Research paper / Praca doświadczalna

Synthesis and properties of a copolymer based on polycaprolactone and hydroxyl terminated polybutadiene
Synteza i właściwości kopolimeru opartego na polikaprolaktonie i α,ω-dihydroksypolibutadienie

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Abstract: *Polycaprolactone (PCL) is a widely used biodegradable and biocompatible polymer. Its use in rocket fuels results in a better oxygen balance and provides additional centres of adhesion of polyurethane binders compared to polyurethanes obtained using Hydroxyl Terminated PolyButadiene (HTPB). Additionally, PCL is used as a phlegmatizer in homogeneous solid rocket fuels. The other raw material used was HTPB used in the production of polyesters and polyurethanes, which gives these materials good mechanical properties. HTPB is the basis of solid rocket fuels used in space and military rocket propulsion.*
The aim of the work was to investigate the copolymerization reaction of HTPB with PCL. PCL-HTPB-PCL copolymer should combine and possess the desired properties of both polymers, i.e. excellent mechanical properties of polyurethanes, low glass transition temperature, and biocompatibility and biodegradability. Two HTPB species with different molecular weights were used in the study. Copolymerization with a ε-caprolactone ring opening (ROP) combines the constituent properties of the polymers. FTIR spectroscopic analysis was performed to confirm the PCL-HTPB-PCL chain structure. The molecular weight of the copolymer was shown to increase after 24 h of reaction, and the construction of the copolymer chain was confirmed, which indicated the correct reaction. Studies confirmed that as the molecular weight increases, the hydroxyl number decreases. The viscosity of the copolymers obtained decreases with increasing temperature. The copolymers obtained on the basis of low molecular weight HTPB had a liquid form. High molecular weight HTPB copolymers were obtained in the form of a wax.

Streszczenie: *Polikaprolakton (PCL) jest powszechnie stosowanym biodegradowalnym i biokompatybilnym polimerem. Wykorzystanie go w paliwach rakietowych skutkuje lepszym bilansem tlenowym i zapewnia dodatkowe centra adhezji lepiszcz poliuretanowych w porównaniu z poliuretanami otrzymanymi z użyciem α,ω-dihydroksypolibutadienu (HTPB). Dodatkowo PCL stosowany jest jako flegmatyzator w homogenicznych stałych paliwach rakietowych. Drugim wykorzystanym surowcem był HTPB używany do otrzymywania poliestrów i poliuretanów, nadaje on tworzywom dobre właściwości mechaniczne. HTPB stanowi podstawę stałych paliw rakietowych, używanych w napędach rakiet kosmicznych i wojskowych.*

Celem pracy było zbadanie reakcji kopolimeryzacji HTPB z polikaprolaktonem. Kopolimer PCL-HTPB-PCL powinien łączyć i posiadać pożądane właściwości obydwu polimerów tj. doskonałe właściwości mechaniczne wytworzonych z nich poliuretanów, niską temperaturę zeszklenia oraz biokompatybilność i biodegradowalność. W badaniach wykorzystano dwa gatunki HTPB o różnej masie cząsteczkowej. Kopolimeryzacja z otwarciem pierścienia ε-kaprolaktonu (ROP) łączy właściwości składowe polimerów. Wykonano analizę FTIR, aby potwierdzić budowę łańcucha PCL-HTPB-PCL. Wykazano wzrost masy cząsteczkowej kopolimeru po 24 godzinach reakcji, oraz potwierdzono budowę łańcucha kopolimeru. Badania potwierdziły, że wraz ze wzrostem masy cząsteczkowej liczba hydroksylowa maleje. Lepkość otrzymanych kopolimerów maleje wraz ze wzrostem temperatury. Kopolimery otrzymane na bazie niskocząsteczkowego HTPB posiadały ciekłą postać. Kopolimery z wysokocząsteczkowym HTPB otrzymano w postaci wosku.

1. Foreword

Copolymers of α,ω-dihydroxylpolybutadiene (HTPB) and polycaprolactone (PCL) combine the properties of their constituent polymers. In the armaments industry, using those copolymers as binders in solid rocket propellants, improves the oxygen balance of the propellant while maintaining good mechanical properties. PCL-HTPB-PCL copolymers can also be used as phlegmatizers in explosives. Improving the adhesive properties of polyurethane may lead to a reduction in the amount of adhesion enhancers in binders, varnishes or polyurethane paints. The research presented here is intended to show the effects of the type and properties of HTPB, used as a component of caprolactone polymerization initiation on the properties of the resultant copolymers.

Copolymerization allows specific characteristics to be achieved – a combination of features of the two homopolymers. The properties may include crystallinity, flexibility, tensile strength, melting point, crystallization temperature and many others. One method of combining two polymers is to mix them together, which may prove difficult, since the phases tend to separate due to incompatibility between most polymers. It is estimated that 36% of global polymer use involves polymer blends [1].

An alternative to physical mixing is the polymerization of two or more monomers, a process referred to as copolymerization. When more than two monomers are used, the product is referred to as a multi-component copolymer, whereas if three monomers are used, the product is called a terpolymer. Adding more than one type of monomer to the mixture increases the complexity of the kinetic reaction mechanism which affects the copolymer composition, distribution of comonomers in the main polymer chain and the molecular weight of the copolymer. As opposed to homopolymerization, copolymerization yields a wide range of properties.

