

Unsaturated Polyesters. V. Polyester from Maleic Anhydride and 1,6-Hexanediol

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SYNOPSIS

The polycondensation reaction between maleic anhydride and 1,6-hexanediol, with *p*-toluenesulfonic acid as catalyst has been carried out. The product has been analyzed spectroscopically and the molecular weight determined by endgroup analysis and gel permeation chromatography. The influence of spatial interactions between condensed groups on the isomerization of maleate into fumarate is discussed, as well as the effects of even- and odd-numbered carbon atom glycols. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

In previous papers of this series,¹⁻⁴ polyesterification reactions involving maleic anhydride and some *n*-methylene glycols has been discussed. Linear glycols, with an even number of carbon atoms, give rise to a higher percentage of isomerization than do the odd ones, if polycondensation is carried out under the same conditions. Temperature is one of the most important parameters that must be taken into account, as shown by Mladen et al.⁵ On the other hand, the time of reaction plays its part, though only in the initial steps of polycondensation, since after a certain time, as shown by Vancso-Szmercsanyi,⁶ the isomerization process shows asymptotic behavior around a particular value that is a function of temperature. There has been some arguments about this, but the assumption that glycols which give greater steric agglomeration have their major effects in the initial stages of polycondensation could settle any discrepancy.⁷ For diols with less steric hindrance, or which give less spatial interaction between condensed groups, it is supposed that parallel polycondensation and isomerization occur, whereupon fumarate contents within the oligomeric chain change continuously with time.⁸

It is also important to emphasize the strong tendency of polyesters based on maleic anhydride and

even-numbered carbon glycols to undergo gelation and cross-linking reactions, leading to a highly intractable jellylike mass that cannot be further characterized. So, when no side reactions interfere, this kind of polyester becomes a transparent fluid resin in contrast to the odd ones, which ends up as a white nonsticky rubberlike solid.

Meanwhile, it may be assumed, as previously suggested,⁹ that olefinic bonds within the polyester, in its fumarate form, are more reactive toward hydroxyl addition or olefinic-olefinic reaction through a cationic intermediate. A radical mechanism, particularly with the latter reaction, may not be completely discarded since it takes place too fast, making it difficult to detect.

EXPERIMENTAL

Reagents

Maleic anhydride (BDH) was crystallized from chloroform solution. 1,6-Hexanediol (Aldrich) and *p*-toluenesulfonic acid (Sigma) were used without further treatment.

Synthesis of Polyester

Polyesterification was accomplished as previously described.¹ The reaction vessel was charged with 14.7517 g (0.1504 mol) of maleic anhydride, 18.0022 g (0.1533 mol) of 1,6-hexanediol, and 0.0327 g

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Table I Data from the Polymerization Process

Sample	Temperature (°C)	Time (Min)	Acid No. ^a
1	114	30	231.2
2	187	120	58.5
3	187	240	39.2
4	187	330	33.5
5	187	450	33.8
6	187	510	33.6
7 ^b	187	580	20.0

^a mg KOH/g of sample.^b Vacuum (≈ 1 Torr) applied to system during first 10 min.

(0.099% *p/p*) of *p*-toluenesulfonic acid. The reaction carried out at the temperature of boiling of ethylene glycol until an acid number between 10 and 20 mg of KOH/g of sample was reached. Vacuum (≈ 1 Torr) was applied a short time before the polycondensation was stopped in order to help water removal from the reaction medium.

Purification of Polyester

The resulting polyester was dissolved in approximately 150 mL of acetone, discarding the nonsoluble fraction that amounted to 3.77 g. The filtrate was warmed nearly to boiling and petroleum ether (60–80) was added dropwise until cloudiness appeared. The solution was left overnight and the upper layer discarded. The lower layer was dried under vacuum (≈ 0.1 Torr) at 60°C for 10 h.

Analytical Techniques

Molecular weight was measured by analytical titration of the polymer endgroups and by gel permeation chromatography (GPC) using chloroform solutions (0.2% *p/p*) at 40°C in a Waters 200 instrument. A Perkin-Elmer 377 apparatus was used for infrared analysis of film samples cast on sodium chloride

Table II Data from Endgroup and GPC Analysis of the Polyester

Endgroup Analysis			GPC		
Acid No. ^a	Hydroxide No. ^a	\bar{M}_n	\bar{M}_n	\bar{M}_w	<i>D</i>
14.80	22.5	3006	2959	4434	1.50

^a mg KOH/g of sample.

discs. A Varian A-60 60 MHz instrument was used for proton magnetic resonance analysis of deuterated chloroform solutions.

RESULTS

Tables I and II describe the polymerization process and values obtained for molecular weight by endgroup analysis and GPC, respectively. IR, NMR, and GPC traces are shown in Figures 1, 2, and 3 respectively. The main absorptions in the IR and NMR spectra are assigned in Tables III and IV, respectively.

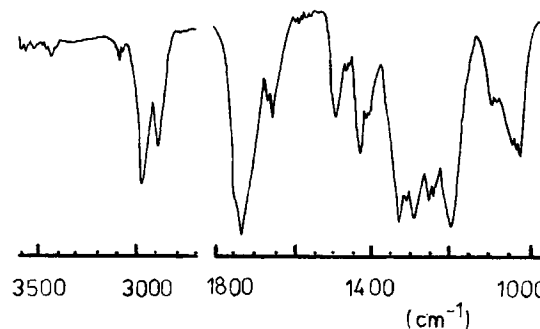
DISCUSSION

As in previous work,¹⁻⁴ considerable isomerization took place, as well as a general tendency of the polymerization system to gelation or cross-linking when a critical value of isomerization was reached.

