Some Unsaturated Polyesters based on Maleic Anhydride

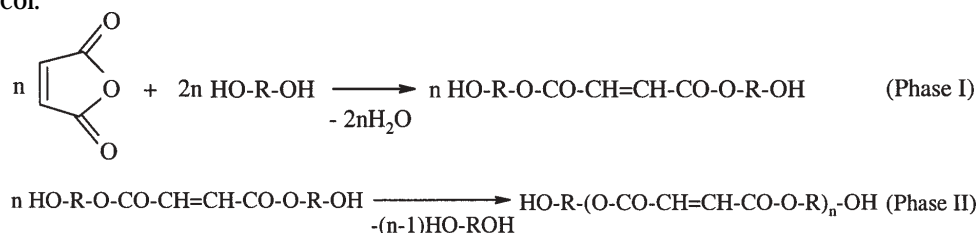## Reaction Mechanism and Kinetic Study

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This paper discusses the reaction mechanism and kinetic study of linear unsaturated polyesters, based on polycondensation reaction of maleic anhydride with different glycols (ethylene glycol, diethylene glycol and neopentyl glycol) utilized for the fabrication of polyurethanes. This polyester-diols with relatively high molecular weight (1000-1500) were characterized by IR, H-NMR, GPC, end groups analysis, as well as by the double bond content determination.

Keywords: unsaturated polyester, reaction mechanism, kinetic study

The synthesis of unsaturated polyesters resulting from maleic anhydride and saturated diols is relatively complicated, as side and branching reactions may occur. The polycondensation process, carried out under normal conditions (through the melt method), is accompanied by an isomerization reaction of maleate to fumarate form [1]. Increasing of the fumarate form percentage in the final product is due to the glycol segments favoring *cis-trans* isomerization [2,3]. As a consequence of methylene groups numbers [4] increasing, this isomerization became weaker in the ethylene, diethylene and neopentyl glycol (*cis-trans* rapport 2:1 to 1:3). In the maleic anhydride based unsaturated polyesters synthesis process, branching reactions may occur, because of the glycol segments or OH end groups, addition to the double bond [3-6]. Some authors [1,7] consider that in this reaction about 15 % of polymeric chain unsaturation might be consumed. These results suggest that the intramolecular spatial interactions appear also as a consequence of the neighboring position of the ester groups, and not only as a result of the steric hindrance of the hydroxyl group, or due to the length of the glycol.

Synthesis of polyesters

Glycols react with maleic anhydride to give linear unsaturated polyesters [8,9]. Glycol and maleic anhydride combine to form the following repeating unit. This reaction is the first step in industrially important polyester resin production, and in second step the reaction of transesterification is placed.

The reaction was carried out in a 250 cm³ four-necked flask, equipped with mechanical stirring, contact thermometer and bubbling tube for dry nitrogen.

The unsaturated polyesters were obtained from maleic anhydride and glycol (ethylene glycol, diethylene glycol or neopentyl glycol) to a molar ratio of 1:2.

The melting method of polycondensation was effectuated in two stages: first when water is removed and second when glycol is eliminated by transesterification.

The kinetic study was effectuated for both phase by measurement of time and removal quantity of water and respectively glycol.

The final composition of the polyesters was determined by H-NMR and IR spectral analysis. The acidities of the

Scheme 1. The general reaction of prepared unsaturated polyesters based on maleic anhydride

where:

R: -CH₂-CH₂- ; -CH₂-CH₂-O-CH₂-CH₂- ; -CH₂-C(CH₃)₂-CH₂- ;

Experimental part

Materials

- maleic anhydride (MA); $C_4H_2O_3$; M_w 98.06; mp 52.85°C; bp 202°C; recrystallized from chloroform;
- ethylene glycol (EG); $C_2H_6O_2$; M_w 62.07; mp -12.9°C; bp 192°C; refluxed with sodium for 1 hour, then distilled at atmospheric pressure, the 190-192 °C fraction being collected;
- diethylene glycol (DEG); $C_4H_{10}O_3$; M_w 106.12; mp -10°C; bp 244-245°C;
- neopentyl glycol (NPG); $C_5H_{12}O_2$; M_w 104.2; mp 124°C; bp 210°C.

polyesters were determined by titration method. The molecular weights distribution of the polyesters was determined by GPC at 20 °C. Tetrahydrofuran (THF) was used as the mobile phase, and narrow MWD polystyrene standards (Du Pont, Pierce) used in the linear calibration method.

