Synthesis of HTPB using a semi-batch method
Otrzymywanie HTPB metodą półperiodyczną

Michał Chmielarek*, Wincenty Skupiński, Zdzisław Wieczorek

Abstract: Hydroxyl-terminated polybutadiene is widely used in industry for both civil and military applications. In munitions, HTPB is mostly used as a binder for heterogenic rocket propellants and as a component of plastic bonded explosives, as well as a phlegmatizer in explosives sensitive to friction and impact. The wide range of HTPB applications results from the good mechanical properties of HTPB-based polyurethanes, in particular at temperatures down to –40 °C.

A synthesis method for HTPB, different from the commonly used semi-batch and continuous methods, is presented. The effect of parameters including reaction temperature, 1,3-butadiene pressure and hydrogen peroxide concentration on the properties of the obtained polymer is determined. The synthesis conditions enabling new HTPB species to be obtained, which meet the requirements for binders used in solid rocket propellants, are specified.

Streszczenie: Polibutadien zakończony grupami hydroksylowymi (HTPB) ma szerokie zastosowanie w przemyśle światowym. Wykorzystywany jest zarówno w przemyśle cywilnym jak i wojskowym. HTPB w przemyśle zbrojeniowym wykorzystywany jest głównie jako lepiszcze heterogenicznych paliw rakietowych ale wykorzystuje się go również jako składnik plastycznych materiałów wybuchowych i flegmatyzator do wrażliwych na tarcie i uderzenie materiałów wybuchowych. Szczególnie w niskich temperaturach dochodzących do –40 °C.

Przedstawiamy inną metodę syntez HTPB niż powszechnie stosowane w przemyśle metody periodyczna i ciągła. Określa wpływ parametrów takich jak temperatura reakcji, ciśnienie 1,3-butadienu oraz stężenie nadtlenku wodoru na właściwości otrzymywanego polimeru. Wyznaczono parametry syntezy prowadzące do otrzymania nowego gatunku HTPB spełniającego wymagania stawiane lepiszczom stosowanym w stałych paliwach rakietowych.

Keywords: synthesis of hydroxyl-terminated polybutadiene, HTPB, polymerization of 1,3-butadiene, semi-batch method

Słowa kluczowe: synteza α,ω-dihydroksypolibutadienu, HTPB, polimeryzacja 1,3-butadienu, metoda półperiodyczna
1. Introduction

Due to its properties, hydroxyl-terminated polybutadiene (HTPB) is widely used in munitions and civil industry. In the latter, it is used in the production of adhesives and coatings, golf balls, tennis balls etc. [1]. In munitions, HTPB is used as a component of composite rocket propellants [2], a component of plastic bonded explosives and as a phlegmatizing agent. When used as a component of plastic bonded explosives, it allows the formation of malleable compounds which show good adhesion to different substrates. These properties are particularly useful at low temperatures. The main advantage of HTPB is a low glass transition temperature (approx. −75 °C) providing excellent strength properties of HTPB-based polyurethanes at low temperatures. HTPB is mostly used for obtaining polyurethanes (PU) as a product of reaction with diisocyanates. The reaction and the properties of the product depend on the physical and chemical properties of HTPB which, in turn, depend on the synthesis method and conditions used [3]. Outside of its basic applications, HTPB can also be chemically modified. The double C=C bond of the polybutadiene chain is chemically active and is subject to typical reactions, including hydrogenation or epoxidation. A hydrogenated HTPB derivative is used as a component of chemical-resistant and thermal-resistant polyurethanes. The epoxidation product can be further modified. The reaction of epoxidized (EHTPB) with N₂O₅ yields HTPB with nitroester groups (NHTPB) [4]. The nitro NHTPB derivative is used as a high-energy alternative to HTPB in composite rocket propellants [5].

Hydroxyl groups are other commonly modified components of the HTPB structure. They show typical reactivity, used mainly in reactions with diisocyanates, to obtain polyurethanes and polyesters in reaction with acids, acid chlorides or anhydrides. The polymers thus obtained can be used as [6, 7]:
- modifiers of thermoplastic polymers, including polyamides, PET, PBT and others,
- epoxy resin modifiers,
- adhesive additives,
- coatings in laminated circuit boards,
- components of sealants and cements (due to chemical resistance).

In military applications, it is used as a component of solid composite rocket propellants (used in space rockets) or as a component of solid propellant for gas generators.

