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Unsaturated polyester

4. Polyester from maleic anhydride and 1,5-pentanediol

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Summary

The polyesterification reaction between maleic anhydride and 1,5-pentanediol, using p-toluenesulphonic acid as catalyst, was carried out. The material was characterized spectroscopically and its molecular weight measured. Besides isomerization of maleate to fumarate, some sort of intramolecular ring closure between polymer end groups may be occurring, since there is little agreement between molecular weight measurements by end group analysis and gel permeation chromatography, and very weak absorption is observed for hydroxyl group.

Introduction

Spatial interaction between condensed groups in unsaturated polyester based on maleic anhydride has a remarkable effect on both the cis-trans (1) isomerization and the physical properties (2) of the final product. In previous work (3-5) it has been reported that polyesters with glycol segments with an even number of carbon atoms gives a higher degree of isomerization than those with odd numbers.

Unsaturated polyester with a low degree of isomerization reaches a high degree of polymerization and a high molecular weight. In these cases the polycondensation is less affected by side reactions like gelation and crosslinking.

Polyesters with even numbers of carbon atoms in the glycol segments are relatively hard waxy materials, while those with odd numbers are fluid resins. Structural agglomeration in both cases seems to be responsible for much of the isomerization. Chain mobility and energy transfer together with agglomeration, are critical for reaching linear high molecular weight polymer.

Experimental

Reactants.

Maleic anhydride was recrystallized from chloroform solution. 1,5-Pentanediol was vacuum distilled, the intermediate fraction being collected. p-Toluenesulphonic acid was used without further treatment.

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Synthesis of polyester.

Polymer was synthesized as described in an earlier paper (3). The reactor was charged with 6.1481g (.0627mol) of maleic anhydride, 6.70ml (.0639mol) of 1,5-pentanediol, and .0169g of p-toluensulphonic acid (.13% p/p). The reaction was carried out at the temperature of boiling ethylene glycol (185°C), heating was continued until no appreciable change in acid number was observed.

Purification of polyester.

The viscous transparent resin was dissolved in acetone and filtered through a sintered glass funnel. The filtered solution was warmed up and petroleum ether (60-80) added carefully till a cloudness appeared. The mixture was allowed to stand overnight, the upper phase was drained off, the lower one was dried under vacuum (.1 Torr.) at 60°C for 6 hours.

Analytical techniques.

Molecular weight was determined by end group analysis and gel permeation chromatography (3). Infrared analysis was carried out on a Perkin Elmer 377 instrument, and proton magnetic resonance on a Varian A-60 instrument (3).

Results

Tables 1 and 2 summarise data for the polymerization process and molecular weight determination, respectively.

Table 1.
Polycondensation data

Sample	Temperature, °C	Time, min.	acid number^a.
1	183	20	85
2	185	80	32,5
3	185	160	16.1
4	185	260	13.7
5	185	300	11.3

(a)mg KOH/g of sample.

Table 2.
Data from end group and gpc analysis of polyester.

End group analysis.			Gel permeation chromatography		
A. number^a.	Hydrox. number^a.	$\bar{M}n$	$\bar{M}n$	$\bar{M}w$	D
8.85	2.75	9670	3307	5960	1.80

(a) mg KOH/g of sample.

Traces from infrared, proton magnetic resonance, and gel permeation chromatography are shown in Figures 1,2 and 3, respectively.

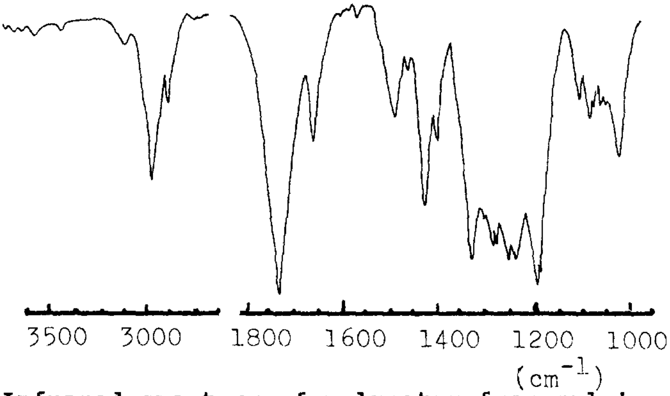

Figure 1. Infrared spectrum of polyester from maleic anhydride and 1,5-pentanediol.