Analytical techniques

Molecular weight of the polyester was determined by quantitative measurements of the OH and COOH end groups' content.

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Acidity was determined by dissolving a sample of polyester in a mixture of solvents, and then by titration with 0.1 N KOH solution.

For the determination of OH number, a precisely measured amount of product has been refluxed for 130 min in 10 mL of acetylation mixture (pyridine: acetic anhydride), then the acetic anhydride excess was titrated with a 0.1 N KOH solution.

The average molecular weight ($\overline{M}_n$) was calculated with the following relation:

$$\overline{M}_n = \frac{2 * 56.11 * 1000}{I_{AC} + C_{OH}} \quad (mgKOH/g)$$

Double bond content was determined accordingly by the sulfite method [10].

IR spectra were recorded on a Specord M80 Carl Zeiss Jena Spectrometer using KBr pellet technique.

Gel permeation chromatographic analyses (GPC) were carried out on a PL-EMD 950 Evaporative Mass Detector instrument using THF as eluant after calibration with polystyrene standards.

H-NMR spectroscopy samples were analyzed in CDCl$_3$ on a C 80 HL type High Resolution NMR Instrument, using tetramethylsilane as internal standard.

Result and discussion

In non catalytic system, the reaction mechanism of ester group formation depends on protons concentration of reaction medium. This is function of acid and hydroxyl groups amount from glycol and the water resulted from reaction, as per equations 1-3:

$$HOH \rightleftharpoons H^+ + HO^- \quad (1)$$
$$-COOH \rightleftharpoons H^+ + -COO^- \quad (2)$$
$$-ROH \rightleftharpoons H^+ + -RO^- \quad (3)$$
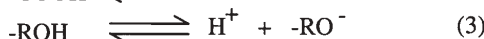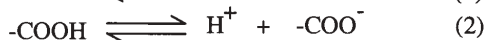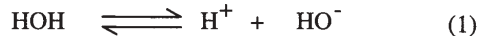
The process of polyesterification can be realized easily by control of the water and respectively glycol amount, which must be eliminated.

The kinetic equation should to take into a count each concentration of the ions from systems, very hard to achieve in practice. When is working in solution, the solvent is permanently hydrated with a water amount, which can't may be measured with accuracy.

Water elimination

The experimental data for PEF, PDEF and PNF were presented in table 1. All polyesters were synthesized by melting polycondensation method. The molar ratio of maleic anhydride and glycols was of 1:2. Kinetic order of the esterification phase of water elimination is one, just as arises from the graphic representation (fig. 1).
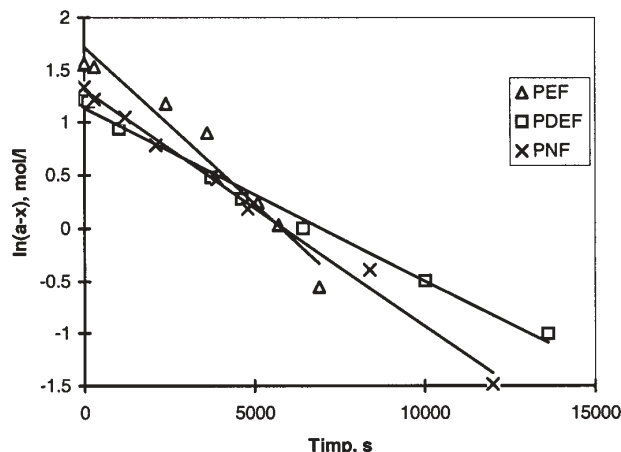

Fig. 1. Kinetic curves of PEF, PDEF and PNF (removal water phase)
$K_{PEF} = 2.9673.10^{-4}$ s^{-1}; $K_{PDEF} = 1.635.10^{-4}$ s^{-1}; $K_{PNF} = 2.2446.10^{-4}$ s^{-1}
ln a = 1.7173 mol/l (PEF); ln a = 1.1332 mol/l (PDEF); ln a = 1.3241 mol/l (PNF

The experimental data were verified by kinetic equation in the linear form (8).

$$\ln(a-x) = \ln a - kt \quad (8)$$

where:
a - initial amount of MA (mol);
x – amount of product eliminated at one time (mol).

