



Polímeros: Ciência e Tecnologia

ISSN: 0104-1428

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Associação Brasileira de Polímeros
Brasil

Alavi Nikje, Mir Mohammad; Gholi Nataj, Maryam
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Polímeros: Ciência e Tecnologia, vol. 24, núm. 5, septiembre-octubre, 2014, pp. 536-540

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Cloisite 15A^o Nanoclay as an Effective PTC for the Epoxidation of Hydroxyl Terminated Polybutadiene (HTPB)

Mir Mohammad Alavi Nikje

Chemistry Department, Faculty of Science, Imam Khomeini International University

Maryam Gholi Nataj

Chemistry Department, Faculty of Science, Ghaemshahr Islamic Azad University

Abstract: A simple method is reported for the epoxidation of hydroxyl-terminated polybutadiene (HTPB) by using in-situ generated dimethyl dioxirane (DMD) as an oxidant and Cloisite 15A^o nanoclay as a phase-transfer catalyst (PTC). In order to find the optimum reaction conditions, real time analyses of the products as well as epoxidation progress, followed by ¹HNMR and FTIR techniques at various reaction times and different PTC concentrations, were done. Obtained data revealed the selectivity of DMD/ Cloisite 15A^o in predominant cis double bonds epoxidation in comparison with trans and pendant vinyl functional groups.

Keywords: Hydroxyl-terminated polybutadiene (HTPB), epoxidation, dimethyl dioxirane, Cloisite 15A^o.

Introduction

Epoxidation of unsaturated carbon- carbon double bonds and introducing of the reactive three membered oxirane functional groups on the polymer structure lead to significant properties by having broad variety of applications^[1,2]. Among the engineering polymers, the hydroxyl-terminated polybutadiene (HTPB) is widely used as a binder in the formulation of adhesives, solid rocket propellants, elastomers, sealants etc., due to its unique physicochemical properties namely, thermal stability, performances under dynamic load, pyrolysis resistance, elasticity, toughness, and durability^[3]. These properties are performed by introducing of one or more epoxy functional groups in non-polar non-conjugated HTPB main chain^[4]. In this research area, modified hydroxyl-terminated polybutadiene based polyurethane membranes has been prepared and the properties studied by Yang et al.^[5,6]. In the another report, Stenberg and coworkers studied the chemiluminescence properties of thermally oxidized hydroxyl terminated polybutadiene rubber^[7]. The kinetic of epoxidation of hydroxyl-terminated polybutadiene with hydrogen peroxide under phase transfer catalyst studied by Wang research group and the epoxidation yields determined by spectroscopy methods^[8]. In addition, kinetics and mechanism of epoxidation of low molecular weight cis-butadiene rubber has been studied by using tertbutyl hydroperoxide as the oxidant and products identified by ¹HNMR spectra^[9]. *m*-Chloroperbenzoic acid (*m*-CPBA) has been used as the oxidant in epoxidation of internal C=C bonds and data published by Saffers research group^[10].

Akcelrud and his coworkers reported the direct and strait forward HTPB epoxidation reaction for the first time by complete structural elucidation of reaction products. In their study, *m*-Chloroperbenzoic acid has been used as

the oxidant and the corresponded NMR spectra assigned carefully and the progress of epoxidation reaction followed by this technique^[11]. All the reported methods have their own merits and drawbacks. For example, even though peracids appear to be more effective than peroxides in epoxidation reactions, they have harmful effects on human health and gives rise to environmental pollution^[12]. Another drawback in the reported epoxidation reactions is the formation of undesired by-products via side-reactions and the need for high reaction temperatures to achieve higher conversions^[13,14].

