Investigations of the Kinetics of Maleate–Fumarate Isomerization during the Polyesterification of Maleic Anhydride with Different Glycols

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Synopsis

The rate of isomerization during the polyesterification of maleic acid or maleic anhydride depends on the structure of the glycol used: the longer the chain of the glycol, the lower the isomerization rate. The rate constants differ greatly from one case to another. Thus, the difference in the reaction rate constants depends mainly on the steric effects caused by the different types of glycols used in the polycondensation. The isomerization approaches a constant value, which after a certain time depends on the structure of the glycol and the temperature of the condensation. The activation energies calculated from the rate constants would fall at about 20 ± 4 kcal./mole. This value for the activation energy corresponds to that reported in the literature for the transformation of maleic acid into fumaric acid. The reaction apparently follows second-order kinetics due to the catalytic effect of the maleic acid on the isomerization.

Introduction

It is known that the polyester formed in the course of the polycondensation of maleic acid or maleic anhydride with glycols consists partly or wholly of fumarate. There are some differences in the properties of maleates and fumarates, and therefore it is worthwhile to study the isomerization in this case not only from the theoretical but also from the practical point of view.

In one of our earlier papers[1] we reported qualitative results confirming that the degree of isomerization is affected by the type of the glycol as well as modifying monomer used in the polycondensation.

We tried in our recent investigation to complete the picture quantitatively of the *cis–trans* transformation taking place during the polyesterification of maleic anhydride.

It is necessary first to review the theories concerning the transformation of maleic acid into fumaric acid itself.

An evaluation of previous studies of maleic acid isomerization has been published by Davies and Evans.[2] These authors investigated the isomerization of maleic acid at 115 and 170°C. in aqueous solution both with and without hydrochloric acid catalyst. They established the reaction to be second-order and found an evidence of autocatalytic effects if no catalyst

was present. The activation energy was calculated as $E = 18.4$ kcal./mole for the reaction catalyzed by hydrochloric acid and $E = 21 \pm 4$ kcal/mole for the reaction carried out in the absence of catalyst, but in the presence of water.

The same authors agreed with the theory of Nozaki and Ogg[3] for the mechanism of reaction based on the hydration of the carbonyl group. The actual catalysts are H_3O^+ ions formed in the presence of water according to eq. (1);

$$\text{fumaric acid} + HA \quad (1)$$
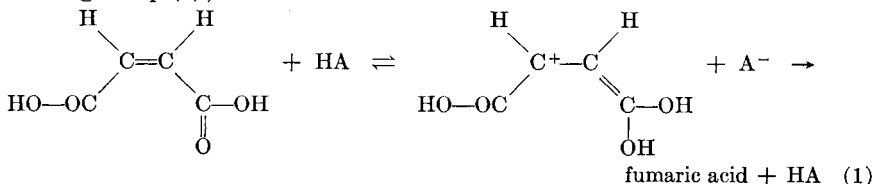
In the case of autocatalyzed reaction the HA represents an H_3O^+ ion which will be formed upon the catalytic effect of a maleic acid molecule (MA) through the addition of one molecule of water. No satisfactory explanation of the mechanism of the hydration itself was found. Nevertheless it was established that the reaction is bimolecular in the absence of an acid catalyst.

With regard to earlier quantitative investigations of the kinetics of isomerization of maleic acid and its esters, the papers by Kistiakowsky and his co-workers[4-6] should be mentioned. They reported 26.5 kcal./mole for the activation energy of the reaction. The maleate–fumarate isomerization involved in polycondensation was discussed later by several authors. Bradley and his co-workers[7] stated that solely maleate is produced from hexanediol and maleic acid by polycondensation carried out at 100°C. Batzer and Mohr[8] obtained a similar result; Voigt, on the contrary, did not obtain pure maleate, the polyester prepared by him contained some fumarate as well.

In the course of his experiments Voigt[9] investigated the isomerization of maleic acid esterified with different glycols and established that the fumarate content of the polyester attained depends on the glycol component; in the case of a glycol with rather long carbon chain, less fumarate was detected. The author explained this finding on the basis of the fact that more time is required to achieve an identical degree of condensation in the case of a glycol with a shorter carbon chain so that the isomerization can proceed further. The findings were only qualitative.

