

Model Esterification of Neopentyl Glycol and Trimethylol Propane with 1,4-*Tert*-Butyl Benzoic Acid

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SYNOPSIS

The esterification kinetics of difunctional neopentyl glycol and trifunctional trimethylol propane with monofunctional 1,4-*tert*-butyl benzoic acid was studied in the melt phase at 200°C in the presence of a metal catalyst. The rate of conversion was monitored via titrations and by determination of the relative concentrations of products and reactants using HPLC with a UV detector. A small but significant positive substitution effect was found for neopentyl glycol ($K_{DA} = 1.15$) and none was found for trimethylol propane. The reaction rate constant of neopentyl glycol with the acid is about 40% higher than that of trimethylol propane with the acid. A second-order overall reaction order was used to compute the rate constants.

INTRODUCTION

Polyesterification is an important polycondensation reaction from both a scientific and a technological point of view. The rate of polycondensation is controlled primarily by the kinetics of the reactions between the functional groups involved, which are usually assumed to be independent of the size of the molecules to which they are attached, and of the reaction state of the other groups belonging to the same monomer. Ample experimental evidence for the correctness of the first assumption is provided in the literature.¹⁻³ However, in several instances experimental results strongly indicate that the principle of equal reactivity of equal functional groups is not obeyed for all monomer sizes: The intrinsic chemical characteristics of a functional group can often be altered by substitution when the substituent is introduced near to that functional group.³⁻⁶

Polyesterification usually occurs through an alternating copolymerization between two- (or higher-) functional alcohols and carboxylic acids via a so-called stepwise intermolecular condensation of the functional groups. Such reactions can be de-

scribed successfully with the statistical theory, originally developed by Flory and Stockmayer^{1-3,7,8} and later extended by Gordon et al.⁹ to more complex systems by using probability generating functions and cascade substitutions as tools. In this way, substitution effects can be taken into account.^{4,5,10}

This approach was recently employed to describe network formation in multistage processes,¹³⁻¹⁵ which are of technological interest in particular for the synthesis of polymers and resins for paints, coatings, adhesives, and construction materials. For a verification of such theoretical models information is required on the reaction kinetics of the starting monomers. If conversion rather than time is the variable of interest, only substitution effects and relative reaction rate constants are required.

This experimental study focuses on these kinetic aspects for a diol and triol, namely, neopentyl glycol (NPG) and trimethylol propane (TMP), which are frequently used in industrial polyesterifications. Small positive substitution effects have been found for pentaerythritol and trimethylol ethane with adipic acid⁴ and with lauric acid.⁵ No substitution effects have been found for TMP with various long-chain carboxylic acids,¹⁶ whereas, for TMP with *p*-tolyl isocyanate, negative substitution effects have been found.⁶ Thus substitution effects apparently depend strongly on the reaction conditions and the type of coreactant. The kinetics of NPG and TMP

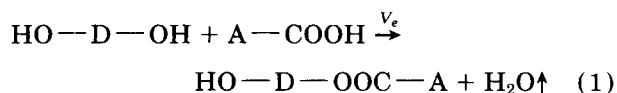
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are studied here as model reactions of these monomers with a monofunctional carboxylic acid, namely 1,4-*tert*-butyl benzoic acid (tBBA), as the monofunctional substitute for terephthalic acid. By measuring the distribution of monomers and oligomers as a function of conversion, substitution effects and relative reaction rates are determined, similar to the work in Refs. 5, 6, and 16.

REACTION KINETICS OF ESTERIFICATION

The rates of polyesterifications are largely controlled by the reaction rates of the functional groups, rather than by the size of the reacting molecules, i.e., their diffusion rates in the system. The similarity in the courses followed by mono- and polyesterifications provides direct evidence for the nondependence of the reactivity on the molecular size.^{1-3,17} The independence of the reaction kinetics on the increase in viscosity or the crossing of the gel point is further strong evidence.

