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Preparation of oligoester diols by alcoholytic destruction of poly(ethylene terephthalate)

N. Halacheva* and P. Novakov
Technological University of Sofia, 8 Kl. Ohridski Blvd., 1756 Sofia, Bulgaria
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The alcoholytic destruction of poly(ethylene terephthalate) (PET) with diethylene glycol (DEG) is studied. The influence of the DEG amount on the structure of the obtained oligoesters is investigated. On the basis of the experimental results, a probable mechanism is proposed for the alcoholysis of PET at large excess of DEG. The molecular weight characteristics of the obtained oligomers are studied and kinetic schemes are assumed for alcoholysis at different molar ratios of the starting components. Optimal conditions are established for the preparation of linear oligoester diols suitable for the synthesis of water-borne polyurethanes.

(Keywords: alcoholysis; poly(ethylene terephthalate); oligoesters)

INTRODUCTION

Polyester polyols are the preferred raw materials in the production of polyurethanes (PU) and paints based on PU. The polyester polyols traditionally used for this purpose are those obtained by polycondensation of aliphatic (aromatic) diols or aromatic (aliphatic) di- or polycarboxylic acids.

Poly(ethylene terephthalate) (PET) is produced in considerable amounts since it finds application in the textile industry. The wastes from PET spinning are not suitable for a second drawing. One possible approach to their reuse consists in their transformation into oligoester polyols by alcoholytic destruction[1–3]. The present study aims to establish appropriate conditions for the preparation of oligoester polyols by alcoholytic destruction of PET. The products should have properties and structure suitable for the synthesis of water-borne PU: they should have a linear structure, –OH end groups and an acid number of less than 10 mg KOH/g.

Reports dealing with the alcoholysis of polymers[4–10] are concerned mainly with establishing the degree of destruction of the starting polymer and with determining the kinetic parameters of the reaction using low-molecular-weight model compounds. For this reason it was of interest to study the structure and properties of the oligoester polyols obtained by alcoholytic destruction with diethylene glycol (DEG). The investigation reported here deals with the influence of the process duration and the PET:DEG molar ratio on the structure and functional groups of the polyester polyols obtained, as well as with the study of the mechanism and kinetics of alcoholytic destruction of PET.

EXPERIMENTAL

PET wastes with molecular weight of 22 200, hydroxyl number of 5.0 mg KOH/g and acid number of 4.6 mg KOH/g were subjected to alcoholytic destruction. The atomic absorption analysis of this material showed the presence of 0.3 wt% of Mn and 0.01 wt% of Sn.

Alcoholysis was carried out in a continuously stirred three-necked flask equipped with a condenser. The temperature of the reaction mixture was kept constant at 230°C. AFter a chosen reaction time, the reaction product was dissolved in ethyl acetate and reprecipitated with hexane. The precipitate was filtered (Schott filter, M02) and dried at 50°C in a vacuum oven at residual pressure of 200–300 mmHg to constant weight.

The contents of hydroxy and carboxy groups of the oligoesters obtained were determined by potentiometric titration on a Mettler automatic titrator. The water content of the oligoesters was determined by the Karl-Fischer method.

Infra-red spectra of the oligoester polyols in the form of thin films were recorded in the range 700–4000 cm^{-1} on NaCl plates using a Specord-71 IR spectrophotometer.

^{1}H and ^{13}C n.m.r. spectra were recorded on a Bruker 250 spectrometer at a frequency of 250 MHz in dimethylfomamide-d$_7$ (DMFA-d$_7$) solutions.

The molecular weights of the oligomers were determined by gel permeation chromatography (g.p.c.) on a Waters 991 chromatograph equipped with a photodiode array detector and a set of three Ultrastyragel columns (one 500 Å and two 100 Å). Chloroform was used as solvent at 40°C and with a flow rate of 0.8 ml min^{-1}. The data were calculated using polystyrene standards and Waters Expert™ software Variant 6.2, on a Waters M860 data station.

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* To whom correspondence should be addressed

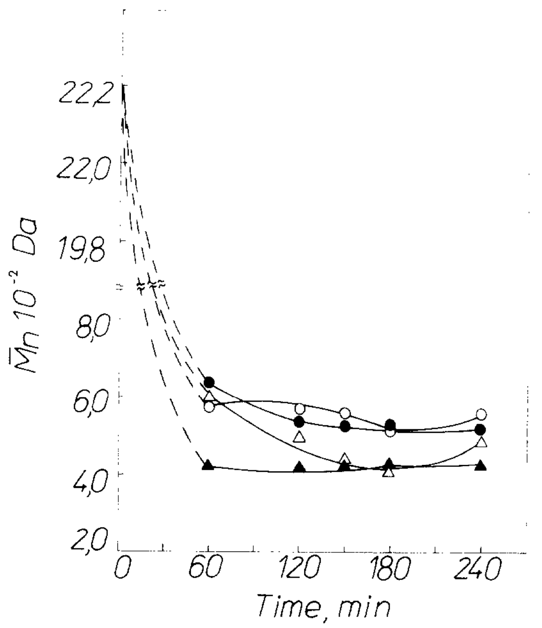
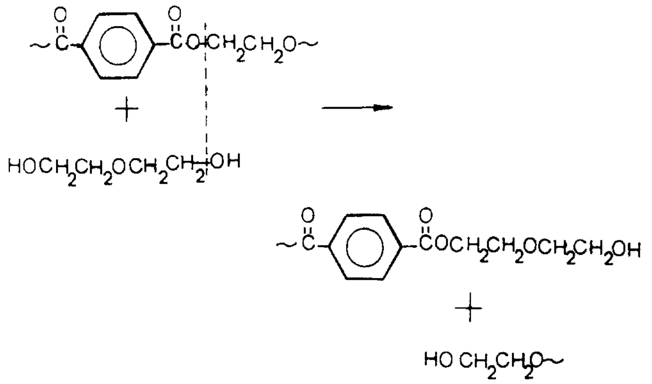