Klaban[10] proceeded further and carried out a kinetic investigation of the isomerization of diesters and polyesters produced from maleic acid upon heating after the completion of the condensation. He stated that the glycol component of the esters would not influence the isomerization. It should be emphasized that this statement refers to diesters and that the investigations of the author are of a quantitative character.

From this short survey of the literature it is seen that data on the kinetics of the *cis–trans* transformation during polycondensation are rather in-

complete.   Our own investigations are thus an attempt to complete the picture in this respect.

Experimental

In the course of our work we investigated the kinetics of maleate–fumarate isomerization taking place simultaneously with the polycondensation at different temperatures with each of the following glycols: ethylene glycol, 1,2-propylene glycol, diethylene glycol, and 1,6-hexamethylene glycol.
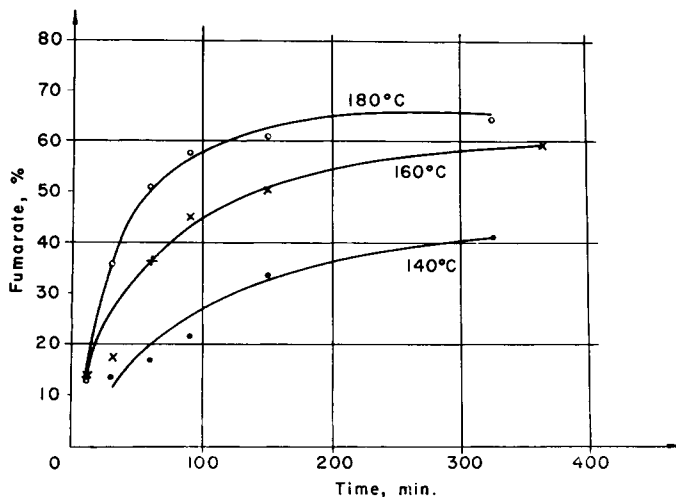

Fig. 1. *cis–trans* Isomerization in the polycondensation of maleic anhydride with ethylene glycol at different temperatures.
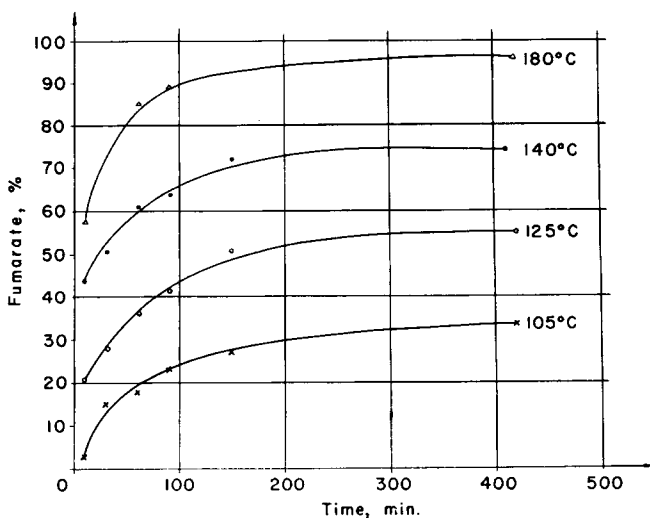

