

The Kinetics of the Ester-interchange Reaction of Poly(ethylene terephthalate)

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Summary

The ester-interchange reaction behaviour of poly(ethylene terephthalate) (PET) was investigated in a new model reaction where the transfer of di(oxyethylene)oxy units from an oligoester to the PET chain is monitored in the temperature range from 200 to 300 °C. In the solid state the reaction rate becomes remarkably high above 225 °C. From the kinetics of the transfer reaction in the melt it is concluded that the reaction is catalyzed by the free carboxylic end groups of the PET.

Introduction

Poly(ethylene terephthalate) (PET) undergoes ester-interchange reactions at elevated temperatures in the solid state and in the melt. As was shown in an extended study by REIMSCHUESSEL (1980) for low molecular weight model compounds, these reactions even occur without transesterification catalysts being present. The free carboxylic end groups which are always contained in PET as a consequence of side reactions during the condensation process act as a catalyst for the ester-interchange reaction.

The kinetics of the ester-interchange reaction is not only of great commercial interest but is also very important for the stability of mixtures of normal PET with perdeuterated samples, which are used in neutron scattering experiments.

We have developed a new model reaction to probe the ester-interchange behaviour of PET. PET films containing 30 wt-% of an oligoester of the structure Bz-T-E-T-DE-T-E-T-Bz (1) were annealed at temperatures between 200 and 300 °C. Here, Bz, T, E, and DE denote the benzyloxy, the terephthaloyl, the oxyethyleneoxy, and the di(oxyethylene)oxy group, respectively. The kinetics of the transfer of DE units from the oligoester to the polymer chain was determined. To avoid the influence of transesterification catalysts which are contained in PET from the melt condensation process, we employed pure, catalyst free PET from a solid state condensation process (DRÖSCHER and WEGNER 1978) for the investigation in the melt.

Experimental PartSynthesis of the oligoester 1:

22,0 g (0,06 mol) of Bz-T-Cl as synthesized according to ZAHN and SEIDEL (1959) were dissolved in 25 ml of dry 1,4-dioxane. 4,2 g (0,04 mol) of diethylene glycol in 5 ml of pyridine were added dropwise under cooling. The mixture was stirred over night and precipitated in water. The aqueous layer was extracted with diethyl ether. The ether layer was dried and the ether evaporated. After recrystallizing the residue from methanol, 17,5 g (75%) of Bz-T-DE-T-Bz (2) were obtained; m.p. 92°C. 17,4 g (0,03 mol) of 2 were dissolved in a mixture of 175 ml of trifluoroacetic acid (TFA) and 17,5 ml of HBr/acetic acid (40 wt-%) and stirred for 90 min. Subsequently, the solution was poured into an excess of water and stirred over night. The precipitate was dissolved in dioxane and again precipitated in water to yield 12,0 g (99%) of HO-T-DE-T-OH (3); m.p. 214°C. 9,1 g (0,023 mol) of 3 were dissolved in 90 ml of SOCl₂ which contained 3 drops of dimethyl formamide. The solution was refluxed for 1 h. Subsequently, the SOCl₂ was evaporated in vacuo. Then, 50 ml of toluene were added and again evaporated in vacuo to yield 10,1 g (98%) of Cl-T-DE-T-Cl which were directly dissolved in 100 ml of dry dioxane. 15,9 g (0,27 mol) of ethylene glycol mixed with 6 ml of pyridine were added dropwise to the solution under cooling and stirring. The reaction mixture was stirred over night, the solvent evaporated and the residue recrystallized from 300 ml of methanol to yield 6,3 g (56%) of H-E-T-DE-T-E-H (4); m.p. 97°C. Finally, 6 g (0,12 mol) of 4 were dissolved in 40 ml of dry sym-tetrachloroethane (TCE) and 10 ml of pyridine. 8,3 g (0,031 mol) of Bz-T-Cl were added dropwise under cooling. The reaction mixture was precipitated in methanol. After recrystallization from toluene 4,8 g (41%) of 1 were obtained; m.p. 139°C.

