

Analiza termiczna polimerycznych cieczy jonowych (z wykorzystaniem technik TGA i DSC)

Thermal analysis of polymeric ionic liquids (using TGA and DSC techniques)

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Abstrakt

W artykule przedstawiono analizę stabilności struktury polimerycznych cieczy jonowych. Za pomocą technik DSC (Differential Scanning Calorimetry) oraz TGA (Thermogravimetric analysis) zbadano nowe polimeryczne ciecze jonowe zawierające grupy poliheksametylenobiguanidyny (PHMB), jako kationy oraz grupy arylokarboksylanowe, jako aniony pochodzące od kwasu benzoowego i salicylowego. Technika DSC polega na pomiarze ciepła pochłanianego bądź wydzielanego przez próbkę podczas zaprogramowanego wzrostu lub zmniejszenia temperatury. Natomiast za pomocą pomiaru termogravimetrycznego (TGA) otrzymuje się tzw. krzywą termogravimetryczną, która opisuje zależność masy próbki od temperatury. Rezultaty uzyskane podczas badań pozwoliły na wyznaczenie entalpii oraz temperatur zeszklenia dla obu próbek.

Abstract

The article presents an analysis of the structure stability of polymeric ionic liquids. Using DSC (Differential Scanning Calorimetry) and TGA (Thermogravimetric analysis) techniques, new polymeric ionic liquids containing polyhexamethylene biguanide (PHMB) groups as cations and aryl carboxylate groups as anions derived from benzoic and salicylic acids were studied. The DSC technique measures the heat absorbed or released by the sample during a programmed increase or decrease in temperature. On the other hand, using thermogravimetric measurement (TGA), the so-called thermogravimetric curve, which describes the dependence of the sample mass on temperature. The results obtained during the tests allowed to determine the enthalpy and glass transition temperatures for both samples.

Słowa kluczowe: ciecze jonowe, poliheksametylenobiguanidyna (PHMB), DSC, TGA

Keywords: ionic liquids (ILs), polyhexamethylene biguanide (PHMB), DSC, TGA

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1. Introduction

Ionic liquids (ILs) are usually defined as compounds entirely composed of ions with a melting point below 100°C. The first ionic liquid, ethylammonium nitrate, was described in 1914 by Paul Walden. The intensive development of this group of compounds took place only after 100 years. After the NATO scientific conference in Heraklion in 2000, there was a flourishing of scientific activity focusing on research on ionic liquids. Due to their unique properties, including non-flammability, high thermal stability and low vapor pressure, they are becoming an increasingly attractive group of chemical compounds. Scientists have already discovered a number of practical applications for ionic liquids in the fields of biotechnology, catalysis, pharmacy and sustainable energy [1], as solvents (an alternative to volatile organic solvents that have a harmful impact on the environment), electrolytes, energy storage materials and lubricants. Among other organic compounds, the melting point is lower than 100°C, and often lower than room temperature. In addition, they are non-volatile, stable in a wide range of temperatures and voltages, they have the ability to dissolve many organic and inorganic substances, they are characterized by different kinetics and thermodynamics of the processes [2].

The above properties make ionic liquids a constant subject of intensive research, and the number of publications concerning both their structures and applications is constantly growing. The largest group of ionic liquids are ammonium, imidazolium, pyridinium and phosphonium salts [3].

A separate group of ionic liquids are polymeric ionic liquids (PILs). Polymeric ionic liquids are created by a polymer having repeating structural units in the polymer chain capable of forming many ion pairs. Compounds built in this way have both the properties of ionic liquids and exhibit characteristics characteristic of

the parent polymer, e.g. increased mechanical strength, durability, processability, etc.

Research on polymeric ionic liquids began in the 1970s, when work on the polymerization of vinyl cationic monomers began [4]. Salts with vinylpyridinium and vinylimidazolium cations turned out to be of particular interest. They have a positive charge located in the aromatic ring connected to the vinyl group [5].

