



## Multiphase Reaction Kinetics of Epoxidation of Polyisobutene

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The kinetics of epoxidation of polyisobutene by peracetic acid generated *in situ* from hydrogen peroxide and acetic acid in the presence of solid acid  $WO_3/ZrO_2$  were studied. The effect of several reaction parameters such as stirring speed, acetic acid-to-double bond molar ratio, temperature and content of catalyst were examined. Dynamic parameters were estimated using nonlinear regression method from the experimental data. A multiphase kinetic model of the epoxidation reaction was developed. There was good agreement between experimental and predicted data and simulation was performed to validate the model.

**Key Words:** Epoxidation, Polyisobutene, Peracetic acid, Kinetics, Model.

### INTRODUCTION

Chemical modifications are the useful ways to obtain new polymeric materials. Of the well-known chemical modifications of materials, epoxidation has been the most promising and advantageous method. Polyisobutene (PIB) as an important polymer is widely used as adhesives, sealants, cable insulation and packing material because of its unique physical properties such as thermal stability, resistance to weathering and UV light, excellent gas barrier properties, elasticity<sup>1-6</sup>. These properties can be modified by introducing epoxy functional groups into polymer chains, which can increase the polarity of the final polymers to expand their applications.

Epoxidation can be carried out by different methods, depending on feedstock, oxidant, catalyst. In recent years, much attention has been paid to the use of hydrogen peroxide as the oxidant because it is relatively low cost, environmentally friendly and safe<sup>7,8</sup>. Likewise, the epoxidation of unsaturated polymers has been attracting much more attention. Nikje and Mozaffazi<sup>9</sup> investigated the epoxidation of hydroxyl-terminated polybutadiene (HTPB) by using *in situ*-generated dimethyldioxirane (DMD) as oxidant and tetra-*n*-butylammonium bromide as a phase-transfer catalyst. The epoxidation of HTPB with hydrogen peroxide was investigated in the presence of phase-transfer catalyst<sup>10</sup>. Some kinetic concerning the epoxidation of several oils with peracetic acid generated *in situ* under homogeneous catalytic conditions, have been carried out in previous years<sup>11,12</sup>. These models were pseudo-homogeneous and established that the peracetic acid generation in the epoxidation was always the rate controlling step which

did not consider the presence of two immiscible phases. On the other hand, the kinetic parameters of the reaction considered as a two-phase liquid-liquid reacting system under the same reaction conditions were reported<sup>13,14</sup>. A heterogeneous kinetic model using acidic ion exchange resins as a catalyst has been presented<sup>15</sup>. The model did not consider the presence of liquid-liquid immiscible phases. Ion exchange resin was prone to swell in the organic phase, which was neglected by researchers.

In this work, polyisobutene oxide (PIBO) was obtained in the presence of  $WO_3/ZrO_2$ . There were three phases in the processes catalyzed by  $WO_3/ZrO_2$ : (1) an aqueous phase (acetic acid, hydrogen peroxide and water); (2) the organic phase; (3) an acidic solid catalyst phase.

This paper studied the kinetics of the epoxidation of PIB and the influence of different reaction parameters (temperature and concentration of acetic acid). Dynamic parameters for the individual steps were obtained from experimental data. The objectives of this study were to: (i) propose a mathematical model for the reaction system; (ii) estimate the model parameters and (iii) compare the model predicted with experimental data.

### EXPERIMENTAL

Polyisobutene (PIB:  $M_n = 1050$ , content of double bond = 0.00085 mol/g). Acetic acid (AR Grade), aqueous hydrogen peroxide (50 wt %) and heptane were obtained from reputed firms. They were used without further purification.

**Catalyst preparation:**  $Zr(OH)_4$  was prepared by precipitation of the solution of  $ZrOCl_2$  with 28 wt % ammonia.  $Zr(OH)_4$  was impregnated with the solution of  $(NH_4)_6W_{12}O_{39} \cdot xH_2O$  at

room temperature. After aging for 24 h, the precipitate was washed with distilled water repeatedly to remove chloride ions completely and dried at 100 °C for 5 h. The product was calcined at 700 °C in air flow for 4 h.

