

Preparation and Mechanical Properties of Crosslinked 1,2,3-Triazole-Polymers as Potential Propellant Binders

Ling Wang,¹ Yuming Song,² Reena Gyanda,² Rajeev Sakhuja,² Nabin K. Meher,² Sureyya Hanci,² Kapil Gyanda,¹ Sindhu Mathai,² Firouzeh Sabri,¹ David A. Ciaramitaro,³ Clifford D. Bedford,³ Alan R. Katritzky,² Randolph S. Duran¹

¹Department of Chemistry, Polymer Research Laboratory, University of Florida, Gainesville, Florida 32611-7200

²Department of Chemistry, Center for Heterocyclic Compounds, University of Florida, Gainesville, Florida 32611-7200

³Office of Naval Research, Arlington, Virginia 22203

Received 4 March 2009; accepted 3 May 2009

DOI 10.1002/app.30753

Published online 27 April 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Thirteen triazole polymers were prepared as potential rocket propellant binders by the reactions of various diacetylenes and diazides. The reaction of E300 dipropiolate (**1**) with diazide (**2**) obtained from tetraethylene glycol was selected to study the effects of concentration of the tetraacetylene functionalized crosslinker (**3**) on the mechanical properties of resulting triazole polymers. The modulus of the polymers increased, whereas the strain (% elongation at failure) decreased with increasing percentage of crosslinker. The resulting triazole polymers

also showed that the desired mechanical properties could be obtained by adjusting the crosslinker concentration during the polymerization. Addition of 43 wt % aluminum filler did not significantly affect the strain. The modulus of these triazole polymers was comparable with typical polyurethane elastomeric matrices for rocket propellants. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 2612–2621, 2010

Key words: strain; mechanical properties; modulus; crosslinking; fillers

INTRODUCTION

Triazole polymers are novel macromolecules that have received growing interest in the area of polymer and material science.¹ They can be synthesized by 1,3-dipolar cycloaddition of azides with terminal alkynes following "Click" chemistry, which has been explored as an efficient tool for the synthesis of functionalized monomers,² polymers,³ and postpolymerization modification of polymers,^{1,4} such as the synthesis of dendrimers, dendronized polymers,^{5,6} biohybrid amphiphiles,⁷ chromophores,⁸ conjugated polymers,⁹ block copolymers,^{10,11} glyco-polymers,¹² macrocyclic polymers,¹³ and adhesives.¹⁴

1,2,3-Triazole-polymers have been studied recently as novel binders for explosives and high-energy propellants.^{15–17} The mechanical properties of solid rocket propellants are important for the functioning of rocket motors.¹⁸ Most composite propellants are composed of fuel and oxidizer held together by a polymeric binder. The binder concentration is minimized in these very highly filled systems. The well-

known polyurethane rocket propellant binders can undergo side reactions during and after polymerization that degrade the mechanical properties of the resulting propellant, e.g., loss of elasticity.¹⁷ Polymerization through triazole linkages proceeds readily and the components of the triazole cure (ethynyl groups and azido groups) react preferentially with each other,¹² which largely avoids the possibility of side reactions.

Reed¹⁷ reported the synthesis of crosslinked triazoles as energetic binders with improved mechanical properties and stability. Huang and coworkers^{19–21} synthesized and characterized series of novel low-temperature curing and heat-resistant polytriazole resins as an advanced composites. Previous work in our group developed strategies for low-temperature synthesis of oligotriazoles as binder ingredients.²² Triazole-cured polymers were prepared with various alkynes and azides without any solvent or copper catalysts under mild conditions near room temperature.¹⁵ However, the mechanical properties of those triazole polymers were not quantified.

The mechanical properties of triazole polymers are significantly influenced by their molecular structures such as the chain length between the triazole groups.¹⁵ Addition of crosslinkers can modify polymer mechanical properties such as tensile strength, modulus, and elasticity by limiting the mobility of individual polymer chains.²³ Crosslinker effects on mechanical properties of conventional

Correspondence to: A. R. Katritzky (Katritzky@chem.ufl.edu) and R. S. Duran (duran@chem.ufl.edu).

Contract grant sponsor: Office of Naval Research (from the Advanced Reactive and Energetic Materials Program); contract grant number: N00014-06-0211.

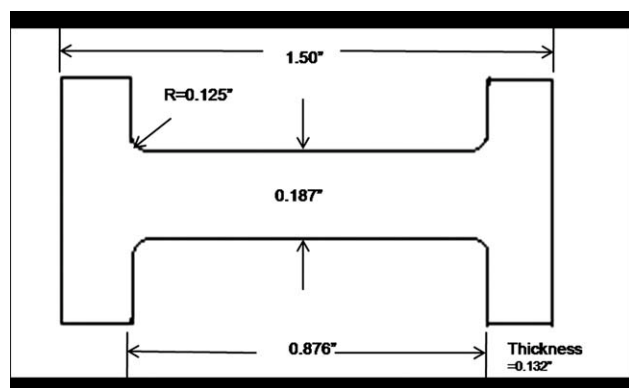


Figure 1 Dimensions of dogbone mold.

rubbers have been studied for many years and are well understood.²⁴ Such studies have not been systematically performed on triazole polymers. The reactions to form triazole polymers are good models to investigate the relationship between crosslinking and polymer mechanical properties since acetylene and azide groups should react with each other at 1 : 1 molar ratio, no small molecules are produced, the reaction should not be influenced by residual moisture, and side reactions should not occur. Understanding the relationship between crosslinking and mechanical properties of triazole polymers, the synthesis was thus optimized to result in polymers with desired mechanical properties.