Reaction speed constants have been determined from figure 1, which for PEF are 1.81 times bigger than for PDEF (K_{PEF}/K_{PDEF}) and 1.32 times bigger than for PNF (K_{PEF}/K_{PNF}).

From H-NMR spectra (fig. 2) can be notices that the biggest proportion of trans 1 : 1 is PEF, while for the other two polyesters the proportion of trans relative to cis is 1 : 1.5 for PDEF, respectivelly 1 : 2 for PNF.

We think that the difference noticed for the raport between the structures cis-trans as well as for the proportion of branchings appear on one side due to the different ionization of the glicols in reaction medium, and on the other side due to the steric and electronic effects of the glycols and maleic anhydride as well as due to the reciprocal solubility of the reaction components.

The glycol removal

After the water removal follows the second phase of glycol removal, by the reaction of the esteric interchanged (transesterification). In this phase the oxygen from OH group of diester molecule attacks, through the non participant electrons, the carbon atom from the group COO-, electrophile mechanism, making an unstable complex that is passed slow in tetra ester with glycol elimination. This slow step determines the speed of reaction. The process was continued in same manner and was checked up by the amount of glycol removed. This is

Table 1
EXPERIMENTAL DATA OF PEF, PDEF AND PNF (WATER REMOVAL PHASE)

| Nr. crt	PEF			PDEF			PNF		
	a-x, mol/l	ln(a-x)	t, s	a-x, mol/l	Ln(a-x)	t, s	a-x, mol/l	ln(a-x)	t, s
1	4.7789	1.564	0	3.3819	1.218	0	3.8206	1.34	0
2	4.6268	1.532	300	3.3275	1.202	120	3.3987	1.223	300
3	3.2479	1.178	2400	2.5546	0.938	1020	2.8541	1.049	1200
4	2.4637	0.902	3600	1.6138	0.479	3720	2.1895	0.784	2100
5	1.2771	0.245	5100	1.3220	0.279	4620	1.5940	0.466	3900
6	1.0334	0.033	5700	0.9975	-0.0025	6420	1.2041	0.186	4800
7	0.5749	-0.554	6900	0.6088	-0.496	10020	0.6755	-0.392	8400
8				0.3669	-1.002	13620	0.2270	-1.483	12000
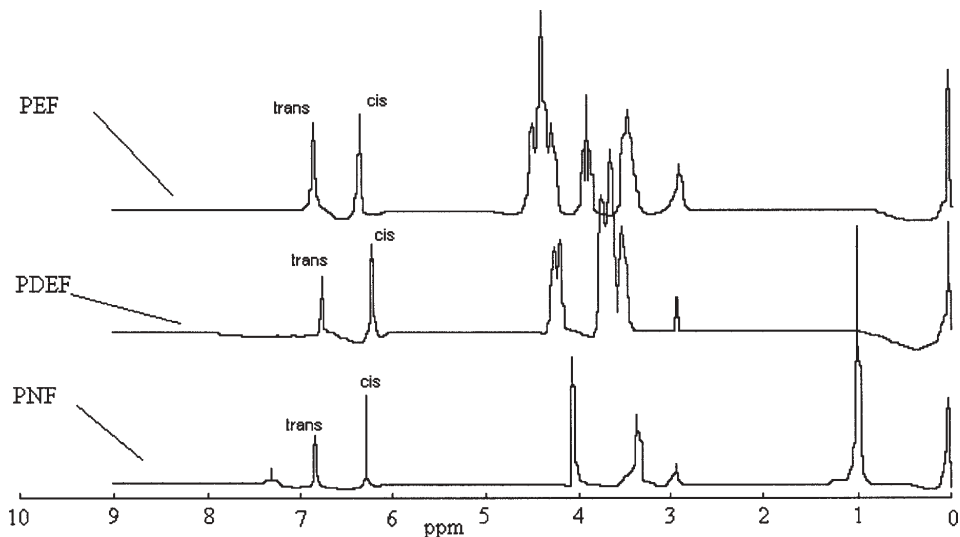
Fig. 2   H-NMR spectra of PEF, PDEF and PNF