**Epoxidation of polyisobutene with peracetic acid generated *in situ*:** Polyisobutene, WO<sub>3</sub>/ZrO<sub>2</sub> and acetic acid were placed into the reactor and heated to the reaction temperature under reflux, using heptane as the diluent of the organic phase. Then, hydrogen peroxide was added, drop by drop (30 minimums in total) under stirring and the reaction was held for several hours to achieve reaction completion. Periodically, samples were taken, centrifuged at 1000 rpm for 10 min and analyzed.

**Phase partition coefficients of acetic acid and peracetic acid between the aqueous and polymeric phases:** Different contents of acetic acid, H<sub>2</sub>O, heptane and PIB were placed into a round-bottom flask, equipped with a reflux condenser. The mixtures were then stirred (500 rpm) for 3 h and later standing for another 3 h at 70 °C until physicochemical equilibrium was achieved, after which the sample was centrifuged and analyzed.

**Analytical techniques:** Iodine value was obtained using the Hanns's method in accordance with the Chinese Standard ZB/B66005.8-1990 by the following equations:

$$IN_{ac} = \frac{0.1269(V_1 - V_2)C_{Na_2S_2O_3}}{m_1} \times 100 \times \frac{1}{2A_I} \quad (1)$$

where  $IN_{ac}$ : iodine number of PIB after epoxidation (mol/100 g); 0.1269: mass of iodine correspond to 1 cm<sup>3</sup> of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (1 mol/cm<sup>3</sup>); V<sub>1</sub>: volume of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> used to titrate blank sample (cm<sup>3</sup>); V<sub>2</sub>: volume of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> used to titrate right sample (cm<sup>3</sup>); C<sub>Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub></sub>: concentration of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution (mol/cm<sup>3</sup>); m<sub>1</sub>: mass of sample (g); A<sub>I</sub>: molecular mass of iodine (g/mol).

Epoxy number was calculated according to the Chinese Standard GB/T4612-2008:

$$EN_{ac} = \frac{100(V_4 - V_3)C_{HClO_4}}{100m_2} \quad (2)$$

where  $EN_{ac}$ : epoxy number of epoxy polyisobutylene (PIBO) (mol/100 g PIBO); V<sub>3</sub>: volume of HClO<sub>4</sub> used to titrate blank sample (cm<sup>3</sup>); V<sub>4</sub>: volume of HClO<sub>4</sub> used to titrate right sample (cm<sup>3</sup>); C<sub>HClO<sub>4</sub></sub>: concentration of HClO<sub>4</sub> solution (mol/cm<sup>3</sup>); m<sub>2</sub>: mass of sample (g).

$$C_{IN} = \frac{IN_{be} - IN_{ac}}{IN_{be}} \times 100 \% \quad (3)$$

where  $C_{IN}$ : conversion of PIB;  $IN_{be}$ : iodine number of PIB before epoxidation;  $IN_{ac}$ : iodine number of PIB after epoxidation.

$$Y_{EN} = \frac{EN_{ac}}{EN_{max}} \times 100 \% \quad (4)$$

where  $Y_{EN}$ : yield of PIBO;  $EN_{ac}$ : epoxy number of PIBO after epoxidation (mol/100 g PIB);  $EN_{max}$ : epoxy number of PIBO calculated from the number of unsaturated bonds.

The concentrations of peracetic acid and H<sub>2</sub>O<sub>2</sub> were determined in accordance with the Chinese Standard GB/T 19108-2003. The principle could be summarized as that H<sub>2</sub>O<sub>2</sub>

was first titrated with potassium permanganate and then peracetic acid was determined iodometrically.

The content of acetic acid was calculated by volumetric titration, using a solution of sodium hydroxide in the aqueous phase and potassium hydroxide in the organic phase.

## RESULTS AND DISCUSSION

Epoxidation runs were conducted with the following range of variables: stirring speed 200-1000 rev/minimums; temperature (60-80 °C); acetic acid-to-double bond ratio (mole per mole) 0.5-1.5; catalyst concentration was expressed as weight percentage of organic phase in the range of 1 %.

