

LINEAR ALIPHATIC UNSATURATED POLYESTERS BASED ON CIS -2- BUTENE -1, 4-DIOL: SYNTHESIS AND CHARACTERIZATION*

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Abstract

A new homologous series of linear aliphatic polyesters, such as poly (cis-2-butenylene carboxylate)s, PBms (m is the number of methylene groups in the acid component, m=2-8 have been synthesized by direct polyesterification reactions in anisole, as solvent. FT-IR, 400 MHz ¹H-NMR, ¹³C-NMR and elemental analysis were used to establish the structure of polyesters. Molecular weight distributions were studied by GPC. The most narrow distributions were found to be for PB2 and PB8, whereas, the average molecular weight for all polyesters, except PB6, was about 3000-4000.

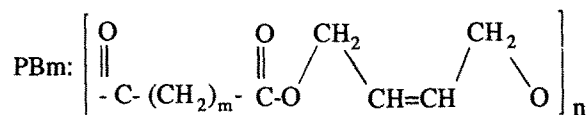
Introduction

By definition, unsaturated polyesters are the polyesterification products of saturated and unsaturated dicarboxylic acids with a glycol [1]. Curing of unsaturated polyesters with vinylic monomers, such as styrene, to form solid thermosetting materials have markedly improved properties [1, 2]. These resins can be mass-cast, laminated, molded, pultruded, and made into gel coats [3,4].

Some scattered reports have shown that when unsaturated bond, C = C, is placed in glycol component rather than in acid, in spite of decreasing its reactivity in curing, the product, when cured with styrene, produces

interesting materials, as non-shrinking bodies [5] or tackfree surfaces [6]. It was found that the presence of an unsaturated diol such as 2-butene-1,4 diol in some segmented thermoplastic polyester elastomers provides plastics with exceptionally good flow characteristics [7].

Our literature survey showed that no systematic study regarding linear aliphatic unsaturated polyesters, based on cis-2-butene-1, 4- diol (PBm) has been reported.



m, is the number of methylene groups in the acid component. In the homologous series PBm, only PB8 is synthesized and characterized by C. S. Marvel in 1951 [8], no data has been published regarding the properties of PB2 [9] and synthesis of PB4 has been reported in

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patent literature [10], briefly. Our final goal has been assessing the chemical and mechanical performance of cross-linked materials based upon these unsaturated polyesters.

In this work, we have investigated the synthesis of PBm ($m = 2-8$) under similar reaction conditions and polyesters obtained have been characterized by elemental analysis, Fourier transform infra-red (FT-IR), ^1H and ^{13}C Nuclear magnetic resonance (NMR) spectroscopy and Gel permeation chromatography (GPC).

Experimental Section

Reagents and materials. 2-butene-1,4-diol (Aldrich, 99.5% *cis*) was used as received.

Pimelic acid was prepared according to standard procedures from salicylic acid [11]. Glutaric acid (Riedel) was used after recrystallization in benzene. Suberic acid (Aldrich), succinic anhydride and other diacids (all Riedel) were used without further purification. Anisole and hydroquinone (Riedel) were used also without further purification.

Synthesis of polyesters. 0.200 mole of dicarboxylic acid (anhydride), 0.219 mole (19.27g, 18ml) of *cis*-2-butene-1,4-diol, 0.04g of hydroquinone as inhibitor and 15ml anisole as solvent were placed in a 200ml four-necked reactor equipped with a silicone-sealed mechanical stirrer, a heating mantle, a contact thermometer, a nitrogen inlet and a Dean-Stark distillation trap. The water formed during the reaction time (16-19hr) at 170°C was separated. Then, the heating was continued at 190°C at reduced pressure (1-10mm Hg) for 0.5-0.7 hr. After pipetting some of the viscous brown polyester for acid value determination, the polymer was dissolved in hot chloroform, filtered, precipitated with an excess quantity of ice-cold methanol, filtered, washed twice with cold methanol, and dried in a vacuum desiccator. All polyesters, except PB3, have soapy-solid state and milky-white color. For purification of PB3, after filtration of chloroform polymer solution, chloroform was distilled and the polymer was shaken several times with fresh methanol and decanted. Then, methanol was completely distilled in vacuum. PB3 was obtained as a viscous clear brown liquid.