Figure 1 Time dependence of the final molecular weight ($\bar{M}_n$) of oligoesters obtained by alcoholysis of PET with DEG at molar ratios of (○) 1:100; (●) 1:120; (△) 1:160; (▲) 1:250

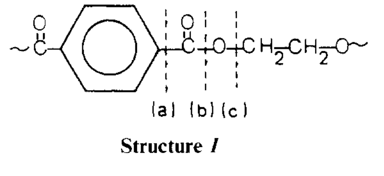
RESULTS AND DISCUSSION

According to literature data[4–6], the alcoholysis of PET with DEG proceeds as shown in reaction (1).



Reaction (1)

The alcoholysis consists of the transesterification of PET and the destruction of its polymer chain, resulting in the decrease of PET molecular weight. Destruction of PET can take place at elevated temperatures by affecting the bonds (a), (b) and (c) in the polymer chain[11]:



Structure *I*

When glycols are used as destructuring agents, the oligoesters obtained have two hydroxy end groups, i.e. oligoester diols are formed.

Some concurrent reactions could take place together with alcoholysis; these could be thermal oxidative breakdown of PET[11–14], oxidation of DEG and ethylene glycol forming acetaldehyde and water[2,13]

Influence of DEG amount on PET alcoholytic destruction

The effect of the amount of DEG on the degree and type of alcoholytic destruction is studied at PET:DEG molar ratios of 1:100, 1:120, 1:160 and 1:250 and reaction times of 1, 2, 3 and 4 h. The molar ratios are chosen in such a way that 0.86 (1:100), 1.03 (1:120), 1.38 (1:160) and 2.15 (1:250) moles of DEG correspond to one monomeric unit of starting PET.

The final molecular weight ($\bar{M}_n$) of the isolated oligoester diols decreases with increasing amount of DEG (*Figure 1*). At a large excess of DEG (1:250) the final molecular weight of the oligoesters is about 410–450 and remains almost unchanged regardless of the reaction time. This value is about 50 times lower than the $\bar{M}_n$ of the starting PET. For PET:DEG ratios of 1:100, 1:120 and 1:160, the optimal reaction time for obtaining a low-molecular-weight oligomer is about 3 h.

The values of hydroxyl numbers of the oligoester diols obtained (*Figure 2*) suggest that the type of destruction depends on the PET:DEG molar ratio. As expected, the hydroxyl number of the oligomer rises with increasing DEG excess. The facts that the maximum hydroxyl number is obtained at the reaction time of 3 h and that the molecular weight of the obtained oligomers reaches its lowest value at the same process duration lead to the assumption that these oligoesters have more than two –OH end groups in their molecules. On the basis of the experimentally determined hydroxyl numbers[15]. The $\bar{M}_n$ values are calculated and compared to those obtained by g.p.c. (*Table 1*).

It is seen that at a large excess of DEG (1:160, 1:250) there is no correlation between the calculated M_n values and those determined experimentally. At the longest reaction times the molecular weight decreases and the –OH percentage increases. It follows that at PET:DEG molar ratios of 1:160 and 1:250, alcoholysis obeys such a mechanism that oligoesters with a higher OH group content are formed.

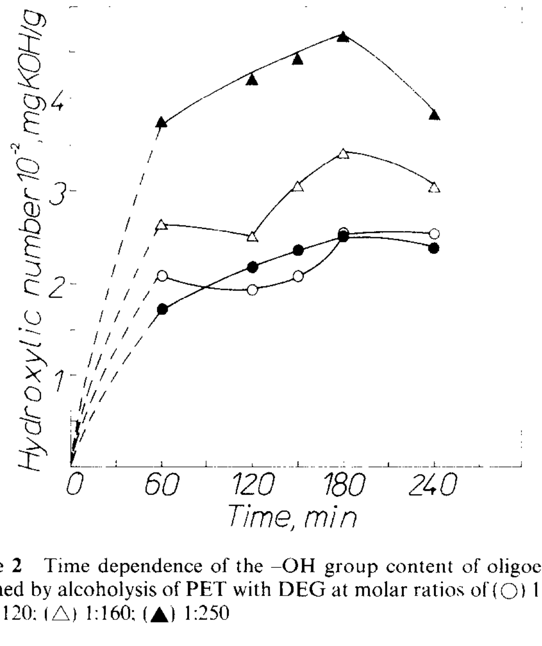


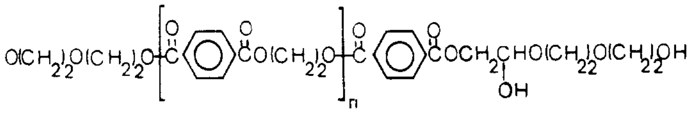
Figure 2 Time dependence of the –OH group content of oligoesters obtained by alcoholysis of PET with DEG at molar ratios of (○) 1:100; (●) 1:120; (△) 1:160; (▲) 1:250

Table 1 Molecular weights ($\bar{M}_n$) of oligoester diols obtained by alcoholytic destruction of PET with DEG

PET:DEG molar ratio	Time (min)	Hydroxy group content (wt%)	Molecular weight ($\bar{M}_n$) obtained: from hydroxyl number	Molecular weight ($\bar{M}_n$) obtained: from g.p.c.
1:100	60	6.31	538	582
	120	5.96	570	573
	150	6.29	540	561
	180	7.76	438	495
	240	8.79	387	559
1:120	60	5.20	654	640
	120	5.57	518	536
	150	6.13	555	528
	180	7.72	440	520
	240	7.25	468	518
1:160	60	8.85	384	602
	120	7.54	450	505
	150	9.18	370	442
	180	10.31	329	414
	240	9.10	370	499
1:250	60	11.55	320	433
	120	12.91	263	418
	150	11.33	300	442
	180	13.79	238	432
	240	11.76	289	429

The i.r. spectra (*Figure 3*) of the oligoesters obtained at a large excess of DEG show a clearly expressed absorption band at 1075 cm^{-1}, corresponding to the deformation vibrations of a secondary –OH group. Bands at $\lambda = 930$ and 820 cm^{-1}, characteristic of triethylene glycol[2], are also observed in these spectra.

