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Selective epoxidation of hydroxyl terminated polybutadiene using *in situ* generated dimethyl dioxirane in the presence of MoO3

Summary — Hydroxyl terminated polybutadiene (HTPB) was epoxidized using *in situ* generated dimethyl dioxirane (DMD) as an oxidant and MoO_3 as a catalyst at 25 °C. Different reaction factors such as reaction time and catalyst concentration were examined. The ability of different C=C geometries toward epoxidation was evaluated in detail at various reaction times and the products were characterized by ^{1}H NMR, ^{13}C NMR and FT-IR techniques and no side reaction were detected. It was found that hydroxyl group of the polymer chain was preserved in the oxidation reaction without using any conditional control and relative reactivity depended on chain microstructure in the following way: 1,4-*cis* > 1,4-*trans* > 1,2-vinyl. This method is easy, environmentally friendly, convenient and the reaction conditions are straightforward.

Key words: hydroxyl terminated polybutadiene, epoxidation, dimethyl dioxirane, microstructure.

SELEKTYWNE EPOKSYDOWANIE POLIBUTADIENU Z KOŃCOWYMI GRUPAMI HYDROKSYLOWYMI W OBECNOŚCI MoO_3 Z ZASTOSOWANIEM GENEROWANEGO *IN SITU* DIMETYLODIOKSIRANU

Streszczenie — Metodami spektroskopii ^{1}H NMR, ^{13}C NMR oraz FT-IR określono budowę produktów wymienionej w tytule reakcji (rys. 1—9, tabele 1 i 2). Na tej podstawie stwierdzono, że nie towarzyszą jej procesy uboczne a obecne w wyjściowym polimerze grupy wodorotlenowe zostają zachowane. Reaktywność polimerowego łańcucha zależy od jego mikrostruktury i maleje w szeregu ugrupowań 1,4-*cis* > 1,4-*trans* > 1,2-winylowe. Zbadano wpływ stężenia czynnika utleniającego oraz czasu epoksydowania na jego wydajność (tabele 3 i 4). Podkreślono łatwość realizacji i zalety ekologiczne omawianej reakcji.

Słowa kluczowe: polibutadien z końcowymi grupami wodorotlenowymi, epoksydowanie, dimetylodioksiran, mikrostruktura.

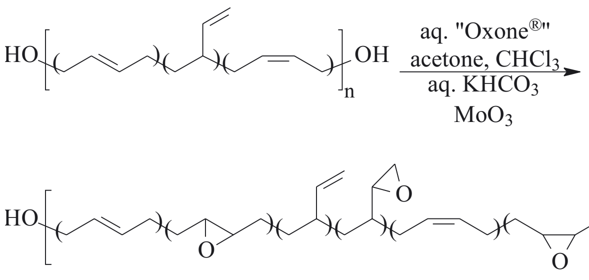
Among many possibilities of chemical modification of polyenes, epoxidation is a simple and efficient method for introducing a new reactive group into polymer backbone leading to the new and useful properties and wide use in a variety of applications [1—3]. The various methods have been proposed for the chain modification of hydroxyl terminated polybutadiene (HTPB) [4—7, 9, 10], such as, for example, thermal oxidation [5], epoxidation using *m*-chloroperbenzoic acid (*m*-CPBA) [6] or oxidation with $Vo(acac)_2$ complex [7b]. In this work the epoxidation process was accompanied by several side reactions and higher temperatures were needed in order to obtain higher conversion degrees. On the other hand, smaller reaction yields can be attributed to the degradation of the polymer [7]. Also, it has been found that at high reaction temperature and longer time, the formation of side product increased [8].

Recently, epoxidation of HTPB-based polyurethane membrane by *in situ* generated peracid method was reported and spectral analysis of the products indicated the formation of side products [9, 10]. The most usual system to epoxidize diene polymers involves the *in situ* formation of peracids generated by the reaction of acetic or formic acids with hydrogen peroxide [11]. It is reported that in these reactions at conversion above 50 % the oxirane ring undergoes ring opening to give formate esters and alcohols, and the epoxidation of block copolymers with molecular weights higher than of 60,000 invariably led to gelation [12]. Nevertheless, traces of unreacted acid can be present in the polymer, reducing its stability, if they are not properly removed.

