Unsaturated Polyesters. III. Polyester from Maleic Anhydride and 1,4-Butylene Glycol

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SYNOPSIS

The polyesterification reaction of maleic anhydride and 1,4-butylene glycol was carried out, using p-toluensulphonic acid as catalyst. The resulting material was characterized by IR and H^1-NMR spectroscopy, end group analysis, and gel permeation chromatography. It is shown that there is a relationship between maleate to fumarate isomerization and steric interaction among condensed groups on the one hand and the tendency of the reacting system to crosslink or gel.

INTRODUCTION

In spite of all the work which has been carried out on polycondensation of maleic anhydride (MA) with different glycols, it is not clear why the maleate to fumarate isomerization occurs. Although it is quite certain that the glycol structure plays an important part in the isomerization, which is enhanced when bulky groups are close to the hydroxyls, there has been little work done on series of linear polyesters. In previous work,[1,2] it has been shown experimentally that isomerization diminished in going from ethylene glycol to 1,3-propylene glycol, from around 70 to 15%. The fact that there is one more methylene group, in the 1,3-propylene glycol, may be indicative of less spatial interaction between condensed groups.

Nonetheless, different behavior has been exhibited by glycols with larger numbers of methylene groups, 1,6-hexamethylene glycol and diethylene glycol,[3] where the percentage isomerization is over 35 and 55%, respectively. These results suggests intramolecular spatial interaction between ester groups in close proximity, and not only to steric hindrance around the hydroxyl group, or the length of the glycol chain. With 1,4-butylene glycol, once condensed, there could be some sterical interaction, since the spatial arrangement of two consecutive es-

ter functions might acquire a nonplanar[4] configuration, deviating from the planar zig-zag configuration generally accepted.[5] This deviation could be attributed to the attractive forces within the ester groups.[6]

EXPERIMENTAL

Reactants

Maleic anhydride (MA) was recrystallized from chloroform, mp 52°C. 1,4-Butylene glycol (Aldrich) was purified by distillation, using only the fraction distilling in the range 216–218°C, which was collected. Monohydrated p-toluenesulfonic acid (Sigma) used without further purification.

Synthesis of Polyester

The polymerization was carried out as previously described.[1] To 4.903 g (0.05 mol) of MA, 4.90 mL (0.055 mol) of 1,4-butylene glycol and 0.0115 g (0.11% p/p) of p-toluenesulphonic acid were added. The reaction mixture was heated at 188–190°C until the acid number reached a value of 10 mg KOH/g sample.

Purification of Polyester

The white waxy-like material was dissolved in acetone, and the resulting solution filtered through a

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Table I Data from Polyesterification Reactions

Sample	Temperature (°C)	Time (min)	Acid Number[a]
1	188	60	312.3
2	188	180	131.6
3	190	360	81.8
4	190	480	14.5
5	190	540	13.6

[a] mg KOH/g sample.

Table II Data from End Group Analysis of the Polyester

Acid Number[a]	Hydroxyl Number	$\bar{M}_n$	% Isomerization
7.3	30.7	2737	39

[a] Mg KOH/g sample.

sintered glass funnel. The filtrate was warmed and petroleum ether added. The mixture was allowed to stand overnight and the upper layer decanted. The remaining material was dried under vacuum (0.1 Torr) at 60°C for 5 h.

Analytical Techniques

Molecular weights were determined by end group analysis and gel permeation chromatography.[1] Thin films were obtained by casting of chloroform solution on NaCl disks, and the IR spectra taken on a Perkin Elmer 377 instrument. Proton magnetic resonance analyses were carried out in a Varian A-60 (60 MHz) spectrometer, samples being dissolved in CDCl₃ and TMS used as internal reference.

Table III Infrared Assignment of Main Absorption Bands

Absorption (cm⁻¹)	Assignment
3550 (small, broad)	Stretching OH terminal hydroxy
3450 (small, broad)	Stretching OH terminal carboxyl
3070 (small, broad)	Stretching C — H olefinic
2980 (medium, sharp)	Stretching C — H methylenic
1725 (strong, sharp)	Stretching C — O ester
1645 (medium, sharp)	Stretching C — C olefinic
1190 (strong, sharp)	Stretching C — O — C ester

Table IV Proton Magnetic Resonance Assignments

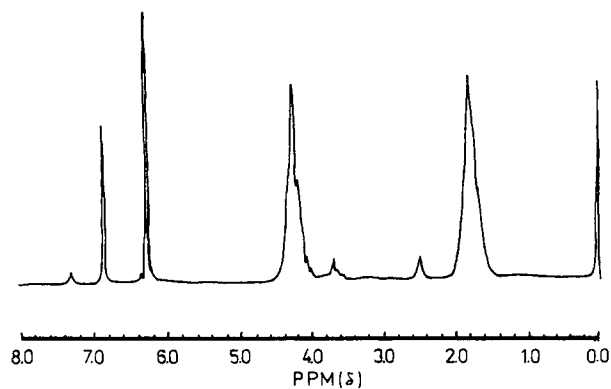| Chemical Shift (ppm)	Assignment
6.85 singlet	—CH=CH— fumarate form
6.27 singlet	—CH=CH— maleate form
4.22 singlet	—C — O — CH₂ CH₂ CH₂ CH₂ O — C —
1.80	—C — O — CH₂ CH₂ CH₂ CH₂ O — C —

