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ORIGINAL PAPER

Synthesis and characterization of terminally functionalized and epoxidized hydroxyl-terminated polybutadiene

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Abstract Pyridyl *N*-oxide derivatives of hydroxyl terminated polybutadiene-pyridine (HTPB-PY) were synthesized via functionalization on terminal carbon atoms of HTPB backbone by 2-chloropyridine and epoxidation of C=C bonds and N atoms using in situ generated dimethyl dioxirane (DMD). ^{1}HNMR, ^{13}CNMR, ^{14}NNMR, and FT–IR spectroscopy techniques used in order to investigate the structural elucidation of products. In this synthesis method, HTPB terminal hydroxyl groups have preserved unchanged without applying any conditional controllers.

Keywords Hydroxyl-terminated polybutadiene (HTPB) · Functionalization · Oxidation · Modification · *N*-oxide

Introduction

The study of terminally polar group functionalized HTPBs, where a polar or ionic functional group is attached to a non-polar polymer chain, has gained much interest because of their unique properties namely, thermal dynamism, pyrolysis resistance, elasticity, toughness, and durability [1–4]. In addition, thiols, e.g., MTPS [5, 6], TGA [7, 8], fluorinated thiols [9, 10], or phosphonated derivatives [11, 12] have been used as the versatile functional groups in functionalization of HTPB what has been used in synthesizing of structurally improved polyurethanes. The solubility in hydrophilic solvents and glass transition temperature of liquid 1,2-polybutadiene (PBL) has also been improved by the functionalization method [13].

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Structural modification of HTPB-based polyurethanes is studied promoting more capable polymeric products. Yang et al. [14] have modified HTPB-based PUs through C=C bonds epoxidation and found that the properties of the modified HTPB-based PU membranes, including the adsorption of fibrinogen and albumin onto the surface, had significantly been changed. In addition [15], they reported synthesis of poly (*N*-isopropyl acrylamide)-modified polyurethane (PUDPANIPAAm) by modification of HTPB-based PUs using *N*-isopropyl acrylamide monomer initiated by UV radiation for biomaterial application. HTPB-based polyurethane urea has been synthesized by terminal addition of toluene 2,4-diisocyanate (TDI) in the presence of dibutyltindilaurate (DBTDL) as a catalyst in a two-step polymerization reaction [16]. HTPB functionalization had also been reported utilizing 3-isopropenyl-α,α-dimethylbenzylisocyanate (TMI) [17], triethoxysilane-functionalized polybutadiene [18] and t-butyldimethylsiloxy [19]. Terminal-functionalization of HTPB involving covalently attaching of 1-chloro-2,4-dinitrobenzene (DNCB) to the polymer backbone has been performed, achieving (HTPB-DNCB) as an energetic binder in formulation of solid rocket composite propellants [20].

Pyridine *N*-oxides (Py–NO) have lately been the center of much attention [21]. Particularly, heterocyclic *N*-oxides are important as catalysts, chemical protecting groups, auxiliary agents in oxidation, and ligands in metal complexes [22]. The N–O bond acts as an electron donor as well as an electron acceptor what cause significant effect on the electronic and physical properties of target molecule [23, 24].

In this study, we report the functionalization of HTPB by covalently attaching of 2-chloropyridine to the terminal carbon atoms of polymer chain in the presence of sodium hydride (NaH) as a base, in order to synthesizing HTPB-PY as the reaction product which is converted to the corresponding Pyridyl *N*-oxide (HTPB-PY-NO) in an oxidation process by using in situ generated DMD as an oxidant.

Experimental

Materials

HTPB by an average Mw of 2,840 (composed by 15% *cis*, 25% *Trans*, and 60% *vinyl* microstructures), Hydroxyl number of 42 ± 2 g/mg KOH, Viscosity at 40 °C $\leq$ 5 Pa s, Water content $\leq$0.1%, and Peroxy content $\leq$0.05% was purchased from Zibo Qilong Chemical Industry Co. Ltd, China and was used as received without any further purification. 2-chloropyridine, Oxone®, sodium hydride, acetone, and other chemicals were purchased from Merck®, Germany and used as received.

Equipment

^{1}H NMR, ^{13}C NMR, and ^{14}N NMR spectra were done on a Bruker CRX-300 Avance by using $CDCl_3$ as a deuterated solvent and tetramethyl silane (TMS) as an internal reference. FT–IR spectra were obtained using a Bruker Tensor 27 FT–IR instrument. All reactions were performed using a water circulator known as Cole Parmer Polystate (model 12101-25).