The acid values were determined by direct titration of polymer dissolved in acetone with methanolic potassium hydroxide, using a special indicator [12]. Reaction

conditions, yields, intrinsic viscosity, $[\eta]$, and elemental analysis are summarized in Table 1.

Measurements. The polymers solution viscosity values were measured at $30 \pm 0.05^\circ\text{C}$ in chloroform using a Cannon-Fenske-type viscometer. A Heraeus CHNO Analyser system was used for elemental analysis. FT-IR spectra were measured by a Bruker ISF88 spectrometer from a thin film of polymers on the NaCl disk. 400MHz ^1H -NMR and 100MHz ^{13}C -NMR spectra were obtained on a Bruker AM-400 using tetramethylsilane as an internal standard (solvent CDCl_3). Average molecular weights and distribution curves were obtained by gel permeation chromatography (GPC). GPC analysis of polymers was performed at 30°C with a Waters 150C system equipped with four μ -styragel columns ($500, 10^3, 10^4, 10^5 \text{ \AA}$), a data processing system and a calibration curve for polystyrene standards. Tetrahydrofuran was used as GPC solvent.

Results and Discussion

Solubility. The solubilities of polymers were examined and are summarized in Table 2. The polymers were soluble in many common solvents, such as AcOH, AcOEt, 1,2-dichloroethane, pyridine, nitrobenzene and benzene, but were insoluble in aliphatic alcohols and hydrocarbons.

FT-IR Spectroscopy. The stretching esteric $\text{C}=\text{O}$ at $1722-1743 \text{ cm}^{-1}$ is the strongest absorption band in the polyesters' IR spectra (Fig.1). The second characteristic band is $\text{C}-\text{O}$ stretching at $1165-1178$ and $1215-1261 \text{ cm}^{-1}$ Out-of-plane $\text{C}-\text{H}$ bending at $669-727 \text{ cm}^{-1}$ scissoring CH_2 bending ($\begin{array}{c} \text{O} \\ | \\ \text{---} \text{C} \text{---} \text{O}-\text{CH}_2 \end{array}$) at $1450-1475 \text{ cm}^{-1}$ and stretching terminal $\text{o}-\text{H}$ at $3435-3460 \text{ cm}^{-1}$ also appear. Aliphatic $\text{C}-\text{H}$ stretching is observed at $2850-2952 \text{ cm}^{-1}$ as two or three sharp peaks. The intensity of these peaks increases from PB2 to PB8 which is due to the increase of the number of the methylene groups. No $\text{C}=\text{C}$ stretching is observed in any of the polyesters. All of the polyesters show a very weak peak at $3031-3033 \text{ cm}^{-1}$. In the FT-IR spectra, this peak is evidence for the presence of $\text{C}=\text{C}$ unsaturation in the polyester backbone.

Some peaks are observed in both regions of 660-730

Table 1. Reaction conditions, yields, elemental analysis and viscosity data for polyesters.

polyester	reaction time(hr)		yield (%)	acid value	repeat unit (formula weight)	elemental analysis				
	h ₁ ^a	h ₂ ^b				%C	%H	%O	[η ^c] (dL/g)	
PB2 ^d	19.0	0.5	71	8.7	C ₈ H ₁₀ O ₄ (170.16)	Found	56.25	5.95	37.30	0.10
						Calcd	56.46	5.92	37.62	
PB3	15.7	3.5 ^e	66	8.3	C ₉ H ₁₂ O ₄ (184.19)	Found	58.40	6.61	33.86	0.09
						Calcd	58.68	6.57	34.75	
PB4	16.0	0.5	75	13.0	C ₁₀ H ₁₄ O ₄ (198.22)	Found	60.07	7.07	32.06	0.15
						Calcd	60.59	7.12	32.29	
PB5	17.2	0.5	68	25.9	C ₁₁ H ₁₆ O ₄ (212.24)	Found	61.47	7.59	30.05	0.09
						Calcd	62.25	7.60	30.15	
PB6	17.0	0.7	74	29.7	C ₁₂ H ₁₈ O ₄ (226.27)	Found	62.90	8.02	28.08	0.13
						Calcd	63.69	8.02	28.29	
PB7	17.5	0.5	71	15.1	C ₁₃ H ₂₀ O ₄ (240.29)	Found	64.55	8.27	26.19	0.21
						Calcd	64.98	8.39	26.63	
PB8	18.0	0.5	73	24.9	C ₁₄ H ₂₂ O ₄ (250.32)	Found	65.43	8.66	24.04	0.16
						Calcd	66.11	8.72	25.17	

^aAnisole as solvent, Dean-Stark arrangement, atmospheric pressure, 170 °C.

