

POLY(EPICHLOROHYDRIN-CO-1,2-EPOXYHEXANE) – A PROMISING PRECURSOR FOR AN ENERGETIC AZIDO POLYMER FOR CAST-CURE PROCESSING

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ABSTRACT

A copolymer of epichlorohydrin (ECH) and 1,2-epoxyhexane (EpH) has been synthesized via cationic ring-opening polymerization using $\text{BF}_3 \cdot \text{Tf}_2\text{O}$ as a catalyst and 1,4-butanediol (BDO) as an initiator. The structure of the resulting PECH copolymer was confirmed by NMR- and IR-spectroscopic methods. The molecular weight distribution was determined by GPC, showing a number average weight of 1607 g/mol. The introduction of n-butyl substituted units into the polyether backbone chain lowers the glass transition temperature, which was confirmed by thermal analysis (DSC- T_g), and also lowers the viscosity of the polymer significantly compared to PECH in the same molecular weight range. A subsequent azidation of the polymer should lead to an energetic prepolymer with interesting properties for cast-cure processing of composite propellants.

INTRODUCTION

Energetic polymers are able to supply additional energy to the combustion process and are therefore attractive binder components for tomorrow's generation of rocket and gun propellants.

One of the most investigated energetic polymers is glycidyl azide polymer (GAP).¹⁻³ It consists of a polyether backbone bearing energy delivering pendant azido methyl side-chains with a high heat of formation of +957 kJ/kg.⁴

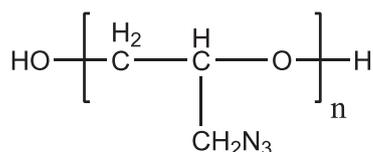


Figure 1: Molecular structure of GAP

GAP is a liquid dihydroxy-terminated telechelic polymer and is typically cured with di- or polyfunctional isocyanates to form energetic rubber like polyurethanes.

One major drawback of GAP is the relative high glass transition temperature of approximately $-45\text{ }^\circ\text{C}$ ^{5,6} compared to HTPB's superior T_g of $-70\text{ }^\circ\text{C}$.¹ High glass transition temperatures may cause brittleness of cured propellants applied at low temperatures. Copolymers of GAP together with non-energetic units will lead to prepolymers with lower energy, but can have improved mechanical properties and lower glass-transition temperatures compared to pure GAP.

So far, there are still only a few literature-described random GAP-Copolymers, mainly GAP-THF⁷⁻⁹ and GAP-BAMO¹⁰⁻¹³.

Therefore we decided to synthesize a copolymer consisting of epichlorohydrin together with 1,2-epoxyhexane, which should work as an internal plasticizer due to the unpolar pendant n-alkyl chain. The resulting copolymer could be azidated in a subsequent nucleophilic substitution with sodium azide leading to an energetic GAP-copolymer suitable for cast-cure applications.

EXPERIMENTAL SECTION

Reagents

Solvents and reagents were purchased from Acros Organics, Sigma-Aldrich or Merck and used as received, unless otherwise stated.

PECH was supplied by 3M and used as received. Dichloromethane (DCM) was refluxed over P_2O_5 for 4 hours, distilled and stored over 4 \AA molecular sieves. Epichlorohydrin and 1,2-epoxyhexane were distilled over CaH_2 and stored under nitrogen atmosphere in a fridge. 1,4-Butanediol was purchased from Sigma-Aldrich and stored over 4 \AA molecular sieves. $\text{BF}_3 \cdot \text{THF}$ was purchased from Sigma-Aldrich, distilled and stored under nitrogen in a fridge.

Instrumentation

IR spectra have been measured on Thermo Scientific Nicolet 6700 (FTIR-Spectrometer) with Durascope diamond ATR accessory. ^1H -NMR spectra were recorded with a Bruker 400 (TR) instrument. The spectra were measured at 25 °C. The chemical shifts are given relative to tetramethylsilane (^1H , ^{13}C) as external standards. Molecular weights have been measured by GPC Agilent Series 1100 with RID detector and a set of four PSS SDV 5 μ columns (50/100/1000/10⁵ Å). THF was used as a solvent and the flow rate was 1.0 ml/min. Polystyrene standards with molecular weights (Mp) from 162 to 1210000 g/mol have been used for calibration. Differential scanning calorimetry (DSC) was performed on a TA instruments Q 1000 using alumina pans. Scans were carried out at scan rates of 10 °C min⁻¹, under nitrogen flux, in a range from -90 °C to 25 °C and the result has been taken at the second cycle. Thermogravimetric analyses (TGA) were measured on a TA Instruments TGA Q5000 under nitrogen atmosphere using a heat rate of 10 °C min⁻¹. Viscosity measurements have been performed on a MCR501 using shear rates ranging from 1 s⁻¹ to 1000 s⁻¹ at stated temperatures.