The IR spectrum of soluble polyester shows small absorption bands for hydroxyl and carboxyl at 3560 and 3450 cm^{-1} , respectively. The low intensity of the hydroxyl band is attributed either to a high degree of conversion of monomer to oligoester or to oligomer cyclization,⁴ though there is not much difference between the molecular weights obtained by the two methods.

The unsaturated nature of the polyester is confirmed by the olefinic absorption at 1650 cm^{-1} and by the inner *cis* (6.24 δ) and *trans* (6.82 δ) isomeric forms of the ester unit.

The percentage of maleate that was isomerized to fumarate, in the soluble fraction, was around 51.3%. It is also important to point out the appearance of the two small signals for outer fumarate (6.78 δ) and maleate (6.20 δ) protons, which have been reported and used for the determination of molecular

**Figure 1** Infrared spectra of the polyester.

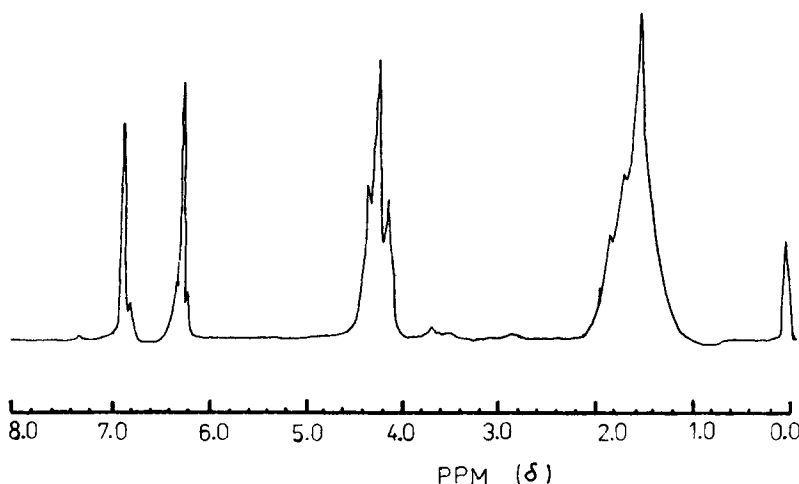


Figure 2 Proton magnetic resonance spectra of the polyester.

weight.⁵ Other NMR signals occur with the expected shifts and ratios.

Though there is quite good agreement between the values for number-average molecular weights (\bar{M}_n) measured by the two methods, endgroup values have always been relatively higher for those polyesters that show two fractions in the GPC trace. The reason for this behavior may be ascribed to intramolecular cyclization of a certain proportion of the polymer chains, which diminishes the amount of countable endgroups without real growth of the molecular weight of the polymer. Separation of the two GPC fractions might help by determining the endgroups within each, though this has yet to be accomplished.

As in earlier reports, this even-numbered carbon glycol may undergo spatial agglomeration near the olefinic bond in the polymer chain, promoting a higher degree of isomerization and, of course, gela-

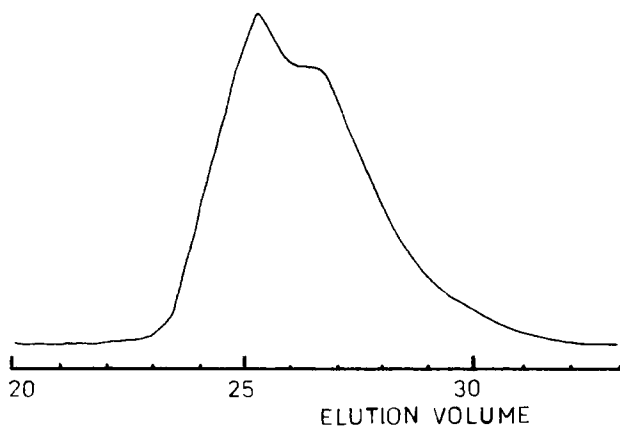


Figure 3 GPC trace of the polyester.

tion and cross-linking, though the reaction was kept below the critical point.

CONCLUSION

Under the conditions used, a small amount of cross-linking or gelation took place, even though the crit-

Table III Main Absorptions from IR Spectra of the Polyester

Absorption (cm ⁻¹)	Assignment
3560 small, broad	Stretching OH terminal hydroxyl
3450 small, broad	Stretching OH terminal carboxyl
3100 small, broad	Stretching =C—H olefinic
2870 strong, sharp	Stretching <i>sym</i> methylene
2800 medium, sharp	Stretching <i>asym</i> methylene
1730 strong, sharp	Stretching C=O ester
1650 medium, sharp	Stretching —C=C— olefinic
1480 medium, sharp	Bend methylene
1185 strong, sharp	Stretching —C—O—C— O

Table IV Absorption Assignment of NMR Bands of the Polyester

Chemical Shift (ppm)	Assignment	Ratio
6.82 singlet	— <u>CH</u> = <u>CH</u> — fumarate	7.8
6.24 singlet	— <u>CH</u> = <u>CH</u> — maleate	
4.22 triplet	—O <u>CH</u> ₂ —(CH ₂) ₄ — <u>CH</u> ₂ —O—	16.5
1.32 multiplet	—OCH ₂ —(CH ₂) ₄ —CH ₂ —O—	33.4

ical point was not reached. In the light of molecular weight measurements, some cyclization may have occurred.

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