2. HTPB and PCL

HTPB is a known and valued polymer used in the production of polyurethanes and polyesters. Thanks to its specific properties, the polymers are frost-resistant and show excellent mechanical properties, in particular at low temperatures (–40 ºC). The obtained polyurethanes are used in the production of frost-resistant adhesives and binders, insulation materials, soles of shoes, as well as propellants for space and military rocket propulsion systems.

PCL is a linear, high-crystalline polyester with physical, mechanical and thermal properties depending on the molecular weight and the degree of crystallinity (≤69%). The dimensions of PCL crystallites,

their orientation and intermolecular distance greatly affect those properties [2]. PCL is widely used as a raw material in injection moulding, extrusion moulding and extrusion blow moulding, and in manufacturing fibres and sutures, also as a compatibilizer of polymer blends and adhesion modifier [3]. Polymers containing polycaprolactone, similar to PCL, are biodegradable and biocompatible. It exhibits a low melting point (T_m = 59-64 °C) and a low glass transition temperature (T_g = –60 °C).

PCL, added to rocket propellants, improves the oxygen balance and provides additional adhesion centres for polyurethane binders compared to polymers obtained using HTPB [4,]. PCL inhibits the decomposition of ammonium dinitramide (ADN) – an oxidiser proposed as a substitute for ammonium perchlorate in heterogeneous rocket propellants. On the other hand, ADN and PCL decomposition products intensify the processes occurring in the flame zone. PCL with the molecular weight M_n = 1000-4500 g/mol has similar applications to HTPB, i.e. it can be used as a comonomer in the production processes of polyurethanes and polyesters [6] and in medicine, as a component of surgical sutures or biocompatible materials [7-9].

3. Polymerization of ε-caprolactone (CL)

There are two methods of obtaining polycaprolactone: a CL (Figure 1) ring-opening polymerization (ROP) and a 6-hydroxyhexanoic acid polycondensation. The PCL terminated with hydroxyl groups is obtained by CL polymerization, also referred to as a living ring-opening polymerization in the presence of initiators containing alkali metals, metal alkoxides, (e.g. stannous octoate (Sn(oct)$_2$), tris(acetylacetonato)aluminium, zinc and rare earth elements) [10]. The methods of obtaining PCL using an initiator in the form of Sn(oct)$_2$ with ethylene glycol complex, are also known [11, 12].
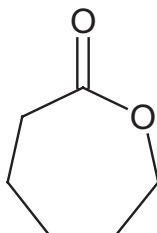

Figure 1. Structural formula of CL

Previous research has shown that polymerization with this initiator and the molecular weight of the product, significantly affects the ratio of all substrates (diol:Sn(oct)$_2$:monomer), process temperature and reaction duration. The structural analyses of ^{1}H NMR showed that ethylene glycol is incorporated in the PCL structure [15, 16].

To initiate controlled polymerization, Sn(oct)$_2$ must be used along with a nucleophile, usually an alcohol. PCL polymerization with ethylene glycol may proceed according to the following diagram.
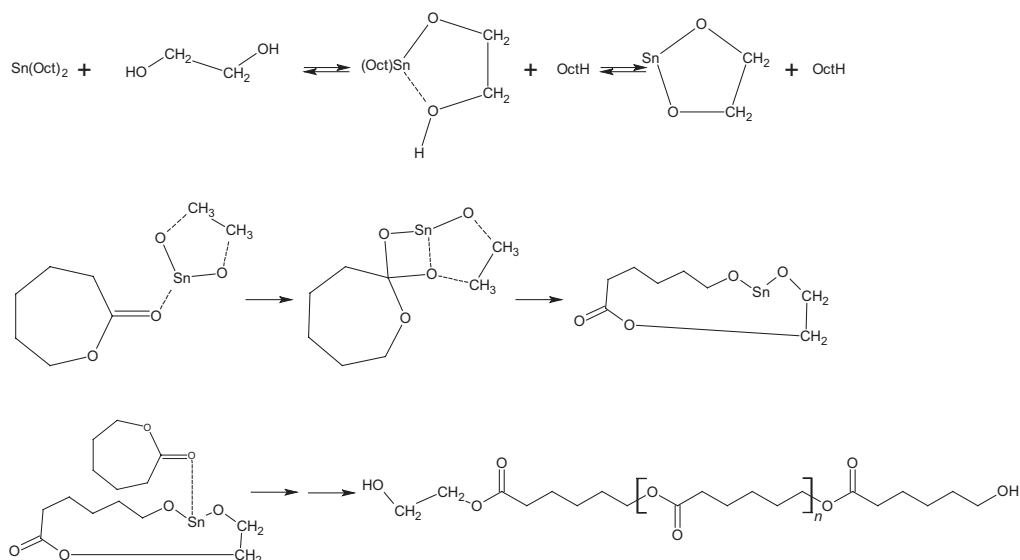
Figure 2. CL polymerization using Sn(oct)$_2$ and ethylene glycol [11]

As a result of the reaction between Sn(oct)$_2$ and ethylene glycol, a polymerization initiator is formed. One of the lactone's carbonyl oxygen forms a complex compound with a metal ion, opening the lactone ring and inserting the monomer into a metal-hydroxyl oxygen bond in the initiator molecule. The reaction extends the polymer chain by a single monomer and restores the active centre of polymerization. An alcohol, e.g. methanol is added to stop the ongoing polymerization and as a result, form the polymer and an inactive form of the initiator.

