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Polymers oxidation with VO(acac)$_2$ complex

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Abstract

The introduction of epoxy groups in the polymer backbone is one of the most promising methods of modifying polydienes. In this work the performance of the classical catalytic system VO(acac)$_2$/*tert*-butylhydroperoxide was evaluated for the epoxidation of polydienes. The polymers investigated were a hydroxylated poly(butadiene), two polybutadienes with high and with low 1,4-content, a poly(isoprene), and a styrene–butadiene copolymer. The epoxidized polymers were characterized by IR, ^{1}H and ^{13}C NMR and GPC techniques. The vanadium system was active for the epoxidation reaction and the reactivity decreases in the order HTPB>PI>1,4-PB>1,2-PB∼SBR. The occurrence of secondary reactions to low extension could be detected by the presence of hydroxyl, carbonyl and alcohol signals in the spectra of epoxidized polymers. Incomplete mass recovery (70–90%) was observed probably due to the chain degradation or modification of the polymer polarity. ©2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Polymers with a carbon backbone and pendant functional groups find extensive use both as base materials and as additives to modify the properties of other materials [1]. Such polymers can be prepared by homo- or copolymerizing monomers containing functional groups or by modification of a polymer introducing new functional groups or changing existing ones [2,3].

Epoxypren®, for example, is a new commercial product obtained by the partial epoxidation (25 and 50%) of natural rubber. The epoxidized material presents higher tensile strength and oil resistance, lower gas permeability and better compatibility with polymers such as PVC, when compared with natural rubber, enlarging its application range as, for example, in tire inside-wall and polymer blends among others.

The introduction of epoxy groups along the polymer backbone is one of the most promising methods of modifying polydienes. The most usual system to epoxidize diene polymers involves the in situ formation of peracids, generated by the reaction of acetic or formic acid with hydrogen peroxide [1,4,5]. 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 polydienes using systems based on transition metals, such as Mo [6], W [7,8], Mn [9].

Complexes of vanadium (IV) or (V) in the presence of an oxidant, like hydrogen peroxide or alkyl hydroperoxides, ROOH, have been extensively used as catalyst for oxidation reactions, such as epoxidation of olefins and allylic alcohols and oxidation of olefins, thioethers, alcohols and hydrocarbons

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[10]. By far the most used compound is the vanadium(IV)acetylacetonate, VO(acac)$_2$, which reacts with H_2O_2 or ROOH forming peroxo complexes that are effective and selective oxidants of organic and inorganic substrates.

In this work we evaluate the performance of the classical catalytic system VO(acac)$_2$/*tert*-butylhydroperoxide in the epoxidation of polydienes, such as hydroxylated poly(butadiene) (HTPB), polybutadienes with high and low 1,4-content (1,4-PB) and (1,2-PB), respectively, poly(isoprene) (PI), and a styrene–butadiene copolymer (SBR).

2. Experimental

2.1. Materials

Commercial polydienes were used in this study, namely 1,4-PB (M_w=56 400, M_n=34 300, PD=1.65, 86% of *cis*/*trans*-1,4), 1,2-PB (13% *cis*/*trans*-1,4), SBR (Buna VLS, 76 wt.% of butadiene and 24 wt.% of styrene), PI (M_w=311 000, M_n=181 100, PD=1.70, 70% *cis*-1,4, 20% *trans*-1,4, 10% 3,4-) and HTPB (Liquiflex H, 80% *cis*/*trans*-1,4). *tert*-Butylhydroperoxide (TBHP) 70% in water (Aldrich) was extracted in dichloromethane or toluene as described in the literature [11]. The hydroperoxide content in the solution was determined by ^{1}H NMR. Toluene and dichloromethane were reagent grade and were used without further purification. VO(acac)$_2$ was synthesized by the method described elsewhere [12].

Epoxidation reaction: In a typical epoxidation reaction, VO(acac)$_2$ was added to 20 ml of the polymer solution in toluene or dichloromethane (10% (w/v) for HTPB and 5% (w/v) for the other polymers). The solution was then cooled in an ice bath and the appropriated amount of TBHP solution was added dropwise under continuous stirring. The amount of VO(acac)$_2$ and TBHP were calculated according to the double bond content of the polymers (100 mol% of polymer double bonds, 1 mol% of VO(acac)$_2$ and 100 or 150 mol% of TBHP. The mixture was kept under constant magnetic stirring in the dark at the required temperature. At the end of the reaction, the solution was filtered in order to separate the catalyst and the polymer was precipitated in ethanol containing 2,6-di-*tert*-butyl-4-methylphenol. The coagulated polymer was then dried at 30°C under vacuum and the samples were characterized by IR, ^{1}H and ^{13}C NMR and GPC techniques.

