Synthesis and characterization of 2,3-dialkyl-1,4-butanediols and copolyesters containing these moieties

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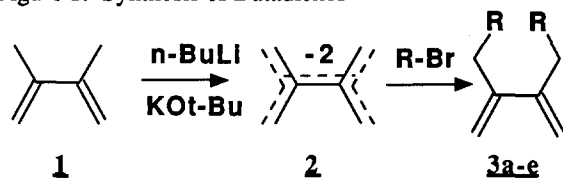Pennsylvania State University, University Park, PA 16802, USA

Summary

Reaction of the 2,3-dimethylene-1,3-butadiene dianion (made using Lochmann's base) with a series of primary alkyl halides yielded 2,3-dialkyl-1,3-butadienes, which were converted to the corresponding 2,3-dialkyl-1,4-butanediols via hydroboration/oxidation. Along with ethylene glycol and dimethyl terephthalate these disubstituted butanediols were incorporated into copolyesters using melt condensation polymerization. The resultant copolymers were characterized by ^{1}H NMR, inherent viscosity, and DSC. From this data the effects of varying the length and amount of alkyl side groups on the copolyester syntheses and properties were studied.

Introduction

Lochmann's base system (n-butyllithium/potassium t-butoxide in pentane) (1) has been shown to cause allylic metalation of 2,3-dimethyl-1,3-butadiene, **1**, to form the delocalized dicarbanion, **2**, cleanly and quickly in yields of greater than 80% (2). The 2,3-dimethylene-1,3-butadiene dianion, **2**, has been reacted with a series of primary alkyl bromides (1-bromo-butane, 1-bromododecane, and 1-bromooctadecane) to form 2,3-dialkyl-1,3-butadienes, **3**, in high yield (3,4). By reacting dianion **2** with additional alkyl bromides, this series of dialkyl butadienes has been expanded. Subsequent 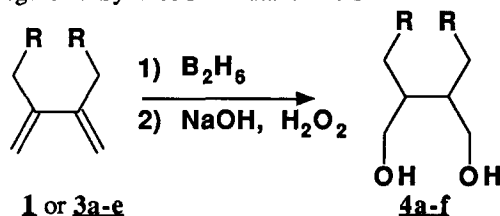hydroboration/oxidation of these compounds with diborane (B_2H_6) (5,6) and alkaline hydrogen peroxide (7) gives the corresponding 2,3-dialkyl-1,4-butanediols, **4**. The effects of alkyl side groups on the syntheses and properties of polyesters has been briefly studied (8-12). These previous attempts to incorporate alkyl side groups into polyesters met with limited success in that polymeric products were formed; however, the polymers were invariably of low to moderately low molecular weights. Most notable is the case of synthesizing

Figure 1: Synthesis of Butadienes

	R	Recovered Yield
3a	$(CH_2)_3CH_3$	48%
3b	$CH_2CH(CH_3)_2$	41%
3c	$(CH_2)_{11}CH_3$	45%
3d	$(CH_2)_{14}CH_3$	49%
3e	$(CH_2)_{17}CH_3$	57%

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poly (2,3-dialkylbutanediol terephthalates) with alkyl groups ranging from methyl to hexadecyl - in this example it was speculated that a decrease in diol volatility was a possible cause for low molecular weight polymer formation (12). The plan was to synthesize copolyesters of dimethyl terephthalate, ethylene glycol, and the various 2,3-dialkyl-1,4-butanediols via melt condensation polymerization to avoid the problem of low molecular weight polymer formation (by adding an excess of diol and removing the more volatile ethylene glycol) and that the length and amount of alkyl side chains in the polymers could be varied at will. The copolyesters made using this synthetic approach could then be studied for the effects of varying the length and amount of alkyl side groups on polymer properties; specifically, the copolymer compositions, inherent viscosities, and thermal behavior (Tg, Tm, and side chain crystallinity).