Several HTPB grades obtained by radical polymerization reaction using hydrogen peroxide (H₂O₂) as an initiator for semi-batch or continuous reaction, are currently available on the market. In the initiation reactions, the hydroxyl radicals formed as a result of thermal dissociation of hydrogen peroxide, react with 1,3-butadiene form hydroxybutadienyl radicals, during which, at the propagation stage, the chain is extended by the addition of 1,3-butadiene particles. The macro-radicals formed at the termination stage, combine with hydroxyl radicals (shorter chains) or hydroxybutadiene (longer chains) to form HTPB particles [7]. The commercially available products are mostly used as a feedstock for polyurethane based systems. Further studies are currently being carried out to modify HTPB and extend its applicability. Table 1 shows the physical and chemical properties of commercially available HTPBs.

### Table 1. Comparison of properties of commercially available HTPB species [6, 8, 9]

| Parameter                                      | Unit   | R-45HTLO | R-45M  | R-20LM |
|------------------------------------------------|--------|----------|--------|--------|
| Viscosity at 23 °C                             | mPa·s  | 8000     | 7000   | –      |
| Hydroxyl value                                 | meq/g  | 0.84     | 0.72   | 1.8    |
| Number-average molecular weight, Mₐ            | g/mol  | 2800     | 2800   | 1200   |
| Polydispersity, D                              | –      | 2.5      | 2.2    | 2.0    |
| Glass transition temperature, T_g (DSC)        | °C     | −75      | −76    | −70    |

Commercially available polymers differ in the number of –OH groups present and viscosity. R-45HTLO and R-45M species have the same average molar mass (2,800 g/mol), while the molarity of R-20LM is lower, at 1,200. All species have the same number of –OH groups in the particle, and the different quantity in mass is the result of differences in chain length. R-45HTLO has more –OH groups per gram than R-45M; the difference resulting
from the higher number of –OH groups in the chain or the higher number of low molecular weight polyols. HTPB, in its ideal form, consists of a polybutadiene chain with hydroxyl groups in positions α and ω. The polybutadiene chain includes 1,4-cis; 1,4-trans and 1,2-vinyl monomer units. 1,4-cis monomer units provide flexibility, tensile strength and a low glass transition temperature $T_g = -45$ °C of HTPB. 1,4-trans monomer units provide resistance to mechanical stimuli, and 1,2-vinyl monomer units provide relatively high adhesive properties. The 1,2-vinyl isomer content affects the viscosity [8].

A semi-batch HTPB synthesis method using hydrogen peroxide as a reaction initiator, different from the commonly used semi-batch and continuous methods, is presented in the study. The continuous and semi-batch HTPB synthesis methods were presented in [10]. The methods for obtaining HTPB by polymerization of butadiene using different pathways are known: initiation with organodilithium compounds, initiation with hydroxyl radicals obtained by thermal dissociation of hydrogen peroxide, initiation with radicals-containing groups hydrolysed to hydroxyl groups [8, 11]. Depending on the hydroxyl-terminated polybutadiene synthesis method, i.e. initiator type, initiator/monomer ratio, solvent, polymerization temperature, reaction time, pressure and temperature, polymers with different molecular weight, polydispersity, different number of hydroxyl groups and 1,4-cis, 1,4-trans and 1,2-vinyl blocks can be prepared [2, 3].

2. Raw materials

All raw materials used in the process are readily available on the Polish market. The following raw materials were used in the experiment:
- 1,3-butadiene, technically pure (supplier: PKN Orlen),
- 2-propanol pure (supplier: Chempur), and
- $\text{H}_2\text{O}_2$ 60% pure (supplier: Chempur).

The largest manufacturer of 1,3-butadiene is PKN Orlen S.A. in Płock, and the hydrogen peroxide is manufactured by Nitrogen Production Plant in Puławy. The solvent is also manufactured locally. In the event of any limitations in raw material imports, there is no risk that production will be interrupted. A unique situation may involve a crisis on the market of raw fossil materials used to obtain 1,3-butadien. A butadiene production process is planned in the Synthos plant, using butadiene biosynthesised from sugar by genetically-modified bacteria. Another biobutadiene synthesis method involves ethanol. This production process will be a step towards ending dependence on raw fossil materials.

