SYNTHESIS AND PROPERTIES OF RANDOM CO-POLYMER POLY-(GA/BAMO) AS ENERGETIC BINDER

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ABSTRACT

Random copolymer with monomer units from glycidyl azide (GA) and 3,3-bis-azidomethyloxetane (BAMO) has been synthesized to produce a material for potential application as energetic binder for solid rocket propellant.. The former synthesized halogen precursor copolymer epichlorohydrin/3,3-bis-bromomethyl-oxetane (ECH/BBrMO) has been converted to an energetic polymer via azidation reaction with NaN_3. The introduction of poly-BAMO units in the GAP chain has the advantage of an increasing number in azide groups and consequently in the energetic content of the material, but to a limited value that preserves the amorphous morphology of the polymer. The synthesis has been up-scaled to 1.1 kg quantity and the resulting polymer has been characterized via IR-spectroscopy, thermal analysis (DSC, TGA, Tg), impact sensitivity, end group analysis, molecular mass measurement (GPC), density, viscosity, heat of combustion and elemental analysis.
This study has been done under the EDA project “Formulation and Production of New Energetic Materials” (FPNEM) PA No B-0585-GEM2-GC.

INTRODUCTION

Energetic binders are polymers for propellants and explosives that bear energetic functional groups along their polymer backbone which provide additional energy to the energy balance of the system. Such energetic groups are azido ($-N_3$), nitro ($-NO_2$), nitrate ester ($-ONO_2$) and nitramino ($-N-NO_2$) groups. From these the energetic binders with azido groups approved to be the most intensive studied modern energetic polymers. These binders are liquid oligomers with hydroxyl end groups which will be cured with isocyanates after the explosive fillers, oxidizers and metallic fuels are mixed homogeneously with the binder. The curing reaction of the hydroxyl end groups with the isocyanates build up a polyurethane network. To achieve a cross linked network, the binder polymers and/or the isocyanates have to be at least trifunctional. Another possibility to achieve crosslinking in case the polymers and the isocyanates are difunctional is the adding of triols. The cured binder embeds the explosive fillers, oxidizers and metallic fuels in an elastomeric matrix which keeps the shape/geometry of the propellants and the explosives. Furthermore these binder matrix is responsible for reducing the sensitivity of the energetic material by absorbing hazardous mechanical stimuli or shock waves within the elastomeric binder matrix and protecting so the explosive fillers from accidentally ignition/initiation. Due to the energetic contribution from the binder the explosive filler can be reduced, still keeping the overall performance of the energetic material and also getting reduced sensitivity to external stimuli. Of course using energetic binders instead of inert binders and keeping the filler content unchanged the performance can be increased.

From energetic binders with azido groups glycidyl azide polymer (GAP) is the only one that is commercial available in Western Europe. GAP has a nitrogen content of 42.41 % (= monomer unit), high positive heat of formation (+957 $kJkg^{-1}$) [1] and low glass-transition temperature (Tg = -48 °C). Besides, GAP shows good compatibility with high-energy oxidizers like ammonium perchlorate (AP) and ammonium dinitramide (ADN). Another well known azido binder is poly-BAMO which has even higher nitrogen content of 49.98 % (= monomer unit) and higher heat of formation (+2209 $KJ\ kg^{-1}$) [2] than GAP. Unfortunately poly-BAMO is solid at room temperature and so it can not be used for cast cured processing of energetic materials. However, when BAMO units are randomly spread along a GAP chain the resulting copolymer stays liquid if the BAMO content does not get too high. Due to the higher nitrogen content in poly-BAMO the copolymer glycidyl azide-r-(3,3-bis(azidomethyl)oxetane) (poly-GA/BAMO) should be more energetic than pure GAP. The copolymer poly-GA/BAMO has been mentioned in literature first time in 2006 [3] but no properties of the copolymer have been given. Later this copolymer has been synthesized in an international cooperation project from Barbieri and Kawamoto et. al. [4] [5] as part of European project CEPA 14; RTP 14.10. The copolymers had BAMO contents from 20 to 25 mol-%, showed higher energy content than GAP and were liquid. However these copolymers contained up to 10 mass-% cyclic oligomers, had low molecular weights and OH-functionalities of around 1.5 which gives some limitations for the processing of energetic materials (functionality of isocyanate > 3). The properties of the copolymers have been also evaluated in rocket propellant formulations [6] [7] [8]. Another research group evaluated a GA/BAMO copolymer concerning its thermal decomposition and its properties as energetic thermoplastic elastomer [9].

The objectives of this work were to modify the synthesis of copolymer GA/BAMO that the oligomers should be avoided or the amount should be at least reduced. Further, the functionality of the copolymer should be increased to 2 and the synthesis should be up-scaled to provide enough material for evaluation of the modified copolymer in rocket propellants. The results from evaluation of the up-scaled GA/BAMO-copolymer as binder for Al/AP-based propellants are presented also on this conference [10].

The work has been done in the European EDA project “Formulation and production of new energetic materials – FPNEM (PA NoB-0585-GEM2-GC).