Thus attempts have been made to epoxidize olefinic double bonds using systems based on transition metals such as Mo [13], W [12, 14], Mn [15] or V [7]. Molybdenum (VI) complexes are probably the best catalysts for epoxidation with alkyl hydroperoxides as oxidants. Several references are available about molybdenum-catalyzed epoxidation [16—19] and the mechanism of action of Mo(VI) complexes as catalysts in this process was demonstrated.

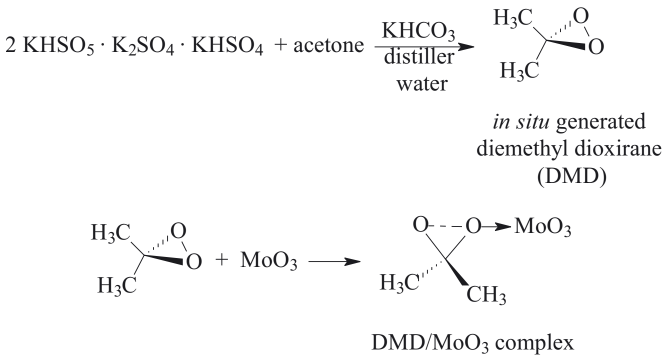
Also in a recently published paper [20] methyltrioxorhenium-CH_2Cl_2/H_2O_2 diphase catalytic system was used for the epoxidation of polydienes such as polybutadiene, polyisoprene, random styrene-butadiene rubber (SBR) and low-molecular liquid hydroxylated polybutadiene (LHPB). Authors obtained 87 % epoxidation yield after 36 h for LHPB. In that report there was no consideration about oxidation or preservation of hydroxyl groups.

In the continuation of our experiments on organic materials oxidation using potassium peroxymonosulfate ($2KHSO_5$, $KHSO_4$, K_2SO_4), commercially sold as "Oxone®", we decided to examine the ability and selectivity of this reagent for oxidation of hydroxyl terminated polybutadiene [21]. "Oxone®" is a convenient, inexpensive and powerful oxidant with a wide range of applications [22—24], soluble in water and nontoxic, therefore it is safe and environmentally friendly reagent. It was also demonstrated that "Oxone®" in the presence of ketones serves as an effective oxidant for a wide variety of substrates.



(1)

Kinetic, stereochemical and ^{18}O-labelling studies established dioxiranes unequivocally as the actual oxygen transfer agents. *In situ* generated dimethyl dioxiranes (DMD) (aqueous "Oxone®"/acetone system) were quickly adopted as remarkably efficient and stereoselective oxidants especially for epoxidation and heteroatom oxidation [25—28]. Aqueous solutions of "Oxone®" can be used to perform oxidation as well in homogeneous solution as in diphase system, using immiscible co-solvent and phase transfer catalyst.



Scheme A. The mechanism of in situ generation of dimethyldioxirane in "Oxone®"/acetone system

In this paper, the epoxidation of hydroxy terminated polybutadiene by using *in situ* generated DMD, in the presence of molybdenum trioxide (MoO_3) is reported [Equation (1)]. The mechanism of *in situ* generation of DMD in "Oxone®"/acetone system is shown in Scheme A. We aimed to determine the selectivity of "Oxone®" in epoxidation of C=C bonds without oxidation of C-OH groups of polymer chain.

EXPERIMENTAL

Materials

— HTPB (average $\overline{M}_n$ = 2000, containing 20 % *cis*, 60 % *trans* and 20 % vinyl) purchased from Sartomer Company (the trade name "Krasol-LBH").

— HTPB (average $\overline{M}_n$ = 2840, containing 15 % *cis*, 25 % *trans* and 60 % vinyl) purchased from Chinian Zibo Qilu Chemicals Co. Ltd. (named HTPB "Zibo" in this text).

— "Oxone®", MoO_3 and other auxiliary chemicals were purchased from Merck and were used as received.

