Polyesterification and isomerization of maleic anhydride and 1,6-hexane diol as studied by ^{1}H and ^{13}C n.m.r.

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The polyesterification and isomerization reaction of 1,6-hexane diol and maleic anydride in a melt without catalyst was studied by ^{13}C and ^{1}H n.m.r. spectroscopy. The structure and concentration of oligoester species during the polyesterification and isomerization were determined depending on the reaction temperature and time. According to the number and configuration of repeating units determined from ^{1}H n.m.r. spectra kinetics of both reactions were also considered. The degree of isomerization is continuously increasing in the investigated reaction range.

(Keywords: ^{13}C nuclear magnetic resonance; ^{1}H nuclear magnetic resonance; polyesterification; *cis–trans* isomerization; reaction kinetics; 1,6-hexane diol; maleic anhydride)

INTRODUCTION

The kinetics of the polycondensation reaction of maleic anhydride and different glycols with or without catalyst has been the subject of numerous investigations[1–5]. However, various interpretations of the results depending on the reaction media and reaction treatment have been discussed[6,7].

In the course of the polyesterification reaction the *cis–trans* isomerization of the maleic anhydride takes place[8]. According to the previous results[9–11] the isomerization process is affected by the glycol component, its stereochemical structure and chain length. However, the results concerning the change of fumarate content during the polyesterification are not univocal. From the findings of Vancsó–Szmercsanyi *et al.*[11] *cis–trans* isomerization, after the elapse of a certain time, approaches a constant value. This contradicts the results that the fumarate content changes continuously with the time of polycondensation[9]. In order to contribute to a better understanding of both polyesterification and isomerization processes, reaction of 1,6-hexane diol–maleic anhydride system in the absence of solvent was studied through the microstructure of the growing polyester chain as deduced from ^{1}H and ^{13}C n.m.r. spectra.

The study was carried out with two objectives: (a) to study polyesterification reaction following the type and length of polyesters formed during the reaction at different temperatures and (b) to follow simultaneously the isomerization reaction depending on the reaction temperature, reaction time and the length of the growing polyester chain.

EXPERIMENTAL

The polyesterification of equivalent amounts (1 mole) of reagent grade 1,6-hexane diol (Aldrich) and maleic anhydride (Kemika, Zagreb), used without further purification, was carried out without catalyst in a melt under nitrogen gas with continuous stirring. The reactants were mixed at room temperature and then heated to the reaction temperatures 120°C, 140°C, 160°C and 180°C, respectively. The aliquots were taken from the reaction mixture at different reaction time intervals. For each aliquot the acid number of oligoester was determined by a standard method and the corresponding molecular weight by osmometric measurements in methyl ethyl ketone solution on a Mechrolab 301 A osmometer.

^{13}C n.m.r. spectra were recorded at 25.05 MHz on a JEOL FX-100 spectrometer using the internal deuterium lock. The spectral width was 6000 Hz giving a digital resolution of 0.75 Hz for 16000 sampling and transformation points. However, due to variations in temperature and sample concentrations chemical shifts are quoted as mean values of several measurements to one decimal place only. The samples, dissolved in deuteroacetone immediately after the aliquots were taken, were measured at room temperature in 5 mm tubes with tetramethyl silane (TMS) as internal standard.

^{1}H n.m.r. spectra of the same samples dissolved in DMSO-d$_6$ were recorded at 89.55 MHz on a JEOL FX-90Q spectrometer. The spectral width was 1000 Hz and the digital resolution 0.24 Hz.

RESULTS AND DISCUSSION

The ^{1}H n.m.r. spectra of polyesters of maleic anhydride and various glycols show two well separated absorption regions of fumaric and maleic olefinic protons, respectively[12]. The number of peaks and their chemical shifts in each subregion are dependent on the glycol structure and the nature of the solvent. In the case of 1,2-propylene glycol a great number of overlapping peaks ($\Delta\delta \sim 0.08$ ppm) are observed[13] while in the ethylene glycol and some related polyesters two types of proton absorptions can be resolved[14]. Polyesters of maleic anhydride (MAn) and 1,6-hexane diol (HD) in acetone