In this study, it was assumed that HTPB as a diol, will substitute ethylene glycol, i.e. it will react with Sn(oct)$_2$ forming a polymerization initiator which will initiate polymerization after adding CL. Similarly to ethylene glycol, HTPB is also incorporated into the PCL structure. Depending on the amount of Sn(oct)$_2$, monomer/HTPB ratio, HTPB molecular weight, the number of OH groups in HTPB and polymerization conditions, a PCL-HTPB-PCL copolymer with different properties (molecular weight, T_g, T_m, viscosity etc.), should be obtained. With CL and HTPB as the raw materials, the polymerization reactions can be expressed as follows:
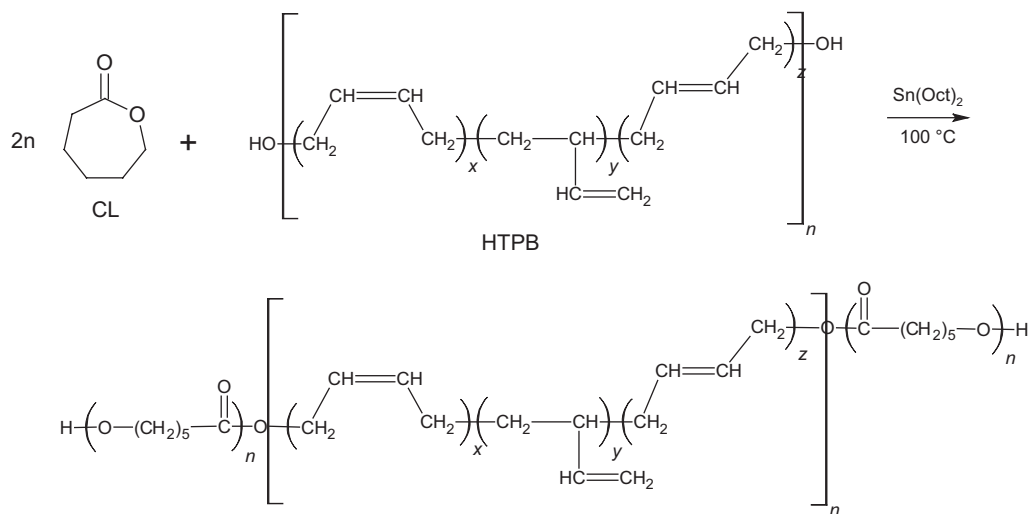
Figure 3. HTPB and PCL copolymerization diagram

4. Experimental section

4.1. Raw materials

Two different HTPB grades, synthesised in accordance with PL224488 [13], were used in the experimental study. Both HTPB grades show different properties, each is characterised by a different molecular weight and hydroxyl number. Using different HTPB grades, the effect of the amount of PCL combined with HTPB on the properties of the copolymer, can be determined.

Raw materials used were:

– HTPB A: M_n = 2800 g/mol, OH = 58 mgKOH/g,
– HTPB B: M_n = 4800 g/mol, OH = 30 mgKOH/g,
– calcium hydride (CaH$_2$): >97% purity, Sigma Aldrich,
– CL: 97%, Sigma Aldrich,
– Sn(oct)$_2$: >92.5%, Sigma Aldrich,
– 2-propanol: pure, Avantor.

CL is a cyclic ester with a 7-membered ring (Figure 1), a colourless liquid soluble in most organic solvents which slowly hydrolyses in the presence of water to 6-hydroxycaproic acid. To prepare the CL monomer for polymerization, the monomer was dried by adding CaH$_2$ and stirring at room temperature for 24 h. The monomer was distilled under reduced pressure. All impurities and moisture were removed from the HTPB under reduced pressure, at approx. 100 ºC with high-speed stirring for approx. 4 h.

4.2. Standard copolymerization reaction procedure

10 g of purified polymer – HTPB – was added to a 50 ml three-neck flask in an oil bath with magnetic stirrer, connected to a vacuum/argon system. A catalyst, Sn(oct)$_2$ in a quantity of 0.01 ml or 0.02 ml was added and stirred for 30 min at 40 ºC. After 30 min, CL was added and reacted for 24 h at 110 ºC. The resulting product was rinsed with 2-propanol to deactivate the catalyst.

The liquid or solid polymer was rinsed with water and dried under vacuum to remove the solvent and unreacted CL. The amount of unreacted CL was used to determine the yield of reaction. Each copolymer sample was obtained under the same conditions to determine the effect of the amount of catalyst and CL on the properties of the final polymer product. The same amount of HTPB (10 g) was used.

4.3. Analytical methods

The following analytical methods were used to test the obtained PCL-based and polybutadiene-based copolymers:

- **determining the hydroxyl number by titration:** The method involves acetylation of HTPB hydroxyl groups using acetic anhydride and pyridine. The copolymer was dissolved in a pyridine-acetic anhydride solution and heated for 2 h. The sample was titrated with KOH/EtOH solution with bromothymol blue as an indicator.
- **determining the average molecular weight and its distribution:** An analysis using gel chromatography (SEC) technique was carried out using an Agilent 1260 Infinity liquid phase chromatograph with RID detector, PLgel MiniMIX-E 250 x 4.6 mm (Agilent) column at 50 °C. The calibration curves were obtained using polystyrene standards with molecular weights covering the range of the column used.
- **FTIR analysis:** The spectra were recorded using a Nicolet 6700 by Thermo Scientific with a diamond ATR attachment. Spectra in the 600-4000 cm^{-1} infrared range were obtained.
- **determining the viscosity:** The viscosity was determined using a Brookfield DV2T viscometer with an attachment for determining viscosity in low-volume samples. Each sample was thermostated in a measuring chamber. The viscosity was determined at 25 to 60 ºC using SC4 no. 21 spindle with a speed set depending on the viscosity of the polymer being analysed.
- **DSC analysis:** The analysis was carried out using a DSC Q2000 V24.10 Build 122 with 50 ml/min nitrogen flow and sample heating rate of 10 °C/min.