3. Apparatus

The plant includes two feedstock feeding lines, a polymerization reactor and a reaction mixture collection line. A butadiene batching line connects a liquid gas tank with an autoclave. The gas is supplied from the tank with a pressure booster. A batching line for $\text{H}_2\text{O}_2$ alcohol solution includes a solution tank and a $\text{H}_2\text{O}_2$ pump. A polymerization reactor is a 1000 cm³ autoclave from Autoclave Engineers made of acid-resistant steel with a cover with adjustable butadiene and $\text{H}_2\text{O}_2$ solution inlet valves and an adjustable valve for removing the post-reaction mixture. The reaction mixture is cooled by a steel water cooler connected to the drain valve. The reactor is heated electrically with a heating band attached to the reactor vessel. The process rate and temperature are monitored and adjusted. All lines, both providing raw materials and removing the reaction mixture are made of acid-resistant steel tubing. The plant meets EX requirements and is resistant to 1,3-butadiene and concentrated $\text{H}_2\text{O}_2$.

4. Description of semi-batch HTPB synthesis method

As part of the research on HTPB synthesis discussed in the foreword (semi-batch and continuous), attempts were made to modify the methods to achieve better yield, while maintaining the physical and chemical parameters of the polymer. A new synthesis method was developed using $\text{H}_2\text{O}_2$ as an initiator of the 1,3-butadiene polymerization reaction.
In current 1,3-butadiene polymerization methods, the properties of hydroxyl-terminated polybutadiene are determined by the reactant concentration, reaction time, temperature and pressure. Obtaining high molecular weight α,ω-dihydroxyl butadiene polymers using those solutions requires a relatively long process, resulting in large energy expenditures.

Synthesis reactions using the semi-batch method are carried out cyclically at a constant concentration of 1,3-butadiene in the system. On completion, any unreacted 1,3-butadiene is left in the reactor after each cycle. The method produces hydroxyl-terminated polybutadiene highly efficiently in any required molecular weight, in a significantly shorter time compared to those presented in the literature (semi-batch and continuous method). The synthesis were carried out in accordance with the reaction given in patent application [12]. A certain amount of H$_2$O$_2$ solution in the solvent was transferred to the reactor. The reactor was heated to a specified temperature (over 100 °C), and 1,3-butadiene was supplied by a pressure booster. The reaction time was measured after the required pressure was reached in the reactor. During the process, constant 1,3-butadiene pressure was maintained (constant pressure in the reactor). After the reaction, using a bottom drain vale, the product, solvent, unreacted H$_2$O$_2$, water and solvent-absorbed butadiene mixture were collected. The mixture was cooled in a steel water cooler and transferred to the reaction mixture vessel. The reaction mixture was collected from the reactor, leaving the unreacted 1,3-butadiene. Excess H$_2$O$_2$ solution in organic solvent was added to the reactor and heated to over 100 °C; after reaching the temperature, 1,3-butadiene was added. The process was repeated cyclically, as required. The unreacted 1,3-butadiene left in the reactor can be used in the next cycle, without capturing, condensing or storing to save time and energy. Specific properties of the polymer can be obtained by modifying the reaction time, H$_2$O$_2$ and butadiene amount (concentration). The reaction mixture included two fractions: low molecular mass and high molecular mass fraction. After gravitational separation, the solvent, water and H$_2$O$_2$ were distilled under vacuum from the high molecular mass fraction. The product was vacuum dried at 100 ºC. The polymer properties were analysed.

Each HTPB synthesis carried out under specific conditions was repeated several times. Average properties of the polymer obtained from a minimum of three repeatable syntheses were presented. The yield of reaction was determined as an average amount of HTPB obtained from a single reaction (for a minimum of three repeatable reactions).

5. Product analysis

FTIR – the polymer chain structure was analysed using Fourier-transform infrared spectroscopy. The spectra over a range of wavelengths (400-4000 cm$^{-1}$) were compared with the spectra for commercially available products.

H$^1$ NMR – the components and the structure of polybutadiene chain and –OH groups were determined using proton magnetic resonance spectroscopy.

Gel chromatography – gel chromatography (GPC) technique was used to determine the average molecular mass and molecular-mass distribution.

Hydroxyl value was determined by titration. The method involves acetylation of HTPB hydroxyl groups using acetic anhydride and pyridine. HTPB was dissolved in pyridine-acetic anhydride solution and heated for 2 h. The unreacted anhydride was hydrolysed and the acetic acid was titrated with KOH/EtOH solution using phenol red as an indicator.

