# **Equilibria in the Alcoholysis Reactions of Terephthalic Esters and Chemical Valorization of Polyethyleneterephthalate Waste. I. Equilibrium Constants Determination**

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**ABSTRACT:** The depolymerization of polyethyleneterephthalate (PET) by alcoholysis is an easy operation and gives interesting prospects for the valorization of wastes. The reactive species being composed of esters and alcohols, all possible alcoholysis reactions happen, whether wanted or not. Finally, a complex blend of many molecules follows.

Practically, two great types of reactions occur: a reaction called "interchange," and a reaction called "polycondensation." We have determined the values of global equilibrium constants of those two types of reaction. The values of polycondensation equilibrium constants are close to those estimated from the "equireactivity" principle. We did not observe any particular behavior of monomer species. When reactants are the di- or mono-propylene glycols, the molar proportion of these glycolic radicals is higher in the free glycols than in the polyester chains. Both proportions are similar, when diethylene glycol or 2-ethylhexanol are used. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 329–340, 1999

**Key words:** alcoholysis reactions; equilibrium constants; terephthalic esters; waste valorization; polyethyleneterephthalate waste

# **INTRODUCTION**

Because of the new regulations setting up itself gradually at the national, European, and world level, the valorization of the polymer wastes becomes a priority. Chemical valorization has advantages on physical regeneration (tolerance of the impurities and existence of copolymers, diversification of the outlets) and on energy valorization (economy of the raw materials, safeguard of the ecological and commercial value of the matter).

The PET is an important source of wastes, $<sup>1</sup>$ </sup> whose collection is now well organized for the bottles and X-ray films. This waste is a natural source of terephthalic groups, for which Europe shows a deficit. Thus, waste PET is potentially a raw material very attractive, giving access to new intermediate compositions in the field of materials.

PET is a polyester. The functions ester can be cleaved by reagents, such as water (hydrolysis), alcohols (alcoholysis), amines (aminolysis), acids (acidolysis), etc. According to reagents used for the waste processing PET (in fact, it is a destruction of the macromolecule), various products are obtained.1 Indeed, either the process makes it possible to return to the monomeric reagents of the PET synthesis, or it allows the synthesis of

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intermediate chemical species of the basic chemicals (processes based mainly on alcoholysis). For the second process (that we are studying here), the principal known products are the polyols<sup>2</sup> (intermediate of the synthesis of polyurethanes), the unsaturatedpolyesters,<sup>2</sup>andthedialkylterephthalates (plasticizer).3

The polyols and the unsaturated polyesters, obtained from PET, are generally prepared in two stages: a glycolysis [use of a mixture of diols introduced in excess; idealized reaction: eq. (1)] followed by an esterification with elimination of formed water [use of a mixture of acids introduces at fault—eq. (2)]. The glycols usually used are the monopropylene glycol (MPG), the diethylene glycol (DEG), and the dipropylene glycol (DPG). For unsaturated polyesters, the maleic acid (AM) is used. For polyols, the adipic acid (AA) and phthalic anhydride (AP) are used.

$$
\begin{aligned} \mathrm{PET} + 2 \; \mathrm{HOZOH} &\rightarrow \\ \mathrm{glycol} &\rightarrow \\ \mathrm{HOZO_{2}C} \text{---} \mathrm{C_{6}H_{4}} \text{---} \mathrm{CO_{2}ZOH} \\ &+ \mathrm{HOCH_{2}CH_{2}OH} \\ \mathrm{MEG} \qquad \qquad (1) \end{aligned}
$$

glycolysis product + dicarboxylic acid  $\rightarrow$ 

polyester(diol) + H<sub>2</sub>O  $\mathcal{A}$  (2)

For the synthesis of the dialkylterephthalates, the PET alcoholysis is carried out with a monoalcohol [introduced in slight excess—eq. (3)].