^b1-10mmHg, 190 °C.

^cIn CHCl₃, 30 + 0.05 °C

^dSuccinic anhydride, instead of succinic acid was used.

^eThis time also includes the distillation time of chloroform and methanol in the purification step.

Table 2. Solubility of Polyesters^a

polyester	H ₂ SO ₄ ^b	HCOOH	m-Cresol	NMP ^c	DMF ^d	DMSO ^e	PhCl	xylene	HMPA ^f	CCl ₄	CS ₂
PB2	++	++	++	++	++	++	+	+	+	--	--
PB3	++	++	++	++	++	++	++	++	++	--	--
PB4	++	++	++	++	++	++	++	+	+	--	--
PB5	++	++	++	++	++	++	++	++	+	--	--
PB6	++	++	++	++	++	++	++	++	++	++	--
PB7	++	++	++	++	++	+	++	++	++	++	--
PB8	++	++	++	++	++	+	++	++	++	++	+

^aAt room temperature, (++) soluble, (+-) soluble by heating, (--) insoluble.

^bSolutions were colored to clear brown.

^cN-Methyl -2-Pyrrolidone

^dN,N-Dimethylformamide

^eDimethylsulfoxide

^fHexamethylphosphoramide

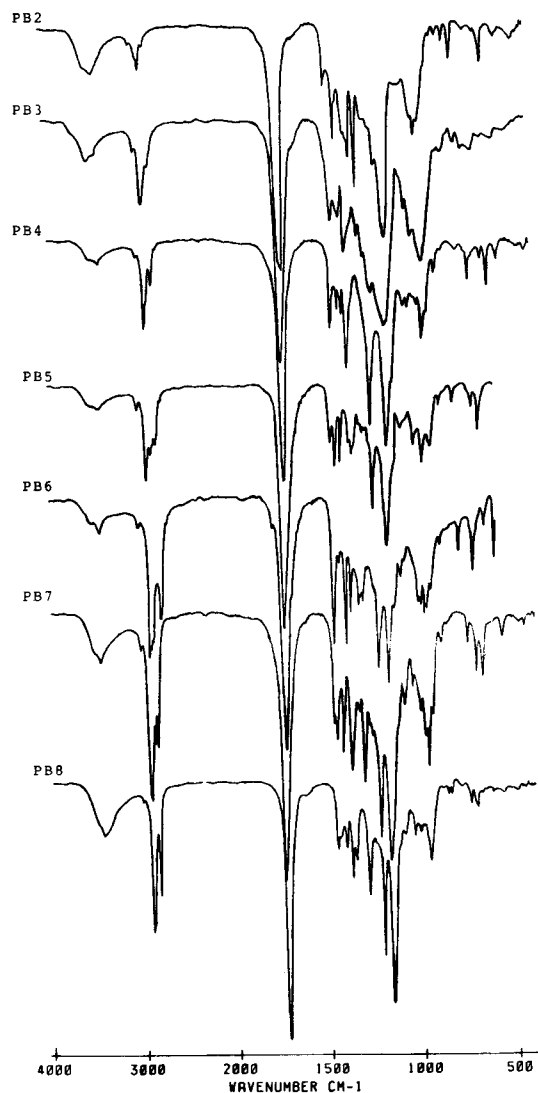


Figure 1- FT- IR spectra of polyesters.

Table 3. FT- IR data of polyesters.

wave number due to vibration type (cm⁻¹)

polyester	C=O	C-O	C-H (aliphatic)	C-H (olefinic)	OH	C : C-H (out-of-plane)	CH ₂ (scissoring)
PB2	1722	1165,1217	2889,2941	3032	3435	681	1469
PB3	1734	1169,1238	2880,2947	3033	3535	698	1450
PB4	1728	1178,1261	2875,2952	3033	3437	669	1469
PB5	1741	1171,1246	2854,2897 2947	3033	3460	690	1458
PB6	1730	1178,1236	2860,2939	3031	3442	727	1469
PB7	1743	1173,1225	2856,2885 2925	3033	3458	686	1458,1475
PB8	1734	1171,1215	2850,2929	3032	3446	721	1464

and 960-980 Cm^{-1} which are due to the in plane C-H bending *cis* and *trans* olefins, respectively [13]. Therefore, geometric isomery of the double bond, could not be concluded from FT-IR spectra. The presence of weak and broad absorbtion bands due to terminal OHs, suggest that the number of terminal OHs are considerably more than terminal COOHS. Some of the important FT-IR data are summarized in Table 3.