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solution exhibit unresolved or slightly overlapped peaks in these subregions. In DMSO-d_6 solution two types of olefinic proton absorptions (*Figure 1*) have been observed regardless of *cis–trans* isomerization:

A type: HOOC–CH=CH–COOR
B type: ROOC–CH=CH–COOR

R denotes the hexane diol unit or polyester chain. Both protons in the A type, although chemically not identical, have the same chemical shift. Consequently, the absorption regions of the A and B types are proportional to the acid end groups and repeating units in the chain, respectively[15]. The peaks of free maleic and fumaric acid are present only at the beginning of the polycondensation reaction. From the olefinic absorptions a concentration of the corresponding species during the polyesterification can be followed. Furthermore, the molecular weight as well as the kinetics of polycondensation and *cis–trans* isomerization can be determined.

Molecular weight of oligoesters

The oligoester with n repeating units has $\frac{n-1}{n}\cdot 100$ per cent of B type olefinic protons. At low molecular weights (below 1500) where the concentration of end groups is relatively significant, the molecular weight $\bar{M}_n$ can be determined with the great accuracy from the ^{1}H n.m.r. spectra using the relation:

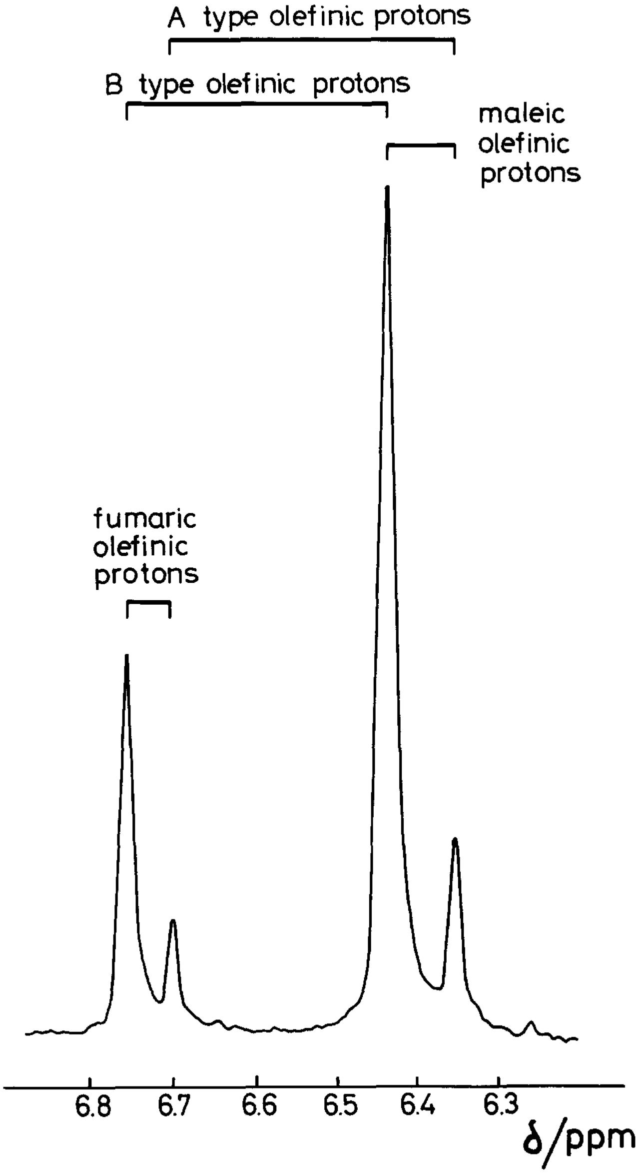


Figure 1 ^{1}H n.m.r. olefinic absorptions of DMSO-d_6 solution of an oligoester prepared at 160°C