In order to resolve the epoxidation reaction drawbacks, some experiments designed to epoxidize of double bonds by using *in-situ* generated dimethyl dioxirane (DMD)^[15,16]. In-situ generated DMD is cyclic peroxide known as a powerful, reactive and useful oxidizing agent. DMD is generally obtained from the reaction of acetone and aqueous Oxone[®] (2KHSO₅, KHSO₄, K₂SO₄)^[17]. Oxone[®] is soluble in water and its oxidation process is simple and requires readily available cheap reagents in eco-friendly conditions. Oxone[®] performs oxidations in biphasic systems using immiscible co-solvents in mixture with a phase-transfer catalyst (PTC)^[18,19]. Previously, we reported polybutadiene and HTPB epoxidation using in-situ generated DMD in the presence of tetra-*n*-butyl ammonium bromide as a phase transfer catalyst (PTC)^[20,21], MoO₃^[22], transition metal salts^[23], copper (II) complex^[24], Nano TiO₂^[25] and Cloisite 30B as a PTC^[26,27]. In the continuation of our previous works on epoxidation reactions, we decided to epoxidize HTPB using modified nanoclay called Cloisite 15A^o as the phase-transfer catalyst. Based on our literature survey, the epoxidation of HTPB by using in-situ generated DMD and Cloisite 15A^o is reported for the first time and can be included as a simple and convenient method in epoxidation reactions.

Corresponding author: Mir Mohammad Alavi Nikje, Chemistry Department, Faculty of Science, Imam Khomeini International University, PO box 288, CP 34149-16818, Qazvin, Iran, e-mail: drmm.alavi@gmail.com

Experimental

Materials and methods

HTPB (M_n 2840, containing 15% cis, 25% trans and 60% vinyl) was purchased from Chinese Zibo Qilu Chemicals. Cloisite[®] 15A, obtained from Southern Clay Products, is a natural montmorillonite modified with a quaternary ammonium salt. Oxone[®] and other auxiliary chemicals, bought from Merck, were used as received. ¹HNMR and ¹³CNMR spectra were obtained using a Bruker CRX-300 Avance instrument at 300 MHz and room temperature using CDCl₃ as a solvent. FT-IR spectra were obtained on a Bomem MB-100 instrument.

Epoxidation reactions

All reactions took place in a five-necked glassy reactor at 25 °C ± 0.1 °C using the Cole Parmer Polystate temperature regulator (Model 12101-25). HTPB (0.5 g) and CHCl₃ (20 ml) were poured into the reactor and mixed until the polymer was completely dissolved. Then, acetone (10 ml) and 60 ml of potassium bicarbonate solution (5.68 g of KHCO₃ in distilled water) were added to the reactor. Next, 60 ml of the Oxone[®] solution (7.8 g of Oxone[®] in distilled water) was mixed with different percentages of

Cloisite 15A^o /Oxone (w/w). The mixture was then poured into the reactor and vigorously agitated until obtained a clear diphasic system. At specified times, 10 ml of the mixture was selected and the organic phase was dried under vacuum at 55-60 °C for 10 h for analysis. Epoxidation of HTPB using in situ-generated DMD in the presence of Cloisite 15A^o is shown in Figure 1.

Results and Discussion

Epoxidation reactions in the presence of Cloisite 15A^o

The epoxidation of HTPB using in-situ generated DMD as an oxidant and Cloisite 15A^o as a phase-transfer catalyst is presented in Figure 2. In the epoxidation process, the HSO₅⁻ anion is formed from the dissolution of Oxone[®] in water that cannot penetrate into the polymer contained organic phase. Its reaction with acetone in the solvent phase is minimal and needs the use of a phase-transfer catalyst. In the present research, Cloisite 15A^o acts as the phase-transfer catalyst that has quaternary ammonium salt with two long unbranched aliphatic tails and has the ability to transfer HSO₅⁻ from aqueous phase to solvent phase. As shown in Figure 2, the ion-exchange process

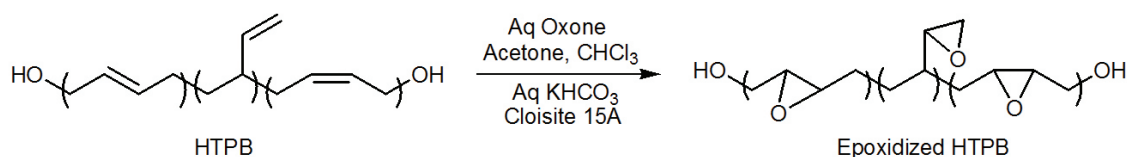


Figure 1. Schematic representation of epoxidation reaction.

