A New Homologous Series of Linear Aliphatic Unsaturated Hydroxypolyesters as Polyol Soft Segments for Polyurethanes: Synthesis and Characterization

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ABSTRACT: Synthesis and characterization of a new series of low molecular weight (MW = 500–3000) OH-terminated linear aliphatic unsaturated polyesters based on *cis*-2-butene-1,4-diol and oxalic to sebacic acid were investigated. Direct polycondensation and transesterification methods were used for the syntheses. The latter was recognized to be the preferable method due to its lower reaction temperature and time, lower diol/diacid ratio, absence of decarboxylation, and formation of a product with low polydispersity ($\bar{M}_w/\bar{M}_n = 1.3–2.7$). Elemental analysis, GPC, FTIR, ^{1}H-NMR, DSC, and WAXD were used for the investigations. A segmented polyurethane based on poly (*cis*-2-butylene adipate) glycol was also synthesized and spectroscopically identified. ©1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 173–183, 1998

Key words: *cis*-2-butene-1,4-diol; synthesis; hydroxy-terminated polyester; transesterification; segmented polyurethane

INTRODUCTION

Low molecular weight linear aliphatic polyesters that are traditionally used in PVC plastisizers[1] were recently used for the delivery of active agents (i.e., pharmaceuticals, agrochemicals) in proper environment through biodegradation controlled release.[2]

Hydroxy-terminated polyesters (hydroxypolyesters) as macroglycols or polyols are used for preparation of block copolyesters[3] and polyester-based urethane rubbers.[4] They reacted either alone or in combination with diols or diamines to give segmented polyurethanes, which are marketed as aqueous dispersions, solutions, or as powders that are thermoplastically processable or soluble in special solvents. They may be combined on site with polyisocyanates and various additives to form soft to hard foams, elastomers, adhesives, flexible coatings, and joint fillers.[5] On the other hand, polyurethanes have found many applications as biomaterials due to their excellent physical properties and relatively good biocompatibility.[6] Polyurethanes based on linear OH-terminated polyesters, diphenylmethane-4,4′-diisocyanate (MDI), and glycol chain extenders (with a 1 : 1 ratio of NCO and OH groups), usually have excellent elastomer properties and can be processed as thermoplastics. Thermoplastic polyurethane elastomers are now well established as synthetic rubbers as well as engineering plastics for a multitude of applications mentioned above, and also as compounds for polymer alloys.[7]

In the polyesters area itself, inclusion of the C=C bond in the polymer backbone (often in an acid component) to permit a subsequent curing process, results in polymeric materials with improved physico-chemical properties.[8] Replacement of the C=C unsaturation with the diol component in polyester chains has been our research

Table I   Optimized Reaction Conditions, Elemental Analysis, Yield, Viscosity, and Other Specifications of OH-PBms

Polyester	B2D[a]	Reaction Temp., °C	App[b]	Yield, %	OH-V[c]	$\bar{M}_n$[d] (egt)	$\overline{DP}_n$[e] (egt)	$[\eta]$[f], dL/g	Calcd.[g], %			Found, %		
									C	H	O	C	H	O
OH-PB0	110	120	ms	55	214	520	3.0	0.26	52.7	5.14	41.99	50.70	4.20	45.10
OH-PB1	30	125	bl	56	127	870	5.0	0.05	54.98	5.62	39.60	53.80	5.20	41.00
OH-PB2	30	120	ws	85	55	1940	10.9	0.27	56.66	6.05	36.99	56.45	5.94	37.61
OH-PB3	30	125	bl	68	50	2100	10.9	0.28	58.95	6.67	34.34	58.42	6.76	34.82
OH-PB4	30	130	cs	88	38	2870	14.0	0.30	60.68	7.16	32.03	60.00	7.20	32.80
OH-PB5	30	130	ws	81	45	2380	10.8	0.44	62.41	7.62	30.05	62.20	7.50	30.30
OH-PB6	30	130	cs	70	90	1200	4.9	0.40	63.74	8.13	27.90	63.58	8.10	28.32
OH-PB7	50	128	ws	75	37	2900	11.7	0.41	64.80	8.37	26.46	64.92	8.40	26.68
OH-PB8	30	130	cs	78	35	3090	11.8	0.55	65.96	8.69	25.05	66.00	8.80	25.20

[a] Mol % of excess B2D.
[b] Product appearance: ms = milky solid, bl = brown liquid, ws = white solid, cs = cream solid.
[c] Hydroxyl value (mg KOH/g).
[d] obtained from end-group titration (egt).
[e] based on $\bar{M}_n$ (egt).
[f] in CHCl$_3$; 30 ± 0.05°C.
[g] The elemental analyses were calculated from the whole chain parts of each polyester based on structure 1 and average of $\bar{M}_n$ (egt) and $\bar{M}_n$ (GPC).
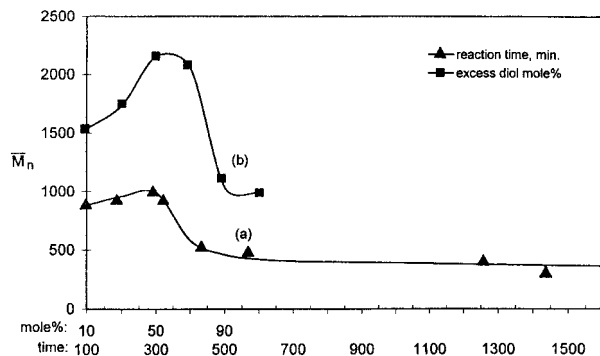
Figure 1 Molecular weight variation with a reaction time and excess diol mol % in the direct polyesterification of sebacic acid and *cis*-2-butene-1,4-diol in anisole, at 170°C; (a) in 110 mol % of excess diol, (b) in a reaction time of 300 min.