Table 2

VALUES OF H-NMR SPECTRA, *CIS-TRANS* RATIO AND EMBRANCHEMENT PROPORTION OF PEF, PDFE AND PNF

Polyester	Peak, ppm	Attributive	Obs.	*cis-trans* ratio, mol	Proportion of embranchment, %
PEF	2,90 3.70-3,90 4.20-4,40 6,30 6,85	-OH -CH$_2$- -CH$_2$- -CH=CH- -CH=CH-	exterior interior *cis* *trans*	1 : 1	10-12
PDEF	2,90 3,5-3,8 4,1-4,4 6,25 6,85	-OH -CH$_2$-CH$_2$- -CH$_2$-CH$_2$- -CH=CH- -CH=CH-	exterior interior *cis* *trans*	1,5 : 1	1-2
PNF	1.00 2,95 3,35 4,10 6,25 6,80	-CH$_3$ -OH -CH$_2$ -CH$_2$ -CH=CH- -CH=CH-	exterior interior *cis* *trans*	2:1	5-6
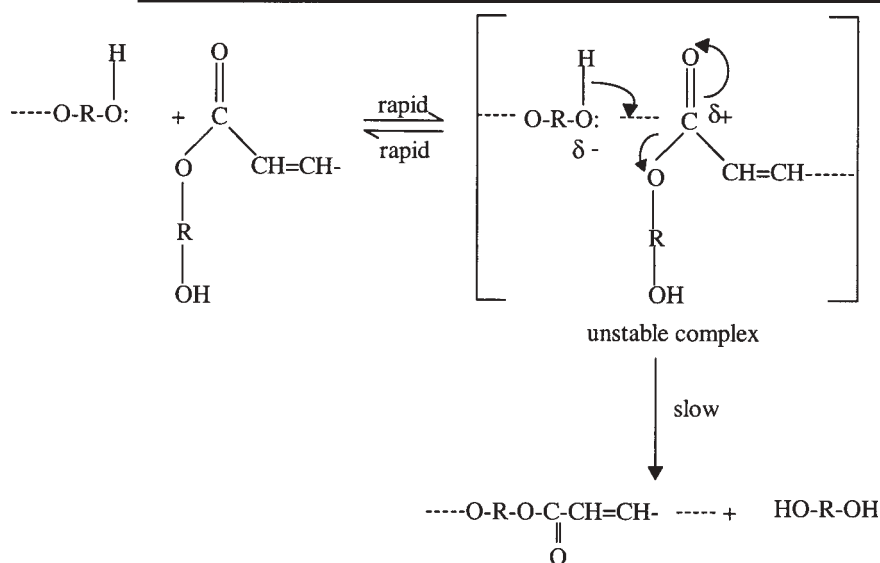
Scheme 2. SN$_2$ mechanism for forming of the chain of unsaturated polyester

the order two nucleofil substitute mechanism of (SN$_2$) and it can be represented as in scheme 2.

The mechanism is based on experimental data (table 3), which is dominated by a order two kinetic low, the equation 9.

$$dx/dt = K(a-x)^2 \qquad (9)$$

where:
a= initial concentration of diester (mol/L);
x = amount of glycol removal (mol/lL) for moment t.
After the separation of the variables and direct integration, the equation becomes:

$$1/(a-x) = 1/a + Kt \qquad (10)$$

Table 3
EXPERIMENTAL DATA OF PEF, PDEF AND PNF (GLYCOL REMOVAL PHASE)

Nr. Crt.	PEF		PDEF		PNF	
	1/(a-x), l/mol	t, s	1/(a-x), l/mol	t, s	1/(a-x), l/mol	t, s
1	0.176	600	0.275	600	0.8	3600
2	0.244	2700	0.314	1200	1.1	5400
3	0.292	4800	0.382	2100	1.6	7200
4	0.4	6600	0.467	3000	2.3	10800
5	0.5	9000	0.565	4500	3.0	14400
6	0.65	11400	0.711	6600		
7	0.8	13200	0.811	8400		
8	1.1	16800	0.88	9600		
9			0.948	10200		
10			1.091	11400		