The ^{1}H and ^{13}C n.m.r. spectral data (*Figures 4* and *5*, *Table 2*)[16–21] also confirm the assumption that the oligoesters obtained at a large excess of DEG have the structure shown in Structure *II*, where $n = 1$–4.



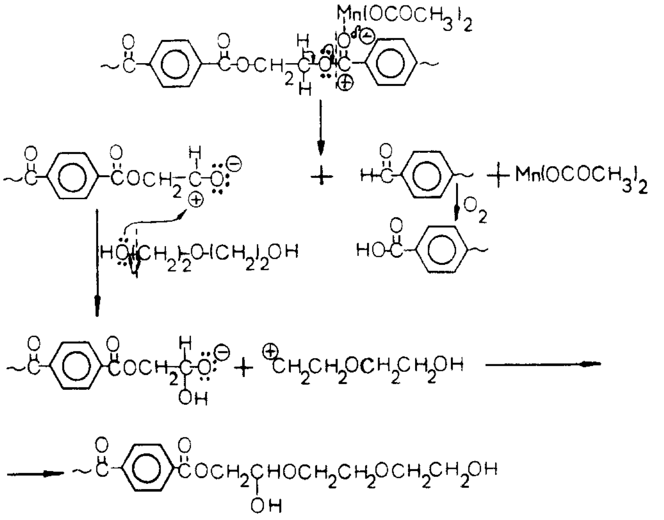
Structure *II*

A secondary hydroxyl group can be formed in polyester chains by oxidative breakdown[12,13]. If this is the case in the present study, all oligoesters obtained should have a structure similar to *II* regardless of the DEG amount in the reaction mixture. However, our spectral data clearly show that such structures are characteristic of the products obtained at a large excess of DEG (1:160 and 1:250). For this reason the mechanism shown by reaction (2) could be assumed in this case.

The benzaldehyde end groups formed according to reaction (2) are readily oxidized to carboxy groups; this is an explanation of the rise in acid number of the oligoesters at a PET:DEG ratio 1:160 (*Figure 6*). The lower acid numbers at a molar ratio of 1:250 could be explained by the fact that some carboxy groups undergo esterification due to the large excess of DEG.

Kinetics of the alcoholytic destruction of PET with DEG

Alcoholysis proceeds by random cleavage of the PET chains with the formation of oligomers. The bonds (a) and (b) in Structure *I* are most often cleaved. It could be assumed with some approximation that the probability



Reaction (2)

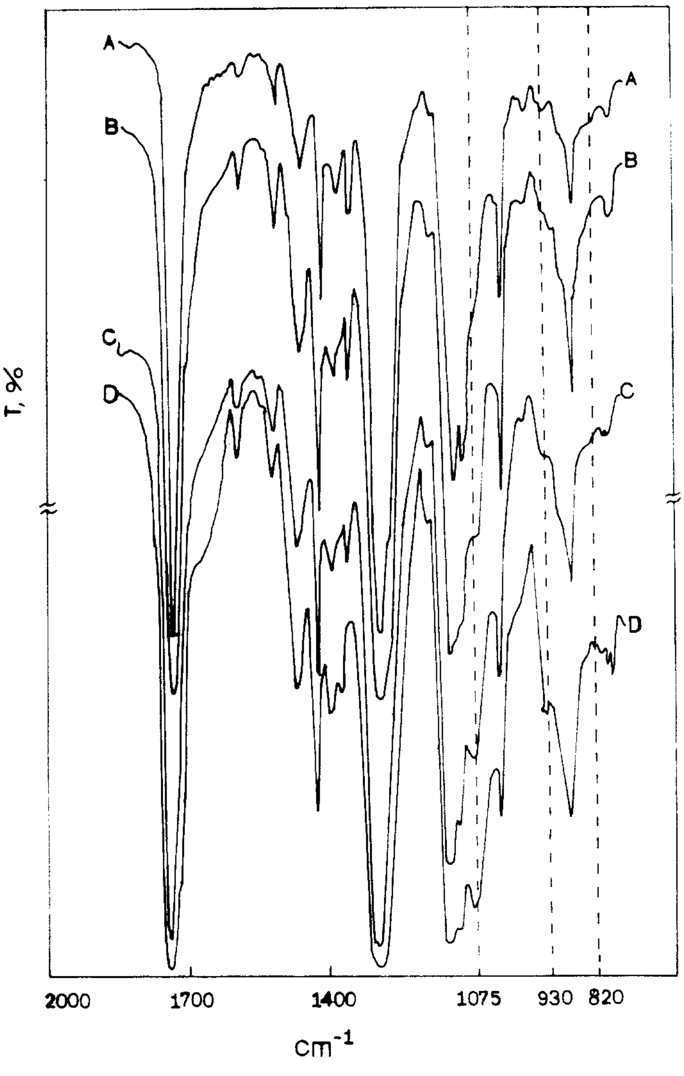


Figure 3 I.r. spectra of oligoesters obtained by alcoholytic destruction for 120 min of PET with DEG at molar ratios of (A) 1:100; (B) 1:120; (C) 1:160; (D) 1:250