SYNTHESIS OF COPOLYMER GA/BAMO

The synthesis of copolymer GA/BAMO involves two steps. First the halogenated precursor is synthesized from a monomer mixture of epichlorohydrin (ECH) and 3,3-bis(bromomethyl)oxetane (BBrMO) via cationic polymerization using BF_3-THF as catalyst and 1,4-dioxane as solvent. This synthesis and the characterization of the copolymer ECH/BBrMO have been already published [11]. For revision the following Table 1 shows some properties of the halogenated precursor copolymer ECH/BBrMO.

Table 1: Properties of the halogenated precursor copolymer ECH/BBrMO

copolymer ECH/BBrMO	results from GPC analysis				end group analysis	DSC analysis
	Mw	Mn	D	Mp	Eq. Wt. [g/mol-OH]	Tg [°C]
	7362	2038	4.63	7618	4479	-38.4

The second step in the synthesis is the nucleophilic substitution reaction for replacing the halogen groups by azido groups. This azidation reaction is done with NaN_3, using DMSO as solvent at 100 °C to give the desired copolymer GA/BAMO. The azidation reaction of the copolymer ECH/BBrMO has been up-scaled to 1.1 kg.

The reaction equation for the azidation process can be seen at Figure 1.

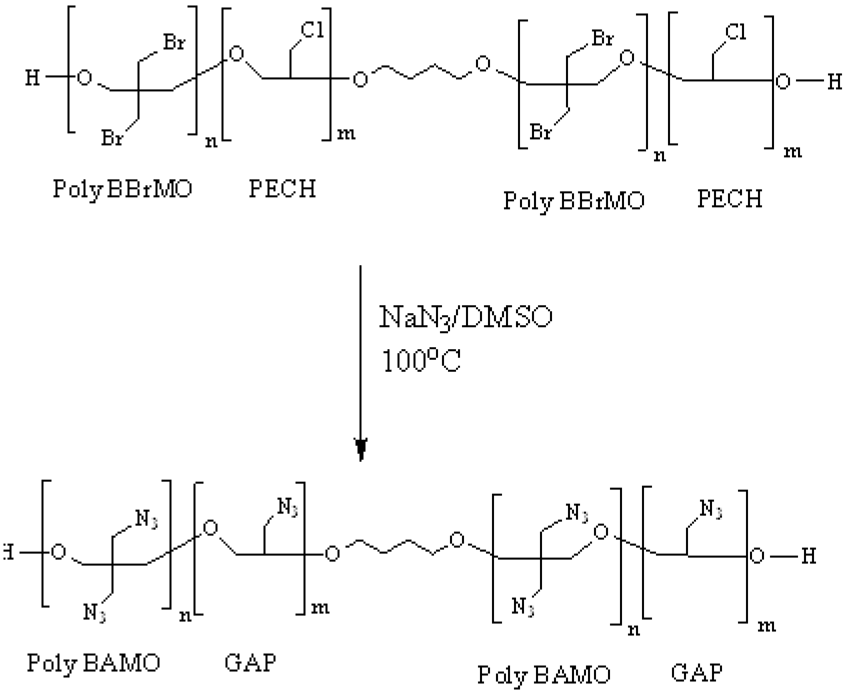

Figure 1: Synthesis of copolymer GA/BAMO

- Experimental:

Copolymer ECH/BBrMO has been synthesized according literature [11]. DMSO and NaN_3 have been used as received from chemical supplier.

Copolymer ECH/BBrMO (1119 g) was added to a 30 liter double jacket reactor with 13 l of DMSO and water (650 ml) and heated to 60 °C. To this mixture, sodium azide (1233 g) was added in portions under stirring. The adding took about 25 minutes. Then the temperature has been increased to 100 °C and stirring has been continued for 167 h. Then the temperature has been reduced to 60 °C and around 15 L of water has been added to the reaction mixture under stirring. The copolymer separates from the mixture. The aqueous phase with DMSO, NaBr/-Cl and NaN_3-residues is removed and the polymer has been washed with water at a temperature of 60 °C five times more. Then the copolymer is dried at the rotavapor at 60 °C under vacuum to give a high viscous dark brown and clear product. Yield 928.2 g copolymer. Waste from washing operation; aqueous phase with DMSO/, NaBr/-Cl and NaN_3-residues 100 liters.

The water content of the polymer has been measured via Karl-Fischer titration. The water content was 0.07 %. The following Figures give some aspects from the azidation reaction and from purification.

