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Unsaturated polyesters

1. Polyester from maleic anhydride and ethylene glycol

Larez V. Cristobal and Perdomo Mendoza Gilberto A.

Universidad de los Andes, Facultad de Ciencias, Departamento de Quimica,
Merida 5101, Venezuela

Summary

Polyesterification of maleic anhydride with ethylene glycol, using p-toluensulphonic acid as catalyst, has been carried out under very well controlled conditions to obtain a linear polyester with a relatively high molecular weight. The polyester was characterized by ir, nmr, end group analysis, and gpc. Isomerization of the maleate to the fumarate form takes place to a great extent in a reaction which runs parallel to the polycondensation process. An addition reaction could interfere with the polycondensation since some glycol segments may react with the cationic intermediate during the isomerization of maleate to fumarate.

Introduction

The synthesis of unsaturated polyester of relatively high molecular weight, derived from maleic anhydride (MA), seems to reach a point at which side reactions and branching occur through the unsaturation within the polymer structure. These reactions take place to a variable extent depending on whether the glycolic segment promotes the isomerization (cis-trans) reaction which is responsible for the increase in the percentage of fumarate in the final product (1). It has been proved (2), when a resin is cured with a vinyl monomer, that the fumarate form is highly reactive towards crosslinking reactions compared to the maleate form. Moreover, it has been found during the curing process of an unsaturated resin with styrene, when the ratio of styrene to unsaturation is small, that crosslinking through fumarate-fumarate forms take place to a considerable extent. In the absence of styrene or free radical initiators, the gelation reaction has been attributed to addition of glycol or any hydroxyl terminated group to a double bond (3) within the polymer chain; this reaction might use up to 15% of the unsaturations.

The purpose of this work is to synthesize a linear unsaturated polyester with an acid number less than 40, by limiting the amount of crosslinking during polyesterification. Below this point the condensation becomes slow and extended heating and temperature increase may favour fumarate-fumarate crosslinking, since polyesterification with ethylene glycol encourages maleate-fumurate isomerization (4).

Experimental

Reagents.

Maleic anhydride (BDH) was recrystallized from chloroform (m.p. 52°C). Ethylene glycol (BDH) was refluxed with sodium for an hour, then distilled at atmospheric pressure, the 190-192°C fraction being collected.

Monohydrated p-toluenesulphonic acid (SIGMA) was used without further treatment.

Synthesis of polyester.

The reaction was carried out in a tube, consisting of a bulb and a long tube with a side arm one inch below the top, for collecting the water formed during the reaction. A steady stream of dry nitrogen was bubbled through a fine tube, bubbling during the whole polymerization, in order to stir the reaction mixture and to remove the water formed. This bubbling tube was also useful for taking samples out from the reaction vessel. To 4.9385g of maleic anhydride (0.050 mol), 3ml of ethylene glycol (0.055 mol) and 0.0075g of p-toluenesulphonic acid (0.091% p/p) were added. The mixture was precondensed at 92°C during 4 1/2 hours and the temperature then raised to 192°C. The reaction was stopped when differences between two measurements of acid number were very small. The temperature is lowered to 110°C and the mixture dried under vacuum until no more bubbles were evolved.

Purification of polyester.

Once the polymerization was finished the polyester was dissolved in acetone and filtered through a sintered glass funnel. The solution was then heated to boiling and petroleum ether (60-80°C) added until cloudyness was just mantained. It was then allowed to cool till two well separated layers were formed. The solvent was drained off and the polyester dried under vacuum (0.5 mm Hg) at 60°C for 5 hours.

Analytical techniques.