This article focuses on the investigation of the relationship between crosslinker concentration and mechanical properties of unfilled and filled triazole polymers in terms of elongational strain (% elongation at break) and elastic modulus (Young's modulus). Triazole polymers, as a potential propellant binders, with desired mechanical properties (strain > 50%, modulus > 1.4 Mpa)²⁵ were obtained by tuning crosslinker concentration.

EXPERIMENTAL

General

Commercially obtained reagents were used without further purification. All monomers except **14** were prepared following reported procedures.^{15,22,26} Solvents were distilled by standard methods. ¹³C and ¹H NMR spectra were recorded at 75 and 300 MHz, using tetramethylsilane (TMS) as an internal standard. In view of the stringent stoichiometry requirements for step polymerization, the monomers were systematically dried by azeotropic distillation and lyophilization. The uniaxial test specimen was a standard microtensile dogbone, with dimensions 0.88" × 0.19" × 0.13"²⁷ (Fig. 1). Strain (% elongation at break) and elastic modulus (Young's modulus) were measured by Instron Universal Tensile Testing

Machine (Upgrade package, Model no. 1122), with a strain rate of 20 mm/min. Each data point in the figures (Figs. 5 and 6) is an average of at least two measurements. The error bars indicate cumulative standard errors for each data set.

Linear triazole polymer synthesis using different diacetylenes and diazides

The 1 : 1 mol equivalents of the two monomers were mixed in an aluminum pan until homogenous. The pan was cured in a vacuum oven under the conditions described in Scheme 1. The reaction conditions were standardized on the basis of time of reaction, curing temperature by monitoring the course of these reactions with ¹H NMR. The reaction condition avoids the use of any solvent or catalyst. The physical behavior of the resultant linear triazole polymers (**P1–P13**) were studied and mentioned in Scheme 1.

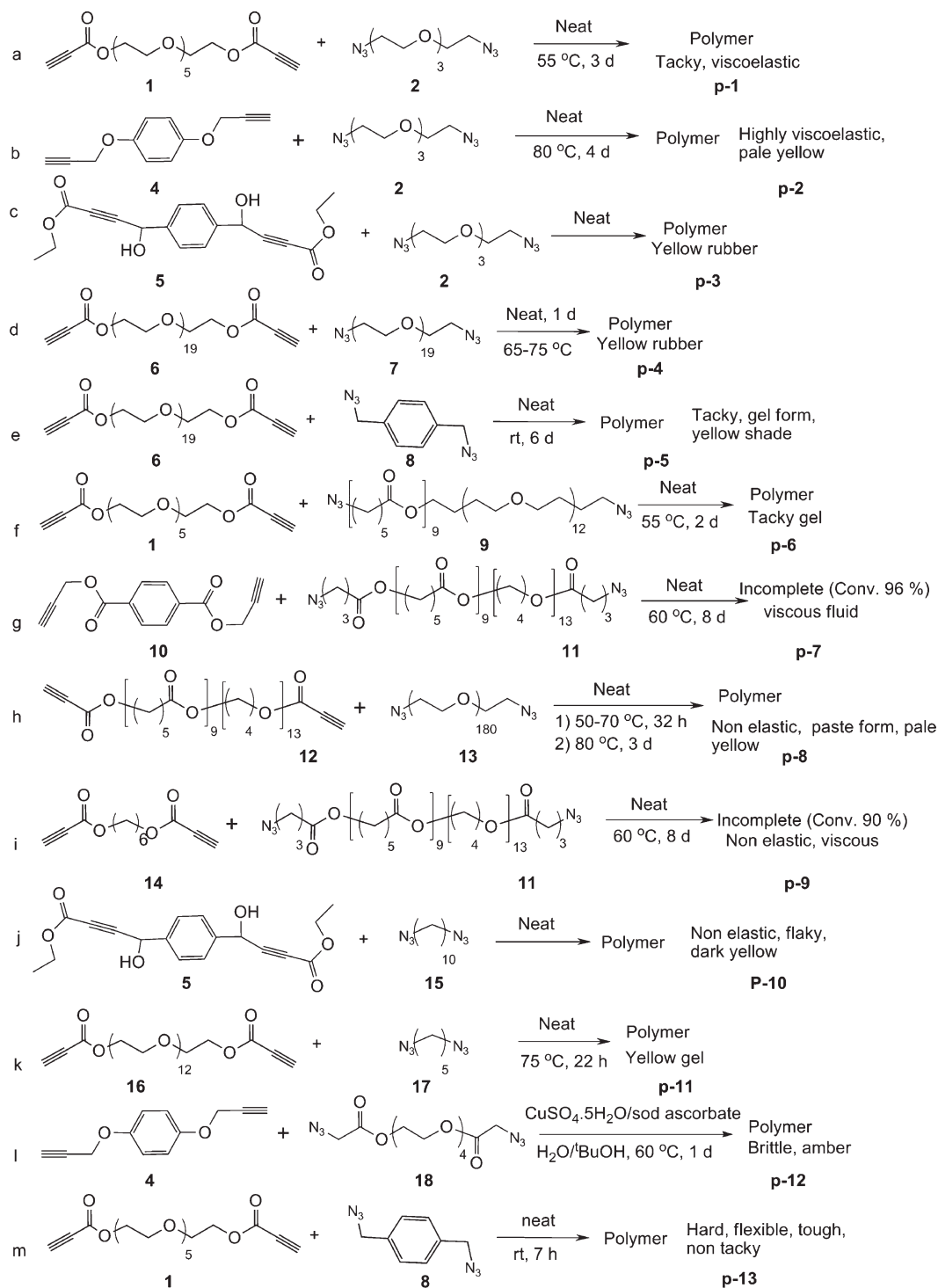
Among the entire monomers synthesized, compound **14** was novel and we now report the characterization data along with its method of preparation. The spectral analysis of the 13 polymers (**P1–P13**) is also reported.