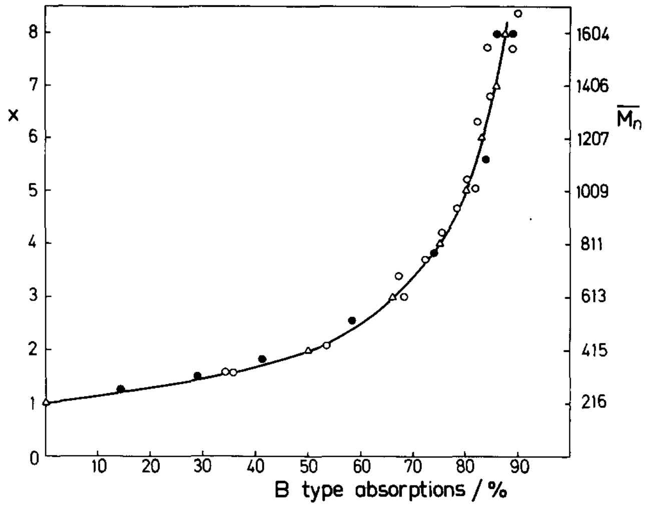


Figure 2 The number of repeating units (x) and molecular weight ($\bar{M}_n$) of various oligoesters as a function of B type olefinic absorptions in ^{1}H n.m.r. spectra: calculated (△), determined by osmometry (○) and acid number measurements (●)

$$\bar{M}_n = \frac{198.2}{1 - B\cdot 10^{-2}} + 18.0$$

where B is the percentage of the olefinic B types in all the oligoester olefinic protons, 198.2 and 18.0 are the molecular weights of repeating unit and end groups, respectively. Molecular weights of the samples determined from the osmometric or acid number measurements are presented in *Figure 2* along with the values calculated from the ^{1}H n.m.r. spectra. The curve in *Figure 2* represents the calculated number of repeating units (or $\bar{M}_n$) vs. B type n.m.r. absorptions. Molecular weights of a number of samples determined by osmometric and acid number measurements with the corresponding percentage of the B type absorption are in a good agreement with the calculated curve. $\bar{M}_n$ was calculated from the acid number according to the relation:

$$\bar{M}_n = \frac{56\,100}{\text{acid number}}\cdot 1.167$$

An increase of the theoretical value (taken into account by the factor 1.167) which has a very small influence at higher molecular weights is due to the nonequivalent concentration of carboxyl and hydroxyl end groups in the early stages of the polycondensation reaction[16]. $\bar{M}_n$ of oligoesters after 400 min of the reaction were $5\cdot 10^2$, $8\cdot 10^2$, $1.2\cdot 10^3$ and $2\cdot 10^3$ at 120°C, 140°C, 160°C and 180°C, respectively. The fumarate contents at the corresponding reaction temperatures were 10, 21, 29 and 55%, respectively.

Polycondensation reaction

The reaction steps and growth of the oligoester chain were followed by ^{13}C n.m.r. spectroscopy. Similarly as for the reaction of maleic anhydride and 1,2-propylene glycol[13] the monoester and free maleic acid (MAc) are formed at the beginning (*Figure 3*). The subsequent reaction steps are characterized by the presence of the Mal-HD-Mal diester and higher oligoesters with partially isomerized acid moiety. Unlike the oligoesters derived from 1,2-propylene glycol, where maleic and fumaric carbon atoms are sensitive to different ester configurations, the symmetry of HD permits only one ester form. Consequently, the ^{13}C n.m.r. spectra represent absorptions of the diol and diacid units depending on their relative positions along the chain (*Figure 4*). In the diacid absorption region *cis* and *trans* isomers are distinguished. All the ^{13}C chemical shifts of characteristic signals are listed in *Table 1*. Furthermore, in the spectra of the oligoesters having approximately two repeating units some additional hexane diol and maleic olefinic peaks are observed which are probably due to the interactions between specific oligoester conformations in the solution.

The number of repeating units determined from ^{1}H n.m.r. spectra were attempted to attribute to the kinetics of polycondensation reation. It has been shown by Fradet and Marechal that the kinetical consideration based on the experimental data of polycondensation may lead to a quite different conclusion[6]. Generally, it depends on whether the whole reaction course is considered or certain reaction regions separately. It is known[5,17] that the initial stage (up to 80% conversion) and later stage of the reaction (above 93% conversion) kinetically differ from the middle conversion region. Furthermore the overall order is influenced by the polarity of the reaction medium and the presence of catalyst[7]. Our results for the middle conversion region (*Figure 5*) are in agreement with the third order reactions found in the stoichiometric non-catalysed reactions of diols and diacids, diols and monobasic acids and alcohols and monobasic acids[6]. However, this finding is in disagreement with the second order reaction found earlier for the same system[1].