interest. We have recently studied a series of linear polyesters based on *cis*-2-butene-1,4-diol (B2D).[9–12] Some of these polyesters had already been prepared through a direct polyesterification method.[13–15] Marvel has reported the synthesis of similar polyesters using polyesterification of dimethyl sebacate and butyne diol in the presence of litharge as a catalyst.[16] Smith et al. have synthesized some similar aliphatic oligoesters via both mentioned methods.[17]

B2D, the most available aliphatic unsaturated diol, is used to produce some valuable polymers such as graftable unsaturated segmented polyurethanes[18] and some crosslinkable polyesters for biomedical composites.[19] New segmented thermoplastic terephthalate/B2D-based polyester elastomer, named Gaflex®, has been prepared and commercialized.[20] Study of a similar copolyester[21] and thermal behavior of some C_4 aliphatic polyoxalates are reported elsewhere.[22] Moderate reactivity of C=C unsaturation in the B2D-based macromers has been the base of some chemically modified polyesters[23] or epoxidized poly(ester-amide)s.[15,24] We found that there are just scattered reports on unsaturated diol-containing polyesters, and OH-terminated polyesters based on the *cis*-2-butene-1,4-diol (OH-PBms) has not been studied so far. This article describes an attempt to optimize the preparation conditions of the complete series of the low molecular weight polyesters with hydroxy-terminated chains and low polydispersity (Structure 1). In addition, to use as unsaturated polyester polyol soft segment in urethane polymers, these macromolecules are expected to have potential applications in several mentioned areas; e.g., other block copolymers, thermosetting

resins, plasticizers, and biodegradable and controlled-release systems.

$$HO—CH_2CH=CHCH_2—[—OOC—(CH_2)_m—$$
$$COO—CH_2CH=CHCH_2—]_n—OH$$
$$(OH-PBm; m = 0–8)$$
$$\mathbf{1}$$
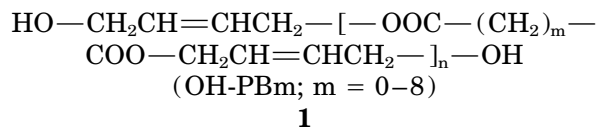
Syntheses were carried out through both direct polyesterification (in anisol as solvent) and the ester-interchange (transesterification or dealcoholation) methods. In the latter, diethyl carboxylates were dealcoholized with *cis*-2-butene-1,4-diol in the presence of PbO as the catalyst.

The hydroxypolyesters have been characterized by elemental analysis, Fourier transform infrared (FTIR), and ¹H-nuclear magnetic resonance (NMR) spectroscopy. Gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and wide-angel X-ray diffraction (WAXD) were also used for the investigations.

A representative poly(ester urethane) based on OH-PB4 ($\overline{M}_n$ = 2870, hydroxy value = 38), MDI, and 1,4-butanediol (as a chain extender) was also synthesized and analyzed by infrared spectroscopy.

EXPERIMENTAL SECTION

Materials

2-Butene-1,4-diol (Aldrich, 99.5% *cis*) was used as received. A three-step synthesis was applied to prepare pimelic acid from tetrahydropyran.[25]
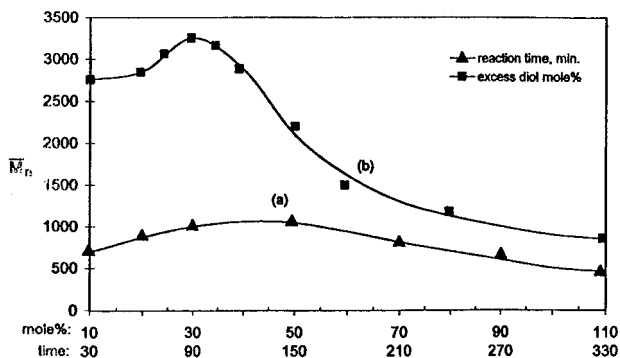

Figure 2 Molecular weight variation with reaction time and excess diol mol % in the polycondensation of diethyl adipate and *cis*-2-butene-1,4-diol through transesterification at 130°C; (a) in 110 mol % of excess diol, (b) in a reaction time of 130 min.
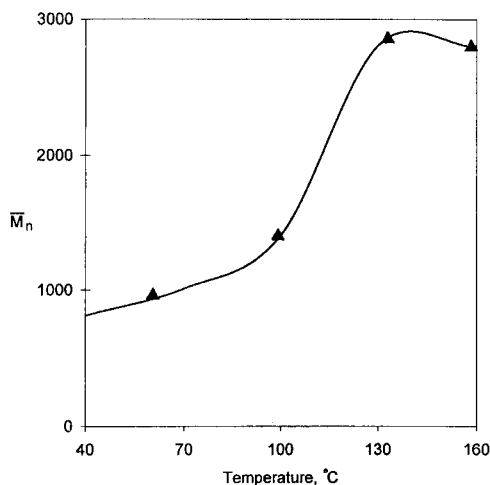
Figure 3 $\bar{M}_n$–temperature curve for the synthesis of poly(*cis*-2-butenylene adipate) in a reaction time of 120 min and an excess diol mol % of 40.