NMR Spectroscopy. In 400 MHz $^1\text{H-NMR}$, olefinic protons of polyesters are observed in 5.74 or 5.75 PPM. The coupling constant of these protons, 4Hz confirms *cis* geometry for the double bonds (coupling constant for similar *cis* isomers is equal to 6-12 Hz, while for *trans* isomers is equal to 12-18 Hz [13]). Therefore, in contrast to polymaleates, these polyesters have not been exposed to *cis-trans* isomerization during the polyesterification.

The CH_2O protons of PB4 to PB8 were observed at 4.68 PPM. These protons in PB3 and PB2 appear at

4.69 and 4.70 PPM, respectively. Decreasing distance between two carbonyl groups, in PB3 and PB2, causes a little deshielding in the chemical shifts of CH_2O protons. $^1\text{H-NMR}$ spectral data, in 400MHz, are given in Table 4, and the spectrum of one of the series (PB5, as an example) is presented in Fig. 2 (a). In the case of methylene groups in acid component, α and β -methylene protons are the most deshielded and γ and δ -methylene protons are the most shielded ones. Also, from the integrated peak areas and according to the method of Baddar *et al.* [14], the percent mole ratio of the glycol to the acid is calculated and included in Table 4. In spite of a 9.5 mole percent excess of the diol in the polyesterification reaction, a glycol loss is evident from the table.

It is well known that decarboxylation is a side reaction that may occur according to equation (1), during the synthesis of polyesters. Decarboxylation reactions may be particularly important for the preparation of

Table 4. 400 MHz $^1\text{H-NMR}$ spectral data of polyesters.

polyester	component	chemical shift (PMM)	assignment	integrated peak area	mol%
PB2	Glycol	4.70, 5.75	2 (CH_2O), CH=CH	42.2, 21.1	49.1
	Acid	2.65	2 ($\alpha\text{-CH}_2$)	43.7	50.9
PB3	Glycol	4.69, 5.75	2 (CH_2O) CH=CH	34.4, 17.2	48.3
	Acid	2.39, 1.96	2 ($\alpha\text{-CH}_2$), $\beta\text{-CH}_2$	36.8, 18.4	51.7
PB4	Glycol	4.68, 5.74	2 (CH_2O), CH=CH	48.6, 24.3	48.4
	Acid	2.34, 1.66	2 ($\alpha\text{-CH}_2$) 2 ($\beta\text{-CH}_2$)	51.8, 51.8	51.6
PB5	Glycol	4.68, 5.74	2 (CH_2O), CH=CH	75.6, 37.88	48.6
	Acid	2.33, 1.64	2 ($\alpha\text{-CH}_2$), 2 ($\beta\text{-CH}_2$)	79.8, 79.8,	51.4
		1.35	$\gamma\text{-CH}_2$	40.0	
PB6	Glycol	4.68, 5.75	2(CH_2O), CH=CH	46.2, 23.1	47.5
	Acid	2.31 1.63	2 ($\alpha\text{-CH}_2$) 2 ($\beta\text{-CH}_2$)	49.1, 51.9	52.5
		1:34	2 ($\gamma\text{-CH}_2$)	51.9	
PB7	Glycol	4.68, 5.74	2 (CH_2O) CH=CH	38.7, 19.3	47.6
	Acid	2.30, 1.61	2($\alpha\text{-CH}_2$) 2 ($\beta\text{-CH}_2$)	42.6, 42.6	52.4
		1.31	2 ($\gamma\text{-CH}_2$) $\delta\text{-CH}_2$	63.9	
PB8	Glycol	4.68, 5.75	2 (CH_2O), CH=CH	35.2, 17.6	48.4
	Acid	2.31, 1.62	2 ($\alpha\text{-CH}_2$), 2 ($\beta\text{-CH}_2$)	37.5, 37.5	51.6
		1.30	2 ($\gamma\text{-CH}_2$), 2 ($\delta\text{-CH}_2$)	75.1	