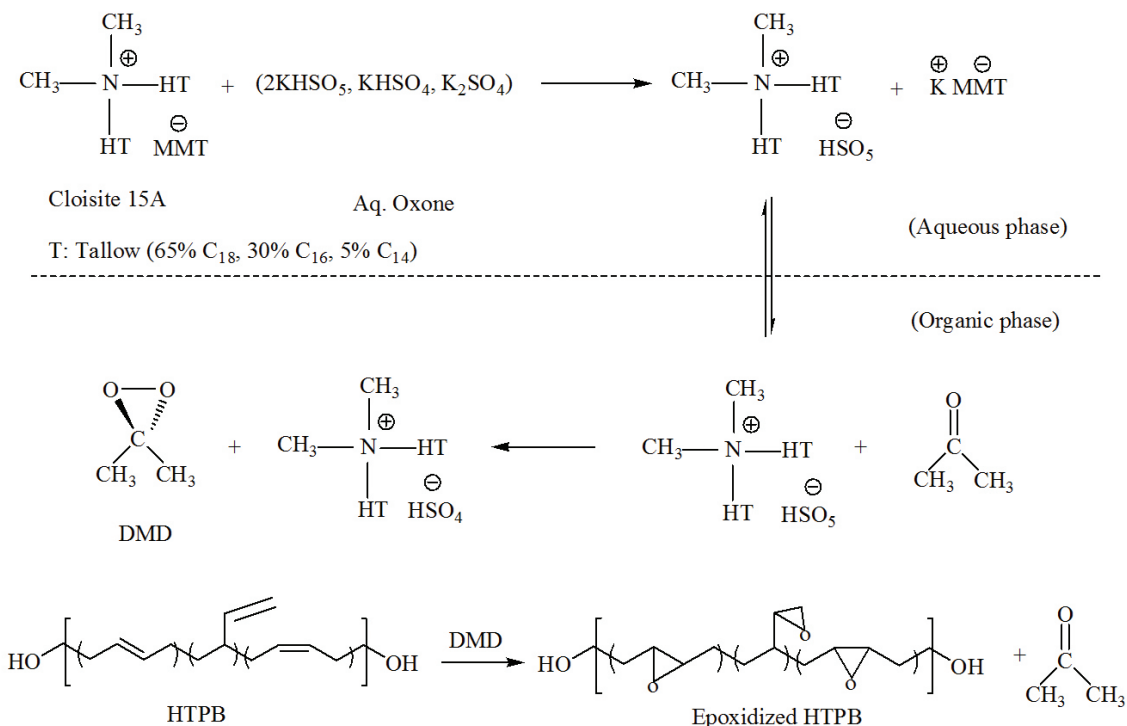


Figure 2. Biphasic epoxidation of HTPB in the presence of Cloisite 15A^o.

between Cloisite 15A^o and Oxone[®] is an important step in the formation of a new oxidant that acts as a surfactant and transfers peroxysulfate ion into the organic phase. The reaction between this new oxidant and acetone in the organic phase leads to the formation of DMD that is responsible for the epoxidation reaction. As the electron-rich double bonds attach to unstable electrophile three-member DMD rings, HTPB C=C bonds oxidized and HTPB converted to the epoxidized HTPB. Recently, similar reaction mechanism has been reported by Kachasakul et al. who used Oxone[®] as an oxidant in combination with tert-butyl ammonium persulfate as the PTC^[16].

Characterization of the epoxidized polymers

The assignment of HTPB and epoxidized HTPB protons was done on ¹HNMR spectra as shown in the Figure 3. According to our obtained results from spectra, the findings are similar to previously reported data by elsewhere^[28]. In addition, the assignment of cis, trans and vinyl epoxy groups in the epoxidized products were based on the data reported by Gemmer and Golub^[29] and Zuchowska^[30]. A comparison of epoxidized and unepoxidized HTPB in the ¹HNMR spectra showed that signals at 5.3 ppm, 5.4 ppm, 4.9 and 5.6 were pertained to cis, trans, and vinyl double bonds, respectively. These signals were respectively, shifted to about 2.9, 2.7, 2.5, and 3.0 ppm in the epoxidized HTPB. Of course, we did not observe vinyl epoxy in the ¹HNMR, which was due to the lower reactivity of vinyl bonds in comparison to cis and trans double bonds^[29]. This indicates that vinyl double bonds are rarely epoxidized.

