

SYNTHESIS OF BRASSILIC ACID POLYESTERS OBTAINED BY OZONOLYSIS OF ERUCIC ACID AND A TRIAL OF THEIR APPLICATION TO POLYURETHANES PRODUCTION

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Syntheses of brassilic acid polyesters with 1,4-butylene, diethylene, ethylene and 1,2-propylene glycols were carried out. The obtained polyesters were applied to cast urethane elastomers production.

INTRODUCTION

Polyesters obtained by reactions of glycols and dicarboxylic acids have found a wide usage in fibres and synthetic plastics industries. The most common acids used in the synthesis are: adipic, phthalic and other dicarboxylic acids like e.g. sebacic acid.

At our work the brassilic acid obtained by ozonolysis of erucic acid was applied to the synthesis of polyesters [2, 5]. Kind of glycol and acid as well as the molecular weight of obtained compound influence on the properties of the polyester [4].

We intended to use the obtained brassilic acid polyesters to the polyurethane elastomers, and because of that we aimed at obtaining the compounds of molecular weight in the region 1.500-3.000 because only such polyesters can be used here.

RESULTS

The polycondensation reaction was carried out in three stages in the neutral gas atmosphere. The first stage has begun after reaching 140°C temperature of the reaction mixture. At that temperature the reaction was carried out until distinct diminishing of the decrease of acid value

what generally occurred at an A. V. of about 100. Then the temperature of the reaction mixture increased to 200°C, and the reaction was continued under vacuum. At these conditions the process went on until diminishing the acid value to ca 2.

Table 1

Changes of acid values during the polycondensation reaction of brassilic acid with 1,4-butylene glycol, diethylene glycol, ethylene glycol and 1,2-propylene glycol

Stage	Time (hours)	Polyester of brassilic acid with glycol			
		1,4-butylene	diethylene	ethylene	1,2-propylene
Acid value					
I					
140°C atm. pressure	0	322.2	306.1	355.1	337.9
	5	91.4	113.0	97.8	130.0
II					
140°C—200°C atm. pressure	9	40.0	35.4	20.0	49.5
III					
200°C 5 mmHg pressure	22	0.7	1.0	1.6	1.4

Reagents ratio: glycol/acid = 1.15 mole/mole

The course of the first stage is shown in Figure 1. We presented there the change of acid value in dependence on the reaction time for brassilic acid polycondensation with following glycols: 1,2-propylene glycol, ethylene glycol, diethylene glycol and 1,4-butylene glycol at catalyst presence and without it. As it result from the curves the acid value at the first reaction stage increases very quickly and later only slight changes can be observed. Further application of the same para-

Table 2

Characterization of polybrasilates of: 1,4-butylene, diethylene, ethylene and 1,2-propylene glycols

Kind of glycol	Molecular weight <i>M</i>	Contents of OH groups (%)	Acid value	Melting point °C
1,4-butylene glycol	2148	1.58	0.7	66.0—67.5
Diethylene glycol	1735	1.88	1.0	40.5—41.0
Ethylene glycol	1990	1.73	1.6	68.0—68.5
1,2-propylene glycol	2820	1.20	1.4	22.5—23.5

Glycol/acid = 1.15 mole/mole.