4.4. Effect of copolymerization conditions on the properties of obtained copolymers

Two HTPB grades with different molecular weights and hydroxyl numbers were used in the study to determine the effect of molecular weight of the polymer on the ability to initiate the polymerization reaction with Sn(oct)$_2$. HTPB B has a higher molecular weight M_n and a lower hydroxyl number OH, whereas, HTPB A has a lower molecular weight and a higher hydroxyl number OH. In the syntheses, the catalyst load was modified and its effect on the molecular weight of copolymer was analysed. The same amount of CL was used in all cases and the catalyst concentration in the system was increased to analyse the effect of an increased amount of the initiator obtained from HTPB on the molecular weight of the resulting copolymer. To ensure repeatability of synthesis conditions, the same amount of HTPB was used (10 g). In the preliminary study on the possibility of obtaining the copolymers, reaction systems using non-purified and non-dried raw materials were used. Immediate gelation of the reaction system was observed, indicating that dried raw materials are required. A non-uniform polymer containing solid PCL and liquid HTPB was obtained.

Table 1.   The effects of polymerization process parameters on copolymer properties PCL-HTPB B-CL

Sample	Amount of CL [ml]	Amount of catalyst [ml]	Mole ratio Sn(Oct)$_2$/CL	M_n [g/mol]	M_w [g/mol]	OH [mgKOH/g]
R2	0.88	0.01	1:260	5567	14675	29
R3	1.77	0.01	1:520	5927	14553	25
R4	2.65	0.01	1:780	6524	15187	22
R5	3.52	0.01	1:1000	6812	15894	18
R6	4.4	0.01	1:1280	6823	19097	15
R7	2.65	0.02	1:320	6280	15919	23
R8	8.8	0.02	1:1060	10372	18046	10
R9	8.8	0.04	1:530	9241	17526	12
R10	8.8	0.06	1:355	7554	16612	13

For samples R2 to R6, the catalyst load was increased gradually by increasing the CL amount in the reaction system. For sample R2, the minimum required amount to terminate the HTPB B chain of CL was used, yielding a liquid PCL-HTPB B-PCL copolymer. In subsequent syntheses, the amount of CL was increased to elongate the PCL chain. Initially, liquid copolymers were obtained (samples R2-R7). Once the molecular weight of $M_n = 7500$ g/mol was exceeded, the obtained polymers were liquid at the reaction temperature and solid at room temperature (samples R8-R10). The hydroxyl number decreased with an increase in the molecular weight M_n of polymers. Chain elongation results in a different ratio between the number of hydroxyl groups per 1 g of polymer. An increase in the amount of catalyst (samples R8-R10) and the initiator in the initial polymerization phase resulted in a gradual decrease in the molecular weight M_n with a simultaneous increase in the hydroxyl number. The yield of the reaction was 90% for samples R2-R7 and 98% for samples R8-R10. The effect of the amount of catalyst in the system can be observed by comparing samples R3 and R9. Despite a similar catalyst to CL ratio, the polymers show different molecular weights M_n and hydroxyl numbers. For sample R3 obtained with a 90% yield, CL did not react completely, and for the R9 sample, the larger amount of the initiator yielded a longer PCL chain.

Table 2. Effects of the polymerization process parameters on copolymer properties PCL-HTPB A-PCL

Sample	Amount of CL [ml]	Amount of catalyst [ml]	Mole ratio $Sn(Oct)_2$/CL	M_n [g/mol]	M_w [g/mol]	OH [mgKOH/g]
R11	0.88	0.01	1:260	3700	6466	55
R12	1.77	0.01	1:520	3916	6552	53
R13	2.65	0.01	1:780	4129	6939	50
R14	3.52	0.01	1:1000	4734	7372	45
R15	4.4	0.01	1:1280	4650	7241	47
R16	2.65	0.02	1:320	4763	7476	44
R17	8.8	0.02	1:1060	6017	8881	35
R18	8.8	0.04	1:530	5978	8764	38
R19	8.8	0.06	1:355	4564	7166	42

In case of HTPB A, the procedure was identical as for HTPB B with the same amounts of catalyst and CL used. The study verified the possibility of a copolymerization reaction using HTPB with lower M_n and higher number of OH groups per 1 g of polymer. In all cases, liquid copolymers were obtained with the yield of reaction similar to previous syntheses. In the synthesis of samples R11-R16, the yield was 92%, in other cases it was 98%. The study showed that the form of the obtained copolymer depends on the amount of catalyst and CL used. Those copolymers with a M_n over 7500 g/mol at room temperature are in the form of a white wax. Using HTPB with low molecular weight and high hydroxyl number, results in liquid copolymers, even if multiple CL molecules are attached to the HTPB chain. Thus the applicability of the copolymer is increased. Choosing the right molecular weight and related hydroxyl number enables polymers with desired mechanical properties to be obtained.