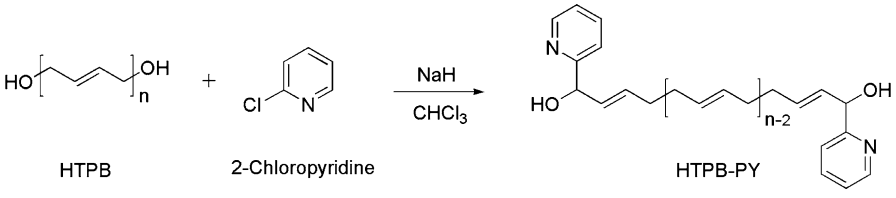
Functionalization of HTPB by 2-chloropyridine

HTPB (3.345 g, 0.062 mol) was dissolved in chloroform (10 mL) and stirred for 30 min in order to obtaining a clear solution. NaH (0.223 g) and 2-chloropyridine (0.113 g, 0.001 mol) were added to the solution and stirring was continued overnight what the color of the solution changed to dark brown by formation of an oily product (Fig. 1). The oily product collected, washed by distilled water (3 × 10 mL), dried under vacuum and characterized by spectroscopy methods. Scheme 1 illustrates the formation HTPB-PY from the reaction of HTPB and 2-chloropyridine.

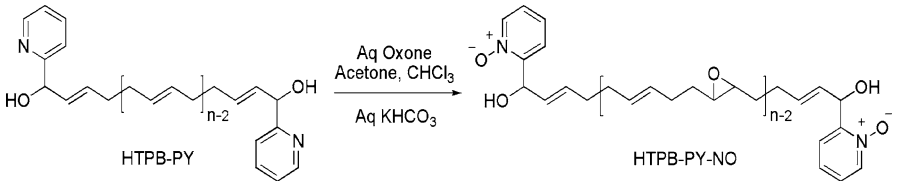
Oxidation of HTPB-PY

Oxidation was carried out in a five-necked glassy reactor at 25 ± 0.1 °C. In a general procedure, HTPB-PY (0.5 g) was dissolved in $CHCl_3$ (20 mL). Acetone (5 mL), $KHCO_3$ solution (containing 5.68 g in 60 mL distilled water) and Oxone® solution (7.8 g in 60 mL distilled water) were added to the reaction mixture and the mixture vigorously stirred in order to formation of split phases [25]. The organic phase (HTPB-PY-NO) was separated and dried under vacuum at 55–60 °C for 10 h and characterized. The reaction path is shown in Scheme 2.

Fig. 1 Photographs of HTPB (*left* colorless), HTPB-PY (*middle* dark brown), and HTPB-PY-NO (*right* pale yellow)



Scheme 1 Formation of HTPB-PY from the reaction of HTPB and 2-Chloropyridine



Scheme 2 Formation of HTPB-PY-NO from the oxidation of HTPB-PY by in situ DMD

In addition, Fig. 1 shows the photographs of the starting material as well as reaction products.

Results and discussion

Functionalization of HTPB with 2-chloropyridine

In this study, HTPB was functionalized via covalently attaching of 2-chloropyridine in the presence of NaH as a catalyst. The functionalization product (HTPB-PY) was characterized using ^{1}H NMR and ^{13}C NMR spectroscopy techniques and the obtained results were compared to those of unmodified HTPB (Fig. 2a, b). As shown in Fig. 2a, the peaks at 1.0–2.2, 3.8, and 4.4–5.4 ppm are related to –CH,