Epoxidation reactions (general procedure)

All reactions were carried out in five-necked glassy reactor at 25±0.1 °C, using Cole Parmer Polystate contant temperature regulator (model 12101-25). In a typical reaction, polymer (1 g) and $CHCl_3$ (40 ml) were poured into the reactor and agitated until the complete dissolution of a polymer. Acetone (10 ml) and potassium bicarbonate solution (118 ml) (11.36 g of $KHCO_3$ in 118 ml distilled water) were charged to the reactor. "Oxone®" (15.6 g), distilled water (118 ml) and MoO_3 (at specified amounts as in Table 3) were poured to the reactor and vigorously agitated until the complete dissolution giving clear diphase system. At specified times 25 ml of reaction mixture was selected for analyses of epoxidation reactions at various reaction times. For each run, the two layers were separated, and the organic phase was dried under vacuum at 55—60 °C for 10 h. Finally the samples were removed and their FT-IR (in $CHCl_3$), ^1H NMR and ^{13}C NMR (in $CDCl_3$) spectra were obtained.

Samples characterization

^1H NMR and ^{13}C NMR spectra were performed using Bruker "CRX-300 Avance" FT-NMR Instrument, using $CDCl_3$ as deuterated solvent and tetramethylsilane (TMS) as internal standard. FT-IR spectra were registered using "Bruker Tensor 27" FT-IR instrument. All compounds were known and compared with standards.

RESULTS AND DISCUSSION

Characterization of epoxidized products

NMR spectra

The chemical shifts observed by ^{1}H NMR and ^{13}C NMR for initial polymer (HTPB "Krasol-LBH") presented in Tables 1 and 2, respectively, and Figures 1 and 2 were based on previously reported data for similar HTPB ("Liquiflex H") [6].

Table 1. Assignment of chemical shifts (δ) in ^{1}H NMR spectrum of HTPB ("Krasol-LBH")$^{a)}$

δ, ppm	Hydrogen
5.7—5.1	-CH= (1, 2) + -CH=CH- (1, 4)
5.4	-CH=CH- (1, 4)
5.1—4.8	=CH- (1, 2)
4.2	-**CH$_2$**-OH (G$_{OH}$)
4.1	-**CH$_2$**-OH (H$_{OH}$)
3.7—3.4	-**CH$_2$**-OH (V$_{OH}$)
2.5—1.7	-CH$_2$- (1, 4) + -CH- (1, 2)
1.7—1.0	-CH$_2$- (1, 2)

$^{a)}$ G$_{OH}$: OH-CH$_2$-CH=C<; H$_{OH}$: HO-CH$_2$-CH=CH-CH$_2$-; V$_{OH}$: OH-CH$_2$-CH-(CH=CH$_2$).

Table 2. Assignment of chemical shifts (δ) in ^{13}C NMR spectrum of HTPB ("Krasol-LBH")$^{a)}$

δ, ppm	Carbon
142.5	-CH= (V isolated)
134—128	-CH=CH- (1, 4)
115	=CH$_2$ (V isolated)
67	-CH$_2$-OH (V$_{OH}$)
64	-CH$_2$-OH (H$_{OH}$)
58.4	-CH$_2$-OH (G$_{OH}$)
47	-CH- (V)
44	-CH- (V isolated)
39	-CH$_2$- (V isolated)
35	-CH$_2$- (V)
33	-CH$_2$- (1, 4T)
31	-CH$_2$- (1, 4) (VT)
28	-CH$_2$- (1,4C)
25	-CH$_2$- (1, 4) (VC)

$^{a)}$ H$_{OH}$: HO-CH$_2$-CH=CH-CH$_2$; V$_{OH}$: HO-CH$_2$-CH<(CH=CH$_2$); G$_{OH}$: HO-CH$_2$-CH=C=; T: *trans*, C: *cis*, V: vinyl.

The assignment of *cis*, *trans* and vinyl epoxy groups was based on data reported by Gemmer [29], Zuchowska [11], and Akcelrud [6]. Also by comparison with the *cis*-polybutadiene ^{1}H NMR spectrum, it was found that epoxy hydrogen absorption at 3.0 ppm was related to the *cis*-epoxy hydrogen, therefore the one at 2.7 ppm was related to the *trans*-epoxy hydrogen (Fig. 3). The absorption of pendant epoxy group hydrogens was overlapped with *cis* and *trans* epoxy group hydrogen absorptions and are in agreement with Akcelrud [6].