Figure 2: Copolymer ECH/BBrMO in a 30 liter reactor with DMSO and water

Figure 3: Third washing operation after azidation reaction

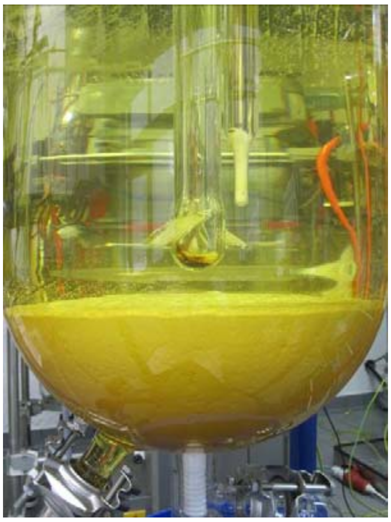

Figure 4: Phase separation after fourth washing operation of copolymer GA/BAMO

Figure 5: Copolymer GA/BAMO at the rotavapor for drying

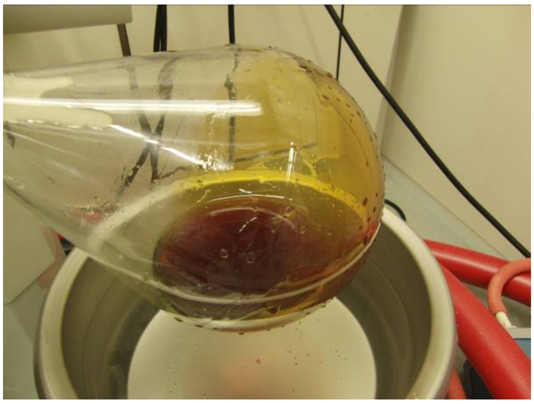

Figure 6: Copolymer GA/BAMO at the rotavapor – finished drying

ANALYSIS OF COPOLYMER ECH/BBRMO

- Experimental:

IR spectra have been measured on Thermo Scientific Nicolet 6700 (FTIR-Spectrometer) with Durascope diamond ATR accessory.

Molecular weights have been measured by GPC Agilent Series 1100 with detector DAD (Diode Array Detector) Agilent 230 nm and a set of four PSS SDV columns (50/100/1000/105 Å). The solvent was THF and the flow rate was 1.0 mL/min. Polystyrene standards with molecular weights (Mp) from 162 to 246000 g/mol have been used for calibration.

Differential scanning calorimetry (DSC) was done to measure the glass transition temperature (Tg). The measurements were performed on a TA instruments Q 1000 using aluminum pans. Scans were carried out on each sample at scan rates of 5 °C/min, under nitrogen flux, in the -90 to 25 °C range and the result has been taken at the second cycle.

The heat of combustion has been measured with an IKA 2000 calorimeter at sample weights of around 1.0 g.

The end groups have been analyzed via classical titration method following the procedure described in DIN 53240-2; Determination of hydroxyl value - Part 2: Method with catalyst. The end group analysis has been done with 6 g samples.

Impact sensitivity of copolymer GA/BAMO

The impact sensitivity testing has been done with BAM drop hammer apparatus following the NATO STANAG 4489. Impact sensitivity of copolymer GA/BAMO was 20.0 Nm (5 kg hammer, 0.4 m height, 4 of 6 trials positive, weak bang). With this impact sensitivity copolymer GA/BAMO is quite insensitive and it can be handled with usual precaution for handling of explosives.

IR-spectroscopy of copolymer GA/BAMO

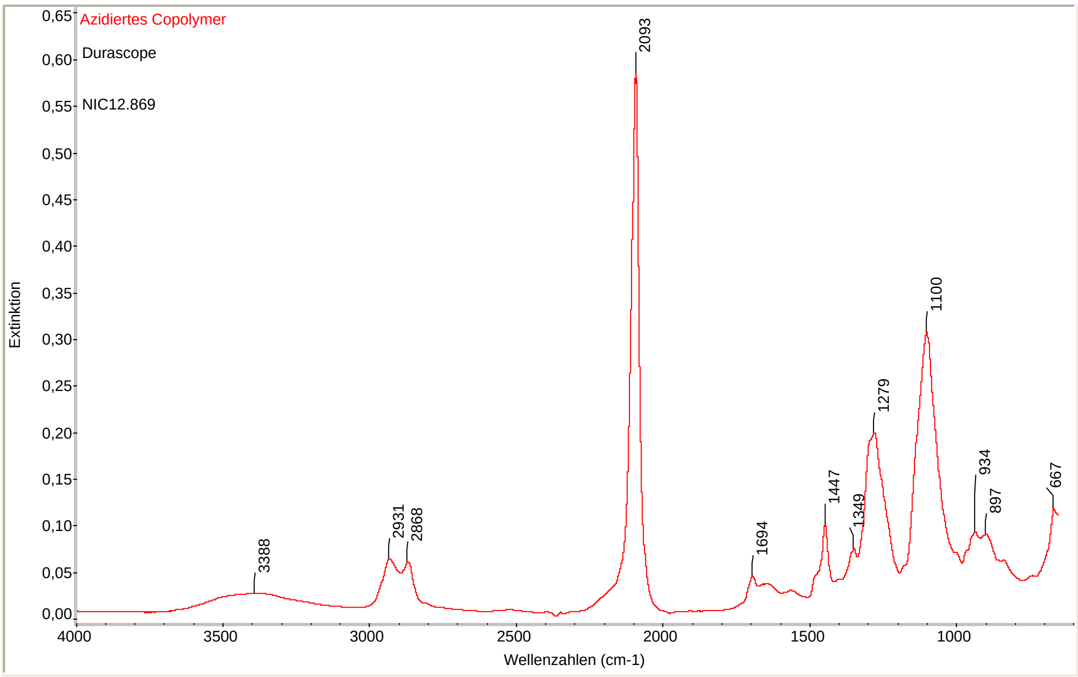

Figure 7: IR spectra of copolymer GA/BAMO

The IR-spectra shows the strong azido band at 2093 cm^{-1} and the broad and wide hydroxyl band at 3368 cm^{-1}. The peak at 1100 cm^{-1} is from the ether bonds. All peaks from the halogen vibrations which can be seen at 692 and 745 cm^{-1} at the IR-spectra of the copolymer ECH/BBrMO has been disappeared.