RESULTS AND DISCUSSION

Table I summarizes the details of the polymerization process; Table II and V refers to the characterization of reprecipitated polyester. The percentage isomerization was obtained from NMR spectra. IR and NMR spectra are shown in Figures 1 and 2, and the main assignments are given in Tables III and IV.

Spectroscopic and solubility results confirm the linearity of this polyester. The two absorptions at 6.27 and 6.85 ppm indicate the isomerization of maleate to fumarate, and NMR measurements indicate that it reaches 39%. End group analysis indicates a relatively high molecular weight and GPC shows two fractions (Fig. 3). The fractions could not be easily separated by normal reprecipitation.

Unsaturation was confirmed by olefinic absorptions at 3070 cm⁻¹ (H—C=) and 1645 cm⁻¹ (C=C) in the IR spectra, and from fumarate (6.85 ppm) and maleate (6.27 ppm) shifts in the NMR spectra. The polyester is mainly hydroxy terminated as shown by end group analysis and IR absorption at 3550 cm⁻¹.

The relatively high percentage of isomerization lies between those for the polyesters from 1,3-propylene glycol and 1,2-ethylene glycol. Though there is one more methylene group in 1,4-butylene glycol,
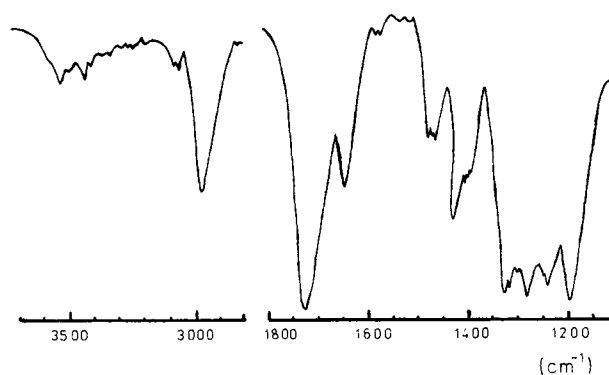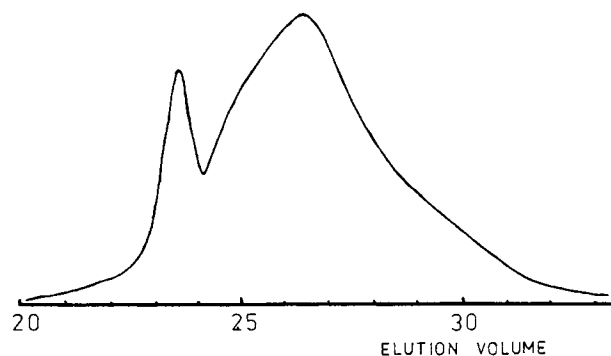

Figure 1 Infrared spectra of the polyester.

Figure 2 Proton magnetic resonance spectra of the polyester.

Table V   Data from GPC Analysis

$\bar{M}_n$	$\bar{M}_w$	D
2544	4673	1.84

MA, the glycol chosen as counterpart for the polyesterification must not endure other side reactions such as that of cis–trans isomerization, which normally proceed together with polymerization. So, the addition of glycol segments to double bonds (mainly to fumarate) and, fumarate–fumarate double bond reaction, is avoided. The last two reactions lead to limited polymerization.

CONCLUSIONS

The spatial configuration of polyester chains is even more important than methylene groups within the glycol chain for cis–trans isomerization to occur. When it is impossible to inhibit this isomerization, it could be harmless to polyesterification if the critical point for gelation or crosslinking is restrained.

the higher degree of isomerization, in comparison with the polyester from 1,3-propylene glycol,[2] may be explained as being due to spatial interactions between ester groups in close proximity. The glycol segment, within the polymer chain, could be arranged in a twisted zig-zag in such a way that some sort of ringlike structure is formed nearby where those close ester groups may undergo spatial repulsion, thus enhancing isomerization.

There may also be a critical point at which side reactions like gelation and crosslinking become kinetically or energetically more relevant even than isomerization or esterification, since the progress of the polyesterification reaction is quite slow, as measured by acid number, without any perceptible sign of any other process than conversion of maleate into fumarate forms. In other words, whenever it is desired to obtain a high molecular weight polyester of

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Figure 3 Gel permeation chromatographic trace of the polyester.