4.5. FTIR analysis of raw materials and selected copolymers

The HTPB spectrum (Figure 4) includes signals in the 2800-3000 cm^{-1} wave number range indicating the presence of C–H bonds in the methylene groups. The signal at 964 cm^{-1} is indicative of the 1,4-*trans* isomer, 910 cm^{-1} of the 1,2-*vinyl* isomer, and 730 cm^{-1} of the 1,4-*cis* isomer. In the FTIR spectrum of CL (Figure 5), characteristic signals can be observed at 2944 cm^{-1} which correspond to the asymmetric stretching vibrations of CH_2, and at 2864 cm^{-1} which correspond to the symmetric stretching vibrations of CH_2. The signal at 1720 cm^{-1} is indicative of the stretching vibrations of C=O, and at 1470 cm^{-1} of the symmetric deformation vibrations of CH_2. Within 1150-1290 cm^{-1}, the signals correspond to the symmetric and asymmetric stretching vibrations of C–O–C bonds in the crystalline and amorphous phase.
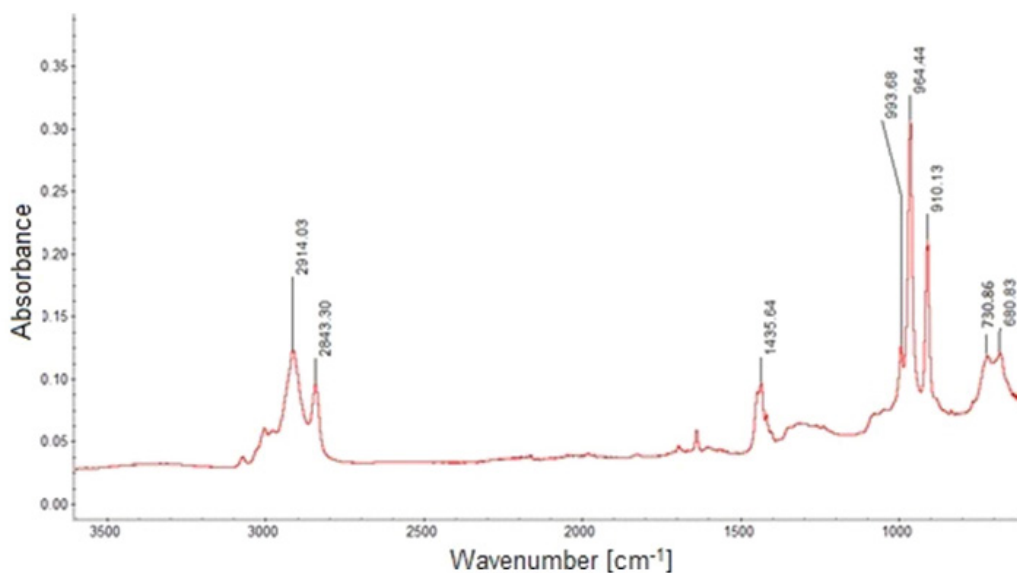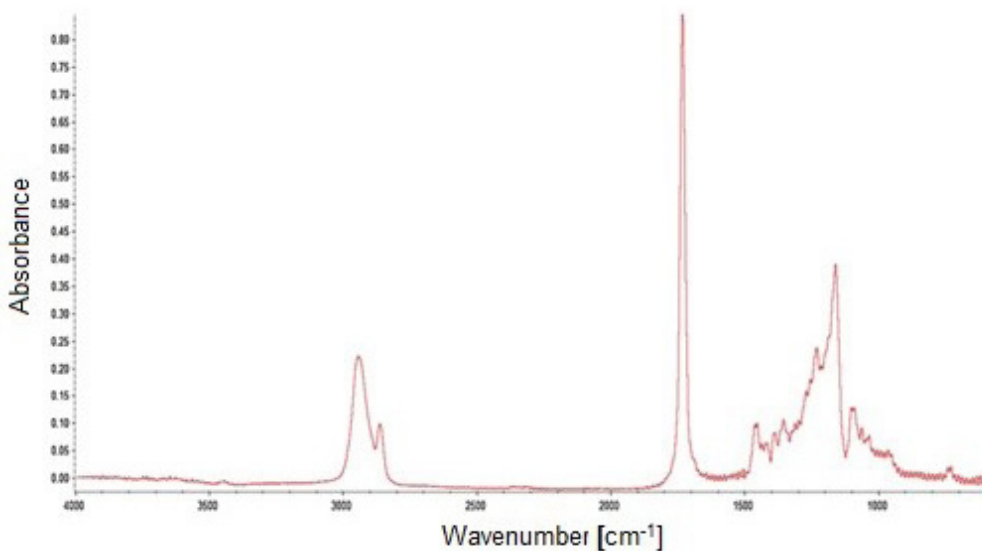
Figure 4. FTIR spectrum of the HTPB polymer

