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Unsaturated polyesters

2. Polyester from maleic anhydride and 1,3-propylene glycol

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Summary

The polymerization of maleic anhydride and 1,3-propylene glycol was carried out using p-toluenesulphonic acid as catalyst. The resulting material has been characterized by ir and H^1nmr spectroscopy, end group analysis and gel permeation chromatography. The percentage isomerization of maleate to fumarate has been correlated with the extension of polycondensation and the steric hindrance between the condensed functional groups.

Introduction

The synthesis of an unsaturated linear polyester from maleic anhydride (MA) and ethylene glycol (EG), using p-toluenesulphonic acid as catalyst has previously been reported (1). The polycondensation reaction is affected, in the later stages of polymerization by side reactions which divert the main reaction from achieving higher degrees of polymerization. Apparently, these side reactions are closely related to the cis-trans isomerization process which occurs in parallel with polycondensation. The structure of the glycolic segment exerts an influence on isomerization. It has been shown (2) that those glycols which facilitate ester groups to appear within the polymer chain, strongly affect the amount of double bonds which undergo interconversion, resulting in higher percentages of isomerization among polyesters with higher steric hindrance within the condensed funtional groups.

This work was carried out in order to clarify some of the aspects of the isomerization process, since it appears to be the most prominent driving force of side reactions which prevent the formation of high molecular weight polymer. If this is so, then the polycondensation of maleic anhydride and a glycol which leads to less steric hindrance between condensed funtional groups than ethylene glycol, may result in lower isomerization and thus in a higher degree of polymerization. A low percentage of isomerization suggests a smaller amount of side reactions which take place through a carbocationic intermediate.

Experimental

Reagents.

Maleic anhydride (BDH) was recrystallized from chloroform (m.p. 52°C). 1,3-Propylene glycol (ALDRICH) was distilled at atmospheric pressure, the fraction which boils at 204-206°C. being collected. Monohydrated p-toluenesulphonic acid (SIGMA) was used without further purification.

Synthesis of polyester.
The synthesis of polyester was carried out as described earlier (1).The reaction vessel was charged with 4.935g (.050 mol) of maleic anhydride, 4.00ml (.055 mol) of 1,3-propylene glycol, and 0.0128g (.14% p/p) of p-toluenesulphonic acid. The bulb then placed in boiling ethylene glycol vapour, kept at 188-190°C, and the reaction continued until the change in the acid number was hardly perceptible.

Purification of polyester.
The reaction product, a rather viscous resin with a light yellowish color, was dissolved in 30ml of acetone and the solution filtered through sintered glass. The filtrate is heated to its boiling point and petroleum ether (60-80°C) is added dropwise till cloudiness is just mantained. The mixture is then allowed to cool and two well separated layers are formed. The upper layer is drawn off and the lower layer, containing the polymer, is vacuum dried (0.1Torr.) for 5 hours at 60°C.

Analytical techniques.
Molecular weight averages were measured by end group analysis and gel permeation chromatography, as described earlier (1). Spectroscopic analysis was carried out by ir and H^1nmr. A Perkin Elmer 377 ir instrument was used to analyse a polymer film, cast on a CsBr disc, and samples dissolved in deuterated chloroform samples were analysed by a Varian A60 of 60MHz nmr spectrometer.

Results

Table 1 shows the main features of the polymerization process and Table 2 shows the results of end group analysis and percentage isomerization of maleate to fumarate deduced from nmr spectra.

Table 1
Data from polyesterification

Sample	Temperature, °C.	Time, min.	Acid number[α]
1	188	15	118.1
2	188	160	38.2
3	188	232	27.2
4	190	295	21.2
5	190	355	16.5
6	190	390	15.2

(α) in mg of KOH/g of sample.

Table 2
Data from end group analysis.

Sample	acid number[a]	Hydroxyl number[a]	$\bar{M}n$	% isomerizat.
non reprecip.	15.2	72.9	1274	14
Reprecipitat.	10.6	32.0	2634	15

(a)mg of KOH/g of sample.

Figure 1 and Table 3, show the infrared spectra and the assignments of the main absortions.

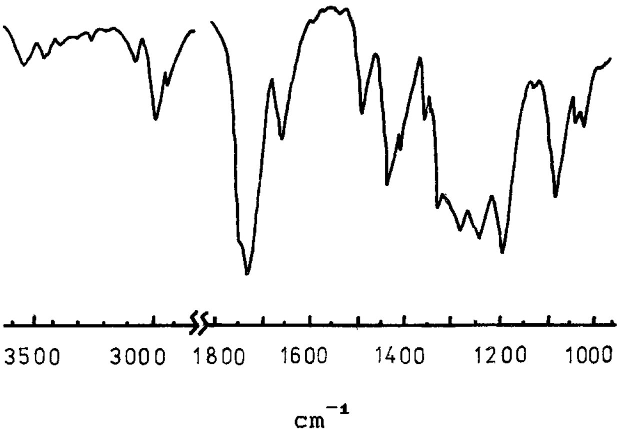

Figure 1. Infrared spectrum of the polyester.

