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Epoxidation of hydroxyl-terminated polybutadiene with hydrogen peroxide under phase-transfer catalysis

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ABSTRACT

The phase-transfer catalytic epoxidation of hydroxyl-terminated polybutadiene (HTPB) by hydrogen peroxide was investigated by using quaternary ammonium salts, ammonium tungstate hydrate and phosphoric acid as the phase-transfer catalyst and cocatalysts, respectively. The influences of quaternary ammonium salts, the amount of Aliquat 336 and hydrogen peroxide, the molar ratio of phosphoric acid to ammonium tungstate hydrate (PO_4^{3-}/WO_4^{2-}), pH value and organic solvents on the conversion of double bonds in HTPB polymer were studied in detail. The kinetic of epoxidation of HTPB was also discussed and the apparent activated energy for epoxidation of HTPB was estimated to be 21.04 kJ/mol.

1. Introduction

Chemical modifications are the useful way to obtain new polymeric materials. Of the well-known chemical modifications of polydiene materials, epoxidation has been the most promising and advantageous method [1–5]. Hydroxyl-terminated polybutadiene (HTPB) is widely used as adhesives and sealants, especially as fuel binder in composite solid propellants currently because of its unique physicochemical properties such as thermal dynamic, pyrolysis, elasticity, toughness and durability [6–11]. These properties can be modified by introducing epoxy functional groups into the non-polar polymer chains, which can increase the polarity of the final polymers to expand their applications [12]. The conventional methods for epoxidizing HTPB are to use a stoichiometric amount of peracids such as *m*-chloroperbenzoic acid (MCPBA) [13–15]. However, the employments of peracids usually give rise to environmental pollution due to the waste acid disposal. In recent years, much attention has been paid to the use of hydrogen peroxide as the oxidant because it is relatively cheap, environmentally friendly and safe [16,17]. The oxidation of organic compounds with an aqueous solution of hydrogen peroxide is very advantageous in view of chemical technology and synthesis.

For the olefin epoxidation with hydrogen peroxide, two-component associates containing tungsten and phosphate ions under acidic conditions were used, in which the associates were in situ formed in the reaction mixture by introducing the two components in the form of sodium tungstate and orthophosphoric acid. It was found to be a valuable catalytic system, as is the case of the well-known Venturello–Ishii phase-transfer catalysis system [18–24]. The applications of this catalytic system to different compounds have been carried out by many groups up to now [25–30]. Recently, the epoxidation of unsaturated polymers by Venturello–Ishii method has been attracting much more attention. However, most of the work was focused on the polymers such as styrene–butadiene–styrene triblock copolymer (SBS) and polybutadiene [27–33]. The epoxidation of hydroxyl-terminated polybutadiene using sodium tungstate, orthophosphoric acid and quaternary ammonium salts as the catalyst was first reported by Fan et al. [34]. Alavi Nikje and Mozaffazi [35] 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. However, this catalytic system was not efficient even though HTPB was successfully epoxidized, and the oxidant DMD is not available.

In this work, ammonium tungstate hydrate was used to replace sodium tungstate in the PTC catalyst. The epoxidation of HTPB with hydrogen peroxide was investigated in the presence of the PTC catalyst formed from ammonium tungstate hydrate, phosphoric acid and quaternary ammonium salts. Special emphasis was placed on the study of the effects of reaction variables on the conversion of double bonds in HTPB. The influences of catalytic systems and quaternary ammonium salts on the HTPB epoxidation were investigated. The influences of Aiquat 336 amount, PO_4^{3-}/WO_4^{2-} molar ratio and H_2O_2 to double bond molar ratio, pH value and the nature of organic solvents on epoxidation of HTPB were also studied.

