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Salih Yildiz[a]; U. Sancar Vural[a]; Refika Kurbanova[a]
[a] Faculty of Arts and Sciences, Department of Chemistry, SelçLuk University, Konya, Turkey

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THE INTERACTION OF EPOXY TOLUENE OLIGOMER CONTAINING CHLOROMETHYL GROUPS AND P-TERT-BUTYLCALIX[6]ARENE

Salih YILDIZ, U. Sancar VURAL and Refika Kurbanova

Selçuk University, Faculty of Arts and Sciences,
Department of Chemistry, 42079 Konya/Turkey

ABSTRACT

Oligomeric toluene material which has epoxy group (ETO) was prepared through reaction of toluene and epichlorohidrine in the presence of BF_3. Epoxy toluene oligomere containing chloromethyl groups (ETOC) was synthesized from the treatment of NaOH and ETO for 6-8 hours. The macromolecular derivative of oligomer (ETOC-I_6) was obtained from the reaction of ETOC and p-tert-butylcalix[6]arene (I_6) in the presence of CH_3ONa. When the concentration of ETOC is greater than I_6, the reaction was observed as pseudo first order, benzene was used as solvent. The activation energy and rate constant of the reaction were calculated as 25.082 kj.mol^{-1} and 3.155.10^{-5} s^{-1}, respectively. The amounts of chlorine in ETOC-I_6 was determined 6.37% by Schöniger Method, and its molecular weight was determined as 2778.84 g.mol^{-1} by cryoscopic method using benzene as solvent.

INTRODUCTION

Epoxy toluene oligomers (ETOC) are very important substances due to effective functional groups in their structure and are especially used as polymer additives[1]. The chlorine atoms in the functional groups of oligomeric compound increases the stability of the polymer materials against burning and heat. The number of chlorine in the oligomer depends on the reaction temperature, reaction time and especially on the ratio of the reactivities[2].

The calixarenes (I_n), n=4 to 8, are macrocyclic oligomers that can be obtained by the base-catalysed condensation of p-substituted phenols with formaldehyde, which are bridged by methylene in ortho-position[3]. An important feature of this class of macrocyclic is their cylindrical molecular geometry, and this feature is now finding wide applications in various fields of chemistry such as host-guest chemistry, selectivity for some metal ions, and catalytic effect[4], i.e.

EXPERIMENTAL

Chemicals

Stiren, toluen, epichlorohydrine and other chemicals were analar grade obtained from Merck Chem. Corp. Solutions were prepared without any further purification. p-tert-butylcalix[6]arene were synthesis according to Gutsche Procedure.

The synthesis of ETOC

1 mol of toluen in flask was reacted with 3 mol of epichlorhidrine in the presence of $BF_3(C_2H_5)O$ as 2% by stirring and heating at 40°C for 2 hours. Then,

temperature was inscreased to 60°C and 1.2 mol of 40% NaOH was added to the reaction mixture and was heated for 6-8 hours. At the end of the reaction, obtained material was cooled to the room temperature, the excess toluen was removed under low pressure, then it was washed, and dried,. Finally a viscous product with orange yellow colour was obtained.

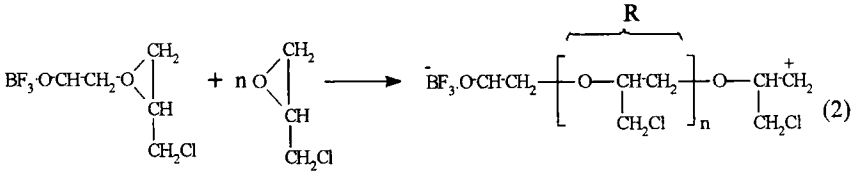
The synthesis of ETOC-I_6

0.76 g of ETOC was reacted with 0.095 g I_6 by using chloroform as solvent in the presence 0.0028 g of CH_3ONa, at 20-25°C. ETOC-I_6 precipitated as a white solid. After removing the solvent under vacuum, the precipitate was filtered off and washed with methanol.