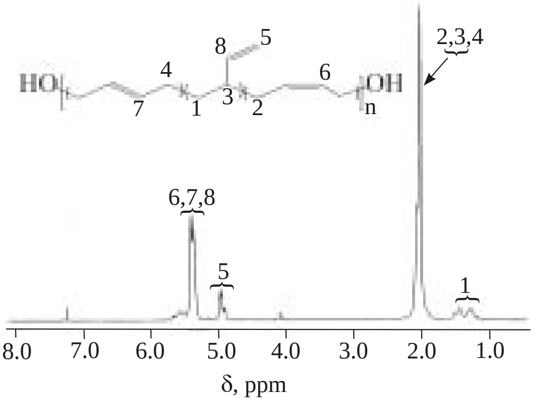


Fig. 1. ^{1}H NMR spectrum of unepoxidized HTPB ("Krasol-LBH")

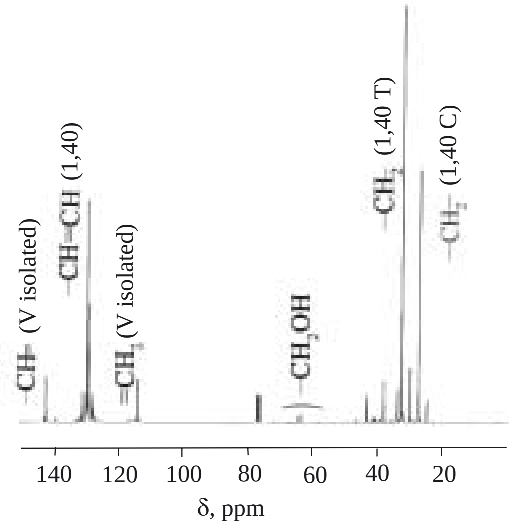


Fig. 2. ^{13}C NMR spectrum of unepoxidized HTPB ("Krasol-LBH") (V, C and T stand for vinyl, cis and trans double bonds microstructures, respectively)

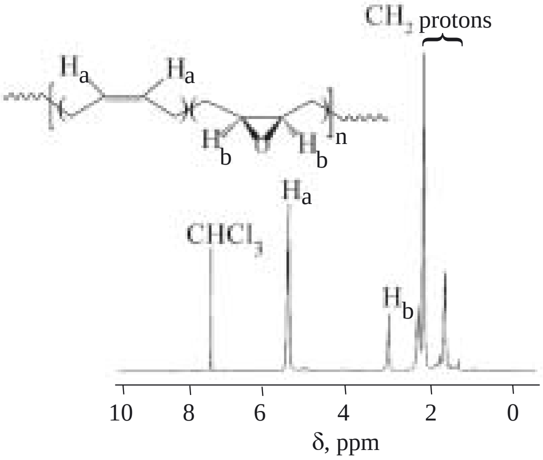


Fig. 3. ^{1}H NMR spectrum of epoxidized polybutadiene HTPB ("Zibo") after 1 h of the reaction time

Figure 4 shows the spectrum of the epoxidized HTPB ("Krasol-LBH") after 1 h of reaction time. The signals at

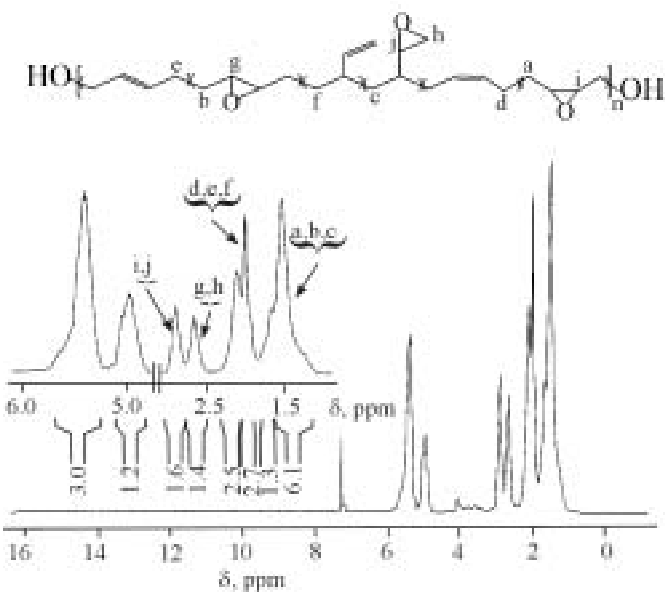


Fig. 4. ^{13}C NMR spectrum of epoxidized HTPB ("Krasol-LBH") after 1 h of the reaction time