End group analysis: the number average molecular weight ($\bar{M}_n$), of the unsaturated polyester was determined by measuring quantitatively the carboxyl and hydroxyl end groups. The number of carboxyl groups was measured by weighing 0.2-0.3g of sample, dissolving in pyridine and titrating with standardized KOH solution (≈ 0.01M). To determine the number of hydroxyl groups, 0.2-0.3g of sample was refluxed during 1 hour with 5ml of acetylating mixture, (pyridine:acetic anhydride, 400:6), and titrating the excess of acetic anhydride with KOH solution (≈ 0.1N). The end point of both titrations were indicated by color change of thymol blue, and the results are expressed as mg of KOH/g of sample. The molecular weight was calculated by using the following equation

$$\bar{M}n = \frac{2 \times 56.11 \times 10^{3}}{\text{acid number} + \text{hydroxyl number}}$$

Gel permeation chromatography: A Waters 200 instrument with five Styragel columns and a calibration curve obtained with low dispersity polypropylene glycol with molecular weights ranging between 800-4000 was utilized. Chloroform solutions were used at 40°C.

Infrared spectroscopy: Samples were film cast on CsBr discs from chloroform solution, and spectra taken using a 377 Perkin Elmer infrared spectrometer.

NMR spectroscopy: Samples were dissolved in $CDCl_3$ with TMS, and spectra taken using a 60 MHz Varian a-60 apparatus.

Results

Table 1 shows the experimental data of the polycondensation process

Table 1
Data from polycondensation.

Temperature(°C)	Purification	Time (h)	A.N.(mg KOH/g sample)
92	no	4 1/2	256
187	no	4 1/2	31
110	no	8	25
60	reprecipitat.	5	23

The ir and the nmr spectra for the reprecipitated polyester are shown in Figures 1 and 2, and the main absorptions are assigned in Tables 2 and 3, respectively. Table 4 shows the end group analysis data before and after reprecipitation, and the proportion of isomerization determined from the nmr spectra.

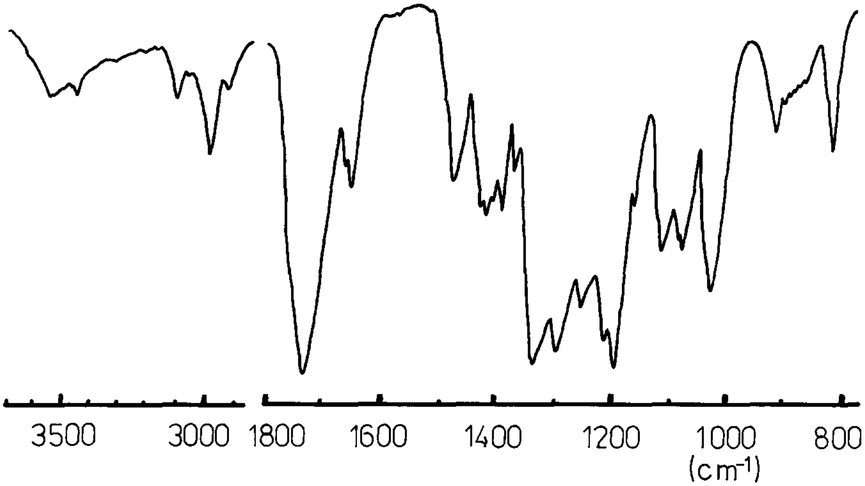


Figure 1. Infrared spectrum of the polyester from maleic anhydride and ethylene glycol.