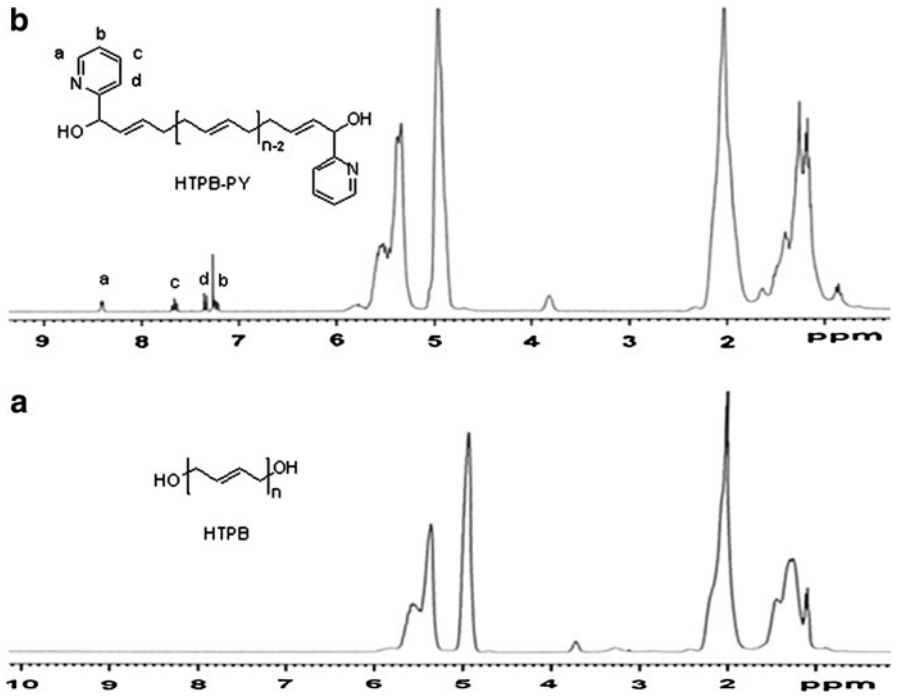


Fig. 2 ^{1}H NMR spectra of HTPB (**a**) and HTPB-PY (**b**)

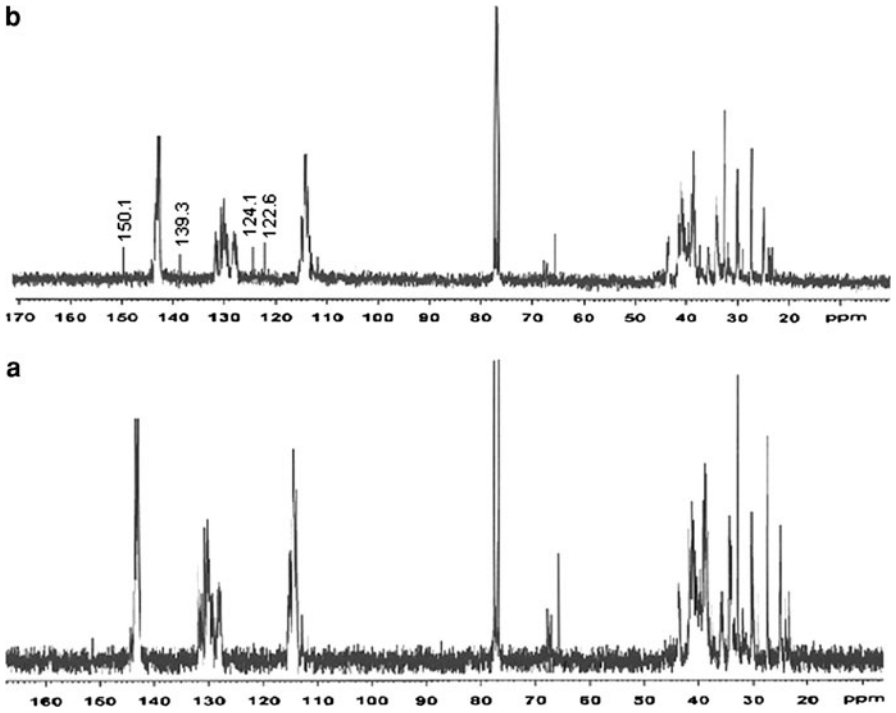


Fig. 3 ^{13}C NMR spectra of HTPB (**a**) and HTPB-PY (**b**)

–OH, and =CH protons in the HTPB backbone, respectively [26, 27]. According to the Fig. 2b, some additional peaks which are associated with aromatic protons are appeared at 7.2 (t, 2H), 7.3 (d, 2H), 7.6 (t, 2H), and 8.4 (d, 2H) ppm what reveal the introducing of the pyridine moieties on the HTPB backbone.

In order to confirmation of results from ^{1}H NMR studies, ^{13}C NMR (Fig. 3a, b) spectra was used and data compared by unmodified HTPB one. In Fig. 3a, the peaks at 25–43 ppm and 114–142 ppm are related to –CH and =CH carbon atoms, respectively [28, 29]. In Fig. 3b, some additional carbons were observed at 122.6, 124.1, 139.3, and 150.1 ppm and are assigned as aromatic ring carbon atoms. The ^{1}H NMR and ^{13}C NMR spectra of HTPB-PY prove that HTPB has been successfully functionalized.

