

INTERNAL PLASTICIZED GLYCIDYL AZIDE POLYETHERS FOR SOLID PROPELLANT BINDERS

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ABSTRACT

Copolymers of epichlorohydrin and *n*-alkyl substituted oxiranes were synthesized by the application of cationic ring-opening polymerization (CROP) using a BF₃ complex as a catalyst and 1,4-butanediol as a co-initiator, followed by a subsequent azidation. The introduction of nonpolar side chains shows an internal plasticizing effect by lowering the glass-transition temperatures (T_g) and the viscosities of the synthesized copolymers compared to a commercial sample of GAP. Due to the improved low temperature properties of the prepolymers, they are interesting candidates for the formulation of composite rocket propellants.

The contribution has to be considered as an extended abstract, the full paper will be published elsewhere.

INTRODUCTION

By replacing HTPB with an energetic polymer, additional energy for the combustion process of composite propellants can be provided. Several energetic polymers are published and discussed in the literature, but all of them suffer from different drawbacks, mostly because of poor mechanical properties and bad low temperature properties.^{1,2} For the formulation of composite propellants, the most extensively studied energetic prepolymer is glycidyl azide polymer (GAP) but its glass transition temperature (T_g) of approximately - 45 °C is still too high for many applications.^{3,4} To

meet the requirements, the formulations often have to contain high amounts of plasticizers that can lead to severe issues because of plasticizer migration phenomena.

As a novel approach, glycidyl azide polymers containing *n*-alkyl side chains acting as internal plasticizers were synthesized and characterized with emphasis on the use as prepolymers for energetic binder systems applied at composite propellants.

EXPERIMENTAL SECTION

Reagents

Solvents and reagents were purchased from Acros Organics, Sigma-Aldrich or Merck and used as received, unless otherwise stated. Dichloromethane (DCM) was refluxed over P₂O₅ for 4 hours, distilled and stored over 4 Å molecular sieves. Epichlorohydrin (ECH) and all comonomers were distilled over CaH₂ and stored under nitrogen atmosphere in a fridge. 1,4-Butanediol (BDO) was purchased from Sigma-Aldrich and stored over 4 Å molecular sieves. BF₃·THF was purchased from Sigma-Aldrich, distilled and stored under nitrogen in a fridge.

Instrumentation

IR spectra were measured on a Thermo Scientific Nicolet 6700 (FTIR-Spectrometer) with Durascope diamond ATR accessory. 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 (M_p) from 162 to 1210000 g/mol have been used for calibration. Differential scanning calorimetry (DSC) was performed on a TA instruments Q 1000 using aluminum pans. Scans were carried out at scan rates of 5 °C min⁻¹, under nitrogen flux.

General Method for Polymerization ⁵

To a stirred mixture of 1,4-butanediol and DCM, BF₃·THF was added under nitrogen atmosphere. The resulting emulsion was stirred for 15 minutes at 20 °C. A solution consisting of epichlorohydrin (75 mol %), the respective comonomer (25 mol %) and DCM was added slowly using a dosing pump at a temperature of 10 °C.

After complete addition, the resulting clear viscous was stirred at 10 °C for 12 h. DCM was added to dilute the mixture and distilled water was added for quenching the reaction. Then saturated NaHCO₃ solution was added and stirring was continued for additional 15 minutes. The organic layer was separated and washed three times with distilled water. Neutralization was checked with pH-paper. After drying over MgSO₄, the solvent was evaporated at a maximum temperature of 80 °C under reduced pressure. The products were obtained as clear colourless viscous liquids.