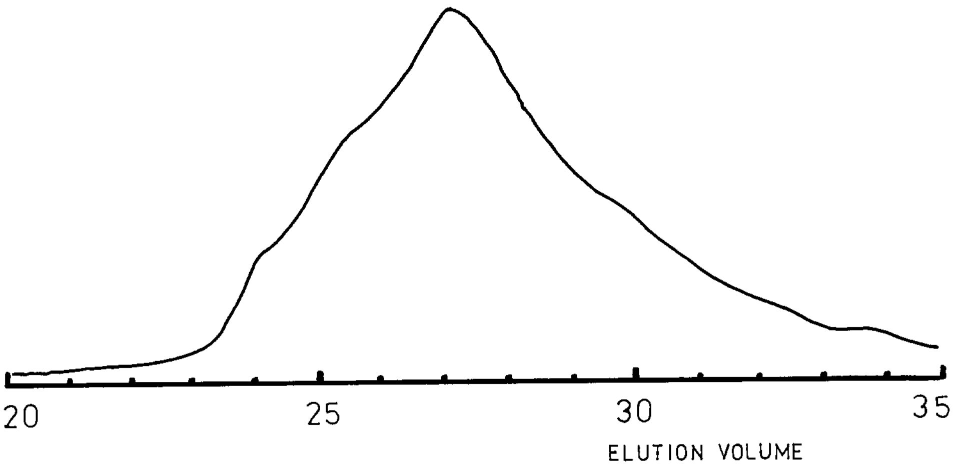


Figure 3. Gpc trace for the polyester.

Table 4
Data from end group analysis.

Sample.	Acid number	Hydroxyl number	$\bar{M}n$	% isomeriz.
crude	25.3	73.6	1135	68
repreci.	23.4	55.6	1421	67

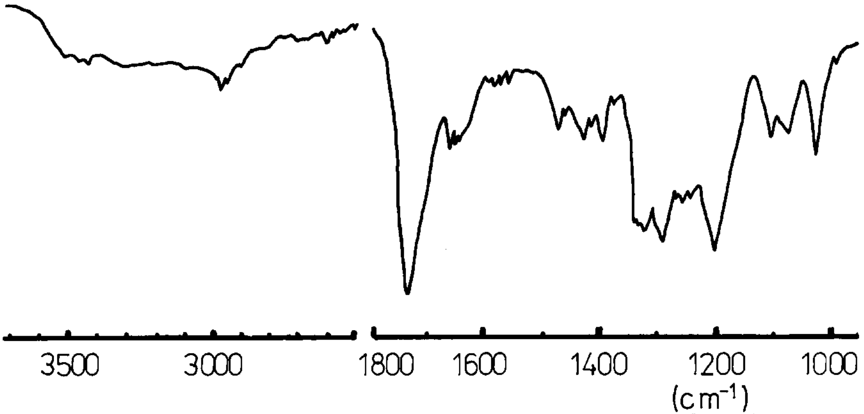


Figure 4. Infrared spectrum of gelled polyester

Table 5
Data from gpc analysis.

Sample	$\bar{M}n$	$\bar{M}w$	$\bar{M}w/\bar{M}n$
Repreci.	1450	3090	2.13

Table 2
Infrared assignments of main absorption bands.

Absorption (cm^{-1})	Assignment.
3550 (small, broad)	Stretching (OH) terminal hydroxyl.
3460 (small, broad)	Stretching (OH) terminal carboxyl.
3110 (small, sharp)	Stretching H — C = C — olefinic.
2995 (medium,sharp)	Stretching —CH₂—CH₂— ethylenic.
1730 (strong,sharp)	Stretching C = O ester.
1650 (medium,sharp)	Stretching — C = C — olefinic.
1185 (strong,sharp)	Stretching - CO - O - C ester.
815 (medium,sharp)	Bending — HC = CH — fumarate.