Fig. 2. *cis–trans* Isomerization in the polycondensation of maleic anhydride with 1,2-propylene glycol at different temperatures.
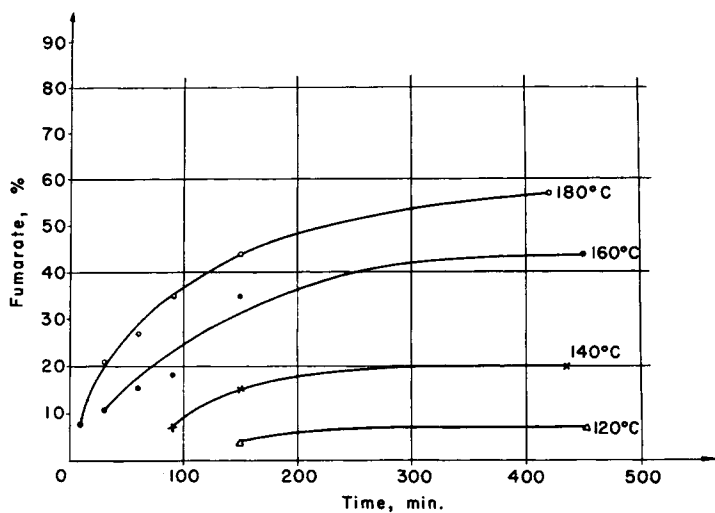
Fig. 3. *cis–trans* Isomerization in the polycondensation of maleic anhydride with diethylene glycol at different temperatures.
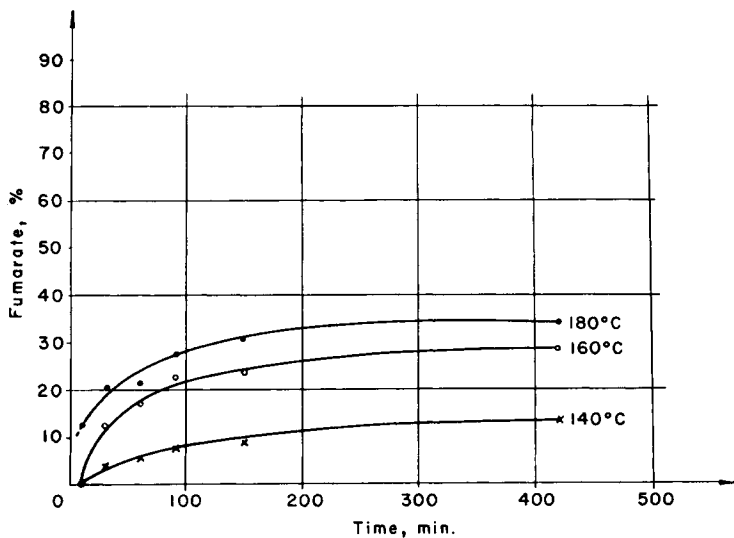

Fig. 4. *cis–trans* Isomerization in the polycondensation of maleic anhydride with 1,6-hexamethylene glycol at different temperatures.

In the course of polycondensation the acid number of the aliquots was determined. The ratio of maleic acid to fumaric acid was then polarographically assigned[11] after cold saponification.

The results are presented in Figures 1–4.

The curves are identical in shape, and they differ only in height, which depends on the temperature and the type of glycol used. The highest degree of isomerization appears in the case of 1,2-propylene glycol. The
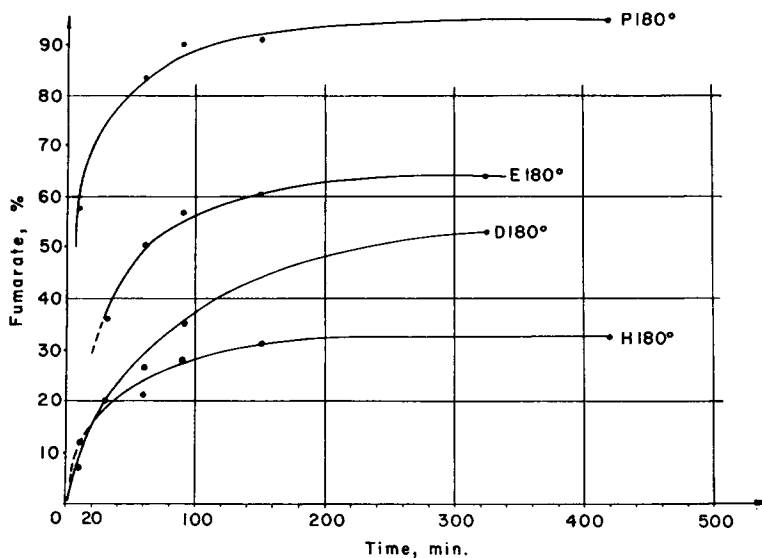
Fig. 5. *cis–trans* Isomerization in the polycondensation of maleic anhydride with various glycols at 180°C.
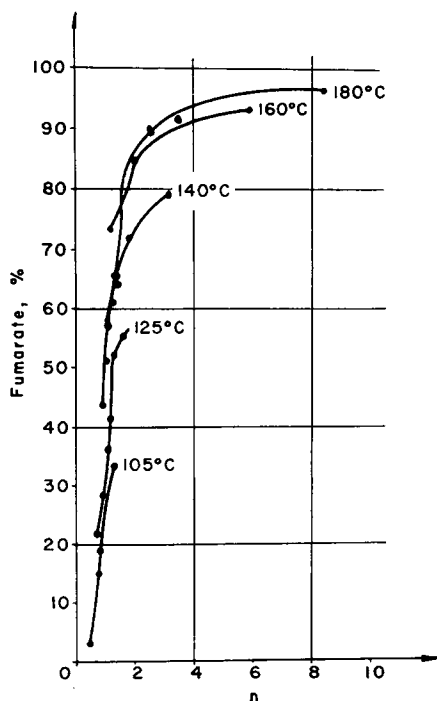

