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SYNTHESIS OF HYDROXYL-TERMINATED POLY(BUTADIENE-CO-ALLYL CHLORIDE) VIA H_2O_2/ISOPROPANOL RADICAL COPOLYMERIZATION AND ITS CONVERSION TO HYDROXYL-TERMINATED POLY(BUTADIENE-CO-ALLYL AZIDE)

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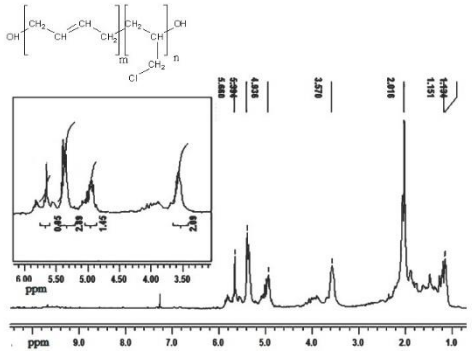
This study introduces an innovative approach for modifying hydroxyl-terminated polybutadiene HTPB by incorporating allyl chloride into the polybutadiene backbone. This method involves the one-pot synthesis of hydroxyl-terminated poly(butadiene-co-allyl chloride) (HTPB-Alc) using the reaction of butadiene and allyl chloride as starting materials in the presence of hydrogen peroxide and isopropanol at 120 °C. The resulting polymer was characterized using fourier-transform infrared spectroscopy (FT-IR), proton nuclear magnetic resonance (^{1}H-NMR), gel permeation chromatography (GPC), and differential scanning calorimetry (DSC). The results indicated that the incorporation of allyl chloride led to a reduction in both the number-average molecular weight ($\bar{M}n$) and weight-average molecular weight ($\bar{M}w$). The DSC thermogram of HTPB-Alc showed a glass transition temperature (*Tg*) similar to that of unmodified HTPB, with a slight increase. The ^{1}H-NMR spectra confirmed the successful incorporation of allyl chloride. Finally, HTPB-Alc undergoes a nucleophilic substitution reaction in the presence of sodium azide and dimethylformamide at 100 °C, leading to the production of hydroxyl-terminated poly(butadiene-co-allyl azide) (HTPB-Az), which was validated by FT-IR.



INTRODUCTION

Hydroxyl-terminated polybutadiene (HTPB) is a semi-transparent, low-molecular-weight liquid with a waxy paper-like appearance.[1–3] It is obtained through the simple and cost-effective polymerization of butadiene monomers.[4,5] Due to the presence of hydroxyl end groups in its polymer chains, HTPB serves as an excellent precursor for the synthesis of polyurethanes that exhibit good low-temperature resistance and high hydrolytic stability.[6,7]

Due to its abundance of functional groups, including double bonds and terminal hydroxyl groups, HTPB readily undergoes modification through various chemical reactions. These