To summarize, the products of reaction are an ester and an alcohol. There is no reason for these two products not to react further by other alcoholytic reactions. We will separate them in two classes: $4$  "interchange" reactions [eq. (4)] and "polycondensation" reactions [eq. (5)].

$$
-C-OZ1OH + HOZ2OH \n\begin{array}{c}\n-C-OZ2OH + HOZ1OH & (4) \\
0 & -C-OZ2OH + HOZ1OH & (4) \\
0 & 0 \\
-C-OZ1OH + HOZ2O - C \n\end{array}
$$

Taking into account various equilibria, the glycolysis/esterification leads to a complex mixture of molecules, $4$  differing on the one hand in polymerization degree, and on the other hand in radicals distribution. For example, with three glycolic radicals and three diacidic radicals, there are 18 different monomer species, 60 different dimer species, etc. Similar equilibrated reactions are well known in the polyesters from DMT synthesis processes.5,6 They are rather omitted in depolymerization processes, although recently a detailed kinetic study in the glycolysis of PET by bisphenol A was published<sup>7</sup> showing a complex scheme with multiple alcoholysis reactions. However, although several kinetic studies and reviews<sup>8</sup> are from time to time published, little is known on the final composition of such systems at thermodynamic equilibrium.

We will report, in the present part I of the relative to alcoholysis reactions articles our investigations on the different equilibria occurring in typical PET depolymerizations of industrial interest. The next article<sup>9</sup>—part II—will describe some applications and processes adaptations, to respect the specifications desired for the final products.

## **EXPERIMENTAL**

The same PET source (scraps of not contaminated bottles preforms made with the "B95A Laser" PET resin of ICI) was used for all the experiments described in this article. Chemical grade DPG (mixture of isomers) was purchased from Merck. All the other reactants were pure (laboratory grade) products purchased from market.



**Figure 1** SEC chromatogram of oligomer of BHEET: Polyol = HODe-(TDe)<sub>n</sub>-OH— Individual degree of polymerization in superscript.

All polyols were prepared according to the previously described procedure:4 glycolysis with an excess of glycol(s) (DEG + DPG + MEG), and then esterification with a defect of diacids (AA 1 AP). The reactions were conducted under a nitrogen blanket, at 200–240°C, and with the catalyst tetrabutylorthotitanate (TBT—0.5 g per 100 g PET). Unsatured polyesters were prepared by the same procedure, except that the reactants were MPG and maleic anhydrid. Dioctylterephthalate was prepared from 2-ethylhexanol in slight excess, followed by vacuum distillation of the alcohols.

The final reaction products where characterized, as previously described: $4$  (a) hydroxyl and acid number by chemical titration; (b) free glycols analysis by gas chromatography; (c) polyester molecular distribution by SEC chromatography, with tetrahydrofuran elution at 0.5 mL/min and 254 nm absorbance detection. Merck Lichrogel PS4 (5  $\mu$ m) and Knauer SDV 100 ( (5  $\mu$ m) columns were utilized, the latter being more selective.

#### **SEC Chromatograms**

The attribution of peaks to pure polyalkyleneterephthalate oligomers was very easy. Figure 1 shows the chromatogram of oligomers of BHEET, bis-hydroxyethoxyethylterephthalate (obtained from  $DMT+DEG$ , from which we could detect the monomer, dimer, trimer, etc., peaks [see eq.  $(6)$ .

From the chromatograms of BHEET and BHET oligomers, we were able to draw the calibration curve, given by  $log(M)$  in function of re-

tention volume. This curve is a straight line (see Fig. 2).

No significant elution volume modifications were observed in chromatograms of similar polyols, also containing adipic and phthalic radicals.

However, the elution volumes of the different oligomers from polyols, obtained with DPG as the only glycolic radical (see Table II), do not agree with the above calibration curve. The molecular weight of Dp must be taken as 145, instead of 100, to fit the above calibration curve.

Figure 3 shows the chromatograms of four polyols obtained from PET at constant values of x and y (see Scheme 1 and Table I), but with variable DEG/DPG ratios. For the monomeric and dimeric species, assignments were made with the help of the calibration curve and with the probable proportions of individual species calculated as described in Table I. We could conclude that the partition of the chromatograms into monomers, dimers, trimers, etc., zones is relatively sure when the Dp mol fraction is low, but very unsafe in the others cases.

## **MATHEMATICAL TREATMENT**

A list of abbreviations and particular notations is given at the end of the text.

With these symbolisms the formula of PET becomes (TMe)*n*.

