Design of an Ammonium Dinitramide Compatible Polymer Matrix

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ABSTRACT: To enable future environmentally friendly access to space by means of solid rocket propulsion a viable replacement to the toxic ammonium perchlorate (AP) oxidizer is needed. Ammonium dinitramide (ADN) holds great promise as a green replacement. Unfortunately compatibility issues with many polymer binder systems have hampered the development of ADN-based formulations. Herein we present proof-of-concept of a polymer cure system based on hyperbranched copolymers of 3-ethyl-3-(hydroxymethyl)oxetane (TMPO) and tetrahydrofuran (THF). The partly alkyne-functionalized macromolecules were synthesized in a one-pot procedure. TMPO and THF are found to polymerize in exact ratios, indicating a kinetically controlled buildup of nonrandom composition copolymers. Several of the materials show excellent compatibility with ADN, and rapid curing of the energetic polyglycidyl azide polymer (GAP) have been demonstrated through 1,3-dipolar cycloaddition at 75°C. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 1–11, 2011

Key words: ADN; cationic polymerization; compatibility; copolymers; curing of polymers; ring-opening polymerization

INTRODUCTION

There is an environmental incentive towards replacing the harmful chemical ammonium perchlorate, NH_4ClO_4, (AP), which is a widely used oxidizer in solid rocket propellant formulations. AP is the main component in several large-scale solid rocket booster systems, such as the American Space shuttle[1] and the European Arianne 5 launch vehicle,[2] and produce large amounts of hydrochloric acid (HCl) upon combustion. Ammonium dinitramide, $NH_4N(NO_2)_2$, (ADN) is an energetic and chlorine free oxidizer, and constitutes one of the few real alternatives to AP.[3,4] It has been estimated that if ADN was to replace AP the lift capacity of large space launchers would increase by $\sim$ 8%, while significantly reducing their environmental impact.[5]

An ADN-based liquid propellant is currently being tested in low earth orbit, in the navigational thrusters of the PRISMA satellite.[6] However, incompatibility issues with commonly used polymer binder systems still hinder the development of solid ADN-based propellants. Many polymer matrices used in today's solid rocket propellants are made through the urethane-bond forming reaction between isocyanate-based curing agents and hydroxyl groups, present in polyols such as hydroxyl terminated polybutadiene (HTPB) or hydroxyl terminated polyether (HTPE). Unfortunately the isocyanate functionality has proven incompatible with ADN.[7,8]

The 1,3-dipolar cycloaddition reaction[9] between alkyne and azide is considered a viable alternative to isocyanate-based cure (crosslinking) chemistry, and several patents and articles based on this idea have been published.[10–13] Unfortunately, the issue of ADN-compatibility has rarely been addressed. The cycloaddition approach has in recent times been applied to ADN by Menke et al.,[14,15] who reported curing of the energetic poly(glycidyl azide) polymer (GAP, H-(O-$CH(CH_3N_3)CH_3)_n$-OH)[16] using bispropargyl succinate (BPS).[14,15,17] Aside from an unfortunate high thermal sensitivity, and an early tendency to deflagration, these formulations are reported to be comparable to similar AP-formulations.[15]

The synthesis and basic properties of hyperbranched poly-(3-ethyl-3-(hydroxymethyl)oxetane) (poly-TMPO, Fig. 1) has been reported during the last decade.[18–23] Recent studies show that materials derived from the TMPO monomer holds promise in

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a variety of applications and processes, such as surface modification,[24,25] anion recognition,[26] protein separation,[27] organic electronics,[28,29] and catalysis[30] to name a few.

As ADN is an energetic compound its thermal decomposition and reactions with its chemical surrounding are expected to be exothermic. Heat flow calorimetry (HFC) is a standard method for determining the thermal stability of propellant formulations.[31] We have recently reported that hyperbranched poly-TMPO is remarkably stable when evaluated for use with ADN.[32] Our earlier HFC-study also revealed ADN to be exceedingly incompatible with poly(ethylene glycol) (PEG), and various other chemicals.[32] The experimental findings are in good agreement with quantum chemical calculations, which argue for the importance of hydrogen bond donating chemical environments for ADN-compatibility.[33] In the research that followed we have pursued various alkyne-functionalized poly-TMPOs and copolymers of TMPO and tetrahydrofuran (THF).

The copolymerization of oxentanes with THF has been well established by Penczek et al.[34] and Vandenberg et al.[35] Similarly, copolymers of THF and energetic monomers such as bis azido methyl oxetane (BAMO) have also been reported.[36] Many other copolymers including hyperbranched and linear segments are known.[37–39]

We have investigated how inclusion of THF can increase the flexibility of our hyperbranched systems (i.e., reduce their glass transition temperature). Our efforts have been aimed towards a material that can be used as a curing agent with the ADN-compatible GAP polymer. Similar to the work of Menke et al.,[15] we have chosen to work with alkyne groups situated on a propargyl ester functionality, as such mildly electron poor alkynes enables fast reaction rates at moderate temperatures.[40]

After that the regioselective cupper(I) catalyzed 1,3-dipolar cycloaddition reaction was discovered by Sharpless[41] and Meldal[42] with coworkers, it has successfully been marketed within the field of "click chemistry."[43,44] The reaction has received considerable attention in many disciplines of chemistry, where it provides straightforward and atom efficient synthetic steps.[45] The Cu(I) catalyst enables predominantly 1,4-regioisomers of the triazole product and fast reaction rates at mild conditions. Unfortunately Cu(I) forms a highly sensitive explosive together with the dinitramide anion. Because of this the use of this metal together with ADN should be avoided. As regioselectivity is not necessary for our purposes we have instead performed all curing cupper-free, at elevated temperature (75°C).

The 1,3-Dipolar cycloaddition reactions between alkynes positioned on hyperbranched macromolecules, with the pendant azide group of GAP constitutes a novel approach to propellant cure systems. In contrast to more conventional cure chemistry, in which low molecular weight curing agents are used (e.g., BPS, in the case of Menke et al.[15]), this method has the advantage of increased design flexibility. The relatively low viscosity of hyperbranched structures[46] provides good processability, while a large number of functional groups enable efficient tailoring of multiple properties, such as compatibility, elasticity, and reactivity. The goal of this work has been to provide proof-of-concept for a propellant cure system based on easily modifiable hyperbranched macromolecules. The presented materials are easily attained through one-pot syntheses using commercially available and affordable chemicals, such as THF and TMPO, and their work-up utilizes nontoxic solvents, such as water and ethanol.

EXPERIMENTAL

Materials

Propargyl alcohol (99%), succinic anhydride (99%), 4-(dimethylamino)pyridine (≥99%) (DMAP), $NaHSO_4$, *N,N′*-Dicyclohexylcarbodiimide (99%) (DCC), tri(ethylene glycol) monoethyl ether (tech), methanesulfonyl chloride (≥98%), and NaN_3 (≥99.5) were all purchased from SigmaAldrich. THF (p.a.) and CH_2Cl_2 (p.a.) were purchased from Merck. 3-ethyl-3-(hydroxymethyl)oxetane (TMPO) was kindly supplied by Perstorp AB. Boron trifloride diethyl etherate, BF_3OEt_2 was purchased from Fluka and kept cold under argon. Por 7 38mm dialysis tubing (1K MWCO) was purchased from Spectrumlabs. GAP diol (batch 904S99, M_n = 1750 g/mol, M_w = 1950 g/mol) was purchased from SNPE, France. Ammonium dinitramide (batch 20079002, ≥99.4%) (ADN) was purchased from EURENCO Bofors AB. All glassware was dried over night at 150°C before use.