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2. Experimental

2.1. Materials

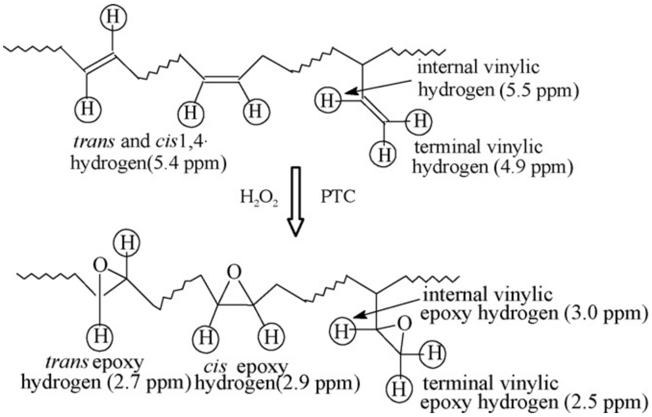
Hydroxyl-terminated polybutadiene ($M_n = 2800$, double content = 0.0171 mol/g) was obtained from Zibo Qilu Chemicals Co. Ltd. (China) and purified according to the procedure proposed by Kurusu et al. [36]. HTPB (10 g) was dissolved in dichloromethane (100 mL), stirred at room temperature for 48 h and then added into the cooling methanol or ethanol (200 mL) to precipitate the HTPB polymer. After separated and dried at 35 °C under vacuum for 72 h, pure HTPB was obtained with a recovery of more than 90%. Methyltrioctylammonium chloride (Aliquat 336) was purchased from Aldrich. Cetyltrimethylammonium bromide (CTAB), dodecyltrimethylammonium bromide (DTAB) and tetrapropylammonium bromide (TPAB) were guaranteed grade (G.R.) chemicals. Ammonium tungstate hydrate, $(NH_4)_5H_5[H_2(WO_4)_6]\cdot H_2O$, was purchased from Merck. 85 wt% phosphoric acid, dichloromethane, toluene, 1,2-dichloroethane, carbon tetrachloride, chloroform, cyclohexane, *tert*-butyl alcohol, 30 wt% hydrogen peroxide and *m*-chloroperbenzoic acid were all G.R. chemicals and were used as-received. The concentration of H_2O_2 was determined by iodometric titration.

2.2. Epoxidation procedure

The epoxidation of HTPB was carried out in a 100 mL three-neck round bottom flask. In a typical run, 1 g purified HTPB was dissolved in 20 mL dichloromethane and then introduced into the reactor which was placed in a well-controlled thermostatic water bath. Known quantities of quaternary ammonium salts, ammonium tungstate hydrate and 85 wt% phosphoric acid were completely dissolved in a 34 wt% hydrogen peroxide aqueous solution. Then the mixture was put into the reactor under stirring to start the reaction. The reaction was carried out at the set temperature for 2 h. Cold methanol was used to interrupt the reaction. The precipitated polymer (EHTPB) was isolated and dried at 35 °C under vacuum for 72 h.

The epoxy-functionalized HTPB product with yellow color was characterized by ^1H NMR with a Varian XL-300 spectrometer operating at 500 MHz at room temperature. Samples were analyzed in deuterated chloroform solution. The corresponding chemical shifts for the HTPB and EHTPB are shown in Scheme 1. Using a previously reported equation [15] and peak area integrations at 2.5, 2.7, 2.9, 4.9 and 5.4 ppm from ^1H NMR data, the double bond conversion (X) can be calculated as follows:

$$X = \frac{A_{2.7} + A_{2.9} + 0.5 \times A_{2.5}}{A_{2.7} + A_{2.9} + 0.5 \times A_{2.5} + A_{5.4} + 0.5A_{4.9}} \times 100\%$$



Scheme 1. Schematic representation of original and epoxidized HTPB and ^1H NMR chemical shifts.

However, the epoxidation degree should be maintained below 75%, because it was found that higher yields rendered the polymer insoluble in $CDCl_3$.

3. Results and discussion

3.1. Influence of catalysis systems

The epoxidation of HTPB was carried out by the conventional peracid method and the phase-transfer catalysis method. The results are listed in Table 1. Compared with the conventional peracid method, phase-transfer catalysis was much more effective for the epoxidation of HTPB. 66.3% conversion of the double bond epoxidation was obtained by the phase-transfer catalysis, which is much higher than that of the peracetic acid method (only 6.9%) and MCPA method (54.4%) under the same experimental conditions. Moreover, when the reaction time was prolonged in the case of peracetic acid as the oxidant, the ring opening of the epoxide would occur and the hydroxyl value of the epoxidized HTPB would increase. These results are consistent with the results reported in Refs. [37,15]. Therefore, investigation of the role of these oxidants, phase-transfer catalysts, and cocatalysts is necessary to improve the reaction. Usually, sodium tungstate and phosphoric acid are used as the cocatalyst in the Venturello–Ishii catalytic system. However, it is valid only when applied to the epoxidation of cycloolefins in order to obtain a relatively high yield. The conversion of long-chain olefins was low when sodium tungstate and phosphoric acid were used as the cocatalyst [38]. Thus, ammonium tungstate hydrate ($(NH_4)_5H_5[H_2(WO_4)_6]\cdot H_2O$), rather than sodium tungstate, was employed as the cocatalyst in the epoxidation of HTPB. Phos-