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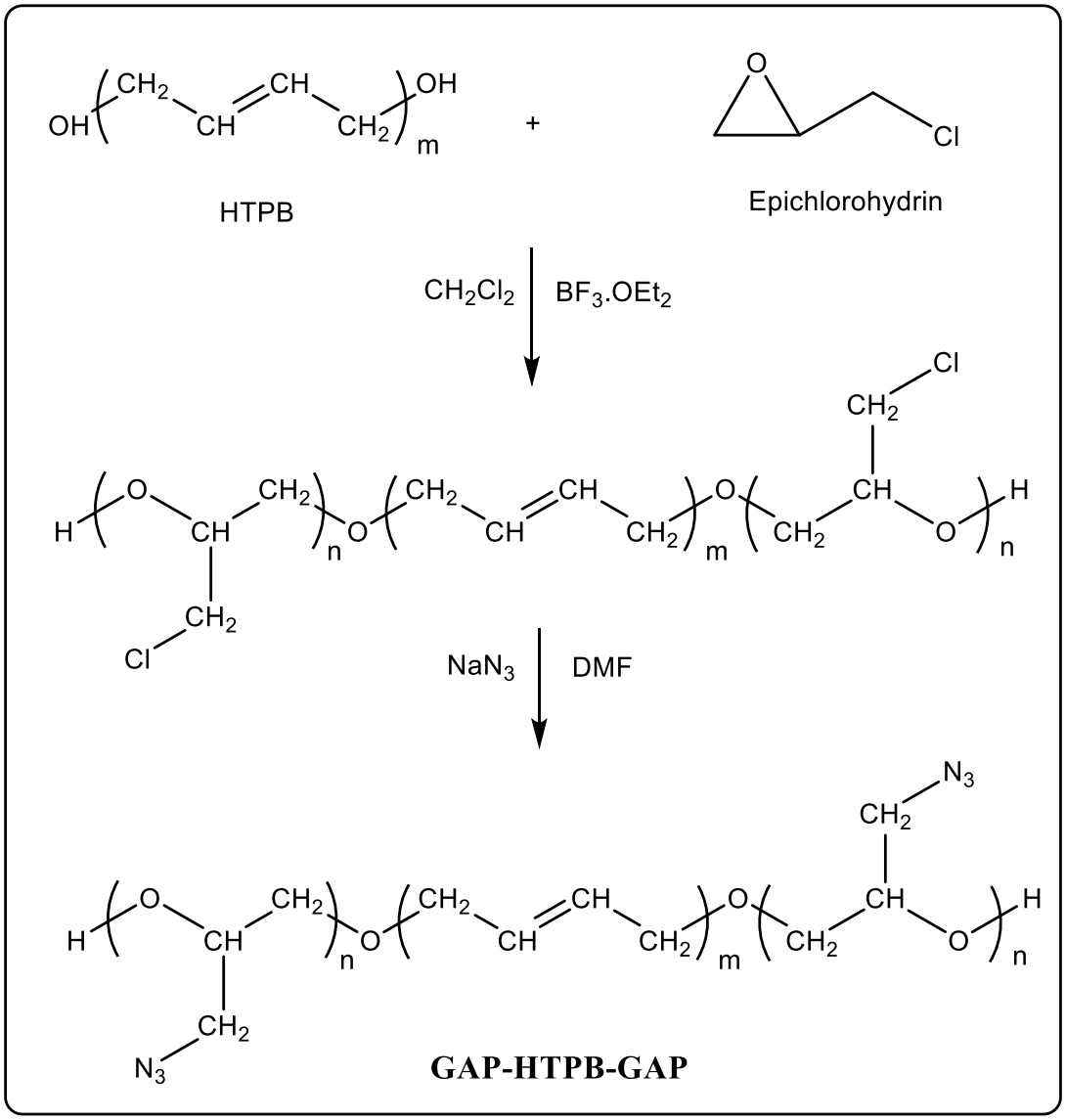
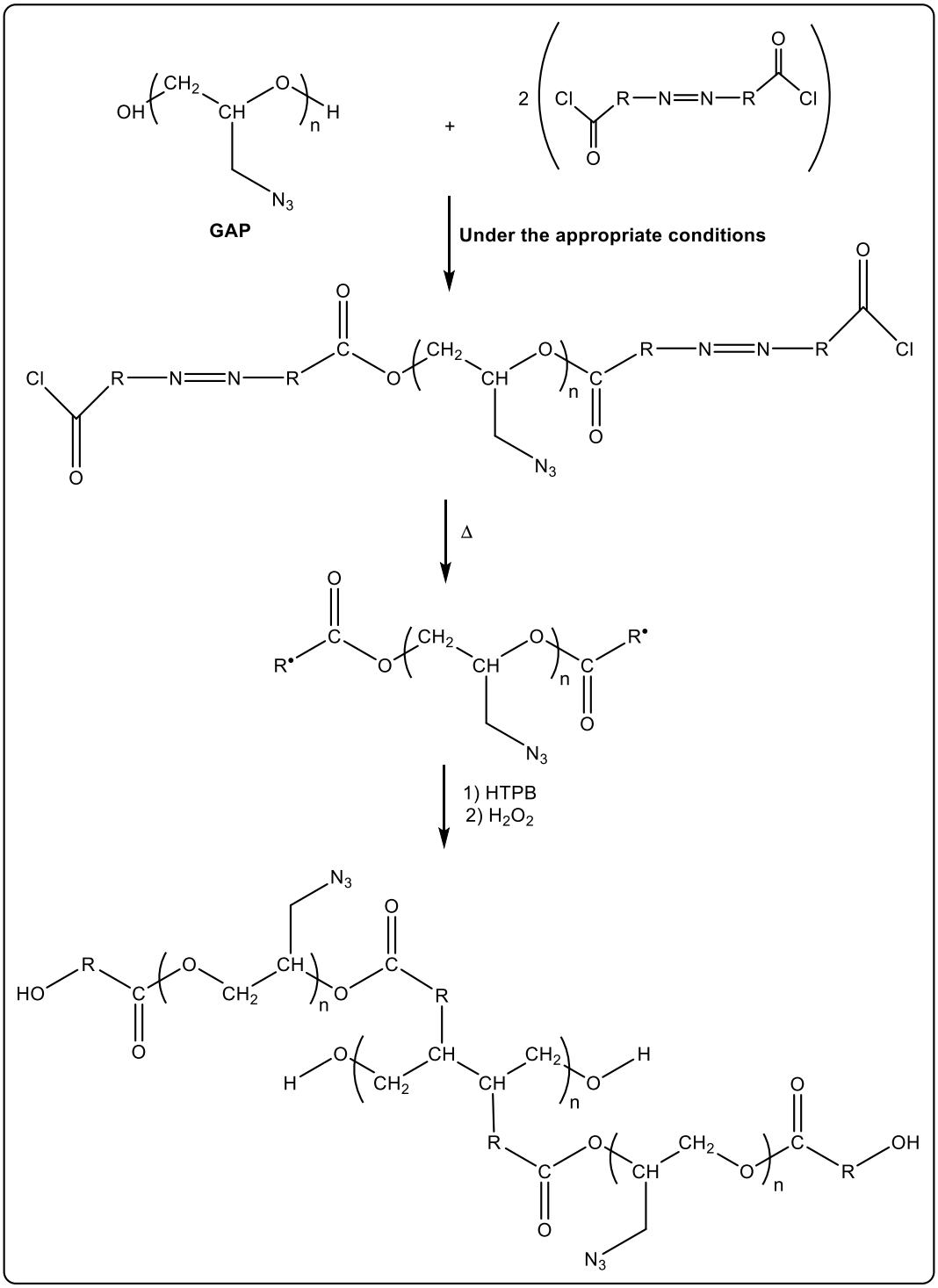
modifications can involve reactions with the double bonds, such as hydrogenation,[8] epoxidation,[9] nitration,[10] and thiol-ene reactions,[11] or reactions with the hydroxyl groups, such as esterification, and the preparation of polyurethanes, poly(urethane-imide)s, poly(urethane-urea)s, and poly(ester-imide)s.[12–15] Furthermore, it is possible to convert the terminal groups to carboxyl (carboxyl-terminated polybutadiene, CTPB) or amine (amine-terminated polybutadiene, ATPB), as well as to functionalize the terminal carbon atoms of the main chain.[16,17]

Beyond its extensive applications as a pre-polymer in various industries, HTPB has also been utilized as a conventional and widely used binder in the production of composite solid propellants.[18] This material, categorized as a non-polar and non-energetic (inert) binder, exhibits limited compatibility with polar energetic plasticizers due to its inherent nature. Given HTPB's pivotal role as a binder in solid propellants, its development and optimization are crucial for achieving higher energy levels and enhancing its physicochemical properties. This limitation has guided researchers towards innovative modification strategies.[19–24] In recent years, one such approach involves the chemical modification of HTPB through grafting with other compounds, such as polyglycidyl azide (GAP), which has garnered significant attention from researchers. However, the resulting copolymers tend to be more heterogeneous than random copolymers.[25-27] Examples of synthetic routes for preparing the grafted copolymer of polyglycidyl azide (GAP-HTPB) are illustrated in scheme **1A** and **1B**.