In the structure of the described ionic liquids, a guanidino group often appears. The authors describe e.g. synthesis and properties of tetraalkyldimethylguanidinium salts. The authors presented the synthesized compounds as a new generation of ionic liquids, showing physicochemical properties comparable to, and in some cases complementary to, widely used ionic liquids [6, 7, 8, 9]. Compared to e.g. imidazolium liquids, liquids with guanidine have much better thermal stability [8].

Taking into account the possibility of synthesizing ionic liquids based on guanidine and the possibility of synthesizing polymeric ionic liquids [10, 11, 12, 13, 14] as part of own research at Łukasiewicz - ŁIT, polymeric ionic liquids built of from polyhexamethylene biguanidine (PHMB) cation and anions derived from benzoic and salicylic acid with the structures shown in Fig. 1. and Fig. 2.

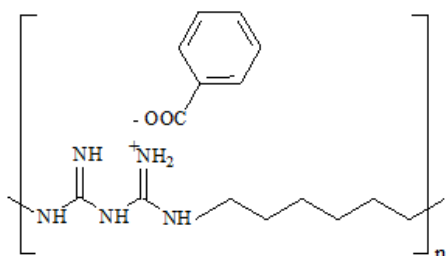


Fig. 1. Benzoate PHMB.

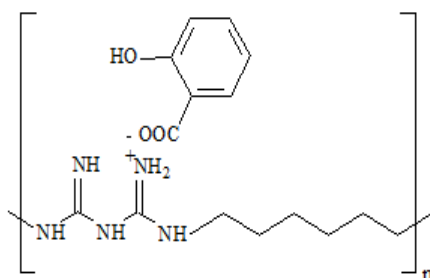


Fig. 2. Salicylate PHMB.

Their method of obtaining and use as a bioactive substance for modifying textile products in order to give them antibacterial and antifungal properties was reserved in the Patent Office, the application was marked with the number: P.440793. Research is still underway to expand the spectrum of applications of new ionic liquids. Research was conducted on the use of PHMB salicylate as an additive to polyvinyl alcohol film [15]. PHMB benzoate was tested for use in the production of bioactive polyethylene films. These compounds are thermally stable and do not dissolve in water, which allows them to be used in polymer processing.

2. Experimental part

2.1. Research materials

The following reagents were used for synthetic work:

- 20% aqueous solution of PHMB in the form of hydrochloride - Lonza
- Ethyl alcohol 96% - Alchem
- sodium salicylate pt. d.a. – Pol Aura
- Sodium benzoate pure pure - Pol Aura

Synthesis of poly(hexamethylene biguanide) salicylate ionic liquid:

The flask was charged with 1092.5 parts by weight of a 20% (1 mol) aqueous solution of polyhexamethylene biguanidine hydrochloride and 316 parts by weight of ethyl alcohol. The whole was stirred for 0.5 h, then a solution of 160 g of sodium salicylate (1 mol) in 200 ml of water was added dropwise over 2 h. The content was stirred for another 1 h at 20-30°C with pH = 6.5 - 7. The resulting two-layer mixture was poured into a separatory funnel and left for 12 h for more effective separation of liquid layers. The product of the reaction is the lower layer, which was washed twice with two portions of 150 ml of water. The product obtained in this way was dried in a vacuum dryer at 40°C for 10 h. 256 g of a polymeric ionic liquid was obtained in the form of an oily, crystal-clear, slightly straw-colored, high viscosity and melting point of 99°C. The yield of the reaction was 80%. The structure of the polymeric ionic liquid was confirmed spectroscopically (¹H NMR oraz FTIR).

¹H NMR (700MHz; MeOD): δ = 1,307 (br s, PHMB); 1,505 (br s, PHMB); 3,181 (br s, PHMB); 6,796-6,835 (arom. 1H); 6,846-6,847 (arom. 1H); 7,297-7,322 (arom. 1H); 7,853-7867 (arom. 1H).