OH-equivalent weight of copolymer GA/BAMO

The hydroxyl groups of the polymer have been acetylated and then titrated with methanolic KOH. From the copolymer three samples and two blank samples have been analyzed and the average value has been calculated. The following Table 2 shows the results for the three samples.

Table 2: Equivalent weight of copolymer GA/BAMO

	Eq. Wt. [g/mol-OH]
Sample 1	3557
Sample 2	3821
Sample 3	3695
Average from sample 1-3	3691
Average from sample 1, 3	**3626**

Result for sample 2 is clear different from the other both samples. So the average for sample 1 and sample 3 has been calculated. It is **3626 g/mol**. This equivalent has been used for calculating the stoichiometry for curing with isocyanates in formulations.

Molecular mass measured via GPC

From the copolymers ECH/BBrMO and GA/BAMO the molecular masses have been measured via GPC method with poly-styrene standards. Figure 8 shows the molecular weight distribution and Table 3 gives the details for the different molecular weight numbers. The molecular weight shows a broad distribution with a high poly-dispersity (D = 4.6) and the peaks of the GPC curves shifted from 7618 g/mol for the halogenated copolymer to 11097 for the azido copolymer. This shift to higher molecular mass is due to substitution of the halogens for azide. The amount of low molecular mass oligomers is quite low.

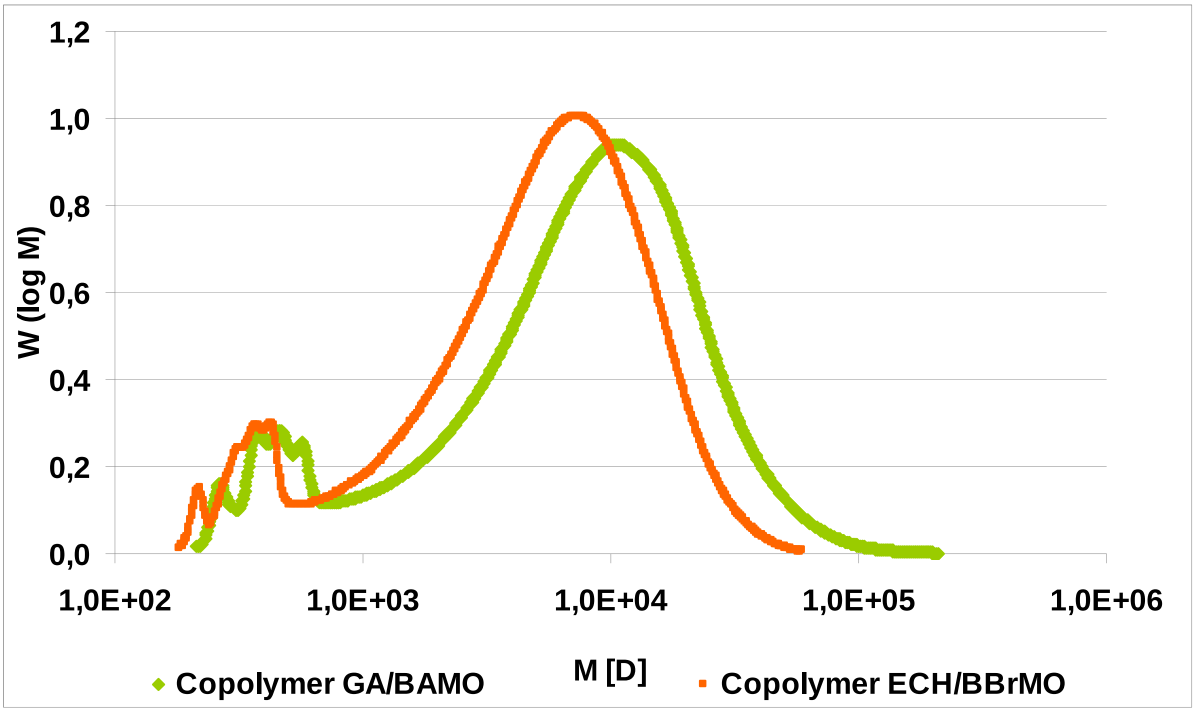

Figure 8: GPC curves of copolymers ECH/BBrMO and GA/BAMO

Table 3: Molecular weight details for copolymers ECH/BBrMO and GA/BAMO

	Mw	Mn	D	Mp
Copolymer ECH/BBrMO	7362	2038	4.63	7618
Copolymer GA/BAMO	11775	2505	4.69	11097

DSC of copolymer GA/BAMO

The copolymer GA/BAMO shows exothermic decomposition starting at around 180 °C with peak maximum at 247 °C and an energy release of 2110 J/g. Following Figure 9 shows the DSC measuring curve.