## **Mol Ratio**

x mol glycols added per mol PET;  $x = x_2 + x_3$  $+$  (x<sub>1</sub> - 1)



**Figure 2** SEC calibration curve:  $\Box$  oligomers of BHET; HOMe-(TMe)<sub>n</sub>-OH;  $\bullet$  oligomers of BHEET; HODe-(TDe)<sub>n</sub>-OH; + oligomers of BHPPT; HODp-(YDp)<sub>n</sub>-OH; Y  $= T/AP = 5/2/2.$ 

- $x_1$  mol ethanediyl/mol terephthalic (Me/T)<br> $x_2$  mol ethoxyethanediyl/mol terephthalic
- $x_2$  mol ethoxyethanediyl/mol  $(De/T)$
- x3 mol propoxypropanediyl/mol terephthalic  $(Dp/T)$
- y mol diacids added per moles PET;  $y = y_1 +$  $y_2$
- y1 mol *o*-phthalic/mol terephthalic (P/T)
- $y_2$  mol adipic/mol terephthalic (A/T)
- *n* polymerization degree  $(\geq 0)$

 $\mathrm{RM} \ \mathrm{molar} \ \mathrm{ratio}, \ \mathrm{RM} = \frac{\mathrm{moles}Z}{\mathrm{moles}Y}$ 

$$
=\frac{(x+1)}{(y+1)}=\frac{(\bar{n}+1)}{\bar{n}}
$$

## **Chemical Equations Writing**

The reaction of PET with a mixture of MEG, DEG, and DPG, phthalic and adipic acids may be written as:

1/n (TMe)<sub>n</sub> + (x<sub>1</sub> - 1)HOMeOH + x<sub>2</sub> HODeOH  
+ x<sub>3</sub> HODpOH + y<sub>1</sub> HPH + y<sub>2</sub> HAH  
+10Z+(YZ)<sub>n</sub>OH + 2y H<sub>2</sub>O<sup>3</sup> (6)  
+10Z+(YZ)<sub>n</sub>OH = 
$$
\begin{vmatrix} HOZOH & \text{free glycols} \\ + \\ HOZ + YZ + _{n'}OH & n' = 1, 2, 3, ... \\ + \\ HOZ + YZ + _{n'}OH & n' = 1, 2, 3, ... \end{vmatrix}
$$

In the case of unsaturated polyols, the writing is the same, apart that it appears Mp and U radicals.

In the case of dioctylterephthalate preparation, the reaction may be written as:

 $1/n$  (TMe)<sub>n</sub> + x EhOH  $\rightarrow$  Ester + free glycols

free glycols  $=$  EhOH  $+$  MEG

Ester = 
$$
R(TMe)TR
$$
  $R = \begin{vmatrix} Eh \\ MEOH \end{vmatrix}$ 

\nNote:  $n' = 0$   $R = Eh$   $: DOTP$ 

\n $n' = 0$   $R = MeOH$   $: BHET$ 

# **Balances and Determination of the Polyester Fraction Composition**

With the following hypothesizes, the polyester fraction composition may be indirectly determined from some experimental data and from balances (initial reactants composition)/(free glycols analysis). The general calculation procedure is summarized in Scheme 1. Hypothesis:

(a) negligible molar amounts of the terminal functional groups in initial PET. (b) No side reactions (etherification, thermolyse, etc.) affecting the concentration of terminal functional groups. Each oligomer contains two



**Figure 3** SEC chromatograms of polyols synthesized with variable DEG/DPG ratio in glycol reactants. Polyols:  $1$  PET + 2.24 glycols (DEG/DPG) + 0.8 diacids (AA/AP = 1/1). Monomers (two glycolic radicals):  $M1 = Me$ ,  $Me$ ;  $M2 = Me$ ,  $De$ ;  $M3 = De$ ,  $De$ ;  $M4 = Me$ ,  $Dp'$ ,  $M5 = De$ ,  $Dp$ ;  $M6 = Dp$ ,  $Dp$ . Dimers (three glycolic radicals):  $D1 = Dp$  poor;  $D2$  $=$  Dp rich; D3  $=$  Dp, Dp, Dp. Trimers (four glycolic radicals): T1  $=$  Dp poor. Note: probable proportions of individual species are given in Table I.



**Figure 3** (*Continued from the previous page*)

OH terminal groups. (c) The glycolic and acidic radicals are statistically distributed inside the different polyester oligomers. (d) In the SEC chromatogram, the UV signal is assumed to be proportional to the total molar concentration of acidic radicals Y. Balances: (a)  $Polyol = (initial reactants charge)$  $-(\text{distributed } H_2O); \text{ polyol} = \text{free}$  glycols + polyesters.

The whole polyol composition was known by the initial reactants charge, whereas the free glycols composition was obtained experimentally.