Figure 2: Synthesis of Butane Diols

	R	Recovered Yield
4a	H	60%
4b	$(CH_2)_3CH_3$	58%
4c	$CH_2CH(CH_3)_2$	69%
4d	$(CH_2)_{11}CH_3$	67%
4e	$(CH_2)_{14}CH_3$	55%
4f	$(CH_2)_{17}CH_3$	62%

Experimental

Potassium t-butoxide, n-BuLi solution in hexane (2.2-2.6 M), and borane-tetrahydrofuran complex (1.0 M) were used as received from Aldrich Chemical Co. 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. Dimethyl terephthalate was recrystallized from absolute ethanol, dried in a vacuum oven for 24 hr, and 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 either purified by standard methods or used as received.

The [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). ^{1}H NMR spectra of monomers were run in CDCl3, polyesters were run as 2% polymer solutions in either CF3COOH or D5PhNO2. Liquid chromatography was performed on a Waters Prep LC/System 500A Liquid Chromatograph equipped with a one inch SemiPREP column packed with silica gel (grade 633, 200-425 mesh). Polymer inherent viscosities were measured using a Cannon-Ubbelohde viscometer (size 50) suspended in a water bath at 30°C using 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.

2,3-dimethylene-1,3-butadiene Dianion (2)

Dianion **2** was prepared by adding 4.4 ml (40 mmol) 2,3-dimethyl-1,3-butadiene (**1**) in 50 ml pentane to a mixture of 8.96 g (80 mmol) KOt-Bu, 100 ml pentane, and 32 ml (80 mmol)

2.5 M n-BuLi in hexane in a nitrogen-filled flask. After 20 min of stirring the dianion salt was allowed to settle, the liquid was removed via syringe, and the salt was blown dry with a stream of nitrogen. For reaction the dianion was suspended in 100 ml THF.

2,3-dipentyl-1,3-butadiene (3a)

The flask containing dianion 2 in THF was placed in an ice water bath and a solution of 8.6 ml (10.96 g, 80 mmol) 1-bromobutane in 40 ml THF was added dropwise. The reaction mixture was stirred while warming to room temperature. The solution was extracted three times with an aqueous saturated sodium chloride solution, then the aqueous layers were combined and back extracted two times with THF. The organic layers were combined and dried over magnesium sulfate, filtered, and the organic solvent removed via rotary evaporation. The product was purified by vacuum distillation (bp 55°C at 0.3 mm) in 48% yield. ^{1}H NMR (CDCl$_3$) δ 0.9 (t, 6H), 1.5 (s, 12H), 2.3 (t, 4H), 4.8 (s,2H), 5.0 (s, 2H).

2,3-diisopentyl-1,3-butadiene (3b)

This compound was prepared in the same manner as 3, with 8.7 ml (10.96 g, 80 mmol) 1-bromo-2-methylpropane in 40 ml THF. The product was purified by vacuum distillation (bp 60°C at 0.3 mm) in 41% yield. ^{1}H NMR (CDCl$_3$) δ 0.9 (t, 12H), 1.3 (m, 4H), 1.6 (m, 2H), 2.2 (t, 4H), 4.8 (s, 2H), 5.0 (s, 2H).

2,3-ditridecyl-1,3-butadiene (3c)

This compound was prepared in the same manner as 3 with 19.2 ml (19.9 g, 80 mmol) 1-bromododecane in 40 ml THF. The product was purified by recrystallization from diethyl ether (mp 42°C) in 45% yield. ^{1}H NMR (CDCl$_3$) δ 0.9 (t, 6H), 1.4 (s, 44H), 2.3 (t, 4H), 4.8 (s, 2H), 5.0 (s, 2H).

2,3-dihexadecyl-1,3-butadiene (3d)

This compound was prepared in the same manner as 3 with 23.2 ml (23.3 g, 80 mmol) 1-bromopentadecane in 40 ml THF. The product was purified by recrystallization from diethyl ether (mp 52°C) in 49% yield. ^{1}H NMR (CDCl$_3$) δ 0.9 (t, 6H), 1.3 (s, 56H), 2.3 (t, 4H), 4.8 (s, 2H), 5.0 (s, 2H).