Figure 5. FTIR spectrum of CL

The spectra are similar for both HTPB A-based and HTPB B-based copolymers. In those spectra, the bands at 2918 cm^{-1}, corresponding to the asymmetric stretching vibrations of CH$_2$, and at 2845 cm^{-1}, corresponding to the symmetric stretching vibrations of CH$_2$, can be observed. Analysis of the spectra shows an increase in the intensity of the signal characterising of the carbonyl group in the PCL at 1720-1736 cm^{-1} for PCL-HTPB A-PCL sample while the change in intensity of the signal at 3400 cm^{-1}, characterises the OH groups. Signals validating the polybutadiene chain structure – 1,4-*cis* isomer at 730 cm^{-1}, 1,4-*trans* isomer at 967 cm^{-1} and 1,2-*vinyl* isomer at 911 cm^{-1}, can be observed. The intensity of the signals indicative of the PCL part is affected by the amount of polymer attached to the HTPB.
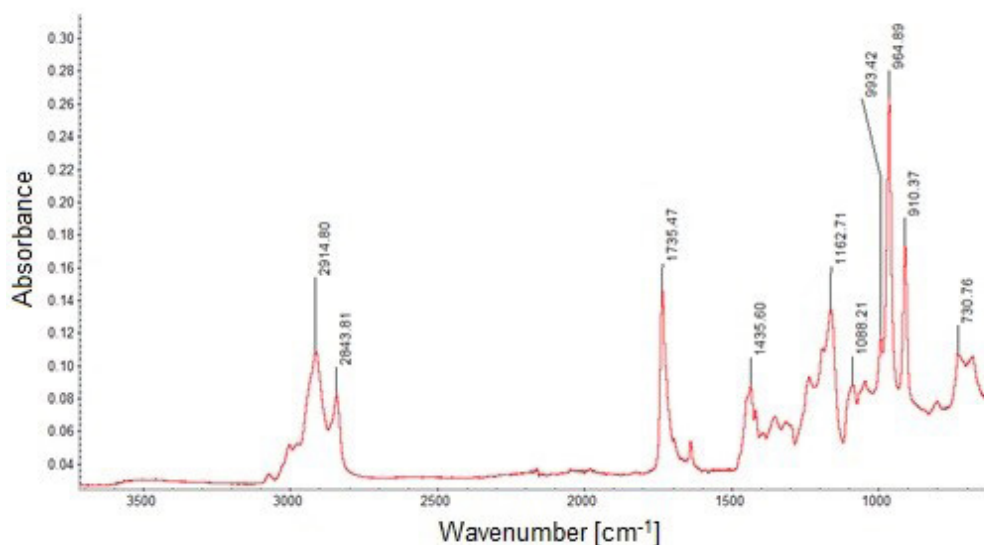
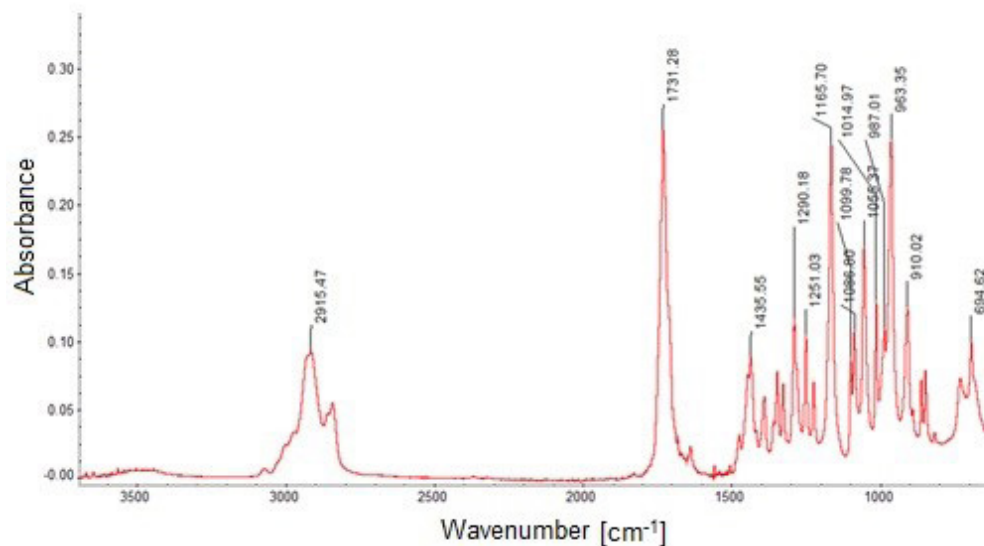**Figure 6.** FTIR spectrum of PCL-HTPB B-PCL copolymer