Apparatus

^{1}H-NMR spectra were obtained on a 500MHz Bruker spectrometer using DMSO-d_6 and $CDCl_3$ as solvents. Quantitative ^{13}C-NMR spectra were obtained on the same machine, utilizing an inversely gated and proton decoupled pulse sequence, with an 8 s relaxation delay and noise suppression. Size exclusion chromatography (SEC) was performed on a Viscotek TDA Model 301 with THF as mobile phase (1 mL min^{-1}, 35°C). The instrument was equipped with two GMH_{HR}-M columns with TSK-gel from Tosoh Biosep, a VE 5200 GPC autosampler, a VE 1121 GPC solvent pump, and a VE 5710 GPC degasser (all from Viscotek corp.). A conventional calibration method was created using narrow linear polystyrene standards. Corrections for the flow rate fluctuations

were made using toluene as an internal standard. Differential scanning calorimetry (DSC) was used to thermally characterize the samples, which were ramped twice between −60 and 150°C using a heating/cooling rate of 10°C min^{-1}. The glass transition temperatures, T_g, were obtained from the second heating scans. Thermogravimetric analysis (TGA) was performed in oxygen atmosphere, between 25 and 500°C, at a heating rate of 10°C min^{-1}. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) experiments were attempted on a Bruker UltraFlex with a SCOUT-MTP Ion Source equipped with a N_2 laser (332 nm), a gridless ion source and reflector design. Spectra were recorded using a reflector-positive method with an acceleration voltage of 25 kV and a reflector voltage of 26,3 kV. 9-Nitroanthracene with sodium trifluoroacetate, 2,5-dihydroxy-benzoic acid (DHB), 2-(4-hydroxy-phenylazo)benzoic acid (HABA), 2-cyano-4-hydroxyl-cinnamic acid (HCCA), indoleacrylic acid (IAA) and 2,4,6-trihydroxyacetophenone monohydrate (THAP) in methanol, were tried as matrices. The thermal stability of ADN and GAP was measured using a Thermometric TAM 2277 heat flow calorimeter. The measurements were performed at 75°C for 19 days according to STANAG 4582,[31] where a heat flow below 63.1 μW g^{-1} is used as a criterion for sufficient thermal stability/compatibility. Approximately 0.2 g sample was used in each measurement. Curing behavior was studied using a StressTech Melt HR rheometer (Reologica AB, Sweden). Viscosity of mixtures of GAP and materials **9** and **10** was measured at 75°C using a StressTech Melt HR Rheometer. The curing process (complex viscosity measurement) was studied using the oscillating strain control mode. The temperature was held constant at 75°C, the frequency was set to 0.1 Hz and the strain was 0.001 during all measurements.

Synthesis of TMPO homopolymer (1)

TMPO (10 g, 86 mmol) was added to a three-necked round bottom flask with a magnetic stirrer, which was lowered into a preheated oil bath set to 90°C. The system was flushed with dry nitrogen gas for 30 min. BF_3OEt_2 (40 mg, 0.28 mmol) was dissolved in dry toluene (1 mL) and added to the reaction vessel. Toluene was seen to boil of, as the exothermic polymerization takes place rapidly. After 20 min, stirring had completely halted and a highly viscous and transparent polymer was formed. After an additional hour the crude polymer was dissolved in hot ethanol and precipitated in cold water. The pure polymer was dried under vacuum at 50°C over night.

^{1}H NMR (500 MHz, DMSO-*d*6): δ 4.14-4.15 (m, 1H, -O*H*), 3.27-3.28 (s, 2H, -C-CH_2-OH), 3.15 (s, 2H, -CH_2-O-CH_2-C-), 1.27 (m, 2H, CH_3-CH_2-), 0.79 (m, 3H, CH_3-CH_2-) ppm.

^{13}C NMR (125 MHz, H-decoupled, DMSO-*d*6): δ 73.31, 71.57, 70.34 (-O-CH_2-C-), 62.03, 61.39, 60.73 (-C-CH_2-OH), 43.47, 43.32, 43.27, 43.12, 43.01 (-*C*-), 23.14(D), 22.56(L), 21.98(T) (-C-CH_2-CH_3), 7.58, 7.16 (-C-CH_2-CH_3) ppm. D, L and T denotes dendritic, linear and terminal units.

Synthesis of TMPO-THF copolymers (3-8)

Polymers **3-8** (Scheme 1) were all prepared using identical equipment and pretreatments as polymer **1**. Because of the slower reaction rate of the THF containing system, the catalyst BF_3OEt_2 could be added nondiluted and drop wise using a thin needle. All experiments, except **3**, used approximately 40 mg (0.28 mmol, ∼ 0.1 wt %) of BF_3OEt_2 catalyst. Polymer **3** was prepared using 50% less catalyst. The temperature in all experiments, except for **4**, varied between 66°C in the first hours (due to boiling of THF, which was refluxed), towards 90°C in the later stages. All experiments showed 100% conversion of the TMPO monomer. Unless otherwise stated the crude reaction mixtures were dissolved in ethanol and purified by precipitation in cold water. All final materials were dried under vacuum at 50°C during at least 48 h.