A)



B)

Scheme 1 – A) Synthesis of tri-block copolymer GAP-HTPB-GAP; B) Synthesis of graft copolymer HTPB-GAP.

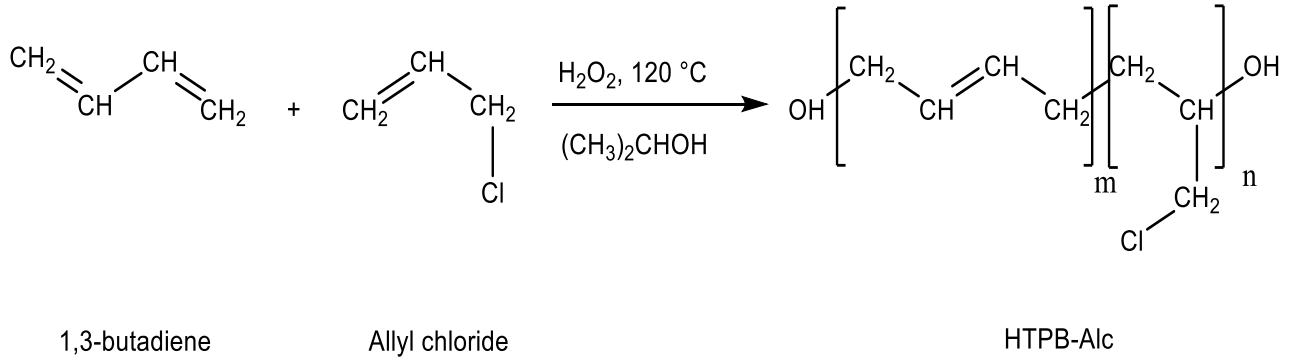
These copolymers were synthesized with the goal of increasing the energy content and improving the polarity of HTPB, making them promising for use as energetic binders in propellant technology. However, GAP-HTPB also faces several challenges, including phase separation, solubility issues, the presence of two distinct glass transition temperatures (–74.03 °C and –35.84 °C), low interaction parameter values, nonlinear behavior in physical properties, and low

yield in its complex synthesis process (involving five steps and resulting in low yields).[26–30] Another effective method for enhancing the properties of HTPB is to modify its structure by adjusting the polybutadiene backbone during polymerization.[31–33] Therefore, efforts to improve the structural modification of GAP-HTPB through various routes are still ongoing.

In continuation of our ongoing research on polymer synthesis and the investigation of their compatibility with energetic plasticizers,[34–42] this research aims to present a novel method for modifying HTPB by incorporating allyl chloride into the polybutadiene backbone. This method involves the one-pot synthesis of hydroxyl-terminated poly(butadiene-co-allyl chloride) (HTPB-Alc) using the reaction of butadiene and allyl chloride as starting materials in the presence of hydrogen peroxide and isopropanol at 120 °C. Subsequently, HTPB-Alc undergoes a nucleophilic substitution reaction in the presence of sodium azide and dimethylformamide at 100 °C, leading to the production of hydroxyl-terminated poly(butadiene-co-allyl azide) (HTPB-Az). To the best of our knowledge, synthesis of HTPB-Alc *via* H_2O_2/isopropanol radical copolymerization and its conversion to HTPB-Az have not been previously reported in the literature. The following sections will delve into a detailed discussion and analysis.

RESULTS AND DISCUSSION

The synthesis of HTPB involved the radical polymerization of 1,3-butadiene at 120 °C, utilizing isopropanol as the solvent and hydrogen peroxide as the initiator. To identify the optimal temperature for the copolymerization of hydroxyl-terminated poly(butadiene-co-allyl chloride) (HTPB-Alc), the reaction was performed under identical conditions but with temperatures adjusted between 80 and 130 °C. It was noted that temperatures exceeding 120 °C led to the breakdown of allyl chloride, producing a green-colored solution. Scheme 2 illustrates the synthesis of HTPB-Alc through the reaction between 1,3-butadiene and allyl chloride in the presence of hydrogen peroxide (H_2O_2) and using isopropanol as the solvent at 120 °C. According to the results obtained from the synthesis of HTPB-Alc, a range of colors appeared in the reaction medium with increasing temperature. In these reactions, when the temperature was varied from 80 to 120 °C, some yellow to red viscous products were obtained after drying under vacuum.



Scheme 2 – Synthetic method for the preparation of HTPB-Alc pre-polymer via radical copolymerization of 1,3-butadiene and allyl chloride.

HTPB and HTPB-Alc were immiscible; when the co-polymerization product was added to HTPB, the mixture spontaneously separated into two phases. The chloride ion concentration was determined by titration (Mohr's Method–ASTM D 1726-03), and the result was positive. The hydroxyl number of the pre-polymer (d_2), measured for formulating polyurethane systems, was found to be 43.6 mg KOH/g. The hydroxyl terminated polybutadiene prepolymers have excellent physical properties such as low glass transition temperature. For determination of variation in T_g value in synthesized copolymer, differential scanning calorimetry was performed on the samples. DSC thermo gram for HTPB-Alc as in HTPB, showed one peak (T_g), to some degree shifted to upper temperature (Fig. 1). This observation is another reason for formation of only one HTPB-Alc copolymer during polymerization reaction.