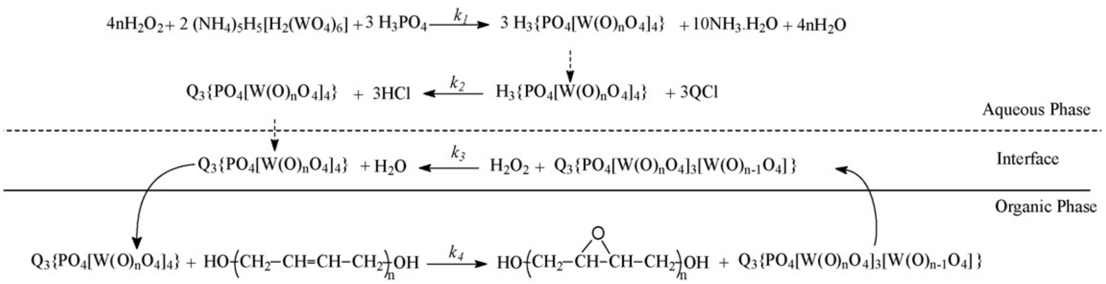
Table 1
Effect of oxidants and phase-transfer catalysts on epoxidation of HTPB.

Entry	Oxidants and catalysts	Reaction temperature (°C)	Reaction time (h)	Conversion of C=C (%)
1	$CH_3COOH + H_2O_2$[a]	50	4	6.9
2	*m*-Chloroperbenzoic acid[b]	50	4	54.4
3	$H_2O_2 + A336 + H_3PO_4 + (NH_4)_5H_5[H_2(WO_4)_6]\cdot H_2O$	50	4	66.3
4	$H_2O_2 + A336 + H_3PO_4 + (NH_4)_5H_5[H_2(WO_4)_6]\cdot H_2O$	50	2	49.0
5	$H_2O_2 + A336 + H_3[PO_4(W_2O_7)_4]$	50	2	40.0
6	$H_2O_2 + A336 + (NH_4)_5H_5[H_2(WO_4)_6]\cdot H_2O$	50	2	9.5
7	$H_2O_2 + A336 + H_3PO_4$	50	2	10.8
8	$H_2O_2 + A336$	50	2	11.1

Reaction conditions: HTPB 1.0 g (containing 0.0171 mol double bonds), $CHCl_3$ 10 mL, 34 wt% H_2O_2 45.0 mmol, Aliquat 336 0.52 mmol, H_3PO_4 1.1 mmol, $(NH_4)_5H_5[H_2(WO_4)_6]\cdot H_2O$ 0.17 mmol.

[a] Reaction conditions is similar to Ref [37]: HTPB 1.0 g (containing 0.0171 mol double bonds), $CHCl_3$ 10 mL, CH_3COOH 0.1 mol, $CH_3COOH/H_2O_2 = 1:1$ (mol ratio).

[b] Reaction conditions is similar to Ref [15]: HTPB 1.0 g (containing 0.0171 mol double bonds), $CHCl_3$ 10 mL, *m*-chloroperbenzoic acid 10 mmol.



Scheme 2. The possible scheme of epoxidation of HTPB under phase-transfer catalysis.

photungstic acid ($H_3P[W_2O_7]_4$) and phosphoric acid (H_3PO_4) were also examined. As shown in Table 1, $(NH_4)_5H_5[H_2(WO_4)_6]\cdot H_2O$ and H_3PO_4 as the cocatalyst had a higher catalytic activity than $H_3P[W_2O_7]_4$. A high conversion of the double bonds was obtained in the presence of $(NH_4)_5H_5[H_2(WO_4)_6]\cdot H_2O$, H_3PO_4, H_2O_2, and A336. But the conversion greatly decreased in the absence of any of the components. This might be due to the fact that the ion-pair compound $Q_3\{PO_4[W(O)_nO_4]_3[W(O)_nO_4]\}$, the active intermediate [39,25], could not form in these reactions. As shown in Scheme 2, the ion-pair compound $Q_3\{PO_4[W(O)_nO_4]_3[W(O)_{n-1}O_4]\}$ (the regenerated catalyst) reacted with hydrogen peroxide to form the true oxidant $Q_3\{PO_4[W(O)_nO_4]_3[W(O)_nO_4]\}$ (the active catalyst) in the aqueous solution. The true oxidant $Q_3\{PO_4[W(O)_nO_4]_3[W(O)_nO_4]\}$ was then transferred into the organic phase by the phase-transfer catalyst (Q^+) for further reaction. Therefore, the formation of the true oxidant $Q_3\{PO_4[W(O)_nO_4]_3[W(O)_nO_4]\}$ was important to the epoxidation of HTPB. In our preliminary experiments, it was found that the addition sequence of $(NH_4)_5H_5[H_2(WO_4)_6]\cdot H_2O$, H_3PO_4, H_2O_2, and A336 had no effect on the conversion of double bonds in HTPB. These results indicated that the synthesis of the true oxidant $H_3\{PO_4[W(O)_nO_4]_3[W(O)_nO_4]\}$ in the aqueous phase was fast. The organic-phase reactions were obviously the rate-controlling steps.