Isomerization reaction

In the previous papers the influence of various glycols on the maleate–fumarate isomerization during the polycondensation was investigated polarographically after cold saponification[9–11]. However, the statement of Vanscó-Szmercsanyi *et al.*[11] that the *cis–trans* isomerization after the elapse of a certain time approaches the constant value contradicts the results that the fumarate content of polyesters changes with a change of the time of polycondensation as reported by Voigt[9]. In order to solve this contradiction a nondestructive method such as ^{1}H n.m.r. was applied. The extent of the *cis–trans* isomerization was determined from the concentrations of four characteristic acid sequences throughout the whole course of the polycondensation reaction (*Figure 1*). These four olefinic absorptions corresponding to the A and B ester sequences are present during the reaction in each of the four syntheses performed, regardless of the reaction temperature. However, the concentration ratio of these species (expressed as the numerical fraction of repeating units) during the reaction is temperature dependent. The numerical fraction of repeating units of the four species as a function of the reaction time for the synthesis carried out at 160°C is illustrated in *Figure 6*. In the investigated reaction range comparable to the previous experiments[11] a continuous increase of both fumaric types, as well as a growth of the maleic B type ester is observed. The amount of maleic end groups is slightly decreasing which indicates their conversion into the fumaric form. A similar behaviour of the oligoesters growth was observed at other

