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Kinetic study of cis-polybutadiene epoxidation by using ^{1}HNMR spectroscopy in buffered oxone® solution with tetra-n-butyl ammonium bromide as phase transfer catalyst (PTC)

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Abstract

Cis-polybutadiene was functionalized using in–situ generated DMD as oxidant and tetra-n-butyl ammonium bromide as phase transfer catalyst (PTC). The epoxidation process was investigated by ^{1}HNMR spectroscopy. ^{1}HNMR spectrum analysis of products confirms the absence of ring opening side products in epoxidation reaction. Various factors such as reaction temperature, reaction time and the concentrations of oxidant, PTC and polymer are also examined in detail. Kinetic study showed that the catalytic epoxidation reaction of cis-polybutadiene is first-order with respect to double bonds and activation energy for the reaction is 22.82 KJ/mol.

Keywords: Kinetic study; Polybutadiene; Oxone®; Epoxidation; Dimethyldioxirane; *Tetra*-n-butyl ammonium bromide.

1. Introduction

Polybutadiene is one of the most popular elastomers widely used in the industry because of its unique, physical properties as elasticity, toughness and durability [1, 2]. These properties can be modified by introduction of epoxy functional groups into non-polar polymer chains. This will improve the polarity of the final polymers and expand their applications, particularly in polymer alloys [3]. New processes for epoxidation of olefin double bonds have been developed with respect to environmental considerations to replace the chlorohydrins method. Green chemistry demands chemical processes for epoxide production via direct oxygen insertion into C=C bonds. Oxygen sources include molecular oxygen, hydrogen peroxide, organic hydroperoxides and peracids [4].

The conventional method for the epoxidation of diene polymers mostly utilizes peroxy acids as epoxidizing agent, who often results in significant side reactions and gelation at high epoxidation levels because the oxiran first formed is easily ring – opened in acidic media [5]. Also hydroxyl-terminated polybutadiene (HTPB) based polyurethane (PU) solution was prepared by reacting equal equivalent of 4,4-methylene diphenyl diisocyanate (MDI) and HTPB with 1,4-butanediol (BDO) as chain extender. The PU was then cast into membrane. The kinetic of

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epoxidation of HTPB-based PU membrane by an in-situ generated peracid method was studied by infrared spectroscopy [6]. Styrene-butadiene-styrene linear block copolymer (SBS) was epoxidized using hydrogen peroxide (H_2O_2) and a phase transfer catalyst [7]. Epoxidation of 1, 4-bis (allyloxy) butane by hydrogen peroxide under phase transfer catalysis and transition metal salts was investigated. The most advantageous conditions for the epoxidation were determined (temperature, reaction time, the type and amount of phase transfer catalyst, molar ratio of hydrogen peroxide to 1,4-bis (allyloxy) butane, the amount and molar ratio of ($H_3PO_4.Na_2WO_4$ $2H_2O$) [8]. Cis-Polybutadiene has been transformed to the corresponding polyepoxide, a polyalcohol precursor, with chloro or acetato-manganese (III) tetra phenyl porphyrin [Mn (III) (TPP) Cl, Mn (III) (TPP) OAc], acting as a catalyst in association with two different oxygen donors, sodium hypochlorite and iodosylbenzene [9]. Hay et al claimed that diene polymers can be epoxidized with hydrogen peroxide in the presence of methyltrioctylammonium tetrakis (diperoxo- tungsto) phosphate (3-) as the phase transfer catalyst in a biphasic system [10].

One of the main advantages of catalytic epoxidation is to adopt acid-free material as epoxidizing agent and thus avoid oxirane ring opening side reactions catalyzed by acid. Recently, we found that cis-polybutadiene could be effectively epoxidized by a simple and commercially available system, which is composed of tetra-n-butyl ammonium bromide and Molybdenum oxide (MoO_3) and oxone® [11, 12]. This paper will report the preliminary investigation results, including the main influencing factors such as reaction temperature, reaction time and the concentrations of oxidant and catalyst and polymer and the kinetic analysis.