\*Note: if starting from DMT, the calculations are analogous except  $MW = 194g$  for DMT and 64g CH<sub>2</sub>OH cyacuated in the distillate

Thus, the polyesters composition was determined according the Scheme 1.

Remark: the above treatment shows more equations than unknowns. Thus, the fact that different modes of calculation leads to the same values, ascertains the validity of analytical values. Examples are given in Table II.

## **RESULTS AND DISCUSSION**

# **Polycondensation Equilibrium Constants Determination**

Following eq. (5), there are as many equilibria as pairs of species. The terminal OH of polyester, the esters, and the free glycols are reacting. According to our terminology, the reaction may be written:

$$
-YZOH + HOZY - \rightleftharpoons -YZY - + HOZOH \quad (7)
$$

$$
K_p = \frac{2[\text{HOZOH}][\text{Internal.ester}]}{[Z_t \text{OH}]^2} \tag{8}
$$

where  $K_p$  is a average equilibrium constant; HOZOH is the free glycol (coefficient 2, because free glycol is difunctional); ZtOH is the OH terminal function of polyester chainl; Internal ester is all esters, except the two terminal ones; and [ ] is the concentration—any unit, because *K* is dimensionless.

The polyol of global formula  $HOZ(YZ)_nOH$ , is a mixture of free glycols HOZOH, and polyester

	Whole Polyester <sup>a</sup>			Monomers						
Probability	Me a	De b	Dp $\mathbf{c}$	$(Me)_2$ $a^2$	Me-De 2ab	$(De)_2$ $h^2$		$Me-Dp$ 2ac	$De-Dp$ 2bc	$\mathrm{(Dp)}_2$ $c^2$
$0\%$ DPG 18% DPG 50% DPG	0.31 0.32 0.33	0.69 0.58 0.36	$\theta$ 0.11 0.31	0.09 0.10 0.11	0.43 0.37 0.24	0.48 0.33 0.13	$\theta$	0.07 0.20	$\mathbf{0}$ 0.12 0.22	$\mathbf{0}$ 0.01 0.09
100% DPG	0.35	$\mathbf{0}$	0.65	0.12	$\mathbf{0}$	$\mathbf{0}$		0.46	$\mathbf{0}$	0.42
	Dimers									
Probability	$(Me)_3$ $a^3$	$(Me)2$ De $3a^2b$	$Me(De)_{2}$ 3ab <sup>2</sup>	$(Me)_{2}Dp$ $3ac^2$	$(De)_3$ $b^3$	$Me-De-Dp$ 6abc	$(De)_{2}Dp$ $3b^2c$	$Me(Dp)_{2}$ $3ac^2$	$De(Dp)_{2}$ $3bc^2$	$(Dp)_3$ $c^3$
$0\%$ DPG 18% DPG 50% DPG 100% DPG	0.03 0.03 0.04 0.04	0.20 0.17 0.12 $\overline{0}$	0.44 0.31 0.13 $\mathbf{0}$	$\theta$ 0.03 0.10 0.24	0.33 0.19 0.04 $\mathbf{0}$	$\theta$ 0.12 0.22 0	$\Omega$ 0.11 0.12 0	$\Omega$ 0.01 0.10 0.44	$\theta$ 0.02 0.10 0	$\Omega$ 0.001 0.03 0.27

**Table I Polyols Synthesized with Variable DEG/DPG Ratios: Statistically Probable Molar Fractions of the Individual Species in the Global Monomers and Dimers**

Polyols: 1 PET + 2.24 glycols (DEG/DPG) + 0.8 diacids (AP/AA = 1/1).<br><sup>a</sup> a, b, c = molar fraction of Me, De, Dp glycolic radicals, deducted from the balance between hole polyol and free glycols (see Scheme 1).

Calculations principle: hypothesis, that the molar fractions of the glycolic radicals are the same into all fractions of different polymerization degree, and purely statistical distribution of the radicals.

 $HOZ(YZ)n \cdot OH$ , containing  $[2(n'-2)+2]$  internal esters for 2 terminal OH.

From equation 8: 
$$
K_p = \frac{2[\text{HOZOH}](n'-1)}{[Z_t \text{OH}]}
$$
 (9)

According to Scheme 1, [HOZOH] is directly accessible by analysis;  $n'$  is the average polymerization degree of polyester fraction, and  $[Z_tOH]$  are accessible by SEC, and from the balance (molar and mass) between the whole polyol and the free glycols.