Synthesis of poly(Epichlorohydrin-co-1,2-Epoxyhexane)

To a stirred mixture of 1.79 ml (20.25 mmol) 1,4-butanediol and 1.0 ml DCM was added 0.17 ml $\text{BF}_3 \cdot \text{THF}$ under nitrogen atmosphere. The resulting emulsion was stirred for 15 minutes at 20 °C.

A solution consisting of 35.19 ml (450.00 mmol) epichlorohydrin, 18.08 ml (150.00 mmol) 1,2-epoxyhexane and 28 ml DCM was added with a feed rate of 0.200 ml/min using a dosing pump at a temperature of 20 °C.

After complete addition, the resulting clear viscous solution was stirred at 20 °C for 6 h. 50 ml DCM was added to dilute the mixture and 20 ml distilled water was added for quenching the reaction. After adding 20 ml of sat. NaHCO_3 solution and stirring for additional 15 minutes, the organic layer was separated and washed three times with distilled water. Neutralisation was checked with pH-paper. After drying over MgSO_4 , the solvent was evaporated at a maximum temperature of 90 °C under vacuum. The product was isolated a clear viscous polymer with a yield of 55.04 g (94 %).

IR: 745 cm⁻¹ ($-\text{CH}_2\text{Cl}$), 1190 cm⁻¹ (C-O-C), 2875 cm⁻¹ ($-\text{CH}_2-$), 3380 cm⁻¹ ($-\text{OH}$)

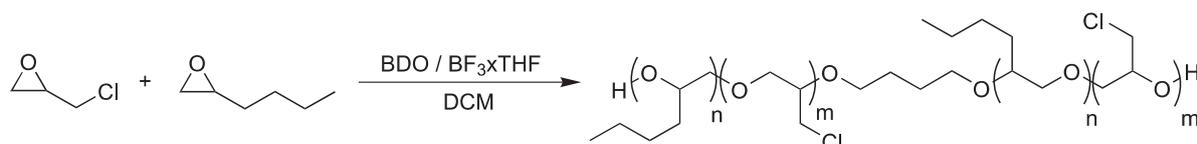
$^1\text{H-NMR}$ (400 MHz, CDCl_3). Repeating units $\delta = 3.97 - 3.18$ (polymer backbone, 10H), 1.57 (-CH-CH₂-CH₂-CH₂-CH₃, 2H), 1.41 (-CH-CH₂-CH₂-CH₂-CH₃, 2H), 1.26 (-CH-CH₂-CH₂-CH₂-CH₃, 2H), (-CH-CH₂-CH₂-CH₂-CH₃, 3H) ppm.

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3). Repeating units $\delta = 80.8-77.6$ (-OCHCH₂R-), 72.1-68.8 (-OCHCH₂R-), 46.5-42.8 (-CH₂Cl), 31.4 (-CH-CH₂-CH₂-CH₂-CH₃), 27.7 (-CH-CH₂-CH₂-CH₂-CH₃), 22.8 (-CH-CH₂-CH₂-CH₂-CH₃), 14.1 (-CH-CH₂-CH₂-CH₂-CH₃) ppm.

RESULTS AND DISCUSSION

The copolymer synthesis of epichlorohydrin and 1,2-epoxyhexane was performed by cationic ring-opening polymerization in DCM solution using $\text{BF}_3 \cdot \text{Tf}_2\text{O}$ as a catalyst and 1,4-butanediol as an initiator (see Scheme 1).

Scheme 1: Synthesis of Copolymer of Epichlorohydrin and 1,2-Epoxyhexane



Performing the polymerization in solution has the advantage of easy stirring and good heat exchange, especially when focusing on very small scale synthesis using magnetic stirring bars. Effective stirring of high viscous bulk polymerizations with mechanical stirrers can be difficult and overheating may lead to discoloration of the products.¹⁴ Since epichlorohydrin is typically polymerized by cationic ring-opening polymerization one has to deal with the formation of low molecular impurities.¹⁵ In order to avoid the formation of a high content of cyclic oligomers, reaction conditions were chosen where the activated monomer mechanism stated by Penczek et al.¹⁴ should be favored over the activated chain end mechanism.