2. Experimental

2.1. Materials

Cis-polybutadiene (Mw = 2000000-3000000, Tg = -102 °C, 98% cis content) was obtained from Aldrich chemical company. Tetra-n-butyl ammonium bromide, potassium bicarbonate ($KHCO_3$), CH_2Cl_2, oxone® (potassium peroxymonosulfate) and acetone were purchased from Merck company and were used as received.

2.2. Analysis of the products

^{1}HNMR and ^{13}CNMR spectra of the products were obtained by using a BRUKER AVANCE 300 MHz instrument with $CDCl_3$ as solvent. All products were known and characterized by comparision of their physical and spectrometric data with those of authentic samples.

2.3. Catalytic epoxidation procedure of cis-polybutadiene

The required amount of cis-polybutadiene was dissolved in 25 ml. dichloromethane. Then 5 ml. of acetone was added to the solution. The required amount of $KHCO_3$ (3.5 equiv to 1.0 equiv Oxone®) was dissolved in distilled water and then added to the reaction mixture. Then the PTC was added to the mixture and the required amount of oxone® (the source of DMD) was dissolved in distilled water and then added to the reaction mixture. The reaction was carried out in a five-necked reactor fitted with a reflux condenser in which temperature was thermostatically controlled within ±0.05 °C by circulating water and using a Cole-Parmer cooling/heating instrument (Model 12101-15). The solution was continuously stirred with using a magnetic bar. At various intervals of time, specific amount of reaction mixture was withdrawn and washed with cold distilled water and dried at 323 K under vacuum for at least 24 h. ^{1}HNMR and ^{13}CNMR spectra were obtained for each sample.

3. Results and discussion

Fig. 1 shows ^{1}HNMR spectrum of unepoxidized cis- polybutadiene (a) and epoxidized cis-polybutadiene at different epoxidation degrees [(b) 33.02%, (c) 43.89% and (d) 60.66%].