Synthesis of poly(hexamethylene biguanide) benzoate ionic liquid:

The flask was charged with 915 parts by weight of a 20% (1 mol) aqueous solution of poly(hexamethylene biguanide) hydrochloride and a solution of 144 g of sodium benzoate (1 mol). 280 ml of water were added dropwise, then the whole was stirred at 20-30°C for 1 h at pH = 6.5-7. The resulting two-layer mixture was placed in a separatory funnel and left for 12 h. The reaction product was the lower layer, which was washed with water. The product obtained in this way was dried in a vacuum dryer at 40°C for 10 h. 245 g of a polymeric ionic liquid was obtained in the form of an oily, crystal-clear, slightly straw-colored and highly viscous. The

yield of the reaction was 80%. The structure of the polymeric ionic liquid was confirmed spectroscopically (^1H NMR oraz FTIR).

^1H NMR (700MHz; MeOD): δ = 1,430 (br s, PHMB); 1,627 (br s, PHMB); 3,329 (br s, PHMB, OH); 7,465-7,491 (arom. 2H); 7,589-7,612 (arom. 1H); 8,025-8,039 (arom. 2H).

2.2. Research methodology

Thermogravimetric analysis (TGA)

Thermogravimetric analysis is a technique that allows you to measure the change in sample weight as a result of a given temperature range. The measurement consists in placing the sample in a platinum or aluminum oxide pan. Then the whole thing is placed in a stove connected to a thermobalance. The sample is heated to the set temperature at a certain rate. Verification of the temperature is possible thanks to the thermocouple, which is located directly next to the pan with the sample. The TGA measurement was carried out in an inert atmosphere (N_2). A very important aspect of the whole test is the properties of the sample being analyzed, because it cannot be flammable, explosive or rapidly changing volume when heated.

Thermogravimetric analysis (TGA) and thermogravimetric first derivative (DTG) were performed using a thermal analyzer (TGA Q500 V20.13 Build 39). First, the samples were heated in the temperature range of 0–600°C in an N_2 atmosphere at a heating rate of 20°C/min [16].

Differential Scanning Calorimetry (DSC) analysis

Differential scanning calorimetry analysis is a technique that measures the heat absorbed or released by a sample (enthalpy ΔH measurement) as a result of a programmed increase or decrease in temperature. Such heat exchange is associated

with endothermic or exothermic transformations taking place in the sample. The measurement consists in placing the sample in an aluminum pan.

The pan are closed with a special press and put into the oven, where they are analyzed in accordance with the set temperature program. The temperature difference between the samples is measured. If the temperature of the tested material is higher than the temperature of the reference material, exothermic changes will occur in the sample. The opposite situation will indicate an endothermic transformation. However, if the temperature in the test sample and the standard sample changes analogously in the measurement conditions, no changes occur in the tested material.

Differential scanning calorimetry (DSC) analysis was performed using a calorimeter (DSC Q2000 V24.11 Build 124). First, the samples were heated in the temperature range (-90)-50°C in an N₂ atmosphere at a heating rate of 20°C/min [17].

¹H NMR – nuclear magnetic resonance spectroscopy. The analysis was performed on a Bruker Avance™ 600 MHz NMR spectrometer with an UltraShield Plus™ magnet. Deuterated methanol was used as the solvent.