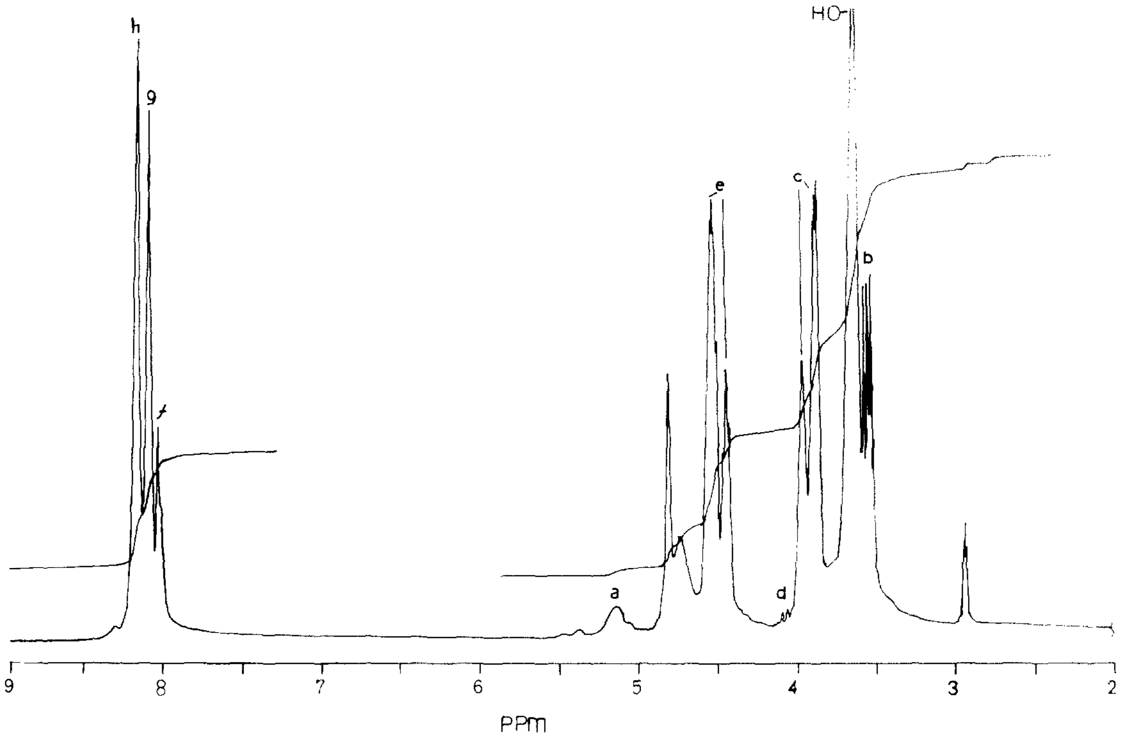


Figure 4 ^{1}H n.m.r. spectrum (250 MHz, solvent DMFA-d_7) of the oligoester obtained by alcoholytic destruction for 120 min of PET with DEG at a molar ratio of 1:160