Similarly, the evaluation of epoxidation reactions studied by comparing the carbons chemical shifts (δ) of HTPB and epoxidized HTPB samples as shown in the ¹³CNMR spectra in Figure 4. In HTPB, cis and trans double bonds had their signals at 129 ppm, but as the epoxidation reaction progressed, additional signals appeared at 56 ppm

and 58 ppm, which were pertinent to cis and trans epoxy, respectively. The obtained results are similar to the results obtained by Gemmer and Golub^[29]. Focusing on the 114 ppm and 141 ppm regions in the ¹³CNMR spectra, we found that vinyl carbons remained unchanged due to their low electron density.

Another way for comparing epoxidized and unepoxidized HTPB is FT-IR spectroscopy. By comparing FT-IR spectra of unepoxidized and epoxidized HTPB, we observed the repeated symmetrical stretching and contraction of the epoxy rings as expected. The stretching and contraction of all ring bonds were observed at around 1262 and 834 cm⁻¹, respectively, after 1 h of reaction (Figure 5). In HTPB, we observed (Figure 5A) the signals related to cis double bonds at 725 cm⁻¹, those related to trans double bonds at 966 cm⁻¹, and the signals related to vinyl double bonds at 912 cm⁻¹. A great majority of cis and trans double bonds disappeared as a result of epoxidation, but only a small number of vinyl double bonds were epoxidized. It is worth noting that the broad signal detected at 3400-3600 cm⁻¹ related to the vibration stretching of hydroxyl functional group of HTPB chain and preserved unreacted during epoxidation process.

The relationship between PTC percentages and epoxidation yields

Through a formerly reported equation^[28] and peak area integrations at 2.7-3.0 and 4.9-5.6 ppm in the ¹HNMR spectra, the double bonds conversion can be calculated. For this purpose, HTPB was epoxidized in the attendance of different percentages of Cloisite 15A^o at different reaction times (Figure 6). As is clear in Figure 6, there are low conversion yields (up to 29%) whether with or without a catalyst. This can be attributed to low reactivity of vinyl bonds in comparison with the cis and trans geometries. Indeed, the vinyl microstructure reacted significantly

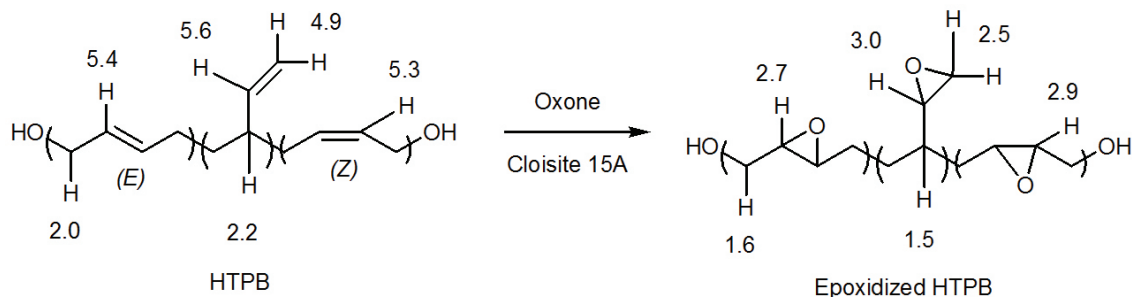


Figure 3. Assignment of chemical shifts (δ ppm) of HTPB and epoxidized HTPB in the ¹HNMR spectra.

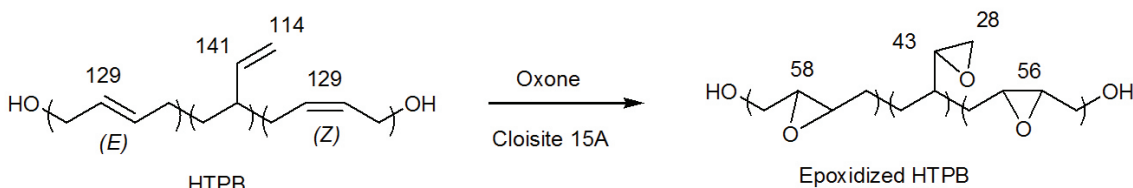


Figure 4. Assignment of chemical shifts (δ ppm) of HTPB and epoxidized HTPB in the ¹³CNMR spectra.