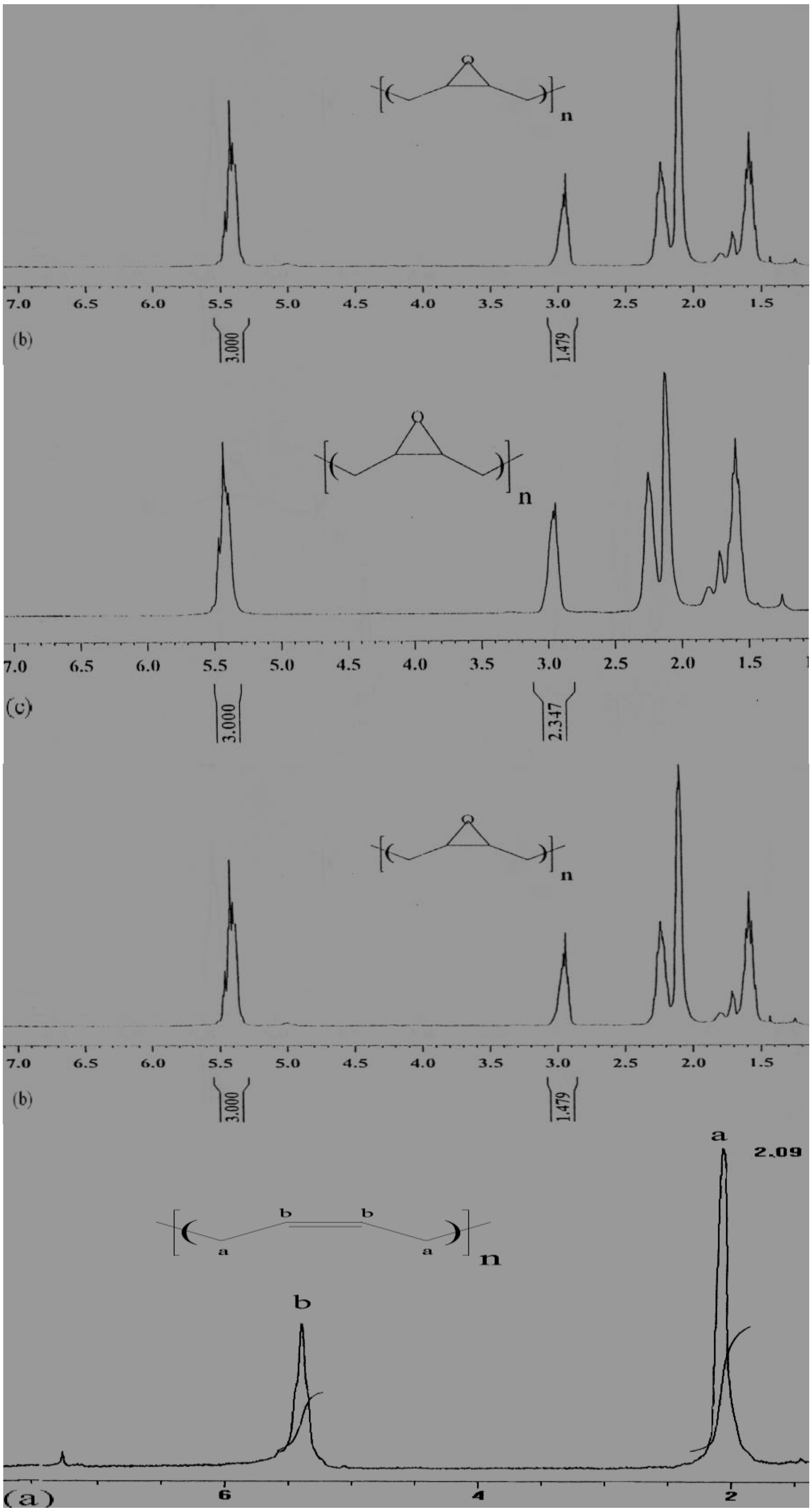


Fig. 1. ^{1}HNMR spectra of cis-polybutadiene (a) and epoxidized cis-polybutadiene [(b), (c) and (d)]

As indicated in Fig. 1, in the ^{1}HNMR spectrum of the unepoxidized cis- polybutadiene (a) there are two peaks at 5.5 ppm and 2.1 ppm that are assigned to the protons of double bonds (vinyl protons) and CH_2 protons, respectively. On the other hand, the epoxidized cis-polybutadienes [(b), (c), and (d)] show four new signals, at 2.9-3 ppm and 1.6, 1.7, 1.8 ppm in ^{1}HNMR spectra, which are assigned to the epoxy ring and attached methylene protons to carbon-carbon double bonds, respectively. An additional peak appeared during the epoxidation reaction at 2.25 ppm and was assigned to the attached methylene protons to the epoxy functional groups. From spectroscopy data, we concluded that side reactions due to ring opening of epoxy group and over oxidation reactions had occurred. On the other hand, spectral results manifest the successful epoxidation of cis-polybutadiene. Moreover, from NMR spectra no significant side reactions, such as ring opening and gelation, occur in this epoxidation system because of no observable characteristic absorption of any side products at 3-4.5 ppm in ^{1}HNMR, assigned to attach OH group.

When the epoxidation reaction progressed, the intensity of the vinyl proton signals decreased and additional signals appeared at 2.9-3 ppm, which was assigned to the epoxy ring protons. Using equation (1), we can calculate the conversion of double bonds, X, to the epoxy functional group:

$$X= I_e / I_e + I_d \qquad (1)$$

where I_e is the peak area of the epoxy group proton at 2.9-3 ppm and I_d is the peak area of vinylic protons at 5.5 ppm, respectively [7]. Fig. 2 shows the effects of PTC concentration on the conversion of double bonds. An important observation in this reaction was the dependence of the epoxidation yields to the PTC concentrations. On the other hand, it should be pointed out that in the absence of the catalyst no epoxidation occurs.