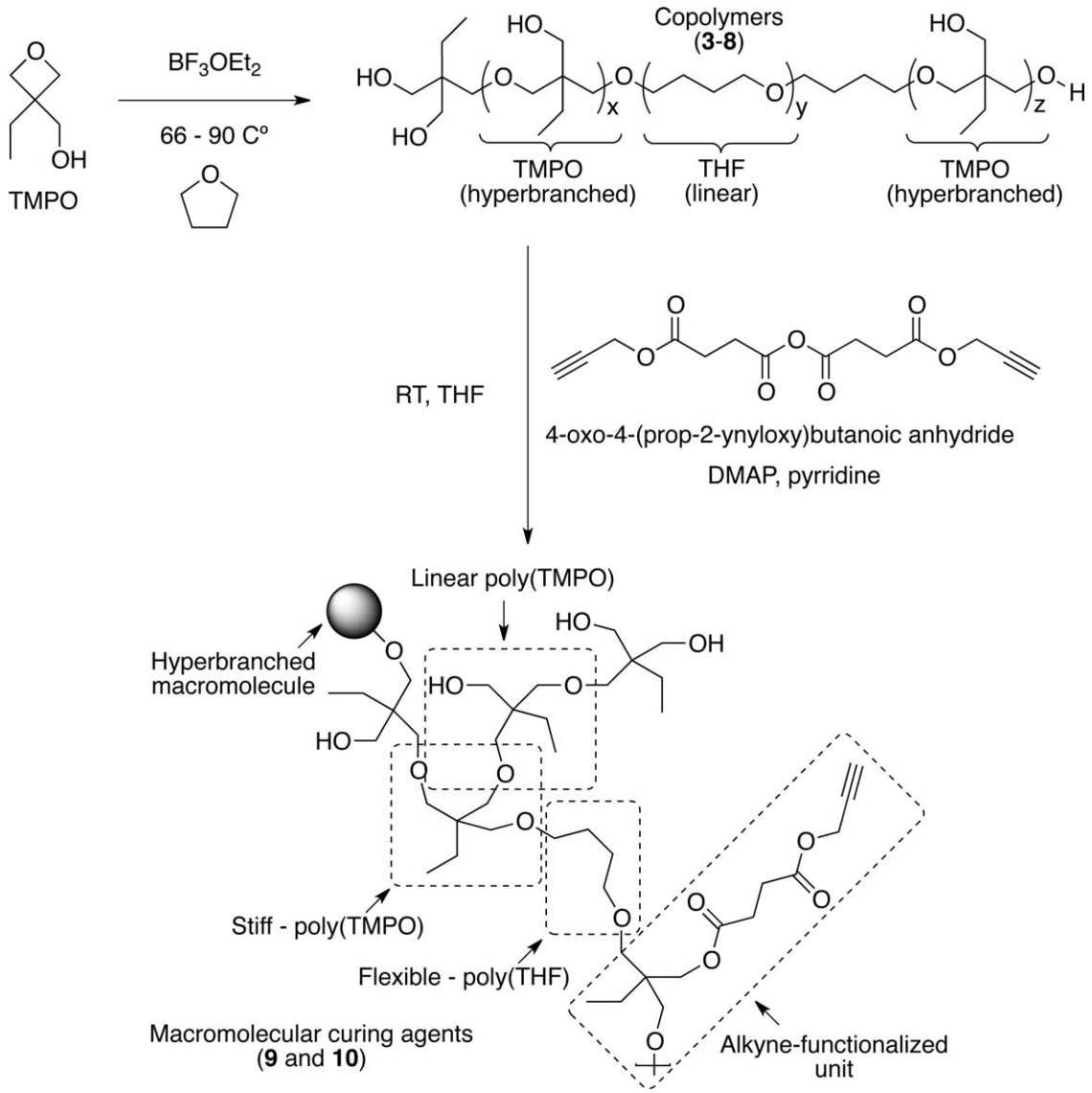
Polymer **3** was prepared by slow drop wise addition of TMPO (10 g, 86.2 mmol) to THF (10 mL, 123.5 mmol) during three hours. The catalyst amount (and concentration) was half of that used in experiments **4-8** (i.e., ∼ 20 mg). After one hour the viscosity was too high for efficient stirring, and extra THF (10 mL) was added. This was repeated 1 h later.

Polymer **4** was prepared by drop wise addition of TMPO (9 g, 77.6 mmol) to a solution of TMPO (1 g, 8.6 mmol) and THF (10 mL, 123.5 mmol), during 4 h. Because of heightened viscosity extra THF (10 mL) was added after 3 h, and again (5 mL) after one additional hour. In contrast to all other materials **4** was prepared at a constant temperature of 60°C.

Polymer **5** was prepared by drop wise addition of TMPO (9 g, 77.6 mmol) to a solution of TMPO (1 g, 8.6 mmol)) and THF (10 mL, 123.5 mmol), during two and a half hours. Because of heightened viscosity extra THF (10 mL) was added after 1 h, and again 30 min later.

Polymer **6** was prepared by bulk polymerization of TMPO (10 g, 86.2 mmol) and THF (2 mL, 24.7 mmol). 100% conversion of TMPO was reached in less than 2 h.

Polymer **7** was prepared by bulk polymerization of TMPO (10 g, 86.2 mmol) and THF (6 mL, 74.1 mmol). 100% conversion of TMPO was reached in less than 4 h.



Scheme 1 Hyperbranched poly-TMPO-*co*-poly-THF copolymers have been constructed using cationic ring-opening polymerization. Some of the materials were partly functionalized by alkynes. Branching points have been omitted for clarity (a majority of the TMPO units are dendritic).

Polymer **8** was prepared by bulk polymerization of TMPO (10 g, 86.2 mmol) and THF (60 mL, 740.8 mmol). As full conversion of TMPO was not reached after 24 h, additional BF_3OEt_2 (20 mg, 0.14 mmol) of was added. Totally, 100% conversion was reached after 20 additional hours. The high viscosity and consequential low T_g of the polymer prohibited precipitation, and the nonreacted THF was removed under vacuum and 90°C, during 2 h, followed by drying at 50°C during 48 h.

^{1}H NMR (500MHz, DMSO-*d6*): δ 4.26$^{(b)}$ (m, 1H, -O*H*), 4.15-4.16$^{(a)}$ (m, 1H, -O*H*), 3.31-3.32$^{(b)}$ (s, 4H, -O-C*H*$_2$-C$_2$H$_4$-C*H*$_2$-O-), 3.26-3.27$^{(a)}$ (s, 2H, -C-C*H*$_2$-OH), 3.14$^{(a)}$ (s, 2H, -CH$_2$-O-C*H*$_2$-C-), 1.50$^{(b)}$ (s, 4H, -C*H*$_2$-C*H*$_2$-) 1.27$^{(a)}$ (m, 2H, CH$_3$-C*H*$_2$-), 0.79$^{(a)}$ (m, 3H, C*H*$_3$-CH$_2$-) ppm. (a) and (b) denotes signals originating from TMPO and THF-segments, respectively

^{13}C NMR (125 MHz, H-decoupled, DMSO-*d6*): δ 73.48$^{(a)}$, 71.71$^{(a)}$, 71.82$^{(b)}$, 70.74$^{(a)}$, 69.89$^{(b)}$ (-O-CH$_2$-C-), 62.29$^{(a)}$, 62.00$^{(b)}$, 61.62$^{(b)}$ (-C-CH$_2$-OH), 43.54-42.93$^{(a,b)}$ (-C-), 26.26$^{(b)}$, 26.17$^{(b)}$ (-O-CH$_2$-CH$_2$-CH$_2$-CH$_2$-O-), 23.27(D), 23.13(D), 22.99(D), 22.83(D), 22.69(L), 22.52(L), 22.32(L), 22.12(T), 21.90(T) (-C-CH$_2$-CH$_3$)$^{(a)}$, 7.63$^{(a)}$ (-C-CH$_2$-CH$_3$) ppm. D, L and T denotes dendritic, linear and terminal units.

Synthesis of 4-oxo-4-(prop-2-ynyloxy)butanoic acid

Propargyl alcohol (20.0 g, 353 mmol) and DMAP (8.6 g, 70.6 mmol) was dissolved in CH_2Cl_2 (200 mL) in a 500 mL round bottom flask [Fig. 2(a)]. Succinic anhydride (38.9 g, 387 mmol) was added and the reaction was allowed to proceed over night. To quench the excess anhydride water (20 mL) was

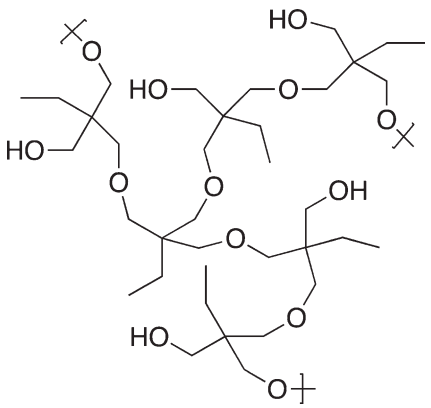


Figure 1 Schematic representation of hyperbranched poly-TMPO.

added and the reaction was left over night. The solution was subsequently extracted with aqueous $NaHSO_4$ (3 × 50 mL, 10 wt %), dried with $MgSO_4$ and evaporated and dried under vacuum to yield a light brown solid. Yield 47.6 g (86%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 2.50 (t, 1H, J = 4 Hz, *H*C≡C-), 2.66-2.74 (m, 4H, -CO-C*H*$_2$-C*H*$_2$-CO-), 4.71 (d, 2H, J < 1 Hz, ≡C-C*H*$_2$-O) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ 28.77, 28.96, 52. 51, 171.55, 178.41 ppm.