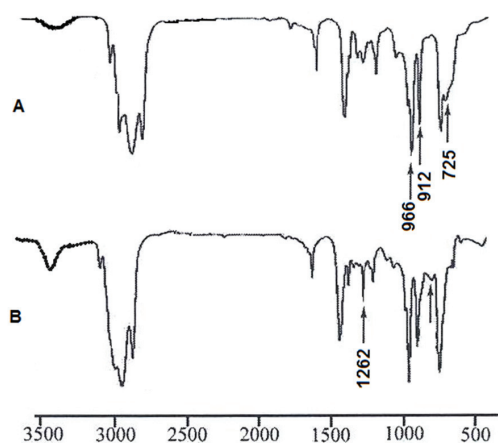


Figure 5. FT-IR spectra of unepoxidized (A) and epoxidized HTPB (B).

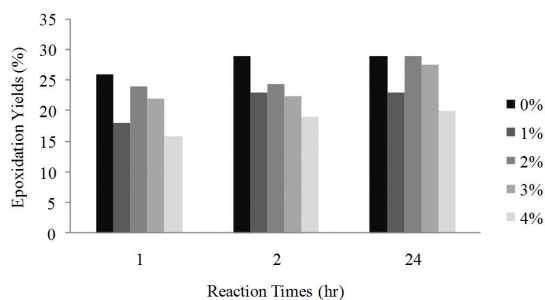


Figure 6. Epoxidation yields of HTPB in the presence of no, 1%, 2%, 3%, 4% Cloisite 15A° as a phase-transfer catalyst at different reaction times.

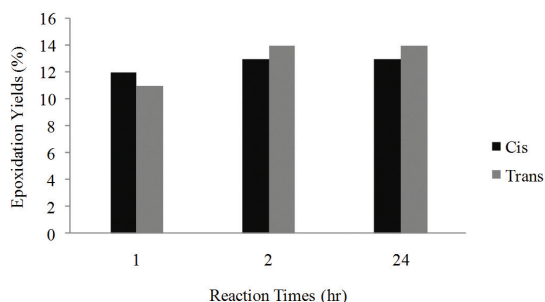


Figure 7. Comparison of cis and trans epoxy in non-catalyzed reactions.

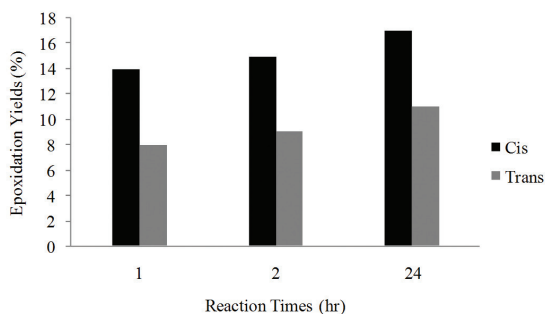


Figure 8. Comparison of cis and trans epoxy in catalyzed reactions (3%).

less than did the cis and trans microstructures. This low reactivity is probably a result of the lower nucleophilicity of the vinyl group^[30].

Another significant point that can be detected from the chart is the amount of epoxidation yields (in %) in non-catalyzed and catalyzed reactions. Epoxidation yield declined nearly in the catalyzed reactions with different percentages of Cloisite 30B than in the non-catalyzed reaction. For example, after 2 h of reaction, 29% of the HTPB was epoxidized in the absence of Cloisite 15A° in comparison with 22% of epoxidation in the presence of 3% Cloisite 15A°. These results show that Cloisite 15A° is particularly selective toward one kind of double bonds. To provide further confirmation, we separated cis epoxy from trans epoxy in non-catalyzed and catalyzed reactions. The results are shown in Figures 7 and 8, respectively.