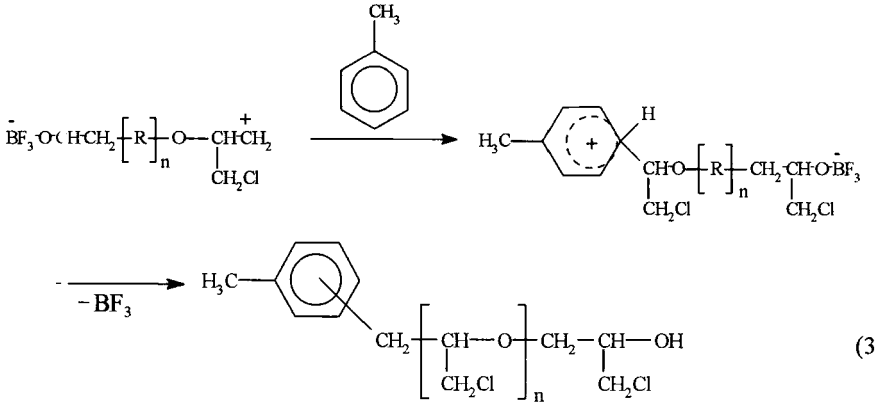
RESULTS AND DISCUSSION

Oligomeric toluene material which have epoxy group (ETO) was obtained by heating toluene with epichlorohidrine at 40°C in the presence of BF_3 for 2 hours. The mechanism of the interaction between epichlorohidrine and BF_3 is suggested as follows

(1)



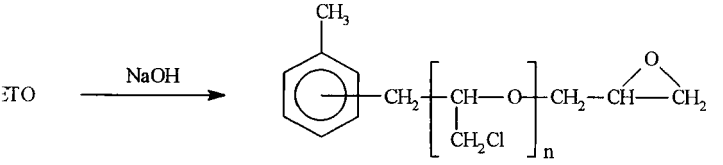
(2)



(3)

ETO

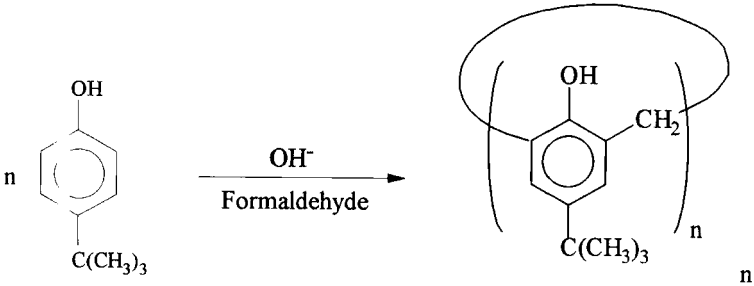
When ETO is reacted with 40% NaOH for 6-8 h, the reaction is



(4)

ETOC

p-tert-butylcalix[6]arene was synthesised by heating p-tert-butyl phenol and formaldehyde in the presence of NaOH, for 4 hours in xylene.

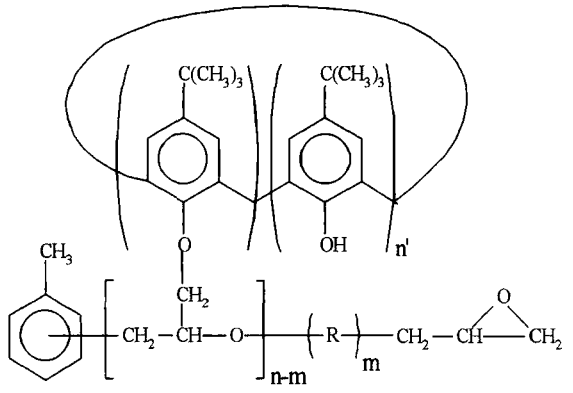


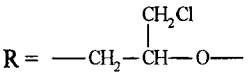
(5)

n : 4 to 8

I_n

ETOC-I_6 was obtained from the reaction of p-tert-butylcalix[6]arene and ETOC in benzene, at room temperature in the presence of CH_3ONa.