Synthesis of 4-oxo-4-(prop-2-ynyloxy)butanoic anhydride

4-Oxo-4-(prop-2-ynyloxy)butanoic acid (29.2 g, 187 mmol) was dissolved in CH_2Cl_2 (100 mL) in a 250 mL round bottom flask [Fig. 2(b)]. The flask was cooled with an ice bath followed by the slow addition of DCC (19.3 g, 93.5 mmol). The reaction was allowed to proceed over night whereby the formed DC-urea side product was filtered off, the solvent evaporated and the product dried under vacuum to yield a light brown solid. Yield 24.6 g (89%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.51 (s, 1H, J = 4 Hz, *H*C≡C-), 2.69-2.84 (m, 4H, -CO-C*H*$_2$-C*H*$_2$-CO-), 4.71 (d, 2H, J = 4 Hz, ≡C-C*H*$_2$-O) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 28.42, 30.20, 52. 59, 167.78, 171.04 ppm.

Synthesis of alkyne-functionalized TMPO-THF copolymers (2, 9, and 10)

Polymers **2**, **9** and **10** (Scheme 1) were all performed using identical equipment and pretreatments as polymers **1**, **3**-**8**. The temperature in all experiments varied between 66°C in the first hours (due to boiling of THF, which was refluxed), to 90°C in the final stages. All experiments showed 100% conversion of the TMPO monomer. The obtained materials were dried under vacuum at 50°C during at least 48 h.

Polymer **2** was prepared by initial bulk polymerization of pure TMPO monomer (5 g, 43.1 mmol). The BF_3OEt_2 catalyst (10 mg, 70 μmol) was diluted by dry DCM (0.5 mL) and added to the reaction vessel (50% lower catalyst concentration compared to most other reactions). The reaction mixture was left at 90°C over night to ensure 100% conversion of TMPO and dying of the catalyst. After 24 h the solid transparent polymer, now at room temperature, was dissolved in THF (8 mL). To functionalize 20% of the hydroxyl groups with alkynes pyridine (0.67 mL, 8.65 mmol) and DMAP (211 mg, 1.73 mmol) was added, followed by 4-oxo-4-(prop-2-ynyloxy)butanoic anhydride (2.54 g, 8.65 mmol). After 24 h ^{1}H-NMR confirmed 100% conversion of the anhydride and 22% functionalization of the hydroxyl groups. The crude reaction was diluted by THF (5 mL), and precipitated in cold water. 1 wt % of DMAP remained in the material after precipitation.

Polymer **9** was prepared by initial bulk polymerization of TMPO (5 g, 43.1 mmol) and THF (5.6 mL, 69.1 mmol) (1 : 1 weight ratio), using BF_3OEt_2 catalyst (20 mg, 0.14 mmol). After 24 h, the reaction mixture was dissolved in THF (12 mL) and taken to room temperature. Similar to reaction **2**, pyridine (0.67 mL, 8.65 mmol) and DMAP (211 mg, 1.73 mmol) was added, followed by reaction with 4-oxo-4-(prop-2-ynyloxy)butanoic anhydride (2.54 g, 8.65 mmol) over night. For more efficient purification the product mixture was dissolved in ethanol (30 mL), and dialyzed thrice using dialysis tubing with a 1000 g mol^{-1} cutoff.

Polymer **10** was prepared from copolymer *8*, in a procedure identical to the one used for polymer **9**.

^{1}H NMR (500MHz, DMSO-*d*6): δ 4.67$^{(c)}$ (s, 2H, ≡C*H*$_2$-OOC-), 4.43$^{(d)}$ (s, 1H, -O*H*), 4.15-4.16$^{(a)}$ (m, 1H, -O*H*), 3.88$^{(c)}$ (m, -O-C*H*$_2$-C-), 3.52$^{(c)}$ (s, 1H, *H*-≡-), 3.31-3.32$^{(b)}$ (s, 4H, -O-C*H*$_2$-C$_2$H$_4$-C*H*$_2$-O-), 3.26-3.27$^{(a)}$ (s, 2H, -C-C*H*$_2$-OH), 3.14$^{(a)}$ (s, 2H, -CH$_2$-O-C*H*$_2$-C-), 2.59-2.57$^{(c)}$ (m, 4H, -OOC-C$_2$*H*$_4$-COO-), 1.50$^{(b)}$ (s, 4H, -C*H*$_2$-C*H*$_2$-) 1.27$^{(a)}$ (m, 2H, CH$_3$-C*H*$_2$-), 0.79$^{(a)}$ (m, 3H, C*H*$_3$-CH$_2$-) ppm. (a), (b) and (c) denotes signals originating from TMPO-segments, THF-segments and

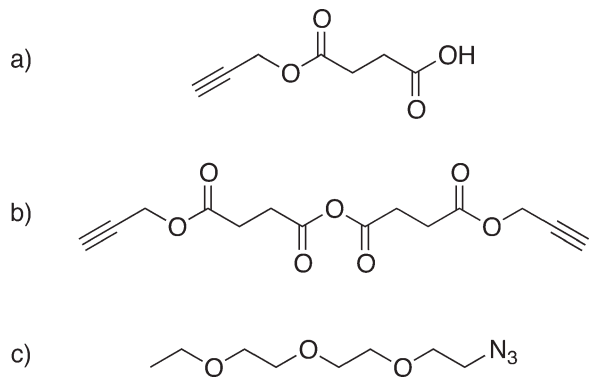


Figure 2 (a) 4-Oxo-4-(prop-2-ynyloxy)butanoic acid, (b) 4-Oxo-4-(prop-2-ynyloxy)butanoic anhydride, (c) 1-azido-3,6,9-trioxaundecane.

propagyl ester groups, respectively. (d) Likely denotes hydroxyl groups on TMPO-segments that have been functionalized.