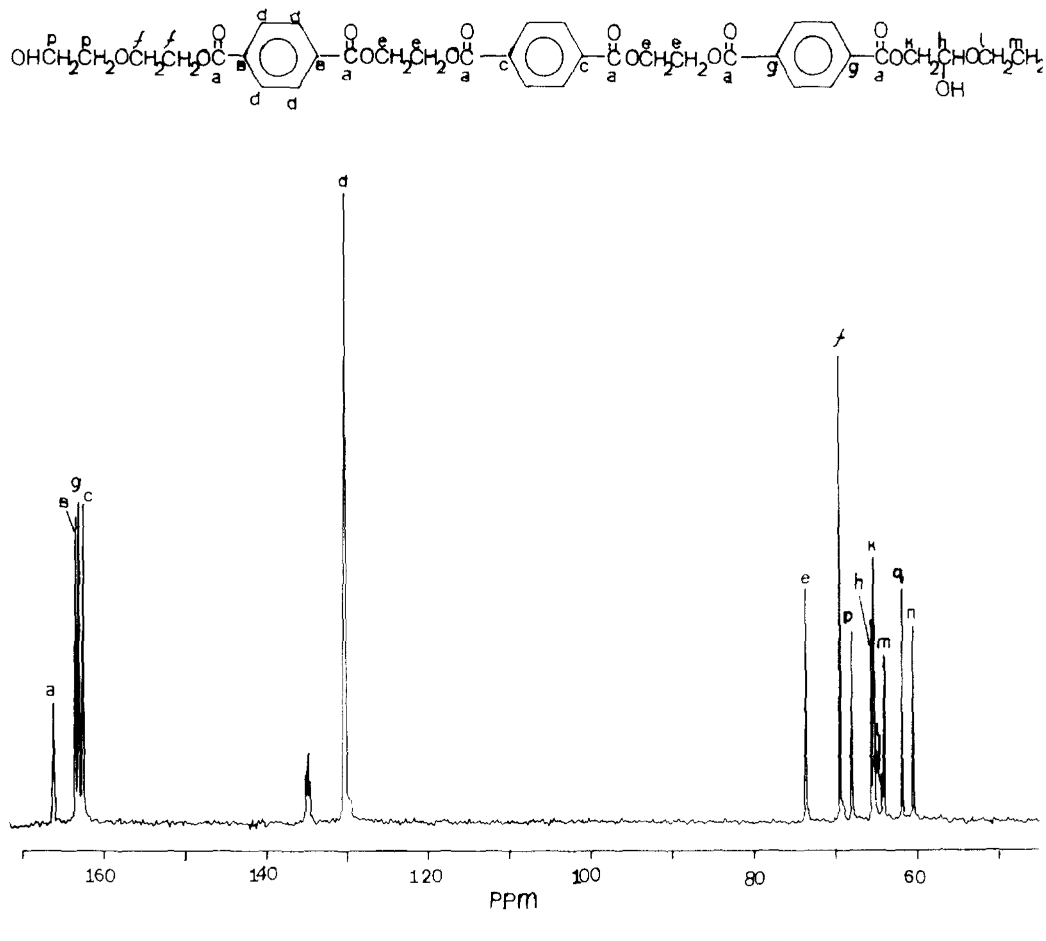


Figure 5 ^{13}C n.m.r. spectrum (250 MHz, solvent DMFA-d_7) of the oligoester obtained by alcoholysis of PET with DEG for 120 min at a mola ratio of 1:160

Table 2 Chemical shifts of the signals in the ^{1}H n.m.r. spectrum of the oligoester formed by alcoholytic destruction of PET with DEG at a molar ratio of 1:160 and reaction time 180 min

Signals	Group[a]	δ(ppm)
a	$\text{-O-CH}_2\text{-}\underset{\text{O}\underline{\text{H}}}{\underset{\mid}{\text{CH}}}\text{-O-}$	5.14
b	$\text{-CH}_2\text{-C}\underline{\text{H}}_2\text{-O-C}\underline{\text{H}}_2\text{-CH}_2\text{-}$	3.5–3.56
c	$\text{-O-CH}_2\text{-CH}_2\text{-O-CH}_2\text{-C}\underline{\text{H}}_2\text{-OH}$ (end DEG)	3.87–3.95
d	$\text{-O-C}\underline{\text{H}}_2\text{-}\underset{\text{OH}}{\underset{\mid}{\text{CH}}}\text{-O-CH}_2\text{-CH}_2\text{-OH}$ (end glycol)	4.05–4.07
e	$\text{-O-C}\underline{\text{H}}_2\text{-C}\underline{\text{H}}_2\text{-O-C}\underline{\text{H}}_2\text{-C}\underline{\text{H}}_2\text{-}$ (bound DEG)	4.41–4.53
f	*p*-substituted Ar in the sequence (DEG–T–DEG)	8.02
g	*p*-substituted Ar in the sequence (DEG–EG–T–DEG)	8.09
h	*p*-substituted Ar in the sequence (DEG–T–EG–T–EG–T–DEG)	8.16–8.18

[a] DEG = $\text{-CH}_2\text{-CH}_2\text{-O-CH}_2\text{-CH}_2$
EG = $\text{-CH}_2\text{-CH}_2$
T = $\text{-O-}\underset{\text{O}}{\underset{\|}{\text{C}}}\text{-Ar-}\underset{\text{O}}{\underset{\|}{\text{C}}}\text{-O}$

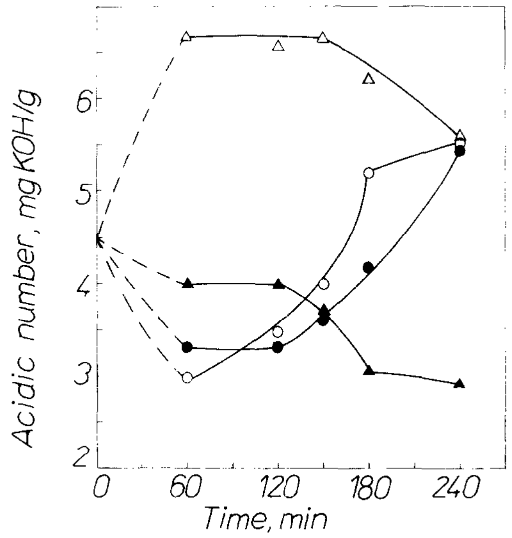


Figure 6 Time dependence of the acid numbers of oligoesters obtained by alcoholytic destruction of PET with DEG at molar ratios of (○) 1:100; (●) 1:120; (△) 1:160; (▲) 1:250

of alcoholytic destruction does not depend on the position of these bonds along the polymer chain[22]. This assumption leads to relatively simple dependences for the rate of alcoholysis and the values of the average degree of polymerization. Since alcoholysis is a first order reaction[6,9,10] with respect to the starting polyester, the following equation is valid for the change of the average degree of polymerization (P_n) with the reaction time at a high extent of destruction[23]:

$$\ln[1-(P_n)^{-1}] = \ln[1-(P_n)_0^{-1}] - k_d[\text{Cat}]\tau \qquad (3)$$

where τ is time. By plotting the time dependence of $\ln[(P-1)/P]$ (*Figure 7*), the values of k_d and $-\ln[1-(P_n)_0^{-1}]$ can be determined. The results are presented in *Table 3*.

During its initial stage (1–60 min), alcoholysis proceeds with a drastic drop of the molecular weight from 22200 in the starting PET to about 600–1000 in the oligoester formed. For this reason, within the reaction time interval studied, the destruction starts by an oligoester of molecular weight that differs from $\bar{M}_n$ of the starting PET ($\bar{M}_n^0$ takes a specific value for each molar ratio studied). It is seen that the rise in the DEG amount results in an increase of the destruction rate. Assuming that destruction at the 1:100 molar ratio proceeds with unit rate, the ratio of the rate constants at molar ratios of 1:120 and 1:250 is 1:1.5:2.4. At the 1:160 molar ratio, destruction starts by an oligomer with higher molecular weight ($\bar{M}_n^0 = 870$) and proceeds at a much higher rate.