Glutaric acid (Riedel) was used after twice recrystallization in benzene. Diethyl malonate, dicarboxylic acids (all Riedel), and lead (II) oxide (Merck) were used without further purification. Diethyl carboxylates were prepared according to standard procedures.[25] Spectral data (NMR, IR) and physical constants (m.p., b.p., refractive index, and density) of all monomers were checked before use. Other chemicals (all from Merck) were used as received.

Measurements

The polymer solution viscosity values were measured at $30 \pm 0.05°C$ in $CHCl_3$ using a Cannon–Fenske-type viscometer. A Heraeus CHNO Analyser system was used for elemental analysis. FTIR spectra were measured by a Mattson 1000 spectrometer. ^{1}H-NMR spectra were obtained on a AC 80 Bruker using tetramethylsilane as an internal standard (solvent $CDCl_3$). GPC analysis of polymers (in THF as solvent) was performed at 30°C with a Waters 150C system equipped with Ultrastyragel columns (500, 10^3, 10^4, 10^5 Å), a data processing system, a RI detector, and a calibration curve for polystyrene standards.

DSC measurements were performed by a DSC PL instrument at a heating rate of 10°C/min. WAXD powder patterns were obtained via a Philips PW 1840-90 system using Ni-filtered Cu-k_α radiation. The scan speed was 0.02 2θ/s.

Polyester Synthesis

Method A: Direct Polycondensation

Dicarboxylic acids were condensed with 2-butene-1,4-diol (110 mol % excess) in anisole as solvent according to the previous description.[10] Under a nitrogen atmosphere, the reactants, solvent, and inhibitor (hydroquinone) were mechanically stirred and heated at 170°C. The condensed water was collected in a Dean-Stark trap. Finally, the heating continued at 200°C under reduced pressure (150 Torr) for 0.5 h. The polymer was dissolved in chloroform, precipitated in cold methanol filtered, and vaccum dried.

Titration methods were applied during the reaction period to determine the acid value (AV) and the hydroxy value (OH-V) for calculating the number average molecular weight, $\bar{M}_n$,[26] using the equation of $\bar{M}_n = 2000 \times 56.11/(AV + OH-V)$. The accuracy of resulted $\bar{M}_n$ values through this method was ±16; according to $\bar{M}_n$ determination of a standard poly(propylene glycol) with known $\bar{M}_n$.

Method B: Transesterification

The known ester-interchange polycondensation procedure[27] was modified and optimized as following. 0.1 mol of diethylcarboxylate, excess amounts (10–110 mol %) of *cis*-2-butene-1,4-diol, 0.1 g of PbO as the catalyst and 0.1 g of hydroquinone as the inhibitor were placed in a four-necked reactor equipped with a silicon-sealed mechanical stirrer, heating mantle, thermometer, nitrogen inlet, and a reflux condenser. The mixture heated at 120–130°C for 150 min. Sample pipetting for $\bar{M}_n$ determination was performed during this period. After changing the arrangement into vaccum distillation, the temperature was increased to 170°C for 30 min under reduced pressure (150 Torr) to remove condensed ethanol and residual diol. The viscous brown liquid was dissolved in hot chloroform, filtered, precipitated in an excess quantity
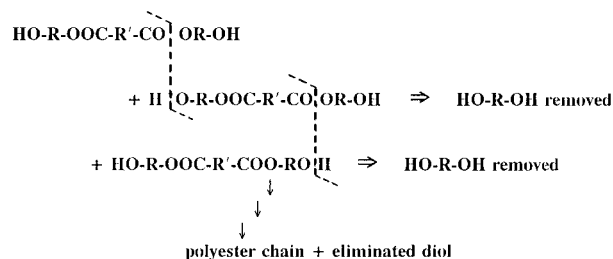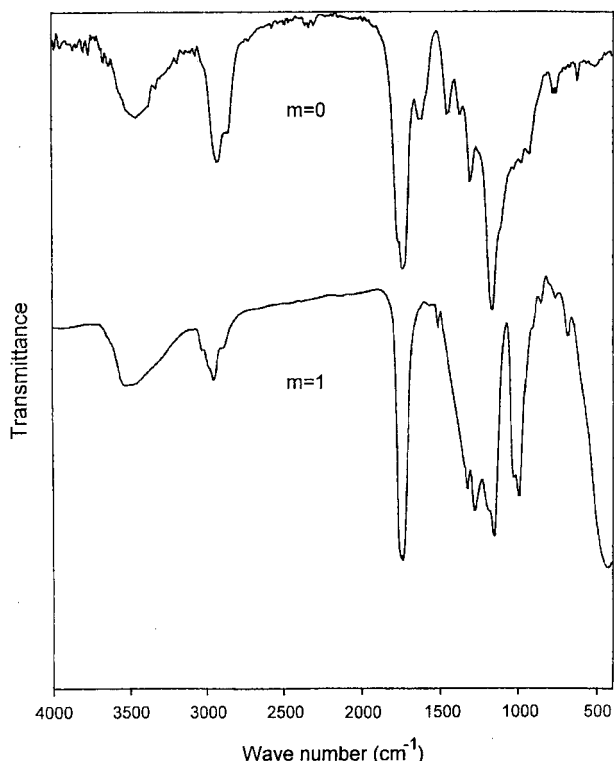

Scheme 1

Figure 4 Typical FTIR spectra of OH-PBm; m = 0,1.

of cold-stirred methanol, filtered, and dried in a vacuum desiccator. All polyesters, except OH-PB1 and OH-PB3 were white-cream solids. OH-PB1 and OH-PB3 were purified through filtration of the CHCl$_3$ solution, removing chloroform by distillation, vigorous shaking with fresh methanol, and decantating. The last two steps were repeated several times, then methanol was completely eliminated by vaccum. Optimized reaction conditions and products specifications are summarized in Table I.