6-(Propiolyloxy)hexyl propiolate (14) A solution of 1,6-hexandiol, (8.27 g, 70 mmol), propiolic acid (2.8 g, 154 mmol), and H₂SO₄ (1 drop) in benzene (250 mL) was heated to reflux using a Dean Stark apparatus for 72 h. Then the reaction mixture was cooled to room temperature and diluted with benzene, washed with NaHCO₃ (2 × 20 mL), water (30 mL), and brine (20 mL). The benzene layer was dried over anhydrous MgSO₄. Filtration and evaporation of the solvent gave 6-(propiolyloxy)hexyl propiolate (14 g, 90 %) as white powder. Mp 42.0–45.0; ¹H NMR (CDCl₃) : δ 1.40–1.45 (m, 4H), 1.62–1.78 (m, 4H), 2.91 (s, 2H), 4.20 (t, J = 6.6 Hz, 4H); ¹³C NMR (CDCl₃) : δ 20.9, 25.3, 25.4, 27.8, 28.0, 28.3, 64.2, 66.1, 74.5, 74.6, 152.7. Anal. Calcd for C₁₂H₁₄O₄ : C, 64.85; H, 6.35 Found: C, 64.96; H, 6.52.

P-1: ¹H NMR (CDCl₃) : δ 3.56–3.67 (m, (–O–CH₂–CH₂–O–)), 3.81–3.95 (m, (–COO–CH₂–CH₂–O) & (–triazole–CH₂–CH₂–O–)), 4.48–4.51 (m, (–CH₂–triazole–)), 4.60–4.63 (m, (–triazole–COO–CH₂–)), 8.34 (s, (–triazole–H)); ¹³C NMR (CDCl₃) : δ 50.4, 64.1, 68.9, 70.3, 70.4, 70.5, 77.2, 130.0, 139.7, 160.8. Anal. Calcd for C₂₆H₄₂N₆O₁₂ : C, 49.52; H, 6.71; N, 13.33 Found: C, 49.38; H, 6.72; N, 13.00.

P-2: ¹H NMR (CDCl₃) : δ 3.44–3.55 (m), 3.82–3.87 (m), 4.48–4.57 (m), 5.10–5.12 (m), 6.83–6.92 (m), 7.64 (s), 7.78 (s); ¹³C NMR (CDCl₃) : δ 48.6, 50.2, 59.5, 62.4, 62.5, 69.3, 69.9, 70.3, 70.3, 70.4, 103.3, 103.3, 115.7, 115.8, 115.9, 116.0, 124.0, 133.7, 133.7, 143.7, 143.9, 152.1, 152.7, 153.2. Anal. Calcd for C₂₀H₂₆N₆O₅ : C, 55.80; H, 6.09; N, 19.52 Found: C, 55.98; H, 6.41; N, 19.18.

P-3: ¹H NMR (CDCl₃) : δ 1.26–1.40 (m), 3.38–3.51 (m), 3.76–3.88 (m), 4.31–4.52 (m), 4.85 (br s), 5.54 (br



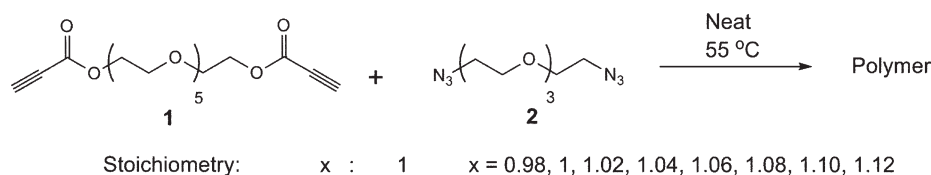
Scheme 1 Linear triazole polymer synthesis using different diacetylenes and diazides.

s), 6.20–6.22 (m), 6.62 (br s), 7.21–7.32 (m); ^{13}C NMR (CDCl_3): δ 13.6, 13.9, 14.1, 21.2, 49.3, 50.2, 61.6, 62.2, 65.1, 68.3, 69.1, 69.9, 70.0, 70.2, 70.3, 124.6, 125.6, 125.7, 126.0, 126.5, 126.8, 128.5, 128.9, 129.9, 136.0, 139.5, 139.8, 141.3, 141.6, 142.6, 143.8, 152.9, 158.6, 162.1. Anal. Calcd for $\text{C}_{26}\text{H}_{34}\text{N}_6\text{O}_9$: C, 54.35; H, 5.96; N, 14.63 Found: C, 54.24; H, 5.78; N, 13.31.

