

Kinetics of Transesterification of Dimethyl 2,6-Naphthalenedicarboxylate with 1,3-Propanediol

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ABSTRACT: The kinetics of transesterification of dimethyl 2,6-naphthalenedicarboxylate (2,6-DMN) with 1,3-propanediol has been studied in the presence of various catalysts. The reaction was followed by measurement of the amount of methanol released, and the formation of oligomers with time. The oligomers obtained were quantitatively determined by high-pressure liquid chromatography (HPLC). Interpretation of the experimental data showed that the transesterification followed Schulz-Flory statistics. Therefore, one kinetic constant was sufficient to describe the kinetics of transesterification of 2,6-DMN with 1,3-propanediol. The kinetic constants observed, when different catalysts were employed, revealed the following activity sequence for the transesterification: Co(II) < Ti(IV) < Mn(II) < Zn(II). © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2039–2046, 2001

Key words: poly(trimethylene 2,6-naphthalenedicarboxylate); transesterification kinetics; Schulz-Flory statistics

INTRODUCTION

The most common polyester in use today is poly(ethylene terephthalate) (PET). It can be prepared in a two-step process by melt transesterification of dimethyl terephthalate (DMT) with ethylene glycol followed by a polycondensation stage to form a polymer with high molecular weight. A relatively new family of polyesters is based on dimethyl 2,6-naphthalenedicarboxylate (2,6-DMN) and aliphatic diols, with poly(ethylene 2,6-naphthalenedicarboxylate) (PEN) being best known. PEN has gained increasing commercial importance as a valuable engineering thermoplastic material with excellent properties.^{1–3}

Because little is known about poly(trimethylene 2,6-naphthalenedicarboxylate)^{4–7} (PTN), we performed a systematic investigation of its syn-

thesis. The present article focuses on a detailed kinetic study of the first stage, i.e., the melt transesterification of 2,6-DMN with 1,3-propanediol in the presence of various catalysts (Zn(II), Mn(II), Ti(IV), and Co(II)). These studies also illustrate the utility of Schulz-Flory statistics to analyze the evolution of oligomers with time.

Lei et al.^{8–10} and Santacesaria et al.¹¹ have shown by HPLC analysis that during melt transesterification of DMT with ethylene glycol three types of compounds differing in their two terminal groups are formed: Molecules carrying two terminal methyl ester groups (X-type), two terminal hydroxyl groups (Y-type), or one terminal methyl ester and one terminal hydroxyl group (Z-type), respectively.

Santacesaria et al.¹¹ developed a kinetic model to simulate the evolution with time of all oligomers and of the methanol release. They reported that two kinetic parameters and two equilibrium constants are necessary to describe the melt transesterification of DMT with ethylene

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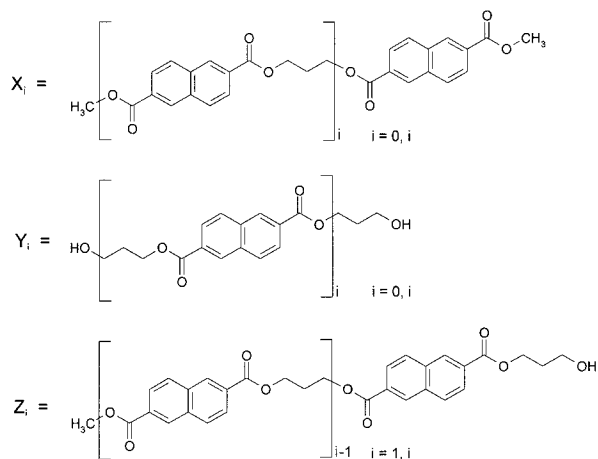


Figure 1 Molecules that are formed during the transesterification of 2,6-DMN with 1,3-propanediol.

glycol. One rate constant k_1 is related to the reaction of a methyl ester group with a hydroxyl group of ethylene glycol, while the other rate constant k_2 corresponds to the reaction of a methyl ester group with a terminal hydroxyl group of a chain. Santacesaria et al.¹¹ found that the activation enthalpies of both kinetic constants k_1 and k_2 are quite similar. Thus, the difference in reactivity of a methyl ester group reacting with a hydroxyl group of an ethylene glycol molecule or with that of an oligomer chain is mainly due to the difference of the preexponential factor in the Arrhenius equation.