**Influence of stirring speed:** To investigate the effect of mass transfer resistance, the reactions were performed carried out at stirring speeds of 200, 500, 1000 rpm. In these studies, the following parameters were fixed: temperature of 70 °C, reaction time of 3 h and the molar ratio of reagents of PIB/H<sub>2</sub>O<sub>2</sub>/AcOH = 1:5:1.5. Similarly, the amount of catalyst was 0.5 wt % in relation to the PIB. It was found that the highest yield of PIBO was achieved at stirring speed of 500 rpm (Table-1).

TABLE-1  
YIELD OF PIBO AT DIFFERENT STIRRING SPEED

	Stirring speed (rpm)					
	200		500		1000	
Time (min)	120	180	120	180	120	180
Iodine value (g/100 g)	13.5	10.87	11.79	8.32	11.8	8.52
Iodine conversion (%)	34.3	47.1	42.7	59.6	42.6	58.6
Yield of PIBO	32.5	44.2	39.6	55.7	39.1	54.9

It can be seen that the oxirane formation rate was not affected by stirring speeds in the range beyond 500 rpm. Direct effect of stirring speed on mass transfer process was mainly the interfacial area of mass transfer. Increased stirring speed beyond 500 rpm reached the "saturation effect" and may not result in increased interfacial contact area.

Hence, it was assumed that the reaction was free from mass transfer resistance under the given conditions. However, all subsequent experiments were performed at a stirring speed of 600 rpm to ensure that there was no resistance to mass transfer at interfaces.

**Effect of intra-particle diffusion resistance:** There was a variation in particle sizes of WO<sub>3</sub>/ZrO<sub>2</sub> to assess the influence of intra-particle diffusion resistance under otherwise similar reaction conditions.

The experimental data obtained are presented in Table-2. The results showed that any of the particle sizes gave practically same results. Hence, it proved that there was no intra-particle diffusion resistance on the catalyst (particle size < 0.3 mm).

TABLE-2  
EFFECT OF INTRA-PARTICLE  
DIFFUSION ON IODINE CONVERSION

	Particle size (mm)			
	0.3		0.074	
Time (min)	120	240	120	240
Iodine value (g/100 g)	11.76	5.33	11.58	5.4
Iodine conversion (%)	42.8	74.1	43.6	73.7
Yield of PIBO	39.6	68.5	40.7	67.8

**Influence of molar ratio of acetic acid to PIB:** The influence of the acetic acid to double bond molar ratio was investigated at different ratios: 0.5:1, 1:1 and 1.5:1. It showed the effect of acetic acid concentration on yield of the PIBO (Fig. 1). Increasing the acid concentration was found to increase a faster reaction rate. It has been observed that at the high mole ratio of CH<sub>3</sub>COOH, the stability of the oxirane ring was poor as the acid promotes the hydrolysis of the epoxide.

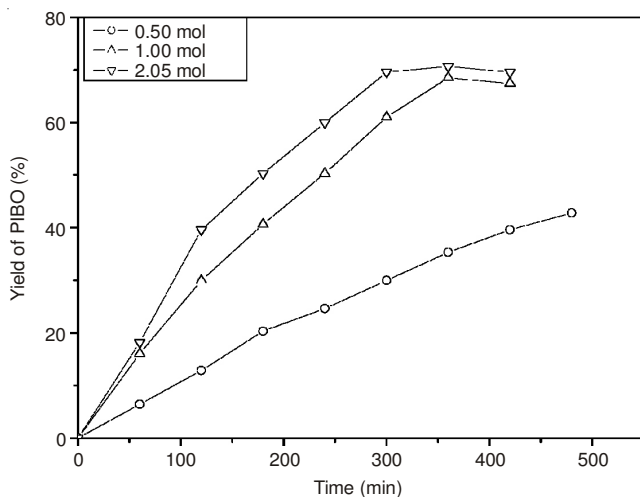
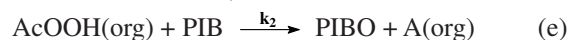
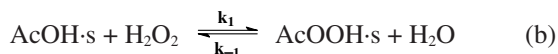