The reactions studied here are simple esterifications, i.e., the reaction of an alcohol functional group with a carboxyl functional group in the presence of a metal catalyst forming an ester bond and a water molecule:



where V_e represents the rate of change of concentration of products or reactants. For an ideal, closed, isothermal, constant-volume reaction system,¹⁸ one can express the rate of increase or decrease of the concentration of P by

$$d[\text{P}]/dt = \pm aV \quad (2)$$

where a is the stoichiometric coefficient of [P] with respect to the overall chemical reaction and V is often incorrectly called the rate of reaction but is strictly the rate of increase or decrease of [P].¹⁹ The rate of increase of [P], $d[\text{P}]/dt$, is experimentally determined and is often expressed as

$$V = kc_1^{n_1}c_2^{n_2} \cdots c_j^{n_j} \quad (3)$$

where k is the reaction rate constant, c_j is the concentration of reactant j , and the sum of the exponents $n = \sum_j n_j$ is the order of reaction.

In this study the reactions were carried out in the absence of solvent, which results in considerable

changes in local concentrations and polarity. Furthermore, the high concentrations are thermodynamically nonideal and the system used is open. The experimental conditions all result in making the application of eqs. (2) and (3) tenuous. In fact for this type of reactions eq. (2) is not valid, but for simplicity it is used, as in various other similar studies. In contrast to other studies^{1,2,17} kinetic results were obtained during the complete course of the reaction and not only in the later stages, similar to work described in Refs. 5 and 6.

Since the primary variable of interest in this study is conversion and not time, the order of the reaction is not of main interest. Considering the conditions of the majority of esterification studies, i.e., nondilute and open, and complicating factors like substitution effects and intramolecular reactions,⁴ it is not surprising that the order of reaction for esterification is a source of considerable dispute. Early studies indicate an overall order of 3, 2 with respect to the carboxylic and 1 with respect to the alcohol concentration, for noncatalyzed systems and 2 for acid catalyzed reactions.^{1-5,17}

However, in a recent study, which also involved TMP, a partial order of 1.5 with respect to the acid was assumed.¹⁶ In another extensive, recent study on esterification with model monomers at high temperature in the melt phase, the reaction rate of the esterification process in the presence of a metal catalyst is expressed by $V = V_u + V_m$, where V_u corresponds to the uncatalyzed reaction, described by²⁰

$$V_u = k_u[\text{acid}]^2[\text{alcohol}] \quad (4)$$

and V_m to the reaction catalyzed by the metal compound

$$V_m = k_m[\text{metal}][\text{acid}]^x[\text{alcohol}] \quad (5)$$

with $x = 0$ or 1, depending on the type of metal catalyst. Under these conditions the overall order of reaction for esterification in the melt phase is somewhere between 2 and 3, determined by experiment. In our calculations (see below) an overall order of 2 is assumed, 1 with respect to [acid] and 1 with respect to [alcohol].

RANDOM REACTIONS AND SUBSTITUTION EFFECTS

The mole fractions m_i of products (and NPG molecules) carrying i ester groups in the random reaction, free from substitution effects, between NPG

and a monoacid are given by the Bernoulli distribution:

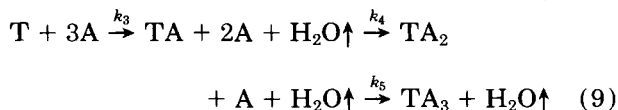
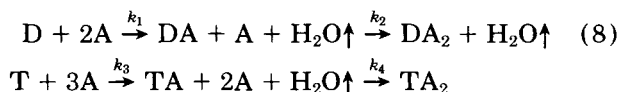
$$m_i = \binom{2}{i} \alpha^i (1 - \alpha)^{2-i}, \quad i = 0, 1, 2. \quad (6)$$

For TMP these mole fractions, denoted by n_i , read

$$n_i = \binom{3}{i} \alpha^i (1 - \alpha)^{3-i}, \quad i = 0, 1, 2, 3. \quad (7)$$

Thus m_i and n_i represent the mole fractions of NPG and TMP, respectively, with i bonds reacted.

The presentation and the following discussion are condensed by assigning each reactant a single alphabetical letter (see Table I) and representing the products with a combination of two reactant symbols. The reactions investigated are thus simply represented by

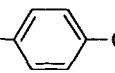


where k_i represent the respective reaction rate constants. In the absence of substitution effects $k_1 = k_2$ and $k_3 = k_4 = k_5$. The substitution effect parameter $K_{DA} = k_2/k_1$ (or $K_{TA} = k_4/k_3$) represents the factor by which the reaction rate constant for a monomer D (or T), which reacted already once with a monomer A, is increased (K_{DA} or $K_{TA} > 1$, i.e., a positive substitution effect) or decreased (K_{DA} or $K_{TA} < 1$, i.e., a negative substitution effect) with respect to k_1 (or k_3).^{4-6,10,15} For linear substitution effects $K_{TA_2} = (K_{TA})^2 = k_5/k_3$.^{4,5,10}