All of the polyesters were soluble in many common solvents, such as AcOH, AcOEt, 1,2-dichloroethane, *m*-cresol, NMP, DMF, and benzene, but insoluble in aliphatic alcohols and hydrocarbons. FTIR and ^{1}H-NMR spectral data of the OH-PBms are summarized as the following.

OH-PB0, IR(KBr) 3440, 3030, 2931, 2870, 1746, 1638, 1461, 1315, 1169 cm^{-1}, ^{1}H-NMR δ 4.11(d), 4.91(m, *J* 6 Hz), 5.89 (m, *J* 4 Hz). OH-PB1, IR (liq. film) 3462, 3031, 2954, 2870 1738, 1500, 1320, 1277, 1164, 992, 498 cm^{-1}, ^{1}H-NMR δ 3.36(s), 4.18(d), 4.70 (m, *J* 6 Hz), 5.73 (m, *J* 4 Hz). OH-PB2, IR (KBr) 3454, 3031, 2938, 1738, 1462, 1377, 1223, 1162, 985 cm^{-1}; ^{1}H-NMR δ 2.42(s), 4.05(d), 4.50 (m, *J* 6 Hz), 5.55 (m, *J* 4 Hz). OH-PB3, IR (liq. film) 3470, 3023, 2931,

2862, 1738, 1461, 1377, 1246, 1177, 985, 769 cm^{-1}; ^{1}H-NMR δ 2.15 (m), 2.50 (t), 4.40 (d), 4.85 (m, *J* 6 Hz), 5.90 (m, *J* 4 Hz). OH-PB4, IR (KBr) 3446, 3033, 2946, 2877, 1731, 1638, 1469, 1385, 1269, 1177, 1069, 985 cm^{-1}; ^{1}H-NMR δ 1.78 (m), 2.48 (m), 4.40 (d), 4.84 (m, *J* 6 Hz), 5.90 (m, *J* 4 Hz). OH-PB5, IR (KBr) 3454, 3032, 2946, 2876, 1746, 1470, 1431, 1362, 1246, 1169, 1080, 969, 690 cm^{-1}; ^{1}H-NMR δ 1.31 (m), 2.14(t), 4.07 (d), 4.50 (m, *J* 6 Hz), 5.55 (m, *J* 4 Hz). OH-PB6, IR (KBr) 3453, 3031, 2938, 2862, 1738, 1469, 1392, 1362, 1238, 1177, 1030, 985, 795, 731 cm^{-1}; ^{1}H-NMR δ 1.30 (m), 1.60(m), 2.30(t), 4.20(d), 4.60 (m, *J* 6 Hz), 5.68 (m, *J* 4 Hz). OH-PB7, IR (KBr) 3431, 3023, 2931, 2854, 1738, 1615, 1462, 1385, 1292, 1225, 1177, 1058, 977, 769 cm^{-1}; ^{1}H-NMR δ 1.30 (m), 1.50 (m), 2.27 (t), 4.20(d), 4.60 (m, *J* 6 Hz), 5.67 (m, *J* 4 Hz). OH-PB8, IR (KBr) 3454, 3032, 2931, 2854, 1738, 1469, 1385, 1300, 1223, 1169, 1064, 969, 731 cm^{-1}; ^{1}H-NMR δ 1.27 (m), 1.57 (m), 2.28 (t), 4.21(d), 4.63 (m, *J* 6 Hz), 5.69 (m, *J* 4 Hz).

Polyurethane Synthesis

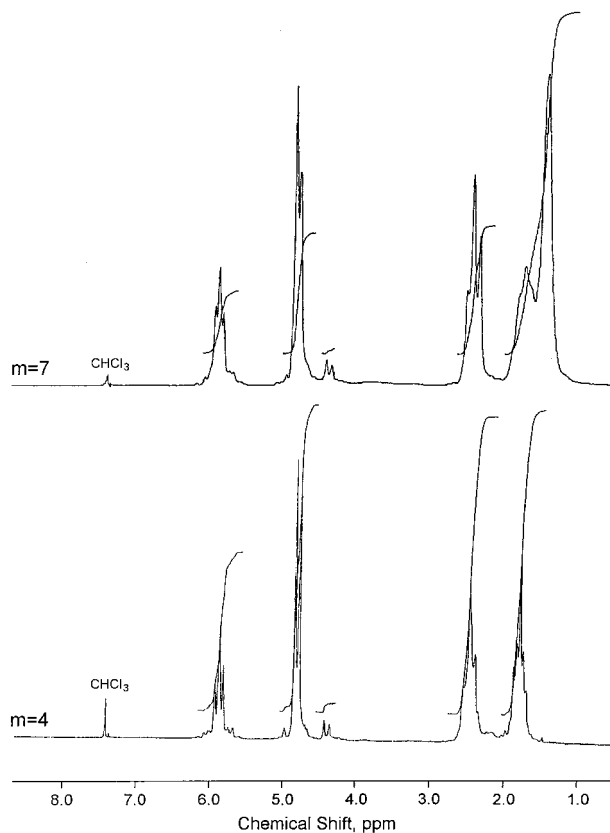28.50 g (0.01 mol) OH-PB4 (MW = 2870) was added to a three-necked reactor equipped with

Figure 5 Typical ^{1}H-NMR spectra of OH-PBm; m = 4,7.