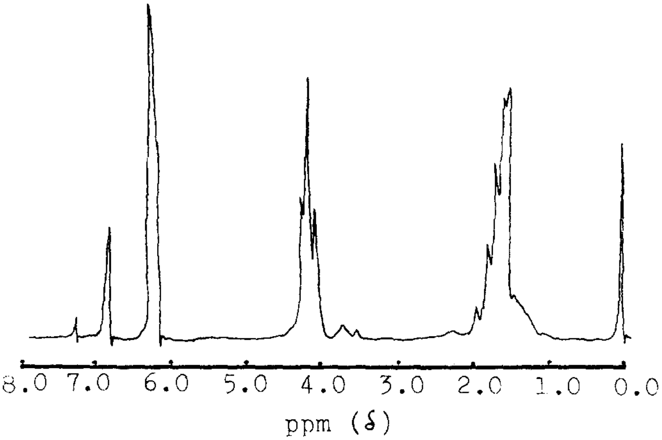

Figure 2. NMR spectrum of polyester from MA and 1,5-pentanediol

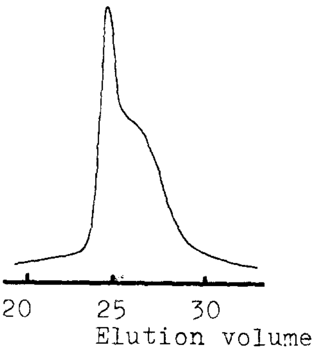

Figure 3. GPC trace of polyester from MA and 1,5-pentanediol.

Tables 3 and 4 relate to ir absortions and H^1nmr resonances.

Table 3.
Main absortions from ir spectra of polyester.

Absortion, cm^{-1}.		Assignment.	
3080	small, broad	Stretching	$-C\underline{H}=C\underline{H}-$
2970	strong, sharp	Stretching	$-C\underline{H}_2-C\underline{H}_2-$
1730	strong, sharp	Stretching	$C=O$ ester
1655	medium, sharp	Stretching	$-C=C-$
1190	strong, sharp	Stretching	$-\underset{\underset{O}{\Vert}}{C}-O-C-$

Table 4.
Main nmr resonances of polyester.

Chemical shift, ppm.	Assignment		ratio
6.85 singlet	$-C\underline{H}=C\underline{H}-$	fumarate	4.1
6.25 singlet	$-C\underline{H}=C\underline{H}-$	maleate	
4.20 triplet	$-O-C\underline{H}_2-(CH_2)_3-C\underline{H}_2-O-$		8.1
1.58 multiplete	$-O-CH_2-(C\underline{H}_2)_3-CH_2-O-$		12.7

Discussion

An unsaturated reasonably high molecular weight polyester was obtained, as compared with that obtained with lower glycols (3-5). The large difference between the molecular weight values, measured by end group analysis and GPC, combined with other observations (e.g.) solubility and fluidness, cannot be due to gelation or crosslinking. The formation of macrocycles by end group reactions within a polymer chain may account for the difference in the polymer molecular weights, that leaves only a small amount of free analytically countable end groups.

The ir spectrum shows very weak absorption of hydroxyl and carboxyl groups; this is not the case for similar polyesters with shorter glycol segments (3-5). The presence of olefinic unsaturation by ir and nmr spectra indicate the absence of side reactions, like crosslinking and gelation. The ratio between nmr maleate-fumarate signals is 17% as measured from the integral.

Conclusion

A soluble unsaturated polyester was obtained. The material is not completely linear, as inferred from the disagreement in molecular weights determined by end group analysis and gel permeation chromatography. Cyclic and linear polyester chains derived from the polycondensation reaction, or degradation (6) processes may explain the observations.

Isomerization occurs but to a diminished extent; this is expected since the spatial interaction among condensed groups is lower when odd carbon atoms glycol is used.

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