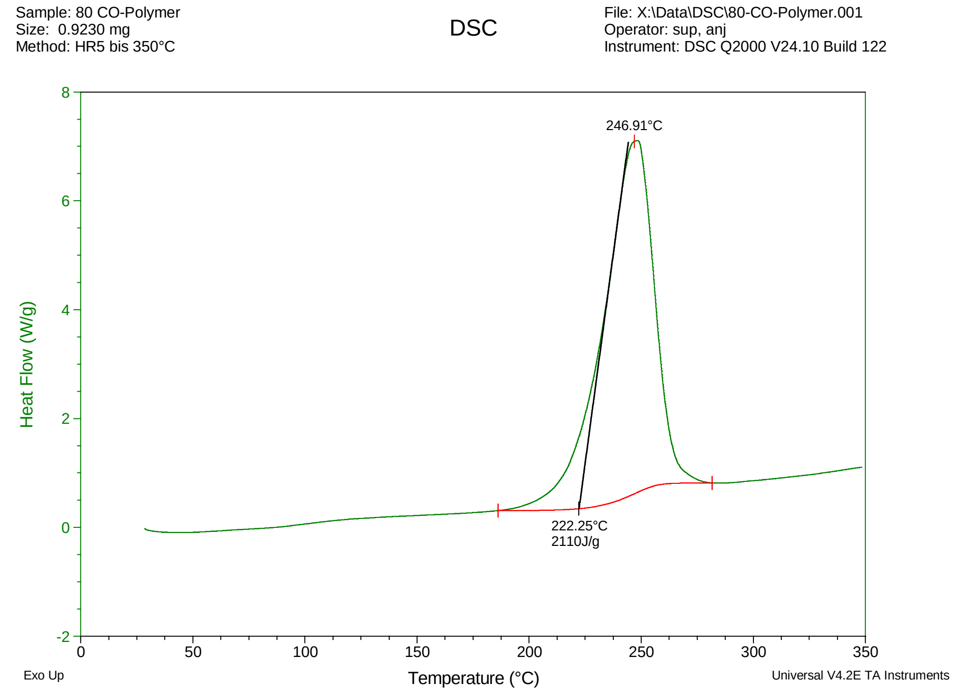

Figure 9: DSC of copolymer GA/BAMO

TGA of copolymer GA/BAMO

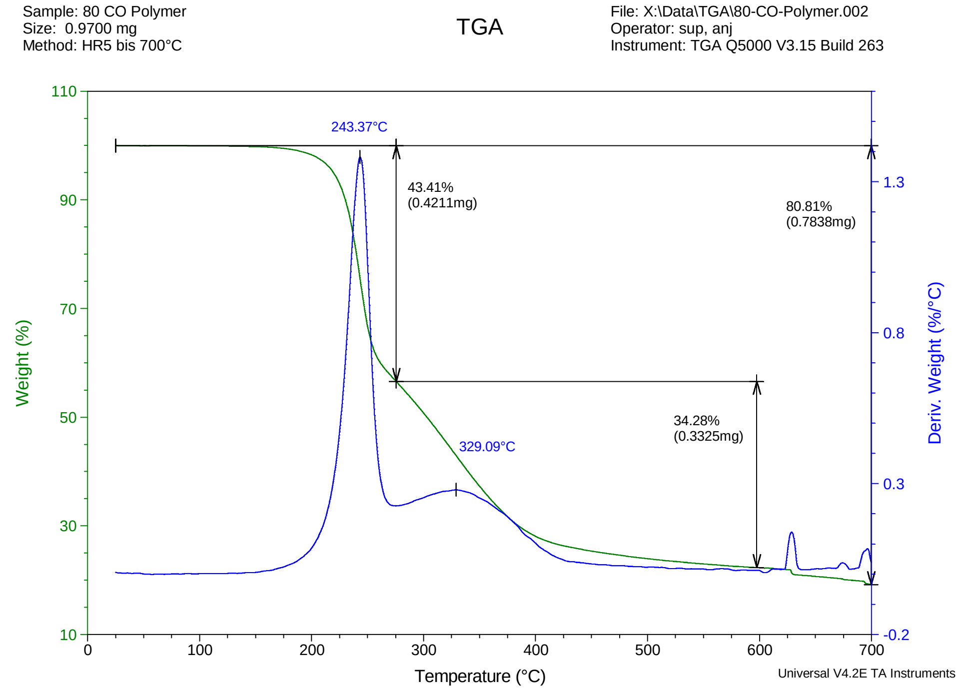

Figure 10: TGA of copolymer GA/BAMO

The copolymer GA/BAMO shows weight loss from temperatures above 160 °C. The weight loss occurs in two steps. A fast weight loss of 43 mass-% between 190 to 250 °C and a second slowly weight loss of 34 mass-% between 250 to 600 °C. This decomposition behavior is typical for azido polymers. During the first step of weight loss the azido groups decompose and evolve nitrogen. At higher temperatures the degradation of remaining residues and the polymer backbone occurs.