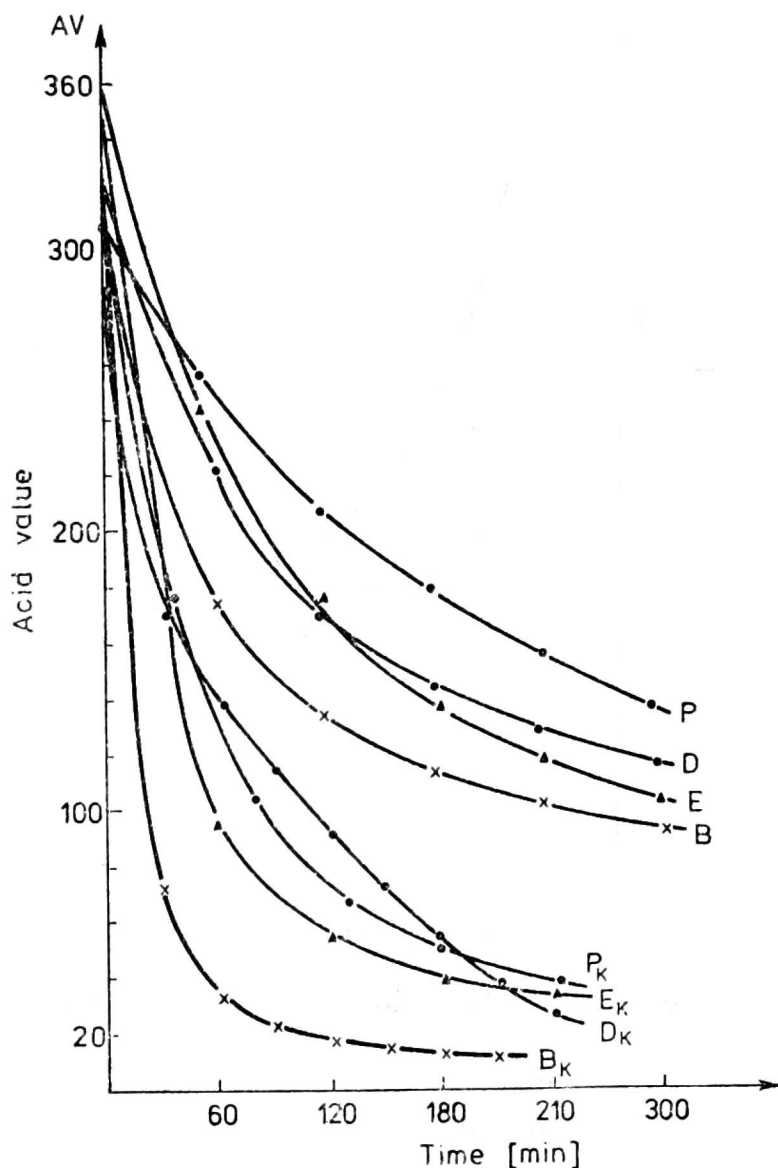


Fig. 1. Changes of acid values during the I stage of polycondensation reaction of brassilic acid with glycols: 1,4-butylene (B , B_K); ethylene (E , E_K); diethylene (D , D_K); 1,2-propylene (P , P_K). B_K , E_K , D_K , P_K — policondensations with catalyst

meters would distinctly lengthen the reaction time and therefore in the II stage temperature was increased to 200°C .

p-toluenesulfonic acid was applied in our work as the catalyst which even at 0.1% concentration showed distinct reaction rate increase.

Characterization of the polyesters obtained at reagents molar ratio 1.15 : 1 (glycol : acid) are presented in Table 2. As it comes from the inserted data, though the same reaction conditions occurred for individual glycols, the esters were of different molecular weights. Similar melting points were only for ethylene and 1,4-butylene polybrassilates. 1,2-propylene polybrassilate was of the lowest melting point.

The molar ratios 1.05; 1.10; 1.15; 1.20 glycol : acid were used to obtain polyesters which differ in molecular weight and therefore in properties.

To determine the reaction order and activation energy the diethylene glycol and ethylene glycol were polyesterified with brassilic acid at one stage until reaching the reaction extent equal 0.9. As it is known,

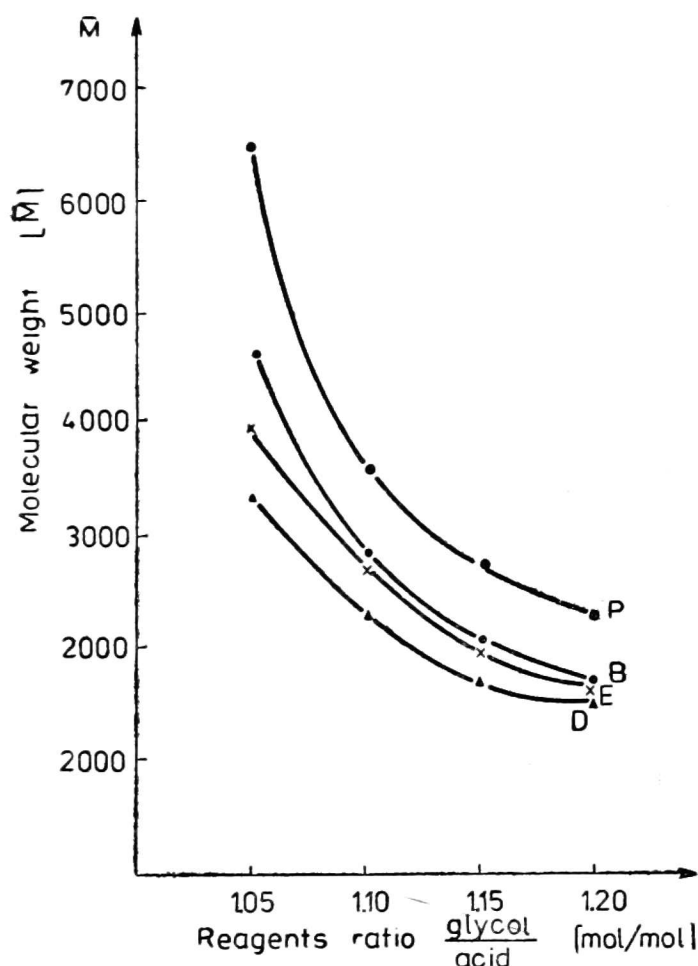


Fig. 2. The influence of reagents ratio on molecular weight of polyesters

the reaction extent is a measure of the process rate. It is defined as the ratio of functional groups number of one kind, which reacted at given time, to the number of the same kind of groups present at the reaction beginning [5].

One of the possibilities to determine the degree of reaction extent, if it is polycondensation, lies in determination of the acid value of the reaction mixture and calculation of the reaction extent. Figures 3 and 4 present the dependance of the reaction extent on the process time at different temperatures in case of polycondensation ethylene and diethylene glycols with brassilic acid.