Furthermore, Di Serio et al.¹² showed that the two rate constants k_1 and k_2 depend on the nature of the catalyst employed. They defined a selectivity S_1 regarding the formation of oligomers with terminal hydroxyl groups:

$$S_1 = \frac{k_1}{k_1 + k_2} \quad (1)$$

and the activity A of a catalyst as:

$$A = k_1 + k_2 \quad (2)$$

Reaction Scheme

Figure 1 shows the molecules formed during the transesterification of 2,6-DMN with 1,3-propanediol. With regard to the end groups, the molecules can be divided in X_i -, Y_i -, and Z_i -types. X_0 corresponds to 2,6-DMN, Y_0 to 1,3-propanediol, Z_1 to methyl-(3-hydroxypropyl) 2,6-naphthalenedi-

carboxylate (MHPN) and Y_1 to bis-(3-hydroxypropyl) 2,6-naphthalenedicarboxylate.

The transesterification can be considered as a combination of many simultaneous and sequential reactions. After each reaction step the product can be the starting compound of the next reaction. The first reaction stage is the reaction of 2,6-DMN (X_0) and 1,3-propanediol (Y_0) to the molecule MHPN (Z_1) under release of methanol. In the second stage the MHPN (Z_1) can react with another MHPN molecule (Z_1) or with 1,3-propanediol (Y_0) or with 2,6-DMN (X_0). Hence, three different products (X_1 , Y_1 , and Z_2) and methanol can be formed. Figure 2 illustrates the reaction scheme, which is shown up to the third reaction stage.

Transesterification Process

Catalysts are applied to accelerate the transesterification of 2,6-DMN with 1,3-propanediol. This raises the question as to whether the oligomer distribution is influenced by the nature of the catalyst employed. Therefore, different catalysts were employed (Mn(II), Ti(IV), Zn(II), and Co(II)), and the reactivity as well as the oligomer formation with time were investigated. All transesterification experiments were carried out under identical conditions: a concentration of $4 \cdot 10^{-4}$

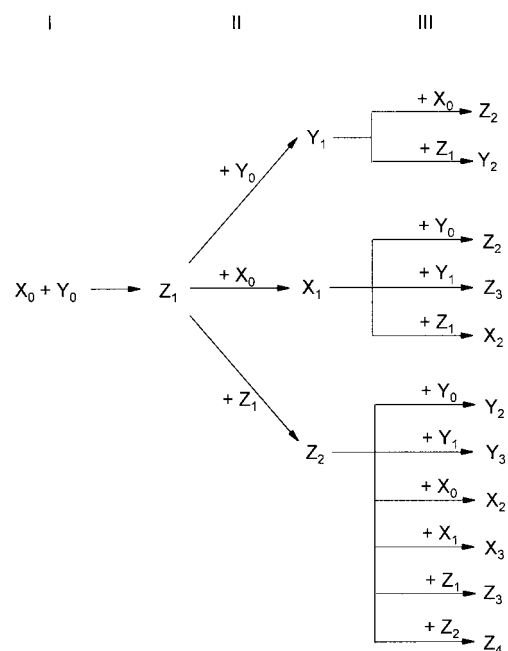


Figure 2 Reaction scheme¹¹ of oligomer formation (shown up to the third reaction stage).

mol catalyst per mol 2,6-DMN, a 1,3-propanediol/2,6-DMN ratio of 2.2, and a reaction temperature of 200°C. The oligomers formed were determined quantitatively by HPLC. Furthermore, the distribution of oligomers was calculated by Schulz-Flory statistics and compared with the experimental data.

EXPERIMENTAL

Transesterification

A 250-mL glass reactor fitted with a stirrer, a distillation system, a supply of nitrogen, and a thermometer was used for the transesterification experiments. The distillation system consisted of two jacketed coil condensers and a graduate receiver. The jacketed coil condenser on the reactor was kept at 80°C by a recirculating thermostated fluid. In this way it was possible to separate methanol quickly from the reaction mixture while 1,3-propanediol was refluxed. The distilled methanol was condensed by a second jacketed coil condenser that was cooled by water and finally conveyed to a graduate receiver. The transesterification experiments were carried out with constant stirring and constant flow of nitrogen. The flow of nitrogen was controlled by a rotameter.