Figure 7. FTIR spectrum of PCL-HTPB A-PCL copolymer

4.6. Determining the viscosity of selected copolymers

Viscosity of the obtained copolymers decreases with increases in temperature. The viscosity decreases more rapidly at lower temperatures. The viscosity was determined for liquid copolymers only. The copolymers in the form of a wax have a melting point of 55-60 °C. Figure 8 shows the relationship between polymer viscosity and temperature.
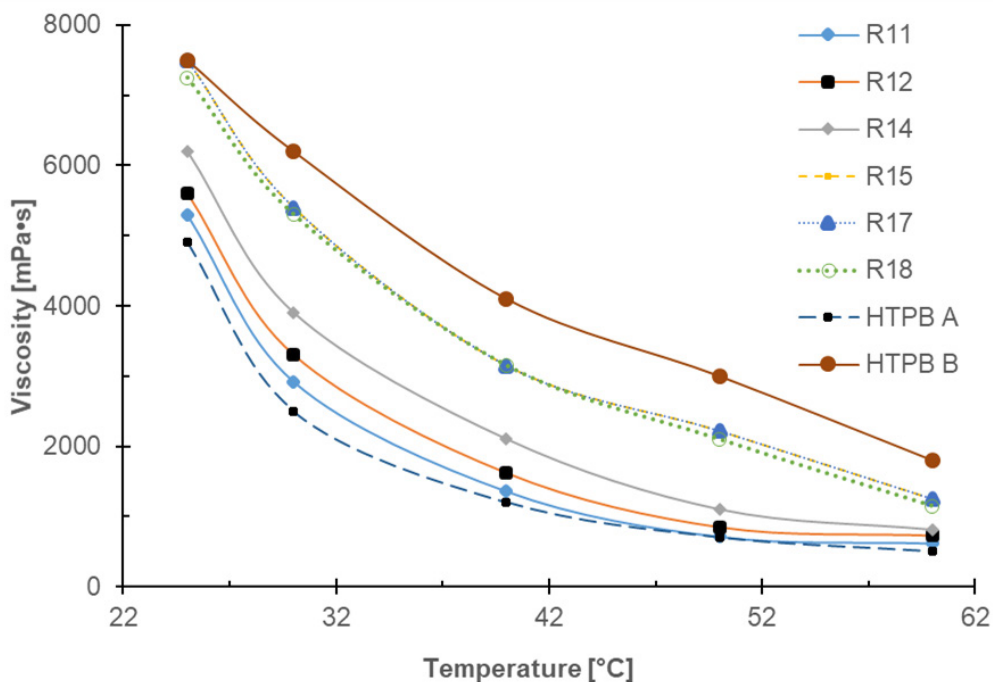
Figure 8. Effect of temperature on the viscosity of polymers

The viscosity of the analysed copolymers decreases with increases in temperature. Analysis of the viscosity of liquid HTPB A-based polymers shows the effect of the type of polymer used, on the copolymer properties. Using HTPB with a lower molecular weight and thus lower viscosity has increased the molecular weight of the copolymer to approx. 6000 g/mol, although, the viscosity of the copolymer is still lower than the viscosity of HTPB B. Using HTPB A allows any amount of PCL to be attached to maintain the essential properties, including viscosity or hydroxyl number. Using HTPB B as an initiator will affect those essential properties. An increase in molecular weight will change the form of the copolymer (wax), decrease its hydroxyl number and affect the mechanical properties of polyurethanes based on this copolymer. A similar correlation was observed for HTPB and GAP copolymerization [14]. An increase in the amount of polyepichlorohydrin attached to the HTPB chain yielded solid copolymers.

4.7. Thermal analysis of the obtained copolymers

DSC was used to determine the melting point of selected copolymers. Figure 9 shows a sample DSC curve for HTPB B-based copolymer with a molecular weight of M_n = 5,500 g/mol. The analysis showed that the amount of CL attached to the HTPB affects its T_g. The higher the amount of CL in the copolymer, the higher the glass transition temperature. The glass transition temperature from –75 to –60 °C was observed at molecular weights ranging from 5,500 to 10,000 g/mol, using HTPB B and from 3,700 to 6,000 g/mol, using HTPB A. The glass transition temperature increases with increases in molecular weight of the copolymer.
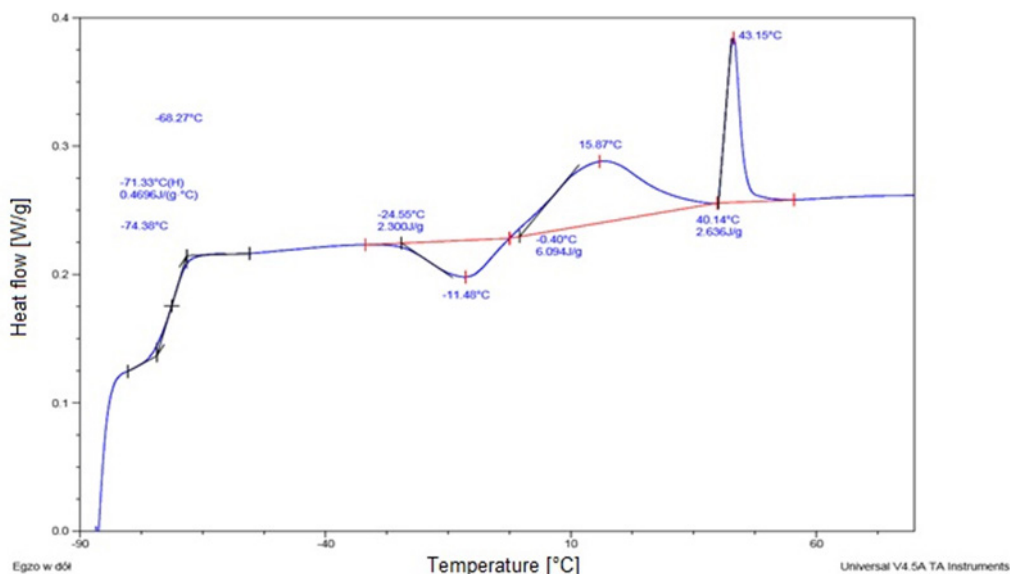
Figure 9. DSC curve of the selected copolymer

5. Summary and conclusions

♦ The study verifies the possibility of a copolymerization reaction between PCL with polybutadiene by opening the CL ring, using stannous octoate as a catalyst.