As shown in Figure 7 the percentage of cis epoxy is more than that of trans epoxy shortly after reaction, the cause being the fact that cis double bonds were more reactive than trans double bonds. Nevertheless, trans epoxy exceeded cis epoxy with the passage of time (it is worth noting that this is a natural phenomenon as HTPB consists of 15% cis, 25% trans and 60% vinyl). For example, after 1 h of reaction, cis epoxy was around 12% while trans epoxy was about 11%. However, after 2 h of reaction, cis epoxy and trans epoxy were around 13% and 14%, respectively.

Data in Figure 8 brings interesting results. Cis epoxy considerably exceeded trans epoxy and the difference remained unchanged with the passage of time. For example, after 1 h reaction, cis epoxy was 14% while trans epoxy was about 8%. However, after 2 h reaction, cis epoxy and trans epoxy were around 15% and 9%, respectively (Figure 9).

Focusing on cis/trans epoxy group ratios, we can detect the high tendency of oxidant towards cis microstructures. For example, after 2 h reaction, the cis/trans epoxy ratio was about 1.8 in the presence of 3% Cloisite 15A° and about 0.8 in its absence. This shows that the cis/trans epoxy ratio increased 2.25 times when Cloisite 15A° was used. In conclusion, catalyzed reactions show more chemoselectivity toward cis double bonds than toward trans double bonds.

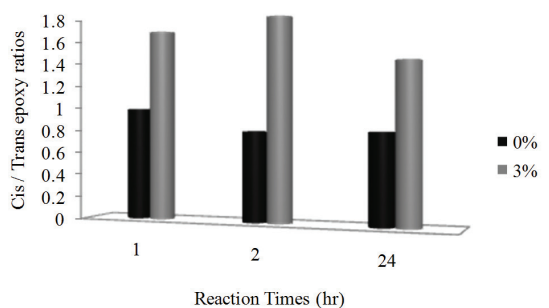


Figure 9. Cis/Trans epoxy group ratios in non-catalyzed and catalyzed reactions (3%).

Conclusions

The epoxidation of HTPB was carried out by using of *in-situ* generated DMD in the presence of nanoclay as the phase-transfer catalyst. Using ¹HNMR, ¹³CNMR and FT-IR, oxidation potential of HTPB and the effect of PTC concentrations on the epoxidizing process were studied at various reaction intervals. The data show that the oxidant was particularly selective toward cis double bonds. This came from the study that the ratio of cis to trans epoxy groups increased when Cloisite 15A^o was present. Overall, this research was successfully performed using both in-situ generated oxidant and Cloisite 15A^o nanoclay for the first time.