One hundred grams (0.409 mol) of 2,6-DMN (Amoco, fiber grade) and 50 g (0.657 mol) of 1,3-propanediol (Degussa, fiber grade) were placed in the reactor and heated up to a reaction temperature of 200°C. Then the catalyst dissolved in 8.5 g (0.243 mol) 1,3-propanediol was added to the melt so that a 1,3-propanediol/2,6-DMN ratio of 2.2 results. In the following, the quantities of catalysts relating to a concentration of $4 \cdot 10^{-4}$ mol catalyst per mol 2,6-DMN are listed:

- 36.0 mg ($1.64 \cdot 10^{-4}$ mol) Zn(II)acetate \cdot 2 H₂O
- 40.2 mg ($1.64 \cdot 10^{-4}$ mol) Mn(II)acetate \cdot 4 H₂O
- 55.8 mg ($1.64 \cdot 10^{-4}$ mol) Ti(IV)butylate
- 40.8 mg ($1.64 \cdot 10^{-4}$ mol) Co(II)acetate \cdot 4 H₂O

The appearance of the first drop of methanol in the condenser was considered as the beginning of the reaction ($t = 0$). Samples were taken at different times and the amount of collected methanol was recorded. The samples were analyzed by HPLC.

Table I Composition of the Mobile Phase Used in the HPLC Analysis

Time (min)	<i>n</i> -Hexane (vol %)	1,4-Dioxane (vol %)
0	70	30
12	70	30
32	47	53
45	47	53

HPLC Analysis

The HPLC method applied was similar to that employed by Santacesaria et al.¹¹ Because of the employment of 2,6-DMN and 1,3-propanediol, a different composition of the mobile phase and a different detection wave length had to be determined.

The samples were prepared by dissolving about 2 mg of the reaction mixture in 10 cm³ of a mixture of chloroform and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) (98 : 2; v/v). The HPLC analyses were carried out with Kroma system 2000 of Kontron Instruments using a Spherisorb Si column and a precolumn of Waters. The column had a length of 25 cm and a diameter of 0.4 cm, and was filled with 5- μ m silica particles. The mobile phase was a mixture of *n*-hexane and 1,4-dioxane, changing the composition with time, as shown in Table I. The flow rate was 1 mL/min. The eluate was detected at 286 nm by a UV detector. This wave length was chosen because bis-(3-hydroxypropyl) 2,6-naphthalenedicarboxylate and 2,6-DMN show maximal absorption at this wave length. Therefore, we could assume that the higher oligomers show a corresponding absorption behavior.

Figure 3 shows a typical HPLC chromatogram of a sample that was taken during the transesterification. It was possible to detect Y₁-oligomers with up to 10 monomer units.

For the quantitative determination of the oligomer distribution, 2,6-DMN was taken as the reference substance. The quantity of every single oligomer was determined by assuming that every naphthalene unit contributes the same amount to the absorption.

RESULTS

The amount of methanol released during the transesterification can be determined in two dif-

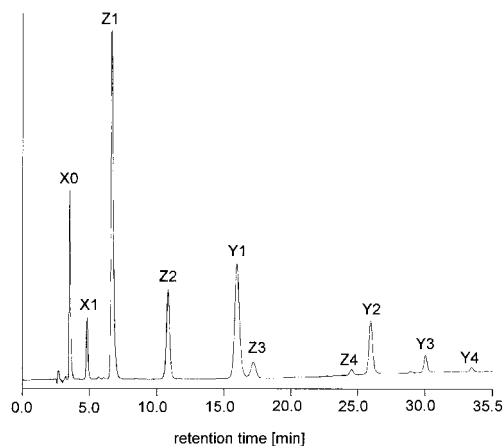


Figure 3 HPLC chromatogram of a sample that was taken during the transesterification.

ferent ways. On the one hand, the volume of the condensed methanol in the receiver can be measured directly. On the other hand, one can calculate the difference of the number of 2,6-DMN methyl ester groups at the beginning of the reaction, and the number of unreacted methyl ester groups remaining after the reaction has been in progress for a time t . The number of molecules with methyl ester groups is obtained from the oligomer distribution as a result of the HPLC analysis.