Influence of alcoholysis duration on the reaction mechanism

The study of the obtained oligoesters by g.p.c. using a photodiode array detector allows the u.v. spectra of the oligomeric fractions prevailing in the oligoesters to be recorded and their respective molecular weights (M_w) and amounts to be determined[24].

Comparison of the u.v. spectra of the oligomeric fractions having the same retention time shows that the fractions with $M_w = 515$ and 420 have the same spectra; they differ, however, from the spectra of the other oligomeric fractions (*Figure 8*). The shifts of the absorption bands are due to the presence of secondary hydroxy groups[25]. For this reason, Structure *II* can be attributed to the oligomeric fractions with M_w of 515 and 420. On the basis of the amounts of oligomeric fractions determined in the oligoesters obtained, the respective kinetic

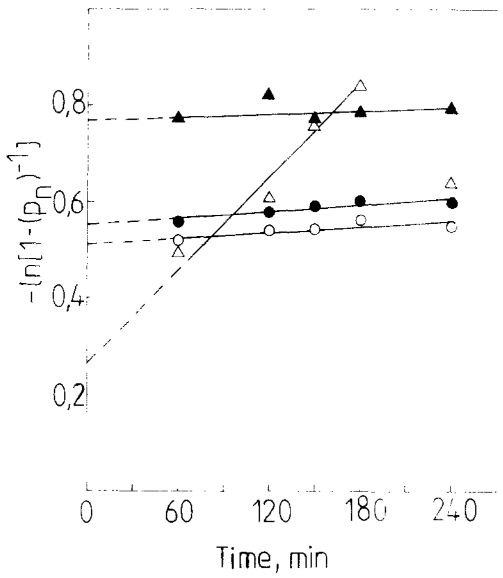


Figure 7 Alcoholytic destruction of PET with DEG at molar ratios of (○) 1:100; (●) 1:120; (△) 1:160; (▲) 1:250

Table 3 Alcoholytic destruction of PET with DEG: kinetic data

PET:DEG molar ratio	$-\ln[1-(P_n)_0^{-1}]$	$\bar{M}_n^0$	$k_d 10^3$ (min^{-1})
1:100	0.52	590	0.19
1:120	0.56	560	0.29
1:160	0.27	870	2.71
1:250	0.77	440	0.46

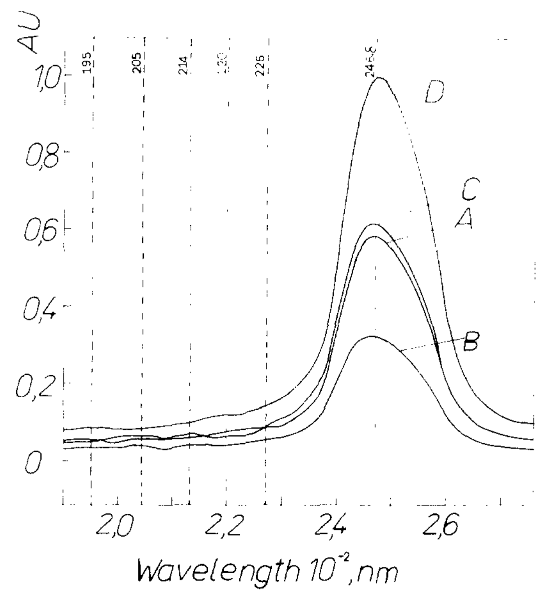


Figure 8 U.v. spectra of the oligomeric fractions (with retention time of 25.3 min and molecular weight of 420) of the oligoesters obtained by alcoholytic destruction for 120 min of PET with DEG at molar ratios of (A) 1:100; (B) 1:120; (C) 1:160; (D) 1:250

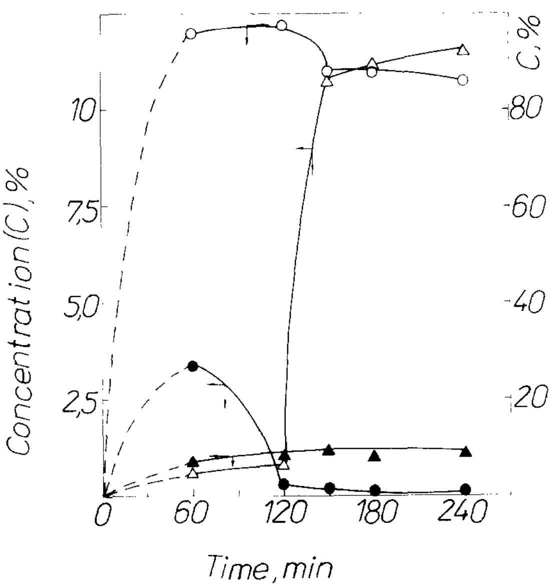


Figure 9 Alcoholytic destruction of the oligomeric fractions of oligoesters obtained by alcoholysis of PET with DEG at a molar ratio of 1:100: (○) $M_w = 1290$; (●) $M_w = 690$; (▲) $M_w = 420$; (△) $M_w = 320$

curves are plotted for the different molar ratios (*Figures 9–12*). The trends of these dependences suggest the following kinetic schemes for the process of alcoholytic destruction:

PET:DEG ratio of 1:100. The trend of kinetic curves (*Figure 9*) suggests that alcoholytic destruction affects mainly the oligomeric fraction with $M_w = 1290$ and the respective reactions can be presented by:

$$\underset{(A)}{\mathrm{PET}_{22200}} \longrightarrow \underset{(B)}{\mathrm{ODEGT}_{1290}} \xrightarrow{k^{I}_{320}} \underset{(C)}{\mathrm{ODEGT}_{320}} \quad (4)$$

where ODEGT is oligo(diethylene glycol terephthalate).