Table II   Some Parameters of the Hydroxypolyesters Resulted from GPC, DSC, and WAXD Measurements

Polyester	GPC[a]				DSC			DC,[b] %
	R_t, min.	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$\bar{DP}_n$	T_m, °C	T_g, °C	ΔH_f, cal/g	
OH-PB0	29.8	563	2.7	3.3	77[c]	—	—	85
OH-PB1	29.4	924	2.1	5.3	—	—	—	0
OH-PB2	28.4	2127	2.2	12.0	62.6	−30	12.04	77
OH-PB3	28.2	2131	17.5	11.0	[d]	−56	—	0
OH-PB4	28.4	2904	2.3	14.2	62.6	−32	13.57	78
OH-PB5	27.6	4543	2.1	21.0	48.6	−41	18.08	59
OH-PB6	29.2	1300	1.3	5.3	49.5	−34	17.51	79
OH-PB7	28.2	3074	1.9	12.4	54.2	−43	21.86	74
OH-PB8	28.5	3169	1.3	12.1	57[c]	—	—	77

[a] From GPC; tetrahydrofuran, 30°C.
[b] Degree of crytallinity resulted from WAXD patterns.
[c] Capillary melting point.
[d] No transition observed.

mechanical stirrer, condenser, and nitrogen inlet. The polyol was heated at 100°C in an oil bath for 2 h under vaccum (150 Torr). The vaccum was broken and 5.0 g (0.02 mol) MDI and 22 μL of T-12 catalyst (4% dibutyltin dilaurate in MEK) were added and the mixture was vigorously stirred at 80°C for 3 h under dry N_2 purge. The reactor was reevacuated and stirred at 70°C for 2 h. The resulting prepolymer was stored under N_2 at 10°C until used.

0.90 g (0.01 mol) 1,4-butanediol was added to the prepolymer in a polyethylene beaker and heated at 80°C for 1 h under mechanically stirring. The resulting viscous polymer (30 g, 87%) has a melting range of 170–180°C and can be molded in a mold preheated at 150°C. The polymer was also synthesized in DMF or chlorobenzene, cast, and dried in vacuum at 50°C to give elastomeric film that was somewhat tacky.

ANAL. calcd. for $[(C_{11}H_{14}O_6)_{14}C_{37}H_{38}N_4O_6]$: C, 56.93, H, 5.81, N, 1.49. Found: C, 57.02, H, 5.85, N, 1.44.

RESULTS AND DISCUSSION

Polyester Synthesis

The basic target in this work has been to obtain low molecular weight, linear OH-terminated polyesters with low polydispersity under more practical and mild conditions.
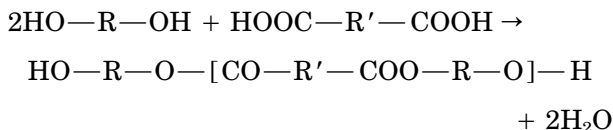
Method A

This method was run in anisole as solvent, without catalyst, while 110 mol % of excess cis-2-butene-1,4-diol was applied. Optimum reaction time, as indicated in Figure 1(a), was 300 min, in which the maximum $\bar{M}_n$ was obtained. To determine the optimum excess diol mol % under the same conditions, various excess diol mol % were reacted with the same diacid at the reaction time of 300 min, which resulted in the highest $\bar{M}_n$ at 50 mol % of excess diol [Fig. 1(b)].

Method B

The same procedure was used for transesterification. As shown in Figure 2, the optimum molecular weight was obtained with 35% excess diol and after 150 min. Regarding $\bar{M}_n-t$ curve (Fig. 3), the optimum reaction temperature was determined to be 130°C.

A comparison between Figures 1 and 2 obviously shows that the transesterification method (B) is preferable to the direct one (A). In transesterification, the reaction time decreases to half (150 min against 300 min) and the excess diol is 20–30 mol % lower than that of the direct process. Meanwhile, the polyester molecular weight is higher (up to 50%).

Ideally, an OH-terminated polyester should be obtained from the completion of the direct reaction between 1 mol diacid and 2 (or more) mol of diol:

$$2HO—R—OH + HOOC—R'—COOH →$$

$$HO—R—O—[CO—R'—COO—R—O]—H$$

$$+ 2H_2O$$

In the early steps of the reaction, a dihydroxy-diester, $HOROOCR'COOROH$, is formed and then ester-interchanged stepwise to produce a polyester chain. Meanwhile, the diol is eliminated at each chainlinking step, as shown in Scheme 1. This method of forcing the polyesterification requires the use of high temperatures for alcoholysis and high vacuum to remove the diol liberated at each step.

In the experimental procedure reported here, the glycol, *cis*-2-butene-1,4-diol, remains in the system and alcoholyzes chain-ester groups, preventing a molecular weight increase. Consequently, the MW increase is gradually stopped and reaches to a maximum amount (Fig. 1). Increasing the time [Fig. 1(a)] or amount of diol [Fig. 1(b)] not only does not increase $\bar{M}_n$, but also causes the self-chain−alcoholysis increase and $\bar{M}_n$ decrease (the negative slopes in the Figs. 1 and 2).