The yields of methanol η can be defined in the following way:

$$\eta = \frac{N(\text{CH}_3\text{OH})}{2N(0)} = \frac{2N(0) - 2 \sum_{i=0}^k N(\text{X}_i) - \sum_{i=1}^k N(\text{Z}_i)}{2N(0)} \quad (3)$$

where $N(\text{CH}_3\text{OH})$ is the number of methanol molecules released, $N(\text{X}_i)$ and $N(\text{Z}_i)$ the number of X_i - and Z_i -molecules after the reaction has been in progress for a time t , and $N(0)$ the number of 2,6-DMN molecules at the beginning of the reaction.

In Figure 4, the methanol yield is shown as a function of time for a reaction where a titanium catalyst was employed. As part of the methanol evaporates and is removed by the nitrogen flow, the yield of methanol determined by HPLC is somewhat higher than the methanol yield determined by direct volume measurement.

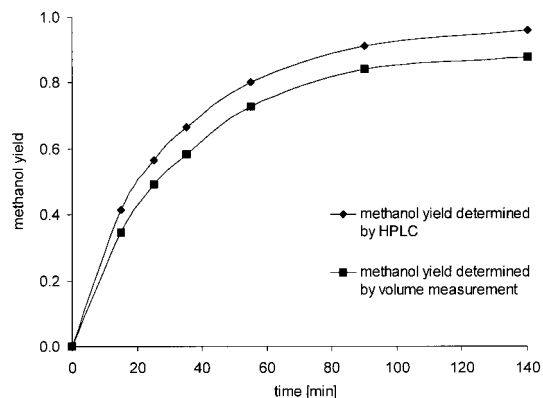
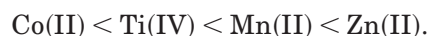


Figure 4 Methanol yield determined by HPLC and volume measurement, related to the catalysis by Ti(IV)butylate.

To compare the reactivity of several catalysts, the amount of methanol released with time will be considered. Many authors have used this method to describe the kinetic processes during transesterification. Figure 5 shows the yield of methanol η determined by volume measurement, related to the transesterification of 2,6-DMN with 1,3-propanediol in the presence of various catalysts. According to Figure 5, the catalytic reactivity can be found to be:



The evaluation of the methanol yield as a function of time gives no information about the evolution of oligomers with time. For such investigations samples have to be taken during the transesterification and analyzed by HPLC. The oligomer formation for the X_i -, Y_i -, and Z_i -types in

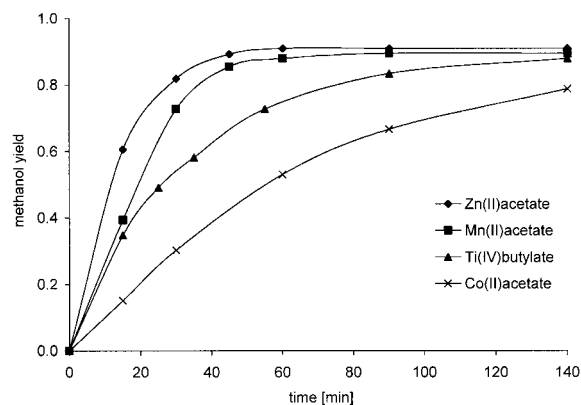


Figure 5 Methanol yield for different catalysts determined by volume measurement.

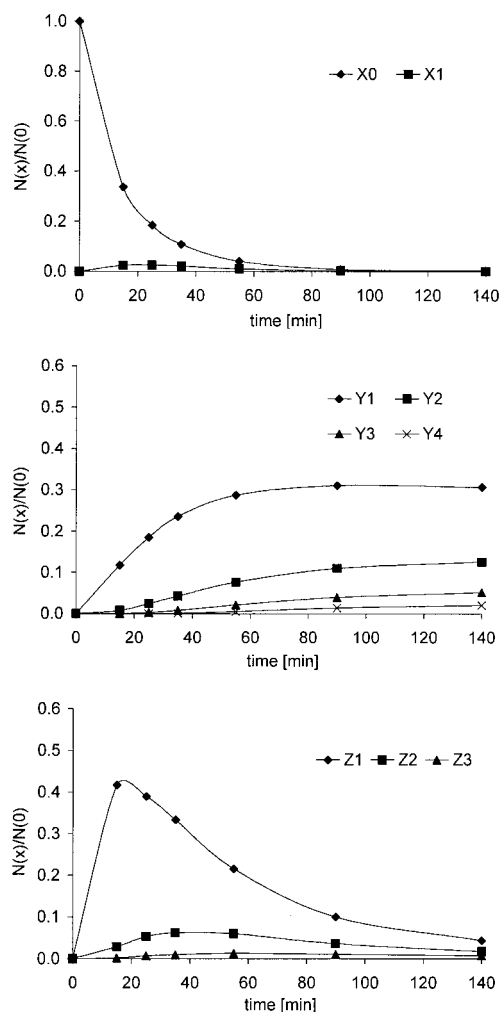


Figure 6 X_i -, Y_i -, and Z_i -oligomer formation as a function of time, related to the catalysis by Ti(IV)butylate.