P-4: ^1H NMR (CDCl_3): δ 2.72 (br s), 3.38–3.41 (m), 3.51–3.78 (m), 3.82–3.86 (m), 3.88–3.95 (m), 4.19–4.24

(m), 4.31–4.34 (m), 4.46–4.53 (m), 4.59–4.62 (m), 4.91–4.95 (m), 8.09–8.15 (m), 8.33 (s); ^{13}C NMR (CDCl_3): δ 50.5, 50.6, 61.6, 62.9, 63.9, 68.8, 68.9, 69.9, 70.2, 70.5, 72.4, 77.2, 128.9. Anal. Calcd for $\text{C}_{86}\text{H}_{162}\text{N}_6\text{O}_{42}$: C, 52.91; H, 8.36; N, 4.30 Found: C, 52.13; H, 8.64; N, 3.85.

P-5: ^1H NMR (CDCl_3): δ 3.59–3.71 (m), 3.78–3.82 (m), 4.31 (br s), 4.36 (s), 4.47 (m), 5.56 (s), 5.60 (s), 5.87 (s), 5.91 (s), 7.23–7.37 (m), 8.05–8.17 (m); ^{13}C



Scheme 2 Different stoichiometry of triazole polymer formation.

NMR (CDCl_3) : δ 51.6, 52.4, 53.2, 53.3, 53.4, 53.7, 53.8, 61.0, 62.5, 63.1, 63.6, 64.3, 68.2, 68.4, 68.6, 69.7, 70.0, 72.2, 127.1, 127.4, 127.6, 128.0, 128.1, 128.1, 128.2, 128.5, 133.7, 133.9, 134.6, 135.1, 135.3, 135.9, 137.9, 139.6, 157.7, 160.0, 160.6. Anal. Calcd for $\text{C}_{54}\text{H}_{90}\text{N}_6\text{O}_{23}$: C, 54.44; H, 7.61; N, 7.05 Found: C, 53.27; H, 8.20; N, 5.96.

P-6: ^1H NMR (CDCl_3) : δ 1.43–1.53 (m), 1.53–1.72 (m), 2.28–2.33 (m), 3.41 (m), 3.64–3.68 (m), 3.82–3.85 (m), 4.04–4.10 (m), 4.40–4.45 (m), 4.49–4.52 (m), 8.13 (s); ^{13}C NMR (CDCl_3) : δ 24.1, 24.5, 25.5, 25.8, 26.2, 26.5, 28.3, 29.9, 33.8, 34.1, 64.1, 68.9, 70.1, 70.6, 75.2, 173.5, 194.5. Anal. Calcd for $\text{C}_{124}\text{H}_{220}\text{N}_6\text{O}_{39}$: C, 61.57; H, 9.17; N, 3.47 Found: C, 61.37; H, 9.39; N, 3.23.

P-7: Incomplete reaction.

P-8: ^1H NMR (CDCl_3) : δ 1.38–1.49 (m), 1.62 (s), 2.29–2.33 (m), 2.90 (br s), 3.42 (s), 3.53 (s), 3.65–3.81 (m), 3.86–3.90 (m), 4.04–4.08 (t, $J = 6.6$ Hz), 4.15–4.19 (m), 4.31–4.38 (m), 4.59–4.64 (m), 8.09–8.10 (m), 8.31 (s); ^{13}C NMR (CDCl_3) : δ 24.5, 25.4, 26.4, 28.2, 34.0, 64.0, 70.1, 70.4, 72.4, 77.2, 173.5. Anal. Calcd for $\text{C}_{474}\text{H}_{920}\text{N}_6\text{O}_{214}$: C, 56.21; H, 9.16; N, 0.83 Found: C, 55.87; H, 9.18; N, 0.66.

P-9: Incomplete reaction.

P-10: ^1H NMR (CDCl_3) : δ 0.83–0.95 (m), 1.18–1.45 (m), 1.60–1.84 (m), 4.17–4.36 (m), 4.64 (br s), 5.54–5.82 (m), 6.21 (br s), 6.42 (br s), 7.19–7.32 (m), 7.52–7.55 (m), 7.69–7.73 (m), 8.65–8.77 (m); ^{13}C NMR (CDCl_3) : δ 14.0, 14.1, 22.9, 23.6, 26.2, 26.3, 28.7, 28.8, 29.0, 29.6, 30.3, 38.6, 49.4, 51.2, 53.4, 61.8, 62.3, 65.3, 68.1, 123.8, 125.8, 126.1, 126.6, 126.8, 128.7, 130.9, 132.3, 136.0, 139.3, 139.8, 141.3, 141.8, 142.9, 143.0, 153.3, 158.5, 162.8, 167.7. Anal. Calcd for $\text{C}_{28}\text{H}_{38}\text{N}_6\text{O}_6$: C, 60.63; H, 6.91; N, 15.15 Found: C, 60.41; H, 7.11; N, 14.96.