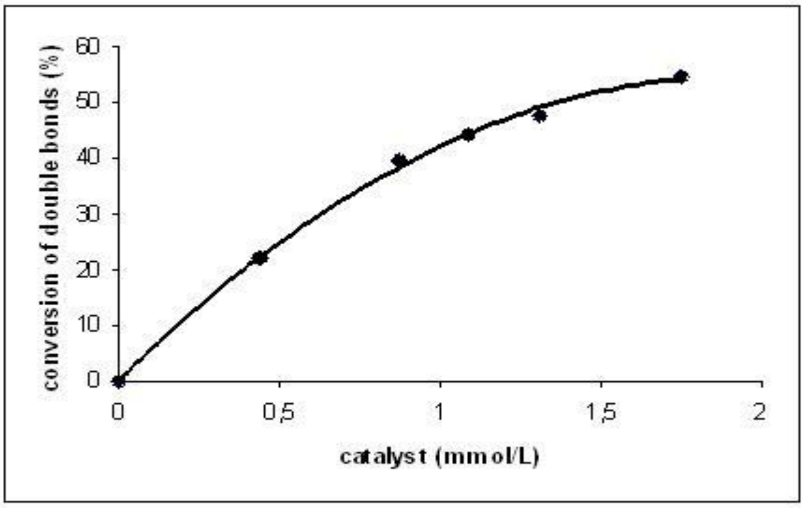


Fig. 2. Conversion of double bonds *vs.* concentration of catalyst, polymer and oxone® are 24 g/L and 0.079 M respectively and reactions were performed at 298 K and 60 min.

The effect of oxone® concentration on the conversion of double bonds is shown in Fig. 3. As the concentration of oxone increases, the conversion of double bonds increases. The effect of the concentration of the polymer on the conversion of double bonds is shown in Fig. 4. As the polymer concentration further increases, the conversion of double bonds decreases. This can be attributed to the fact that the viscosity of the reaction system becomes higher as the polymer concentration increases.

Fig. 5 shows the conversion of double bonds in various reaction times at different temperatures. The conversion of double bonds increases with increasing reaction time at defined temperature. At 303 K the reaction time was longer and reaction time is shorter for the partial epoxidation process, but for further epoxidation the yields were constant due to evaporation of dichloromethane solvent and the precipitation of polymer. Therefore, the optimal temperature as selected was 298 K, at which no evaporation of solvent was observed.

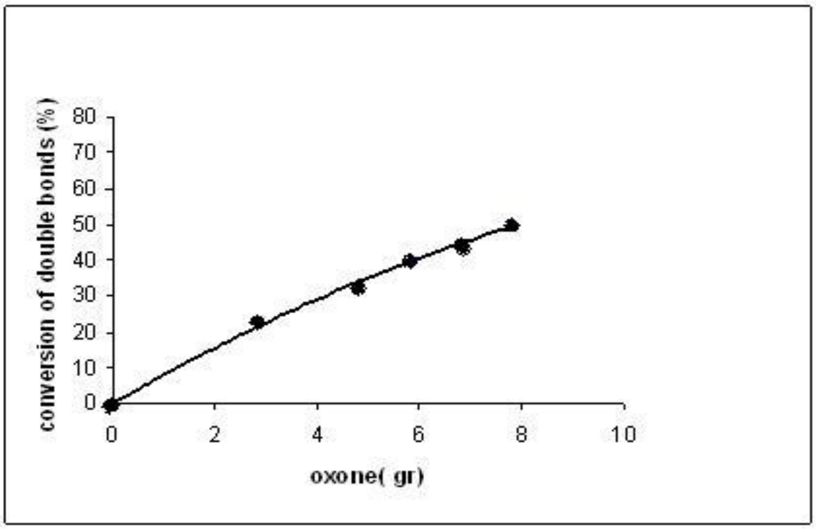


Fig. 3. Conversion of double bonds *vs.* concentration of oxone®. Polymer and catalyst are 24 g L^{-1} and 2.48 mmol L^{-1} respectively and reactions were performed at 298 K and 60 min.