the presence of a titanium catalyst is shown in Figure 6. $N(x)$ is the number of molecules of a certain oligomer, and $N(0)$ is the number of 2,6-DMN molecules at the beginning of the reaction.

Theoretical Description by Schulz-Flory Statistics

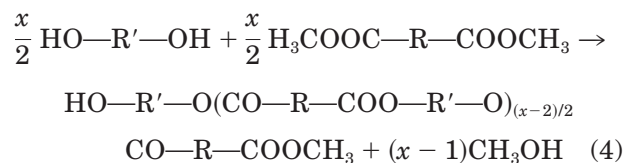
The Schulz-Flory statistics make the fundamental assumption that the reactivity of a functional group is independent of the size of the molecule to which it is attached.¹³⁻¹⁵ It is also assumed that the formation of cyclic compounds (as well as other side reactions) does not occur to an appreciable extent. Based on these assumptions the oligomer formation can be described as a function of the extent of reaction p .

In the following, we show that Schulz-Flory statistics give qualitative agreement with our ex-

perimental data. This is different from what Santacesaria et al.¹¹ have shown. The reasons for the differences being discussed later.

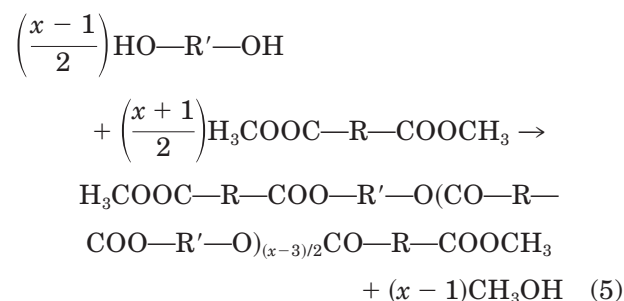
For the description of Schulz-Flory statistics we consider a polyester that is formed by the reaction of a dimethyl ester with a diol where the diol component is in excess. In this case three different types of molecules are formed (X-, Y-, and Z-type). The combination of reactants leading to a molecule with one terminal hydroxyl and one terminal methyl ester group (Z-type), requires an even number of starting molecules x :

Z-Type Molecules:

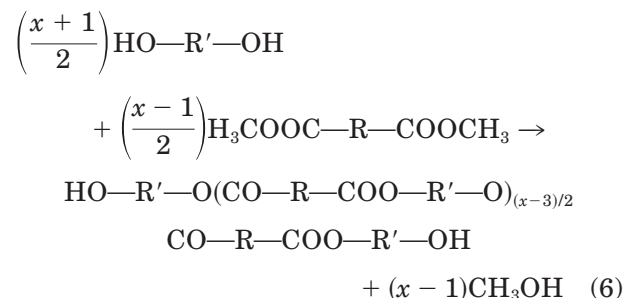


However, the formation of a molecule with two terminal methyl ester groups (X-type) or two terminal hydroxyl groups (Y-type) requires an odd number of starting molecules x .

X-Type Molecules



Y-Type Molecules



To describe the oligomer formation as a function of the extent of reaction p , separate functions must be derived for each of the three kinds of molecules. The probability to obtain a molecule of the X-, Y-, or Z-type is given by:

X-type molecules:

$$\frac{N(x)}{N(0)} (\text{odd}) = p^{(x-1)} \cdot r^{(x-1)/2} \cdot (1-p)^2 \quad (7)$$

Y-type molecules:

$$\frac{N(x)}{N(0)} (\text{odd}) = p^{(x-1)} \cdot r^{(x-3)/2} \cdot (1-rp)^2 \quad (8)$$