General Method for Azidation⁵

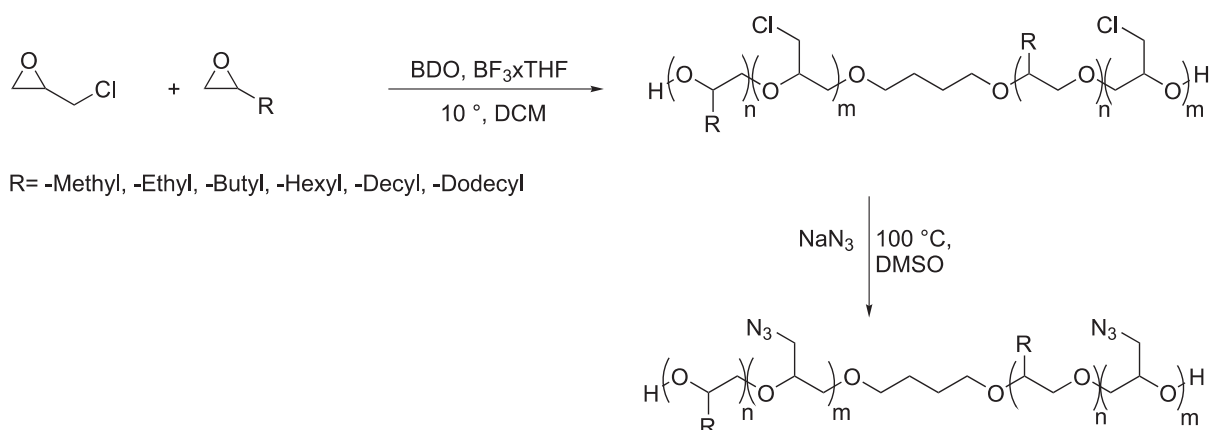
Synthesis should be performed with usual precautions for handling of explosive substances!

The halogenated precursor polymer was dissolved in DMSO and added to a round bottom flask equipped with a condenser and a magnetic stirring bar. The solution was heated up to 100 °C and sodium azide was added to the reaction mixture. The reaction was continued until IR spectroscopy indicated complete conversion (48h). After the reaction was completed, the mixture was cooled down to room temperature, transferred in a beaker and ethyl acetate together with distilled water was added. The organic layer was separated and washed with distilled water several times. After drying over MgSO₄, the solvent was evaporated using a rotary evaporator. Drying was continued under reduced pressure (3 mbar) at 80 °C to remove residues of solvent. The products were obtained as clear, slightly yellow, viscous liquids.

RESULTS AND DISCUSSION

A recent publication discussed the internal plasticizing effect of *n*-butyl chains that were introduced in glycidyl azide polymer (GAP).⁵ In order to study the influence of the side chain length on the polymeric properties, novel glycidyl azide copolymers with a varying side chain length were synthesized and characterized.

Cationic ring-opening polymerization using BF₃·THF as a catalyst and 1,4-butanediol (BDO) as a co-initiator, delivered PECH copolymers that were azidated by using a mixture of DMSO and sodium azide in a subsequent synthesis step (see Figure 1). The resulting products were obtained as clear, slightly yellow viscous liquids, similar to GAP.



R= -Methyl, -Ethyl, -Butyl, -Hexyl, -Decyl, -Dodecyl

Figure 1: Synthesis of glycidyl azide polyethers with nonpolar *n*-alkyl side chains.

The molecular structure and composition of the resulting polymers was checked by NMR and IR spectroscopy. In all cases a molecular composition of 75 mol % glycidyl azide (GA) units and 25 mol % of *n*-alkyl substituted units was targeted, by choosing a suitable comonomer ratio in the synthesis procedure. The final composition in the resulting products was checked by ¹H NMR spectroscopy.

An exemplary IR spectrum of such glycidyl azide copolyethers is shown in Figure 2. The signal at 1108 cm⁻¹ (s) is associated with the C-O-C polyether backbone. The strong signal at 2093 cm⁻¹ (s) belongs to the azido groups. The complete disappearance of a signal at 745 cm⁻¹ (s) that is caused by the C-Cl stretching vibration of the precursor PECH copolymer indicates quantitative substitution, that was also checked by ¹³C NMR spectroscopy and a Beilstein test for all synthesized samples.

Table 1: Copolymers synthesized by CROP using a [M]/[I]=30 ratio and [OH]/[Cat.] ~ 30.