Experimentally, the equilibrium was considered reached when the analytical results stayed at constant values. At these temperatures and with TBT catalysis, we know<sup>4</sup> that the reactions are rapid.

The equilibrium between the global monomers  $(n = 1)$  and the global dimers  $(n = 2)$  is a particular glycolysis reaction. This equilibrium is easier to work with these low molecular weight polyols.10 It corresponds to the reaction:

Monomer + Monomer 
$$
\rightleftharpoons
$$
 Dimer + Glycol (10)

\nM

\nn<sub>1</sub>

\nn<sub>2</sub>

$$
K_{\rm MD} = \frac{[{\rm D}][{\rm HOZOH}]}{[{\rm M}]^2} \tag{11}
$$

where [M], [D], and [HOZOH] were obtained by direct analysis.

If all the hydroxyl functions and all the esters groups have the same reactivity (equireactivity hypothesis), the two equilibrium constants should be equal to 1.

#### **Polyols with Only One Glycolic Radical**

We have prepared a polyol by transesterification of pure DMT and pure DEG, at  $RM = 2$ , distilling off methanol. From the free glycol analysis and the SEC chromatogram shown in Figure 1, we obtained the following equilibrium values:

$$
K_{\rm MD}=0.98 \qquad K_p=1.12
$$

Furthermore, we were able to examine the reactions between an *i*-mer and the monomer:

$$
\frac{i\text{-mer}}{n_i} + \frac{\text{Monomer}}{n_1} \rightleftharpoons \frac{i+1\text{-mer}}{n_{i+1}} + \frac{\text{Glycol}}{n_0} \quad (12)
$$



0.463/ 257

0.389/ 208

0.290/ 153

0.220/ 115 0.359/ 332

0.472/ 457

0.609/ 670

0.603/ 781

**Table II Composition of Polyols (1000g theoretic) and Inferred Equilibrium Constants**

92 Polyols:  $1$  PET + x glycols (DEG/DPG = 4.6 mol/mol) + 0.8 diacids (AP/AA = 1/1 mol/mol).

260

220

110

[OH] is defined in eq and weight (w) in g, <sup>a</sup>from composition, <sup>b</sup>from  $I_{OH}$ , <sup>c</sup>free glycols + polyester.

From eq. (12), it follows:

 $\log[n_i] - \log[n_i + 1] = \log[n_0]/[n_1]$  $-$  log( $K_{\text{Mi}}$ ) (13)

2.1 6.64 6.42 1.74/176 0.797/

1.8 5.37 5.29 1.24/126 0.701/

1.5 3.81 3.20 0.529/50 0.358/

1.3 2.49 2.50 0.244/24 0.301/

If  $K_{\text{Mi}}$  is independent of *i*, then:  $\log[n_i] - \log[n_{i+1}]$  $=$  constant.

Figure 4 shows a good agreement with the assumption, and from the slope we determined  $K_{\text{Mi}}$  $\approx$  constant  $\approx$  1.08.

Finally, *K* value for the reaction of two dimers (giving tetramer + free glycol) was found as  $\approx 1.28.$  Therefore, we could conclude that, for this system, the equireactivity hypothesis could be accepted for all species: free glycols, monomers, and higher oligomers.

The analytic data of two others polyols, made by glycolysis of PET with MEG or of DMT with

DPG and esterification with adipic and phthalic acids, are given in Table IIa.

1.86 6.72 1025 1.31 0.93

2.14 5.59 1011 0.98 0.90

3.00 3.53 984 1.15 0.81

3.64 2.74 1011 0.59 0.59

The same results as for the previous polyol were obtained: equilibrium constants close to 1, a constant ratio  $[n_i]/[n_{i+1}]$  for a given polyol. Thus, the equireactivity hypothesis may be convenient for all equilibrium concerning an oligomer of bishydroxyalkylterephthalate, including the DPG esters. So our previously estimated $4$  high values of these constants, with DPG esters, were wrong, due to erroneous interpretation of chromatograms for these systems.

## **Polyols with Several Glycolic Radicals**

Due to unequal hydrodynamic volumes of the glycolic radicals, there are broadening and overlapping of SEC peaks of the *i*-mer, and thus the determination of amounts of the different oligomers becomes less accurate.



**Figure 4** *i*-mers amounts;  $[n_i]$  in mol/kg of the polyol, oligomers of BHEET (see Fig. 1).  $\Box$ : imprecise values.