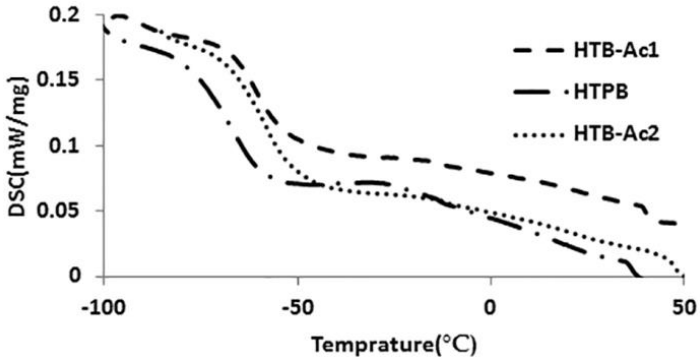


Fig. 1 – DSC curves of HTPB & two samples of HTPB-Alc

Co-polymer composition can be determined very easily by NMR, particularly ^{1}H-NMR, and the method is usually more accurate than other traditional analytical methods, such as elemental analysis.[43,44] Figure 2 illustrates the 500 MHz ^{1}H-NMR spectrum of the HTPB-Alc copolymer. The insertion of allyl chloride in polymer structure can be monitored by ^{1}H-NMR spectroscopy by following the appearance of the peak at 3.5 ppm (due to –C$\underline{H}_2$Cl group) and 1.5 ppm (due to –C$\underline{H}_2$CHCH$_2$Cl group). The most important fundamental relationship of quantitative NMR is the signal intensity in a spectrum directly proportional to the number of nuclei responsible for any specific resonance (eq. 1).

$$Ix = Ks \times Nx \quad (1)$$

where *Ks* is the spectrometer constant in an NMR spectrum which remains the same in all resonances. The areas under 3.5 ppm peak (arise from allyl chloride, 2H) divided to the sum of the areas under the peaks of olefinic protons (arise from butadiene, 2H for [1, 4]-*cis* or *trans* and 3H for [1, 2]) can be used to calculate the mole ratio of allyl chloride to butadiene in copolymers as in eqs. 2–5.

$$[1, 2] + [1, 4] = 1 \quad (2)$$

$$[1,4] = \frac{3B}{2B+3A+C} \quad (3)$$

$$[1,2] = \frac{2A+2C}{2A+3B+2C} \quad (4)$$

$$\left(\frac{Ac}{B}\right) = \frac{3D}{3B+3D+2A+2C} \quad (5)$$

A, B, C in eq. (2) are areas under a, b, c olefinic proton related to butadiene and D is areas under the d protons peaks related to allyl chloride (Fig. 2).

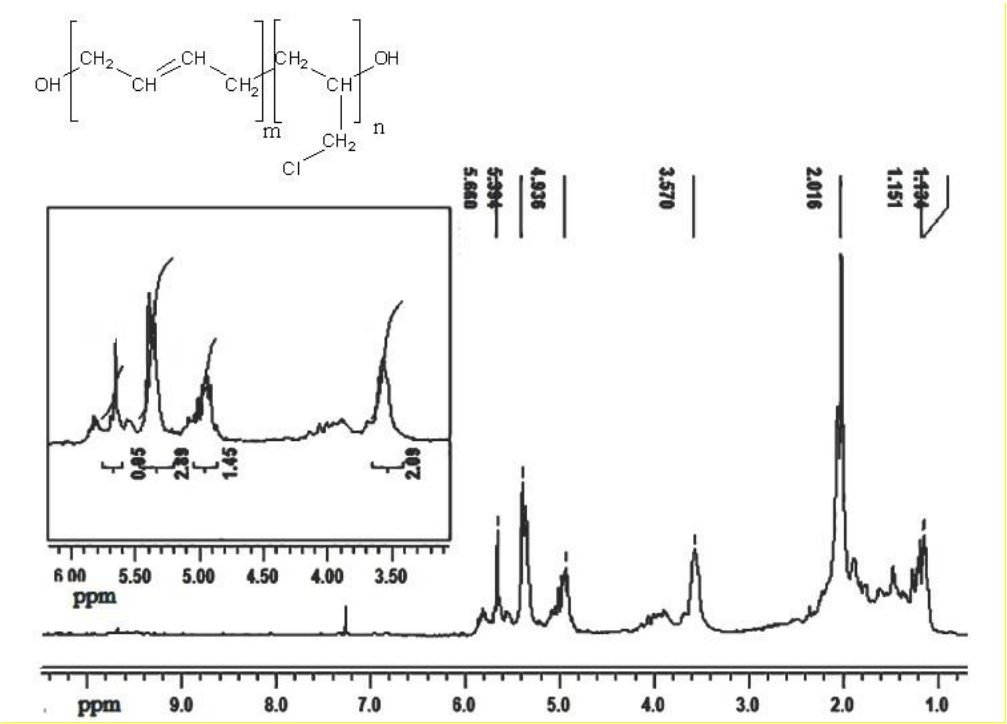


Fig. 2 – ^{1}H-NMR (500 MHz, DMSO d_6) spectra HTPB-Alc copolymer.

In fixed reaction conditions for synthesis of HTPB-Alc such as ratio of monomers in feed (3:1 butadiene to allyl chloride), polymerization temperature (120°C), initiator concentration (0.115 mol), polymerization time and stirring rate were evaluated and found that after 6 h, the rate of conversion of monomers to copolymer was constant. So polymerization time and stirring rate were kept constant and other parameters in copolymerization processes were checked. The number-average molecular weight $\bar{M}_n$, weight-average molecular weight $\bar{M}_w$ and index of polydispersity $\bar{M}_w/\bar{M}_n$, were obtained from GPC (1643, 2718 and 1.65 respectively) (Fig. 3), and yield , mole ratio of allyl chloride to butadiene in copolymer and the ratio of [1,4]/[1,2] addition were obtained from ^{1}H-NMR (28%, 0.39 and 2.01).