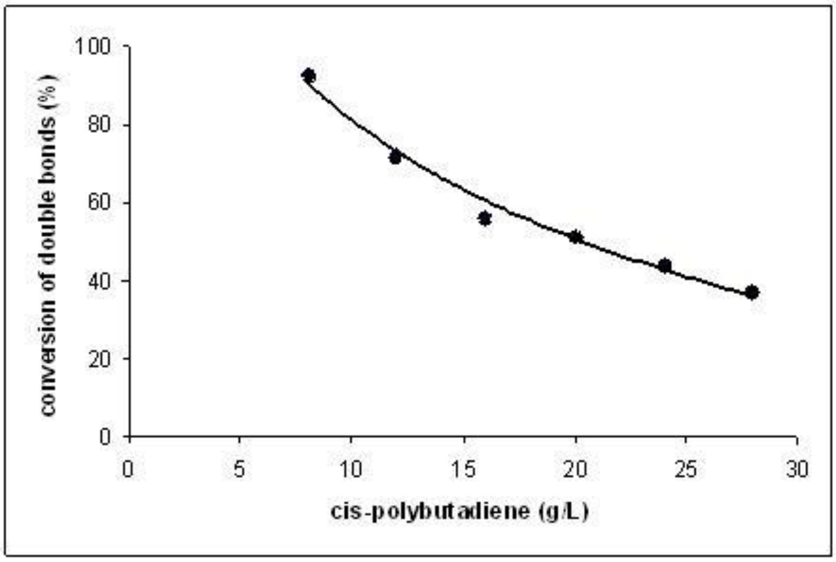


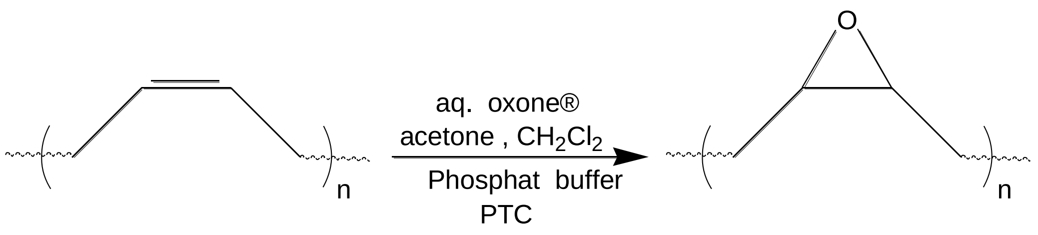
Fig. 4. Conversion of double bonds *vs.* concentration of polymer, oxone® and catalyst are 0.079 M and 2.48 mmol L^{-1} respectively and reactions were performed at 298 K and 60 min.

3.1. Kinetic analysis

The epoxidation of cis-polybutadiene with DMD in the presence of tetra-n-butyl ammonium bromide can be described by Scheme 1. If we assume that the epoxidation of cis-polybutadiene is first order relative to the double bonds the reaction rates can be simply expressed as eq. (2):

$$- d [C=C]/dt = k_{ap1}[C=C] \qquad (2)$$

where k_{ap1} is the apparent first-order rate constant for epoxidation of cis-polybutadiene and is a function of PTC and oxone® concentrations. The concentrations of PTC are constant during the reaction.



Scheme 1 Catalytic epoxidation of cis-polybutadiene.