A complex mechanism is assumed, involving consecutive reactions: the basic one is that illustrated by reaction (4). The reactions affecting the oligomeric fraction with $M_w = 690$ are taking place to a much lower extent since the amount of this fraction is about 3 wt%.

By means of the least squares method[20] the values of the rate constant are determined. In the present case (molar ratio of 1:100) the rate constant of reaction (4) takes the value:

$$k^{I}_{320} = 0.54 \times 10^{-3} \pm 0.003 \, (\mathrm{min}^{-1})$$

PET:DEG ratio of 1:120

$$\underset{(A)}{\mathrm{PET}_{22200}} \longrightarrow \underset{(B)}{\mathrm{ODEGT}_{1290}} \xrightarrow{k^{II}_{420}} \underset{(E)}{\mathrm{ODEGT}_{420}} \quad (5)$$

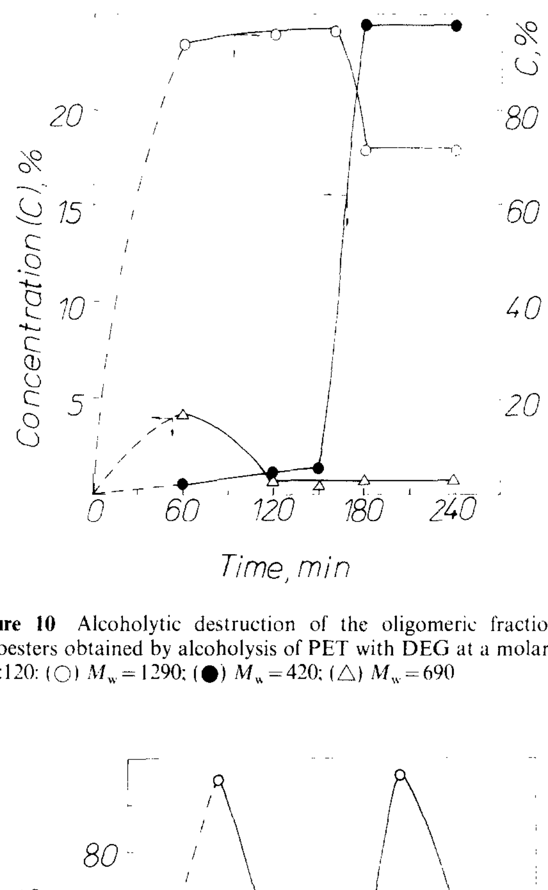


Figure 10 Alcoholytic destruction of the oligomeric fractions of oligoesters obtained by alcoholysis of PET with DEG at a molar ratio of 1:120: (○) $M_w = 1290$; (●) $M_w = 420$; (△) $M_w = 690$

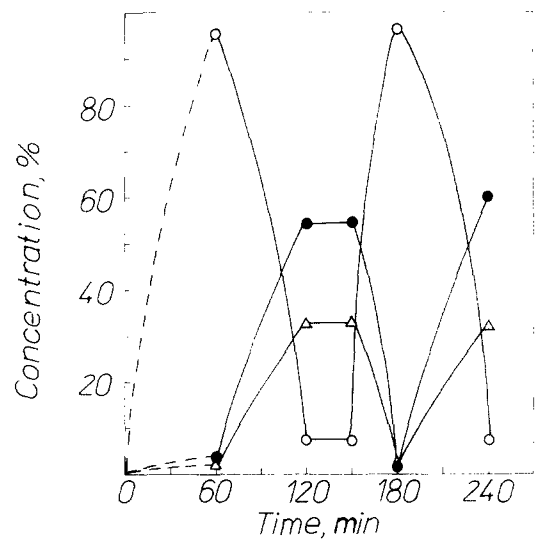


Figure 11 Alcoholytic destruction of the oligomeric fractions of oligoesters obtained by alcoholysis of PET with DEG at a molar ratio 1:160: (○) $M_w = 1290$; (●) $M_w = 815$; (△) $M_w = 420$

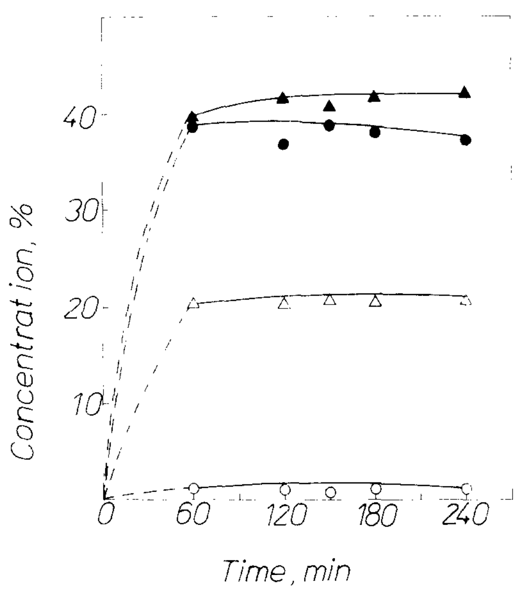


Figure 12 Alcoholytic destruction of the oligomeric fractions of oligoesters obtained by alcoholysis of PET with DEG at a molar ratio 1:250: (○) $M_w = 1290$; (●) $M_w = 690$; (△) $M_w = 515$; (▲) $M_w = 420$

The respective rate constant is:

$$k_{420}^{II} = 1.365 \times 10^{-3} \pm 0.01\,(\mathrm{min}^{-1})$$

This molar ratio is characterized by the occurrence of alcoholytic destruction leading to the formation of an oligoester of higher molecular weight containing secondary –OH groups.