References

1. Chadiri, M.; Farzaneh, F.; Chandi, M. & Alizadeh, M. - J Mol Catal A Chem., **233**, p.127 (2005)
2. Park, J. S. & Ruckenstein, E. - Polymer, **31**, p.175 (1990). [http://dx.doi.org/10.1016/0032-3861\(90\)90371-5](http://dx.doi.org/10.1016/0032-3861(90)90371-5)
3. Ganesh, K.; Sundararajan, S.; Kishore, K.; Ninan, K. N.; George, B. & Surianarayanan, M. - Macromolecules, **33**, p.326 (2000). <http://dx.doi.org/10.1021/ma990423p>
4. McGrath, M. P.; Sall, E. D. & Tremont, S. J. - J Chem Rev., **95**, p.381 (1995). <http://dx.doi.org/10.1021/cr00034a004>
5. Yang, J. M.; Lin, H. T. & Lai, W. C. - J Membr. Sci., **208**, p.105 (2002). [http://dx.doi.org/10.1016/S0376-7388\(02\)00180-1](http://dx.doi.org/10.1016/S0376-7388(02)00180-1)
6. Yang, J. M.; Lai, W. C. & Lin, H. T. - J. Membr. Sci., **183**, p.37 (2001). [http://dx.doi.org/10.1016/S0376-7388\(00\)00550-7](http://dx.doi.org/10.1016/S0376-7388(00)00550-7). Ahlblada, G.; Reitberger, T.; Terselius, B. & Stenberg, B. - Polym Degrad Stab., **65**, p.179 (1999).
8. Wang, Q.; Zhang, X.; Wang, L. & Mi, Z. - Ind. Eng. Chem. Res., **48**, p.1364 (2009). <http://dx.doi.org/10.1021/ie800875h>
9. Koshelev, N. A.; Sapunov, V. N.; Turov, B. S.; Popova, V. V. & Ustavshchikov, B. F. - Polym Sci USSR, **22**, p.2642 (1980).
10. Saffer, A. & Johnson, B. L. - Ind Eng Chem., **40**, p.538 (1948). <http://dx.doi.org/10.1021/ie50459a045>
11. Aguiar, M.; Menezes, S. C. D. & Akcelrud, L. - Chem Phys., **195**, p. 3937 (1994).
12. Lee, H. & Neville, K. - "Handbook of epoxy resins", cap. 5, McGraw-Hill, New York (1967).
13. Martinez-Mandez, S.; Henriques, Y.; Domingues, O.; Ornelas, L. D. & Krentzien, H. - J Mol Catal A Chem., **252**, p.226 (2006).
14. Roy, S.; Gupta, B. R. & De, S. K. - "Elastomer technology handbook", cap. 17, CRC Press, Boca Raton, p. 635-660 (1993).
15. Jian, X. & Hay, A. S. - J Polym Sci Polym Lett., **28**, p.285 (1990). <http://dx.doi.org/10.1002/pol.1990.140280903>
16. Kachasakul, P.; Assabumrungrat, S.; Praserttham, P. & Pancharoen, U. - Chem Eng J., **92**, p.131 (2003). [http://dx.doi.org/10.1016/S1385-8947\(02\)00127-4](http://dx.doi.org/10.1016/S1385-8947(02)00127-4)
17. Brown Ripin, D. H.; Cai, W. & Brenek, S. J. - Tetrahedron Lett., **41**, p.5817 (2000).
18. Aggarwal, V. K.; Lopin, C. H. & Sandrinelli, F. - J. Am. Chem. Soc., **125**, p.7596 (2003). PMID:12812501. <http://dx.doi.org/10.1021/ja0289088>
19. Asensio, G.; Biox-Bernardini, C.; Andreu, C.; Gonzalez-Nunez, M. E.; Mello, R.; Edwards, J. O. & Carpenter, G. B. - J. Org. Chem., **64**, p.4705 (1999). <http://dx.doi.org/10.1021/jo982512q>
20. Alavi Nikje, M. M.; Rafiee, A. & Haghshenas, M. - Des Monomers Polym., **9**, p.293 (2006).
21. Alavi Nikje, M. M. & Mozaffari, Z. - Des Monomers Polym., **10**, p.67 (2007). <http://dx.doi.org/10.1163/1568555077797636322>. Alavi Nikje, M. M. & Mozaffari, Z. - Polymer, **52**, p.28 (2007).
23. Alavi Nikje, M. M. & Mozaffari, Z. - Des Monomers Polym., **11**, p.271 (2008). <http://dx.doi.org/10.1163/156855508X316872>
24. Alavi Nikje, M. M. & Mozaffari, Z. - J Elastomers Plast., **41**, p.41 (2009).
25. Alavi Nikje, M. M. & Hajifatheali, H. - J. Elastomers Plast., **45**, p.457 (2012). <http://dx.doi.org/10.1177/00952443124578026>. Alavi Nikje, M. M. & Hajifatheali, H. - Des Monomers Polym., **14**, p.155 (2011). <http://dx.doi.org/10.1163/138577211X555794>
27. Alavi Nikje, M. M. & Hajifatheali, H. - Polym Plast Technol Eng., **50**, p.1071 (2011). <http://dx.doi.org/10.1080/03602559.2011.5579228>. Vilar, W. D.; Menezes, S. M. C. & Akcelrud, L. - Polym Bull., **33**, p.563 (1994). <http://dx.doi.org/10.1007/BF00296165>
29. Gemmer, R. V. & Golub, M. A. - J Polym Sci., **16**, p.2985 (1978).
30. Zuchowska, D. - Polymer, **21**, p.514 (1980). [http://dx.doi.org/10.1016/0032-3861\(80\)90217-7](http://dx.doi.org/10.1016/0032-3861(80)90217-7)

Received: Nov. 16, 2013

Revised: Apr. 13, 2014

Accepted: May 15, 2014