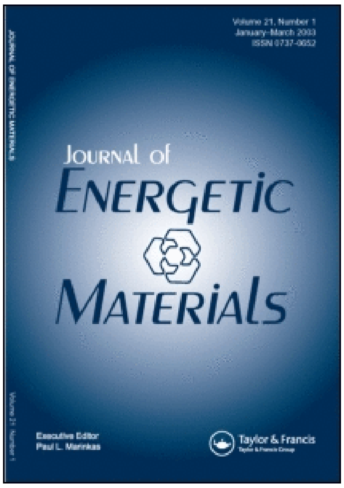

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Dendtritic Azido Ester: A Potential Energetic Additive for High Energy Material (HEM) Formulations

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A second-generation [G-2] terminally azido functionalized dendritic ester has been synthesized from a commercially available dendritic polyol BOLTORN® H20. Structural features were confirmed by IR, ^{1}H NMR, and elemental analysis. The differential scanning calorimetry (DSC) analysis shows an acceptable thermal stability for practical applications in high energy material formulations.

Keywords: azidoesters, BOLTORN, dendrimers, differential scanning calorimetry, energetic additive, energetic materials, lubricant, plasticizers, polymeric binders, processing aid, toughening agent

Introduction

A recent trend in the field of energetic material formulations - (explosives/propellants) is to replace inert binders (*viz.*, HTPB, CTPB, HTPE, etc.) by energetic azido polymeric binders like GAP, BAMO, AMMO, etc., to impart additional energy to the system.

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But these azido-polymeric binders have certain drawbacks associated with them such as poor processibility, low solid loading, and inferior mechanical properties in energetic formulations. In order to overcome these problems there is a great need for suitable additives, which can act as processing aid and toughening agent.

Azido-ester plasticizers have received much attention in order to improve processibility and solid loading of azido-polymeric binders. Compared to known nitrate ester plasticizers, e.g., TMETN and BTTN, azido-ester plasticizers have been reported to have better stability and good compatibility with binders like GAP [1].

Dendrimers are repetitively branched three-dimensional (3D) molecules with all bonds emanating from a central core. The compact 3D structure of dendrimers lets them flow easily past each other under applied stress. They show low T_g and low viscosity due to lack of restrictive inter-chain entanglement in contrast to most linear polymers. The dendrimer additives are able to behave as a lubricant during processing and as a toughening agent in the final blend formulation [2,3].

Considering the above facts it was attempted to combine the unique properties of dendrimers and that of azido-ester plasticizers in the same molecule. A second-generation [G-2] terminal azido functionalized dendritic ester has been synthesized from a commercially available dendritic polyol BOLTORN® H20. The azidated BOLTORN® H20 has 16 terminal azide groups.

Experimental

Methods

Reactions were monitored by precoated silica gel 60 F_{254} (Merck) thin layer chromatography (TLC) plates. The spots on TLC plates were visualized by iodine vapors or under UV light. ^{1}H NMR spectra were recorded on Bruker-300 MHz instrument using tetra methyl silane (TMS) as an internal reference and $CDCl_3$ as solvent. IR spectra were recorded on Perkin Elmer FT-IR 1605 spectrophotometer as a neat sample. Elemental analyses were carried out on Perkin Elmer Elemental Analyzer EA-1110. BOLTORN® H20 was obtained from Perstorp Specialty Chemicals AB Sweden [4,5] and used as such.