Nevertheless, we found again equilibrium polycondensation constants equal to about unity. Data reported in Table IIb concern polyols prepared within a wide range of RM, and with sufficient low DPG proportion to allow adequate interpretation of the chromatograms. For higher DPG proportions, the accuracy of the *i*-mers amounts determination from SEC are too low, but we can see from Figure 3 that the molecular weight distributions remained similar at constant RM. Moreover, calculations of  $n'$  and  $K_p$  from the whole polyol/free glycols balance gave homogeneous results for the four polyols. From these results, we concluded that all equilibria involving oligomers with average polymerization degree from 1 to 3 were correctly described under the equireactivity hypothesis.

The main consequence of the polycondensation reactions is to produce polydispers polyol: formation not only of monomers, but also dimers, higher oligomers and free glycols. An example of distribution curves is given in Figure 5. We have previously shown<sup>4</sup> that, at a given number-average molecular weight, more polydispers polyols lead to more viscous products. Otherwise, a material more homogeneous in the distribution of molecular dimensions creates in the final polyurethane better crosslinking densities. $^{11}$ 

#### **Interchange Equilibrium**

Interchange reactions that involve terminal ester groups and free glycols [see eq. (4)], lead to a



**Figure 5** Distribution curves of polyols  $HOZ(YZ)$ <sub>n</sub>OH. Polyols: 1 PET + x glycols  $(DEG/DPG = 4.6) + 0.8$  diacids  $AP/AA = 1$ ; x = variable.

random redistribution of the glycolic radicals in the polyester and free glycols fraction.

We note,  $K_{\rm HOZ2OH/Z1}$ , the equilibrium constant relative to reaction.<sup>4</sup> If  $K$  is equal to unity, the molar proportions of the glycolic radicals are the same in the two fractions. Glycolic  $Z_1$  radicals are enriched in the free glycols, for *K* values higher than 1. In our case, experimental data are available by analysing the SEC chromatogram of the monomers region for polyols prepared with two different glycolic rests (see, e.g., Fig. 2). Overlapping of the peaks made precision poor. We found:  $K_{\text{DEG/ Me}} \sim 1.$ 

Enrichment of  $Z_1$  radical in the free glycols fraction may also arise from a polycondensation reaction [eq. (5)], if: (a)  $Z_1$  terminal ester group, or  $Z_2$ OH hydroxyl function are the more reactive in condensation reactions; or  $HOZ_{2}OH$  is the more reactive free glycol in the inverse glycolysis reaction.

We note,  $K'_{\text{HOZ2OH/Z1}},$  the ratio:  $\left(\mathrm{[Z}_{\mathit{2}}\text{]/[\mathrm{Z}_1]}\right)_{\text{polyester}}$  $\left(\left[\mathrm{Z}_{2}\right]/[\mathrm{Z}_{1}]\right)_{\text{free glycols}}$ .

Figure 6 shows that this ratio is nearly constant (parallel curves) and close to 1 in the case of the De/Me pair, but clearly below 1 for Dp/Me and Dp/De pairs.

Values of  $K'_{\text{HOZ2OH}/\text{Me}}$  for different alcohols, at RM  $\sim$ 2, are given below:

$$
K'_{\rm DEG-Me} = 0.86 \qquad K'_{\rm DPG-Me} \sim 0.4
$$
 
$$
K'_{\rm MPG-Me} \sim 0.7 \qquad K'_{\rm EhOH-Me} \sim 1
$$

Thus, radicals derived from propylene oxide based glycols (MPG, DPG) are in lesser amount incorporated in polyester chains.

One of the major technical problem encountered in manufacture of polyols from PET, rich in ethanediyl radicals, is a long-term phase separation of solids materials.<sup>12</sup> We have observed<sup>13</sup> that this phenomenon is related with high values of the Me radicals proportion in the polyester fraction. Otherwise, unsaturated polyesters resins made from MEG are known to have poor compatibility with styrene.<sup>14</sup>