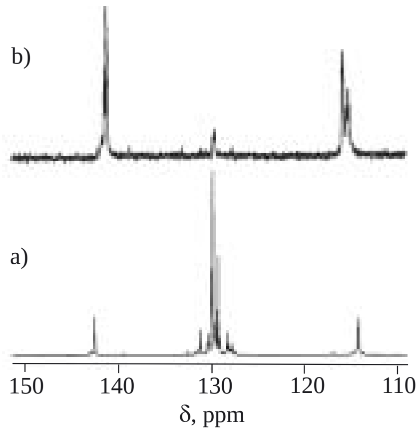


Fig. 5. ^{13}C NMR spectra of unepoxidized (a) and epoxidized HTPB ("Krasol-LBH") after 72 h at the reaction time (b) (range of δ = 115—150 ppm)

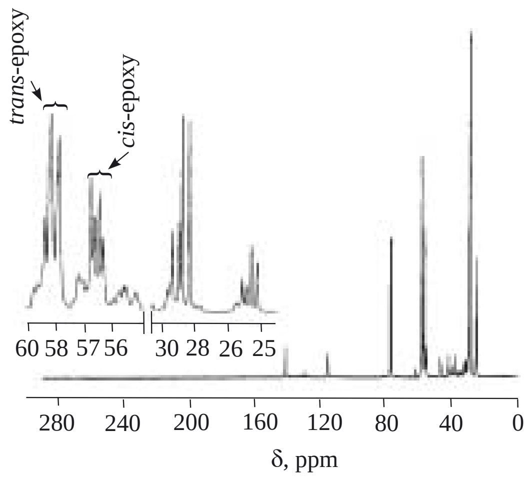


Fig. 6. ^{13}C NMR spectrum of epoxidized HTPB ("Krasol-LBH") after 72 h of the reaction time (range of δ = 20—80 ppm)

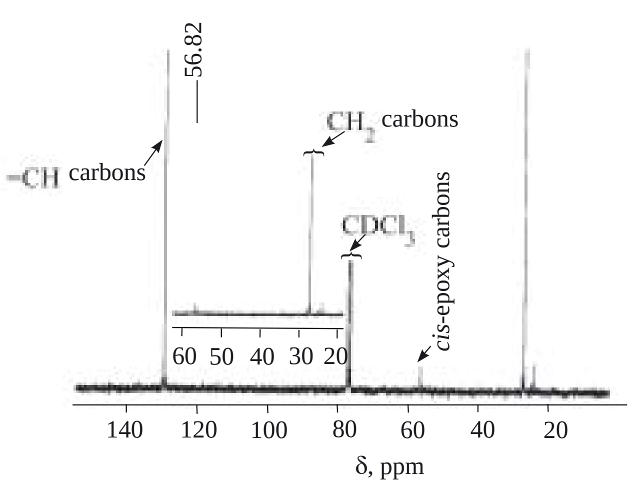


Fig. 7. ^{13}C NMR spectrum of epoxidized HTPB ("Zibo") after 1 h of the reaction time

5.1—4.8 ppm [1,2-vinyl hydrogens (=CH_2)] and 5.7—5.1 ppm [(1,2-vinyl (-CH=), 1,4-*cis* and 1,4-*trans* hydrogens] in ^{1}H NMR spectrum of unepoxidized HTPB are shifted to about 3.0—2.7 ppm and the signal at 2.0 ppm attributed to -CH_2- protons is shifted to about 2.2—2.1 ppm in the epoxidized polymers (Figs. 1 and 4).