Because the mechanism of the transesterification method is more or less similar to that of direct polycondensation, curve features in Figures 2 and 1 are the same. In transesterification, a dialkyl ester reacts with a diol in the presence of a catalyst:

$$HO—R—OH + R''OOC—R'—COOR'' \xrightarrow{\text{cat.}}$$

$$HO—R—O[CO—R'—COO—R—O]H$$

$$+ 2R''OH$$
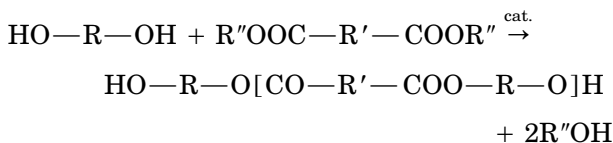
As outlined in Scheme 1, this process generally happens in two steps; the formation of the dihydroxy-diester followed by polycondensation. Again, the same phenomenon ($\bar{M}_n$ decrease) occurs in this method (Fig. 2), because of the same reasons mentioned above. In fact, according to the mechanism, in the first step of the reaction (absence of vacuum) we deal with some OH-terminated oligomers. To achieve a desired OH-terminated polymer, in addition to selection of a proper diol/diacid (or diester) ratio and duration of the first stage, the magnitude of vacuum and its duration (in the second stage) are critical, because the eliminated diol is removed and $\bar{M}_n$ increases rapidly under the vacuum and higher temperatures. As another viewpoint, these facts are based on the
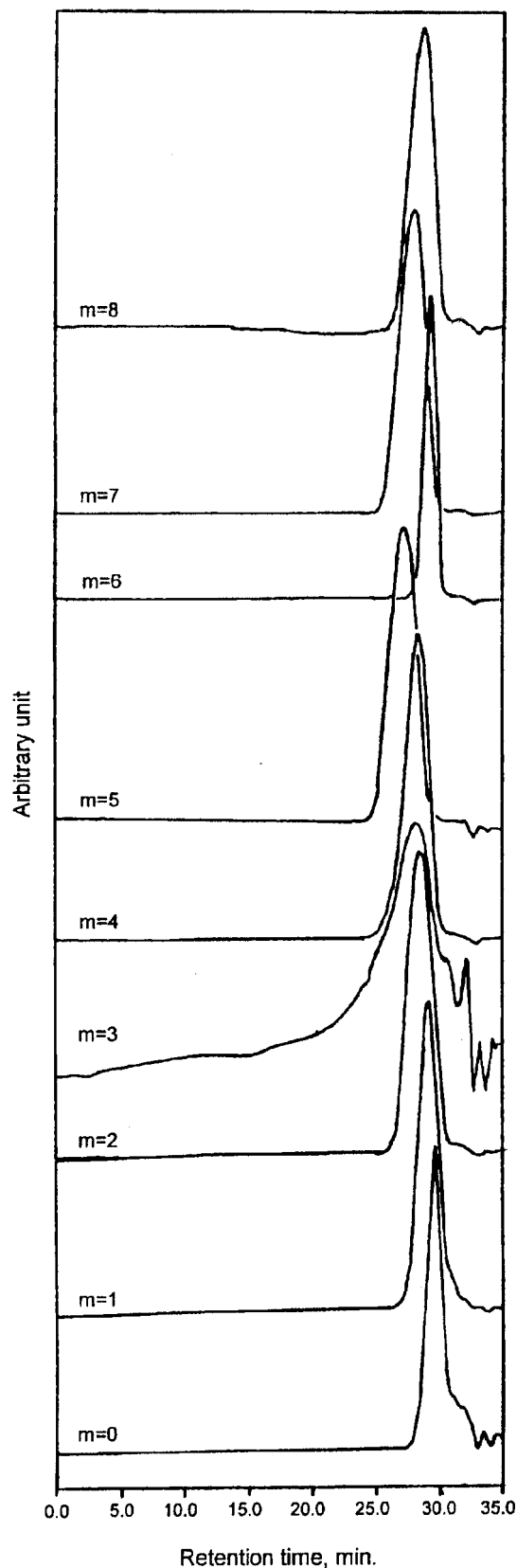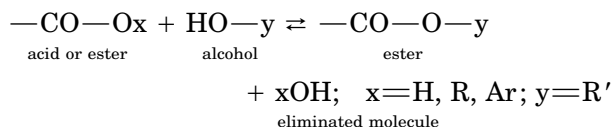

Figure 6 GPC chromatograms of the OH-PBms.

reversibility nature of formation and dissociation of esteric bond:

$$-CO-Ox + HO-y \rightleftharpoons -CO-O-y$$
<div align="center">acid or ester   alcohol   ester</div>

$$+ xOH; \quad x=H, R, Ar; y=R'$$
<div align="center">eliminated molecule</div>

The le Chatelier principle will determine the equilibrium status: removing xOH causes the reaction progress. Fortunately, the boiling point of *cis*-2-butene-1,4-diol (235°C) is low enough to have a short and mild reaction in the second period (30 min, 170°C, 150 Torr).

From the process control viewpoint, transesterification is preferred to the direct polycondensation due to its lower rate of $\bar{M}_n$ decreasing (smaller negative slope in Fig. 2 in comparison to Fig. 1). Additionally, in method A, any imbalance between the molecular proportions of the reactants, whether caused by insufficient accuracy of initial weighing, or by loss of some amount of one or more reactants by volatilization or probable side reactions, will lead to nonterminated chains and high polydispersity. Generally, some advantages can be mentioned for method B in comparison to method A: (a) the esters of many dicarboxylic acids are more readily refined and purified than the correspondent acid, (b) condensation of diesters with some unreactive diols proceeds more readily than with the acids, (c) diesters normally have a lower melting point and are more miscible with other reagents. In addition, condensed alcohol is more volatile than water and is removed easily. According to the literature, in spite of the higher cost of diesters, transesterification is often prefered to prepare polyesters having extremely low value of carboxyl end groups.[3]