Irrespective of substitution effects, the conversions of NPG and TMP are given by

$$\alpha_D = (m_1 + 2m_2)/2 \quad (10)$$

Table I Reactant Notation

Symbol	Chemical Name	Chemical Formula
A	1,4- <i>Tert</i> -butyl benzoic acid (tBBA)	$(CH_3)_3C$  $-COOH$
D	Neopentyl glycol (NPG)	$HOCH_2-C(CH_3)_2-CH_2OH$
T	Trimethylol propane (TMP)	$(HOCH_2)_3-C-CH_2CH_3$

and

$$\alpha_T = (n_1 + 2n_2 + 3n_3)/3 \quad (11)$$

respectively. The presence of substitution effects is verified by comparing experimental $m_i(\alpha)$ and $n_i(\alpha)$ values with the theoretical relations given in eqs. (6) and (7). If systematic deviations occur, the value of the substitution effect parameter K is estimated with nonlinear regression analysis and the set of differential equations given in the Appendix. In a similar way (intermolecular) differences in reactivity between D and T with A are concluded from the values of k_1 and k_3 or their ratio.

EXPERIMENTAL

Chemicals

The 2,2-dimethyl-1,2-propanediol (i.e., neopentyl glycol or NPG) and the 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (i.e., trimethylol propane or TMP) were synthetic grade purchased from Merck-Schuchardt Co. The 1,4-*tert*-butyl benzoic acid (tBBA) was reagent grade from Hoechst, and the metal catalyst was from a usual tin type. All chemicals were used as received without further purification.

Reaction Vessel

The glass reaction vessel was approximately 1 L in capacity. A flat Teflon washer was used between the lid and the vessel. A stainless steel stirring rod was used for mixing at roughly 300 rpm. Nitrogen was used to purge the system and to aid in the removal of waver vapor produced during the reaction. The vessel was heated using a heating mantle which was continuously regulated via a "Microrecorder III" (an I/O device) with a "K-class" thermocouple located in the reaction melt. The reaction temperature was fixed at $200 \pm 2^\circ C$.

Reaction Procedure

The total quantity of reactants was between 250 and 350 g. The materials were weighed to within 0.1% except for the catalyst which was weighed to within 1.0% due to the small quantities used (0.15% by mass compared to NPG). The glycol and/or triol and the acid were mixed in the reaction vessel which was then heated to $150^\circ C$ under nitrogen. The catalyst was then added and $200^\circ C$ reaction temperature was reached within 10 min and maintained to

within $\pm 2^\circ\text{C}$. The variability in temperature was this large due to rapid production of water and its imperfect removal.

Samples were removed using a combination burette-pipette. About 10.2 mL samples were taken over the entire reaction run. The typical reaction was run for roughly 6 h and the time to reach 50% conversion measured by the consumption of free acid groups averaged 2 h.

Acid Determination

The conversion was calculated from the initial and actual mass percentages of acid in a sample. The mass percent of free (unreacted) acid was determined by titration in THF with 0.1 M KOH in methanol solution using cresol-phenolphthalein as an indicator. The samples were titrated in duplicate.

HPLC

As with many kinetic studies the rate of reaction was not measured directly, but the concentrations of the products and the aromatic acid were monitored as functions of conversion (and time). High performance liquid chromatography was used to separate the samples into their constituents and a UV detector allowed the quantitative analysis of all aromatic components.

The extinction coefficients of A, DA₂, and TA₃ were determined experimentally at 240 nm (at a maximum in the absorption curve) in acetonitrile with a Philips PU 8720 UV/VIS spectrophotometer. The tri- and tetramer were purified by repeated dissolution in acetonitrile and precipitation with water and subsequent repeated recrystallization from methanol and ethanol, respectively; titrations and HPLC measurements yielded a purity of over 99.5 and 99.7%, respectively. A linear regression analysis yielded the extinction coefficients of A as a function of n , the number of A groups in the same molecule: $(15.5 + 0.4n) 10^2 \text{ m}^2 \text{ mol}^{-1}$.