Z-type molecules:

$$\frac{N(x)}{N(0)} (\text{even}) = 2 \cdot p^{(x-1)} \cdot r^{(x/2-1)} \cdot (1-p) \cdot (1-rp) \quad (9)$$

where the following notation is used:

p = extent of reaction or the probability that a methyl ester group has reacted

$$p = \frac{N_0(\text{CH}_3) - N(\text{CH}_3)}{N_0(\text{CH}_3)} \quad (10)$$

with $N_0(\text{CH}_3)$ being the number of methyl ester groups at the beginning of the reaction and $N(\text{CH}_3)$ being the number of unreacted methyl ester remaining after the reaction has been in progress for a time t

r = ratio of the number of methyl ester and hydroxyl groups at the beginning of the reaction

$$r = \frac{N_0(\text{CH}_3)}{N_0(\text{OH})} \quad (r < 1) \quad (11)$$

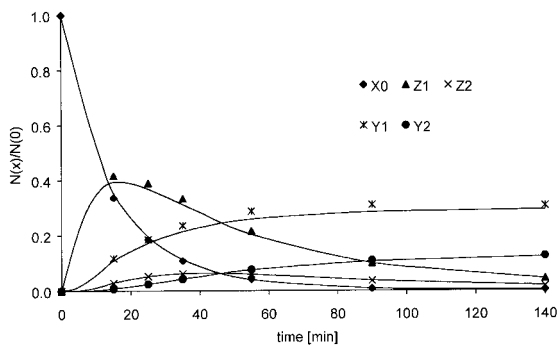


Figure 7 Oligomer formation as a function of time, related to the catalysis by Ti(IV)butylate (symbols represent the experimental values, whereas the lines are calculated).

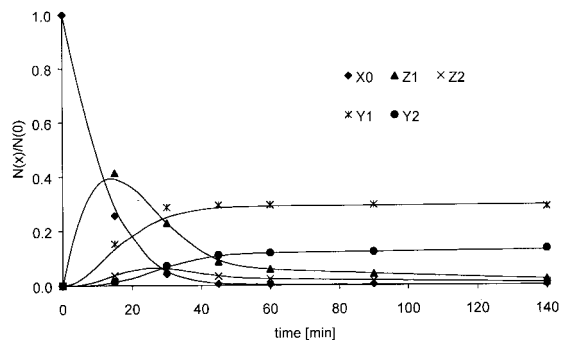


Figure 8 Oligomer formation as a function of time, related to the catalysis by Mn(II)acetate (symbols represent the experimental values, whereas the lines are calculated).

According to eqs. (7) to (9) the oligomer formation can be calculated if the extent of reaction p is known. The extent of reaction p is equal to the methanol yield η determined by HPLC analysis. Figure 7 shows a very good agreement between the theoretical and experimental data for the titanium catalysis. With reference to Figure 7, the symbols represent the experimental values, whereas the lines are calculated with eqs. (7) to (9). The same agreements can be found when a zinc, manganese, or cobalt catalyst is applied (Fig. 8 to Fig. 10).

Regarding eqs. (7) to (9) it has been assumed that the reactivity of the functional groups are independent of the size of the molecule. As the experimental result corresponds very well with the theoretical one, the reactivity of a hydroxyl group in a 1,3-propanediol molecule has to be almost equal to the hydroxyl group in a growing chain. Thus, one single kinetic constant k is suf-

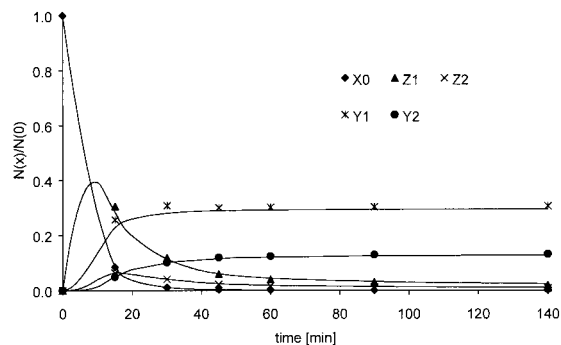


Figure 9 Oligomer formation as a function of time, related to the catalysis by Zn(II)acetate (symbols represent the experimental values, whereas the lines are calculated).