P-11: ^1H NMR (CDCl_3) : δ 1.30–1.50 (m), 1.78 (s), 1.98–2.03 (m), 3.44 (s), 3.64 (br s), 3.82–3.85 (m), 4.40–4.51 (m), 4.70–4.80 (m), 8.13–8.16 (m); ^{13}C NMR (CDCl_3) : δ 23.1, 29.2, 29.4, 49.7, 50.1, 64.0, 64.7, 68.6, 68.8, 70.4, 127.6, 138.1, 139.8, 160.5. Anal. Calcd for $\text{C}_{37}\text{H}_{64}\text{N}_6\text{O}_{16}$: C, 52.35; H, 7.60; N, 9.90 Found: C, 51.48; H, 7.79; N, 9.26.

P-12: ^1H NMR (CDCl_3) : δ 1.60–1.66 (m), 2.15–2.23 (m), 3.58–3.69 (m), 4.28–4.33 (m), 5.10–5.12 (m), 5.19 (s), 5.29 (s), 6.81–6.94 (m), 7.68 (s), 7.78 (s); ^{13}C NMR (CDCl_3) : δ 49.8, 50.7, 59.6, 62.3, 65.1, 68.5, 70.4, 103.3, 115.8, 115.9, 124.5, 133.4, 133.5, 133.7, 133.8,

144.3, 144.4, 151.8, 152.3, 152.7, 153.2, 166.4. Anal. Calcd for $\text{C}_{24}\text{H}_{30}\text{N}_6\text{O}_9$: C, 52.74; H, 5.53; N, 15.38 Found: C, 52.52; H, 5.59; N, 15.09.

P-13: Insoluble polymer. No NMR data available due to the poor solubility of the polymer in CDCl_3 , DMSO, MeOH, acetone, and water. Anal. Calcd for $\text{C}_{26}\text{H}_{34}\text{N}_6\text{O}_9$: C, 54.35; H, 5.96; N, 14.63 Found: C, 53.93; H, 6.06; N, 13.53.

Polymer selection as model system

Among these polymers, the polymer **P1** (Entry 1) obtained by the polymerization of E300 dipropiolate (**1**) with diazide (**2**) obtained from tetraethylene glycol was selected as a model binder system due to its appreciable elasticity, nature and availability of its starting monomers, time of reaction, temperature conditions, and ease of scaling up. A detailed study (stoichiometrically and mechanistically) was done on polymer **P1** to improve its mechanical properties as potential rocket propellant binders.

Preparation of mini samples for stoichiometric studies

The purpose of the preparation of the mini samples was simply for initial screening of diacetylene (**1**) and diazide (**2**) at various stoichiometric concentrations to obtain corresponding linear triazole polymers. This was important because we had no information regarding the physical nature of the polymers that would be obtained by varying the stoichiometry ratios of the monomers (E300 dipropiolate, and tetraethylene glycol diazide) (Scheme 2) and the corresponding variation trends of their modulus and strain. Although the manual testing of these mini samples affords only approximate results, these manual tests helped us to know how strain and modulus changed with different ratios of the two monomers other than exact values of strain and modulus. This also uses lesser starting monomers (< 300 mg) as compared with the larger samples (approximately 2 g) that were done later with specific concentrations in standard dogbone molds based on these preliminary results and were tested by Instron Tensile Testing Machine.

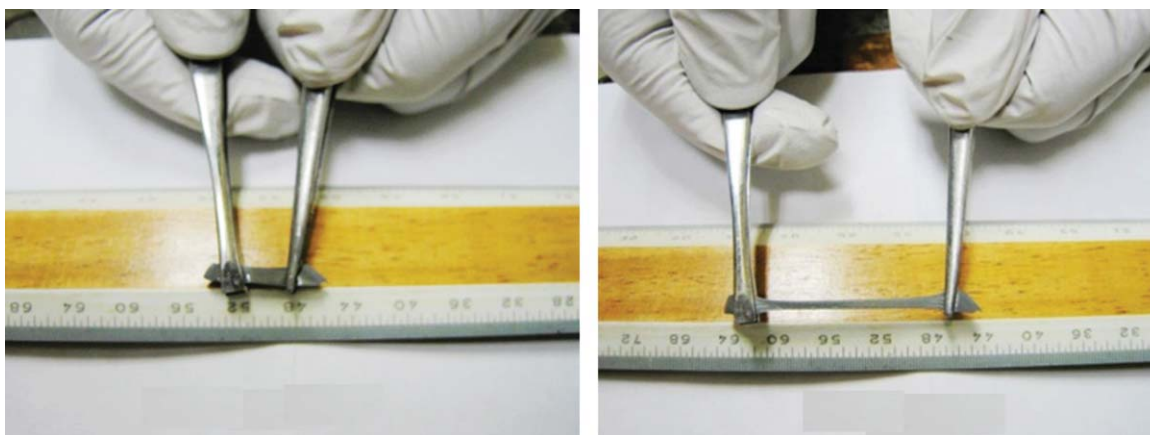


Figure 2 Method for manual tests of strain. (a) original sample, (b) sample under extension.