Fig. 1. Effect of acetic acid per mole of double bond on yield of PIBO

**Kinetic model of the epoxidation reaction:** The mechanism of formation PAA by reacting organic acid with hydrogen peroxide in aqueous solution was known<sup>16</sup>. Zhao<sup>17</sup> claimed that the reaction was carried out *via* a protonated carbonyl oxygen of acetic acid and this protonated intermediate reacted with H<sub>2</sub>O<sub>2</sub> to form the PAA and water. According to the above results, the reacting system has three immiscible phases. The mechanism for the *in situ* epoxidation in the presence of solid catalyst is described as follows: (i) formation of peracetic acid and decomposition of H<sub>2</sub>O<sub>2</sub> in the aqueous phase in the presence of a catalyst; (ii) transfer of peracetic acid from the aqueous phase to the oil phase; (iii) reaction of peracetic acid in the oil phase to produce epoxide and to release acetic acid; (iv) transfer of acetic acid from the oil phase back to the aqueous phase.

In present study, an attempt has been made to develop a model for the formation of peracetic acid. The classic Langmuir-Hinshelwood-Hougen-Watson (LHHW) model was applied to the reaction mechanism. When WO<sub>3</sub>/ZrO<sub>2</sub> is used as a catalyst, the reaction proceeds on the active catalyst site as follows: (1) adsorption of acetic acid on the active catalyst site, (2) surface chemical reaction between acetic acid and H<sub>2</sub>O<sub>2</sub> and (3) desorption of the products. Hence, all the rate equation of the epoxidation reaction was deduced as follows:



Considering our set-up as a well-stirred, ideal isothermal batch reactor in the slow kinetics regime, where (1) the individual volumes of each liquid phase remain nearly constant, (2) the concentration gradients at three phase interface s were negligible, (3) degradation of the epoxide ring was neglected. (4) adsorption and desorption of reactants and products were fast and were therefore at equilibrium.

For the surface reaction controlled peracetic acid formation, the adsorption and desorption steps are very fast in the overall conversion process. As such, the surface concentrations of component may be written as:

$$K_{AA} = \frac{[\text{AcOH} \cdot s]}{[\text{AcOH}][s]} \quad K_{PA} = \frac{[\text{AcOOH} \cdot s]}{[\text{AcOOH}][s]} \quad (5)$$

where  $K_{AA}$ : adsorption equilibrium constant;  $K_{PA}$ : desorption equilibrium constant.

The total concentration of the sites,  $C_t$  expressed as

$$C_t = [s] + [\text{AcOH} \cdot s] + [\text{AcOOH} \cdot s] \quad (6)$$

where  $[s]$  is the concentration of vacant site on the surface.

Substituting the values of  $[\text{AcOH} \cdot s]$  and  $[\text{AcOOH} \cdot s]$  into eqn. 2, gives

$$[s] = \frac{C_t}{1 + K_{AA}[\text{AcOH}] + K_{PA}[\text{AcOOH}]} \quad (7)$$

For the surface reaction controlled peracetic acid formation, the rate of reaction of hydrogen peroxide may be expressed as:

$$\begin{aligned} & -\frac{d_{\text{H}_2\text{O}_2}}{dt} \\ &= \frac{C_t(k_1 K_{AA}[\text{AcOH}][\text{H}_2\text{O}_2] - k_{-1} K_{PA}[\text{AcOOH}][\text{H}_2\text{O}])}{(1 + K_{AA}[\text{AcOH}] + K_{PA}[\text{AcOOH}])} \quad (8) \end{aligned}$$

where  $k_1$  is the forward rate constant;  $k_{-1}$  is the reverse rate constant

$$R_1 = \frac{C_t(k_1 K_{AA}[\text{AcOH}][\text{H}_2\text{O}_2] - k_{-1} K_{PA}[\text{AcOOH}][\text{H}_2\text{O}])}{(1 + K_{AA}[\text{AcOH}] + K_{PA}[\text{AcOOH}])}$$