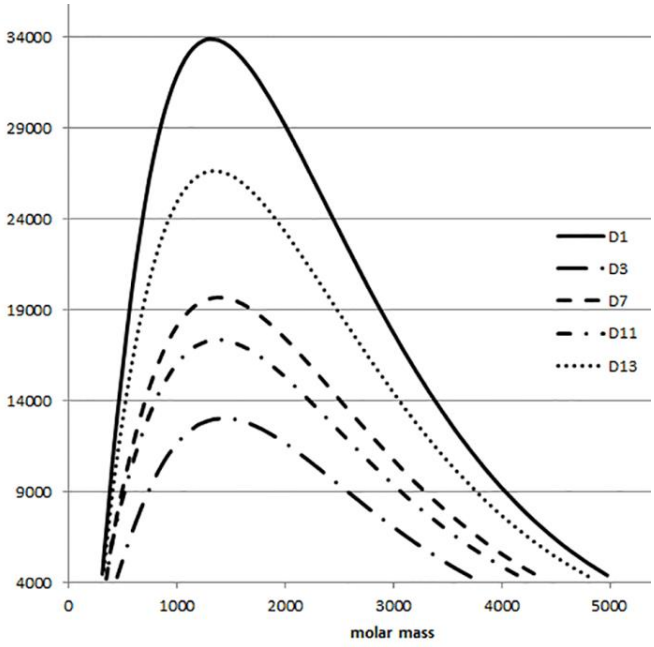


Fig. 3 – GPC curves of HTPB-Alc.

It seems that in presence of allyl chloride, the butadiene radical prefers addition at [1, 2] rather than [1, 4], the feature that was seen in the anionic polymerization method of HTPB pre-polymer production. In addition, molecular weight of products has been reduced in copolymerization reactions because their strong ability of allyl monomer undergoes chain transfer reactions. Also DSC results showed one peak (T_g), that was related to allyl chloride contents and it slightly shifted to higher temperature the case that confirmed the y_2 amounts (Fig. 4).

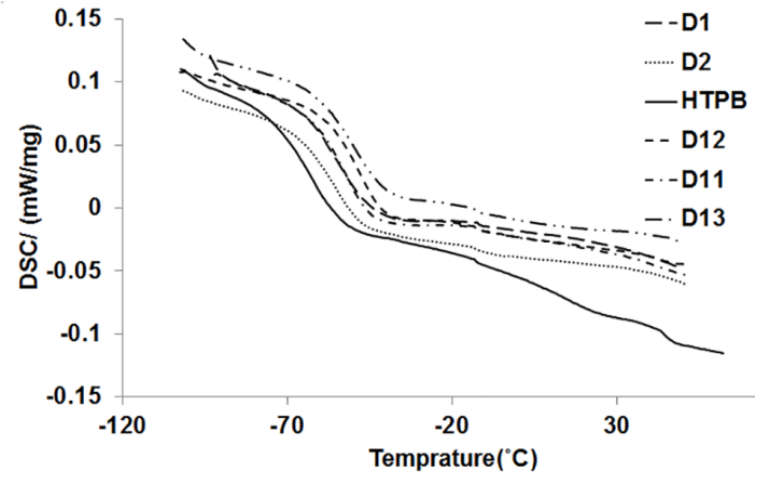


Fig. 4 – DSC curves of HTPB & HTPB-Alc.

The transformation of HTPB-Alc to HTPB-Az was tracked using FT-IR spectroscopy. The FT-IR spectrum displayed in Fig. 5 reveals a reduction in absorbance at 736 cm^{-1}, corresponding to the $–CH_2Cl$ functional group, along with the emergence of a pronounced band at 2095 cm^{-1}, attributed to the $–CH_2N_3$ group. These changes effectively confirm the success of the synthesis process.