Use of an equation (2) reported in [6], and integration values use of 2.7 ($A_{2.7}$) and 3.0 ppm ($A_{3.0}$) lead to 21 % conversion of *cis* double bonds and 19.7 % conversion of *trans* double bonds for the corresponding polyepoxides.

$$\text{Mol \% epoxy} = \frac{A_{2.7} + A_{3.0}}{A_{2.7} + A_{3.0} + A_{5.0} + A_{5.5}} \cdot 100 \qquad (2)$$

From these results and the initial amounts of double bonds (20 % *cis*, 60 % *trans* and 20 % vinyl) in the initial polymer, it was demonstrated for the same reaction times, conditions and constant temperature (even including overlapping of pendant epoxy group hydrogen absorption) that the 1,4-*cis* units of HTPB were found to react virtually fully, whereas 1,4-*trans* units reacted less than it, despite the fact that concerned HTPB had 60 % of 1,4-*trans* units and only 20 % of 1,4-*cis* units.

1,2-Vinyl microstructure reacted significantly less than 1,4-*cis* and 1,4-*trans* microstructures. These results confirm the high reactivity of *cis* C=C bonds in comparison with *trans* and vinyl microstructures. Low reactivity of 1,2-vinyl microstructure is probably a result of lower nucleophilicity of vinyl group and is shown in ^{13}C NMR spectrum (see Fig. 7).

Figure 5 shows that after 72 h of the reaction time, 1,4-*cis* and 1,4-*trans* units which are presented in 130.0 ppm, reacted completely, but 1,2-vinyl units (115.0 ppm and 142.5 ppm) reacted partially. These observations suggest that the presence of the electron donors-alkyl groups enhance reactivity of double bonds. The substitution of one hydrogen atom by one alkyl group (electron donor) increases the rate by a factor of 25 without

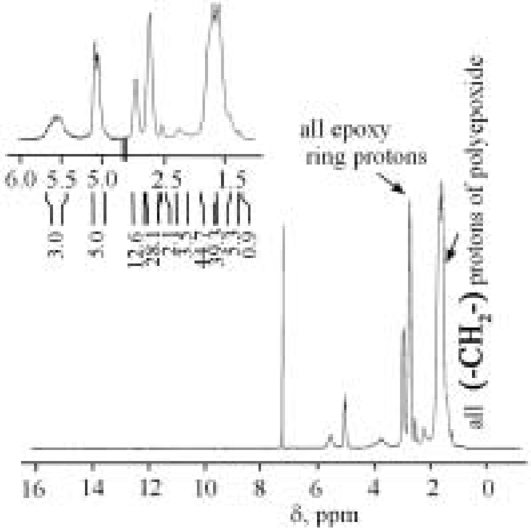


Fig. 8. ^{1}H NMR spectrum of epoxidized HTPB ("Krasol-LBH") after 72 h of the reaction time

any influence on the branch relation to ethylene whereas two alkyl substituents increased the rate by a factor of 500—600 in relation to ethylene [6].

The assignment of *cis* and *trans* epoxy groups in the ^{13}C NMR spectra in Fig. 6 bases on the data reported by Gemmer [29]. He demonstrated that *cis* and *trans* epoxy carbon absorptions were presented at 56.5 and 58.5 ppm, respectively.

It was also found from *cis*-polybutadiene ^{13}C NMR spectrum that epoxy carbon absorption at 56.5 ppm was related to the *cis*-epoxy carbon, therefore the one at 58.5 ppm was related to the *trans*-epoxy carbon (Fig. 7), what is in agreement with [29].

Figure 8 shows ^{1}H NMR spectrum of epoxidized HTPB ("Krasol-LBH") after 72 h of the reaction time. Having looked to the region of spectrum in the range of δ = 16—9 ppm, we found that no signal is present in this region that was attributed to H-CO of aldehydes or H-OCO of acids. The ^{13}C NMR spectrum of the epoxidized product also shows no signal in the region of δ = 220—170 ppm, which is attributed to carbonyl groups of aldehydes or acids (Fig. 6). From these results we concluded that the initial hydroxyl groups at polymer backbone were preserved in the epoxidation and no side reaction was carried out. On the other hand, the action of oxidant has been selective regarding reaction sites and the electron density of reaction sites played the main role in the epoxidation reactions.