Fig. 6. *cis–trans* Isomerization in the polycondensation of maleic anhydride with 1,2-propylene glycol at different temperatures as a function of the average number of ester bonds.

fumarate content reaches about 35% in condensation at 105°C., whereas at 180°C., this content amounts to 95%.

In the case of ethylene glycol there was a low degree of isomerization at 120°C., while at 180°C. the ultimate value was 65% fumarate.
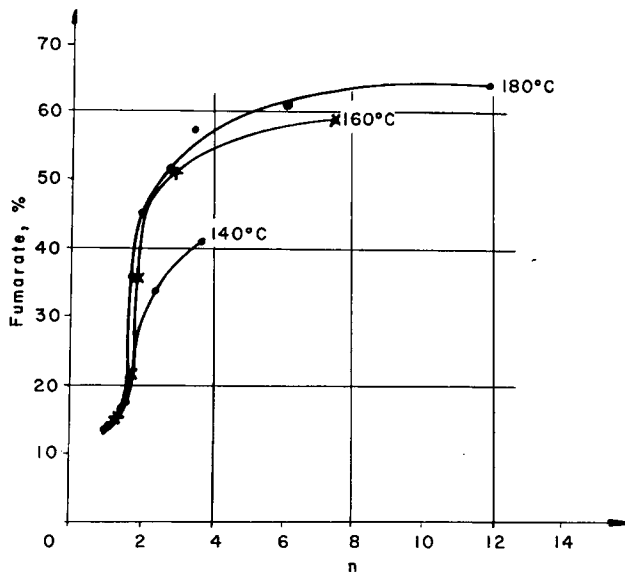

Fig. 7. *cis–trans* Isomerization in the polycondensation of maleic anhydride with ethylene glycol at different temperatures as a function of the average number of ester bonds.
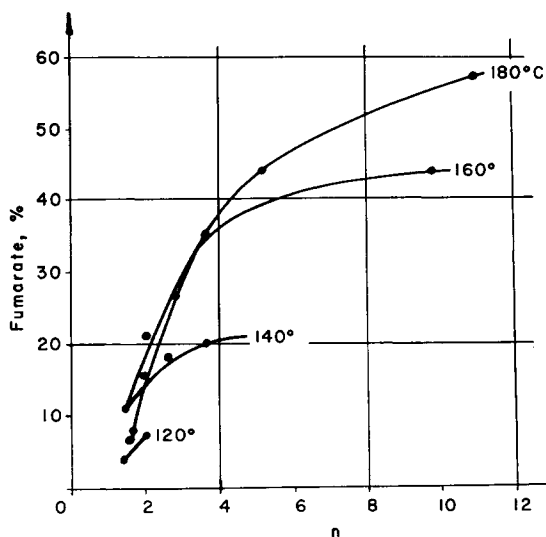

Fig. 8. *cis–trans* Isomerization in the polycondensation of maleic anhydride with diethylene glycol at different temperatures as a function of the average number of ester bonds.

With glycols having longer carbon chains, such as diethylene and 1,6-hexamethylene glycols, the level of isomerization falls. In the case of the former glycol the ultimate isomerization at 180°C. is about 55%, while in the case of the latter it is only 35%.

The fumarate content in per cent refers to the maleic acid initially present in the reaction mixture.