As it comes out from the presented figures both in the polycondensations of brassilic acid with ethylene glycol and with diethylene glycol, the temperature exerts a very essential effect upon the reaction time. The higher the process temperature, the shorter the reaction time. But the temperature increase can not be unlimited because of the possibility of by-reactions like destruction, decarboxylation or oxidation.

To determine the reaction order it should be ascertained, which one among the theoretical dependences, is covered by the experimental results. As it is known, the graphic determination of the reaction order is connected with following functions:

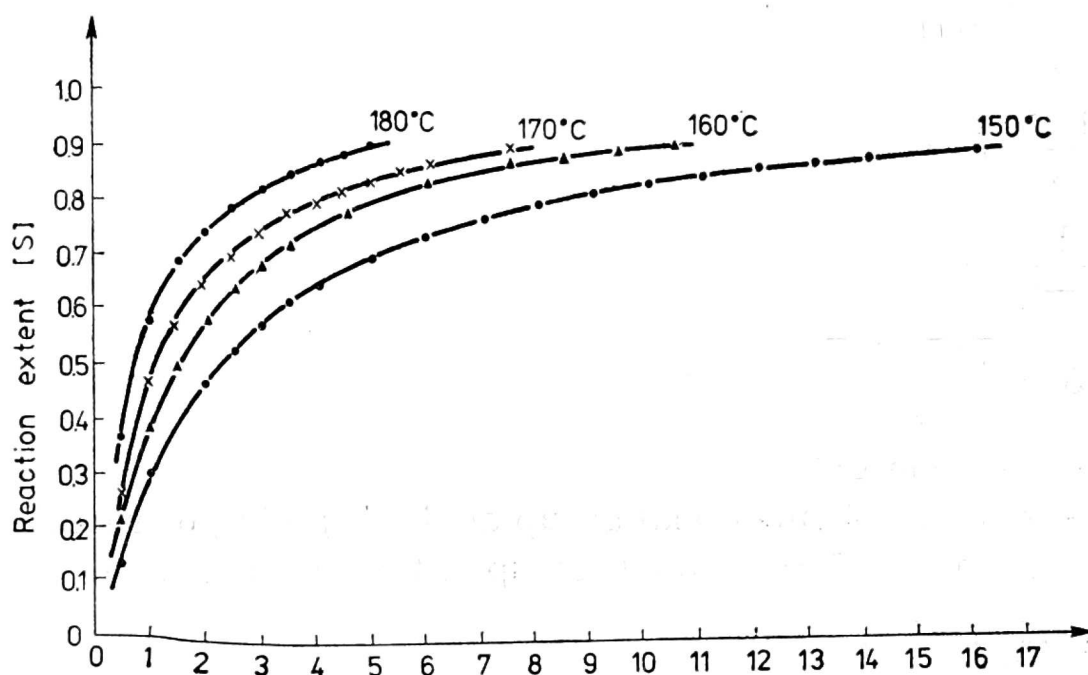


Fig. 3. Changes of the reaction extent at different temperatures as function of time. Polycondensation of brassilic acid with diethylene glycol. Reagents ratio:
 $\frac{\text{glycol}}{\text{acid}} = 1,15 \left(\frac{\text{mole}}{\text{mole}} \right)$