From the HPLC/UV areas and the extinction coefficients, the ratios of [DA]/[A] and [DA₂]/[A] or [TA]/[A], [TA₂]/[A], and [TA₃]/[A] were determined. The mole fractions of unreacted glycol and triol, which are inactive in the UV range studied, were deduced from this information under the assumption that no material was lost by evaporation. In this respect the system was thus assumed to be closed, which is not strictly valid since the system remains open and reactants and products are subject to losses; the error of this approximation was estimated from a material balance to be less than 3%.

To insure that this loss of material (in particular glycol) during the reaction was not significant, a comparison of the conversion from the HPLC and the conversion from the acid titration was made as well, as shown in Figure 1. Obviously the deviation from linearity is not significant; if loss of material was significant, a convex increase with increasing conversion would be expected.

The HPLC included an HP 1050 pump, a Spark Promis automatic sampler and injector (5 μL), a Machery and Nagel 100×4 column of 120–5 μm Nucleosil C₁₈ and the detector was a Lambda Max Model 481 absorbance detector manually set at 240 nm.

The solvent was a mixture of two, i.e., acetonitrile and 0.01 M phosphoric acid, which changed in ratio during the run from 40/60 initially to 100/0 v%/v% after 10 min. This gradient affects baseline separation clearly and nonoverlapping. The integration was computer-assisted and the mole fractions calculated were plotted as a function of the conversion of hydroxyl groups. A typical HPLC chromatogram from a "combined experiment" (vide infra) is shown in Figure 2.

RESULTS AND DISCUSSION

The esterification reactions were carried out in bulk under nonideal conditions. During sampling the reaction kinetics may be influenced (both in the sample and the bulk), so that the uncertainty in total reaction time t is larger than that in the overall conversion determined by titration. The concentrations of the reactants and products are thus better considered in terms of extent of conversion, i.e., $d[\]$

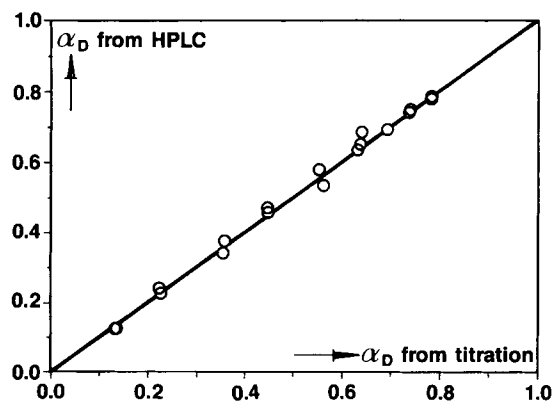


Figure 1 Comparison of conversion of the diol determined from HPLC/UV areas (y-axis) and from acid titrations (x-axis).

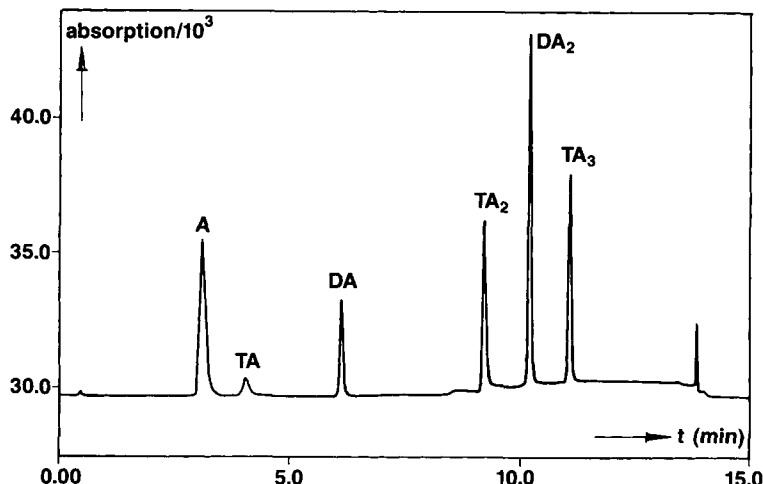


Figure 2 Typical HPLC chromatogram for a sample from a combined experiment (see Table I for symbols).

da. These data are sufficient to yield the ratios of rate constants required. Only with more scepticism are the absolute rate constants considered from the rate of reactions, i.e., $d[]/dt$.