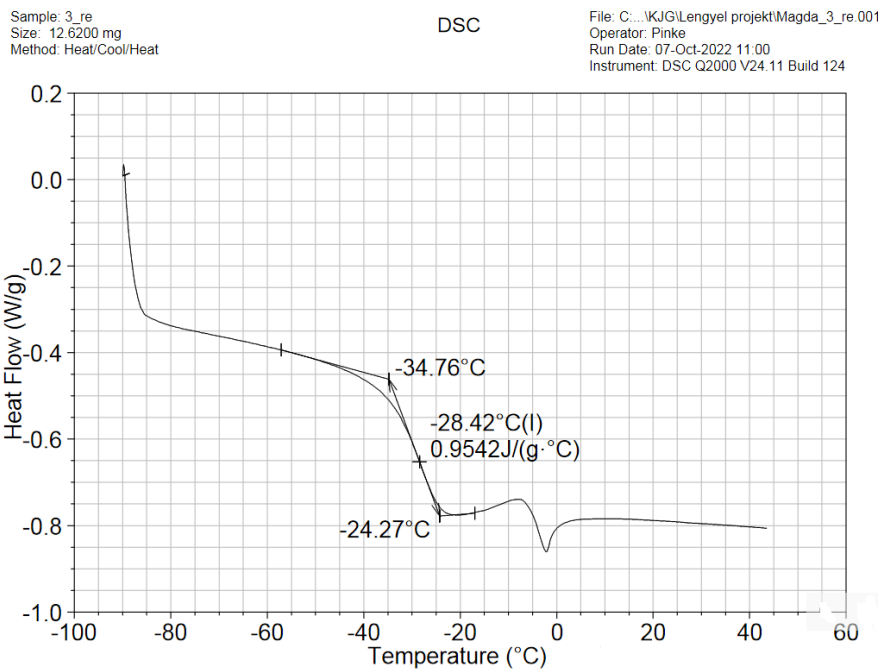
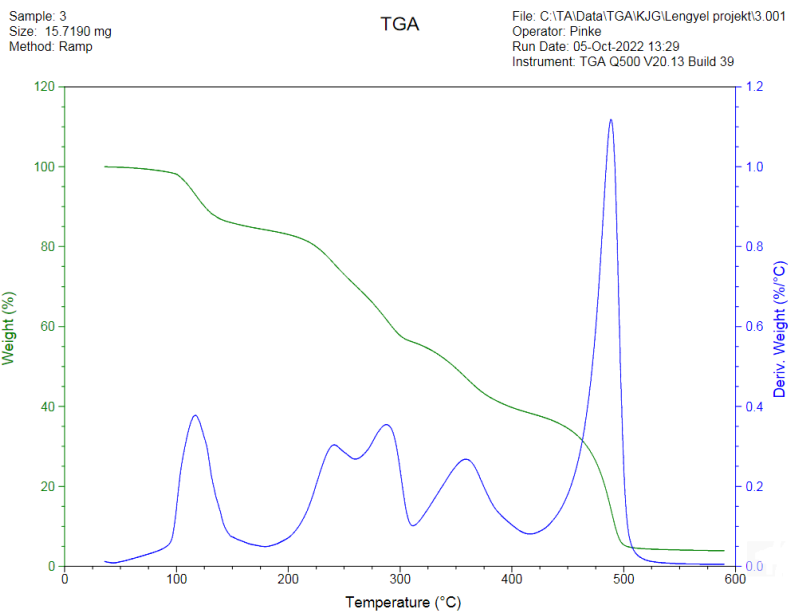
FTIR – Fourier transform infrared spectroscopy. The analysis was performed on a Thermo Scientific Nicolet 6700 FT-IR spectrometer equipped with Smart Orbit ATR (Waltkam, MA, USA).

3. Results and discussion

The synthesized new polymeric ionic liquids (PHMB benzoate, PHMB salicylate) with the structures described in Fig. 1 and Fig. 2 were subjected to thermal analysis using TGA and DSC techniques.