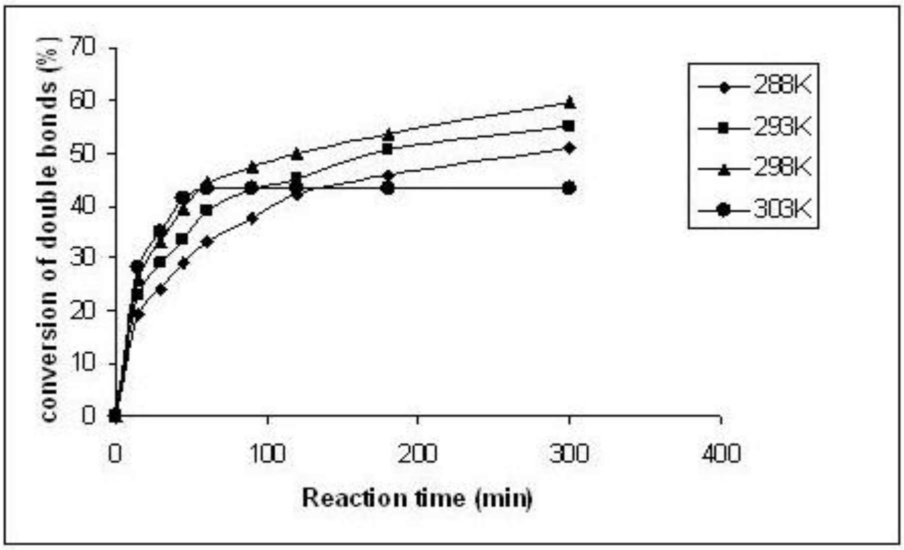


Fig. 5. Dependence of double bonds conversion on reaction time at different temperatures, polymer, catalyst, oxone® are 24 g L^{-1}, 2.48 mmol L^{-1}, 0.079 mol L^{-1}, respectively.

At lower conversion of double bonds the concentration of oxone® is approximately constant when the molar ratio of oxone® is several times in excess of the concentration of double bonds [7]. Integrate [C=C] over t, then

$$H = \ln [C{=}C]_0/[C{=}C]_t = k_{ap1}t \tag{3}$$

or

$$H = \ln 1/1-X = k_{ap1}t \tag{4}$$

where $[C{=}C]_0$ and $[C{=}C]_t$ represent the concentration of double bonds at the beginning of the reaction and defined time , respectively, and X is the conversion of double bonds defined time. Fig. 6, shows the plots of H at different temperatures against reaction time and gives a linear relationship. This indicates that the epoxidation of cis-polybutadiene with DMD in the presence of tetra-n-butyl ammonium bromide as the catalyst is a first-order reaction relative to the double bonds.

The apparent first-order rate constants k_{ap1} at different temperatures were determined from the slops of H versus reaction time curves at the corresponding temperatures and are listed in Table 1. The dependence of reaction rate constant in relation to temperature is expressed by a logarithmic from of the Arrhenius equation:

$$\text{Ln } k = \ln k_0 - (Ea / (RT)) \tag{5}$$

where k_0 is a constant related to the number of collisions between molecules per unit of time and E_a is the activation energy that represents the minimum energy required for the reaction to occur.

The plot of lnkap1 against 1/T of this reaction system is shown in Fig. 7. The activation energy can be obtained from the slope and is about 22.82 KJ/mol.