C₅₄H₄₆O₁₇ (967,0); calc. C 67,10, H 4,80; found C 66,91, H 4,87

Preparation and characterization of the PET film:

The PET sample (M_n ≈ 22000) was prepared in a solid state condensation process as described elsewhere (DRÖSCHER and WEGNER 1978, DRÖSCHER 1980). For the investigations carried out below the melting temperature of the film, commercial PET (BASF AG, M_n ≈ 24000) was employed. This sample contained about 4 mol-% of DE units and an unknown amount of ester-interchange catalysts. Films of PET and 1 were cast from TFA solution (about 5 wt-%) by evaporating the solvent. The films were stored in vacuo for at least three days. The melting properties were determined by DSC (DSC-2, Perkin-Elmer Corp.) in unsealed aluminium pans under a dry nitrogen atmosphere.

Ester-interchange reaction:

About 200 mg of the film in a porcelain boat were placed into a glass tube which was evacuated and refilled with dry nitrogen three times. Then, the evacuated tube was quickly heated to the reaction temperature which was maintained with an accuracy of ±0,5 K. Finally, the sample was quenched in air and stirred in chloroform for 1 h to dissolve the low molecular weight material. The polymer was filtered off and dried carefully. It was then dissolved in TFA to determine the concentration of the DE units by ¹H-NMR.

Model Reaction

Unlike commercial PET samples, PET prepared in our catalyst free solid state condensation process (DRÖSCHER and WEGNER 1978) can be stored in vacuo at 300°C for 24 hours without the formation of DE being observed. Hence, an ester-interchange reaction between the DE containing oligoester and the DE free polyester can be easily monitored by the determination of the amount of DE units transferred from the oligoester to the polyester chain. A suitable oligoester for this reaction is the compound 1 which is soluble in chloroform. Fig. 1 shows a DSC curve for a PET film containing 30 wt-% of 1 as cast from TFA solution. The melting temperature of the film is found to be 520 K, 10 K lower than for melt crystallized pure PET. It should be noted as well that no melting peak of the oligomer is observed, thus implying, the oligoester is fully dissolved in the PET matrix.

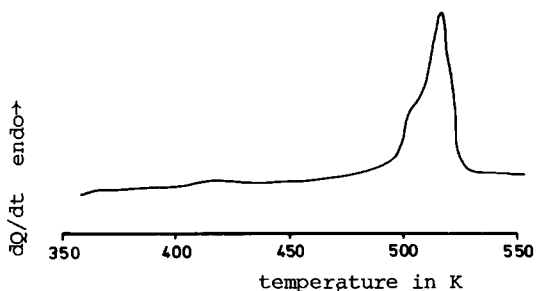


Fig. 1 DSC trace for a solution cast PET film containing 30 wt-% of Bz-T-E-T-DE-T-E-T-Bz (1). Sample weight 4 mg, heating rate 40 K/min

Upon heating of this film to temperatures above 200°C ester-interchange reactions occur as pointed out in the Scheme below.



Scheme 1 Example of the ester-interchange reaction between PET and the oligoester 1

In Scheme 1 we have not considered back reactions to occur. Because, only those back reactions which involve a chain end of the polyester would yield soluble material. At a degree of polymerization of about 115 the probability for reactions near the chain end is low enough to be neglected. Reactions of the oligoester alone do not yield insoluble products. After annealing the pure oligoester at 275°C for several hours, the sample was still fully soluble in chloroform.

Ester-interchange Reactions in the Solid Film

To determine the rate of ester-interchange reactions in the solid state, films of commercial PET and the oligoester 1 were annealed at 200 and 225°C. Tab. 1 lists the annealing times and the amount

of DE units transferred.