ETOC-I_6

Molecular weights

Molecular weights of ETOC and ETOC-I_6 were calculated as 1038.73 $g.mol^{-1}$ and 2778.84 $g.mol^{-1}$, respectively, benzen was used as the solvent. Cryoscıopic method was used for the determination of molecular weights.

The determination of chlorine numbers by Schöniger Method

Schöniger method is based on the burning of the organic substances and polymer materials in a container filled oxygen[5].

$$2\,RX \xrightarrow[Pt]{O_2} X_2 + n\,CO_2 + m\,H_2O \qquad (6)$$

$$X_2 + 2\,KOH + H_2O_2 \longrightarrow 2\,KX + O_2 + 2\,H_2O \quad (7)$$

$$2\,KX + Hg(NO_3)_2 \longrightarrow HgX_2 + 2\,KNO_3 \quad (8)$$

where R is organic sample, and X is halogene. To carry out this, 3-20 mg of sample is placed in the burning stick with platin tin by rolling (winding) with a filter paper. 10 mL of distilled water, 1 ml of 2 N KOH solution an 3 drops of H_2O_2 are added to burning flask which is filled with oxygen. After that, filter paper containing sample on the stick was burned completely. The flask is shacked until all the gases occurring in the flask are completely observed (5-10 minutes). Later, the flask is opened and the contents was poured into another 100 mL flask. It is boiled for five minutes and then allowed to cooling, 0.5 N HNO_3 is added to the solution until pH becomes between 2.3-2.5. The samples are titrated with 0.01 N $Hg(NO_3)_2$ after adding 2-3 droplets of diphenylcarbazone. The same process is repeated the blank and effect of the filter paper is ignored. Calculations are done by the following formula:

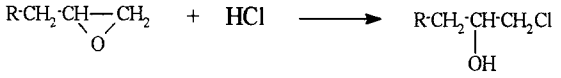
$$N_{Cl} = \frac{(V_2 - V_1)\,K\,m\,100}{W} \quad (9)$$

where N_{Cl} is percentage of chlorine in the sample, V_1 and V_2 are the volumes (mL) of 0.01 N $Hg(NO_3)$ in titrations procedures for blank and sample, respectively, K is a titration factor for 0.01 N $Hg(NO_3)_2$, m is the equivalent amount of halogen to 1 mL of 0.01 N $Hg(NO_3)_2$ (this is 0.35457 for Chlorine), and W is the amount of the sample in mg.

Analyses are performed according to Schöniger method, and chlorine percentage in ETOC and ETOC-I_6 were found to be 37.54 % and 6.37 %, respectively.

The determination of epoxy numbers

The numbers of epoxy groups in sample is determined according to the following reaction[6].



(10)

The mixture of the reaction was titrated with NaOH and the number of epoxy groups is estimated from the reacting HCl amount with the following formula:

$$N_{EPO} = \frac{(V_2\text{-}V_1)\ 0.0043\ K\ 100}{W} \qquad (11)$$

where N_{EPO} is percentage of epoxy groups in the sample, V_2 is the volume of KOH that equals to blank sample. V_1 is the volume of KOH that equals to free acid remaining at the end of the reaction, W is the amount of the sample (g), K is a titration factor for 0.1 N KOH, and 0.0043 value at the right hand side of the equation (11) is the number of epoxy groups the corresponding to 1 mL of 0.1 N KOH. It was found that there was 8% epoxy groups in oligomere structure.

The analyses results are given in Table 1. These results were demonstrated that the amount of the remained chlorine is 11%. Thus, it was understood that the ratio of remained hydroxyl and reacting hydroxyl numbers is 1.