Synthesis of 1-azido-3,6,9-trioxaundecane

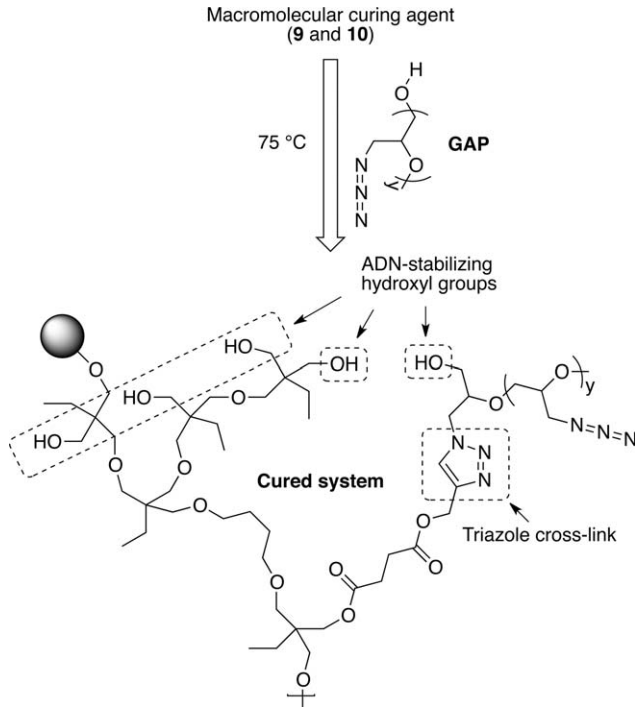
A 500-mL round bottom flask equipped with a stir bar was charged with tri(ethylene glycol) monoethyl ether (Et-TEG-OH) (20.0 g, 112 mmol), THF (200 mL) and methanesulfonyl chloride (16.7 g, 146 mmol) [Fig. 2(c)]. The flask was cooled using an ice bath and EtN_3 (22.7 g, 224 mmol) was slowly added using an addition funnel. After 1 h the ice bath was removed and the reaction was allowed to proceed for additionally 4 h followed by filtration to remove the formed salt. Following the evaporation of the solvent, DMSO (150 mL) and NaN_3 (36.5 g, 561 mmol) was added and the reaction was heated to 80°C and allowed to proceed over night. The reaction was subsequently poured into THF (200 mL) and filtered to remove the excess NaN_3 and the Na-Mes side product. After evaporation of the solvent and drying under vacuum the product was received as a yellow oil. Yield 21.0 g (92%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 1.22 (t, 3H, J = 12 Hz, CH_3-CH_2-), 3.40 (t, 2H, J = 12 Hz, -CH_2-N_3), 3.53 (q, 2H, J = 20 Hz, CH_3-CH_2-O-), 3.59-3.70 (m, 10H, -O-CH_2-CH_2-O- and -O-CH_2-CH_2-N_3) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ 15.16, 50.67, 66.62, 69.81, 70.02, 70.64, 70.70, 70.75 ppm.

RESULTS AND DISCUSSION

A straightforward method for preparing ADN-compatible polymer matrices using 1,3-dipolar cycloaddition curing of GAP is presented. The materials were made utilizing a novel type of hyperbranched macromolecular curing agents, which were prepared using cationic ring-opening polymerization of TMPO and THF monomers in a one-pot procedure. The inclusion of THF into poly-TMPO-*co*-poly-THF copolymers proved important for lowering the T_g of the materials. A schematic representation of the macromolecular curing agents, their preparation and the curing process, is shown in Schemes 1 and 2.

The excellent ADN-compatibility of poly-TMPO can, on the basis of experimental testing[32] and theoretical studies,[33] be attributed to its ability to stabilize the surface of ADN through the donation of multiple hydrogen bonds. Contrary to many related linear polymer systems, the high concentration of hydroxyl groups on the surface of the globular hyperbranched poly-TMPO structure likely results in more favorable polymer-ADN interfaces.

To make use of the stabilizing effect in a curing agent, poly-TMPO was initially functionalized with a sizable amount of alkynes, by reaction with 4-oxo-4-(prop-2-ynyloxy)butanoic anhydride (22% of hydroxyl groups functionalized, c.f. **2** in Table I). We argued that the embedding of necessary, but somewhat ADN-incompatible, alkyne groups among stabilizing hydroxyl groups, could retain overall compatibility, as long as similar physical interactions were maintained between solid ADN and the surrounding polymer. Encouragingly this appeared to be a valid assumption, and **2** showed no visual sign of incompatibility when evaluated with ADN in a heating block at 75°C over 19 days, or when tested using heat flow calorimetry (HFC) using the same conditions.



Scheme 2 ADN-compatible polymer matrices can be realized using GAP and hyperbranched macromolecular curing agents, utilizing the 1,3-dipolar cycloaddition reaction beween alkynes and azide groups.

Unfortunately subsequent experiments showed that **2** was unable to efficiently cure GAP. It was argued that low mobility and flexibility of the hyperbranched structure ($T_g \sim 5$°C) reduced access to the functional groups, especially as the crosslink density increased.

To make a new set of TMPO-based hyperbranched materials with increased mobility (lower T_g) we attempted the copolymerization of TMPO and THF. The resulting materials, which were made through BF_3OEt_2-catalyzed cationic ring-opening polymerization, are shown as **3** through **8** in Table I. Materials **3**, **4,** and **5** were formed by drop-wise addition of TMPO monomer to a bulk solution of THF. Additional THF had to be added in various amounts in later stages of the polymerizations, to enable 100% conversion of TMPO (see experimental section for

TABLE I
Characteristics of the Materials

Sample	Monomer ratio[a] TMPO : THF	Reaction conditions[a]	M_n[b] (g/mol)	M_w[b] (g/mol)	M_w/M_n	DF[c] (%)	T_g (°C)	Molar ratio TMPO:THF in product[c]	Wt % of TMPO in material[c]	Yield of TMPO[d] (%)
1	1 : 0	Bulk	1800	4200	2.3	–	+34	–	100.0	93
2	1 : 0	Bulk	3000	7400	2.5	22	+5	–	79	96
3[e]	[a]	Drop wise	–	–	–	–	+13	20:3	92	91
4	[a]	Drop wise	2600	14800	5.7	–	−1	8:3	81	78
5	[a]	Drop wise	–	–	–	–	−10	7:3	79	88
6[f]	5 : 1	Bulk	–	–	–	–	+32	100:3	98	94
7[f]	1 : 1	Bulk	–	–	–	–	+15	20:3	91	93
8[g]	1 : 5	Bulk	–	–	–	–	−20	3:2	71	100[g]
9[h]	1 : 1	Bulk	5000	9500	1.9	18	−7	16:3	76	70
10[h]	1 : 5	Bulk	4400	7700	1.7	22	−29	3:2	60	65

[a] See experimental section for details. TMPO to THF ratios are given by weight. "Dropwise" refers to the addition of TMPO.
[b] Determined with SEC, conventional calibration with linear polystyrene standards in THF.
[c] Degree of functionalization (DF), TMPO:THF molar ratios and wt % TMPO are calculated from ^{1}H NMR
[d] Yield defined as the amount of TMPO recovered in the final product, and calculated from ^{1}H NMR and the weights of the final polymers. Total yield is lower due to excess use of THF.
[e] 0.5 wt % BF_3OEt_2 was used, instead of 1.0 wt %.
[f] Contains <1 wt % EtOH.
[g] Not precipitated, and used directly for preparing **10.**
[h] Purified by dialysis in EtOH. Contains <1 wt % EtOH.

details). Materials **6**, **7,** and **8** were prepared from bulk solutions of TMPO and THF monomers. Subsequently two additional alkyne-functionalized curing agents (**9** and **10**) were synthesized and evaluated with GAP and ADN.

