, slightly rubbery material.

After isolation of the polymer it was discovered that it would not redissolve in methanol. This could be due to either a small amount of post-reaction oxidative crosslinking or it could be due to the fact that in the precipitation of the original reaction mixture the high amount of unreacted monomer acted as a cosolvent to help solvate the polymer. The polymer swelled greatly in benzyl alcohol and DMF, but would not dissolve. DSC revealed that this polymer had

a Tg of -6°C, exhibited no melting peaks above -40°C, and degraded at temperatures greater than 145°C. Due to the insolubility of the polymer it could not be analyzed by any other method.

Thus, under mild conditions, the free radical diene polymerization in bulk of 4,5-dimethylene-1,8-octanediol (3) was successful in that a polymer was obtained, the % conversion was kept low, and the polymer as initially made could not have been crosslinked, due to its solubility both in monomer and in a monomer/methanol mixture. From DSC it can be inferred that the polymer is amorphous; however, the polymer defies a detailed analysis of its structure owing to its insolubility after isolation. Further work needs to be done on this polymer if its structure is to be determined and its properties to be investigated.

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