In this work, all of poly(*cis*-2-butenylene carboxylate)s were successfully prepared as OH-terminated polymers with low polydispersity ($\bar{M}_w/\bar{M}_n = 1.3–2.7$). The range of the hydroxyl value and acid value of the polyesters were determined to be 35–215 and 0.3–3.5, respectively (Table I). Meanwhile, oxalate and malonate polyesters are also finely synthesized without the decarboxylation problems that had occurred previously.[10]

Polyurethane Synthesis

The polyurethane synthesis was representatively carried out using OH-PB4 as the polyol soft segment ($\bar{M}_w/\bar{M}_n = 2.3$, $\bar{M}_n = 2870$, hydroxyl value = 38, acid value = 1.0) and 1,4-butane diol as the chain extender, through a two-step process. Prepolymer was first prepared by reacting OH-PB4 with an excess of MDI in the presence of an organometallic catalyst (dibutyltin dilaurate), followed by a chain extension with 1,4-butanediol. The overall stoichiometry was 1 mol polyol, 2 mol diisocyanate, and 1 mol diol (Structure 2).

2
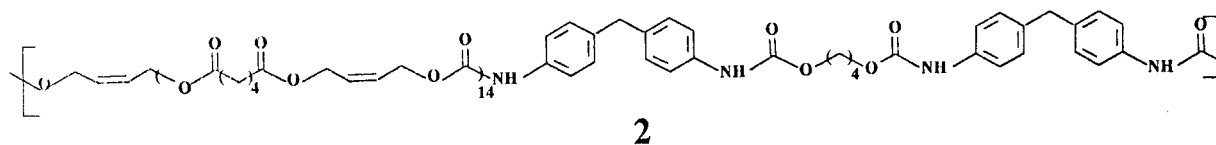
Characterization

Spectral data of all OH-PBms are similar to of those reported previously for PBms.[10] Figure 4 shows FTIR spectra of OH-PB0 and OH-PB1, which are the new members of the series of poly-(*cis*-2-butenylene carboxylate)s. The characteristic esteric C=O at 1746 cm^{-1} (for OH-PB0) and at 1738 cm^{-1} (for OH-PB1) are the strongest absorption band. A very weak peak at about 3030 cm^{-1} due to the olefinic C—H stretching is the only evidence for the presence of C=C unsaturation in all polyester backbones in IR spectra. Broad bands at 3400–3500 cm^{-1} with medium intensity prove the terminal hydroxy groups.

Figure 5 shows the NMR spectra of OH-PBm, m = 4,7. Peaks in 5.50–5.90 are due to CH=CH.

Peaks of the OH groups ($\sim$ 4.6 ppm)[10] are hidden by the multiple peaks of CH$_2$OOC, which appears in the range of 4.4–5.0 ppm. Peaks of OC(CH$_2$)$_m$CO (if any) appear in 1.24–4.36 ppm (see Experimental).

All polyesters, except OH-PB0 and OH-PB7, were prepared through method B with 40 mol % of excess diol. When using the same amount of excess diol for OH-PB0 and OH-PB7, as NMR showed, the chains were not OH-terminated, so 110 and 50 mol % of excess diol were chosen out of a series of experiments. Figures 4 and 5 are typical spectra of hydroxy-terminated polyesters. Figure 3 shows that the optimum reaction temperature is 130°C. Tables I and II present the final reaction conditions and polymer properties. Some definite evidences that may prove the presence of
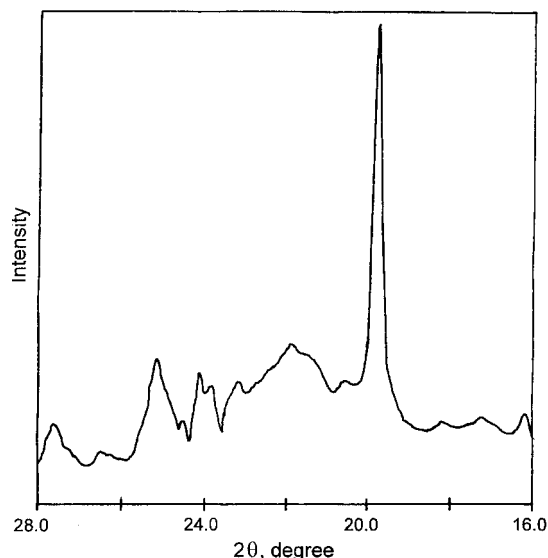
Figure 7 WAXD powder pattern of OH-PB0.

a hydroxy group in the ends of all of these linear polyester chains are: OH broad band in IR spectra in $3400–3500$ cm^{-1} (Fig. 4), approximate equality of $\bar{M}_n$ obtained from end-group titration, egt-, and GPC-based $\bar{M}_n$ (Table I), and in a practical viewpoint, successful stoichiometric reaction with a diisocyanate (see Experimental).

Number average molecular weight ($\bar{M}_n$) of the polyesters was determined using both GPC and end-group titration. Some GPC analytical data are summarized in Table II. GPC chromatograms are also presented in Figure 6.