Glass transition temperature of copolymer GA/BAMO

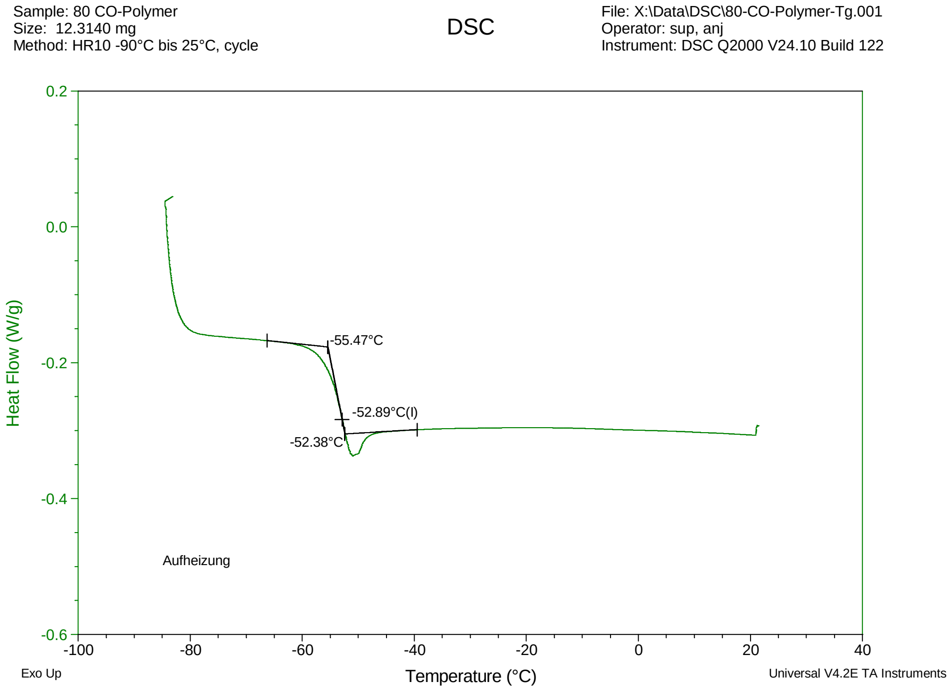

Figure 11: Glass transition temperature of copolymer GA/BAMO

The Tg of copolymer GA/BAMO lays at -52.9 °C which is useful for propellant formulations.

Density of copolymer GA/BAMO

Table 4: Density of copolymer GA/BAMO

Measuring of density with He-Gas pycnometer at 20°C system XS		
Sample	**Density (g/cm³)**	**Volume (cm³)**
Copolymer GA-BAMO sample mass = 3.7439 g	1,2510	2,9927
	1,2503	2,9945
	1,2507	2,9934
	1,2500	2,9952
	Average 1,2505	***2,9939***

The density of copolymer GA/BAMO is 1.25 g/cm³ and slightly lower than the density of GAP which is given with 1.29 g/cm³ [12].

Viscosity of copolymer GA/BAMO

The viscosity of copolymer GA/BAMO has been measured at three different temperatures at shear rates from 10^{-1} to 10^3 s^{-1}. The copolymer shows the behavior of a Newtonian fluid at 40 and 60 °C. At 20 °C the polymer showed reduced viscosity at shear rates higher than 10^2 s^{-1} (thixotropic behavior).