The first part of this study was the *separate* kinetic experiments of D or T with A, primarily meant for determining substitution effects, but also useful for comparing the reactivities of D and T with A. These experiments were repeated under stoichiometric conditions. A typical set of results of D + A is given in Figure 3 together with the results predicted by random reaction, i.e., $K_{DA} = 1$. The values of K_{DA} and K_{TA} were calculated in terms of $d[]/d\alpha$, and with respect to $d[]/dt$ as well. For the parameter estimations the "principal" measuring data were

used, i.e., m_1, m_2 , and α_D or t for NPG and n_1, n_2, n_3 , and α_T or t for TMP. A relative tolerance of 3% was accepted for m_1 , and 2% for m_2 and α_D ; for n_1, n_3 , and α_T this was fixed at 3% and for n_2 at 2%. The absolute tolerance in the time was estimated to be 1 min. A measure for the fit is the sum of the squared eccentricities, $\sum e^2$, where e is defined by the ratio of the correction between measured and calculated values and the absolute tolerance:

$$e_x = (x_{\text{meas}} - x_{\text{calc}}) / \text{absolute tolerance.}$$

The results of the two independent experiments of NPG and tBBA are presented together in Figure 4. The mole fractions determined from the mea-

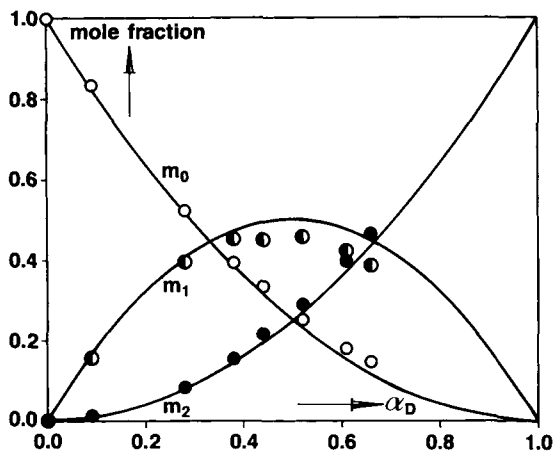


Figure 3 Comparison of experimental reaction states of NPG at 200°C, m_i (symbols), with the Bernoulli distribution (smooth curves).

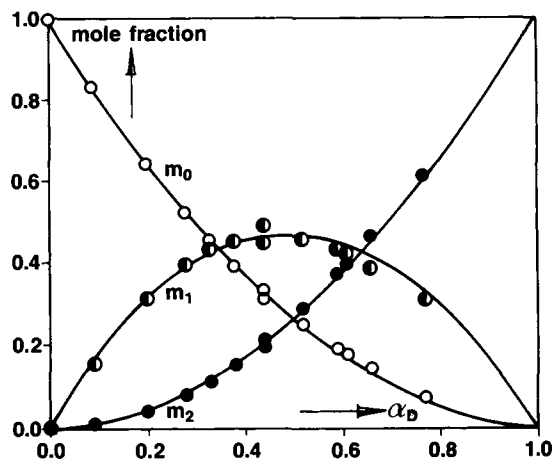


Figure 4 Combined results of the two separate experiments of NPG at 200°C; experimental m_i values (symbols), fitted with equations given in the Appendix with $K_{DA} = 1.18 \pm 0.02$.

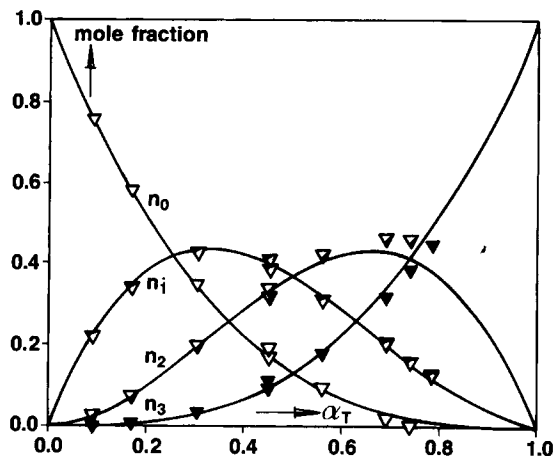


Figure 5 Experimental reaction states of TMP at 200°C, n_i (symbols), fitted with equations given in the Appendix with $K_{TA} = 1.06 \pm 0.01$.

measurements are plotted as point symbols and the curves are based on the optimum K_{DA} value determined with least squares analysis.

