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Quantitative Methyl Esterification of Carboxyl End Groups of Polyethylene Terephthalate*

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Summary

For esterification of its carboxyl end groups in heterogeneous phase, polyethylene terephthalate was treated with boron trifluoride/methanol and with diazomethane in chlorobenzene, respectively. Whereas treatment with boron trifluoride/ methanol in some cases was accompanied by polymer degradation, reacting the polyester with diazomethane resulted in complete methyl esterification without any detectable side reaction.

Introduction

According to the currently most important process for producing polyethylene terephthalate (PETP) - transesterification of terephthalic acid dimethyl ester with an excess of ethylene glycol followed by polycondensation - the polycondensate should only have hydroxyl end groups besides some methyl ester end groups. As a third type of end group, however, carboxyl groups which are produced by thermolytic degradation processes (BUXBAUM 1968) are to be found. These carboxyl groups can interfere during reactions at the hydroxyl groups for analytical purposes. Furthermore the carboxyl end groups have a detrimental effect on the hydrolytic stability

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of polyesters (BATZER 1950, RAVENS and WARD 1961). For these reasons we looked for a method of blocking the carboxyl groups quantitatively.
In the literature, data exist on methyl esterification of carboxyl end groups by reacting aliphatic polyesters with diazomethane (STAUDINGER and SCHMITT 1940, BATZER 1950, BATZER and LANG 1955). It could not be foreseen, however, if this esterification method could be transferred to PETP without difficulties, as the esterification of the aliphatic polyesters was carried out in solution. This is not possible with PETP due to the lack of suitable solvents.
In this communication we describe some experiments to achieve a methyl esterification of the carboxyl end groups of undissolved PETP by means of diazomethane as well as boron trifluoride/methanol.

Experimental

For our investigations, a commercial polyethylene terephthalate fiber, both in unchanged form and after reprecipitating from phenol/ tetrachloroethane (1:1, vol:vol) with diethyl ether, was used. The reprecipitated material was well washed with ether and dried.

Procedure for esterification catalysed by BF_3:
5 g PETP are mixed with water-free methanol. After adding 13 ml boron trifluoride-dimethyl etherate the mixture is boiled for 6 h. Then the polymer is filtered off, washed with methanol and dried. For comparison, 2,5 g PETP are boiled in 50 ml dry methanol for 6 h, filtered off and dried.

Procedure for esterification by diazomethane:
1 g PETP are swollen for 12 h with 40 ml o-dichlorobenzene. Then 5 ml of a solution of diazomethane in di-

ethylether,prepared from 0,1 mol nitrosomethylurea (ORGANIKUM 1976), are added at this temperature, then another 2 ml of the diazomethane solution are added, and the mixture is held for another 24 h at 0°C. The polymer is then filtered off, washed thoroughly with ether and dried. For comparison PETP is treated in an analogous way, but without addition of diazomethane.

Viscosity measurements were made following the recommended method from Schweizer Normenvereinigung (SNV 195590, 1965).
Determinations of carboxyl group contents were kindly performed by BASF Aktiengesellschaft, Ludwigshafen, West Germany.

Results and Discussion

Viscosity measurements showed that the boron trifluoride method is not suitable for carboxyl group esterification. Admittedly, the non-reprecipitated commercial fiber shows no decrease in solution viscosity after being treated with BF_3; however, with the reprecipitated material, a distinct decrease could be detected (Table 1).

TABLE 1

Material	$[\eta]$ $[ml\ g^{-1}]$
Fiber	52,1
Fiber, treated with CH_3OH	51,8
Fiber, treated with BF_3/CH_3OH	52,4
Reprecipitated material	52,0
Reprecipitated material, treated with CH_3OH	52,2
Reprecipitated material, treated with BF_3/CH_3OH	31.5

Since it is obvious that, during treatment with BF_3, degradation reactions can take place to a fairly large extent (probably by BF_3-catalysed transesterifications), this way was not pursued farther.

As medium for the reaction of the polyester samples with diazomethane we selected o-dichlorobenzene, which has a swelling effect on PETP. Thus a disaggregation of the non-crystalline regions - where, as is well known, most of the end groups are located - and in that way a better approach for the reagent to these groups ought to be achieved. During these reactions no such degradation occured as was the case with the BF_3-catalysed reactions; the limiting viscosities remained within tolerance (cf. Table 2). For the determination of carboxyl group contents a colorimetric method was chosen, because a titrimetric determination yields, especially in the case of low carboxyl group contents, only rather inaccurate results; these determinations were kindly made by BASF Aktiengesellschaft, Ludwigshafen, West Germany. The results are summarized in Table 2.

TABLE 2

Material	$[\eta]$ $[\mathrm{ml\ g^{-1}}]$	COOH-content $[\mathrm{mval\ kg^{-1}}]$
Fiber	52.1	54
Fiber, swollen in o-dichlorobenzene	52.1	44
Fiber, treated with diazomethane	52.8	<2
Reprecipitated material	52.0	41
Reprecipitated material, swollen in o-dichlorobenzene	50.4	40
Reprecipitated material, treated with diazomethane	52.1	<2

The results show that the PETP-samples, independent of the fine structure in question (native fiber or reprecipitated material) are virtually completely esterified. The decrease in carboxyl group content in the case of the reprecipitated reference samples and the reference samples swollen in dichlorobenzene, respectively, most probably is due to removal of low molecular weight components with acidic groups, present in the polyester.

The results presented here show that methyl esterification of carboxyl groups can be achieved even with "compact" PETP in heterogenous phase. As this esterification can obviously be achieved in a quantitative manner, the possibility arises for specific determination of carboxyl groups in PETP, because a very exact method for the determination of methyl ester groups in PETP exists (ZIMMERMANN and BECKER 1971).

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