3.1. Thermal analysis

Results 1 - PHMB Benzoate No. 3

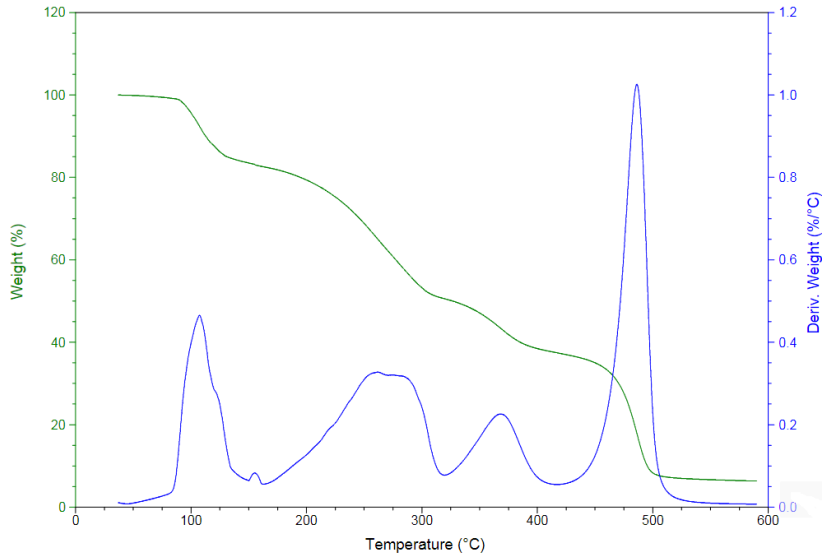


Results 2 - PHMB Salicylate No. 4

Sample: 4
Size: 16.5870 mg
Method: Ramp

TGA

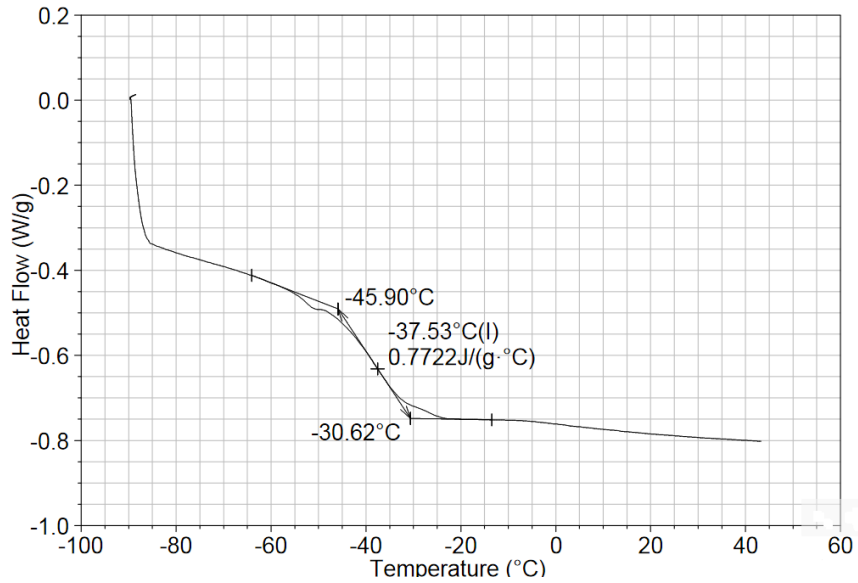
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Operator: Pinke
Run Date: 05-Oct-2022 14:24
Instrument: TGA Q500 V20.13 Build 39



Sample: 4_re
Size: 13.1500 mg
Method: Heat/Cool/Heat

DSC

File: C:\KJG\Lengyel projekt\Magda_4_re.002
Operator: Pinke
Run Date: 07-Oct-2022 14:16
Instrument: DSC Q2000 V24.11 Build 124



The results of analysis obtained for the decomposition of PHMB benzoate and PHMB salicylate in N₂ are presented.

Tab. 1. Thermal analysis results.

Substance	Glass transition temperature T (°C)	Enthalpy J/(g*(°C))
PHMB benzoate	-28.42	0.9542
PHMB salicylate	-37.53	0.7722

3.2. NMR analysis

The structure of polymeric ionic liquids was confirmed spectroscopically by nuclear magnetic resonance analysis H¹NMR.

Benzoate PHMB

H¹NMR (700MHz; MeOD): $\delta = 1,430$ (br s, PHMB); 1,627 (br s, PHMB); 3,329 (br s, PHMB, OH); 7,465-7,491 (arom. 2H); 7,589-7,612 (arom. 1H); 8,025-8,039 (arom. 2H).

There were three characteristic signals of polyhexamethylene biguanide H¹NMR (MeOD) protons 1.430, 1.627, 3.329 ppm and signals of five aromatic benzoate anion protons 7.465 (2H), 7.589 (1H), 8.025 (2H) ppm, which confirms the structure of the obtained ionic liquid.