That means, the ratio $[\text{BDO}]/[\text{Monomers}]$ has to be high from the beginning until the end of the reaction. Therefore the monomer mixture of ECH and 1,2-epoxyhexane in DCM was added slowly drop wise over a period of 8 hours using a dosing pump. A $[\text{monomer}]/[\text{DCM}]$ volume ratio of 2:1 was chosen and a feed rate of 0.200 ml/min led

to a clear, viscous copolymer poly(Epichlorohydrin-co-1,2-Epoxyhexane) with a moderate molecular weight dispersity.

Molecular weight analysis

The suitable molecular weight range of prepolymers in the preparation of cast-cure propellant technology is ranging from 1000 to 4000.⁸ Therefore, a detailed analysis of the molecular weights is necessary. The molecular weight of the halogen precursor was evaluated by GPC relative to polystyrene standards.

Figure 2 shows the molecular weight distribution. Only a small amount of low molecular impurities has been formed. A number average weight of $M_n=1607$ g/mol and a moderate dispersity of $PDI=1.75$ was achieved. Table 1 shows the detailed data summarized.

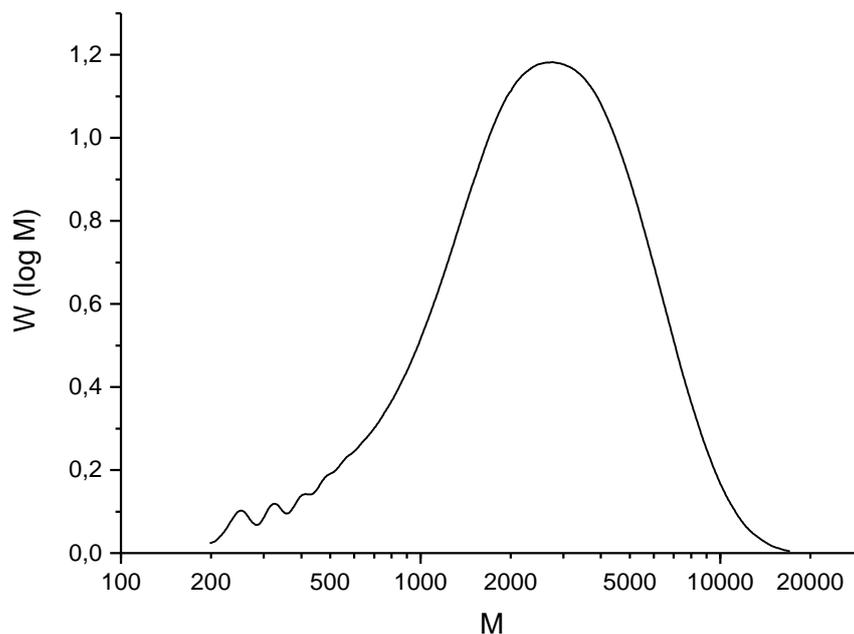


Figure 2: Molecular Weight Distribution of poly(ECH-co-1,2-EpH)

	M_n	M_w	M_p	PDI
poly(ECH-1,2-EpH)	1607	2811	2655	1,75

Table 1: Data of molecular weight analysis

Spectroscopic analysis

Figure 3 shows the IR spectrum of the poly(ECH-co-1,2-EpH) copolymer. It confirms the assumed polyether structure. The C-Cl stretching vibration gives a strong band at 745 cm^{-1} , the band at 1102 cm^{-1} appears from the C-O-C ether bonds and at 3400 cm^{-1} a broad band appears from the terminal hydroxyl groups.