2,3-dinonadecyl-1,3-butadiene (3e)

This compound was prepared in the same manner as 3 with 27.3 ml (26.6 g, 80 mmol) 1-bromooctadecane in 40 ml THF. The product was purified by recrystallization from diethyl ether (mp 55°C) in 57% yield. ^{1}H NMR (CDCl$_3$) δ 0.8 (t, 6H), 1.2 (s, 68H), 2.3 (t, 4H), 4.8 (s, 2H), 5.0 (s, 2H).

2,3-dimethyl-1,4-butanediol (4a)

In a nitrogen-filled flask was placed 11.3 ml (8.2 g, 100 mmol) 2,3-dimethyl-1,3-butadiene (1) in 100 ml THF. The flask was placed in an ice bath and 50 ml 1.0 M B$_2$H$_6$ in THF was added dropwise. After warming to room temperature the excess hydride was decomposed by dropwise addition of distilled water. The organoborane was oxidized at 30-50°C by the addition of 24 ml 3 N NaOH, followed by dropwise addition of 24 ml 30% H$_2$O$_2$. After 1 hr potassium carbonate was added until two layers formed. The organic layer was separated and

the aqueous layer was extracted two times with THF. The organic layers were combined and dried over magnesium sulfate. Following filtration and removal of the solvent by rotary evaporation the product was purified by vacuum distillation (bp 105-106°C at 2 mm) in 60% yield. ^{1}H NMR (CDCl$_3$) δ 0.9 (t, 6H), 1.8 (s, 2H), 3.5 (d, 4H), 4.7 (s,2H).

2,3-dipentyl-1,4-butanediol (4b)

This compound was prepared in the same manner as **4a** using 5.08 g (26mmol) **3a** in 75 ml THF, 20 ml 1.0 M B$_2$H$_6$ in THF, 10 ml 3 N NaOH, and 10 ml 30% H$_2$O$_2$. The product was purified by prep HPLC (solvent: 4/1 hexane/ethyl acetate) in 58% yield. ^{1}H NMR (CDCl$_3$) δ 0.9 (t, 6H), 1.3 (s, 16H), 1.9 (m, 2H), 3.5 (d, 4H), 4.0 (s, 2H).

2,3-diisopentyl-1,4-butanediol (4c)

This compound was prepared in the same manner as **4a** using 2.85 g (15 mmol) **3b** in 75 ml THF, 14 ml 1.0 M B$_2$H$_6$ in THF, 7 ml 3 N NaOH, and 7 ml 30% H$_2$O$_2$. The product was purified by prep HPLC (solvent: 4/1 hexane/ethyl acetate) in 69% yield. ^{1}H NMR (CDCl$_3$) δ 0.9 (d, 12H), 1.4 (m, 10H), 1.8 (m, 2H), 3.3 (s, 2H), 3.5 (d, 4H).

2,3-ditridecyl-1,4-butanediol (4d)

This compound was prepared in the same manner as **4a** using 4.18 g (10 mmol) **3c** in 50 ml THF, 10 ml 1.0 M B$_2$H$_6$ in THF, 5 ml 3 N NaOH, and 5 ml 30% H$_2$O$_2$. The product was purified by prep HPLC (solvent: 6/1 hexane/ethyl acetate) (mp 41°C and 48°C) in 67% yield. ^{1}H NMR (CDCl$_3$) δ 0.9 (t, 6H), 1.3 (s, 48H), 1.8 (m, 2H), 2.8 (s, 2H), 3.6 (d, 4H).