FT-IR spectra

By comparison of FT-IR spectra of epoxidized and initial polymers, the expected symmetrical stretching or contracting frequency of the epoxy rings has been found. All ring bonds, stretching and contracting in phase, were observed at about 1262 cm^{-1} and 834 cm^{-1} for the corresponding epoxide rings (Fig. 9) in FT-IR spectra of epoxidized polymers after 1 h, 10 h and 72 h of the reaction time (Fig. 9). In the spectra of unepoxidized initial polymer the signals at 725 cm^{-1} related to 1,4-*cis* double bonds, 966 cm^{-1} related to 1,4-*trans* double bonds and 911 cm^{-1} related to 1,2-vinyl double bonds are present. In the FT-IR spectra of products after reaction lasted 72 h, the position of 1,4-*cis* and 1,4-*trans* double bonds were virtually removed, but the position of 1,2-vinyl double bonds partially was retained. It is noteworthy that the broad signal at 3400—3600 cm^{-1} related to OH (H-bonded) of HTPB was preserved after 72 h of epoxidation reaction.

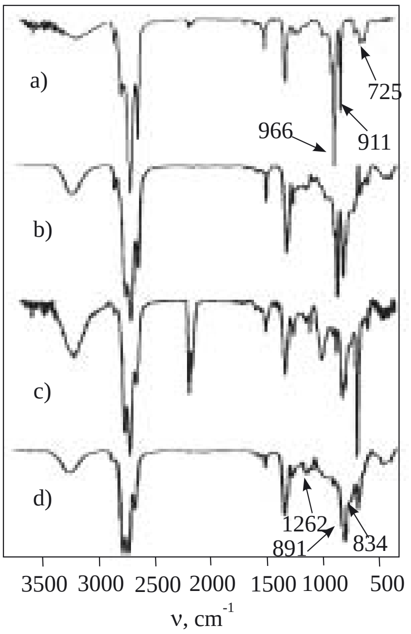


Fig. 9. FT-IR spectra of unepoxidized (a) and epoxidized HTPB ("Krasol-LBH") after 1 h (b), 10 h (c) or 72 h (d) of the reaction time

Determination of epoxidation yields after various reaction times

In Figure 10 the ^{1}H NMR spectra of polyepoxides which were produced by the epoxidation reaction after various reaction times are compared. This comparison shows the increasing absorptions at 2.7 ppm and 3.0 ppm due to the progress of epoxidation reaction.

Integration of intensity values of hydrogen atoms lead to the conversion and described how the degree of epoxidation varied with the change of catalyst concentration, at constant temperature (25 °C) and time (3 h) of reaction (Table 3).

The results showed that the epoxidation of HTPB by DMD includes oxygen transfer and highest reaction yield can be achieved by using about 0.13 % of MoO_3/"Oxone®" (w/w). At catalyst concentrations smaller and higher than 0.13 % decrease in epoxidation yield is observed. The interpretation of reaction yield decreasing can be achieved with the help of the MoO_3/DMD complex obtained through reaction between MoO_3 and

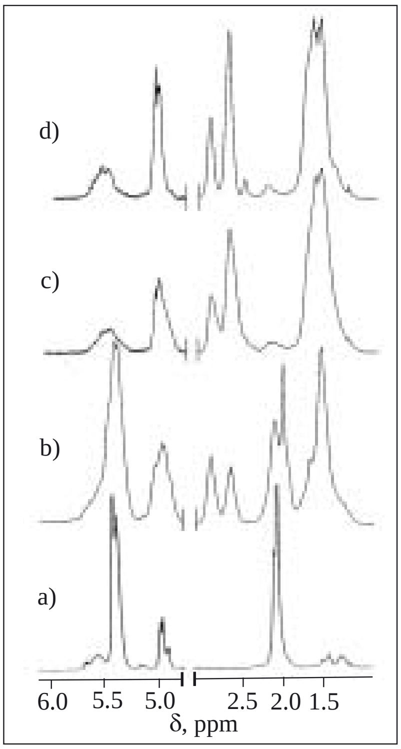


Fig. 10. ^{1}H NMR spectra of unepoxidized (a) and epoxidized HTPB ("Krasol-LBH") after 1 h (b), 10 h (c) or 72 h (d) of the reaction time

DMD (Scheme A). Possibly, at MoO_3 concentrations smaller than 0.13 %, the formation of complex cannot be completed and at MoO_3 concentrations higher than 0.13 %, degradation reaction of active oxidant takes place, probably due to complexation of active oxidant with hydroxyl group of HTPB or by interaction with other MoO_3 molecules.