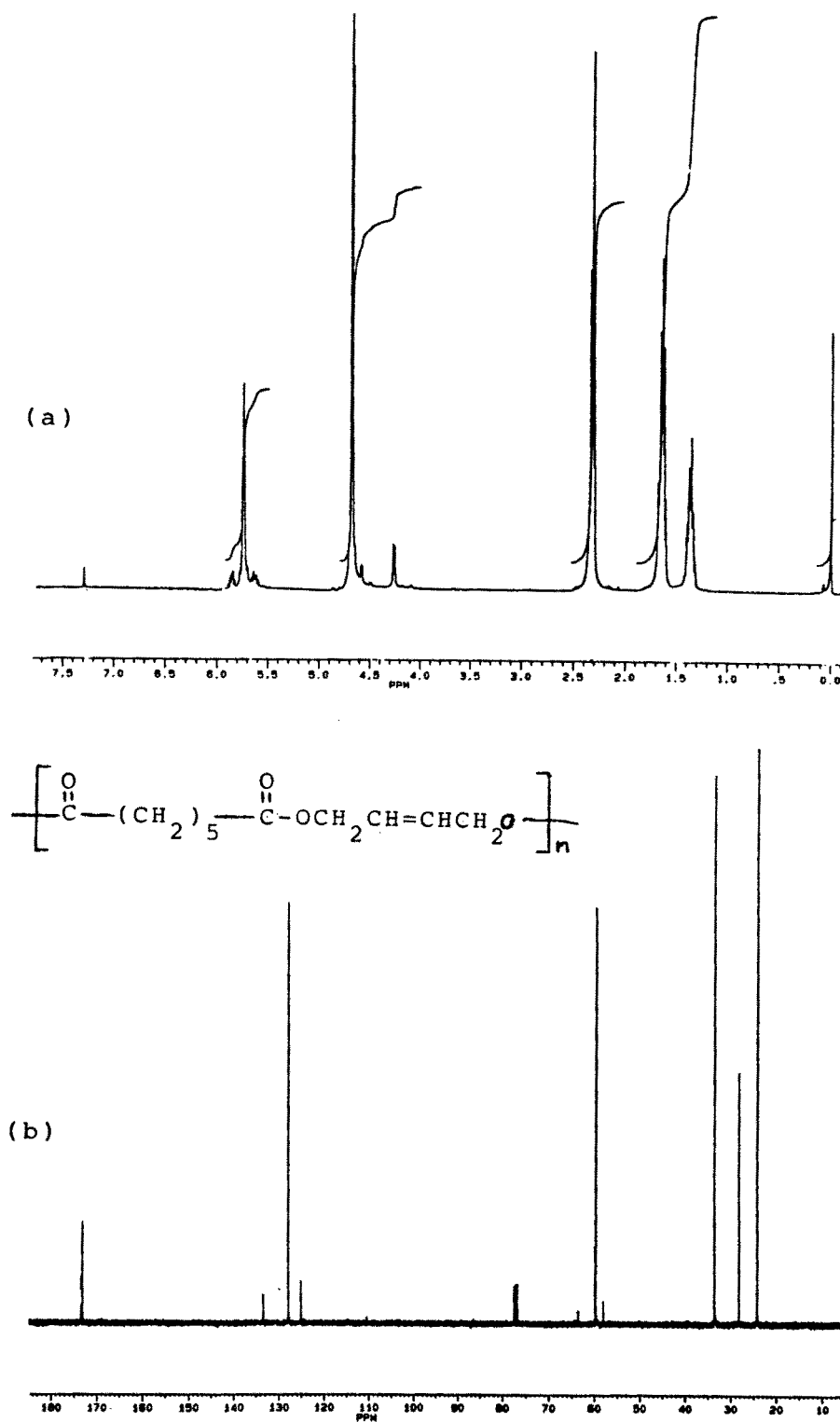
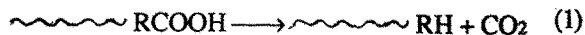


Figure 2. (a) 400 MHz ¹H-NMR Spectrum of PB5; (b) 100.614 MHz ¹³C-NMR Spectrum of PB5.

polyesters from aliphatic dicarboxylic acids and glycols [15]. Thus, a decrease in the number of terminal COOH causes the corresponding band ($2500-3300 \text{ Cm}^{-1}$) not to appear in the FT-IR spectra.