The results of the two independent runs of TMP with tBBA are in good agreement with the random reaction prediction, but the least squares analysis gives a very slight positive substitution effect, as demonstrated in Figure 5. The upper part of Table II gives an overview of the K values determined from the separate experiments.

An estimation of the absolute rate constants for the separate experiments, based on second-order reaction kinetics, is presented in the upper part of Table III. These data (which should be treated with more scepticism than the ratios, see above) indicate that k_1 is about 30% larger than k_3 , which suggests that NPG will react preferentially with tBBA in the

presence of TMP. This result is confirmed by the combined experiments discussed below.

The second part of this study involves the *combined* kinetic experiments of D and T with A. In the combined kinetic experiments the uncertainties in the absolute rate constants remain, but these cancel in the ratio of k_1/k_3 , because the experimental conditions (actual times) are identical. Primarily these experiments were thus meant to determine the reactivity ratio k_1/k_3 of NPG and TMP, respectively, with tBBA (see the Appendix). But these reactions also permitted an independent verification of the substitution effects obtained with the separate reactions. For these reactions stoichiometric ratios were chosen with $[NPG] = 1.5[TMP]$, so that $[-COOH] = [-OH]$ and also that $[-OH]_{NPG} = [-OH]_{TMP}$. A typical HPLC chromatogram for this type of combined reaction has been presented in Figure 2.

A first indication of differences in reaction kinetics is obtained by plotting α_{NPG} and α_{TMP} determined from the HPLC results versus $\alpha_{overall}$ determined from titration, as shown in Figure 6. These data confirm qualitatively that NPG has a higher reactivity than TMP, although part of the difference is caused by the positive substitution effect in NPG.

The ratios k_1/k_3 for the two combined experiments are presented in Table III together with the separate values for k_1 and k_3 . The results are in agreement with those of the separate experiments, but their variation is relatively large. The mean value of k_1/k_3 amounts to 1.4 ± 0.2 .

Apart from these intermolecular differences in reactivity, the present data also enable the determination of K_{AD} and K_{AT} . The results are collected in the lower part of Table II. It should be noted here that in the plots of $m_i(\alpha)$ and $n_i(\alpha)$ versus α the

Table II Substitution Effect Parameters for NPG and TMP Derived from Model Experiments ($T = 200^\circ\text{C}$)

Reaction	$K_{DA} = k_2/k_1$		$K_{TA} = k_4/k_3 = (k_5/k_3)^{1/2}$	
	From $d[\]/d\alpha$	From $d[\]/dt$	From $d[\]/d\alpha$	From $d[\]/dt$
D + 2A	1.23 ± 0.02	1.24 ± 0.03	—	—
T + 3A	1.11 ± 0.02	1.13 ± 0.03	—	—
	—	—	1.02 ± 0.01	1.06 ± 0.01
	—	—	1.08 ± 0.01	1.07 ± 0.01
1.5D + T	1.08 ± 0.02	1.09 ± 0.02	0.92 ± 0.01	1.00 ± 0.01
+ 6A	1.09 ± 0.02	1.23 ± 0.02	0.90 ± 0.01	0.94 ± 0.01
Mean	1.13 ± 0.07	1.17 ± 0.07	0.98 ± 0.08	1.02 ± 0.06

Table III Reaction Rate Constants Based on Second-Order Overall Kinetics ($T = 200^\circ\text{C}$)

Reaction	$10^3 k_1$ ($\text{kg mol}^{-1} \text{min}^{-1}$)	$10^3 k_3$ ($\text{kg mol}^{-1} \text{min}^{-1}$)	k_1/k_3
D + 2A	0.84 ± 0.02 1.06 ± 0.01	— —	
T + 3A	— —	0.67 ± 0.01 0.71 ± 0.01	1.3 ± 0.2
1.5D + T + 6A	1.04 ± 0.02 0.93 ± 0.01	0.59 ± 0.01 0.73 ± 0.01	1.8 ± 0.1 1.3 ± 0.1
Mean	1.0 ± 0.1	0.7 ± 0.1	1.4 ± 0.2

individual α_D and α_T were used and not the values of α_{overall} . Figures 7 and 8 show typical results for a combined experiment; the considerably lower values of the eccentricities in the plots versus α_D or α_T compared with those versus α_{overall} are in favor of this approach. The values of the substitution effect parameters compare favorably with those of the separate experiments, so that a mean value was calculated for all experiments combined (see bottom of Table II).