No	Copolymer	Moiety	M _n	PDI	T _g	N [wt. %]
-	GAP (Lot 06S12)	-	2507	1.23	-48.6	41.89
1	P(GA-co-EpP)	-Methyl	2081	1.84	-52.6	33.90
2	P(GA-co-EpB)	-Ethyl	1908	1.80	-54.0	32.62
3	P(GA-co-EpH)	-Butyl	1928	1.85	-56.8	30.36
4	P(GA-co-EpO)	-Hexyl	1972	1.90	-60.5	28.45
5	P(GA-co-EpD)	-Decyl	2308	1.94	-61.7	26.18
6	P(GA-co-EpT)	-Dodecyl	2014	1.65	m.p.	24.22

Table 1 shows details about the molecular weight distributions. The polydispersity indices could be kept below 2, which can be considered as a good result for cationic copolymerization.

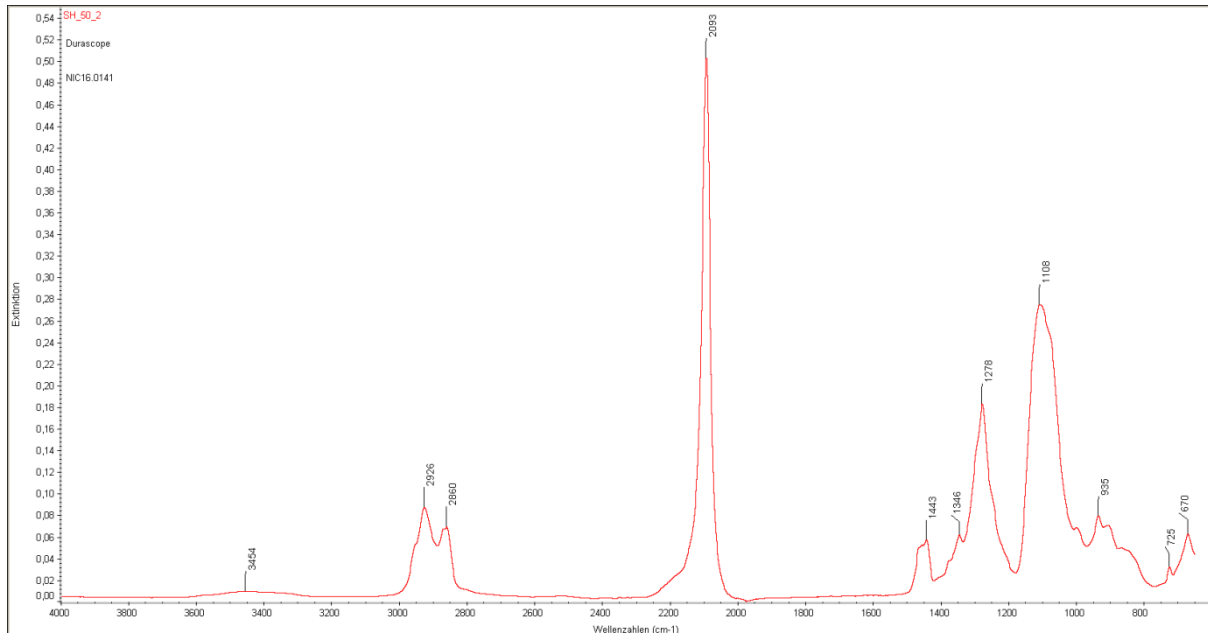


Figure 2: IR spectrum of copolymer sample No. 4

As expected, the glass transition temperature decreased with increasing side chain length from C1 (-methyl) to C10 (-decyl). P(GA-co-EpT) copolymer showed an additional melting point at -28.0 °C, due to phase separation of the nonpolar side chains and the polar polyether backbone and is therefore not suitable for the formulation of propellants (Figure 3). By comparing the achieved T_g with the nitrogen content, that was determined by elemental analysis (Table 1), P(GA-co-EpO) No. 4 was identified as a promising trade-off between improved low temperature properties and loss of energy due to the lower azido content in the molecular structure of the copolymer and will therefore be further investigated concerning the energetic properties and performance in propellant formulations. The results will be published in a separate full paper publication.