2.2. Characterization

IR spectra of the polymers were recorded using a Mattson Galaxy series FTIR 3000 spectrophotometer. The sample was dissolved in chloroform and a thin film was prepared on the KBr disk by evaporating the solvent.

^{1}H and ^{13}C NMR spectra were obtained on a Varian VXR 200 spectrometer operating at 200 MHz at room temperature. The samples were run as approximately 5% (w/v) solutions in $CDCl_3$ in 5 mm tubes using tetramethylsilane as the internal standard.

The molecular weights of all samples were determined by GPC (waters, RI detector, room temperature), using THF as eluent and a calibration curve for polystyrene standards.

The degree of epoxidation was calculated by the integration of the signals in the 2.7–3.0 ppm region of the ^{1}H NMR spectra, corresponding to the *cis* and *trans* epoxy hydrogens [4]. The appearance of peaks at 56.5 and 58.5 ppm in the ^{13}C NMR spectra were assigned to the *cis* and *trans* epoxy groups, respectively [13]. In the IR spectra a shoulder at 880 cm^{-1} indicates the presence of oxirane rings [4,5,14]. No epoxidation products were observed when the reactions were carried out using either VO(acac)$_2$ or TBHP, showing that these compounds are inactive.

3. Results and discussion

Vanadium based systems are known as very active and selective catalysts for the epoxidation of allylic alcohols [10,15]. The exceptional reactivity of the allylic alcohols towards vanadium-alkyl hydroperoxides can be attributed to the fast and strong coordination of alcohol ligands to vanadium, followed by an intramolecular oxygen transfer from the coordinated alkyl to the double bond of the allylic alcohol [16–20].

In this context, the epoxidation of a polymer such as HTPB could be advantageous since the hydroxyl groups of the polymer could help the formation of the active complex.

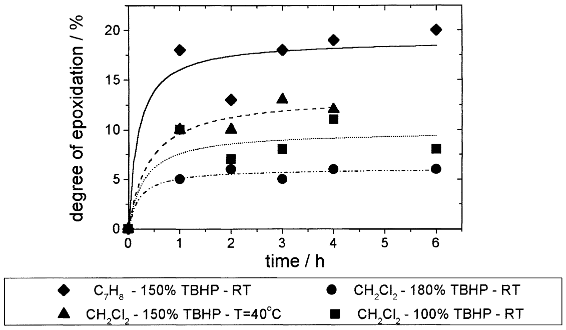

Fig. 1.

Table 1
Molecular weight of epoxidized polymers

Polymer	Epoxidation[a] (%)	M_n	M_w	PD[b]
HTPB	–	3000	5500	1.82
	11	4500	6400	1.40
	8	4500	7460	1.65
	6	4500	7700	1.69
PI	–	181 100	311 000	1.70
	4	22 200	39 100	1.76
1,4-PB	–	34 300	56 400	1.65
	6	17 400	39 800	2.28

[a] Reaction at room temperature, in toluene, 1 mol% of $VO(acac)_2$, 150 mol% TBHP and 100 mol% of polymer double bonds.

[b] $PD=M_w/M_n$.

The results obtained for the HTPB are shown in Fig. 1. As can be seen, under the investigated conditions, the maximum conversion was obtained with toluene. This can be attributed to the lower concentration of chain segments in the polymer coil since toluene is a better solvent for the polymer than dichloromethane. It was also observed that when the reaction is carried out in dichloromethane the degree of epoxidation does not change significantly varying the amount of TBHP and the reaction temperature.

Mass recovery of the epoxidized polymer at the end of the reaction was a problem. Usually only 70–90% could be recovered. It was even more difficult when the reaction was carried out either in dichloromethane or with longer reaction time or with higher temperatures. Such behavior can be explained by the strong modification of the polymer solubility due to chain degradation or to the change in the polymer polarity, caused by the introduction of the epoxy groups.

The molecular weight data obtained by GPC of the epoxidized HTPB (Table 1), indicate that the increase in the polarity of the polymer is the main reason of the low mass recovery. An increase in average numeric molecular weight (M_n) and average ponderal molecular weight (M_w) and a slightly decrease in polydispersity are observed for the epoxidized HTPB. In the GPC-chromatograms it can be observed that there is almost no shift in the peak position. On the other side, the low molecular weight fraction is missing, due to the incomplete coagulation of the polymer, that affects mainly the chains with lower molecular weights.