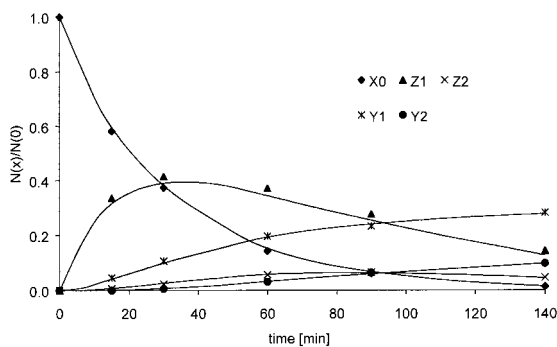
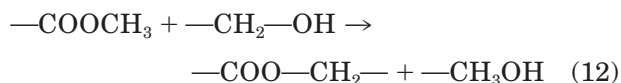


Figure 10 Oligomer formation as a function of time, related to the catalysis by Co(II)acetate (symbols represent the experimental values, whereas the lines are calculated).

ficient to describe the kinetics of transesterification of 2,6-DMN with 1,3-propanediol. Furthermore, this agreement shows that no catalyst forms oligomers of a special type (X_{i-} , Y_{i-} , and Z_{i-} oligomers). Hence, the formation of oligomers clearly follows statistic aspects.

Determination of Kinetic Parameter

We assume an irreversible reaction to describe the kinetics of transesterification, because the methanol is continuously removed from the equilibrium. The transesterification is treated as a reaction of second order with respect to 2,6-DMN and 1,3-propanediol.



The kinetic law of second order

$$\frac{dx}{dt} = k \cdot ([\text{CH}_3]_0 - x) \cdot ([\text{OH}]_0 - x) \quad (13)$$

can be integrated to give

$$\frac{1}{[\text{CH}_3]_0 - [\text{OH}]_0} \cdot \ln \frac{[\text{CH}_3]_0 \cdot [\text{OH}]}{[\text{OH}]_0 \cdot [\text{CH}_3]} = k \cdot t \quad \text{where} \quad \frac{[\text{OH}]_0}{[\text{CH}_3]_0} = \frac{2,2}{1} \quad (14)$$

The kinetic constant k can be determined from the slope in Figure 11. The results are listed in Table II. Thereby the relative rates, when differ-

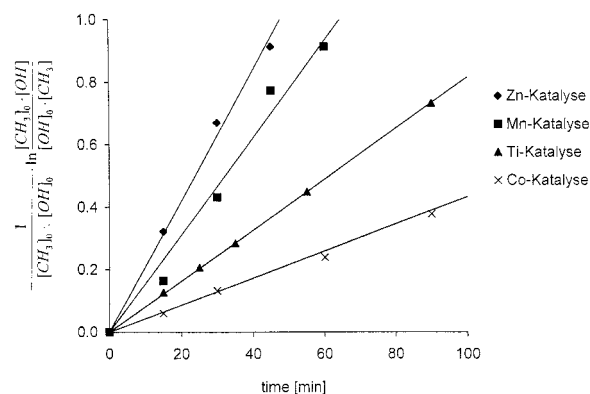


Figure 11 Plot to determine the kinetic constants k for different catalysts, related to the transesterification of 2,6-DMN with 1,3-propanediol.

ent catalysts are employed, reveal the following ratios:

$$\text{Zn(II)} : \text{Mn(II)} : \text{Ti(IV)} : \text{Co(II)} \\ = 1 : 0.74 : 0.39 : 0.21.$$

It is often tried to express the kinetic constant k as:

$$k = k_0 + k' \cdot [\text{cat}] \quad (15)$$

where the constant k_0 takes the uncatalyzed reaction into account and the second term takes care of the catalyzed reaction assuming that the reaction is of first order with respect to the catalyst concentration [cat].

In our case, k_0 can be neglected because the uncatalyzed transesterification does not proceed to an appreciable extent. Kinetic studies at different catalyst concentrations show, however, that there is no linear correlation between catalyst concentration and the kinetic constant k . In Table

Table II Kinetic Constant k for Different Catalysts ($4 \cdot 10^{-4}$ mol/mol 2,6-DMN), Related to the Transesterification of 2,6-DMN with 1,3-Propanediol

Metal	k [$\text{l} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$]
Zn ²⁺	0.021
Mn ²⁺	0.0155
Ti ⁴⁺	0.0082
Co ²⁺	0.0043

Table III Kinetic Constant k Using Ti(IV)Butylate as Catalysts, Related to the Transesterification of 2,6-DMN with 1,3-Propanediol

Concentration [mol/mol 2,6-DMN]	k [$l \cdot mol^{-1} \cdot min^{-1}$]
$2 \cdot 10^{-4}$	0.0057
$4 \cdot 10^{-4}$	0.0082
$6 \cdot 10^{-4}$	0.0093

III, the results for the titanium catalyzed reaction are listed. Thus, the kinetic approach is more complicated than expressed by eq. (15). Many authors^{9–11,16,17} have also observed a nonlinear correlation between reactivity and catalyst concentration. For the melt transesterification of DMT with ethylene glycol, Santacesaria et al.¹¹ observed that the reaction order is about zero for a large concentration range and first order for very low catalyst concentration.