Substitution effects have been determined by Gordon et al.^{4,5} for similar model compound reactions. As in the present work, monofunctional acids were reacted with multifunctional alcohols. For pentaerythritol and trimethylol ethane, reacted separately with adipic acid, values of $K = 1.5 \pm 0.1$ were found in bulk reactions.⁴ Another monofunctional acid, lauric acid, was also reacted with the tetra- and trifunctional alcohols mentioned above, which yielded values of $K = 1.4 \pm 0.1$ and 1.3 ± 0.1 .⁵

In the present study no significant substitution effect was found for the trifunctional alcohol, and a

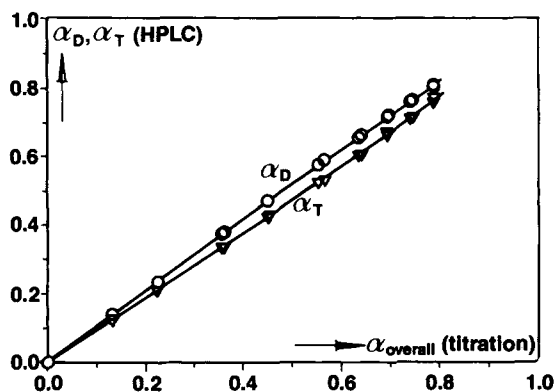


Figure 6 Comparison of α_D and α_T determined from HPLC with α_{overall} determined from titrations.

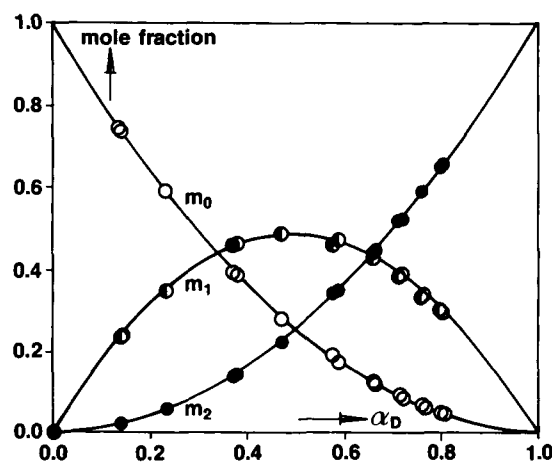


Figure 7a Experimental reaction states of NPG versus α_{NPG} in a combined experiment (symbols), fitted with equations given in the Appendix with $K_{\text{DA}} = 1.08 \pm 0.02$; with $\sum e_{m_1}^2 = 2$, $\sum e_{m_2}^2 = 0.4$, and $\sum e_a^2 = 1$ (17 data).

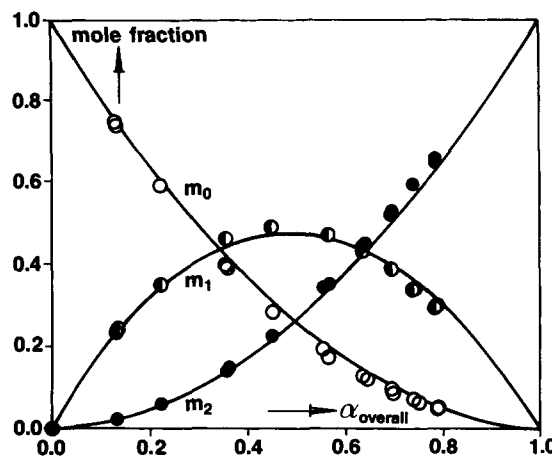


Figure 7b As above but now versus α_{overall} ; $K_{\text{DA}} = 1.15 \pm 0.02$; with $\sum e_{m_1}^2 = 14$, $\sum e_{m_2}^2 = 4$, and $\sum e_a^2 = 17$.