Our optimized conditions resulted in OH-PBms with a low polydispersity index ($1.3–2.7$) and degree of polymerization of $3–14$ (Fig. 6, Table II). The poly(_cis_-2-butenylene oxalate) is the lightest polymer ($\overline{DP}_n \approx 3$). It seems that its tendency to cyclization prevents achieving a higher oligomer, in accordance with the generalization based on the study of a similar oxalate.[28]

Thermal and crystallinity measurements of OH-PBms showed that both DSC and WAXD patterns are similar to those of PBms.[11] Melting temperature (T_m), glass transition temperature (T_g), and heat of fusion (ΔH_f) are listed in Table II. WAXD powder pattern of OH-PB0 is shown in Figure 7. The approximate degree of crystallinity (DC) was calculated[29] and is included in Table II. The changes in T_m values (obtained from DSC), from OH-PB0 to OH-PB5 follow an odd–even dependence on m, but from OH-PB5 to OH-PB8, it increases linearly (Table II). Such a dependence can also be observed in T_g values. WAXD powder

patterns show that polyesters, except OH-PB1 and OH-PB3, are highly crystalline. OH-PB0 has the highest crystallinity (Fig. 7, Table II). An odd–even discrimination in WAXD patterns is observed. The degree of crystallinity varies as zigzag form, i.e., polymers with even m are more crystalline (Table II). Such observations had already been reported as well.[11] An obvious relationship can be recognized between DC and T_g; the lower crystallinity, the lower glass transition temperature. T_g, and DC values will be remarkable parameters in the final properties of poly(ester urethane) product.

The synthesized OH-PB4–based poly(ester urethane) was characterized by infrared spectroscopy (Fig. 8). Assignment of vibrational modes of the polyurethane is summarized in Table III. The major NH absorption appears at 3315 cm^{-1}, typical for hydrogen-bonded NH groups. Two small shoulders on the high-frequency side of this peak, centered around 3420 cm^{-1}, arises from non-bonded NH groups. There exist two additional peaks in the NH regions, occurring at lower frequency. One occurs at 3184 cm^{-1} and is attributed to _cis-trans_ isomeric hydrogen-bonded NH groups in the urethane structure.[30] A second, well-separated small peak at 3115 cm^{-1} may be considered as an overtone of the band representing the NH bending mode mixed with the C—N stretching mode[31] at 1531 cm^{-1}. Other band assignments are listed in Table III.

CONCLUSIONS

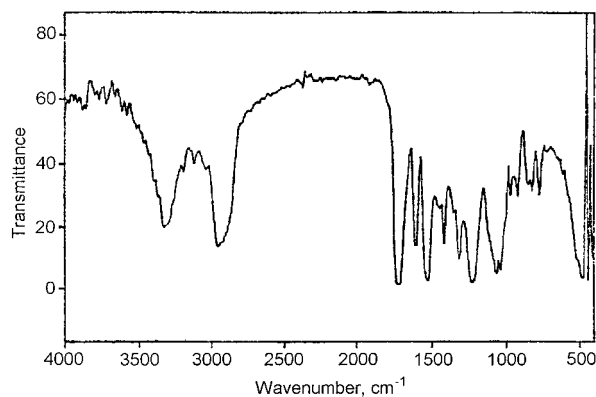Comparison between the results obtained from each two mentioned hydroxy polyester synthetic

Figure 8 Survey FT-IR spectrum of the segmented polyurethane based on OH-PB4.

Table III   Absorption Band Assignments for the Segmented Polyurethane Based on OH-PB4

Wavenumber, cm^{-1}	Relative Intensity[a]	Main Assignments[b]
3420	W, sh	v(N—H); free N—H
3320	S	v(N—H); bonded N—H
3184	W	v(N—H); *cis*-trans isomeric bonded NH
3115	W	Overton of 1531 cm^{-1} band
3030	W	v(C—H) in aromatic ring and olefinic C—H in soft segment
2960	S	v_a(CH$_2$)
2923	S	v_s(CH$_2$)
2890	S, sh	v_s(CH$_2$)
1734	VS	v(C=O) in esteric bond
1704	VS	v(C=O) in urethane bond
1603	S	v(C=C) in aromatic ring
1531	VS	δ(N—H) + v(C—N)
1500–1430	W	δ(CH$_2$)
1415	S	v(C—C) in aromatic ring
1361	M, sh	ω(CH$_2$)
1231	S	δ(N—H) + δ(C—N)
1176	M, sh	v(C—O—C) in soft segment
1079	S	v(C—O—C) in hard segment
1020	S	β(CH) in aromatic ring
820	W	γ(C—H) in aromatic ring
770	W	γ(C=O)

[a] W = weak; M = medium; S = strong; VS = very strong; sh = shoulder.
[b] v = stretching; δ = bending; ω = wagging; β = in-plane bending or rocking; γ = out-of-plane bending or twisting; v_a = asymmetric stretching; v_s = symmetric stretching.

methods proposed that the transesterification is definitely preferred to the direct method due to the following reasons: less excess diol consumption (35 against 50 mol %), lower reaction time (150 against 300 min), lower reaction temperature (130 against 170°C), no use of reaction solvent, lack of decarboxylation, acquisition of higher molecular weight, attainment of lower polydispersity, facile removing of condensed alcohol, and process control facility. Perhaps the only two disadvantages of the transesterification method are use of a catalyst and higher cost of diethyl carboxylates, which should first be prepared from the correspondence diacid and ethyl alcohol. These cases would be important just in large-scale production.

Polyurethane block copolymers based on OH-PBms are one of our research interests to continue this study. Synthesis and identification of a representative polyurethane based on OH-PB4 has reported in this article.

The morphological factors (e.g., hard/soft microphase separation and crystallinity) and thermomechanical behaviors of the OH-PBm−based polyurethane elastomers and some chemical mod-ifications through the C=C unsaturation are under investigation in our laboratory.

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