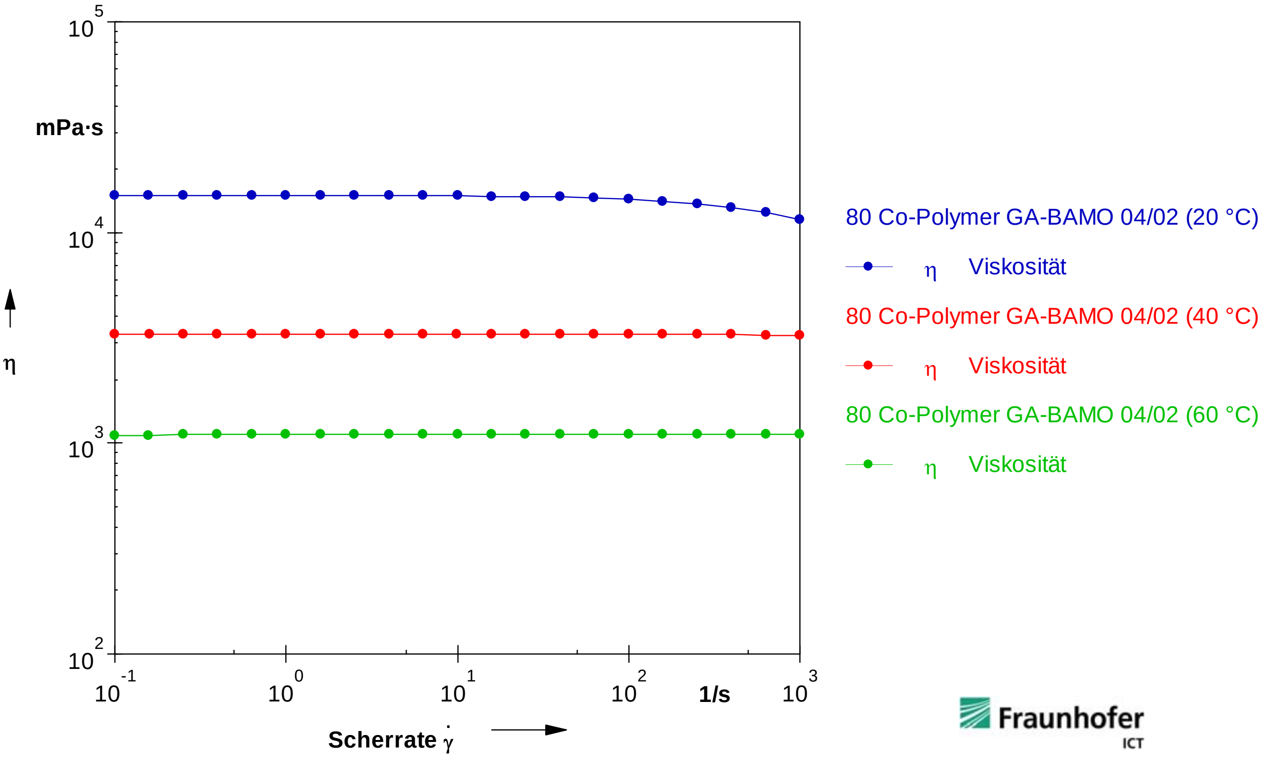

Figure 12: Viscosity of copolymer GA/BAMO

Heat of combustion of copolymer GA/BAMO

The measuring has been done with three samples and the average heat of combustion was 21923 J/g.

Table 5: Heat of combustion of copolymer GA/BAMO

Sample	**Heat of combustion [J/g]**	**Sample weight [g]**	**△T [K]**	**Energy from ignition [J]**	**C-value [J/K]**
	IKA C 2000				
Copolymer GA-BAMO	21919	1,0444	2,5798	120	8920
	21950	0,9909	2,4546	120	8910
	21899	1,1864	2,9261	120	8920
	21923				

Elemental analysis of copolymer GA/BAMO

Table 6: Elemental analysis of copolymer GA/BAMO

Sample	**Content [mass-%]**					**Mass**
	Nitrogen	**Carbon**	**Hydrogen**	**Sulfur**	**Oxygen**	**Balance**
Copolymer GA/BAMO	**35,19**	**40,04**	**5,44**	**0,00**	**18,08**	**98,74**
standard deviation [+/-]	0,186	0,118	0,240	0,000	0,590	

The elemental analysis of copolymer GA/BAMO shows unexpected low nitrogen content. Our copolymer consisting of BAMO and GA units should have higher nitrogen content than GAP. The BAMO unit has 49.98 mass-% nitrogen and the GA units has 42.41 mass-% nitrogen. During the purification of the halogenated precursor copolymer ECH/BBrMO two side compounds have been identified. These were 2-chloromethyl-1,4-dioxane as an oil and crystals from 2,5-bis(chloromethyl)-1,4-dioxane. The 2-chloromethyl-1,4-dioxane is a reaction product built from the monomer epichlorohydrin and dioxane which was the solvent of the polymerization reaction. From this can be concluded that dioxane participated during the polymerization reaction and might have been incorporated into the polymer backbone. This could explain the low nitrogen content. The theoretical elemental analysis has been calculated for the following circumstances:

- 25 to 50 g of epichlorohydrin did not polymerize into the copolymer ECH/BBrMO and instead it was removed as 2,5-bis(chloromethyl)-1,4-dioxane and 2-chloromethyl-1,4-dioxane
- 6.0 to 6.5 moles of –CH2CH2O- units from solvent dioxane have been incorporated into the copolymer backbone

The following Table 7 gives the results for these calculations. From these calculations it can be estimated that between 25 to 50 g epichlorohydrin did not polymerize and around 6 to 6.5 moles CH_2CH_2O units from dioxane were incorporated into the polymer.

Table 7: Calculated elemental analysis of copolymer GA/BAMO

	Content [mass-%]				
		Nitrogen	**Carbon**	**Hydrogen**	**Oxygen**
25 g epichlorohydrin were removed	6 mol CH_2CH_2O have been incorporated in the polymer	36.07	39.93	5.84	18.16
	6.5 mol CH_2CH_2O have been incorporated in the polymer	35.47	40.18	5.90	18.46
50 g epichlorohydrin were removed	6 mol CH_2CH_2O have been incorporated in the polymer	35.93	40.01	5.86	18.2

CONCLUSIONS

Copolymer ECH/BBrMO in molar ratio of 72.5/27.5 (ECH/BBrMO) could be azidated in 1.1 kg scale successfully. The azido copolymer GA/BAMO has been characterized via IR-spectroscopy, thermal analysis (DSC, TGA, Tg), impact sensitivity, end group analysis, molecular mass measurement (GPC), density, viscosity, heat of combustion and elemental analysis. The original aim to synthesize a copolymer with higher energy content than GAP could be not reached. The copolymer showed nitrogen content of 35.1 % which is lower than the nitrogen content of GAP (42.4 %). It seems to be that the solvent dioxane participated in the polymerization and led to incorporation of CH_2CH_2O units in the polymer backbone. This reduced the nitrogen content. However the copolymer showed promising properties during characterization. The polymer is insensitive against impact, has low glass transition temperature, good functionality and low content of cyclic oligomers which are often present in polymers synthesized from cationic polymerization. The copolymer has been evaluated in Al/AP based propellant successfully. Future work will focus on better control of the polymerization and the incorporation of CH_2CH_2O units in the polymer backbone.