Salicylate PHMB

H¹NMR (700MHz; MeOD): $\delta = 1,307$ (br s, PHMB); 1,505 (br s, PHMB); 3,181 (br s, PHMB); 6,796-6,835 (arom. 1H); 6,846-6,847 (arom. 1H); 7,297-7,322 (arom. 1H); 7,853-7,867(arom. 1H).

There were three characteristic signals for polyhexamethylene biguanide H¹NMR (MeOD) protons 1.307, 1.505, 3.181 ppm and signals of four aromatic

salicylate anion protons 6.796, 6.846, 7.297 and 7.853 ppm, which confirms the structure of the obtained ionic liquid.

3.3. FTIR analysis

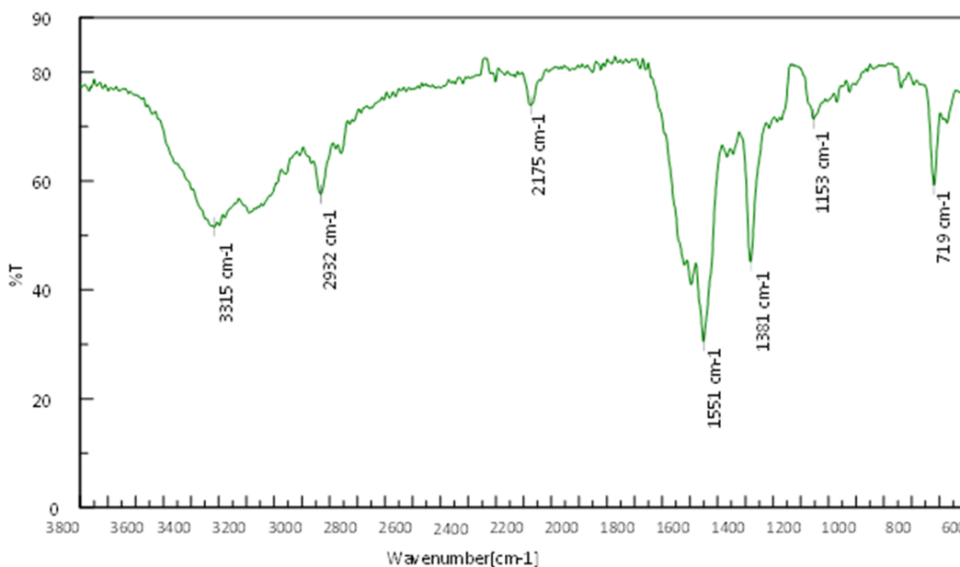


Fig. 3. FTIR analysis.

The IR spectrum also confirms the structure of PHMB benzoate. There are absorption bands attributed to N-H 3315 cm^{-1} stretching vibrations and N-H 1551 cm^{-1} deformation vibrations of polyhexamethylene biguanidine. There are also characteristic absorption bands at the frequency of 2175 cm^{-1} attributed to the C=N stretching vibrations of the polyhexamethylene biguanide. Also visible is the presence of a carboxylate anion that absorbs in a different frequency region than other carbonyl compounds. This is due to mesomerism, as a result of which both C-O bonds become equivalent bonds with an order intermediate between the order of the C=O and C-O bonds and intermediate value of the force constant. The vibrations of these bonds are also strongly mechanically coupled, therefore in the IR spectrum

we observe a band of asymmetric carbon-oxygen stretching vibrations at the frequency of 1381 cm^{-1} and a weaker band of symmetric stretching vibrations at 1153 cm^{-1} . In addition, there are visible absorption bands originating from C-H deformation vibrations in the monosubstituted aromatic ring at the frequency of 719 cm^{-1} and 670 cm^{-1} .