The figures clearly show that *cis–trans* transformation, after the elapse of a certain time, approaches a constant value. This finding contradicts the fact reported in the literature that the fumarate content of the polyesters changes with different glycols with the change of the time of polycondensation.[9]

Figure 5 illustrates the isomerization values attained by different glycols on polycondensation at 180°C.
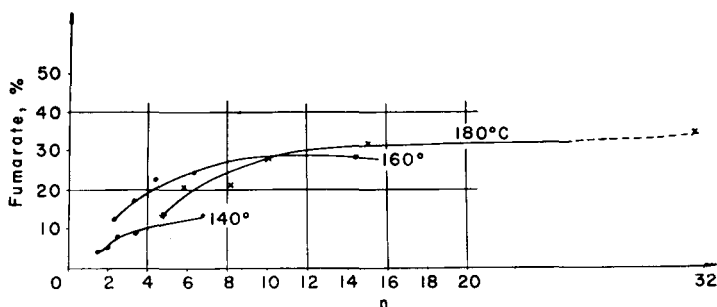

Fig. 9. *cis–trans* Isomerization in the polycondensation of maleic anhydride with 1,6-hexamethylene glycol at different temperatures as a function of the average number of ester bonds.

Since the type of glycol has a direct stereochemical effect on the isomerization process occurring simultaneously with the polycondensation, Figures 6–9 illustrate the isomerization at different temperature, as a function of the average number of ester-bonds.

Figure 6 shows that isomerization with 1,2-propylene glycol occurs predominantly at the different temperatures at a very low value of ester bonds ($n = 1$–2).

Figure 7 demonstrates the stereoisomeric transformation taking place in the course of the polycondensation of ethylene glycol and maleic acid, as a function of the number of ester bonds. In this case the isomerization occurs in a narrow range of n but still a wider range than the number of ester bonds shown in the case of 1,2-propylene glycol.

Figure 8 refers to diethylene glycol. It may be seen that the critical n interval is still wider than in the preceding case.

Figure 9, which refers to 1,6-hexamethylene glycol, shows quite flat, prolonged curves.

Discussion

Depending on their structure the glycols influence the isomerization during polycondensation. The spatial arrangement of the atoms within the ester and polyester molecule, respectively, is more favorable in the case of the fumarates than with the maleates. The molecular strain associated with the maleic molecule depends on the construction of the
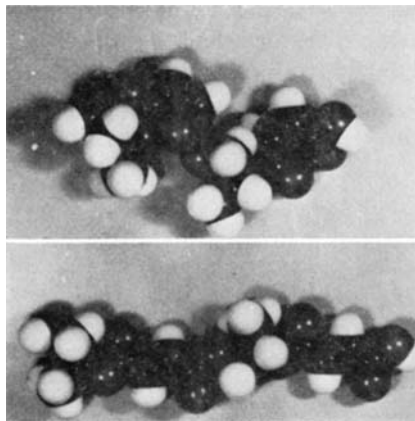

Fig. 10. Molecular models of 1,2-propylene glycol maleate (top) and fumarate (bottom).
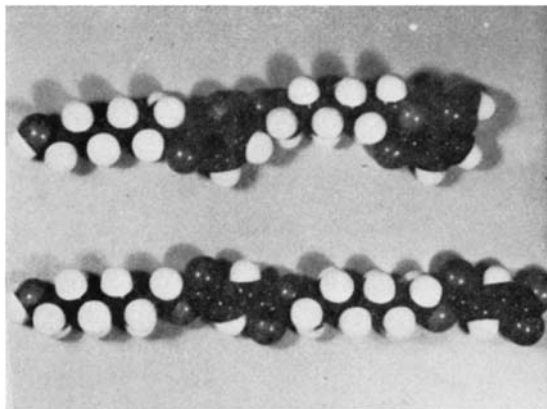

Fig. 11. Molecular models of 1,6-hexamethylene glycol maleate (top) and fumarate (bottom).

whole polyester molecule, that is, on the glycol used. Thus, for instance, in the case of 1,2-propylene glycol, a rather strained structure exists. Such a molecule with a rather metastable state would bear a transformation to a more stable configuration. This transformation can be clearly explained if we imagine the fixing double bond holding the maleate to open; the molecule would thus be free to rotate and to attain the stable fumarate configuration. The greater the molecular strain is, the greater

becomes the probability for the rotation. A condition which is fulfilled by the compact structure of the glycol molecule used (i.e., 1,2-propylene glycol).