Mass balance for AcOH

$$n_{\text{HAC}} = n_{\text{AcOH}}^{\text{aq}} + n_{\text{AcOH}}^{\text{org}} = [\text{AcOH}]^{\text{aq}} V^{\text{aq}} + [\text{AcOH}]^{\text{org}} V^{\text{org}} \quad (9)$$

The partition equilibrium of AcOH may be written as

$$\phi_{\text{AcOH}} = \frac{[\text{AcOH}]^{\text{org}}}{[\text{AcOH}]^{\text{aq}}} \quad (10)$$

Eqn. 9 can be recast, as follows:

$$\begin{aligned} \frac{dn_{\text{AcOH}}}{dt} &= \frac{d[\text{AcOH}]^{\text{aq}} V^{\text{aq}}}{dt} + \frac{\phi_{\text{AcOH}} d[\text{AcOH}]^{\text{aq}} V^{\text{org}}}{dt} \\ &= \frac{d[\text{AcOH}]^{\text{aq}}}{dt} (V^{\text{aq}} + \phi_{\text{AcOH}} V^{\text{org}}) \quad (11) \end{aligned}$$

Besides:

$$\frac{dn_{\text{AcOH}}}{dt} = (-R_1) V^{\text{aq}} + k_4 [\text{PIB}] [\text{AcOOH}]^{\text{org}} V^{\text{org}} \quad (12)$$

Equivalence between eqns. 7 and 8 rearranging:

$$\frac{d[\text{AcOH}]^{\text{aq}}}{dt} = (V^{\text{aq}} + \phi_{\text{AcOH}} V^{\text{org}})^{-1} [(-R_1)V^{\text{aq}} + k_4[\text{PIB}][\text{AcOOH}]^{\text{org}} V^{\text{org}}] \quad (13)$$

Proceeding in similar fashion as above, the following expression results:

$$\frac{d[\text{AcOH}]^{\text{org}}}{dt} = \left( \frac{V^{\text{aq}}}{\phi_{\text{AcOH}}} + V^{\text{org}} \right)^{-1} [(-R_1)V^{\text{aq}} + k_4[\text{PIB}][\text{AcOOH}]^{\text{org}} V^{\text{org}}] \quad (14)$$

AcOOH was proceeding in similar fashion as above, the following expression results:

$$\frac{d[\text{AcOOH}]^{\text{aq}}}{dt} = (V^{\text{aq}} + \phi_{\text{AcOOH}} V^{\text{org}})^{-1} [R_1 V^{\text{aq}} - k_4[\text{PIB}][\text{AcOOH}]^{\text{org}} V^{\text{org}}] \quad (15)$$

$$\frac{d[\text{AcOOH}]^{\text{org}}}{dt} = \left( \frac{V^{\text{aq}}}{\phi_{\text{AcOOH}}} + V^{\text{org}} \right)^{-1} [R_1 V^{\text{aq}} - k_4[\text{E}][\text{AcOOH}]^{\text{org}} V^{\text{org}}] \quad (16)$$

where

$$\phi_{\text{AcOOH}} = \frac{[\text{AcOOH}]^{\text{org}}}{[\text{AcOOH}]^{\text{aq}}}$$

$$\frac{d[\text{PIB}]^{\text{org}}}{dt} = -k_r[\text{PIB}][\text{AcOOH}]^{\text{org}}$$

Phase partition coefficients of acetic acid for each reaction condition were experimentally determined (Table-3). The values were based on the molar concentration of AcOH in each phase ( $\Phi_{\text{AcOH}} = C_{\text{AcOH}}^{\text{oil}}/C_{\text{AcOH}}^{\text{aq}}$ ). The average value  $\Phi_{\text{AcOH}}$  (0.006) of the experimental values was lower than that in the literature  $\Phi$  (0.035, 0.03)<sup>13,18</sup>. It could be inferred that the value some depend on composition of unsaturated hydrocarbons.