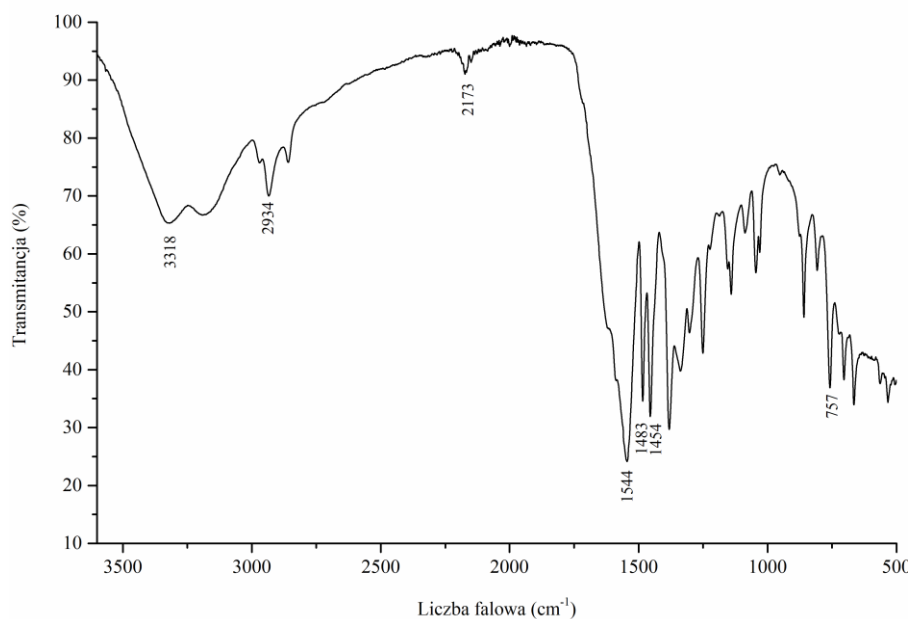


Fig. 4. FTIR analysis.

The IR spectrum also confirms the structure of polyhexamethylene biguanide salicylate. There are absorption bands attributed to N-H 3318 cm^{-1} stretching vibrations and N-H 1544 cm^{-1} deformation vibrations of polyhexamethylene biguanide. There are also characteristic absorption bands at the frequency of 2173 cm^{-1} attributed to the C=N stretching vibrations of polyhexamethylene biguanidine. Also visible is the presence of a carboxylate anion that absorbs in a different frequency region than other carbonyl compounds. This is due to mesomerism as a result of which both C-O bonds become equivalent bonds with an order

intermediate between the order of the C=O and C-O bonds and an intermediate value of the force constant. The vibrations of these bonds are also strongly mechanically coupled, therefore the IR spectrum shows a band of asymmetric carbon-oxygen stretching vibrations at the frequency of 1483 cm^{-1} and a band of symmetric stretching vibrations at 1454 cm^{-1} . In addition, there are visible absorption bands originating from C-H deformation vibrations in the disubstituted aromatic ring at the frequency of 757 cm^{-1}

4. Conclusion

For PHMB benzoate the glass transition temperature is $-28.42\text{ (}^{\circ}\text{C)}$ and for PHMB salicylate the glass transition temperature is $-37.53\text{ (}^{\circ}\text{C)}$. The enthalpy value for PHMB benzoate was $0.9542\text{ J/(g}^{\circ}\text{C)}$, while for PHMB salicylate it was $0.7722\text{ J/(g}^{\circ}\text{C)}$. The application of ionic liquids is very wide and applies to many areas of life and science, including biotechnology, pharmacy and sustainable energy. Due to their unique properties, they can contribute to the development of environmentally friendly technologies. The polymeric ionic liquids presented in the article, which were synthesized in Łukasiewicz-ŁIT (PHMB-BS, PHMB-SA), are ideal for functionalizing textiles in order to give them antibacterial properties. In addition, they can be used as a functional additive in the manufacture of polyethylene film and polyvinyl alcohol film.