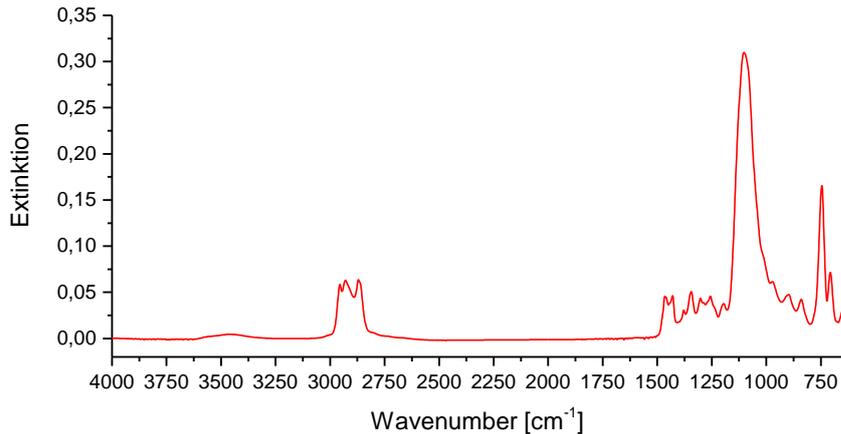


Figure 3: IR spectrum of poly(ECH-co-1,2-EpH)

The assumed molecular structure was also confirmed by $^1\text{H-NMR}$ spectroscopy. The spectrum shows signals in the range of 3.97-3.18 ppm due to protons of $-\text{CH}_2-$ and $-\text{CHR}-$ groups of the polyether backbone as well as the $-\text{CH}_2\text{Cl}-$ chloromethyl units. The four signals caused by the pendant $-\text{butyl}$ sidechain confirm the incorporation of 1,2-Epoxyhexane into the polymer-chain.

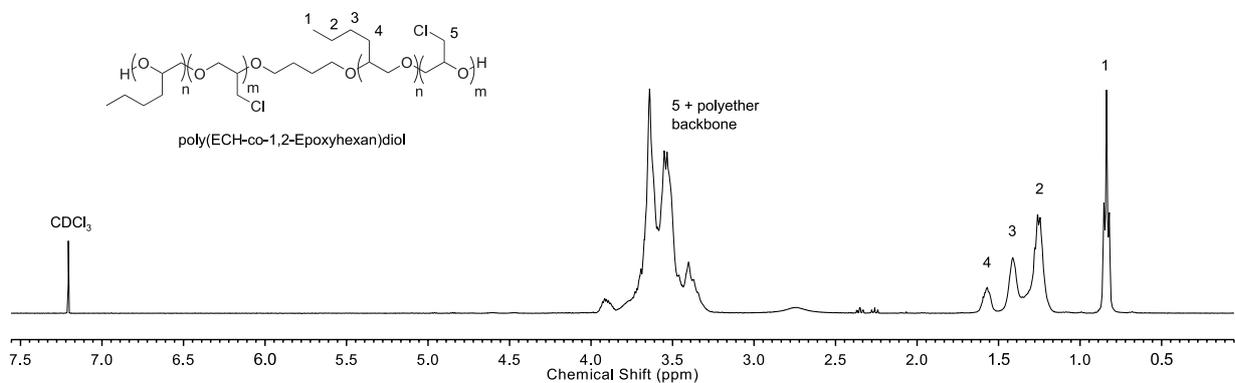


Figure 4: $^1\text{H NMR}$ spectrum of poly(ECH-co-1,2-EpH)

Thermal Analysis

Decomposition Studies

The TGA analysis of the halogen precursor poly(ECH-co-1,2-EpH) shows as expected a one-step degradation of the polymer backbone at 320 °C.

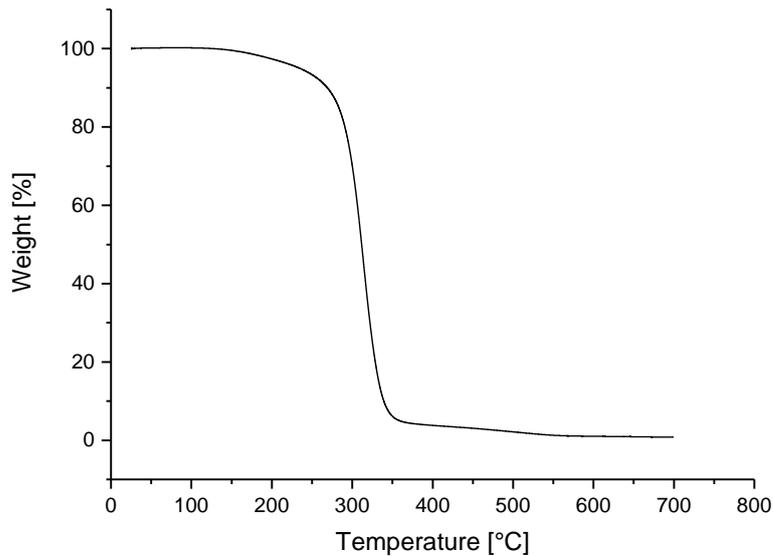


Figure 5: TGA curve of poly(ECH-co-1,2-EpH)

Glass Transition Temperature

The glass transition temperature of a prepolymer plays a crucial role, because it is important for the temperature dependent behaviour of cured binder systems. It has to be as low as possible to avoid brittleness of cured propellants applied at low temperatures.