Try	PIB/H <sub>2</sub> O/AcOH molar ratios	C <sub>AcOH</sub> <sup>oil</sup> (mol/L)	C <sub>AcOH</sub> <sup>aq</sup> (mol/L)	$\Phi = C_{\text{AcOH}}^{\text{oil}}/C_{\text{AcOH}}^{\text{aq}}$
1	1/10.3/1.96	0.046	7.11	0.0065
2	1/5.9/0.42	0.02	3.46	0.0058
3	1/13.6/1.7	0.031	5.28	0.0059

Table-3 also contained the AcOH values predicted using UNIFAC, which were very similar to the measured ones. Therefore, the distribution constant of AcOH was estimated employing UNIFAC. The predicted values of peracetic acid was 0.04.

**Kinetic modelling results:** The surface reaction rate coefficient, desorption and adsorption equilibrium constant were estimated by fitting the experimental data using a non-linear regression (Table-4). The coefficients of determination of the model were 0.97, 0.99 and 0.99 at 60, 70 and 80 °C, respectively.

The kinetic rate constant for the epoxidation of the double bonds by AcOOH in the organic phase was calculated by solving the set of simultaneous ODEs using Euler's numerical method in MATLAB (Table-4).

Parameters	Temperature (°C)		
	60	70	80
k <sub>1</sub> (mol <sup>-1</sup> L min <sup>-1</sup> )	0.047	0.069	0.13
k <sub>-1</sub> (mol <sup>-1</sup> L min <sup>-1</sup> )	0.02	0.034	0.06
C <sub>t</sub> (g mol <sup>-1</sup> L min <sup>-1</sup> )	0.013	0.013	0.013
K <sub>AA</sub> (dm <sup>3</sup> mol <sup>-1</sup> )	2.45	4.9	8.02
K <sub>PA</sub> (dm <sup>3</sup> mol <sup>-1</sup> )	4.8	6.05	12.02
R <sup>2</sup>	0.97	0.99	0.99
Rmsd	0.0001206	0.00004908	0.00009284
K <sub>2</sub> (mol <sup>-1</sup> L min <sup>-1</sup> )	0.1	0.5	0.91

C<sub>t</sub>: Concentration of active site per unit mass of catalyst × constant of surface reaction rate; Rmsd: root-mean-square deviation.

Fourth order Runge-Kutta method was applied for solving the system of differential eqns. 4, 9-12. Experimental value and model curves of double bonds and H<sub>2</sub>O<sub>2</sub> at the different temperature were plotted in Figs. 2 and 3. Figs. 4 and 5 demonstrated the ability of the model with the parameters in Table-4 to correlate the experimental results.

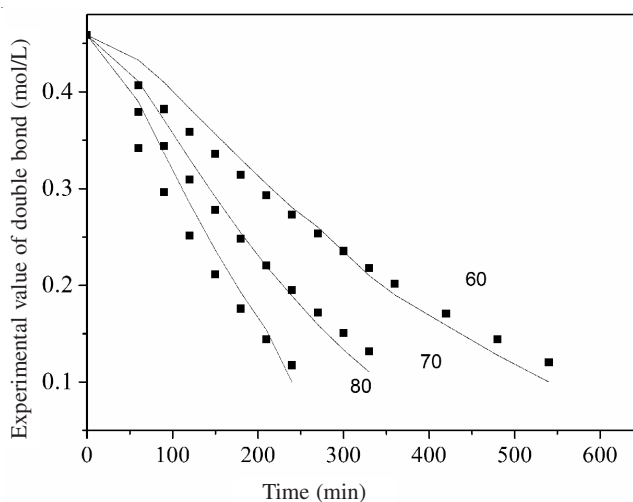


Fig. 2. Comparison of experimental determined points and predicted model curves of double bonds vs. time at different temperature