DISCUSSION

Santacesaria et al.¹¹ have reported that two kinetic parameters and two equilibrium constants are necessary to describe the melt transesterification of DMT with ethylene glycol. One kinetic constant k_1 is related to the reaction of a methyl ester group with a hydroxyl group of ethylene glycol, while the other constant k_2 corresponds to the reaction of a methyl ester group with a hydroxyl group in a chain. In another article, Di Serio et al.¹² reported that the kinetic constants k_1 and k_2 depend on the nature of catalyst employed.

In contrast to these results, the present study shows that only one single kinetic parameter is sufficient to describe the kinetics of melt transesterification of 2,6-DMN with 1,3-propanediol in the presence of various catalysts. These different results are most likely caused by the different number of methylene groups in the diol component. An important point is the mutual influence of the two hydroxyl groups in the diol, and therefore, different electron density distributions in the ethylene glycol and 1,3-propanediol molecules. An increasing number of methylene groups reduces this effect, so that the reactivity of 1,3-

propanediol is similar to the reactivity of an oligomer. According to Santacesaria et al.,¹¹ this is not the case for ethylene glycol.

CONCLUSION

It has been shown that the melt transesterification of 2,6-DMN with 1,3-propanediol simply follows Schulz-Flory statistics. In this way the oligomer formation can be calculated if the extent of reaction is known. Furthermore, the ratio of oligomers to each other at any time of the transesterification is independent of the catalyst employed. The kinetics of transesterification can be described by a kinetic law of second order with respect to 2,6-DMN and 1,3-propanediol. The catalytic reactivity can be found to be: Co(II) < Ti(IV) < Mn(II) < Zn(II).

REFERENCES

- Jager, J.; Juijn, J. A.; van den Heuvel, C. J. M.; Huijts, R. A. *J Appl Polym Sci* 1995, 57, 1429.
- Sharma, N. D.; Jain, S. L. *Man-Made Textiles India* 1995, 38, 406.
- Rim, P. *Chem Fibers Int* 1996, 46, 204.
- Sadanobu, J.; Tsukioka, M. *Annu Tech Conf Soc Plast Eng* 1997, 55, 1567.
- Hwang, S. K.; Yeh, C.; Chen, L. S.; Way, T. F.; Tsay, L. M.; Liu, K. K.; Chen, L. T. *Polym Preprints* 1999, 40, 611.
- How, C.; Forschner, T.; Lowtan, R.; Gwyn, D.; Cris-tea, B. *J Plast Film Sheeting* 1999, 15, 219.
- Tsai, R. S.; Lee, Y. D. *J Polym Res* 1998, 5, 77.
- Lei, G. D.; Choi, K. Y. *Ind Eng Chem Res* 1993, 32, 800.
- Besnoin, J. M.; Lei, G. D.; Choi, K. Y. *AIChE J* 1989, 35, 1445.
- Lei, G. D.; Choi, K. Y. *Ind Eng Chem Res* 1992, 31, 769.
- Santacesaria, E.; Trulli, F.; Minervini, L.; Di Serio, M.; Tesser, R.; Contessa, S. *J Appl Polym Sci* 1994, 54, 1371.
- Di Serio, M.; Tesser, R.; Trulli, F.; Santacesaria, E. *J Appl Polym Sci* 1996, 62, 409.
- Flory, P. J. *J Am Chem Soc* 1936, 58, 1877.
- Schulz, G. V. *Z Physik Chem (B)* 1935, 30, 379.
- Schulz, G. V. *Z Physik Chem (B)* 1939, 43, 25.
- Tomita, K.; Ida, H. *Polymer* 1973, 14, 55.
- Shah, T. H.; Bhatta, J. I.; Gamlen, G. A.; Dollimore, D. *J Macromol Sci Chem* 1984, A21, 431.