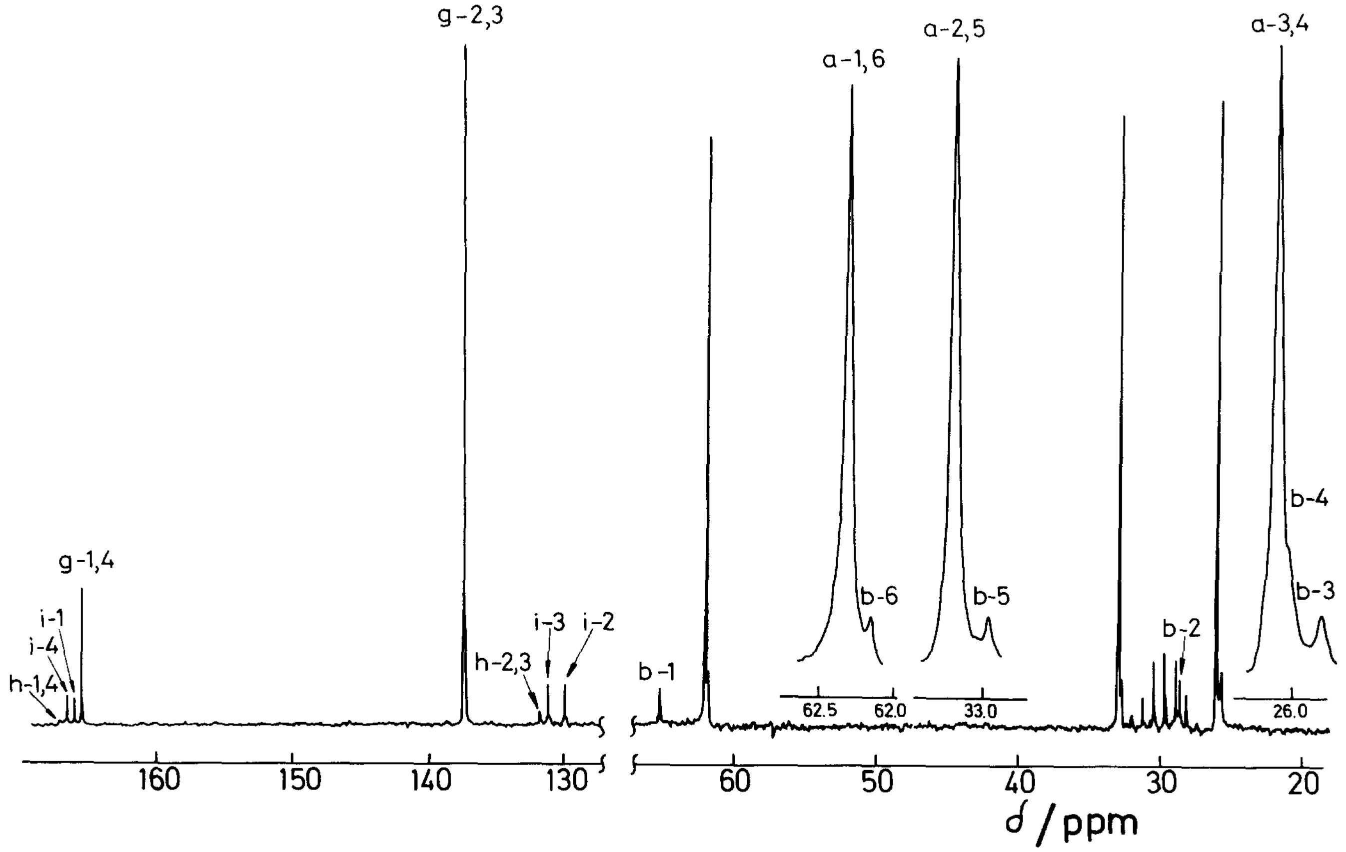


Figure 3 ^{13}C n.m.r. spectrum of the very first sample in the polycondensation reactions. The peaks are denoted as in *Table 1*