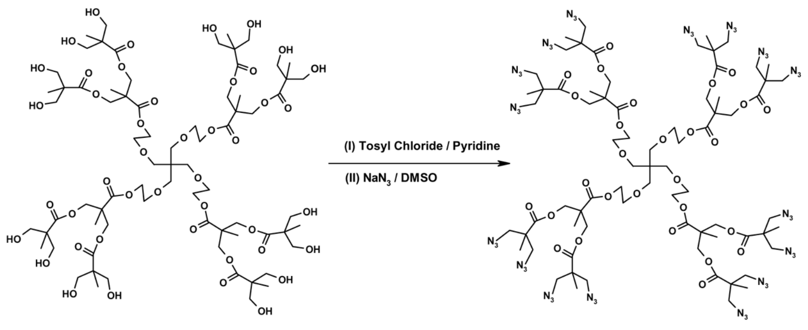
Differential scanning calorimetry (DSC) studies were carried out on a Perkin Elmer DSC-7 instrument operating at a heating rate of 10°C/min in nitrogen atmosphere with 1 to 2 mg of sample. The thermal decomposition studies were also undertaken on Mettler Toledo TG/SDTA-8551. The heat of formation in gaseous state ($\Delta H^{\circ}_{f\,(g)}$) was theoretically predicted by group additivity method [6]. The azido group's contribution to the overall $\Delta H^{\circ}_{f\,(g)}$ was extracted from the reported thermochemical measurements [7]. The sensitivity to impact was determined by the ''drop hammer'' method using a 2-kg drop weight. The results are reported in terms of height for 50% probability of explosion ($h_{50\%}$) of the sample. The friction sensitivity of the compounds was measured on a Julius Peter's apparatus until there was no explosion/ignition in five consecutive test samples at that weight. The results obtained for impact and friction sensitivity were within the uncertainty limits of ±5 cm and ±0.2 kg, respectively [8].

Synthesis

Synthesis involves two steps:

1. Tosylation of BOLTORN® H20 with p-toluene sulfonyl chloride and pyridine.
2. Azidation of tosylated BOLTORN® H20 with NaN_3 and DMSO.

The scheme of the reaction is depicted below:



BOLTORN® H20 Azidated BOLTORN® H20

Scheme 1

Tosylated BOLTORN® H20. To a solution of BOLTORN® H20 (20 g, 11.45 mmol) in 40 mL pyridine and 20 mL chloroform was added a solution of p-toluene sulfonyl chloride (52 g, 275 mmol) in 20 mL pyridine and 100 mL chloroform, drop-wise at 0°C in 1 h. The reaction mixture was stirred at 25°C for 48 h and then poured into crushed ice, neutralized with 5 N HCl, followed by extraction with CH_2Cl_2. The CH_2Cl_2 extracts were washed with saturated aq. $NaHCO_3$ and then 2–3 times with brine followed by drying over Na_2SO_4. Evaporation of solvent yielded tosylated BOLTORN® H20 (46 g, 95%).

Azidated BOLTORN® H20. To the tosylated BOLTORN® H20 (40 g, 9.5 mmol), dissolved in 200 mL DMSO, was added NaN_3 (14.8 g, 228 mmol) with cooling. The reaction mixture was warmed to 75°C and stirred until the completion of reaction (~30 h). The reaction mixture was poured into iced water and extracted with CH_2Cl_2. The CH_2Cl_2 extracts were washed 2–3 times with brine and dried over Na_2SO_4. Evaporation of solvent yielded azidated BOLTORN® H20 (17 g, 85%).

Results and Discussion

The azidated BOLTORN® H20 and the intermediate tosylated BOLTORN® H20 were fully characterized by IR, ^{1}H NMR, and elemental analysis.

Tosylated BOLTORN® H20

IR (neat, cm^{-1}) 3060 (aromatic C−H *str*), 2978 (C-H *str*), 1738 (C=O *str*), 1598 (aromatic C=C *str*). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.87 and 7.47 (Ar-*H*), 4.30–4.20 (CH_2O.OC, CH_2OTs), 3.70–3.50 (CH_2O), 2.35 (Ar-CH_3), 1.22 (CH_3).

Azidated BOLTORN® H20

IR (neat, cm^{-1}) 2942 (C-H *str*), 2108 (N_3 *str*), 1738 (C = O *str*). ^{1}H NMR ($CDCl_3$, 300 MHz) (**Fig. 1**) δ 4.32–4.25 (CH_2O.OC),