The higher conversion observed at room temperature for the HTPB, when compared with the degree of epoxidation obtained for the PI at same conditions (Table 2), suggest that the presence of the hydroxyl groups enhances the reactivity when the vanadium system is used. Higher temperatures are needed in order to obtain higher conversion, that is epoxidation degrees similar to the commercial product (see Table 2). On the other hand, shorter reactions have to be done due to the degradation of the polymer. Different from HTPB, the GPC data of the poly(isoprene) show a significant decrease in the molecular weight (Table 1). The lower molecular weight of epoxidized polymer

Table 2
Epoxidation of polydienes with $VO(acac)_2$/TBHP/toluene

Polymer	TBHP[a] (%)	Temperature	Time (h)	Epoxidation[b] (%)
HTPB	150[c]	Room	1	17
PI	100[c]	Room	1	<5
	100[c]	Reflux	1	11
	150[c]	Room	1	<5
	150[c]	Reflux	1	18
	150[d]	Reflux	1	25
1,4-PB	100[c]	Room	3	<5
	100[c]	Reflux	3	15
	150[c]	Room	5	6
	150[c]	Reflux	5	20
	150[d]	Reflux	5	27
1,2-PB	150[c]	Reflux	2	<5
SBR	150[c]	Reflux	2	<5

[a] Molar ratio: polymer double bonds (100%); $VO(acac)_2$ (1%), TBHP (100 or 150%).

[b] Calculated from ^1H NMR spectra.

[c] TBHP in dichloromethane.

[d] TBHP in toluene.

can be attributed to the occurrence of side reactions that lead to the chain degradation.

For the 1,4-PB, higher temperatures and longer reaction were necessary in order to obtain similar degrees of epoxidation to the PI. Again the decrease in the polymer molecular weight and/or the increase of the polarity of the polymer were responsible for the difficulties in complete coagulation of the polymer.

The degree of epoxidation obtained for the 1,2-PB and SBR polymers were lower than 5% even at higher temperatures and longer reactions. Furthermore, crosslinking of the polymer chain was observed after drying the polymer. The lower reactivity of the 1,2-PB and SBR were expected [4]. The reason is related to the nucleophilicity of the double bonds. Groups which enrich the electron density of the double bonds increase the rate of the epoxidation reaction [1].

In the epoxidation process several side reactions might happen. It has been found that the higher the reaction temperature and time, the higher the extent of secondary product formation [1]. In this work, the spectra of epoxidized polymers show the occurrence of secondary reactions to low extension. The presence of hydroxyl groups in the chain were characterized by the appearance of a broad band in the IR spectra centered at 3450 cm^{-1}. In addition to a very broad signal at 3.8 ppm [7,8] in the ^{1}H NMR spectra, two signals assigned to OH-substituted carbons at 82 ppm (pendant double bonds) and 86 ppm (backbone double bone) in ^{13}C NMR spectra were observed. The presence of these groups suggests the formation of alcoholic groups bounded to the polymer backbone caused by the opening of the oxirane ring [2,14,21].

Besides the hydroxyl groups, the IR spectra show a weak band at 1725 cm^{-1}, assigned to a carbonyl stretching band, which suggest that this system promotes further oxidation reactions [14]. The absence of a characteristic carbonyl resonance in the ^{13}C NMR spectra can be explained bearing in mind that this is a generally weak resonance and is not observed at low concentration of the groups.

In the IR spectra, two bands of medium intensity at 1362 and 1198 cm^{-1} were assigned to $\delta(\text{CH}_3)$ and $\nu(\text{C–O})$, respectively. The intensity of these bands increases when the reactions were longer and were carried out at higher temperatures. The resonance at 1.25 ppm in the ^{1}H NMR spectra and the signal at 26.5 ppm in the ^{13}C NMR spectra were assigned to the protons and carbon of methyl groups of TBHP. The presence of these groups can be attributed to the physical or chemical incorporation of the TBHP in the polymer. In order to verify the nature of the incorporation, a sample of an epoxidized polymer was dissolved in toluene and coagulated in ethanol three times before recording the IR spectrum. Even after this procedure the intensity of the bands did not decrease, suggesting that the TBHP was chemically bounded to the chain.

4. Conclusion

The results show that the VO(acac)$_2$/TBHP is a potential system for the epoxidation of the polydienes. The reactivity obtained follows the order HTPB>PI>1,4-PB>1,2-PB∼SBR, which is similar to that observed for epoxidation systems based on peracids. Exception is the higher reactivity of the HTPB which can be attributed to the presence of hydroxyl groups in the polymer chain. Side reactions, mainly polymer degradation, were observed probably caused by the occurrence of minor further oxidation reactions and/or by the opening of the epoxy group.

Acknowledgements

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