TABLE 1

Ester-interchange reaction in a PET film containing 30 wt-% of Bz-T-E-T-DE-T-E-T-Bz

temperature °C	reaction time min	yield %
200	10	<3
	120	<3
	3780	12
225	33	<3
	180	3
	850	25

Only 12% of the DE units were transferred after annealing for 3780 min at 200°C, and only 25% were transferred after 850 min at 225°C. Thus, it is possible to anneal PET mixtures at temperatures below 200°C for short times without ester-interchange occurring.

Kinetics of the Ester-interchange Reaction in the Melt

The investigations of the ester-interchange reactions in the melt were carried out at 250, 275 and 300°C. As shown in Tab. 2, it took only 5 min at 300°C to transfer 49% of the DE units from the oligoester to the polymer chain.

TABLE 2

Ester-interchange reaction in the melt

temperature °C	reaction time min	yield %
250	7	4
	19	52
	36	65
	66	78
	122	88
	180	90
	360	92
	982	97
275	5	29
	13	53
	16	59
	33	87
	82	92
	175	94
300	5	49
	12	68
	30	91
	70	95

The kinetic data for the reaction in the melt may be analyzed by the generalized Equ. 1 which describes the rate of the DE unit transfer as a function of the concentrations Q and P. Q is the part of the sample which is soluble in chloroform, P the insoluble part.

$$\frac{d(x_{DE})}{dt} = k \cdot P^m \cdot Q^n - k' \cdot P^r \cdot Q^s \quad (1)$$

The mole fraction of DE units in P is denoted by x_{DE} , and k , k' , m , n , r , s are constants.

As already discussed above, we may neglect the back reaction. Thus, the second term in Equ. 1 will vanish. Furthermore, we can assume that P varies only slightly in the course of the reaction and can be considered a constant. Thus, Equ. 1 becomes

$$\frac{d(x_{DE})}{dt} \approx k'' \cdot Q^n = k'' \cdot \{(x_{DE})_{\infty} - x_{DE}\}^n \quad (2)$$

where $(x_{DE})_{\infty}$ gives the maximum conversion.

From a kinetical analysis it was found that the data fit a second order plot as shown in Fig. 2. With $n = 2$ it follows from Equ. 2 that

$$x_{DE} / \{((x_{DE})_{\infty} - x_{DE}) \cdot (x_{DE})_{\infty}\} = k'' \cdot t \quad (3)$$

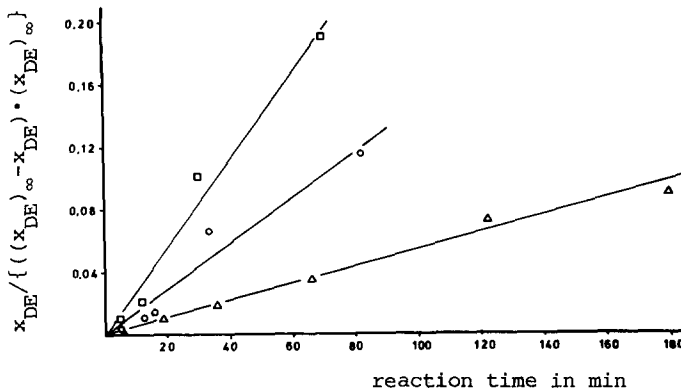


Fig. 2 Kinetics of the ester-interchange reaction in the melt for a PET film containing 30 wt-% of 1: Second order plot according to Equ. 3. Parameter temperature: (Δ) 250°C, (○) 275°C, (□) 300°C

From the temperature dependence of the reaction rate constant k'' an Arrhenius activation energy of 85 kJ/mol was determined. This value is in good agreement with REIMSCHUESSEL's (1980) findings who obtained 91 kJ/mol for the activation energy of the glycolysis reaction of ethylene glycol benzoate in the case of catalysis by

carboxylic acids. For the uncatalyzed reaction he reported an activation energy of 200 kJ/mol.

Conclusion

PET samples undergo ester-interchange reactions at temperatures above 200°C. In the solid state the rate of reaction becomes relatively high only at temperatures above 225°C. As judged from the activation energy observed in the melt, the ester-interchange reaction is catalyzed by free carboxylic end groups of the polyester.

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