Synthesis of Oligomers with Unsaturated End-Groups Based on Dianic Epoxy Resin and Crotonic Acid

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SYNTHESIS OF OLIGOMERS WITH UNSATURATED END-GROUPS BASED ON DIANIC EPOXY RESIN AND CROTONIC ACID

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ABSTRACT

The synthesis of oligomers with unsaturated double end-bonds based on the reaction of dianic epoxy resin and crotonic acid was investigated. Experimental conditions included temperatures from 353-383 K and reaction times from 3.5-4.0h in the presence of quaternary ammonium salts dissolved in various organic solvents. The main kinetic parameters of the reaction were determined.

INTRODUCTION

It is known [1,2], that oligomers with double end-bonds can be obtained by the interaction of acrylic and methacrylic acids with epoxy resins. Oligomers obtained by this way find wide application in the production of polymeric materials [3]. The synthesis of unsaturated oligomers (UO) based on the reaction of dianic epoxy resins (DER) with unsaturated aliphatic acids is carried out in the presence of basic catalysts [4].

Crotonic acid (CA) shows a lower ability for homopolymerization than acrylic and methacrylic acids [5]. This allows the synthesis of UO in the presence of air(i.e. oxygen) without the use of radical polymerization inhibitors. Therefore the obtained oligomers based on CA must exhibit higher stability with respect to oxidation degradation.

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The reaction between CA and DER in the presence of the quaternary ammonium salts was studied in the present work.

The synthesis of UO with terminal double bonds can be illustrated by the following reaction scheme:

$$H_2C-CH-CH_2\left[RCH_2CHCH_2\right]_n-RCH_2-CH-CH_2 + 2\,CH_3-CH=CH-C-OH \xrightarrow{kat.}$$

$$\longrightarrow CH_3-CH=CH-C-O-CH_2-CH-CH_2-\left[RCH_2CHCH_2\right]_2-RCH_2-CH-CH_2-$$

$$-O-C-CH=CH-CH_3 \text{, where}$$

$$R = -O-C_6H_4-C(CH_3)_2-C_6H_4-O-$$

$$n = 0...2.$$

(1)
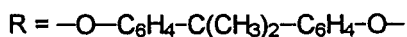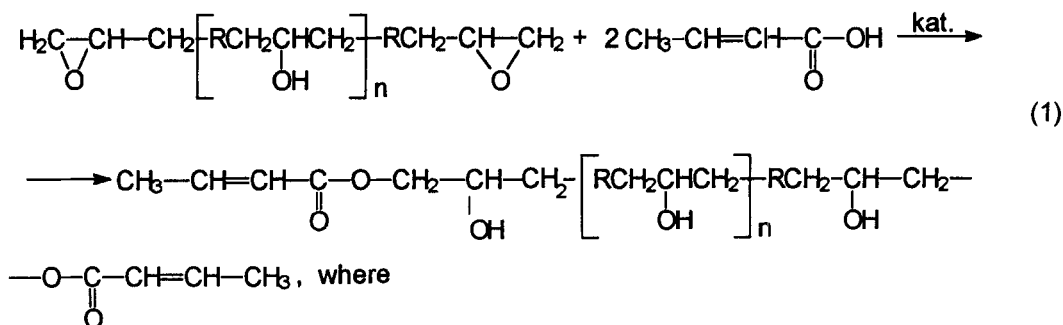
METHODS

The preparation of UO was carried out in a three-necked reactor with a mechanical stirrer, thermometer and reflux condenser. The expulsion of volatile products was carried out under low pressure (1-3 hPa) at 338-343 K. The oligomer yield was calculated as a percentage of the theoretical yield.

The molecular weight was determined by the cryoscopic method in benzene . The iodine number was calculated according to the iodometric titration method .