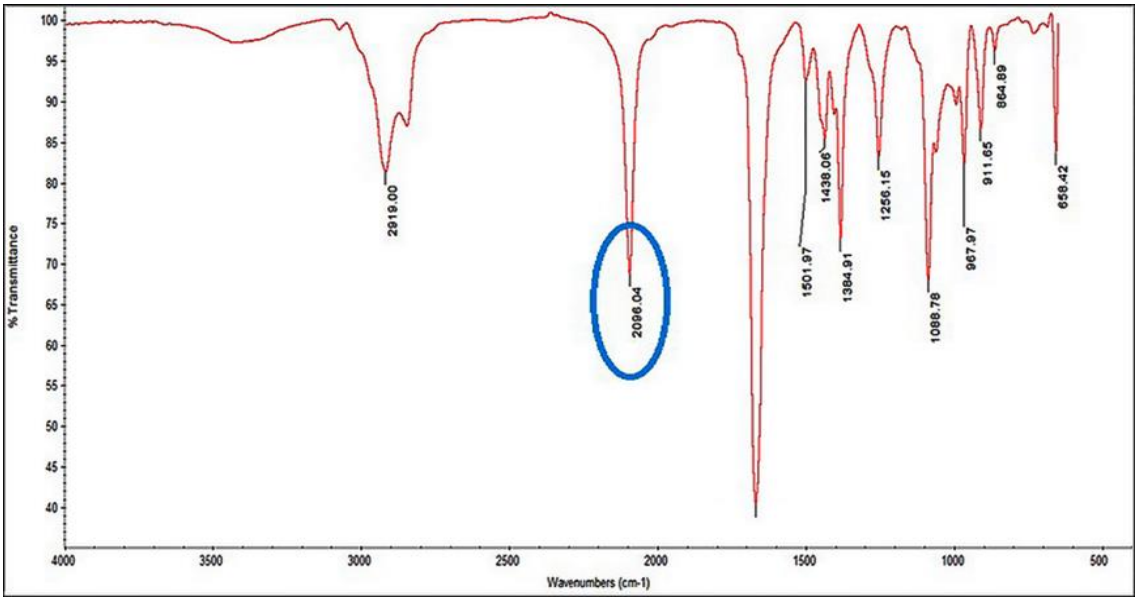
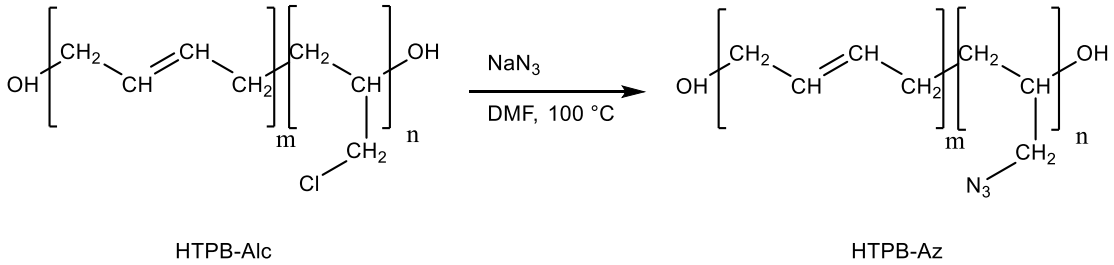


Fig. 5 – FT-IR spectrum of HTPB-Az.

Scheme 3 depicts the reaction of HTPB-Alc with NaN_3 in a DMF solvent at 100°C. This process follows a nucleophilic substitution mechanism, resulting in the formation of HTPB-Az.



Scheme 3 – Synthesis of HTPB-Alc random co-polymer.

EXPERIMENTAL

Materials, apparatus, and measurements

All chemicals were obtained from Merck (Darmstadt, Germany) and Fluka (Buchs, Switzerland) and were used as received, without any additional purification. 1,3-butadiene, hydrogen peroxide (H_2O_2, 30%), isopropanol, allyl chloride, chloroform ($CHCl_3$), tetrahydrofuran (THF), dimethylformamide (DMF), sodium azide, methanol and acetone were purchased from Merck Chemical (Darmstadt, Germany). A three-valve 1-L jacketed stainless steel Buchi reactor, equipped with ‘‘Buchi data system bdsSc 94’’, was used in polymer synthesis, which registered data for variable temperature pressure, and stirring rate during polymerization. The number-average molecular weight ($\bar{M}_n$) and weight-average molecular weight ($\bar{M}_w$) of the products were determined by gel permeation chromatography (GPC). The measurements were performed in THF solvent at 35 °C in a 1 mL/ min flow, using a Shimadzu LC-20A equipped with three PL gel columns (1–10^4, 1–10^3, and 1–500 Å pore size). The calibration curve was obtained with polystyrene standards having an M_w/M_n equal to 1.1 in the molecular weight range of 1060, 2450 and 7000 while RID A, refractive index signal were used as detector. The synthesized oligobutadienes were characterized by ^{1}H-NMR spectroscopy at room temperature. Spectra were recorded on a Bruker AC

500 instruments using deuterated chloroform as the solvent and tetramethylsilane as the reference.

The determination of hydroxyl value (OH_v) of oligobutadiene was carried out with common method (titration of excess anhydride with alcoholic KOH using phenolphthalein as indicator when polymers were acetylated by excess acetic anhydride-ASTM D4274). Differential scanning calorimetry (DSC) was carried out on a Perkin-Elmer DSC 8000over the range –100 to +l00°C at a scan rate of 10 ˚C/min for the lower temperature measurements (glass transition). FT-IR spectral measurements were performed using a Nicolet 6700 Fourier transform from Thermo Electron Corporation. Polymer samples were recorded on liquid films between two KBr disks.

Preparation of hydroxyl-terminated poly(butadiene-co-allyl chloride) via Co-polymerization of 1,3-butadiene and a**l**lyl chloride

All polymerization experiments related to this study were conducted in a stainless steel reactor. The Buchi stainless steel reactor was charged with isopropanol (120 mL), hydrogen peroxide (30%; 13 mL, 0.115 mol), and allyl chloride (77.5 g, 1 mol) under a nitrogen atmosphere. Next, 1,3-butadiene (108 g, 2 mol) was introduced into the reactor under a pressure of 5–6 bar. The polymerization temperature was maintained at 120 °C, and the stirring speed of the reaction mixture was set to 150 rpm. During the 6 h polymerization, the pressure gradually decreased until it stabilized and remained constant. The autoclave was then cooled, and the reaction product was drained from the reactor. The resulting yellow, clear solution was poured into distilled water, and the organic layer was repeatedly washed with water. The organic layer was then separated using a separating funnel. The mixture was stored for 24 h, and the solvent was decanted. Finally, the product was dried under vacuum at 40 °C for 24 h.