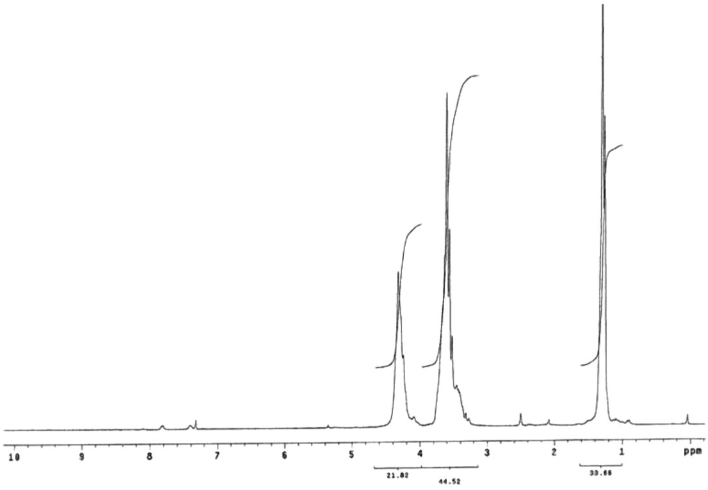


Figure 1. 1H NMR of Azidated Boltron.

3.65–3.52 (CH_2O, CH_2N_3), 1.29 and 1.26 (CH_3). Elemental analysis calculated for $C_{73}H_{108}N_{48}O_{28}$ (2106) C: 41.63%, H: 5.17%, N: 31.92%. Found C: 42.33%, H: 5.13%, N: 32.11%.

IR studies showed complete transformation of OH (*str* 3434 cm^{-1}) groups to N_3 (*str* 2108 cm^{-1}) groups. ^{1}H NMR and elemental analysis data are also in close agreement with the molecular structure. The purity of the sample can be realized by the fact that no significant additional peaks were observed in ^{1}H NMR.

Thermal studies of azidated BOLTORN® H20 by DSC and TG (Table 1) showed thermal stability up to 211°C. DSC (Fig. 2) revealed exothermic decomposition with T_{max} at 248°C and the heat release of the order of 1443 J/g. The glass transition temperature (Tg) was found −35°C. The TG studies showed the weight loss of 61% in the temperature range 211–338°C with the energy of activation of 335 kJ/mol for the decomposition step.

The values for impact and friction sensitivity (Table 1) indicate that the compound is fairly insensitive towards impact and friction stimuli.

Table 1
Properties of Azidated BOLTORN® H20

DSC	
T_{max} (°C)	248
Heat release (J/g)	1443
Tg (°C)	−35
TGA weight loss (%)	61 (211°–338°C)
Energy of activation (kJ/mol)	335
Oxygen Balance (%)	−130.8
Heat of Formation, $\Delta H_f^{\circ}{}_{(g)}$ (kJ/mol)	−141
Impact Sensitivity (cm)	>170
Friction Sensitivity (kg)	36

The azidated BOLTORN® H20 showed good compatibility with azido-polymeric binders GAP and BAMO. Evaluation studies of the compound as an additive in GAP to improve processibility and mechanical properties are in process.

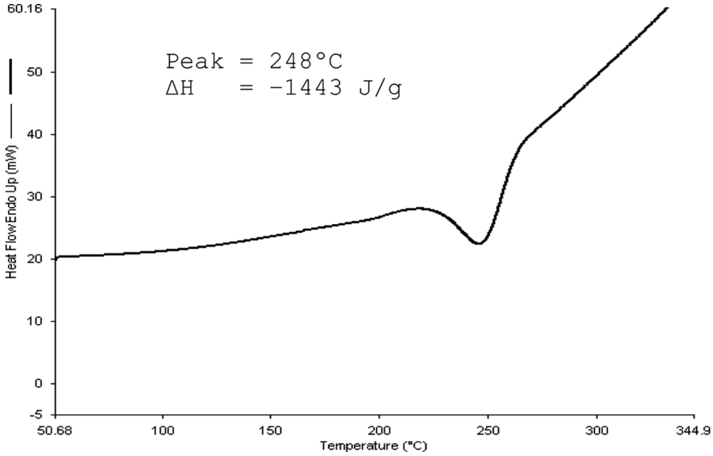


Figure 2. DSC of Azidated Boltron.

Conclusion

A second-generation [G-2] dendritic ester bearing 16 terminal azido functionality was syhthesized successfully from BOLTORN® H20. The intermediate tosylated product and the final azido compound were characterized spectroscopically and thermally.

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