3.2. Influence of quaternary ammonium salts

In the Venturello–Ishii method, quaternary ammonium cation Q^+ is the species bearing the active oxygen which are transported from the organic phase to the aqueous phase to enhance the reaction rate [26]. Usually, the chemical and physical properties of the reactants and the environmental species governed the reaction systems. The hydrophilic and hydrophobic properties of the environmental species would affect the interaction between the reactants and solvents. Therefore, it was important to examine the effect of various quaternary ammonium salts on the conversion of the double bonds and the reaction rate. Methyltrioctylammonium chloride (Aliquat 336), cetyltrimethylammonium bromide (CTAB), dodecyltrimethylammonium bromide (DTAB) and tetrapropylammonium bromide (TPAB) were used as the phase-transfer catalysts in this work. As shown in Fig. 1, the catalytic activity increased with the increase in the total carbon number of the quaternary ammonium salts. Aliquat 336 exhibited the highest catalytic activity among the four quaternary ammonium salts. These results indicated that the total carbon number rather than the anions was the main variable to determine the catalytic activity. When the hydrophilic TPAB was used as the phase-transfer catalyst, it was relatively difficult to bring the nucleophilic reagent and oxygen atom from the aqueous phase to the organic phase. This might be due to the increase in the distribution coefficient of the active catalyst $Q_3\{PO_4[W(O)_nO_4]_3[W(O)_nO_4]\}$ with the increasing total number of carbons of quaternary ammonium salts [38]. The larger the distribution coefficient of the quaternary ammonium salts was, the more active catalysts were present in the organic solution to enhance the reaction.

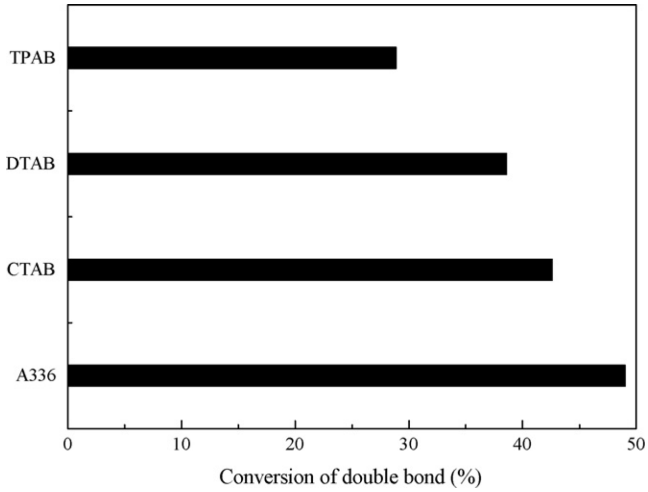


Fig. 1. Effect of quaternary ammonium salt on epoxidation of HTPB. Reaction was carried out under the condition of HTPB 1.0 g (containing 0.0171 mol double bonds), $CHCl_3$ 10 mL, 34 wt% H_2O_2 45.0 mmol, QBr (or QCl) 0.51 mmol, H_3PO_4 1.1 mmol, $(NH_4)_5H_5[H_2(WO_4)_6]\cdot H_2O$ 0.17 mmol, and 50 °C for 2 h.

3.3. Influence of Aliquat 336 amount

The effect of the quaternary ammonium salt, Aliquat 336, on the epoxidation of HTPB was carried out by using a fixed amount of ammonium tungstate hydrate. As shown in Fig. 2, the PTC activity increased with the increase in the amount of quaternary ammonium salt. The conversion of the double bonds increased from 5.3%

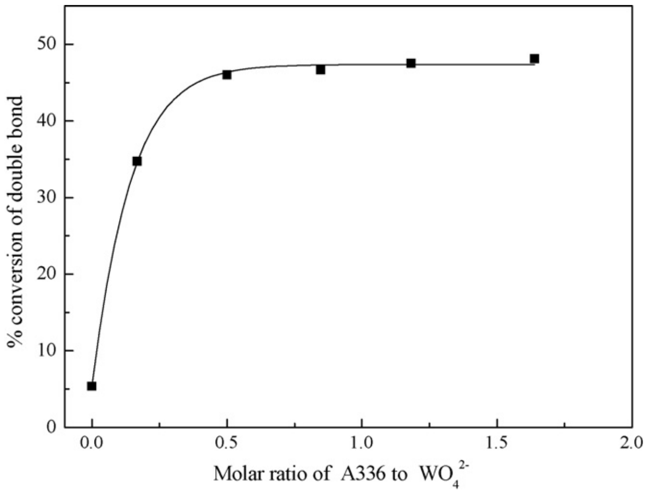


Fig. 2. Effect of the molar ratio of A336 to ammonium tungstate on epoxidation of HTPB. Reactions were carried out under the conditions of HTPB 1.0 g (containing 0.0171 mol double bonds), $CHCl_3$ 10 mL, 34 wt% H_2O_2 45.0 mmol, H_3PO_4 1.1 mmol, $(NH_4)_5H_5[H_2(WO_4)_6]\cdot H_2O$ 0.17 mmol, and 500 °C for 2 h.