Infrared spectra were recorded with a IKS-29 spectrophotometer over the spectral range of 400-4000 cm^{-1}. The UO samples were prepared in the form of films using KBr cells. Oligomer ultraviolet spectra were recorded with a

CF-26 spectrophotometer over the spectral range of 235-350 nm in quartz cells with an optical length of 1 cm, using dioxane as a solvent. The concentration range of the synthesized products varied from 10 to 10 mol/l in dioxane. The reaction rate was followed by monitoring the change of the carboxyl and epoxy groups in the reaction mixture.

MATERIALS

Dianic epoxy resin (DER) with a molecular weight of 370 and an epoxy number 20.1% was used for all investigations. The purity of crotonic acid was verified by its melting point. (T_m) of 344.5 K (99.5 % purity). Toluene, cyclohexanone and chlorobenzene were purified according to a procedure described in [6]; their characteristics subsequently coincided with literature data [6]. The quaternary ammonium salts were of analytical quality.

Table 1. Effective rate constants (k) of the reaction between DER and CA at 373K.

Solvent	Catalyst	Quantity of the catyst, % mol	Molar ratio DER:CA	$k*10^4$ l/mol*s
Toluene	TEBAC	5.0	1:2	3.23
Toluene	TBAI	5.0	1:2	3.68
Toluene	CTMAB	5.0	1:2	1.59
Toluene	TEBAC	2.5	1:2	1.05
Toluene	TEBAC	3.3	1:2	1.32
Toluene	TEBAC	10.0	1:2	6.01
Toluene	TEBAC	5.0	1:4	0.38
Toluene	TEBAC	5.0	1:8	0.22
Toluene	TEBAC	5.0	1:12	0.04
Chlorobenzene	TEBAC	5.0	1:2	2.34
Chlorohexanone	TEBAC	5.0	1:2	3.98

Note: The accuracy of k is estimated to be $\pm 0.04*10^{-4}$ l/mol*s

RESULTS AND DISCUSSION

While studying the influence of the catalyst on the rate of UO formation it was found (Table 1) that the highest reaction rate was observed when using tetra-n-butylammonium iodide (TBAI). The lowest reaction rate was observed using cetyltrimethylammonium bromide (CTMAB). However, due to availability triethylbenzylammonium chloride (TEBAC), with catalytic activity approximately 1.5 times lower than that of TBAI (estimated from the initial rates) was chosen for all the experimentation.

The influence of the amount of catalyst 2.5; 3.3; 5.0 and 10.0 % mol. TEBAC from acid contents) on the reaction rate was first investigated. It was found (see Table 1) that the essential increase of process rate is observed when increasing the catalyst concentration from 5.0 to 10 mol % ralative to the CA concentration.

From Table 2, where the influence of temperature on reaction 1 is presented, it can be seen that the reaction rate between DER and CA increases with increasing temperature. 373 K was found to be and optimum and sufficient temperature, since the energetic expenditures are increased at higher temperature are not economically worthwhile. The activation energy of reaction 1 was determined to be 82.3 Kjoule/mol. It was determined in Arrehenius coordinates based on the constants given in Table 2.

Investigations of the influence of solvent on the reaction of CA with DER, conducted at 373 K, has shown (Table 1). The reaction rate is almost the same in either chlorobenzene and toluene, but considerably higher in cyclohexanone. The initial reaction rate thus increases in the following order: toluene - chlorobenzene - cyclohexanone (Table 3).

Table 2. The effective rate constants and activation energy of the reaction of DER with CA in toluene

Quantity of TEBAC, % mol	$k*10^4$, l/mol*s at T, K				$E_{act.}$, KJoule/mol
	353	363	373	383	
5.0	0.71	1.10	2.23	6.31	82.3

Table 3. The initial reaction rate of DER with CA at 373 K in different solvents

Solvent	$T_{boil.}$, K	W_o*10^3, mol/l*s
Toluene	383	0.167
Chlorobenzene	403	0.245
Cyclohexanone	429	0.378

Since solvent removal is necessary to obtain UO, the solvent with the lowest boiling temperature is desired since the properties of the final products are dependent on the quantity of residual solvent. Therefore, toluene was choosed as the reaction medium for further work, described below.