Table 4
MOLECULAR MASS OH NUMBER AND ACID NUMBER TO PEF, PDEF AND PNF

Product	C_{OH}, mg KOH/g	I_{Ac}, mg KOH/g	M_n (by titration)	M_n (GPC)	M_w (GPC)	Polydispersity M_w/M_n
	219,6	15,0	513	455	1150	2.53
PEF	220,8	16,2	511	450	1020	2.27
	218,9	15,3	515	465	1085	2.33
average	**219,8**	**15,5**	**513**	**450**	**1085**	**2.37**
	220,8	19,7	508	380	850	2.23
PDEF	218,4	20,2	512	415	830	2.00
	219,6	18,6	510	395	810	2.05
average	**219,6**	**19,5**	**510**	**397**	**830**	**2.09**
	222,7	19,8	502	350	750	2.14
PNF	220,1	18,7	508	370	710	1.92
	224,0	20,5	500	390	740	1.90
average	**222,3**	**19,67**	**505**	**370**	**735**	**1.98**

Through graphical representation of experimental data after equation 10, we obtain a series of right lines. From tangent of these lines was deduced the constant of speed (K), and by cut on ordinate axis, the reversed initials concentration (1/a) figure 3.

From figure 3 were determined the speed constants, which showed that the glycol removal phase for PEF and PDEF is much easier than for PNF.
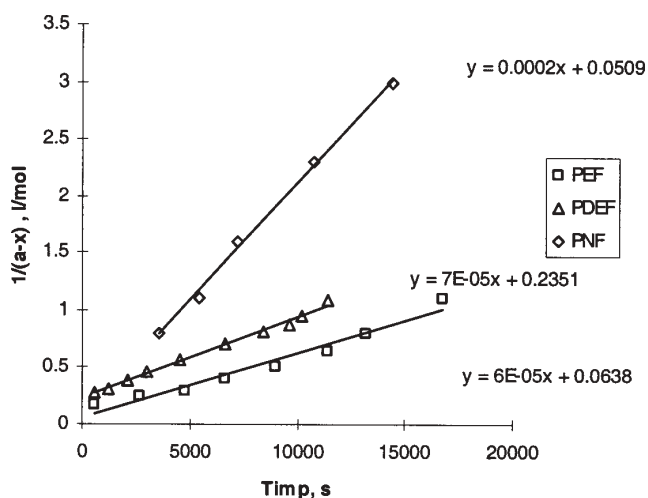

Fig. 3   Kinetic curves of PEF, PDEF and PNF (glycol removal phase)
K_{PEF} = 6.10^{-5} l.mol^{-1}.s^{-1}; K_{PDEF} = 7.10^{-5} l.mol^{-1}.s^{-1}; K_{PNF} = 2.10^{-4} l.mol^{-1}.s^{-1}
1/a = 0.0638 l.mol^{-1} (PEF); 1/a = 0.2351 l.mol^{-1}(PDEF); 1/a = 0.0509 l.mol^{-1}(PNF)

Distribution of molecular mass

The molecular mass of the polyesters synthesized in this study was calculated through end groups' titration method and through GPC. Results of these analyses are presented in the table 4.

In this table is noticed a good correlation between numeric molecular weight found through titration method and by GPC to PEF, which has polydispersity and concentration in the biggest branchings. Probable the polysuccinates, which are formed through the saturation of double bonds, contribute to this distribution of molecular mass.

Conclusion

In this work were discussed the kinetic and reaction mechanism of three unsaturated polyesters based on maleic anhydride and different glycols prepared by poly-condensation reaction. The synthesis of unsaturated polyesters based on maleic anhydride and saturated diols is relatively complicated,on one side also because of the branching reactions that may occur. The polycondensation process, carried out under normal conditions (melt method), is accompanied by an isomerization reaction of maleate to fumarate form. In non catalytic system, the reaction mechanism of ester group formation depends on protons concentration of reaction medium. This is function of acid and hydroxyl groups amount from glycol and the water resulted from reaction. The mechanism is verified by experimental data, which is dominated by a kinetic of order one for water removal phase and order two for glycol removal phase.

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