^{1}H NMR analysis revealed what appear to be specific relative ratios of TMPO and THF in all copolymers. All ratios, except the one in **8**, were exact integers of TMPO units divided by three THF units. **8** instead showed an exact 4.5 : 3 (or 3 : 2) ratio (Table I, Fig. 3). The exact ratios correlated with the relative ratios of TMPO and THF monomers present during the polymerization. For instance, if smaller proportions of TMPO were present during polymerization (e.g., in **4**, **5,** and **8**), then larger amounts of THF were incorporated, in different exact ratios, respectively. Lower catalyst concentration (e.g., in **3**), and reaction temperature (e.g., in **4**) also appears to affect the ratio, in favor of TMPO. This strongly suggests a kinetically controlled build up of nonrandom composition copolymers. The exact ratios are likely a consequence of the trigonal structure of dendritic poly-TMPO. Figure 5 shows four possible secondary structure units of hyperbranched nonrandom composition copolymers of TMPO and THF. Similar structures can be drawn for all other observed ratios. The exact positions of the THF units are unknown, and the positions in Figure 5 have been chosen arbitrary.

Quantitative ^{13}C NMR was used to analyze some of the materials, and confirmed the exact same TMPO to THF ratios as had been seen with ^{1}H NMR. Figure 4 shows the ^{13}C NMR spectra of pure poly-TMPO (**1**) together with copolymer **4**. Hyperbranched TMPO show a splitting of several ^{13}C NMR peaks due to the coexistence of dendritic, linear and terminal TMPO-units in the macromolecule.[32] The methylene carbon at 22.5 ppm gives a clear triplet splitting and has previously been used for calculating the degree of branching in different poly-TMPO segments.[32]

In the copolymers (**3**-**8**) the methylene peak is instead split into nine peaks. There are $3^2 = 9$ ways a linear, hyperbranched or terminal TMPO unit can be constructed and incorporated when bonded to one, two or three other TMPO and/or THF units (2 terminal, 3 linear, and 4 dendritic). The observed splitting pattern (Fig. 4) is a strong indication that TMPO-segments have been covalently bonded to THF-segments, i.e., copolymerization.

All nonsubstituted materials (**1**, **3**-**8**) are likely to be highly polydisperse. However, as some of the materials seemed to adhere and cause problems in the separation column of the size exclusion chromatograph (SEC), only materials **1** and **4** were analyzed in this way. The "stickiness" of the materials is clearly seen in all materials, especially when they are somewhat wetted. This effect is likely caused by the large number of hydroxyl groups present on the surfaces of the hyperbranched structures, and is a testament to their surface active and assumed ADN-stabilizing nature.

Despite extensive efforts MALDI-TOF spectra of the materials **2**-**10** could not be attained (details are given in the apparatus section). It appears that the broad polydispersity and specific structure of the materials hinders effective ionization. The alkyne-

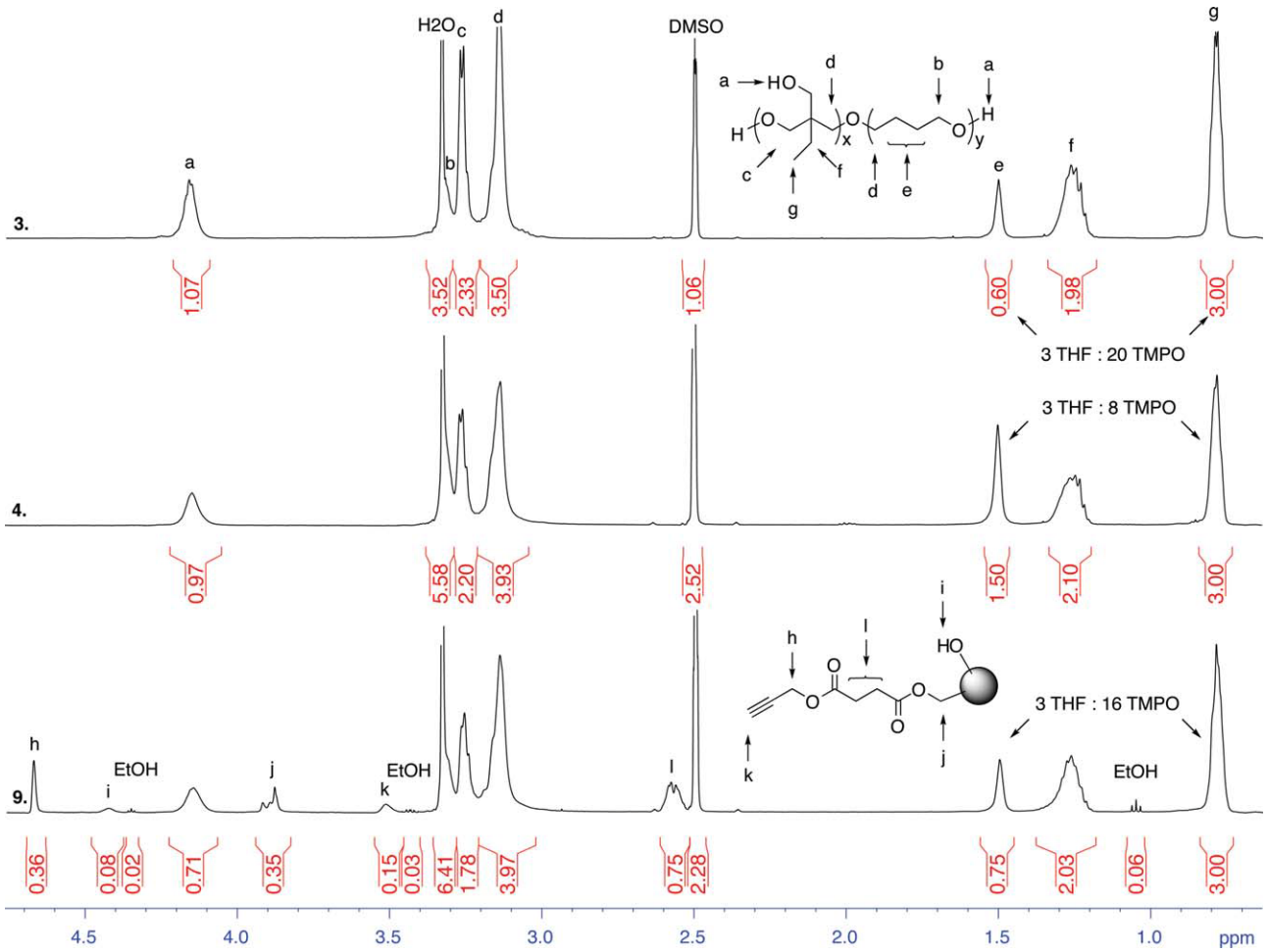


Figure 3 ^{1}H-NMR spectra of copolymers **3** and **4**, and the functionalized material **9**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

functionalized and less polydisperse materials **2**, **9,** and **10** were successfully analyzed using SEC (Table I and Fig. 6). The molecular weights (M_w) were in the range of 7,000 to 10,000 g/mol. **9** and **10** shows narrower polydispersities due to their more extensive purification. Fortunately the envisioned application as propellant polymer matrix does not require a system of narrow polydispersity.