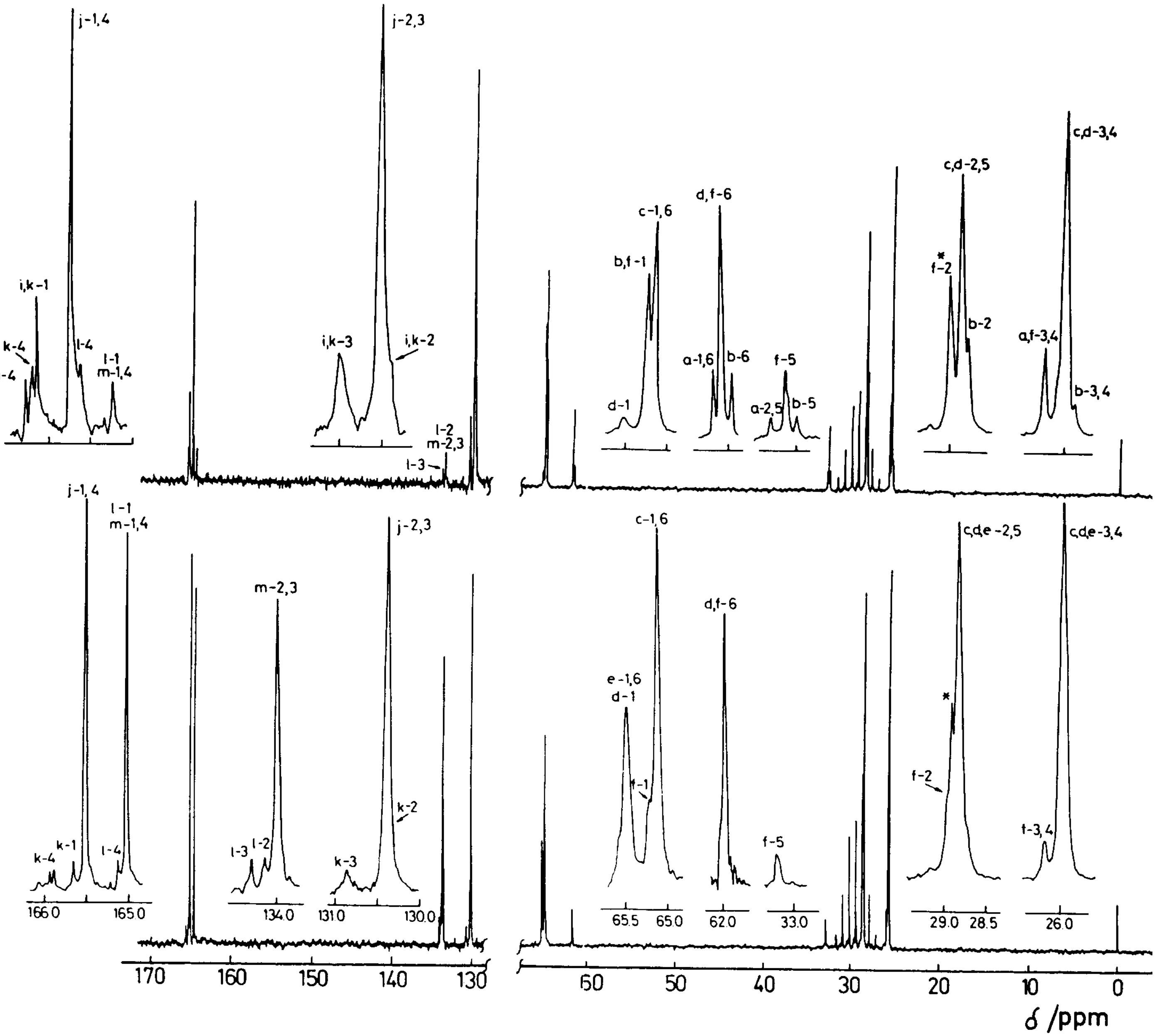


Figure 4 ^{13}C n.m.r. spectra of oligoesters prepared at 120°C (a) and 180°C (b). The peaks are denoted as in *Table 1*. An asterisk denotes acetone-d_6 signals

temperatures. At lower reaction temperatures the number of fumaric ester types is considerably smaller. For instance, at 120°C the amount of both A and B type fumaric ester units equals 10% of the total oligoester chain. On the other hand at 180°C the number of both fumaric ester sequences in the oligoester chain and maleic B type is higher in the same reaction range. A relatively long oligoester chain and high degree of isomerization contribute to the considerable diminishing of the maleic end groups (A type).

Figure 7 represents the parallel change of the repeating maleic and fumaric units for all four syntheses as a function of the reaction time. This presentation enables us to follow at the same time isomerization and polycondensation reaction via overall repeating units at each reaction time. The simultaneous increase of the number of both maleic and fumaric units with the time, as indicated in *Figure 7*, is a consequence of the growth of the chain accompanied by the isomerization. Such a process is strongly affected by the reaction temperature.

This consideration shows that usual presentation of the isomerization reaction in terms of the fumarate percentage is inadequate for describing the details of the reaction. For instance, in the reaction at 180°C the fumarate content is about 51% after both 285 and 345 min, but the numerical fractions of fumaric repeating units (x_i) are different: 3.80 and 4.45, respectively. Hence, in terms of percentage, the content of fumarates stays constant, but actually the total amount of fumarates is increasing with reaction time owing to the continuous isomerization process.

Since both the polycondensation and isomerization reactions occur simultaneously the dependence of the fumaric units on the number of oligoester repeating units (chain length) at different temperatures is shown in *Figure 8*. All the oligoesters consisting of one to approximately three repeating units have similar fumarate content depending on the reaction temperature. However, as the reaction time and temperature increase and the oligoesters chain grows, the fumarate content becomes greater.

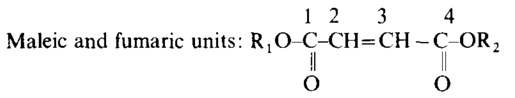
The fumarate content as well as the oligoester chain length depend on the type of glycol. In the case of the symmetric 1,6-hexane diol molecule polycondensation and isomerization reaction occur sumultaneously. However, in the polyesterification of maleic anhydride and 1,2-propylene glycol[13] a significant amount of isomerization, due to the stereochemical effects, occurs already at the initial stage of the reaction when the molecules are mostly in monoester and diester forms, regardless of the temperature of the synthesis.

Table 1 ^{13}C chemical shifts (ppm from TMS) of different acid and diol sequences

1 2 3 4 5 6
1,6-hexane diol units: $R_1O{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}OR_2$
C-atom

Species	R_1	R_2	C-1	C-6	C-2	C-5	C-3	C-4
a	H	H	62.2		33.1		26.1	
b	Mal	H	65.3	62.0	28.7	32.8	25.8	26.0
c	Mal	Mal	65.2		28.9		25.9	
d	Fum	Mal	65.5	62.1	28.9		25.9	
e	Fum	Fum	65.5		28.9		25.9	
f	R'*	H	~65.3	62.1	29.0	33.0	26.1	26.1