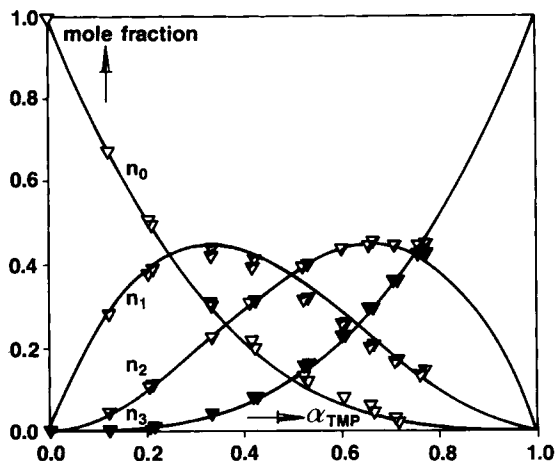


Figure 8a Experimental reaction states of TMP versus α_{TMP} in a combined experiment (symbols), fitted with equations given in the Appendix with $K_{\text{TA}} = 1.00 \pm 0.01$; with $\sum e_{n_1}^2 = 1.6 \times 10^2$, $\sum e_{n_2}^2 = 0.5 \times 10^2$, $\sum e_{n_3}^2 = 1.6 \times 10^2$, and $\sum e_i^2 = 4 \times 10^3$ (18 data).

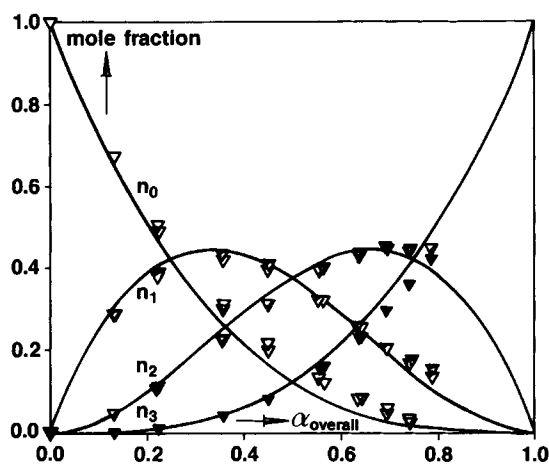


Figure 8b As above but now versus α_{overall} ; $K_{\text{TA}} = 1.00 \pm 0.01$; with $\sum e_{n_1}^2 = 3.9 \times 10^2$, $\sum e_{n_2}^2 = 2.5 \times 10^2$, $\sum e_{n_3}^2 = 1.9 \times 10^2$, and $\sum e_i^2 = 22 \times 10^3$.

small one, $K = 1.15 \pm 0.07$, was found for the difunctional alcohol. The differences between the experimentally determined substitution effects may be in part due to the actual conditions. In the work of Gordon et al.^{4,5} the system was closed and the vapor pressure was used to monitor the reactions. In this work it was open and water was allowed to escape. The presence/absence of water may result in a change of the overall reaction kinetics. How this would affect the value of substitution effects should be further explored. An alternative explanation of the difference in the values of K may be the monoacid coreactant or other experimental conditions which are known to have an important effect.⁶

In summary, substitution effects and relative reaction rates were determined for model esterification reactions of a monofunctional acid and a di- and trifunctional alcohol in an open melt phase reaction. Small substitution effects were found for NPG but none in TMP. The alcohol groups of NPG have a 40% higher reactivity than those of TMP.

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APPENDIX: DIFFERENTIAL EQUATIONS FOR REACTION OF (D + T) + A

$$d[D]/dt = -2k_1[D][A] \quad (\text{A-1})$$

$$d[DA]/dt = +2k_1[D][A] - k_2[DA][A] \quad (\text{A-2})$$

$$d[DA_2]/dt = +k_2[DA][A] \quad (\text{A-3})$$

$$d[T]/dt = -3k_3[T][A] \quad (\text{A-4})$$

$$d[TA]/dt = +3k_3[T][A] - 2k_4[TA][A] \quad (\text{A-5})$$

$$d[TA_2]/dt = +2k_4[TA][A] - k_5[TA_2][A] \quad (\text{A-6})$$

$$d[TA_3]/dt = +k_5[TA_2][A] \quad (\text{A-7})$$

$$d[A]/dt = -2k_1[D][A] - k_2[DA][A] - 3k_3[T][A] - 2k_4[TA][A] - k_5[TA_2][A] \quad (\text{A-8})$$

where $k_2 = k_1K_{DA}$, $k_4 = k_3K_{TA}$, and $k_5 = k_3K_{TA}^2$. Boundary conditions: at $t = 0$, $[D] = [D_0]$, $[T] = [T_0]$, and $[A] = [A_0]$, all other concentrations being equal to zero.