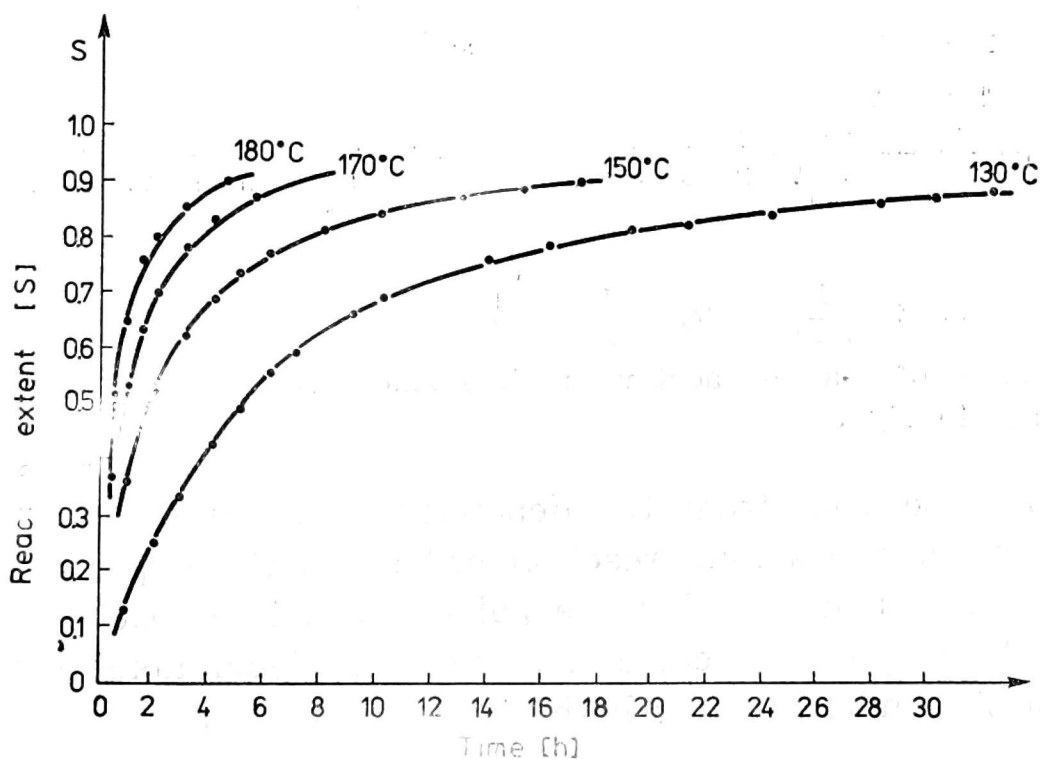


Fig. 4. Changes of the reaction extent at different temperatures as function of time. Polycondensation of brassilic acid with ethylene glycol.
 Explanation as in Fig. 3

$$1) \lg \frac{1}{1-s} = f(t)$$

$$2) \frac{1}{1-s} = f(t)$$

$$3) \frac{1}{(1-s)^2} = f(t)$$

$$\text{where } S = \frac{C_0 - C}{C_0}$$

s — reaction extent,

c_0 — number of functional group at the beginning of reaction,

c — number of functional group after definite time of reaction.

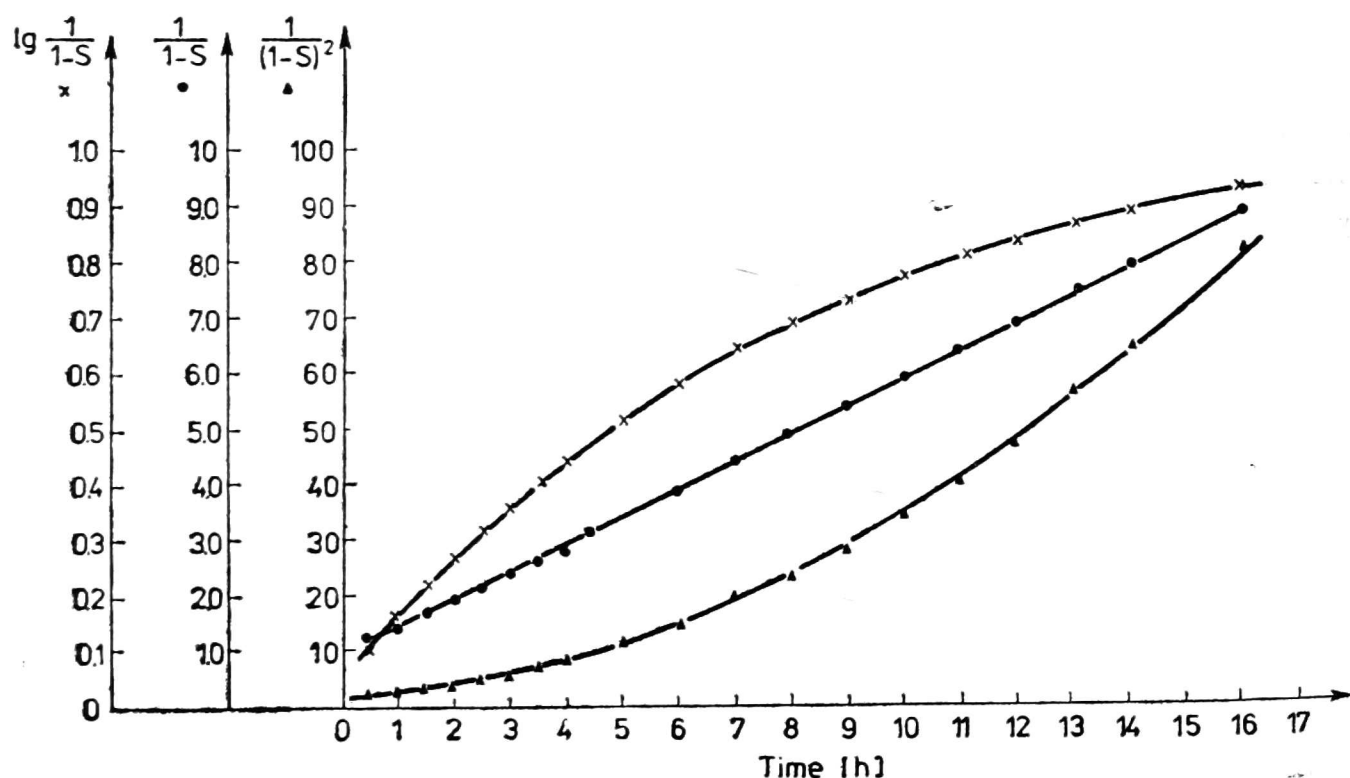


Fig. 5. Functions: $\lg \frac{1}{1-s} = f(t)$; $\frac{1}{1-s} = f(t)$; $\frac{1}{(1-s)^2} = f(t)$

Polycondensation of brassilic acid with diethylene glycol, temp. 150°C

Explanation as in Fig. 3

As it can be seen from the dependences given in figures, only the function for the second reaction order fits the experimental data.