1 2 3 4



Maleic and fumaric units: $R_1O{-}\underset{\underset{O}{\|}}{C}{-}CH{=}CH{-}\underset{\underset{O}{\|}}{C}{-}OR_2$

C-atom

	R_1	R_2	C-1	C-4	C-2	C-3
	Maleic form					
g	MAn		165.6		137.8	
h	H	H	166.9		131.8	
i	HD	H	166.0	166.6	130.3	131.1
j	HD	HD	165.5		130.4	
k	R''†	H	166.0	166.2	~130.3	~131.1
	Fumaric form					
l	R''†	H	165.0	165.1	134.0	134.3
m	HD	HD	165.0		133.9	

* *R'* is the rest of the oligoester chain with the maleate unit as the first neighbour

† *R''* is the rest of the oligoester chain

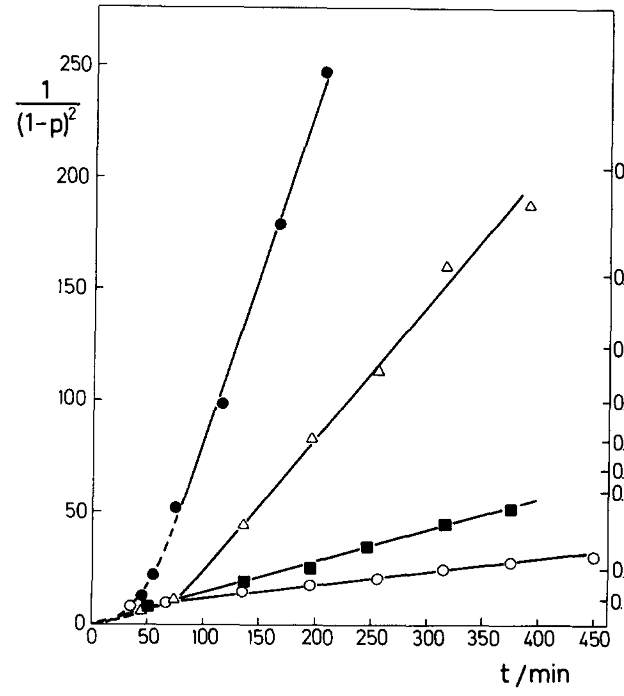


Figure 5 Third order plot of polydensation reactions at 120°C (○), 140°C (■), 160°C (△) and 180°C (●)

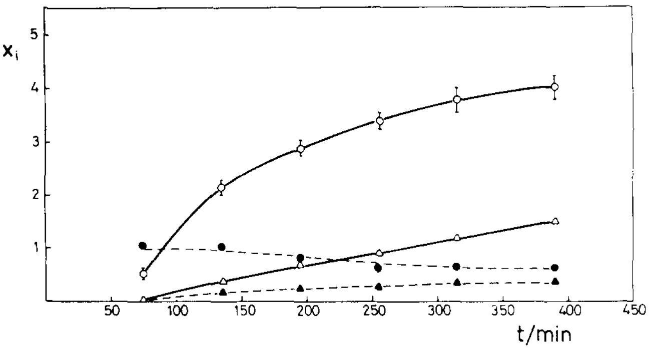


Figure 6 The numerical fraction of repeating units (x_i) for an oligoester prepared at 160°C as a function of the reaction time: maleic A type (●), maleic B type (○), fumaric A type (▲) and fumaric B type (△). The oligoester number of repeating units (x) is the sum of all four x_i

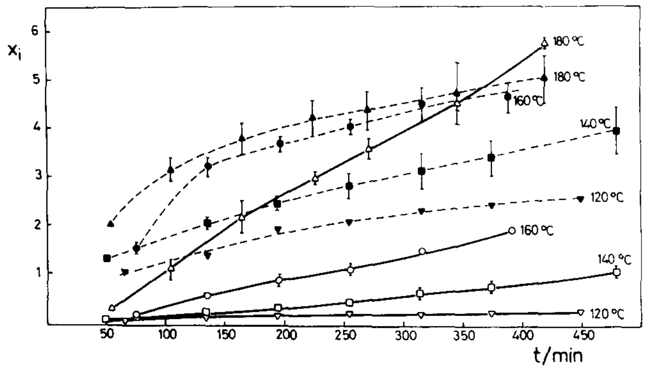


Figure 7 The numerical fraction of repeating units (x_i) for a series of oligoesters prepared at different temperatures as a function of the reaction time. The full line indicates fumarate and dotted line maleate units, respectively