Oxidation of HTPB-PY by DMD

In the next step HTPB-PY was oxidized to pale yellow HTPB-PY-NO by using in situ-generated dimethyl dioxirane (DMD) at 25 °C. For structural elucidation of HTPB-PY-NO, ^{14}N NMR spectra were performed to verify the introducing of *N*-oxide functional groups in the HTPB backbone (Fig. 4a–c). Figure 4a depicts that the peak at −74.58 ppm is associated with the nitrogen atom of 2-chloropyridine. By replacing of the chlorine with carbon atom and formation of HTPB-PY, the attributed peak to the nitrogen atom shifts to −78.60 ppm (Fig. 4b). By oxidation of

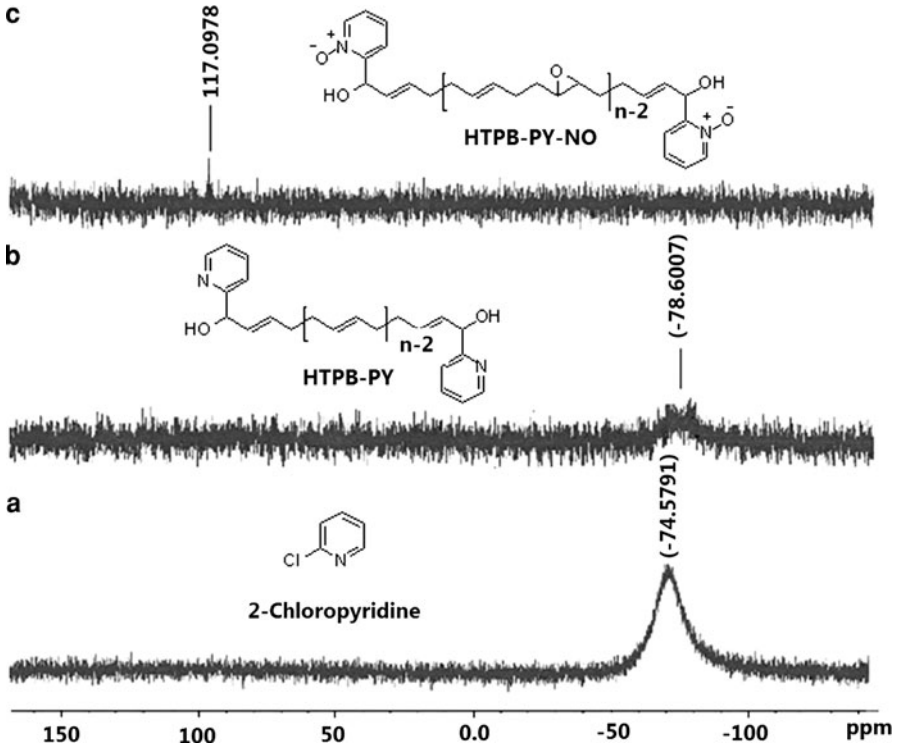


Fig. 4 ^{14}NNMR spectra of 2-chloropyridine (**a**), HTPB-PY (**b**), and HTPB-PY-NO (**c**)

HTPB-PY and converting to HTPB-PY-NO, the electron density of nitrogen atom is decreased in comparison with nitrogen atoms of 2-chloropyridine and HTPB-PY and shifts to downfield. According to the extremely low electron density of the nitrogen atom, it was expected to be observed in the downfield. The obtained spectra proved this expectation by the peak related to the nitrogen atom at 117 ppm (Fig. 4c).

The FT–IR spectra of HTPB were compared to those of HTPB-PY-NO and are shown in the Fig. 5a, b, respectively. Figure 5a shows the stretching vibration of O–H bond at around 3385 cm^{-1}, the C–H aliphatic bond at 2918 cm^{-1}, and the double bonds of HTPB at 1640 cm^{-1}, respectively [20, 30]. Furthermore, the sharp signals at 995, 910, and 688 cm^{-1} are attributed to the 1,4 *Trans*, 1,2 *vinyl*, and 1,4 *cis* microstructures of HTPB, respectively [31, 32]. As is clear in Fig. 5b, the FT–IR spectrum of HTPB-PY-NO demonstrates not only these peaks, but also a strong N–O bond at 1106 cm^{-1} and the found results were similar to the reports [33]. Thus, the presence of O–H stretching in the FT–IR spectrum of HTPB-PY-NO clearly confirms that modification of HTPB backbone by 2-chloropyridne preserve the hydroxyl groups. The terminal O–H of HTPB shows a stretching vibration at 3385 cm^{-1} which is much lower than the expected stretching of the free O–H around 3600 cm^{-1} what reveals the formation of strong intermolecular hydrogen