Table 3
Infrared assignments of main absoption bands.

Absorption, cm^{-1}	Assignment
3550 (small, broad)	Stretching -OH terminal hydroxy
3440 (Small, broad)	Stretching -OH terminal carboxy
3080 (Small, broad)	Stretching C-H olefinic
2995 (Small, sharp)	Stretching C-H methylenic
1730 (Strong sharp)	Stretching C=O ester
1655 (Medium sharp)	Stretching C=C olefinic
1190 (strong sharp)	Stretching C-O-C ester

Figure 2 shows the nmr trace of the polyester, and Table 4 shows the assignments of the main absortion bands. The gpc trace and data are shown in Figure 3 and Table 5, respectively.

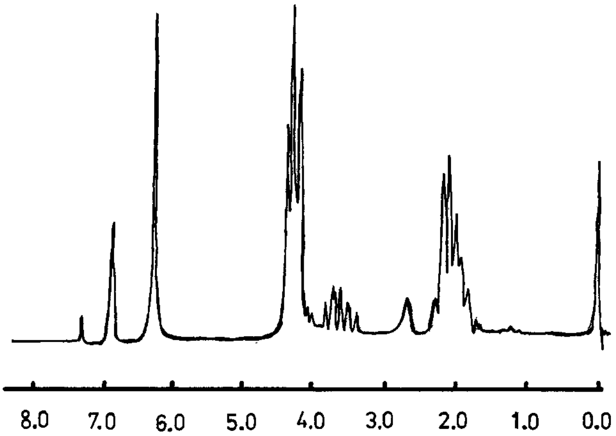

Figure 2. H^1nmr of the polyester.

Table 4
Assignment of characteristic nmr bands of polyester.

Chemical shift (ppm)		Assignment	
6.8	singlet	$- C\underline{H} = C\underline{H} -$	fumarate.
6.25	singlet	$- C\underline{H} = C\underline{H} -$	maleate.
4.25	triplet	$-C\bar{H}_2- CH_2 - C\bar{H}_2-$	internal.
3.60	multiplet	$-C\bar{H}_2- CH_2 - C\bar{H}_2- OH$	terminal.
2.70	singlet	$-OH$	terminal.
2.05	multiplet	$-CH_2- \underline{C}H_2 - CH_2-$	internal.

Table 5
Data from gpc analysis.

$\bar{M}n$	$\bar{M}w$	D
2342	3409	1.46

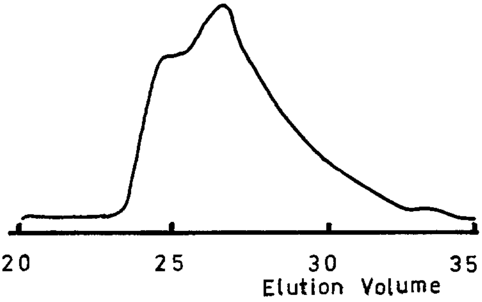

Figure 3. GPC trace.

Discussion

During the polymerization of maleic anhydride with 1,3-propylene glycol, cis-trans isomerization also occurs in the olefinic bonds present in the system (3-6). However, the low percentage (15%) of isomerization is in accordance with expected behaviour of a polycondensation system, namely that the glycol used exerts less steric hindrance between condensed groups, as compared with ethylene glycol (70%) or 1,2-propylene glycol (93%).

It is noticeable that the molecular weight is much higher than when ethylene glycol (1) is used, suggesting an effect of isomerization upon polycondensation. When ethylene glycol is used a great deal of side reactions take place, preventing the polymer attaining a high molecular weight. In the present work, there were no signs of crosslinking or addition reactions though low values of acid and hydroxyl numbers were obtained, and the material was very soluble in the usual solvents (pyridine, acetone, chloroform, etc.), showing no signs of any insoluble residue; at the same time, the dispersity value (lower than 2) also denies gelation.

The polyesterification reaction of maleic anhydride and 1,3-propylene glycol shows a low percentage of isomerization of maleate to fumarate and significant increase in the degree of polymerization. Low values of acid and hydroxyl numbers are achieved without any signs of side reactions such as branching and crosslinking.

It may be stated, in the light of the present results, that all the side reactions observed in this kind of system, namely isomerization, branching, and crosslinking, are closely related, and are probably derived from a common intermediate. Glycols which confer low steric interaction between the condensed groups permit a higher degree of polymerization.

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