On the other hand, the temperature at which this side reaction occurs is particularly low for aliphatic acids containing more carbon atoms [15]. Whereas the polyesters and PBms have been prepared under similar conditions, the amount of CO_2 obtained from PB2 to PB8 should decrease. The acid values presented in Table 1 show good agreement with the above results.

^{13}C -NMR spectra of the polyesters in 25.2 or 100.614 MHz certify the molecular skeleton clearly. Typically, the spectrum of PB5 is presented in Fig. 2(b). The chemical shift changes of CH_2 s of the acid components are comparable to similar changes in corresponding dicarboxylic acids [16] (Table 5).

Molecular weight distributions. GPC analysis shows that the degree of polymerization, DP_n vary between 11 to 22, whereas PB6 has the largest M_n ($\text{DP}_n=56$) and, except PB2 and PB8, other

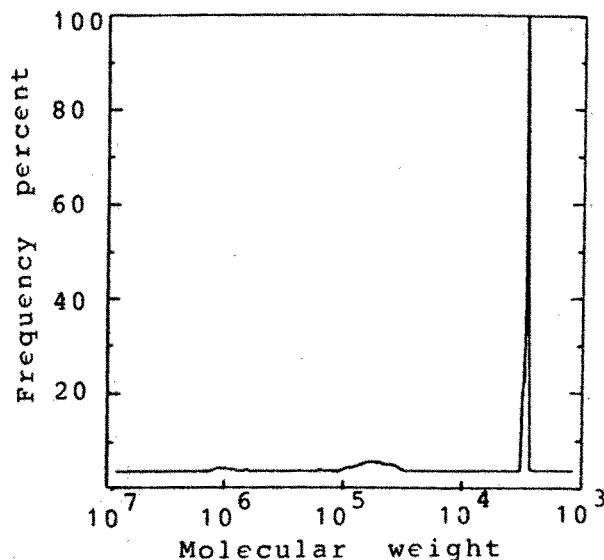


Figure 3. Molecular Weight distribution curve of PB5.

polyesters show a considerable deviation from the dispersity index of one. The GPC analytical data are summarized in Table 6. Molecular weight distribution curves show that PB6 has a continuous distribution from 4000 to about 6×10^5 , a narrow distribution for PB2

Table 5. Chemical shifts in ^{13}C -NMR spectra of polyesters. chemical shift (PPM)

polyester	$\alpha\text{-c}$	$\beta\text{-c}$	$\gamma\text{-c}$	$\delta\text{-c}$	C=O	C-O	C=C
PB2	28.69	-	-	-	171.68	127.72	60.02
PB3	32.70	19.64	-	-	172.19	127.70	59.64
PB4	33.58	24.12	-	-	172.74	127.92	59.80
PB5	33.56	24.15	28.17	-	172.90	127.76	59.58
PB6	33.86	24.47	28.47	-	173.18	127.90	59.69
PB7	34.11	24.78	28.87	28.87	173.40	128.08	59.85
PB8	34.03	24.73	28.92	28.92	173.35	127.99	59.74

Table 6. GPC analytical data for polyesters.

	PB2	PB3	PB4	PB5	PB6	PB7	PB8
\overline{M}_n	3421	4052	3424	3367	12724	3443	2733
\overline{M}_w	3771	44854	63490	33326	92318	91210	2734
\overline{M}_z	70742	693576	1023102	863890	205329	996921	2735
\overline{M}_v	3770	44853	63489	33325	92317	91210	2734
DP_n	20.0	21.9	17.2	15.8	56.2	14.3	10.7

and PB8 is observed. In the other polyesters, molecular weight for most chains is 3000.- 4000, for less than 20 percent of the chains it is about 10^5 and for very little of the chains (less than 10 percent), it is about 10^6 . Thus, in the molecular weight distribution curves of these polyesters, three distinct regions exist (Fig.3). The above heterogeneity may be attributed to the disappearance of carboxyl groups with the formation of unreactive alkyl end-groups corresponding to a decrease in the overall functionality of the system with a consequent effect on the maximum molecular weight attainable [15].

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