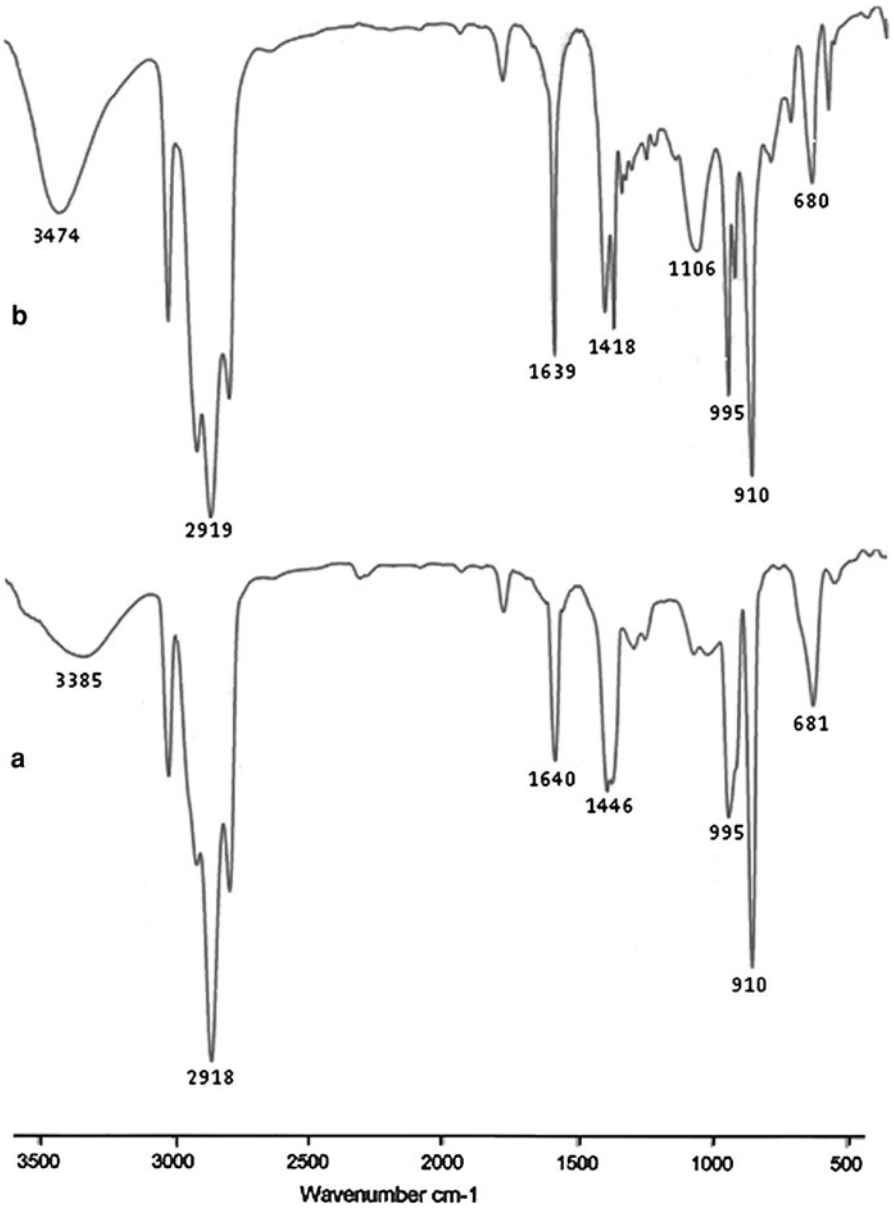


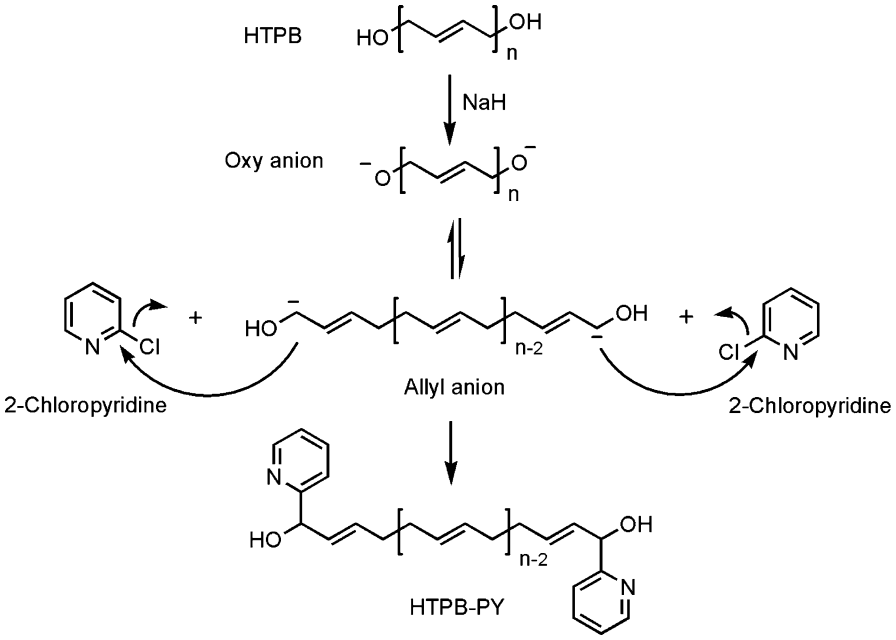
Fig. 5 FT–IR spectra of HTPB (**a**) and HTPB-PY-NO (**b**)

bonds. O–H stretching vibration of the HTPB-PY-NO is appeared at 3474 cm^{-1} which proves that attached 2-chloropyridines to the HTPB, prevent the formation of effective intermolecular hydrogen bonds due to its sizeable structure at the end of the HTPB chain.

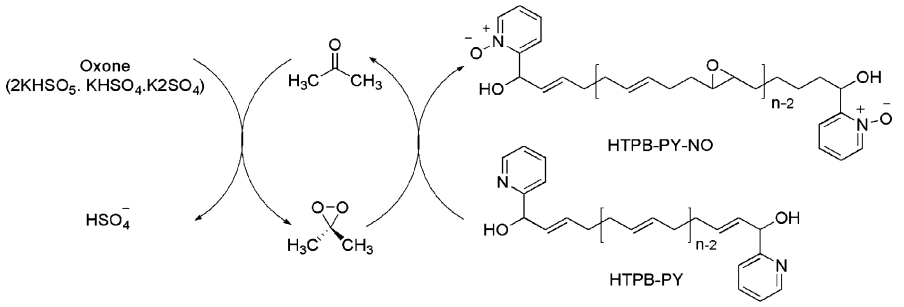
Mechanisms of HTPB-PY and HTPB-PY-NO formation

Investigating the covalent attachment of 2-chloropyridine to the HTPB backbone, a mechanism is proposed through which NaH acts as a strong base and reacts with hydrogen atom of O–H in HTPB and generates alkoxide at both ends of HTPB [20]. Since alkoxide anions are not stable, easily converted to the stable allyl anions by an intermolecular acid–base reaction. This phenomenon is shown in Scheme 3 what the alkoxide anion is converted to the stable allyl anion and the reaction is followed by attaching of HTPB's terminal carbon atom anion as a nucleophiles and replacing of the chlorine leaving group in the substrate.

The oxidation process of HTPB-PY using in situ generated DMD is shown in Scheme 4. In this reaction, the buffer condition is generated by potassium bicarbonate. $KHSO_4/K_2SO_4$ buffer holds the pH constant at 7–8.5, where the low concentration of H^+ and OH^- would not lead to the formation of an open ring