2,3-dihexadecyl-1,4-butanediol (4e)

This compound was prepared in the same manner as **4a** using 5.18 g (10 mmol) **3d** in 75 ml THF, 10 ml 1.0 M B$_2$H$_6$ in THF, 5 ml 3 N NaOH, and 5 ml 30% H$_2$O$_2$. The product was purified by prep HPLC (solvent: 7/1 hexane/ethyl acetate) (mp 52°C and 59°C) in 55% yield. ^{1}H NMR (CDCl$_3$) δ 0.9 (t, 6H), 1.3 (s, 60H), 1.8 (m, 2H), 2.8 (s, 2H), 3.6 (d, 4H).

2,3-dinonadecyl-1,4-butanediol (4f)

This compound was prepared in the same manner as **4a** using 5.86 g (10 mmol) **3e** in 75 ml THF, 10 ml 1.0 M B$_2$H$_6$ in THF, 5 ml 3 N NaOH, and 5 ml 30% H$_2$O$_2$. The product was purified by prep HPLC (solvent: 8/1 hexane/ethyl acetate) (mp 60°C and 65°C) in 62% yield. ^{1}H NMR (CDCl$_3$) δ 0.8 (t, 6H), 1.4 (s, 72H), 1.9 (m, 2H), 2.5 (s, 2H), 3.5 (d, 4H).

General Procedure for the Synthesis of Copolyesters Using Melt Condensation Polymerization

The polymerization apparatus consisted of a 125 ml flat-bottom flask equipped with a magnetic stir bar, claisen adapter, a bent distillation adapter with a vacuum connection, and a 15 ml receiving flask. A firestone valve was used for application of both a nitrogen atmosphere and a vacuum to be alternately placed on the system.

In the flat-bottom flask was placed 1.970 g (0.0100 mol) dimethyl terephthalate, 0.0235 mol total diol, 0.006 g calcium acetate dihydrate, and 0.003 g antimony trioxide (Sb$_2$O$_3$). The flask was placed in an oil bath, flushed with nitrogen, and heated to 195-198°C with stirring. As the reaction proceeded methanol was distilled off and collected in the cooled (ice water bath) receiving flask. Heating and stirring were continued for 2 1/2 hr, keeping the system under a

nitrogen atmosphere. The flask was next heated to 220-225°C for 20 min and then at 265-270°C for 30 min. A vacuum was slowly pulled on the system and the pressure held at less than 0.3 mm while heating and stirring were continued for 3 1/2 hr. (Note: for long reaction time polymerizations, this step was extended to 8 1/2 hr.) During this time excess ethylene glycol was distilled off the the reaction flask and collected. Once the polymerization was complete, the flask was removed from the oil bath and allowed to cool to room temperature, keeping the system under vacuum. The polymer was isolated by dissolving in a 3/5 v/v phenol/tetrachloroethane solvent mixture, followed by precipitation in methanol with stirring. The polymer was collected by filtration and placed in a vacuum oven for 24 hr at 50-80°C to remove any traces of residual solvent.

Results and Discussion

The reaction of dianion **2** with a series of primary alkyl bromides goes rapidly and in very good yields. The reaction scheme, products made, and recovered yields appear in Figure 1. The disubstituted dienes were characterized by ^{1}H NMR, and the results are given in the experimental section. Compared to a previously published procedure (13) this scheme provides an easier and more convenient route to 2,3-dialkyl-1,3-butadienes.

The hydroboration of the resulting dienes, followed by oxidation with alkaline hydrogen peroxide, offers a convenient method for the anti-Markovnikov hydration preparation of disubstituted butandiols. It has been shown that this reaction scheme is easy, quick, and affords high yields of the desired diol for 2,3-dimethyl-1,3-butadiene (**4a**) (5) and 2,3-dinona-decyl-1,3-butadiene (**4f**) (3). Extending this reaction scheme to the series of 2,3-dialkyl-1,3-butadienes (**3a-3e**) it is shown, in Figure 2, that the syntheses of the various 2,3-dialkyl-1,4-butanediols are, also, all facile and of high yield. For all the diols both diastereomers were formed but were not separated prior to subsequent polymerizations. The 2,3-dialkyl-1,4-butanediols were characterized by ^{1}H NMR, and the results are given in the experimental section.