Synthesis of hydroxyl-terminated poly(butadiene-co-allyl azide) (HTPB-Az) from hydroxyl-terminated poly(butadiene-co-allyl chloride) (HTPB-Alc)

3 g of HTPB-Alc and 100 mL of dimethylformamide (DMF) were introduced into a 250 mL two-neck flask, equipped with a condenser, magnetic stirrer, and a calcium chloride guard tube. The reaction mixture was heated gradually until the polymer completely dissolved in the solvent. Then, 0.5 g of sodium azide (in excess relative to the molar ratio) was added slowly, and the temperature was raised to 110 °C. After 8–10 hours of reaction, the polymer solution was cooled to room temperature and filtered to remove salts and any unreacted sodium azide. The filtered polymer solution was then poured into distilled water, where the polymer precipitated and was separated. The obtained polymer was washed several times with distilled water until the washings were free of azide and chloride ions. In the next step, the polymer was dissolved in chloroform ($CHCl_3$) and dried over sodium sulfate (Na_2SO_4). The solvent was removed by vacuum distillation to yield the pure polymer. A total of 2.7 g of HTPB-Az was obtained from the reaction.

CONCLUSION

This study has successfully demonstrated the synthesis of hydroxyl-terminated poly(butadiene-co-allyl chloride) (HTPB-Alc) through radical copolymerization using hydrogen peroxide as an initiator and isopropanol as the solvent. Structural characterization techniques, including FT-IR and ^{1}H-NMR, have confirmed the successful integration of allyl chloride into the polybutadiene backbone. Additionally, results from gel permeation chromatography (GPC) and differential scanning calorimetry (DSC) have shown changes in the polymer's physical properties, such as a decrease in both number-average ($\bar{M}n$) and weight-average ($\bar{M}w$) molecular weights, and a slight shift in the glass transition temperature (*Tg*). Furthermore, by substituting the chloride group with an azide group through nucleophilic substitution, hydroxyl-terminated poly(butadiene-co-allyl azide) (HTPB-Az) was produced. This study highlights the potential of HTPB-Alc as a valuable precursor for subsequent reactions, like "click" chemistry, and its ability to interact with isocyanates to form various curing systems. Overall, this innovative approach improves the chemical and physical properties of the polymer, expanding its potential applications in both industrial and research contexts.

REFERENCES

1. D. Meng, L-P. Sang, Y. Chang, P-G. Zhang, J. Deng, X. Guo, *ACS Appl. Polym. Mater.*, **2024**, *6*, 8235–8243. https://doi.org/10.1021/acsapm.4c01140.
2. M. Irfan, Ch-K. Pu, Zh-Ga. Xiao, J-Ju. Xiao, *Chemistry Select*, **2024**, *9*, e202400656. https://doi.org/10.1002/slct.202400656.