Further it was proved that the polycondensation reaction of brassilic acid with ethylene glycol and diethylene glycol takes place according to the Arrhenius equation both at equimolar conditions and a glycol excess.

Basing on a graph of a function $\lg k = f\left(\frac{1}{t}\right)$ it was determined the value of activation energy for polycondensation brassilic acid with ethy-

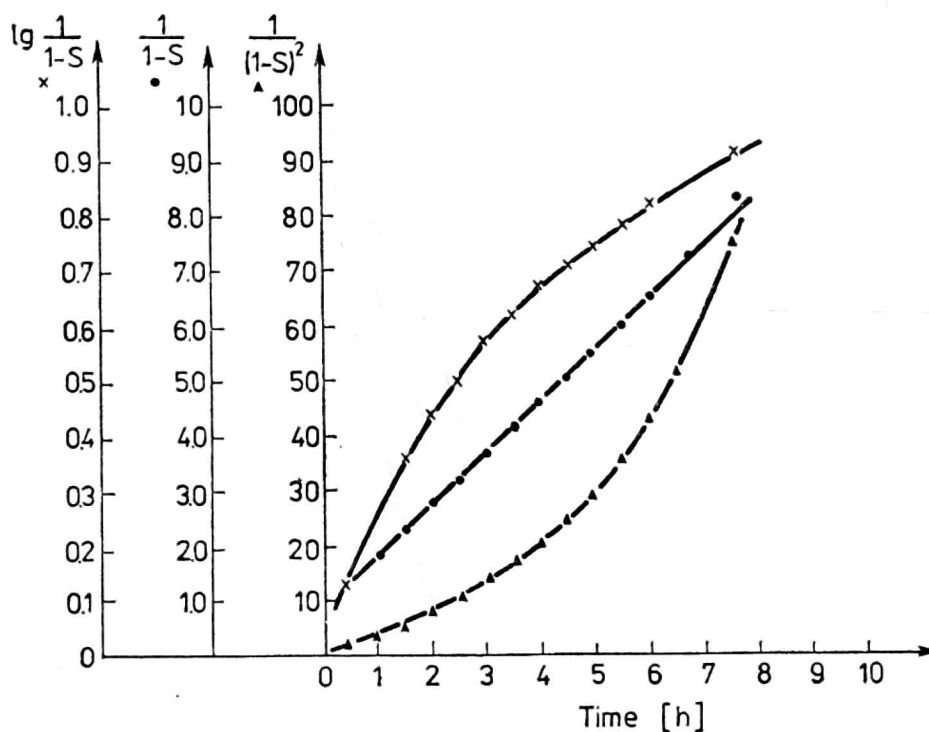


Fig. 6. Functions: $\lg \frac{1}{1-S} = f(t)$; $\frac{1}{1-S} = f(t)$; $\frac{1}{(1-S)^2} = f(t)$

Polycondensation of brassilic acid with diethylene glycol, temp. 170°C
Explanation as in Fig. 3