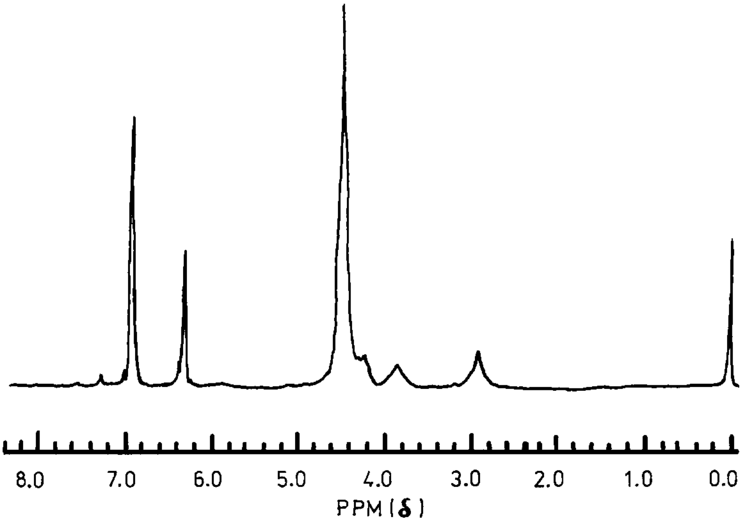


Figure 2. Proton magnetic resonance spectrum of the polyester from maleic anhydride and ethylene glycol.

Table 3
Proton magnetic resonance assignment of absorption bands

Chemical shift (ppm)		Assignment.	
6.85	singlet.	$- C\underline{H} = C\underline{H} -$	fumarate.
6.30	singlet.	$- C\underline{H} = C\underline{H} -$	maleate.
4.40	singlet.	$- C\underline{H_2} - C\underline{H_2} -$	inner.
3.90	multipl.	$- C\underline{H_2} - C\underline{H_2} -$	terminal.
2.90	singlet.	- OH	terminal.

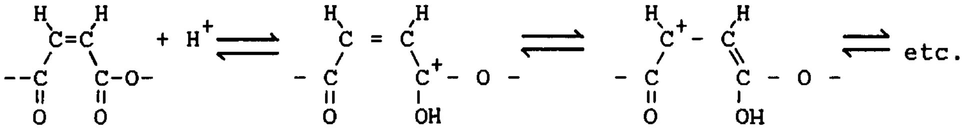
The gel permeation chromatographic trace data are shown in Figure 3 and Table 5, respectively. The effects of gelation are observed in the ir spectrum (Figure 4).

Discussion

The spectroscopic analysis refers basically to a linear polyester. It could be argued for linearity that the nmr espectrum only shows signals for cis (6.30 ppm), trans (6.85 ppm), inner and outer methylene protons, and terminal hydroxyl. This could also be confirmed by the height intensity of olefinic stretching (C = C) at 1650 cm^{-1} in the spectra, which indicates negligible or non existent side reactions though the double bonds, that is crosslinking and addition reactions. In the same way, the very small absorption at 3550 cm^{-1} in the ir spectrum, indicates terminal hydroxyl from polyester rather than hydroxyl groups from glycol chains attached to the polymer backbone.

The solubility of the polymer in common solvents, like acetone, chloroform and pyridine, leaves no doubt about linearity since the material which becomes jellylike and sticky does not dissolve but swells. In addition, the polymer forms very long threads when it is stretched.

Crosslinking is indicated by the broadening of the ir absorption at 3550 cm^{-1} and the intensity reduction at 1640 cm^{-1} which arise from OH and C=C groups respectively, that is a side reaction between hydroxyl and olefinic group is more likely, than by pure olefinic interactions. Gelation may ocur during initial stages similar to cis-trans isomerization, believed to occur by a carbocationic intermediate during initial stages (5)



Once the equilibrium is reached, the carbocation could be formed continuously but, depending on the reaction conditions, it is the addition of hydroxyl group to carbocation which takes over. This provides the drive for gelation.

Conclusions

The synthesis of a linear high molecular weight polyester from maleic anhydride and ethylene glycol is rather difficult. By careful experimentation, however the reaction can be driven to higher conversions as compared to those normally achieved, and in a shorter time of polymerization. Both main reactions are promoted by the protic catalyst used. By careful control of the catalyst amount and the reaction conditions, can be obtained linear polymer. The main obstacle to achieving considerable high molecular weight linear polymer, seems to be due to cis-trans isomerization which runs parallel to polycondensation. The isomerization may lead to a carbocation intermediate which facilitates the addition of hydroxyl groups to olefinic double bonds.

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