The number of available crosslinking groups per molecule is an important property of a curing agent, and vital to the mechanical properties of the final cured material. Classical cure systems, based on fairly small molecules, typically employ di- and trifunctionality. A rough approximation to the number of crosslinking groups per weight for such systems is one per every 100 a.u. ($\sim$ 0.01 a.u.$^{-1}$). If one analyze our much larger curing agents (M_w = 7,000–10,000 g mol^{-1}) in the same way, the number of available groups per weight are reduced one order of magnitude ($\sim$ 0.001 a.u.$^{-1}$). On the other hand the number of crosslinking groups per molecule, is significantly increased in the macromolecules. Based on the molecular weight averages (M_w) obtained with SEC and the ^{1}H NMR analyses, **2** and **9** have $\sim$ 11 alkynes per molecule, whereas **10** have roughly 9 per molecule. By considering this, and the average weight-loadings of curing agent in previous GAP curing studies[17] ($\sim$ 8 wt %), it was argued that fairly high loading of macromolecular curing agent (**2**, **9,** and **10**) should be employed in the initial study. Approximately 10- and 25 wt % was used throughout. Future work, concerned with the optimization of mechanical properties of the materials, will be necessary to find the best possible loading.

As expected the differential scanning calorimetry (DSC) analyses showed significant decreases in T_g with increasing amounts of incorporated THF (Table I). Inclusion of $\sim$ 29 wt % THF in **8** decreased the T_g with 54°C relative to pure poly-TMPO. (1) 22% alkyne-functionalization decreased T_g by an additional 9°C, and **10** showed a T_g of $-$29°C. Curing agent **9**, which later proved the most successful in curing GAP, showed a T_g of $-$7°C. It should be noted that both **9** and **10** contained small residues of ethanol (<1 wt %), which acted plasticizing, and decreased T_g slightly.

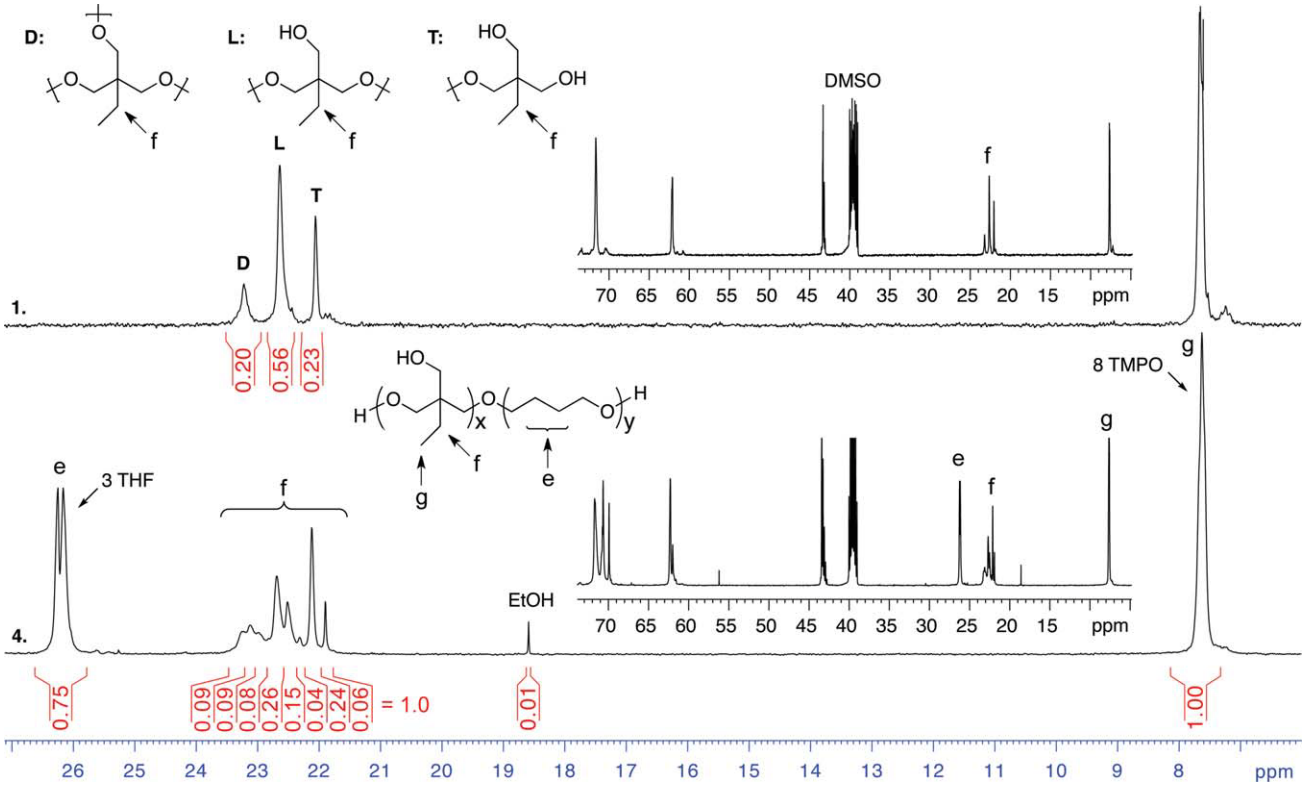


Figure 4 Quantitative ^{13}C-NMR spectra of poly-TMPO (**1**) and copolymer **4**. Copolymerization is evident from the additional splitting of peaks corresponding to dendritic (D), linear (L) and terminal (T) TMPO-units, now covalently linked to THF. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Thermal gravimetric analysis (TGA) of the materials showed a decomposition onset at 190°C, when they were evaluated under oxygen atmosphere. The small difference is explained by the similar molecular constitution (oxygen balance) of all materials (28.1 wt % and 27.6 wt % for TMPO and THF, respectively).

Several of the materials were checked for ADN-compatibility using HFC (Fig. 7). The exothermicity at 75°C, measured over 19 days, provides a valuable measure for the thermal stability of a formulation.[31] Material **4** showed a slightly decreased compatibility with ADN, relative pure poly-TMPO. However, the thermal output was still within the acceptable range after 19 days. Because of the fairly similar structure and composition of the polymers **3**-**7**, all were not analyzed in this manner. If too much THF was included (e.g., in **8**, THF = 30 wt %), the incompatibility did, however, rise above the threshold after six days. As previously mentioned material **2** proved

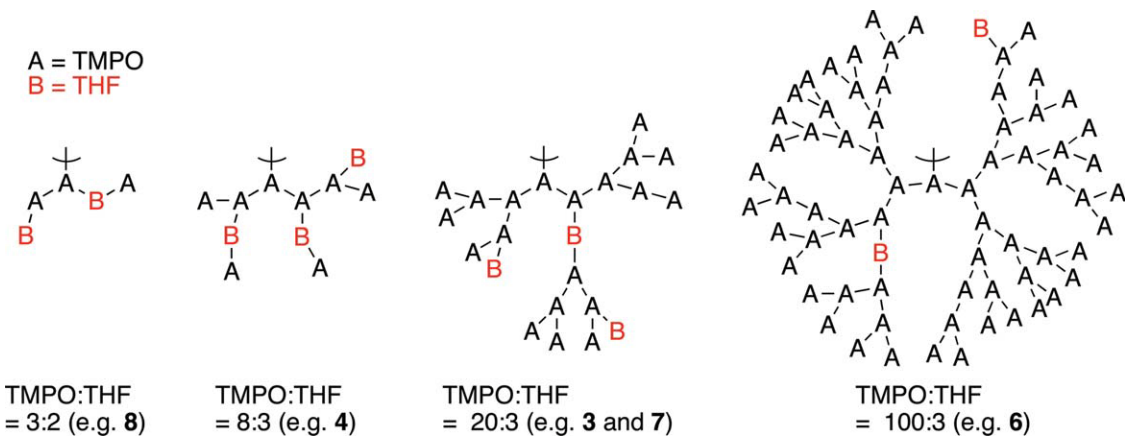


Figure 5 Possible secondary structures of different hyperbranched nonrandom composition poly-TMPO-*co*-poly-THF copolymers. The exact positions of TMPO (A) and THF (B) are unknown. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