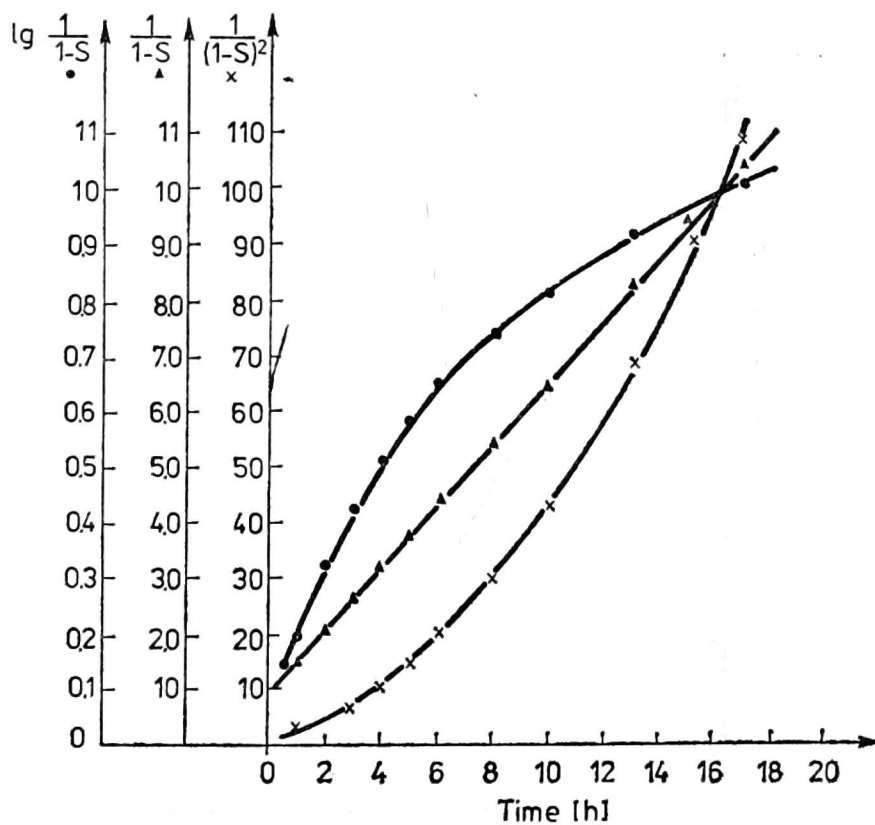


Fig. 7. Functions: $\lg \frac{1}{1-S} = f(t)$; $\frac{1}{1-S} = f(t)$; $\frac{1}{(1-S)^2} = f(t)$

Polycondensation of brassilic acid with ethylene glycol, temp. 150°C
Explanation as in Fig. 3

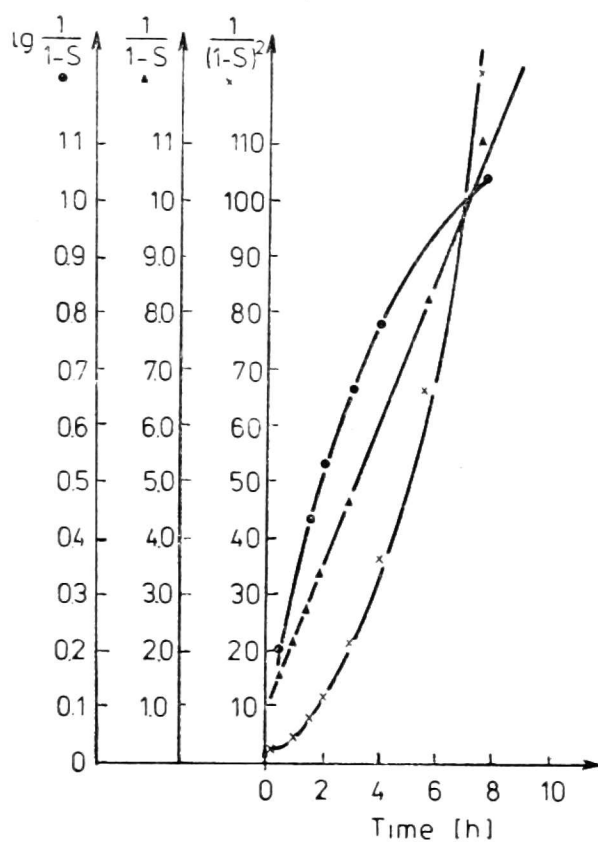


Fig. 8. Functions: $\lg \frac{1}{1-S} = f(t)$; $\frac{1}{1-S} = f(t)$; $\frac{1}{(1-S)^2} = f(t)$

Polycondensation of brassilic acid with ethylene glycol, temp. 170°C
Explanation as in Fig. 3

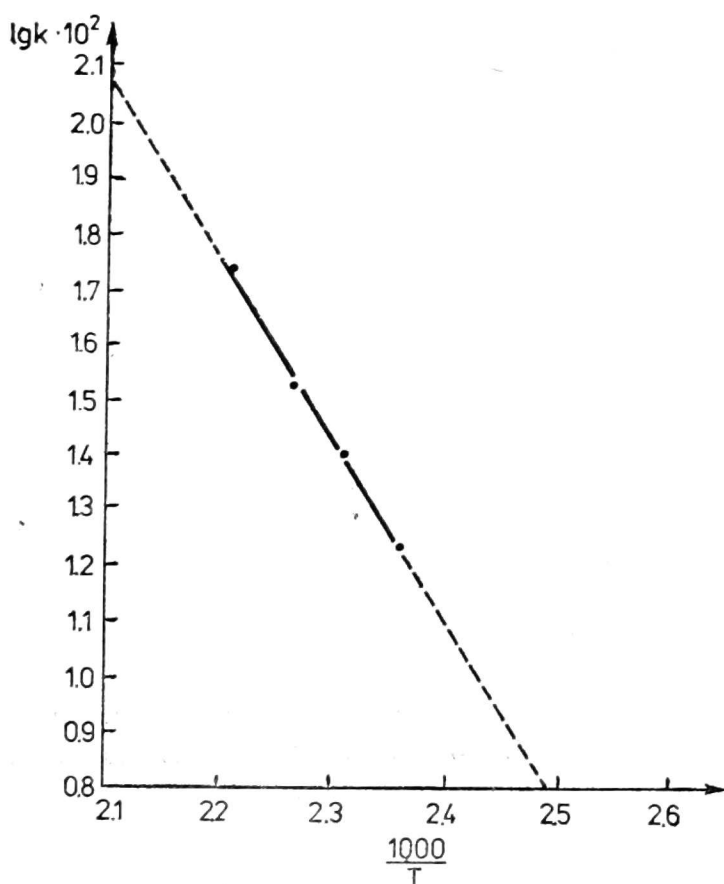


Fig. 9. The dependence of the reaction rate on the temperature. Polycondensation of brassilic acid with diethylene glycol. Explanation as in Fig. 3

lene glycol ($15.2 \frac{\text{kcal}}{\text{mol}}$, reagent ration $1 : 1.15 \frac{\text{acid}}{\text{glycol}}$ and diethylene glycol ($16.2 \frac{\text{kcal}}{\text{mol}}$, reagent ratio $1 : 1.15 \frac{\text{acid}}{\text{glycol}}$).