♦ FTIR spectra show a correct structure of the PCL-HTPB-PCL chain. A polybutadiene chain is characterised by 1,4-*cis*, 1,4-*trans* and 1,2-*vinyl* isomers, a signal indicative of the PCL's carbonyl group and a signal indicative of the hydroxyl groups. No signals indicative of the CL ring were observed.

♦ The molecular weight of the copolymers increases with increases in the amount of monomer and catalyst. The hydroxyl number decreases with increases in molecular weight of the copolymers. Viscosity decreases with increases in temperature. Using a low-molecular weight HTPB A, liquid copolymers were obtained, whereas, using high-molecular weight HTPB B, solid wax copolymers were obtained.

♦ Due to the larger number of OH groups in HTPB A, a larger amount of CL can be attached, yielding a liquid copolymer characterised by a higher PCL content. The study showed that doubling the molecular weight M_n of the copolymer (up to the molecular weight of HTPB) increases the glass transition temperature T_g of the copolymers by 5 ºC. T_g increases with increases in the amount of monomer added to the reaction.

♦ Those copolymers based on low-molecular weight HTPB A, due to their liquid form, can be used in the synthesis of solid heterogeneous rocket propellants without the need of modifying the procedure itself, as is the case with HTPB B, where the copolymer is melted.

References

[1] *Polymer Blends Handbook*. Utracki L.A., Ed., Vol. 1, Dordrecht: Kluwer Academic Publishers, The Netherlands, **2002**.

[2] Chanchai S., Nawee K. *Theoretical Investigation on the Mechanism and Kinetics of the Ring-opening Polymerization of ε-Caprolactone Initiated by Tin(II) Alkoxides*. Berlin-Heidelberg: Springer-Verlag, **2013**.

[3] Joshi P., Madras G. Degradation of Polycaprolactone in Supercritical Fluids. *Polym. Degrad. Stab.*

2008, *93*: 1901-1908.

[4] Ryszkowska J., Auguścik M. Properties of Poliurethane for Application as a Bone Tissue. (in Polish) *Czasopismo Techniczne Mechanika* **2009**, *106*: 287-293.

[5] Bennett J.S., Barnes M.W., Koloako K.J. *Propellant Binder Prepared from a PCP/HTPB Block Polymer*. Patent US 4853051, **1989**.

[6] Ostap R. *Research on the Preparation of α,ω-Dihydrohypolycaprolactone*. (in Polish) Master thesis, Technical University of Warsaw, Warsaw, **2013**.

[7] Filachlone E.M., Fisher Ch.H. *Process for the Manufacture of Esters of Hydroxy Carboxylic Acids*. Patent US 2447693, **1948**.

[8] Lam C.X.F., Teoh S.H., Hutmacher D.W. Comparison of the Degradation of Polycaprolactone and Polycaprolactone-(*β*-tricalcium phosphate) Scaffolds in Alkalinemedium. *Polym. Int.* **2007**, *56*: 718-728.

[9] Sinha V.R., Bansal K., Kaushik R., Kumria R., Trehan A. Poly-ε-caprolactone Microspheres and Nanospheres: An Overview. *Int. J. Pharm*. **2004**, *278*: 1-23.

[10] Chen D.R., Bei J.Z., Wang S.G. Polycaprolactone Microparticles and their Biodegradation. *Polym. Degrad. Stab.* **2000**, *67*: 455-459.

[11] Hedrick J.L., Magbitang T., Connor E.F., Glauser T., Volksen W., Hawker C.J., Lee V.Y., Miller R.D. Application of Complex Macromolecular Architectures for Advanced Microelectronic Materials. *Eur. J. Chem*. **2002**, *8*: 3308-3319.

[12] Joshi P., Madras G. Degradation of Polycaprolactone in Supercritical Fluids. *Polym. Degrad. Stab.* **2008**, *93*: 1901-1908.

[13] Canterberry J.B. *Polycaprolactone-deterred Nitrocellulose Propellant Compositions and Method*. Patent US 4950342, **1990**.

[14] Elzein T., Nasser-Eddine M., Delaite C., Bistac S., Dumas P. FTIR Study of Polycaprolactone Chain Organization at Interfaces. *J. Colloid Interf. Sci*. **2004**, *273*: 381-387.

[15] Skupiński W., Kozakiewicz J. *Application of α,ω-Dihydroxypolybutadiene (HTPB) and Oligomeric α,ω-Dihydroxypolycaprolactone (HTPCL) in the Preparation of Polyurethanes for Special Production*. (in Polish) Industrial Chemistry Institute, Report on Statutory Works – Strategic, **2011**, [unpublished].

[16] Skupiński W., Kozakiewicz J. *α,ω-Dihydroxypolybutadiene (HTPB) and Oligomeric α,ω-Dihydroxypolycaprolactone (HTPCL) in the Preparation of Polyurethanes for Special Production.* (in Polish) Industrial Chemistry Institute, Report on Statutory Works – Strategic, **2012**, [unpublished].

[17] Skupiński W., Chmielarek M., Wieczorek Z., Dziura R. *Method of Obtaining α,ω-Dihydroxypolybutadiene.* (in Polish) Patent PL 224488, **2016.**

[18] Chmielarek M., Maksimowski P., Cieślak K., Gołofit T., Drozd H. Study of the Synthesis of GAP-HTPB-GAP Liquid Copolymer. *Cent. Eur. J. Energ. Mater.* **2020**, *17*(4): 566-583.