The results of the syntheses and characterizations of the copolyesters containing the various 2,3-dialkyl-1,4-butanediols are given in Table 1. For comparison, results for poly(ethylene terephthalate) (PET) made in an identical manner are included. The copolyester compositions were determined from ^{1}H NMR spectra. In all cases, the copolyesters are "enriched" in ethylene glycol relative to the starting ratio of diols in the reaction vessel, which is exactly opposite of what would be expected with ethylene glycol being the more volatile diol. This effect is due to an undesired side reaction - dehydration and cyclization of the disubstituted butanediols to 2,3-dialkyltetrahydrofurans (**5a-f**) during the polymerization (see Figure 3). Three of these compounds have been isolated (**5b** and **5c** from the distillate and **5f** by extraction from the copolyester) and characterized by ^{1}H NMR, with the results given in Table 2.
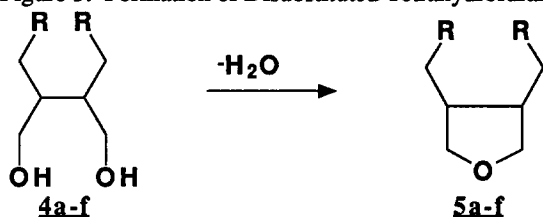
It was found that, regardless of the length of the alkyl side group, 65-70% of the disubstituted butanediol cyclized during the polyesterification. For comparison, during the polymerization of poly(butylene terephthalate) anywhere from 3 to 20% of the 1,4-butanediol cyclizes to form tetrahydrofuran, depending on the reaction conditions (14-16). The much larger percentage of cyclization of the 2,3-dialkyl-1,4-butanediols takes place due to steric factors (Thorpe-Ingold effect) (17,18) - ring formation eases steric strain of the substituents by

Table 1: Copolyester Synthesis and Characterization Data

Diol Used	Initial mole ratio of ethylene glycol / 4	Final mole ratio of ethylene glycol / 4	ηinh (dl/g)	Tg (°C)	Tm (°C)
-	100/0	100/0	1.65	81	253
4a	75/25	86/14	0.51	73	228
	68/32*	80/20*	0.38	60	209
	51/49	70/30	0.44	63	-
	52/48	67/33	0.18	52	180
	26/74	50/50	0.20	44	-
	26/74	43/57	0.21	31	-
	10/90	33/67	0.24	20	-
4b	79/21	89/11	0.38	65	241
	68/32	85/15	0.29	56	229
	68/32*	84/16*	0.27	52	224
	61/39	79/21	0.26	47	218
4c	78/22	93/7	0.22	65	237
	68/32	82/18	0.33	61	225
4d	79/21	90/10	0.46	51	248
	70/30	85/15	0.16	38	246
	68/32*	79/21*	0.20	52	224
	62/38	79/21	0.17	34	242
	51/49	67/33	0.14	0	172
4e	79/21	83/17	0.14	-	13
					250
	61/39	74/26	0.20	-	11
					246
	63/37	72/28	0.26	-	8
					242
4f	79/21	87/13	-	-	34
					250
	69/31	78/22	-	-	33
					251
	69/31*	73/27*	-	-	34
					252
	62/38	70/30	-	-	33
					248

forcing them apart. Also, when there are heteroatoms (in this case oxygen) in the ring to be formed, ring formation is generally easier than for carbocyclic rings, especially in the medium ring region. The major nonbonded repulsion in medium rings is between hydrogens; when the hydrogens are absent (-CH$_2$- is replaced by -O-) the strain is decreased and ease of ring formation increased (19). Therefore, due to the cyclization side reaction, much less disubstituted butanediol is available for the esterification reaction. Varying the length of the alkyl side groups had very little effect on the final copolymer compositions. Again, if there is a slight trend it is that, when the alkyl side chains become very long (hexadecyl and nonadecyl), a slightly higher amount of 2,3-dialkyl-1,4-butanediol becomes incorporated into the copolyester. However, this may be just the effect of the decreasing volatility of the disubstituted butanediols with increasing alkyl side chain length.