The investigation of the influence of the initial reactant ratio on the reaction rate in the presence of toluene shows (Table 1, Fig. 1) that stoichiometric increases of acid in the initial mixture essentially does not increase the rate of this reaction. Therefore, the most effective utilization of the reaction volume is achieved at a molar ratio of initial reactants CA:DER of 2:1.

Based on the above mentioned kinetic investigations using the transformation method [7], it was established that the acid conversion corresponds to the change in the quantity of epoxy groups (Fig. 1), despite a change of the molar ratio DER:CA in the interval 1:(1...12) accordingly. It indicates the absence of the polymerization of resin epoxy groups in this process.

From Fig.1 it can be seen that the kinetic data at different DER:CA ratios give one curve when combined on the same plot. The rate of acid expenditure versus time on the generalized kinetic curve depends on the relative acid concentration in a specific moment of time. This concentration in a specific moment of time is the difference between the absolute concentration and concentration at reaction time (Fig.2).

The obtained results reveal the invariance of the reaction mechanism between DER and CA over the examined acid concentrations range. This suggests first order reaction with respect to acid; it appers that the reaction proceeds in two stages.

The first stage is a rapid complexation reaction leading to [CA-DER] formation. It's concentration in the reaction mixture is equal to the concentration of either the acid or the epoxy resin, depending on which of the two components
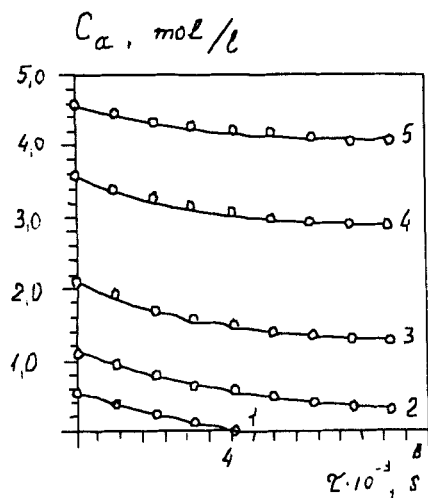
Figure 1. The kinetic curves by following carboxyl groups changes at 373 K in toluene with molar ratios DER:CA of 1:1 (1), 1:2 (2), 1:4 (3), 1:8 (4), 1:12 (5); TEBAC concentration ÷5 % the molar of the acid concentration.
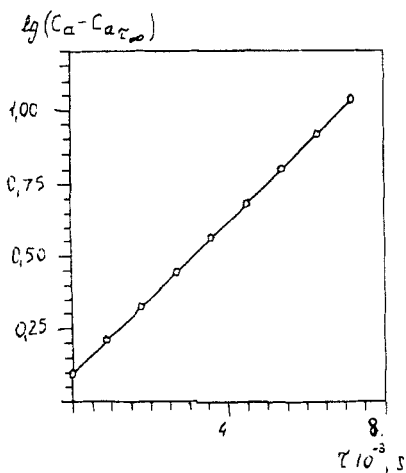

Figure 2. lg $(C_a - C_a\tau_\infty)$ versus time at 373 K in toluene with molar ratio DER:CA = 1:2 and a TEBAC concentration = 5% mol. of the acid concentration.

C_a-present acid concentration determined by base/acid method (8).

appers to be in abundance. The complex formation equilibrium constant appears to be sufficiently high.

The transformation of this complex into the final product takes place in a second, slow stage. This is confirmed by the fact is that the half-logarithmic anamorphosises of the acid's concentration ($\lg (C_a-C_a\tau_\infty)$) versus time is linear (Fig.2).
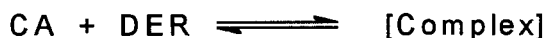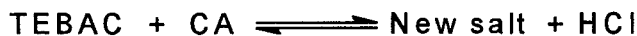
A change in the catalyst concentration leads to a reaction rate change. Using the transformation method [7] (Fig.3, Fig.4), it was found that the transformation coefficient (η), i.e. the rate constant, practically linearly depends on the catalyst concentration. This indicates a first order dependence for ring catalyst.