Table 1. Some analytical results of ETOC, I_6 and ETOC-I_6. The chloroform was used as solvent for the determination of UV spectra at 22°C.

Compounds	λ_{max} / nm	Cl %	Epoxy %	Molecular weight
I_6 ($C_{66}H_{96}O_6$)	305	-	-	977
ETOC ($C_{34}H_{48}O_{12}Cl_{11}$)	252	37	4.139	1038.73
ETOC-I_6 ($C_{166}H_{222}O_{24}Cl_5$)	344	6	1.547	2778.84

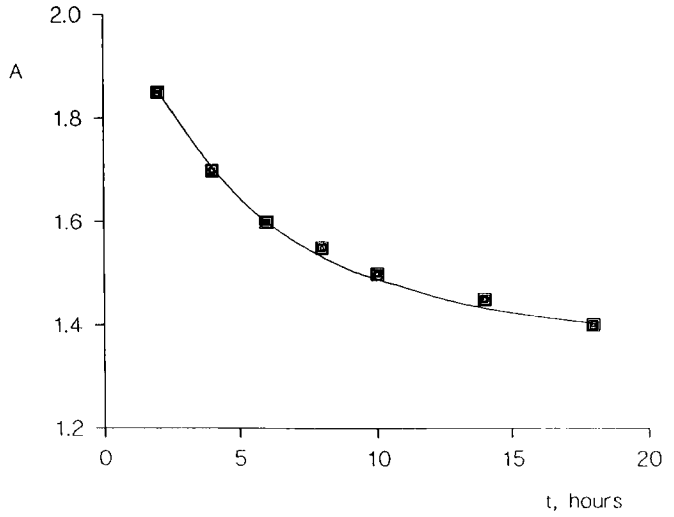


Fig. 1. The absorption values of the reaction between ETOC and I_6 in chloroform, T= 23°C, λ=344 nm.

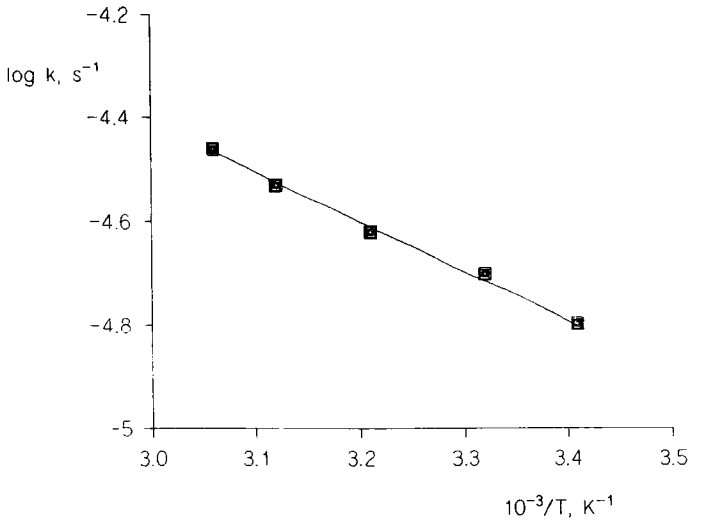


Fig 2. The variation of log k with 1/T for the reaction between . ETOC and I_6 in chloroform, at various temperatures.

Reaction Kinetics

Spectrophotometric measurements were used for kinetic studies. The order of reaction between calixarene and ETOC was determined as pseudo first order when oligomere concentration is greather than that of calixarene in the presence of CH_3ONa. Chloroform was used as solvent. The absorption maximum (344 nm) of the product was used as a measure of concentration changing in time (Fig 1).

The relationship between reaction rate constants and temperature was determined from the changes of absorption values at 344 nm of the product, between 291-306 K. The activation energy of the reaction was calculated by using Arrhennius equation as 25.082 kJ/mol from the slope of the plot drawing log k against 1/T shown in Fig 2.

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