$$\text{Strain} = \frac{L-L_0}{L_0} \times 100\% = \frac{\Delta L}{L_0} \times 100\% \quad (1)$$

The sample was stretched by two tweezers. The original length (L_0) and increased length (ΔL) of the sample were measured by a fine scale. The strain at failure was calculated by eq. (1). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Method of manual testing of strain and modulus

The strain of the polymers was estimated by subjecting much smaller thin film samples to external deformation and measuring the original and increased length of the samples by a fine scale. (Fig. 2) This allowed for the testing of many more compositions on the tens of milligram scale and the concomitant gains in safety, sample waste, and efficiency. The process of tests of modulus on the mini samples is illustrated in Figure 3.

Crosslinker selection

Crosslinkers are known to provide less mobility to the polymer chains, which in turn increases the stiffness of the polymer. Thus, to improve on the mechanical properties of the linear triazole polymers and depending on the structural specificity of the monomers, tetraacetylene functionalized crosslinker (3, tetrapropiolate) was synthesized and selected to study the effect of crosslinker concentration on the mechanical properties of the resulting crosslinked triazole polymers.

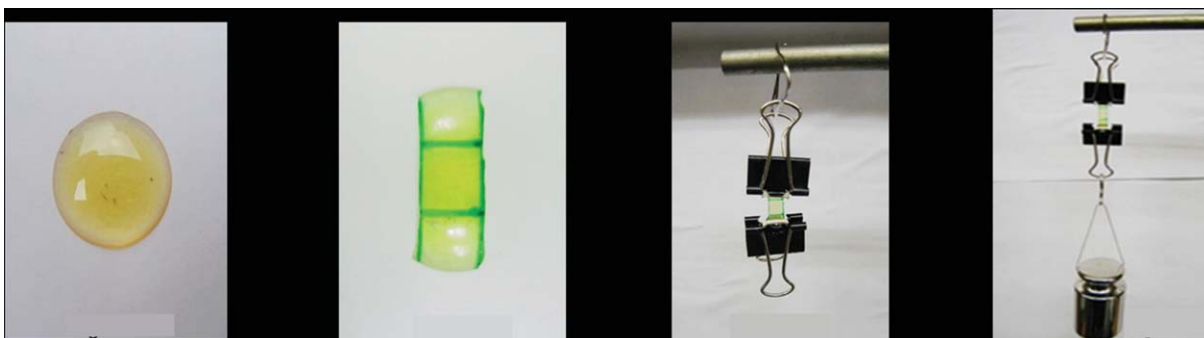


Figure 3 Method for manual tests of modulus. (a) Mini sample film, (b) sample strip, (c) fixed sample, (d) sample under extension.

$$\text{Young's modulus} = \frac{\text{Stress}}{\text{Strain}} \quad \text{stress} = \frac{F}{A_0} \quad (2)$$

(F : force loaded on the sample, A_0 : original area of sample cross section) The original length of the sample is the distance between two green lines. The force loaded on the sample is the weight attached to the sample. The young's modulus can be calculated by eq. (2). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

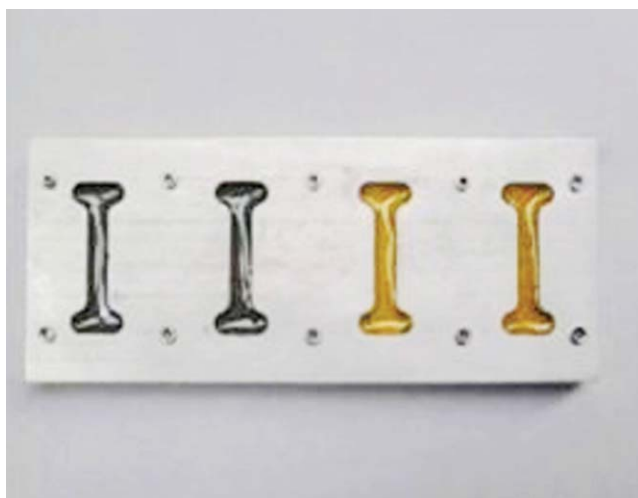
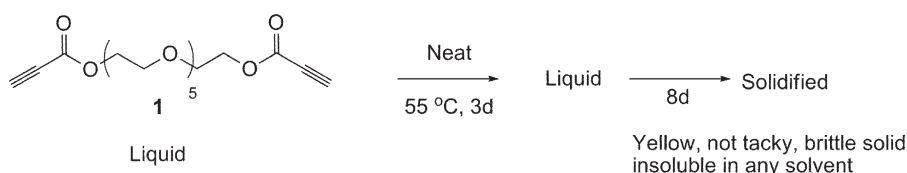