3. H. Enfiajyan, Tran K. L. Hang, D. Kamyab, M. Yoozbashizadeh, F. Tian, J. Kalman, *Energy & Fuels*, **2024**, *38*, 20417–20425. https://doi.org/10.1021/acs.energyfuels.4c03691.
4. P. Santhana, G. Krishnan, K. Ayyaswamy, S. K. Nayak, *J. Macromol. Sci. Chem., A.*, **2013**, *50*, 128–138. https://doi.org/10.1080/10601325.2013.736275.
5. M. Irfan, J-Ju Xiao, *Chemistry Select*, **2024**, *9*, e202402278. https://doi.org/10.1002/slct.202402278.
6. G. Mir Mohamad Sadeghi, J. Morshedian, M, Barikani, *React. Funct. Polym.*, **2006**, *66*, 255–266. https://doi.org/10.1016/j.reactfunctpolym.2005.08.001.
7. W. D. Vilar, S. M. C. Menezes, L. Akcelrud, *Polym. Bull.*, **1994**, *33*: 557–561. https://doi.org/10.1007/BF00296164.
8. Ch. Devi Vara Prasad, P. Kanakaraju, R. Vinu, A. P Deshpande, *Chemistry Select*, **2024**, *9*, e202401883. https://doi.org/10.1002/slct.202401883.
9. L. Meng, F. Xu, M. Zhang, Ch. Yu, Y. Chang, Y. Wei, Y. Sun, H. Wang, Y. Zhu, *Prog. Org. Coat.*, **2023**, *175*, 107334. https://doi.org/10.1016/j.porgcoat.2022.107334.
10. M. Kazazi, M. Hayaty, A. Mousaviazar, *Polym. Bull.*, **2024**, *81*, 9031–9050. https://doi.org/10.1007/s00289-024-05143-x.
11. Q. Zhou, A. Wang, L. Dai, S. Jie, B-G Li, *Polymer*, **2016**, *107*, 306–315. https://doi.org/10.1016/j.polymer.2016.11.033.
12. Ch. Michał, M. Paweł, G. Tomasz, C. Katarzyna, P. Wojciech, T. Waldemar, *Materiały Wysokoenergetyczne (High Energy Materials)*, **2020**, *12*, 203–220. https://doi.org/10.22211/matwys/0168E.
13. N. A. Tahir, S. A. Zubir, *J. Appl. Polym. Sci.*, **2025**, *142*, e56510. https://doi.org/10.1002/app.56510.
14. A. L. Didenko, A. S. Nesterova, T. S. Anokhina, I. L. Borisov, V. V. Kudryavtsev, Membranes and Membrane Technologies, **2024**, *6*, 43–53. https://doi.org/10.1134/S2517751624010037.
15. Z. Xu, Y. Fan, P. Tao, L. Wang, C. Wang, X. Guo, Y. Quan, *ACS Appl. Polym. Mater.*, **2024**, *6*, 6183–619. https://doi.org/10.1021/acsapm.4c01009.
16. B. S. Min, S. J. Kim, H. M. Shim, H. B. Jeon, *Propellants Explos. Pyrotech.*, **2024**, *49*, e202400016. https://doi.org/10.1002/prep.202400016.
17. L. Xu, S. Jie, Z. Bu, B.-G. Li, *Eur. Polym. J.*, **2021**, *15*: 110484. https://doi.org/10.1016/j.eurpolymj.2021.110484.
18. P. Zhang, W. Tan, X. Zhang, J. Chen, J. Yuan, J. Deng, *Ind. Eng. Chem. Res.*, **2021**, *60*, 3819–3829. https://doi.org/10.1021/acs.iecr.0c06172.
19. A. Bhattacharjee, Sh. Saha, J. Patel, Sh. Bhagat, A. Kumar, R.B. Pawar, S.S. Sudhir, A. Chowdhury, *Eur. Polym. J.*, **2024**, *217*, 113330. https://doi.org/10.1016/j.eurpolymj. 2024.113330.
20. D. Meng, L. Sang, P. Zhang, J. Deng, X. Guo, *Def. Technol.*, **2024**, *40*, 199–209. https://doi.org/10.1016/j.dt.2024.04.014.
21. X. Chang, M. Wen, Q. Chu, K.-H. Luo, D. Chen, *Chem. Eng. J.*, **2024**, *497*, 154783. https://doi.org/10.1016/j.cej.2024.154783.
22. M. N. Ganivada, M. Dhara, S. Jana, T. Jana, *J. Macromol. Sci., Part A: Pure Appl. Chem.*, **2022**, *59*, 167–179. https://doi.org/10.1080/10601325.2021.2013730.
23. M. F. Lemos, L. C. Mendes, M. A. Bohn, *J. Appl. Polym. Sci.*, **2021**, *138*, 49981. https://doi.org/10.1002/app. 49981.
24. T. Zhang, J. Shuai, W. Zhang, H. Liu, Z. Gao, Q. Zhu, X. Liu, L. Zhang, H. Li, *Polym. Bull.*, **2023**, *80*, 4611–4624. https://doi.org/10.1007/s00289-022-04620-5.
25. Z. Cao, Q. Zhou, S. Jie, B.-G. Li, *Ind. Eng. Chem. Res.*, **2016**, *55*, 1582–1589. https://doi.org/10.1021/acs.iecr.5b04921.
26. Y. Bayat, H. Kashef Shandi, T. Khanlari, *Polym. Bull.*, **2021**, *78*, 6577–6593. https://doi.org/10.1007/s00289-020-03440-9.
27. S. Touidjine, M. Karim Boulkadid, D. Trache, H. Akbi, D. Guettiche, S. Belkhiri, M. Nourine, *J. Polym. Sci.*, **2023**, *61*, 2254–2275. https://doi.org/10.1002/pol.20230241.
28. L. Shi, X. Fu, Y. Li, S. Wu, S. Meng, J. Wang, *Nanomaterials*, **2023**, *13*, 268. https://doi.org/10.3390/nano13020268.
29. S. Filippi, L. Mori, M. Cappello, G. Polacco, *Propellants Explos. Pyrotech.*, **2017**, *42*, 826–835. https://doi.org/10.1002/prep.201600263.
30. M. Gozin, L. L. Fershtat, *Nitrogen-Rich Energetic Materials*, **2023**, Chapter 6.
31. B. Kumar Sikder, T. Jana, *ACS Omega*, **2018**, *3*, 3004–3013. https://doi.org/10.1021/acsomega.8b00022.
32. Y. Zhang, Y. Tian, Y. Zhang, X. Fu, H. Li, Z. Lu, T. Zhang, Y. Hu, *Polymers*, **2022**, *14*, 5213. https://doi.org/10.3390/polym14235213.
33. Q. Zhang, Y. Shu, N. Liu, X. Lu, Y. Shu, X. Wang, H. Mo, M. Xu, *Cent. Eur. J. Energ. Mater.*, **2019**, *16*, 153–193. https://doi.org/10.22211/cejem/109806.
34. T. Khanlari, Y. Bayat, M. Bayat, *Polym. Bull.*, **2022**, *79*, 709–724. https://doi.org/10.1007/s00289-020-03518-4.
35. T. Khanlari, Y. Bayat, M. Bayat, *Polym. Bull.*, **2020**, *77*, 5859–5878. https://doi.org/10.1007/s00289-019-03051-z.
36. M. Alizadeh, Y. Bayat, *Cent. Eur. J. Energ. Mater.*, **2024**, *21*, 5–21. https://doi.org/10.22211/cejem/184038.
37. Y. Bayat, S. S. Hajimirsadeghi, S. M. Pourmortazavi, *Org. Process Res. Dev.*, **2011**, *15*, 810–816. https://doi.org/10.1021/op200056j.
38. V. Azizkhani, F. Montazeri, E. Molashahi, A. Ramazani, *J. Energ. Mater.*, **2017**, *35*, 314–320. https://doi.org/10.1080/07370652.2016.1190795.
39. Y. Bayat, V. Azizkhani, *J. Energ. Mater.*, **2012**, *30*, 209–19. https://doi.org/10.1080/07370652.2011.562600.
40. Y. Bayat, V. Azizkhani, *Cent. Eur. J. Energ. Mater.*, **2022**, *19*, 231–247. https://doi.org/10.22211/cejem/154723.
41. Y. Bayat, F. Esmailmarandi, V. Azizkhani, *Polym. Bull.*, **2025,** *82*, 1197–1221. https://doi.org/10.1007/s00289-024-05556-8.
42. Y. Bayat, G. Taheripouya, V. Zeynali, V, Azizkhani, *J. Energ. Mater.*, **2025**, *43*, 62–96. https://doi.org/10.1080/07370652.2023.2183435.
43. S. Kumar Bharti, R. Roy, *Trends in Analytical Chemistry*, **2012**, *35*, 5–26. https://doi.org/10.1016/j.trac.2012.02.007.
44. G. Mir Mohammad Sadeghi, J. Morshedian, M Barikani, *Polym. Test.*, **2003**, *22*, 165–168. https://doi.org/10.1016/S0142-9418(02)00065-X.