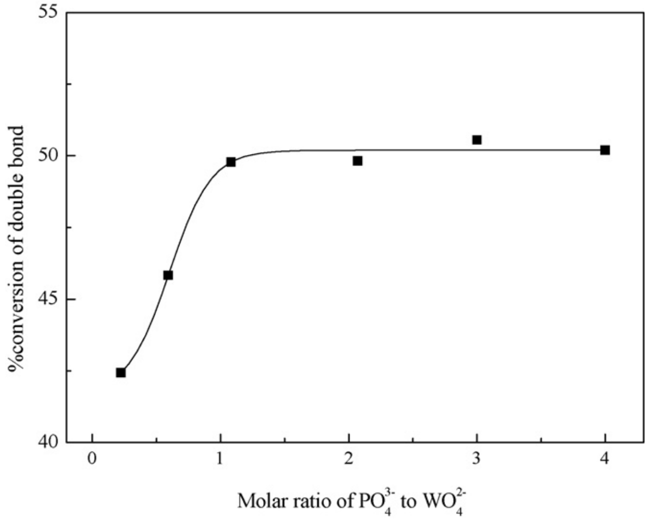


Fig. 3. Influence of the molar ratio of PO_4^{3-} to WO_4^{2-} on epoxidation of HTPB. Reactions were carried out under the conditions of HTPB 1.0 g (containing 0.0171 mol double bonds), $CHCl_3$ 10 mL, 34 wt% H_2O_2 45.0 mmol, Aliquat 336 0.52 mmol, $(NH_4)_5H_5[H_2(WO_4)_6]\cdot H_2O$ 0.17 mmol, and 50 °C for 2 h.

to 46.0% by increasing the molar ratio of Aliquat 336 to WO_4^{2-} from 0 to 0.5:1. A further increase could not enhance the PTC activity. This is accounted for by assuming that only the active intermediate formed from the reaction of phosphoric acid, ammonium tungstate hydrate, Aliquat 336, and hydrogen peroxide possessed high activity. With the amount of phosphoric acid and ammonium tungstate hydrate fixed, the amount of the formed active intermediate would also be kept at a fixed value. An excess amount of Aliquat 336 did not increase the amount of active catalytic intermediate to enhance the activity. In our experiment, the molar ratio of Aliquat 336 to WO_4^{2-} = 1:2 was the optimum value in the epoxidation of HTPB.

3.4. *Influence of PO_4^{3-}/WO_4^{2-} molar ratio*

The molar ratio of PO_4^{3-} to WO_4^{2-} in the epoxidation of HTPB was explored in order to determine the optimum catalyst composition (see Fig. 3). When the molar ratio of PO_4^{3-} to WO_4^{2-} increased from 0.25:1 to 1:1, an increase in the double bond conversion from 43% to 51% was obtained. A further increase in the phosphoric acid amount hardly caused the changes of the double bond conversion of HTPB. This indicates that there is an optimum concentration of phosphoric acid, which was found to be 1:1 for the molar ratio of PO_4^{3-}/WO_4^{2-}, larger than the stoichiometry of the active intermediate catalyst. Since a strong acidic condition was needed to improve the reactivity of the phase-transfer catalyst [40], the excess of phosphoric acid was used.

3.5. *Influence of H_2O_2 to double bond mole ratio*

The influence of the molar ratio of hydrogen peroxide to double bond on the epoxidation of HTPB was also investigated (see Fig. 4). It could be seen that the conversion of the double bonds increased with the increase in the hydrogen peroxide amount and reached the maximum, 60%, at 1.6:1. Although the conversion of the double bonds in HTPB decreased with the molar ratio, further increase in the molar ratio of H_2O_2 to double bond was not significant. In the phase-transfer catalysis, the active catalyst distributed between the organic and the aqueous phases, and most of the active catalysts were dissolved in the organic phase [41]. In our experiment, the volume of the aqueous phase increased with the increase in the amount of H_2O_2. Then the active catalysts in the aqueous phase increased gradually. Correspondingly, the concentration of the active catalyst in the organic phase decreased slightly. However, the reaction between the active catalyst and the reactant or the intermediate took place in the organic phase. Therefore, the conversion slightly decreased with the increase in the amount of hydrogen peroxide.