Table 3. The effect of catalyst concentration on the epoxidation yield of HTPB (temp. 25 °C, time 3 h)

Run	Epoxidation, %		MoO_3/"Oxone®" % w/w
	HTPB ("Krasol-LBH")	HTPB ("Zibo")	
1	58	42	0.06
2	65	46	0.13
3	52	43	0.38
4	43	39	0.63
5	43	38	0.89
6	36	40	1.14

The changes of epoxidation yields as functions of reaction time (1—10 h) are stopped after 5—7 h at a level of about 85 % and 70 % for two studied by us kinds of HTPB, probably due to significant decrements in *cis* and *trans* moieties and low reactivity of vinyl content in HTPB "Krasol-LBH" and HTPB "Zibo", respectively (Table 4).

Table 4. The effect of reaction time on the epoxidation yield of HTPB (temp. 25 °C, MoO_3/"Oxone®" concentration 0.13 % w/w)

Run	Epoxidation, %		MoO_3/"Oxone®" % w/w
	HTPB ("Krasol-LBH")	HTPB ("Zibo")	
1	41	34	1
2	65	46	3
3	83	46	5
4	86	70	7
5	84	72	10

We expected HTPB microstructure containing 15 % *cis*, 25 % *trans* and 60 % vinyl (HTPB "Zibo") being less reactive than the other one, with 20 % *cis*, 60 % *trans* and 20 % vinyl (HTPB "Krasol-LBH"). Maximum epoxidation yields of low *cis* content in HTPB was about 72 % after 10 h whereas the high *cis* one reacted to about 84 % conversion at the same conditions. It is in agreement with our expectations. Probably, when the double bonds have been reacted to the conversion over 84 % the resultant polymer appeared to be insoluble in chloroform and the epoxidation reaction was stopped.

CONCLUSION

The epoxidation of hydroxyl terminated polybutadiene was carried out with *in situ* generated dimethyl dioxirane, with epoxidation yields up to 84 % at constant temperature 25 °C in the presence of molybdenum trioxide (MoO_3) at easy and convenient conditions. ^{1}H NMR and ^{13}C NMR spectra of epoxidized polymer indicated no by-products. The formation of epoxy groups in polymer backbone was confirmed mainly on the basis of ^{13}C NMR spectra which exhibited characteristic resonances in the region 56.5 and 58.5 ppm corresponding to *cis*- and *trans*- epoxy ring carbon atoms, respectively. Also ^{1}H NMR spectra indicated absorptions at 3.0 ppm that was related to the *cis*-epoxy hydrogens whereas the one at 2.7 ppm was related to the *trans*-epoxy hydrogens. ^{1}H NMR, ^{13}C NMR and FT-IR spectra analyses confirm the absence of ring epoxy group opening the side reactions. From FT-IR spectra there were observed no signals suggesting oxidation to aldehydes or acids (2850 cm^{-1}, 2750 cm^{-1} for C-H of aldehydes and broad signal for OH of acids at 2400—3400 cm^{-1}). Also ^{13}C NMR spectra of the products show no signal in the region 220—170 ppm and ^{1}H NMR spectra of epoxidized polymers indicated no signals in 16—9 ppm regions attributed to aldehydes and acids, respectively. In conclusion, epoxidation of HTPB by using *in situ* generated DMD proceeds without any over-oxidation reactions toward OH groups of HTPB and ring opening reactions of three-member epoxy rings. *In situ* generated DMD play chemoselective role in these reactions. The epoxidation reactivity depends on the chain microstructure, and decreases in the following order: 1,4-*cis* > 1,4-*trans* > 1,2-vinyl. The reason is related to the nucleophilicity of double bonds — groups which enriched the electron density of double bonds increase the rate of epoxidation reaction.

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