epoxy group. It is mentionable that, in the oxidation process, the HSO_5^- anion is produced from the dissolution of Oxone in water which reacts with acetone to form in situ generated DMD in the solvent phase [31]. The electron pair of the nitrogen atom is oxidized by unstable and electron deficient DMD and HTPB-PY is converted to the HTPB-PY-NO. It is mentionable that in these reactions only 14% of total double bonds on HTPB are oxidized. The mechanism is illustrated in Scheme 4.



Scheme 3 Proposed mechanism for the formation HTPB-PY



Scheme 4 Proposed mechanism for the formation of HTPB-PY-NO

Conclusion

Hydroxyl-terminated polybutadiene (HTPB) was functionalized by covalent attaching of 2-chloropyridine to the terminal carbon atoms. The synthesized HTPB-PY was converted to the HTPB-PY-NO using in situ generated dimethyl dioxirane (DMD) and via an oxidation process. The structural elucidation data revealed that the terminal hydroxyl groups of the polymer were preserved in both processes without employing any conditional controllers. This modification resulted in the structural diversity of the polymer, enhances its physicochemical properties and introducing of HTPB-PY-NO as a new candidate for the future application purposes.

Acknowledgment We gratefully acknowledge the financial support of the Imam Khomeini International University, Qazvin, Iran.

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