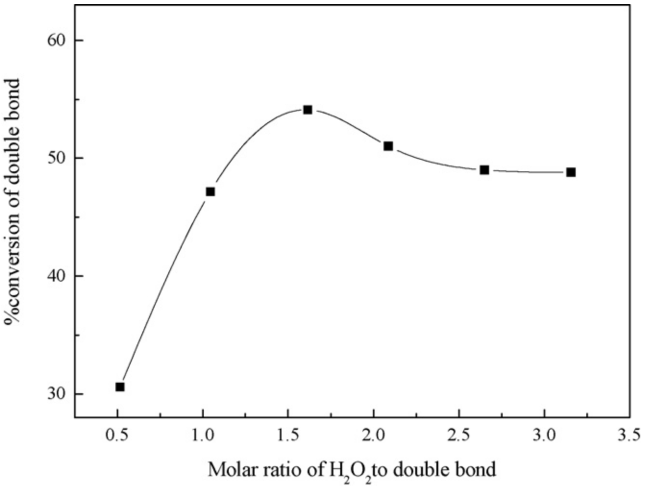


Fig. 4. Influence of hydrogen peroxide on epoxidation of HTPB. Reactions were carried out under the conditions of HTPB 1.0 g (containing 0.0171 mol double bonds), $CHCl_3$ 10 mL, Aliquat 336 0.52 mmol, H_3PO_4 1.1 mmol, $(NH_4)_5H_5[H_2(WO_4)_6]\cdot H_2O$ 0.17 mmol, and 50 °C for 2 h.

3.6. *Influence of pH value*

From the reaction mechanism, ammonia was produced when the active oxidizing agent was synthesized. It was obvious that the acidity of the solution would be an important factor affecting the conversion. Therefore, the effects of pH value on the epoxidation of HTPB were investigated with the molar ratio of Aliqat 336:PO_4^{3-}:WO_4^{2-} at 1:2:2 and the molar ratio of H_2O_2:C=C at 1.6:1. Extra addition of $NH_3\cdot H_2O$ or H_2SO_4 was necessary to adjust the pH value. The results are shown in Fig. 5. In this work, phosphoric acid was employed as the cocatalyst. Under the above optimum conditions, the initial pH value of the reaction solutions was 2.0. When the pH value was above 3.0, the conversion decreased almost lin-

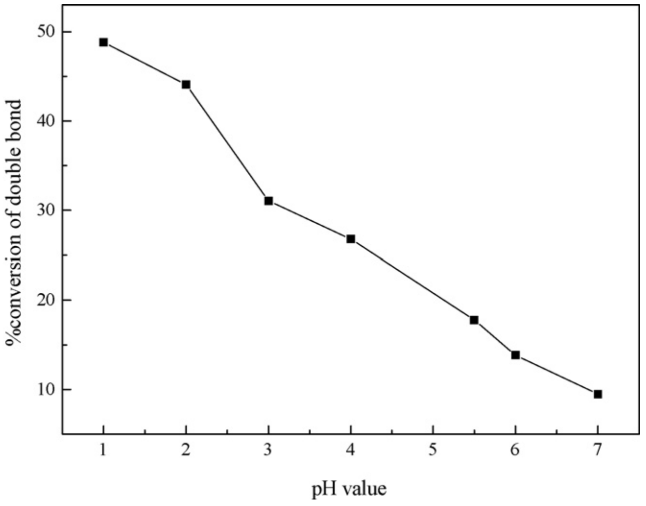


Fig. 5. Influence of pH value on epoxidation of HTPB. Reactions were carried out under the conditions of HTPB 1.0 g (containing 0.0171 mol double bonds), $CHCl_3$ 10 mL, 34 wt% H_2O_2 45.0 mmol, Aliquat 336 0.51 mmol, H_3PO_4 1.1 mmol, $(NH_4)_5H_5[H_2(WO_4)_6]\cdot H_2O$ 0.17 mmol, and 50 °C for 2 h.

Table 2
The polarity and solubility parameters of some solvents used in epoxidation of HTPB [46,47].

Solvents	Dielectric constant, ε	Dipole moment, D	$E_T(30)$ (kcal/mol)	$E_T{}^N$	Solubility parameters, δ (J/cm^3)$^{1/2}$
Toluene	2.4	0.3	33.9	0.099	18.2
1,2-Dichloroethane	10.3	1.8	41.3	0.327	20.1
Carbon tetrachloride	2.2	0.0	32.4	0.052	17.6
Chloroform	4.8	1.0	39.1	0.259	19.0
Dichloromethane	9.1	1.6	40.7	0.309	19.8
Cyclohexane	2.0	0.0	30.9	0.006	16.7
tert-Butyl alcohol	11.2	1.7	43.3	0.389	21.7

early with the increase in pH value. It could be inferred that the acidic conditions would favor the formation of the active intermediate and their transfer from the aqueous phase to the organic phase. These results are consistent with Refs. [42–44]. So it was desirable for the reaction to be carried out in acidic solution with pH value below 3.0.