Sample: SH 128.1
Size: 4.8100 mg
Method: HR10 von -90 bis 25°C

DSC

File: Z:\DSC\SH 128-1-Tg.001
Operator: sup, anj
Instrument: DSC Q2000 V24.10 Build 122

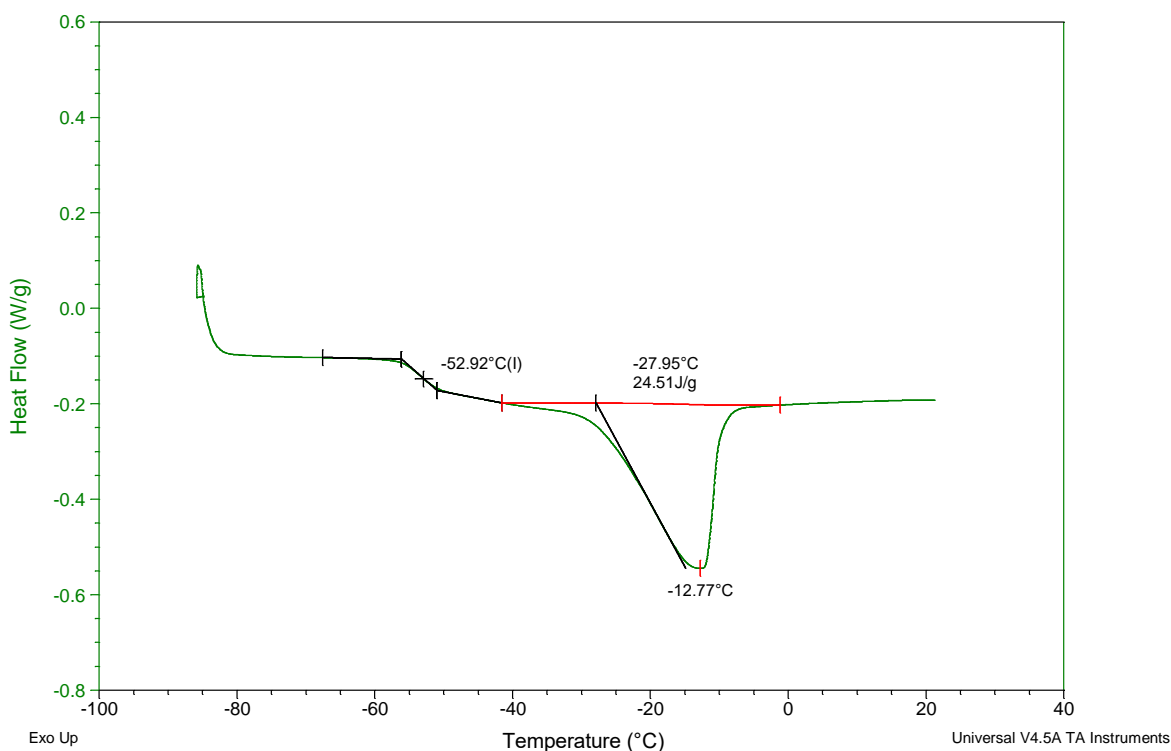


Figure 3: DSC curve of copolymer sample No. 6 (see Table 1) – Melting point due to phase separation.

CONCLUSIONS

The synthesis of glycidyl azide copolyethers with *n*-alkyl side chains showed the desired internal plasticizing effect by lowering the glass transition temperatures and viscosities of the copolymers compared to the reference compound GAP. 1,2-Epoxyoctane was identified as a suitable comonomer for further studies. Based on the analysis results, the copolymer consisting of approximately 75 mol % GA and 25 mol % EpO units is supposed to be an interesting candidate for the formulation of composite rocket propellants. Further results will be published elsewhere.

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
PECH Polyepichlorohydrin
ppm parts per million
RID Reflective index detector
Sec Size exclusion chromatography
T_g Glass transition temperature
TGA Thermogravimetric analysis
THF Tetrahydrofurane

ACKNOWLEDGEMENTS

The authors would like to thank H. Schuppler and J. Aniol for TGA and DSC. H. Popp for measuring sensitivity towards impact, M. Dörich for GPC, W. Schweikert for IR analysis and M. Kleine-Beek for support in the synthesis laboratory.

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