Therefore we determined the T_g of the halogen precursor in order to check if it could be a promising prepolymer after azidation. Figure 6 shows the DSC curves of the synthesized copolymer and Polyepichlorohydrin (PECH) supplied by 3M, which is the halogen precursor of glycidyl azide polymer (GAP).

The copolymer shows a glass transition temperature of - 46 °C. This is significantly lower than the T_g of the Polyepichlorohydrin homopolymer (- 32 °C) and makes the material a suitable candidate for azidation and further studies.

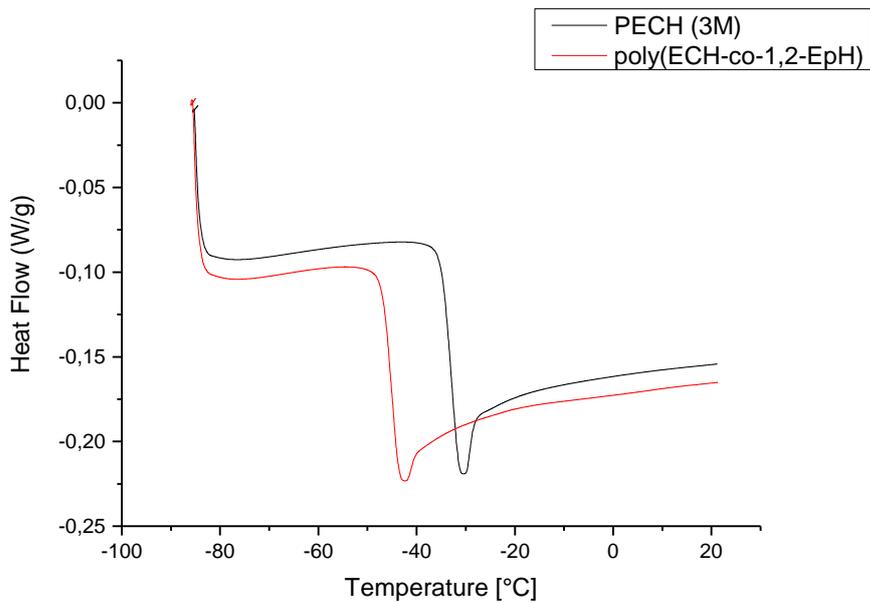


Figure 6: DSC curves of poly(ECH-co-1,2-EpH) and PECH (3M)

Viscosity

The viscosity of the copolymer poly(Epichlorohydrin-co-1,2-Epoxyhexane) was measured at three different temperatures (20 °C, 40 °C, 60 °C) and shear rates ranging from 10^{-1} to 10^3 s^{-1} .

In comparison to PECH of 3M (see Figure 7), the viscosity is significantly lowered particularly at low temperatures, that should lead to a good cast cure process ability of a subsequent azidated copolymer.

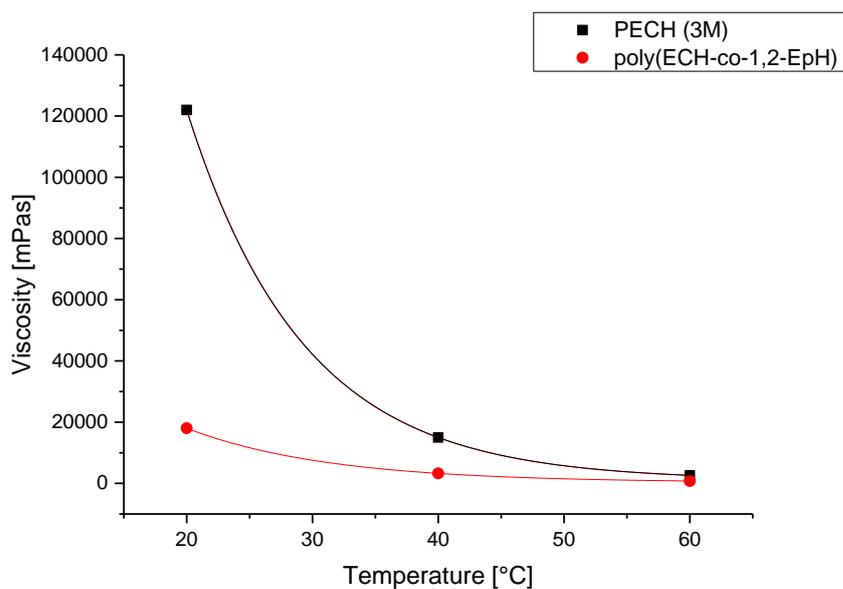


Figure 7: Viscosity measurement at temperatures ranging from 20 °C to 60 °C at a shear-rate of 10 1/s