Figure 3: Formation of Disubstituted Tetrahydrofurans

Table 2: ^{1}H NMR of Disubstituted Tetrahydrofurans

5b		5c		5f	
0.9	(t, 6H)	0.9	(d, 12H)	0.9	(t, 6H)
1.25	(s, 16H)	1.3	(m, 10H)	1.25	(s, 72H)
1.65	(s, 1H)	1.7	(s, 1H)	1.8	(s, 1H)
2.1	(s, 1H)	2.15	(s, 1H)	2.2	(s, 1H)
3.4	(m, 2H)	3.4	(m, 2H)	3.5	(m, 2H)
3.8	(m, 2H)	3.9	(m, 2H)	4.0	(m,2H)

Incorporation of the bulkier 2,3-diisopentyl-1,4-butanediol (as compared to 2,3-dipentyl-1,4-butanediol) monomer into copolyesters had virtually no effect on the final copolymer compositions and properties. The most likely explanation is that the steric hindrance was too far removed from the reaction site to cause any significant effects.

The polyester syntheses which are marked by asterisks are those in which the polymerization time during the second step (heat to 265-270°C and hold under vacuum) was extended from 3 1/2 to 8 1/2 hr. As can be seen in Table 1, in general, there appears to be no major effects on either final copolymer compositions or polymer properties. Increasing the polymerization time further is not practical, due to potential degradation of the copolyesters and/or monomers.

DSC data for the copolyesters appears in Table 1. All samples were given a uniform thermal history - heated to above Tm at 20°C/min, quenched at 200°C/min, then reheated at 20°C/min. The results given are data taken during the second heating run. All polymers which were semicrystalline (except PET) exhibited a recrystallization exotherm in the DSC. Also, Tm was defined as the maximum of the endothermic peak and Tg was defined as the midpoint of the heat capacity change.

Tgs for the copolyesters decreased both as the length and amount of alkyl side chains increased, as would be expected from free volume considerations (20). For the series of copolyesters with methyl side groups, some Tg values are lower than predicted by the copolymer equation (21) $1/Tg = w_1/Tg_1 + w_2/Tg_2$, taking a Tg value for PET of 81°C and a Tg value for poly(2,3-dimethylbutanediol terephthalate) of either 43°C or 32°C (12). Thus some of these copolyesters must be of low molecular weight - low enough to be in a regime where the Tg of the copolymer becomes molecular weight dependent. For copolyesters with hexadecyl and nonadecyl side groups Tgs could not be observed (down to -40°C); it is assumed that the transitions were obscured by the Tm peaks.

Tm peaks due to side chain crystallinity were observed for alkyl side chains containing sixteen and nineteen carbon atoms (at 11°C and 34°C respectively). This is in good agreement with previous results (12) where a Tm of 14°C was obtained for homopolyesters with hexadecyl side chains. Thus, the minimum number of carbon atoms needed to observe side chain crystallinity in these polyesters is greater than thirteen but less than or equal to sixteen.

The Tm peaks obtained for polymer backbone crystallinity were due mainly to recrystallization in the DSC during heating. The samples themselves exhibited little or no residual crystallinity. In general, for copolyesters with the same number of carbon atoms in the side chain, as the amount of alkyl side chains increased the Tm decreased; however, the magnitude of this decrease became smaller as the alkyl side chains became longer. Copolymers with similar compositions exhibited an increase in Tm with increasing alkyl side chain length, which appears to indicate that the copolyesters are becoming blockier. For some copolyesters containing methyl side groups the polymer is amorphous even upon heating in the DSC, which would indicate a random monomer placement. In the cases of very long alkyl side chains (hexadecyl and nonadecyl) the polymer Tm values are very close to that of PET (253°C).

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