6. Results

6.1. Effect of 1,3-butadiene pressure

The effects of butadiene pressure on the properties of the obtained polymer and yield of reaction (quantity of high molecular mass HTPB) were analysed. The reaction used butadiene in the amount corresponding to 15-25 bar pressure. H$_2$O$_2$ solution in 2-propanol was used (2.3 mol H$_2$O$_2$ in 1000 cm$^3$ solution). The reaction time was 30 min. The mixture was stirred at 400 rpm at a temperature 120 °C.
(a) Efficiency [g/cycle] vs. Pressure [bar]

(b) $M_n$ vs. Pressure [bar]
The efficiency of the process increases with an increase in 1,3-butadiene content in the reaction system. The hydroxyl radicals formed at the initial reaction stage initiate many hydroxyl-butadiene radicals. The continuous addition of 1,3-butadiene leads to a further increase in chain length. Increasing the 1,3-butadiene pressure from 15 to 19 bar doubled the yield of HTPB. Further increases in pressure did not affect the process yield. An increase in \(M_n\) polymer molecular mass was also observed. As with the efficiency, further increases in 1,3-butadiene pressure did not affect \(M_n\). The continuous addition of 1,3-butadiene to the system probably increased the probability of reaction of the hydroxyl-butadienyl radical with another 1,3-butadiene particle, rather than the hydroxyl radical or hydroxyl-butadienyl radical. Increasing the 1,3-butadiene pressure in the system resulted in a slight increase in the hydroxyl number of the obtained polymers.

6.2. Effect of reaction time

The effects of reaction time on the properties of the obtained polymers and the yield (quantity of high molecular mass HTPB), were analysed. The reaction time was from 15 to 120 min. The synthesis was carried out with 1,3-butadiene at 19 bar. \(\text{H}_2\text{O}_2\) solution in 2-propanol was used (2.3 mol \(\text{H}_2\text{O}_2\) in 1000 cm\(^3\) solution). The mixture was stirred at 400 rpm at a temperature of 120 °C. Longer reaction times allow the polybutadiene chain to expand further and increase the amount of polymer obtained. Reaction time affects the molecular mass \(M_n\). Increasing the reaction time increases the molecular mass. Less significant differences can be observed between 15-45 min. Extending the reaction time from 45 to 60 min increases the molecular mass \(M_n\) by approximately 25%. At the initial reaction stage, short chains are formed with an increase in molecular mass being observed after 45 min. Further increases in reaction times allow systematic increases in the length of chain formed at the initial stage. Increasing the reaction time and the molecular mass \(M_n\) leads to a decrease in the hydroxyl number. Chain elongation results in a reduced number of –OH groups per 1 g of polymer.
6.3. Effect of H$_2$O$_2$ concentration

The effects of H$_2$O$_2$ concentration on the properties of the obtained polymer and yield (amount of high-molecular weight HTPB), were analysed. The solution (1000 cm$^3$) of H$_2$O$_2$ in 2-propanol contained 0.4 to 3.5 mol H$_2$O$_2$. The reaction time was 30 min; the syntheses were carried out with 1,3-butadiene at 19 bar. The mixture was stirred at 400 rpm at a temperature 120 °C. Increasing the H$_2$O$_2$ concentration in the reaction system decreases the molecular mass. The large number of hydroxyl radicals formed initiate a large number of polybutadiene chains. During the reaction, 1,3-butadiene is used to extend the chains. Increasing the H$_2$O$_2$ concentration in the reaction mixture increases the hydroxyl number. 1 g of product contains more polymer chains characterized by a low molecular mass $M_n$. Increasing the H$_2$O$_2$ concentration in the reaction system increases the yield of reaction. In a 30-minute reaction, a large number of hydroxyl radicals at the initial stage forms a large number of hydroxyl-polybutadienyl radicals and as a result, increases the yield.
Figure 3. The effect of $\text{H}_2\text{O}_2$ concentration on HTPB properties

6.4. Product properties

Using the semi-batch method, polymers with properties similar to commercially available products can be manufactured in less time with less energy expenditure. Table 2 compares the properties of commercially available products (R-45HTLO and R-45M) with the properties of polymers obtained using the semi-batch method (6P60).
### Table 2. Comparison of commercially available HTPB-based products manufactured using a semi-batch method (the commercially available products were analysed along with 6P60 polymer)

| Property                                      | Unit       | R-45HTLO | R-45M  | 6P60  |
|-----------------------------------------------|------------|----------|--------|-------|
| Hydroxyl value                                | meq/g      | 0.84     | 0.72   | 0.81  |
| Number-average molecular weight, $M_n$        | g/mol      | 4046     | 4700   | 4791  |
| Weight-average molecular weight, $M_w$        | g/mol      | 8189     | 11750  | 8051  |
| Polydispersity, $D$                           | –          | 2.01     | 2.5    | 1.68  |
| Glass transition temperature, $T_g$ (DSC)     | °C         | –75      | –76    | –76   |