PET:DEG ratio of 1:160

$$\underset{(\mathrm{A})}{\mathrm{PET}_{22200}} \rightarrow \underset{(\mathrm{B})}{\mathrm{ODEGT}_{1290}} \underset{k_2^{III}}{\overset{k_1^{III}}{\rightleftarrows}} \underset{(\mathrm{E})}{\mathrm{ODEGT}_{420}} + \underset{(\mathrm{G})}{\mathrm{ODEGT}_{815}} \qquad (6)$$

At this molar ratio alcoholysis proceeds as an inverse reaction. The direct reaction leading to the formation of oligomers with $M_w = 815$ and 420 is a first order one while the inverse reaction is of the second order. In the case of PET:DEG molar ratio of 1:160, alcoholysis proceeds as an inverse and equilibrium reaction. By means of the basic kinetic equation describing the inverse and equilibrium reaction[22,26], the following values are obtained for the respective rate constants:

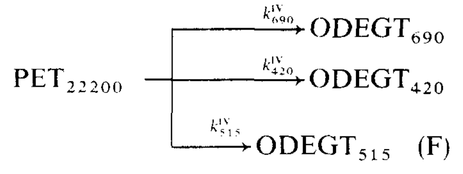
$$k_1^{III} = 5.24 \times 10^{-3}\,(\mathrm{min}^{-1});$$

$$k_2^{III} = 5.09 \times 10^{-3}\,(\mathrm{wt\%}^{-1}\,\mathrm{min}^{-1})$$

$$K = 0.97$$

where K is the equilibrium constant.

PET:DEG ratio of 1:250



$$\mathrm{PET}_{22200} \left\{ \begin{array}{l} \xrightarrow{k_{690}^{IV}} \mathrm{ODEGT}_{690} \quad (\mathrm{B}) \\ \xrightarrow{k_{420}^{IV}} \mathrm{ODEGT}_{420} \quad (\mathrm{E}) \\ \xrightarrow{k_{515}^{IV}} \mathrm{ODEGT}_{515} \quad (\mathrm{F}) \end{array} \right. \qquad (7)$$

Alcoholysis proceeds by concurrent reactins; their respective rate constants are as follows:

$$k_{690}^{IV} = 1.2 \times 10^{-4} \pm 0.006\,(\mathrm{min}^{-1})$$

$$k_{515}^{IV} = 0.72 \times 10^{-4} \pm 0.003\,(\mathrm{min}^{-1})$$

$$k_{420}^{IV} = 1.98 \times 10^{-4} \pm 0.003\,(\mathrm{min}^{-1})$$

The kinetic data on the mechanism of alcoholytic destruction at different ET:DEG molar ratios suggest that the highest molecular weight fraction ($M_w = 1290$) is most affected. At molar ratios of 1:100 and 1:120, alcoholysis results in the formation of oligoesters with $M_w = 320$ and 420, the amount of the higher molecular weight fraction remaining relatively large. At the molar ratio of 1:160 oligomeric products with $M_w = 815$ and 420 are obtained, while at 1:250 three oligomeric fractions are formed with $M_w = 690$, 515 and 420, respectively.

Comparison of the values of the rate constants determined according to the respective kinetic schemes leading to the formation of oligomers with $M_w = 515$ and 420 (containing secondary –OH groups) (*Table 4*) suggests that:

(a) The rise of the DEG amount results in a higher rate of alcoholytic destruction leading to the formation of oligomers containing units with Structure *II*.

(b) At a large excess of DEG (1:250) the rate of alcoholysis resulting in the formation of oligomers with Structure *II* is lower in the reaction time interval studied; this fact can be explained by the formation of these oligomers in substantial amounts during the initial stage (up to 60 min) under these conditions.

The proposed kinetic schemes show that the increased amount of the glycol component renders the mechanism of alcoholysis more complex; the latter proceeds from consecutive reactions through equilibrium and inverse reaction to concurrent ones.

CONCLUSION

The alcoholytic destruction of PET with DEG is a complex process, its path being influenced by the molar ratio of the components. At PET:DEG molar ratios of 1:100 and 1:120, i.e. at 1 mole of DEG corresponding to one monomeric unit of the starting PET (unit probability of destruction), alcoholysis proceeds by consecutive reactions of the first order resulting in the formation of linear oligoester diols with end hydroxy groups and $M_n = 500$–650.

By the addition of DEG in a large excess (1:160 and 1:250), alcoholysis takes place by the complex path of reversible and concurrent reactions. The DEG excess causes an alcoholysis mechanism leading to the formation of oligoesters with secondary –OH groups in their chains; oligoester triols with $\bar{M}_n = 420$–550 are obtained.

Table 4 Alcoholysis of an oligoester fraction with $M_w = 1290$ to oligoesters with $M_w = 515$ and 420 containing secondary –OH groups: kinetic data

PET:DEG molar ratio	$k_{515}\,10^{-4}$ (min^{-1})	$k_{420}\,10^{-3}$ (min^{-1})
1:120	–	1.36
1:160	–	5.24
1:250	0.72	0.20

Since linear oligoester diols are preferred for the synthesis of polyurethanes, the products obtained by alcoholytic destruction of PET with DEG at molar ratios of 1:100 and 1:120 are most suitable to this purpose.

Our study of the process of alcoholytic destruction of PET with DEG results in the establishment of optimal conditions for obtaining oligoester diols serving as raw materials in the synthesis of water-borne PU. Additional information on the mechanism of alcoholytic destruction of PET is also obtained.

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