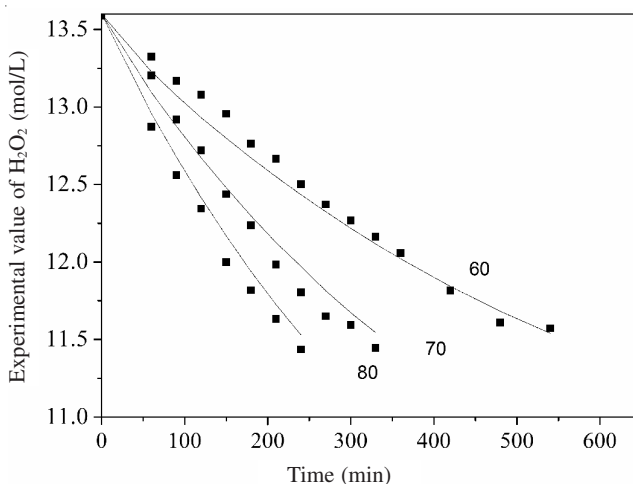


Fig. 3. Comparison of experimental determined points and predicted model curves of H<sub>2</sub>O<sub>2</sub> vs. time at different temperature



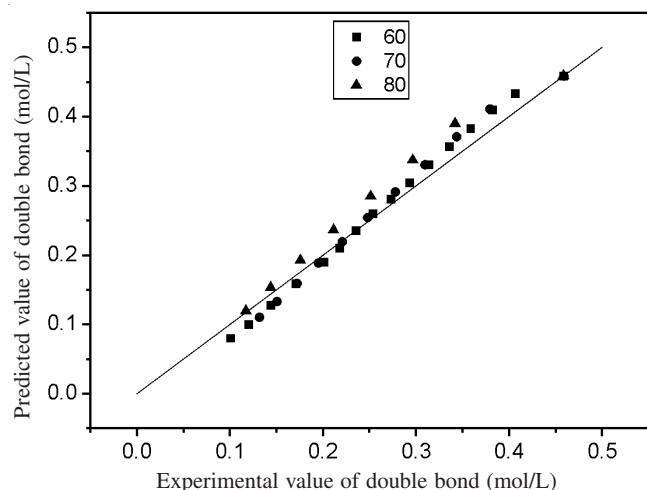


Fig. 4. Parity plot of the experimental and simulated molar fractions double bond (mol/L)

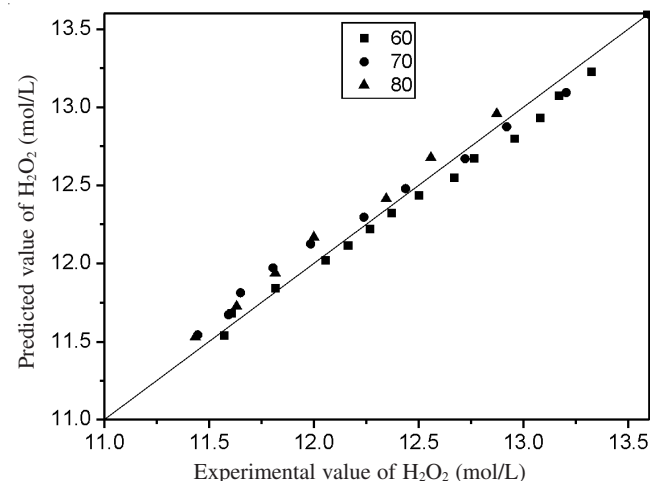


Fig. 5. Parity plot of the experimental and simulated molar fractions of  $H_2O_2$

Clearly, the model fit was very good. Moreover, the data were scattered on both sides of the diagonal indicating the absence of systematic errors. It can be seen that good agreement between the experimental and predicted data validated the proposed model.

## Conclusion

The kinetics of epoxidation of polyisobutene by peracetic acid generated *in situ* from hydrogen peroxide and acetic acid in the presence of solid acid  $WO_3/ZrO_2$  were studied. The classic LHHW model was applied to the reaction mechanism of peracetic acid. The various constants were evaluated from the experimental data. A multiphase kinetic model that described epoxidation was proposed. Comparison of experimental value and model curves validated the model.

## ACKNOWLEDGEMENTS

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