### 7. Conclusions

Each HTPB synthesis method has its pros and cons. The biggest advantage of the semi-batch method is that it is a relatively straightforward process. Correctly charged feedstock and gradual reaction initiation, guarantee a failure-free synthesis. Using 1,3-butadiene to expand the polybutadiene chain results in a gradual pressure drop inside the reactor. The main disadvantage is that the reactor must be drained every time, and the unreacted reactants must be disposed of. The solvent can be easily recovered in a series of distillation processes, however, 1,3-butadiene recovery requires higher energy expenditure and a more complex system.

All methods (batch, continuous and semi-batch) can be used to obtain HTPB which meets market requirements. The semi-batch method allows the products to be obtained faster, with less energy. The method saves the time required to drain the reactor and dispose of the unreacted 1,3-butadiene. Leaving the unreacted 1,3-butadiene in the reactor vessel saves the energy required to recover and store 1,3-butadiene and re-heat the reactor to the required temperature.

### Acknowledgements

The Industrial Chemistry Research Institute hereby informs that the research was carried out with the financial support of project no. 180743 *Badania nad przeniesieniem skali otrzymywania α,ω-dihydroksypolibutadienu (HTPB) z reaktora 1 dm$^3$ do reaktora 10 dm$^3$ oraz badania aplikacyjne otrzymanego HTPB* (Ed. Transl.: Analysis of HTPB Synthesis Scaling from 1 dm$^3$ Reactor to 10 dm$^3$ Reactor and Applicability Analysis of Obtained HTPB.) as part of the Applied Testing Programme.

### References

1. Guery J.-F., Chang I.-S., Shimada T., Glick M., Boursy D., Robert E., Napier J., Wardle R., Pérut Ch., Calabro M., Glick R., Habu H., Sekino N., Vigier G., d’Andrea B. Solid Propulsion for Space Applications: An Updated Roadmap. *Acta Astronaut.* 2010, 66(1): 201-219.
2. Buchalik K., Florczak B., Lipiński M. Solid Rocket Propellants – Current State and Future Perspective. (in Polish) *Przyb. Techn. Uzbrojenia* 2001, 78(3): 129-140.
3. Shankar R.M., Roy T.K., Jana T. Terminal Functionalized Hydroxyl-terminated Polybutadiene: an Energetic Binder for Propellant. *J. Appl. Polym. Sci.* 2009, 114: 732-741.
4. Agrawal J.P. *High Energy Materials*. Wiley-VCH, 2010; ISBN 978-3-527-32610-5.
5. Florczak B., Bogusz R., Skupiński W., Chmielarek M., Dzik A. Study of the Effect of Nitrated Hydroxyl-terminated Polybutadiene (NHTPB) on the Properties of Heterogeneous Rocket Propellants. *Cent. Eur. J. Energ. Mater.* 2015, 12(4): 841-854.
6. Sartomer. *Hydroxyl Terminated Polybutadiene Resin and Derivatives*. Sartomer Product Bulletin, www.sartomer.com [retrieved 2012].
7. *Polymer Chemistry*. (in Polish). Florjańczyk Z., Penczek S. Eds., Warsaw: Oficyna Wyd. Politechniki Warszawskiej, 2001; ISBN 83-7207-265-5.
[8] Goncalez V., Barcia F.L., Soares B.G. Composite Materials Based on Modified Epoxy Resin and Carbon Fiber. *J. Braz. Chem. Soc.* **2006**, *17*(6): 11-17.

[9] *TDS Poly bd R-45HTLO. Technical Data Sheet.* Cray Valley, Oaklands Corporate Center, USA, www.crayvalley.com [retrieved 2015].

[10] Chmielarek M., Skupiński W., Wieczorek Z., Dziura R. α,ω-Dihydroxypolibutadiene (HTPB): Properties and Production. (in Polish) *Przem. Chem.* **2012**, *91*(9): 1803-1807.

[11] Gramov E.I. *Synthetic Rubber.* (in Russian) Leningrad: Izd. Khimiya, **1983**.

[12] Patent application P-404551 (in Polish).

Polish version:
The study was originally published in Polish, in the *Materiały Wysokoenergetyczne (High Energy Materials)* journal **2015**, 7: 110-116.

English version:
– Revised: November 21, 2020
– Published first time online: December 14, 2020