Figure 4 Dogbone mold containing filled and unfilled triazole polymers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Preparation of 3-(Propiolyloxy)-2,2-bis[(propiolyloxy)methyl]propyl propiolate (tetrapropiolate) (3): A solution of pentaerythritol (5 g, 36.72 mmol), propiolic acid (14.91 g, 213 mmol), and conc. H_2SO_4 (0.5 mL) in benzene (75 mL) was heated to reflux using a Dean Stark apparatus for 12.5 h. Then the reaction mixture was ice cooled and neutralized with solid Na_2CO_3 , filtered, washed with ether, and then the filtrate was evaporated to obtain a solid. The solid was dissolved in CH_2Cl_2 (100 mL) washed with saturated $NaHCO_3$ (50 mL), water (50 mL), and brine (25 mL). The dichloromethane layer was dried over anhydrous $MgSO_4$, filtered, and the solvent was evaporated to give pentaerythritol tetrapropiolate (6.5 g, 51%) as white microcrystals. 1H NMR ($CDCl_3$): δ 2.98 (s, 4H), 4.31 (s, 8H); ^{13}C NMR ($CDCl_3$): δ 41.7, 63.3, 73.6, 76.4, 151.8. Anal. Calcd for $C_{17}H_{12}O_8$: C, 59.31; H, 3.51 Found: C, 59.05; H, 3.57.

Preparation of dogbone samples for mechanical studies

In an aluminum pan, E300 diacetylene (1) was weighed and different concentrations of crosslinker (3) were added and stirred until it dissolved. The time of dissolving crosslinker may vary from 5 to 20 min with the increase in the concentration of the crosslinker. This was followed by the addition of



Scheme 3 Reaction of pure acetylene.

TABLE I
Effect of Stoichiometry on Mechanical Properties of Triazole Polymers

Entry	Diacetylene: diazide	Modulus(psi)	Strain (%)	Comparative sample description
1	0.98 : 1	NA	NA	Tacky and soft
2	1 : 1	NA	NA	
3	1.02 : 1	NA	NA	↓
4	1.04 : 1	<1	1470	
5	1.06 : 1	1	3180	Rubbery
6	1.08 : 1	4	2980	
7	1.10 : 1	7	2800	↓
8	1.12 : 1	<1	1580	Tacky and soft

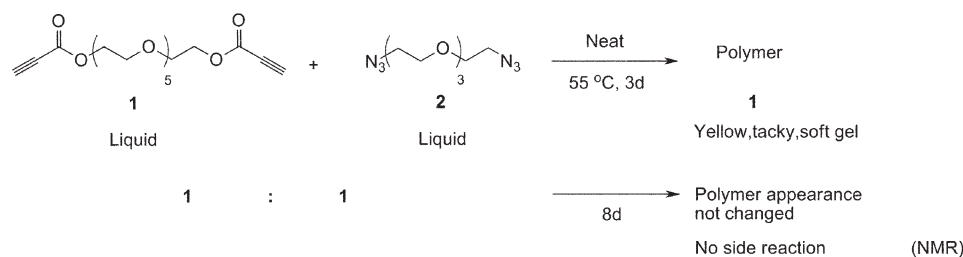
diazide (2), which on stirring gave a homogeneous mixture (Scheme 5). The reactions were carried on a total scale of 2 g (including the three reactants for each dogbone sample) in aluminum pans by taking 100 mol % of diazide (2) and calculating the concentrations of diacetylene (1) and the crosslinker (3) accordingly as shown in Scheme 5, keeping the overall end group stoichiometric ratios 1 : 1. The mixture was casted into a dogbone mold (Fig. 4) and the dogbone mold was degassed under vacuum at room temperature for 15 min and left at room temperature for 3–4 h. The curing was then done in a vacuum oven at 55°C for 72 h. The dogbone samples were carefully removed from the mold. After they cooled, they were tested using a Universal Tensile Testing Machine.

For the filled systems, aluminum powder was added to the homogeneous mixture of diacetylene (1), diazide (2) and crosslinker (3), then mixed uniformly and degassed followed by curing in a vacuum oven at 55°C for 1 h. After that, the mixture was stirred again and cured at 55°C for an additional 71 h.

RESULTS AND DISCUSSION

Selection of model polymer system

As per the specification of rocket propellant binders, the monomers should be reactive at low temperatures (room temperature to 60°C) with no or little side reactions. The polymerization process should proceed in the absence of any solvent or heavy metal catalysts. In addition, the polymerization should be easily scaled up. Accordingly, different



Scheme 4 Reaction of diacetylene and diazide at 1 : 1 ratio.

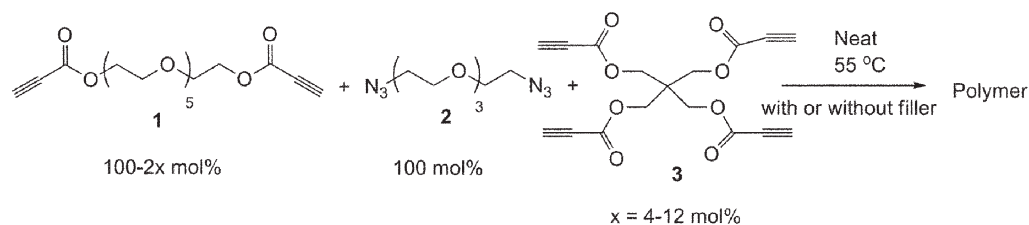
diazides and diacetylenes in Scheme 1 were screened and polymerization conditions were optimized by the criteria mentioned above. As shown in Scheme 1, diacetylenes with acetylene groups connected to electron withdrawing groups showed better activities than propargyl esters or ethers (Reaction b, g, l) that needed higher temperature and/or catalyst to react with azides. Benzyl azides (Reaction e, m) can react with propiolates easily at room temperature. However, the reactions are more vigorous and sometimes too violent. Reactions c and j were also ruled out because of difficulties in scaling up the preparation of starting material (7). Moreover, the reactions of monomers with longer spacers between end groups (Reactions d, f, h, i, k) need higher temperature or longer reaction time. Thus, the reaction of E300 dipropiolate (1) with diazide (2) obtained from tetraethylene glycol (Reaction a) was selected as a model system to study the relationship between crosslinker concentration and mechanical properties of triazole polymers.