ABBREVIATIONS

ADN	ammonium dinitramide
AP	ammonium perchlorate
ATR	attenuated total reflectance
BAM	Federal Institute for Materials Research and Testing - Berlin
BAMO	3,3-bis(azidomethyl)-oxetane
BBrMO	3,3-bis(bromomethyl)-oxetane
BF_3-THF	boron trifluoride complex with tetrahydrofurane
D	polydispersity index of molecular weight
DMSO	dimethyl sulfoxide
DSC	differential scanning calorimetry
ECH	epichlorohydrin
EDA	European Defence Agency
Eq. Wt.	equivalent weight
FPNEM	EDA project “Formulation and Production of New Energetic Materials” PA No B-0585-GEM2-GC
GA	glycidyl azide (monomer unit of GAP)
GAP	glycidyl azide polymer
GPC	gel permeation chromatography
IR	infrared (spectroscopy)
Mn	molecular weight; number average
Mp	molecular weight at peak maximum
Mw	molecular weight; weight average
PECH	poly-epichlorohydrin
poly-BAMO	poly-3,3-bis(azidomethyl)-oxetane
poly-ECH/BBrMO	poly-epichlorohydrin-r-(3,3-bis-bromomethyloxetane)
poly-GA/BAMO	poly-glycidyl azide-r-(3,3-bis(azidomethyl)oxetane)
PSS	Polymer Standards Service (company name)
Tg	glass transition temperature
TGA	thermogravimetric analysis

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LITERATURE

[1] M.Y. Murali, R.M. Padmanabha, R.K. Mohana, Synthesis, Spectral and DSC Analysis of Glycidyl Azide Polymers Containing Different Initiating Diol Unit, J. Appl. Polym. Sci. **2004**, 93, 2157

[2] R.D. Schmidt, G.M. Manser, Heats of Formation of Energetic Oxetane Monomers and Polymers, Proceedings 32nd International Annual Conference of ICT (**2001**), Karlsruhe, Germany, P 140

[3] M.Y. Murali, Y. Mani, R.K. Mohana, Synthesis of Azido Polymers as Potential Energetic Propellant Binders, Des. Monomers Polym. **2006**, 9, 201

[4] U. Barbieri, G. Polacco, R. Massimi, Synthesis of Energetic Polyethers from Halogenated Precursors, Macromol. Symp. **2006**, 234, 51

[5] A.M. Kawamoto, U. Barbieri, T. Keicher, H. Krause, J.A.S. Holanda, M. Kaiser, G. Polacco, Synthesis and Characterization of Glycidyl Azide-r-(3,3-bis(azidomethyl)-oxetane) Copolymers, Propellant, Explos. Pyrotech., **2008**, 33, 365

[6] K. Menke, P.B. Kempa, T. Keicher, A. Kawamoto, J.A.S. Holanda, High Energetic Composite Propellants based on AP and GAP/BAMO Copolymers, Proceedings 38th International Annual Conference of ICT (**2007**), Karlsruhe, Germany, P82

[7] U. Barbieri, G. Polacco, T. Keicher, R. Massimi, Preliminary Characterization of Propellants Based on p(GA/BAMO) and pAMMO Binders; Propellants Explos. Pyrotech. **2009**, 34, 427 – 435

[8] A.M. Kawamoto, M.F. Diniz, V.L. Lourenço, M.F.K. Takahashi, T. Keicher, H. Krause, K. Menke, P.B. Kempa, Synthesis and characterization of GAP/BAMO copolymers applied at high energetic composite propellants; J. Aerosp.Technol. Manag., São José dos Campos, Vol.2, No.3, pp. 307-322, Sep-Dec., **2010**

[9] S. Pisharath and H.G. Ang, Synthesis and thermal decomposition of GAP-Poly(BAMO) copolymer; Polymer Degradation and Stability 92 (**2007**) 1365-1377

[10] V. Gettwert, T. Keicher, A. Franzin, M. Jung, V. Weiser, EVALUATION OF GA/BAMO-COPOLYMER BINDER FOR AL/AP-BASED PROPELLANTS; Proceedings 44th International Annual Conference of ICT (**2014**), Karlsruhe, Germany, P 93

[11] T. Keicher, S. Steinert, M. Dörich, H. Krause, M. Raab, U. Schaller, W. Schweikert, Scale up of the polymerization of copolymer ECH/BBrMO as precursor for an energetic polymer; Proceedings 43th International Annual Conference of ICT (**2013**), Karlsruhe, Germany, P 76

[12] B. Finck, H. Graindorge, New Molecules for High Energetic Materials Proceedings 27th International Annual Conference of ICT (**1996**), Karlsruhe, Germany, V 23