3.7. *Influence of organic solvents*

In the phase-transfer catalytic reaction, the organic solvent provides a medium for the interaction between the reactants and plays the dominant role in influencing the reaction rate and the conversion of the reactants. The polarity of the organic phase, in conjunction with the structure of the anion and the catalyst cation, would affect the selectivity of the phase-transfer catalyst portioning into the organic phase [45]. The epoxidation of HTPB with the molar ratio of Aliquat 336:$PO_4{}^{3-}$:$WO_4{}^{2-}$ = 1:2:2 resulted in the high conversion of the double bonds. In relation to these results, the influences of the nature of the aprotic solvents such as dichloromethane, chloroform, *n*-hexane, cyclohexane, benzene, and toluene, and protic solvent *tert*-butyl alcohol on the epoxidation of HTPB were investigated. The same solvent volume was applied in all experiments. Each of the aprotic solvents ensured the two-phase reaction system. The solubility parameters of these solvents are listed in Table 2. The Hildebrand solubility parameter of HTPB was 17.7 (J/cm^3)$^{1/2}$ [48]. The solubility parameter difference of each HTPB-aprotic solvents pair ($\delta_{\mathrm{HTPB}} - \delta_{\mathrm{solvent}}$) was less than 2.0 (J/cm^3)$^{1/2}$. Therefore, the mixture of HTPB-aprotic solvents had a good miscibility. For protic solvent *tert*-butyl alcohol (solubility parameter 21.7 (J/cm^3)$^{1/2}$), the two-phase reaction was also observed since HTPB is slightly soluble in *tert*-butyl alcohol. Therefore, the degree of the epoxidation of HTPB in *tert*-butyl alcohol solvent was very low. The polarity of the aprotic solvents (in Table 2) was also considered. As shown in Fig. 6, the order of the conversions were: toluene > 1,2-chloroethane > carbon tetrachloride > chloroform > dichloromethane > cyclohexane. The reactivity was independent of the polarity of organic solvent. The same behavior was also reported in Refs. [38,40]. These results indicate that it is unsuitable to use a dielectric constant as the unique index to select an organic solvent. Other factors, such as the solubility of the catalyst in organic solvent, reaction transition state, ion transfer and solvation, were important in affecting the reaction. Therefore, the determination of an appropriate organic solvent was highly dependent on the experimental results.

3.8. *A kinetic study*

From the above results, it could be inferred that the ion exchange and the formation of a complex in the aqueous solution were rapid and in equilibrium. The organic-phase reactions were the rate-controlling steps. Furthermore, the concentration of the active intermediate, which transfers between the two phases, could be considered to be maintained at a constant value because of the large excess of hydrogen peroxide. Thus, a pseudo-steady-state rate law was sufficient to describe the kinetics of the epoxidation of HTPB. The rate of consuming double bonds in HTPB could be expressed as

$$-\frac{dC_A}{dt} = k_A C_{QPWO} C_A = k_{app,A} C_A \quad (1)$$

where C_A is the concentration of double bonds in the organic phase, C_{QPWO} is the concentration of active catalyst, and $k_{app,A}$ is the apparent rate constant = $k_4 C_{QPWO}$.

Integrating Eq. (1), the following expression is obtained

$$\frac{C_A}{C_{A0}} = e^{-k_{app,A} t} \quad (2)$$

Fractional conversion, X, was defined as

$$X = 1 - \frac{C_A}{C_{A0}} \quad (3)$$

Then, Eq. (3) could be rewritten as

$$-\ln(1 - X) = k_{app,A} t \quad (4)$$

The value of $k_{app,A}$ could be obtained by plotting $-\ln(1 - X)$ vs. t obtained experimentally.

In order to obtain the kinetic parameters, the epoxiation of HTPB was carried out with the molar ratio of Aliquat 336:$PO_4{}^{3-}$:$WO_4{}^{2-}$ at 1:2:2 and a molar ratio of hydrogen peroxide to double bond at 1.6:1 under 20 °C, 30 °C, 40 °C, 50 °C and 60 °C. From ^{1}H NMR integration data for the epoxidized HTPB and numerical integration, X_A was calculated for the different reaction times and temperatures (see Fig. 7). The value of $k_{app,A}$ could be graphically obtained from the slope of the straight lines. The results are listed in Table 3. It was obvious that the reactivity was increased by increasing the temperature. Hence, the reaction rate and the conversion of the double bonds were improved at higher temperature. Therefore, the apparent rate constants $k_{app,A}$ also increased with the increase in the temperature. From the Arrhenius plot of $-\ln(k_{app,A})$ vs. $1/T$, the activation energies for $k_{app,A}$ was estimated to be 21.04 kJ/mol.