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References

- [1] Shiflett M.B., Magee J.W., Tuma D.: *Commercial Applications of Ionic Liquids*, Springer International Publishing, USA, 2020, str. 3-29.
- [2] Kraśkiewicz A., Wojcieszak M., Rzemieniecki T., Syguda A., Materna K.: *Ciecze jonowe jako związki o budowie amfifilowej*, VI Szczecińskie Sympozjum Młodych Chemików streszczenie, Z. Lendzion-Bieluń i D. Moszyńskiego (red.), Polskie Towarzystwo Chemiczne, Szczecin, 2021, str. 32-33.
- [3] Dresler E., Kula K., Nowakowska-Bogdan E., Jasiński R.: *Ciecze jonowe jako nowoczesne i przyjazne środowisku medium dla syntezy organicznej*, I Konferencja Naukowo-Techniczna „Innowacje w przemyśle chemicznym” Zaleska A. (red.), Polska Izba Przemysłu Chemicznego, Warszawa, 2018, str. 54-79.
- [4] M. F. Hoover, *J MacromolSci – Chem*, 1970, 4, 1327-1417 Cationic quaternary polyelectrolytes.
- [5] K. Petrak, I. Degen, P. Beynon, *J PolymSci. Polym Chem Ed*, 1982, 20, 783-793, *Journal of polymer science. Part A-1, Polymer chemistry* Volume 20, Issue 3, Mar, Pages 783-793 Some 1- substituted quaternary imidazolium compounds and related polymers: qualitative and qualitative infrared analysis.
- [6] Mateus N.M.M., Branco L.C., Lourenço N.M.T., Afonso C.A.M.: *Synthesis and properties of tetra-alkyl-dimethylguanidinium salts as a potential new generation of ionic liquids*. *Green Chemistry*, 3(2003), str. 347-352.
- [7] Carrera G.V.S.M., Frade R.F.M., Aires-de-Sousa J., Afonso C.A.M., Branco L.C.: *Synthesis and properties of new functionalized guanidinium based ionic liquids as non-toxic versatile organic materials*. *Tetrahedron*, 66(2010), str. 8785-8794.
- [8] Butschies M., Neidhardt M.M., Mansueto M., Laschat S., Tussetschläger S.: *Synthesis of guanidinium–sulfonimide ion pairs: towards novel ionic liquid crystals*. *The Journal of Organic Chemistry*, 19(2013), str. 1093–1101.
- [9] Schlaikjer C.R., inventor, Guanidine derivatives as cations for ambient temperature molten salts in electrochemical power source. European patent 379096. 11.2003.
- [10] Mecerreyes D.: *Polymeric ionic liquids: Broadening the properties and applications of polyelectrolytes*. *Progress in Polymer Science*, 36, 2011, str. 1629–1648.
- [11] Andrzejewska E., Stępnik I.: *Highly conductive solid polymer-(ionic liquid) electrolytes prepared by in situ photopolymerization*. *Polimery*, 51, 11-12, 2006, str. 859-861.
- [12] Ito K., Nishina N., Ohno H.: *Enhanced ion conduction in imidazolium type molten salts*. *ElectrochimActa*, 45, 2000, str. 1295–1298.
- [13] Vygodskii Y.S., Melnik O.A., Shaplov A.S., Lozinskaya E.I., Malyshkina I.A., Gavrilova N.D. *Synthesis and ionic conductivity of polymer ionic liquids*. *Polymer Science Series A*, 49, 2007, str. 256–261.

- [14] Kawano R., Katakabe T., Shimosawa H., Nazeeruddin Md.K., Gratzel M., Matsui H., Kitamura T., Tanabe N., Watanabe M. *Solid-state dyesensitized solar cells using polymerized ionic liquid electrolyte with platinum-free counter electrode*. Physical Chemistry Chemical Physics, 12, 2010, str. 1916–1921.
- [15] Słubik A., Masłowska-Lipowicz I., Wieczorek D., Wyrębska Ł.: *Poly(hexamethylene biguanide) salicylate as a novel ionic liquid with antibacterial properties in the production of poly(vinyl alcohol) films*, Materials Research Express, 9, 2022, str. 1-11.
- [16] Wróbel J., Domańska A.: *Analiza termogravimetryczna materiałów gumowych w praktyce laboratoryjnej*, Laboratorium - Przegląd Ogólnopolski, nr 2, 2021, str. 15-25.
- [17] Gracz B.: *Zastosowanie skaningowej kalometrii różnicowej (DSC) w odlewnictwie*, Laboratorium - Przegląd Ogólnopolski, nr 2, 2021, str. 26-33.