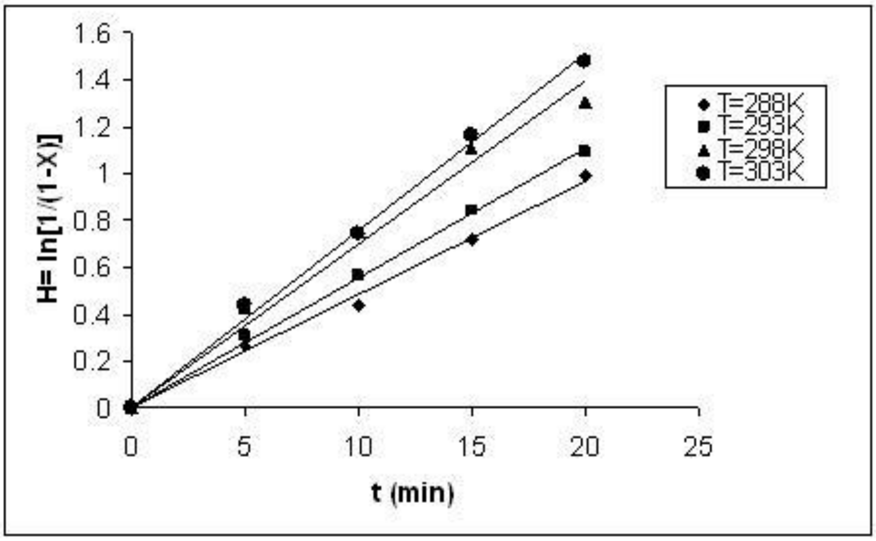


Fig. 6. Plot of H *vs.* reaction time at different temperatures, polymer, catalyst and oxone® are 24 g L^{-1}, 2.48 mmol L^{-1} and 0.079 mol L^{-1}, respectively.

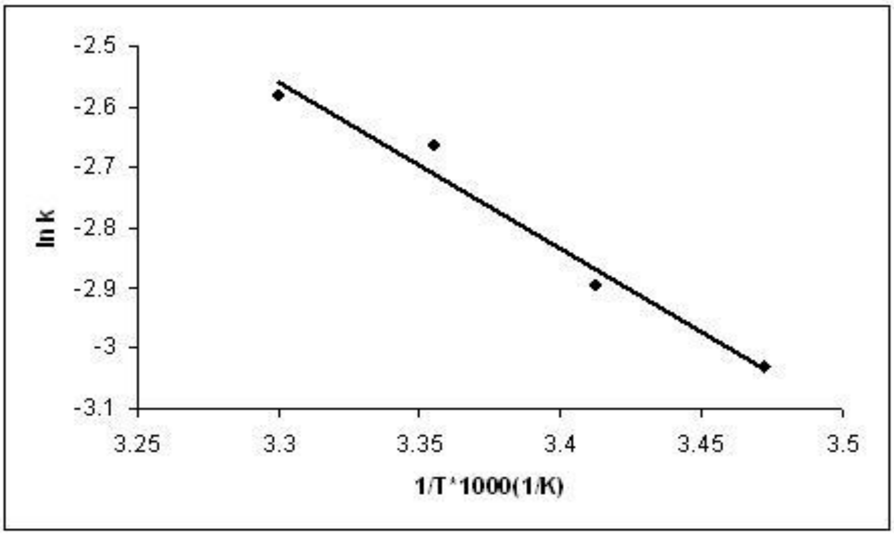


Fig. 7. Arrhenius plot of catalytic epoxidation of cis-polybutadiene.

Table 1
Apparent first-order rate constants k_{ap1} for epoxidation of cis-polybutadiene at different temperatures.

T °(K)	288	293	298	303
(1/T)* 1000(1/K)	3.472	3.412	3.355	3.3
K' * 1000(1/min)	48.3	55.3	69.7	75.5
ln k'	-3.030	-2.894	-2.663	-2.583

4. Conclusions

The transformation of cis-polybutadiene to epoxidized cis-polybutadiene with the help of in–situ generated DMD in association with tetra-n-butyl ammonium bromide was successfully fulfilled for the first time. ^{1}HNMR spectrum analysis confirms the absence of epoxide ring opening side reaction in this system. On the other hand,from NMR spectra no significant side reactions, such as ring opening and gelation, were found in this epoxidation system because of no observable characteristic absorption of any side-products at 3-4.5 ppm in ^{1}HNMR, assignable to the attached OH group. The kinetic analysis reveals that the catalytic epoxidation reaction of cis-polybutadiene is first-order with respect to the concentrations of double bonds, and the apparent activation energy for the reaction is about 22.82 KJ/mol.

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