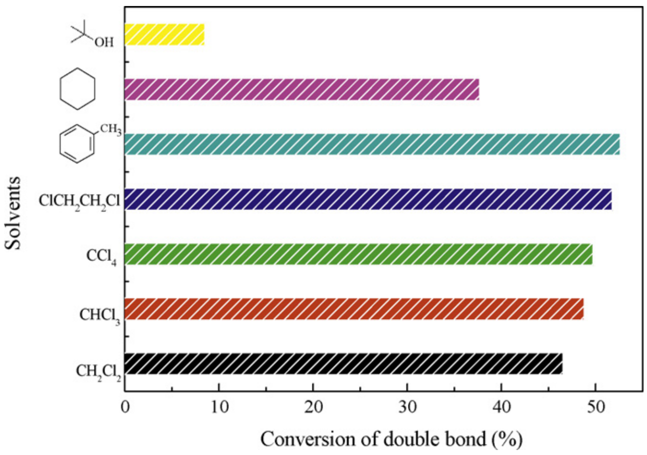


Fig. 6. Effect of organic solvents on epoxidation of HTPB. Reactions were carried out under the conditions of HTPB 1.0 g (containing 0.0171 mol double bonds), solvent 10 mL, 34 wt% H_2O_2 45.0 mmol, Aliquat 336 0.52 mmol, H_3PO_4 1.1 mmol, $(NH_4)_5H_5[H_2(WO_4)_6]\cdot H_2O$ 0.17 mmol, and 50 °C for 2 h.

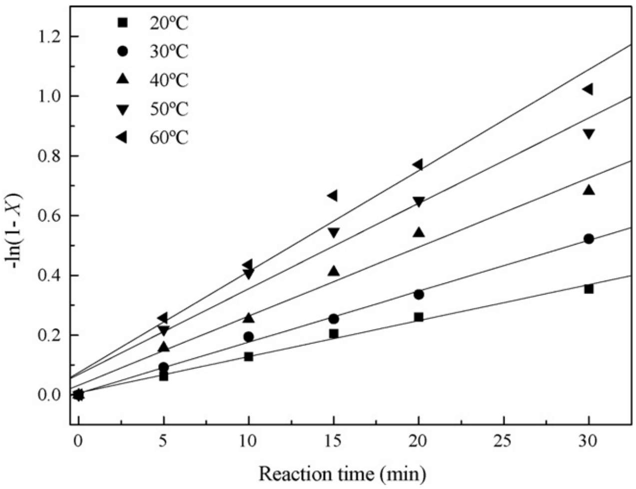


Fig. 7. The conversion of double bonds vs. reaction time in epoxidation of HTPB. Reactions were carried out under the conditions of HTPB 1.0 g (containing 0.0171 mol double bonds), $CHCl_3$ 10 mL, 34 wt% H_2O_2 27.4 mmol, Aliquat 336 0.52 mmol, H_3PO_4 1.1 mmol, $(NH_4)_5H_5[H_2(WO_4)_6]\cdot H_2O$ 0.17 mmol, and 2 h.

Table 3
The apparent reaction rate constant at different temperature in epoxidation of HTPB.

	Temperature				
	20 °C	30 °C	40 °C	50 °C	60 °C
$k_{app,A}$ (min^{-1})	0.0121	0.0171	0.0231	0.0286	0.0338

4. Conclusion

The epoxidation of HTPB by means of 34 wt% H_2O_2 in the presence of quaternary ammonium salts as the phase-transfer catalyst and the epoxidation cocatalyst, ammonium tungstate hydrate and 85 wt% phosphoric acid, and an auxiliary organic solvent was carried out. The catalytic activity increased with the increase in the total carbon number of the quaternary ammonium salt and methyltrioctylammonium chloride (Aliquat 336) had the highest catalytic activity. The catalytic system exhibited the highest reactivity with the molar ratio of Aliquat 336:PO_4^{3-}:WO_4^{2-} = 1:2:2. The acidic conditions with pH value below 3.0 favored the formation of the active intermediate and their transfer from the aqueous phase to the organic phase. The activity had no relation with the polarity of the organic solvent. Toluene as the solvent gave the best results. The epoxidation of HTPB followed the pseudo-steady-state rate law and the apparent activation energy of 21.04 kJ/mol was obtained.

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