Diethylene glycol polyester of $\bar{M} = 1975$, and ethylene glycol polyester of $\bar{M} = 2425$ were applied to manufacture of polyurethane elasto-

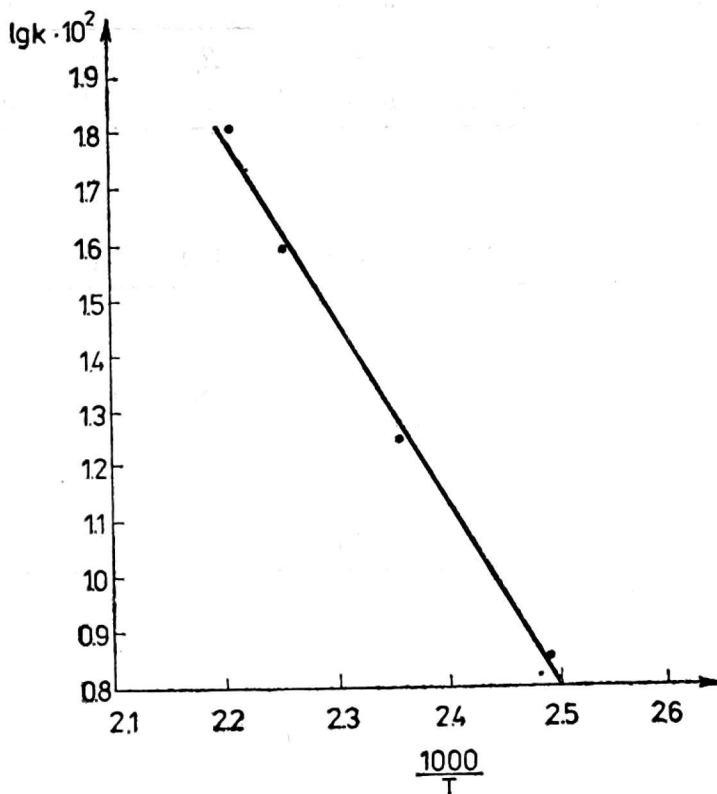


Fig. 10. The dependence of the reaction rate on the temperature. Polycondensation of brassilic acid with ethylene glycol. Explanation as in Fig. 3

mers. The obtained elastomers were examined on their physical and chemical properties and were compared with elastomers obtained from raw materials already applied to industrial manufacture of polyesters: i.e. adipic acid and ethylene glycols.

Looking at data inserted in Table 3 one can notice that elastomers obtained with brassilates do not give much way to mechanical properties of polyurethanes obtained from adipic acid polyesters. As it can be seen, the first elastomers are slightly more rigid and are of greater stable elongation.

The obtained polyurethanes were also examined to study their chemical resistance.

The results inserted in Table 4 show great differentiation in behaviour of individual elastomers in aqueous medium at different temperatures or sulphuric acid and alkaline media. Samples of urethane elastomers obtained from the polybrassilates after their 7-days staying

Table 3

Properties of cast urethane elastomers synthesized with poly(ethylene adipate), poly(ethylene brassilate), or poly(diethylene brassilate) and diphenylmethane-4,4'-diisocyanate cured with 1,4-butylene glycol or 3,3'-dichloro-4,4'-diaminodiphenylmethane

Polyester	Curing agent	Physical properties						
		moduls M_{200} KG/cm ²	tensile strenght R_{r_2} KG/cm ²	elongation		tear strenght R_{rd} KG/cm	hard- nass $Sh A$	elasti- city η
				E_r %	E_t set %			
Poly(ethylene adipate) $\bar{M} = 2000$	1,4-butylene glycol	112	440	560	16	96	87	22
Poly(ethylene brassilate) $\bar{M} = 2425$	1,4-butylene glycol	159	392	420	120	99	97	24
Poly(diethylene brassilate) $\bar{M} = 1975$	1,4-butylene glycol	97	339	520	40	69	93	26
Poly(ethylene adipate) $\bar{M} = 2000$	3,3'-dichloro-4,4'-diamino diphenylmethane	296	390	320	68	161	97	26
Poly(ethylene brassilate) $\bar{M} = 2425$	3,3'-dichloro-4,4'-diamino diphenylmethane	313	351	260	116	143	97	30
Poly(diethylene brassilate) $\bar{M} = 1975$	3,3'-dichloro-4,4'-diamino diphenylmethane	296	367	280	78	154	97	30

$$\frac{\text{NCO}}{\text{OH}_B} = 1.1, \frac{\text{NCO}}{\text{NH}_2} = 1.1.$$

in aqueous medium are of about 40-70% smaller gain in weight than the elastomers synthesized by adipate. Samples staying during 5 hours at 90°C in alkaline medium differ greatly in their chemical resistance. Samples containing adipate lose as much as 56.7% of their mass but those containing polybrassilate change their weight in only 3.5%.