After a analysing this dependence (Fig.4), it was established, that the tangent, extended to the horizontal axis, provides the quantity of "inactive" catalyst, approximately 10-15 %. It was shown on tangent to a curve (fig. 4) and it was cut on the axis ~15 m.%. This indicates that free TEBAC is the true catalyst of the reaction. The segment on the horizontal axis (Fig.4) characterizes the acid-connected TEBAC quantity. Thus the equlilbium

$$\text{TEBAC} + \text{CA} \leftrightarrow \text{New salt} + \text{HCl}$$
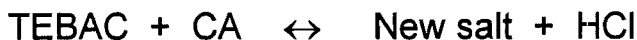
favours reactants. This seems natural since more weak organic acid takes part in the formation of the new salt.

Based on investigations the following reaction scheme for the reaction between CA and DER in the presence of TEBAC is suggested:

$$\text{TEBAC} + \text{CA} \rightleftharpoons \text{New salt} + \text{HCl}$$

$$\text{CA} + \text{DER} \rightleftharpoons [\text{Complex}]$$

$$[\text{Complex}] \xrightarrow{\text{TEBAC}} \text{Product}$$

The effective activation energy of this reaction calculated in accordance with the Arrehenius equation using the transformation method makes up 79.6 Kjoule/mol. This value confirms well with the magnitude of the activation energy, calculated using the rate constants of the second order kinetic equation (82.3 Kjoule/mole).

The obtained kinetic data and the results from the optimization study for obtaining UO based on CA and DER allowed suggestions regarding methods of the synthesis.

The characteristics of the synthesized oligomers are presented in the Table 4.

CONCLUSION

The obtained oligomers are viscous substances, dark-yellow in colour, and soluble in acetone, benzene, chloroform and other organic solvents. Their general structure
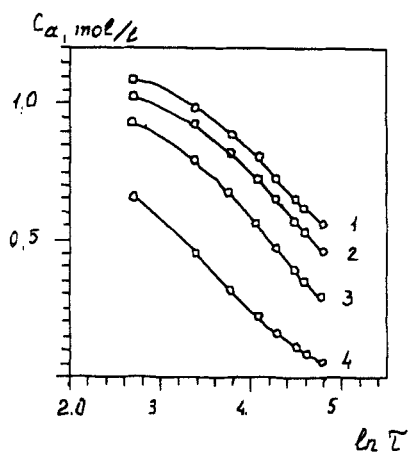
Figure 3. Changes in the carboxyl groups versus $\ln\tau$ at TEBAC concentration = 2.5 (1); 3.3 (2); 5.0 (3) and 10.0 (4) % mol. at 373 K in toluene with molar ratio DER:CA = 1:2; τ - min.
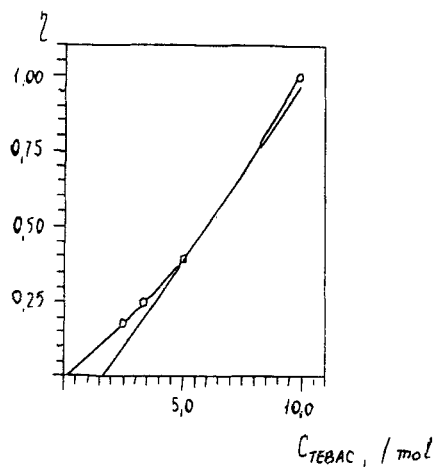
Figure 4. Dependence of the transformation coefficient (η) on the TEBAC quantity at 373 K in toluene with molar ratio DER:CA = 1:2.

Table 4. The characteristics of the unsaturated oligomers based on dianic epoxy resin (DER) and crotonic acid (CA).

Yield	Mol. weight		Iodine number
%	experiment.	theoretic.	g I_2 /100 g
89.8	500	540	94.4

was confirmed by IR and UV spectroscopy. Epoxy and carboxyl groups are absent in UO. Oligomers based on crotonic acid are stable on storage.

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