#### **Discussion on the Equilibrium Constants**

A systematic work on the equilibrium melt polycondensation in the PET system was performed by Challa.15,16 He reported that, in noncatalyzed systems, the equilibrium constant depends only slightly on temperature, but increase markedly with the extent of polycondensation. Thus,  $K_p$  was

found to be 0.4 at degree of polymerization 1.7, and 1.1 at degree of polymerization 6.2. From kinetics data Challa<sup>16</sup> concluded that all ester groups are equally reactive in glycolysis reactions, but that monomer hydroxyl end groups are less reactive than polymer hydroxyl end groups. In the  $Sb<sub>2</sub>O<sub>3</sub>$  catalyzed polymerization of pure trimer, Stevenson and Nettleton<sup>17</sup> have found average value of 0.36 for  $K_p$ , and concluded that BHET can deactivate the catalyst. In all these studies, MEG and BHET were determined by fractional distillation under vacuum. Latter, Reimschuessel<sup>18</sup> published values of the  $Sb<sub>2</sub>O<sub>3</sub>$  catalyzed polycondensation equilibrium constant of 2-hydroxyethyl benzoate varying from 0.78 to 0.38 in the temperature range  $214-254^{\circ}\text{C}$  (Sb<sub>2</sub>O<sub>3</sub>) catalysis).

Baliga and Wong<sup>10</sup> have found a value of 1.13 for  $K_{\text{MD}}$  in zinc acetate catalyzed glycolysis of PET with a large excess of MEG. The degree of polymerization of the polyester was determined from the hydroxyl number of the water washed polyol, and it was assumed that the trimer amount was negligible.

Hsu and Choi<sup>6</sup> reported that the kinetics of  $Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>$  catalyzed transesterification of DMT by butanediol are in agreement with the equal reactivity hypothesis for functional groups. Thus, the literature is confusing, and data are inconsistent, probably because different reaction conditions (catalysis, RM, etc.), and always indirect determination of reactants concentration; it is difficult to ascertain that analytical datas correspond really with the pure equilibrium state (kinetic extrapolation at infinite time, side reactions, experimental incertitude's).

In our  $Ti(OC_4H_9)_4$  catalyzed glycolysis study we found that all polycondensation constants agree with the equireactivity hypothesis. Moreover, we have a picture of the different *i*-mers abundance, and we do not detect any particular behavior for the monomer. However, the lower proportion of Dp radicals in polyester fractions may be related to a lower reactivity of hydroxyl groups bound to Dp radicals. This is the reverse situation of PET glycolysis by bisphenol A.<sup>7</sup>

#### **CONCLUSION**

Transesterification equilibrium play an important role, as well in polyesters manufacture as in depolymerization processes. From our work, we could conclude that: (a) functional group determi-



**Figure 6** Distribution of glycolic radicals in polyester and free glycols fractions. Me:radical derived from MEG; Z: radical derived from either DEG or DPG.  $\blacktriangle$  Z  $=$  radical derived from DEG; free glycols fraction.  $\triangle Z =$  radical derived from DEG; polyester fraction.  $\bullet$  Z = radical derived from DPG; free glycols fraction.  $\circ$  Z = radical derived from DPG; polyester fraction. (a) polyols:  $1$  PET + x glycols (DEG/DPG = 4.6)  $+$  0.8 diacids (AA/AP = 1). (b) polyols: 1 PET  $+$  glycols (DEG/DPG variable)  $+$  0.8 diacids  $(AA/AP = 3)$ .

nation and chromatographic (GC/SEC) analysis are convenient method for alcoholysis equilibrium constants determination. (b) Polycondensation equilibrium constants are close to fit the equireactivity concept. A particular reactivity of "monomer" species was not detected. (c) Interchange equilibrium constants are glycol nature dependent. (d) The knowledge of the thermodynamics of the reactions allows one to adapt the process to wanted properties. The properties may be in certain cases, unfavorable. However, process adaptations are sometimes possible, in order to respect some specifications. Some examples will be described in a forthcoming article.<sup>9</sup>

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# **ABBREVIATIONS**

The following abbreviations are used (see also Mathematical Treatment):

#### **Structural Units**



Thus, with these symbolisms the formula of PET becomes (TMe)<sub>n</sub>.

# **Other Notations**

x mol glycols added per moles PET;  $x = x_2$  $+ x_3 + (x_1 - 1)$ 

- y mol diacids added per moles PET;  $y = y_1$  $+ y_2$
- *n* polymerization degree ( $\geq 0$ ); *n* = 0: free glycol
- $n'$  polymerization degree of polyester chains  $(\geq 1)$
- RM molar ratio,

$$
RM = \frac{\text{moles}Z}{\text{moles}Z} = \frac{(x+1)}{(y+1)} = \frac{(\bar{n}+1)}{n}
$$

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