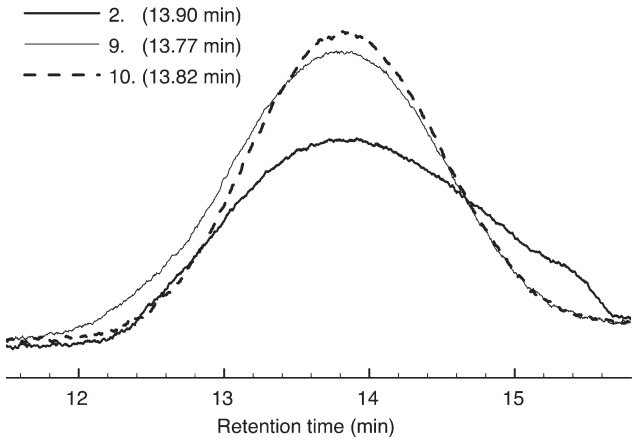


Figure 6 SEC traces of the alkyne functionalized materials **2**, **9,** and **10**.

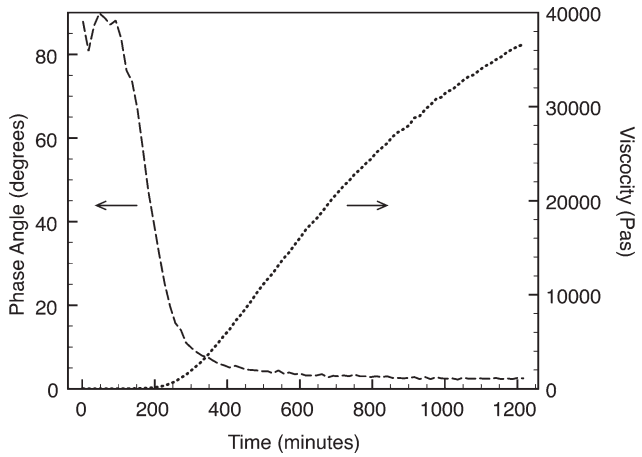


Figure 8 Rapid curing of GAP was observed at 75°C using 25 wt % of material **9**.

exceedingly stable towards ADN. It should be noticed that **2** contained 1 wt % of the DMAP catalyst, which had been enclosed in the rigid structure. Previous computational studies have argued that amines can stabilize ADN by coordinating to radical decomposition intermediates,[33] and the small impurity was left intentionally. Despite the initial promising compatibility results with **2** and ADN, materials **9** and **10** proved incompatible with ADN, as the heat flow exceeded the allowed threshold after ~ 8 h. The increased thermal outputs in these cases seem to be a cumulative effect of both propagyl esters groups and THF (and possibly the lack of the amine base DMAP). However, as the heat-flow was acceptable during the first 8 h it can be argued that a cured system, which is more rigid and where the alkyne-groups have been transformed into more thermally stable triazole-linkages, will be ADN-compatible.

The reactivity of materials **2**, **9,** and **10** with respect to alkynes (i.e., cycloaddition) was first tested using a low viscosity model compound, 1-azido-3,6,9-trioxaundecane [Fig. 2(c)], at 75°C. Since no crosslinking could occur in this case the materials remained soluble, and the reactions were monitored by ^{1}H NMR. 100% triazole formation was observed within a few hours for all materials.

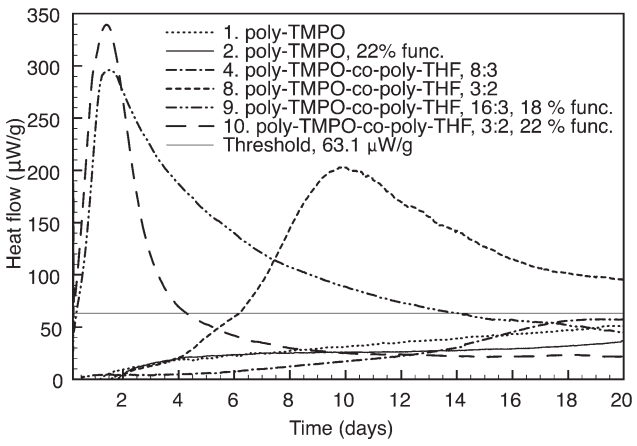


Figure 7 HFC-study of materials **1**, **2**, **4,** and **8-10** with ADN for 20 days at 75°C.

The reactivity of materials **2** and **9** with respect to GAP was tested using a rheometer. 10- and 25 wt % of material **2** or **9** was mixed with GAP and the mixture was allowed to cure at 75°C while monitoring the viscosity. Material **2** did not cure GAP at all, i.e., the viscosity remained unchanged. Material **9** did, however, cure GAP at concentrations of 10 and 25 wt %. Figure 8 shows rapid curing of GAP using material **9** at a concentration of 25 wt %. A curing time in the order of hours is preferable, since it allows for cast curing of a propellant formulation. The observed cure kinetics is also especially preferable for the system under study, since the relatively short cure time limits ADN-incompatibility, arising due to the presence of alkyne groups.

Material **10** was also investigated together with GAP at the same concentrations, however the experiment was performed in an oven at 75°C with no real-time monitoring of viscosity. No curing was, however, observed during a period of five days.

CONCLUSIONS

Isocyanate free curing of the energetic and ADN-compatible GAP-polymer can be realized using alkyne-functionalized hyperbranched curing agents. The materials can be synthesized in a one-pot procedure using cationic ring-opening polymerization of TMPO and THF monomers. With reference to ^{1}H/^{13}C-NMR analyses, it is concluded that TMPO and THF copolymerizes in exact relative ratios, such as 3 : 2, 8 : 3, and 20 : 3 etc. The ratios are influenced by the relative amount of THF present during

polymerization, by temperature, and by catalyst concentration. This strongly suggests kinetically controlled buildup of nonrandom composition copolymers. The incorporation of THF segments into the hyperbranched structure of poly-TMPO can reduce the glass transition temperature down to −20°C.

Alkyne functionalization of poly-TMPO and poly-TMPO-*co*-poly-THF materials were performed by DMAP-catalyzed esterification using 4-oxo-4-(prop-2-ynyloxy)butanoic anhydride. Several of the materials show good compatibility with ADN. This is explained by high surface concentrations of hydroxyl groups on the macromolecules, which provide favorable interactions at interfaces with ADN. The materials provide a feasible route to rapid curing of GAP through the 1,3-dipolar cycloaddition reaction, and to triazole crosslinked polymer matrices.

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