Figures 6–9 showing the relation between the quantity of fumarate and the number of ester bonds n clearly shows the effect of the compact structure of the glycol and the polycondensation rate on the isomerization.

Molecular models referring to the typical cases previously discussed and the spatial arrangement of the atoms are shown in Figures 10 and 11.

It appears from our calculations of the rate constants and activation energies that the isomerization taking place in the course of the polycondensation follows a kinetic equation of a second order. This is in agreement with the theories concerning the kinetics of isomerization of maleic acid into fumaric acid.[2]

The second-order equation used in calculation is

$$k = \frac{1}{t_2 - t_1}\left(\frac{1}{a - x_2} - \frac{1}{a - x_1}\right)$$

where t_1 and t_2 are the reaction times, x_1 and x_2 the fumarate concentrations at time t_1 and t_2, respectively, and a is the initial concentration of maleic acid in moles per 1000 g. mixture of reaction. Table I summarizes the rate constants. The activation energies calculated from the Arrhenius equation fall in the range 20 ± 4 kcal./mole.

TABLE I
Rate Constants for *cis–trans* Isomerization of Maleic Anhydride
Esterified by Different Glycols

Glycol	Rate constants $k \times 10^5$, mole/1000 g./min.[a]				
	105°C.	120°C.	140°C.	160°C.	180°C.
1,2-Propylene glycol	43.2	96.0	243.0	466.2	1260.0
Ethylene glycol	—	5.20	56.6	106.5	163.1
Diethylene glycol	—	2.20	16.6	76.5	109.8
1,6-Hexamethylene glycol	—	—	13.3	39.9	49.9

[a] Rate constants at the beginning of the steep section of the curves.

As it may be seen, the rate constants differ to a great extent from each other in the case of certain glycols.

The activation energies are nearly identical and show very good agreement with the literature data for isomerization of pure maleic acid itself.[2]

It may be assumed that the maleate–fumarate isomerization taking place during polycondensation, follows the same mechanism and has the same activation energy as that of the isomerization of maleic acid itself; it may however increase due to the steric effects due to the type of glycol participating in the molecular structure of the polymer.

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Résumé

La vitesse d'isomérisation maléate–fumarate pendant la polycondensation de l'acide ou l'anhydride maléique est influencée par le glycol utilisé. Plus la molécule du glycol est courte plus le degré d'isomérisation est prononcé. La différence entre les constantes de vitesse d'isomérisation dépend de l'influence stérique des glycols utilisés. Le degré final d'isomérisation atteint une valeur constante influencée par la structure du glycol et par la température de réaction. L'énergie d'activation d'isomérisation maléate–fumarate est 20 ± 4 Kcal/mole. Cette valeur est conforme aux valeurs obtenues concernant l'isomérisation de l'acide maléique en acide fumarique. La réaction paraît être de second ordre; celui-ci peut être attribué à l'influence catalytique qu'exerce l'acide maléique lui-même sur l'isomérisation.

Zusammenfassung

Die Geschwindigkeit der während der Polyesterifizierung von Maleinsäure oder Maleinsäureanhydrid stattfindenden Isomerisierung hängt von der Struktur des verwendeten Glycols ab. Je länger die Kohlenstoffkette des Glycols ist, umso niedriger ist der Isomerisierungsgrad. Der Unterschied der Geschwindigkeitskonstanten der Reaktion ist hauptsächlich durch den sterischen Charakter der verwendeten verschiedenartigen Glycole bedingt. Der Isomerisierungsgrad nähert sich in jedem Falle einem konstanten Wert, der nach einer bestimmten Zeitdauer durch die Struktur des Glycols und ausserdem durch die Reaktions temperatur der Polykondensation bestimmt wird. Aus den Geschwindigkeitskonstanten wurden Werte von 20 ± 4 kcal/Mol für die Aktivierungsenergie berechnet. Dieser Wert ist in guter Übereinstimmung mit den in der Literatur für die Maleinsäure–Fumarsäureumwandlung angegebenen Werten. Die Isomerisierungsreaktion verläuft scheinbar nach zweiter Ordnung, und dies kann die Ursache für die katalytische Wirkung der Maleinsäure selbst auf die Isomerisierung sein.