The changes in weight of the samples caused by sulphuric acid are much smaller for elastomers containing polybrassilate, only 0.24%, than those with polyadipate (-11.9%).

Our work presents only a trial of application the brassilic acid in

Table 4

Results of chemical resistance estimation of received elastomers samples

Polyurethane elastomer	Sample weight changes (%)									
	H ₂ O		10% NaOH						30% H ₂ SO ₄	
	25 °C	40 °C	40 °C	60 °C	100 °C	25 °C	90 °C	25 °C	90 °C	
Poly(ethylene adipate), diphenylmethane-4,4'-diisocyanate, 1,4 butylene glycol	1.31	1.32	1.12	1.12	—	1.51	—	0.75	—	
Poly(ethylene brassilate), diphenylmethane-4,4'-diisocyanate, 1,4 butylene glycol	0.41	0.47	0.64	0.64	0.64	0.18	—3.5	—	—	
Poly(diethylene brassilate), diphenylmethane-4,4'-diisocyanate, 1,4 butylene glycol	0.76	0.33	0.83	—	—	0.40	—	0.47	—	
Poly(ethylene adipate), diphenylmethane-4,4'-diisocyanate, 3,3'-dichloro-4,4'-diaminodiphenylmethane	1.27	1.33	1.31	0.36	3.42	—56.7	0.65	—11.9	—	
Poly(ethylene brassilate), diphenylmethane-4,4'-diisocyanate, 3,3'-dichloro-4,4'-diaminodiphenylmethane	0.45	0.48	0.62	0.37	0.05	—2.5	0.31	0.24	—	

Sample staying time in medium: 7 days in temperatures 25 °C, 40 °C and 60 °C,
5 hours in temperatures 90 °C and 100 °C.

the polyurethane synthesis. They are the group of polymers very intensively developed nowadays because of scientific and practical point of view. As it is known, the properties of the final product depend on the selection of many reagents and process parameters. This gives a wide field for chemists who look for new elastomers with better mechanical and chemical properties.

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SYNTEZA POLIESTRÓW KWASU BRASYŁOWEGO OTRZYMANEGO NA DRODZE OZONOLIZY KWASU ERUKOWEGO I PRÓBA ICH ZASTOSOWANIA DO PRODUKCJI POLIURETANÓW

Streszczenie

Techniczny kwas erukowy poddano utleniającej ozonolizie. Wyodrębniony kwas brasyłowy zastosowano w reakcji poliestryfikacji z glikolami: etylenowym, dwuetylenowym, 1,2-propylenowym i 1,4-butylenowym.

Zbadano wpływ stosunku molowego reagentów i udział ukatalizatora (kwasu p-toluenosulfonowego) na przebieg polikondensacji. W przypadku glikolu etylenowego i dwuetylenowego określono rzędowość reakcji i wartość energii aktywacji.

Przeprowadzono próbę zastosowania otrzymanych polibrasyłanów do syntezy elastomerów poliuretanowych. Elastomery uzyskane w oparciu o poliestry kwasu brasyłowego oraz glikole: etylenowy i dwuetylenowy pod względem niektórych własności fizykomechanicznych dorównywały analogicznym próbom otrzymanym z zastosowaniem poliestrów glikolu etylenowego i kwasu adypinowego, natomiast charakteryzowały się znacznie wyższą odpornością na czynniki chemiczne.

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**СИНТЕЗ ПОЛИЭФИРОВ БРАСИЛОВОЙ КИСЛОТЫ ПОЛУЧЕННОЙ ПУТЕМ
ОЗОНОЛИЗА ЭРУКОВОЙ КИСЛОТЫ И ПОПЫТКА ИХ ПРИМЕНЕНИЯ
В ПРОИЗВОДСТВЕ ПОЛИУРЕТАНОВ**

Резюме

Техническую эруковую кислоту подвергали окисляющему озонлизу. Выделенную брасиловую кислоту использовали в реакции полиэстрификации с этиловым, диэтиловым, 1,2-пропиленовым и 1,4-бутиловым гликолом.

Исследовали влияние молярного соотношения реагентов и участия катализатора (п-толуэносulfоновой кислоты) на ход поликонденсации.

В случае этилового и диэтилового гликола определяли степень замещенности реакции и величину энергии активации.

Предпринималась проба использования полученных полибрасилатов для синтеза полиуретановых эластомеров. Эластомеры полученные на базе полиэфиров брасиловой кислоты, а также этиленового и диэтиленового гликола, равнялись по отношению к некоторым физико-механическим свойствам аналогичным пробам, полученным при использовании полиэфиров этилового гликола и адипиновой кислоты, а с другой стороны характеризовались гораздо высшей устойчивости к химическим факторам.