CONCLUSIONS

A copolymer consisting of epichlorohydrin and 1,2-epoxyhexane was synthesized successfully with low content of cyclo-oligomeric impurities. This was possible by adding the monomers with slow feeding rate and therefore favoring the activated monomer mechanism. The resulting poly(Epichlorohydrin-co-1,2-Epoxyhexane) is a clear colorless viscous polymer. The substance has been characterized by IR-/ NMR-spectroscopy, GPC and thermal analysis. The low glass transition temperature and the low viscosity makes the copolymer a suitable candidate for a subsequent azidation leading to an energetic prepolymer for cast-cure propellant binder applications. This will be the object of future work.

ABBREVIATIONS

ATR Attenuated total reflectance

BDO 1,4-Butanediol

DCM Dichloromethane

DSC Differential scanning calorimetry

ECH Epichlorohydrin

EpH 1,2-Epoxyhexane

GAP Gycidyl azide polymer

GPC Gel permation chromatography, Gel permation chromatographie

IR Infrared

NMR Nuclearmagnetic Resonance

PECH Polyepichlorohydrin

ppm parts per million

RID Reflective index detector

Sec Size exclusion chromatography

T_g Glass transition temperature

TGA Thermogravimetric analysis

THF Tetrahydrofurane

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REFERENCES

- (1) Ang, H. G.; Pisharath, S. *Energetic Polymers*; Wiley-VCH, 2012.
- (2) Provatas, A. No. DSTO-TR-0966. *Def. Sci. Technol. Organ. Melb.* **2000**.
- (3) Colclough, M. E.; Desai, H.; Millar, R. W.; Paul, N. C.; Stewart, M. J.; Golding, P. *Polym. Adv. Technol.* **1994**, 5 (9), 554–560.
- (4) Kubota, N.; Sonobe, T. *Propellants, Explos. Pyrotech.* **1988**, 177, 172–177.
- (5) Nazare, A. N.; Asthana, S. N.; Singh, H. *J. Energ. Mater.* **1992**, 10 (1), 43–63.
- (6) Grant, L. R.; Flanagan, J. E.; Frankel, M. B. *J. Propuls. Power* **1992**, 8 (3), 560–563.
- (7) Lee, B. J.; Bae, I. J.; Kim, J. S.; Kim, S. H. US8871872 B2, 2014.
- (8) Mohan, Y. M.; Mani, Y.; Raju, K. M. *Des. Monomers Polym.* **2006**, 9 (3), 201–236.
- (9) Mohan, Y. M.; Raju, K. M. *Int. J. Polym. Mater.* **2006**, 55 (3), 203–217.
- (10) Barbieri, U.; Polacco, G.; Massimi, R. *Macromol. Symp.* **2006**, 234 (1), 51–58.
- (11) Kawamoto, A. M.; Holanda, J. A. S.; Barbieri, U.; Polacco, G.; Keicher, T.; Krause, H.; Kaiser, M. *Propellants, Explos. Pyrotech.* **2008**, 33 (5), 365–372.
- (12) Kawamoto, A. M.; Diniz, M. F.; Lourenço, V. L.; Takahashi, M. F. K.; Keicher, T.; Krause, H.; Menke, K.; Kempa, P. B. *J. Aerosp. Technol. Manag.* **2010**, 2 (3), 307–322.
- (13) Barbieri, U.; Polacco, G.; Keicher, T.; Massimi, R. *Propellants, Explos. Pyrotech.* **2009**, 34 (5), 427–435.
- (14) Biedron, T.; Kubisa, P.; Penczek, S. *J. Polym. Sci. Part A Polym. Chem.* **1991**, 29 (5), 619–628.
- (15) Goethals, E. *Pure Appl. Chem.* **1976**, 48, 335–341.