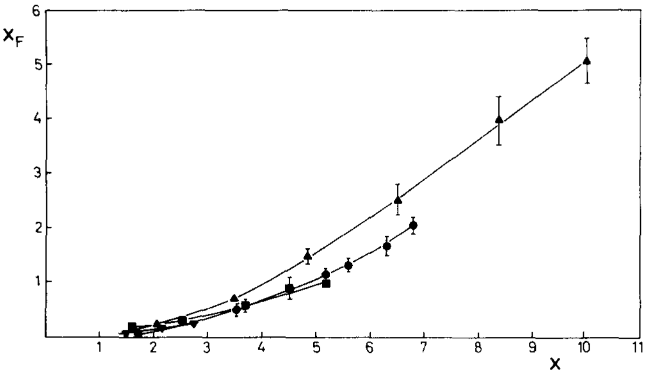


Figure 8 The numerical fraction of repeating fumaric units (x_F) as a function of the oligoester repeating units (x) at different reaction temperatures: 120°C (▼), 140°C (■), 160°C (●) and 180°C (▲)

The isomerization process follows the second order kinetic equation[18]:

$$k=\frac{1}{t}\left(\frac{1}{a-x}-\frac{1}{x}\right)$$

where t is the reaction time, a the initial concentration of maleic anhydride (moles kg^{-1}) and x the concentration of the corresponding fumarate type at time t. The rate constants k during the polyesterification are presented in

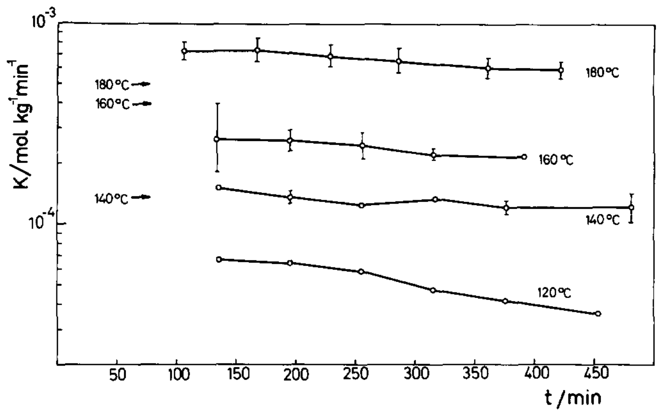


Figure 9 The rate constant k for oligoesters prepared at different temperatures as a function of the reaction time. The arrows indicate values from ref. 11

Figure 9. In this Figure the values of the rate constants reported by Vancsó–Szmercsanyi *et al.*[11] which are determined at the beginning of the steep sections of the isomerization curves are also indicated. Since the temperature during the first stage of the reaction was not stable enough the corresponding data at early sampling times were omitted in *Figure 9*. In order to obtain more accurate data for this stage of the reaction, the preheated system will be studied separately using the same technique. The activation energy calculated from the Arrhenius equation is 63.4 ± 2 kJ mol^{-1}, which is in a good agreement with the values obtained previously using different methods[11,18].

CONCLUSION

The structure of the growing polyester chain, the number of the repeating units and consequently the concentration of different species during the polyesterification at different reaction temperatures can be followed by ^{13}C and ^{1}H n.m.r. spectroscopy. Furthermore, for the oligoesters of lower molecular weights (below 1500) having a symmetric diol component, $\bar{M}_n$ can be determined efficiently with the great accuracy from the olefinic absorptions in ^{1}H n.m.r. spectra.

The number of overall repeating units deduced from the ^{1}H n.m.r. spectra as well as the number of maleic and fumaric units enabled us to follow simultaneously both polyesterification and isomerization reaction quantitatively including reaction kinetics. This paper demonstrates the way how to determine microstructure of the chain and the course of such a reaction by using a single spectroscopic method without additional chemical experiments.

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