Stoichiometry effect on the mechanical properties of linear triazole polymers

The effect of diacetylene to diazide stoichiometry on the mechanical properties of triazole polymers was studied. The ratio of diacetylene to diazide was varied from 0.98:1 to 1.12:1 on mini scale (Scheme 2). Because many of the resulting polymers were too soft and tacky to cast into dogbone molds, the strain and modulus of the polymers were estimated by the manual method described earlier. The results are listed in Table I.

As shown in Table I, the polymers with azide stoichiometry in excess were soft, tacky, and nonelastic.

With slight excess of diacetylene, the polymer becomes comparatively hard and elastic. On further increasing the diacetylene concentration, the modulus increased reaching the maximum value at the ratio of 1.10 : 1 (Entry 7), then finally decreased on further increasing the diacetylene concentration. These results were unexpected because in a step polymerization involving two difunctional monomers, the polymer should give the best mechanical properties at 1 : 1 stoichiometry of the monomers since any imbalance in stoichiometry should significantly lower the degree of polymerization.^{28,29} However, these results showed that the ratio of 1.10 : 1 gave the highest value of modulus and a systematic shift toward excess acetylene was observed despite the purification noted in the experimental section. Side reactions may account for this shift. For instance, it has been reported that the reaction of propiolate coupling to form enyne could be catalyzed by Lewis bases such as aromatic and aliphatic amines due to the lone pairs on the nitrogens.³⁰ In this case, such excess unreacted diacetylenes might then undergo self-condensation or oxidative coupling in the presence of triazole acting as a catalyst to result in internal crosslinking, increase in molecular weight, and ultimately shifting the stoichiometry from the expected 1 : 1 toward excess acetylene. To study this systematic shift toward excess acetylene, two reactions were performed. The first is the self-reaction of pure diacetylene (1) (Scheme 3); the second is the reaction of diacetylene (1) with diazide (2) at 1 : 1 molar ratio (Scheme 4). After 3 days of reaction, the first reaction seemed incomplete, whereas the second reaction gave tacky and soft gel. The first reaction resulted in a nontacky brittle solid on the eighth day, whereas the triazole polymer from the



Scheme 5 Crosslinked triazole polymer formation.

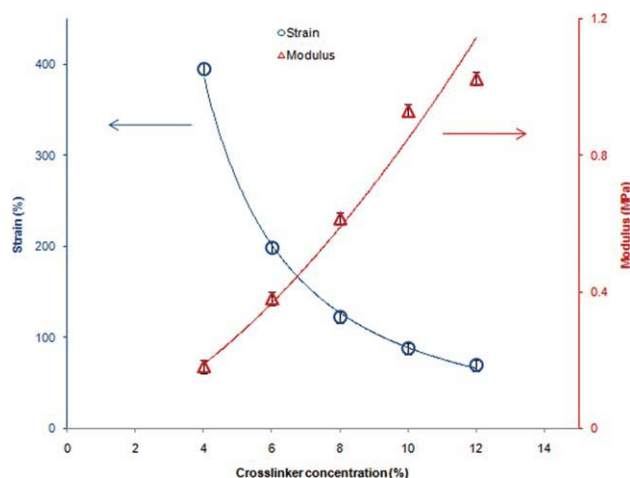


Figure 5 Effect of crosslinker concentration on mechanical properties of unfilled triazole polymers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

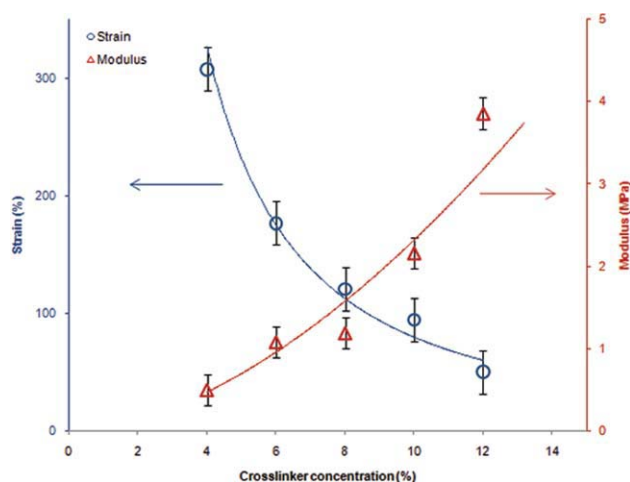


Figure 6 Effect of crosslinker concentration on mechanical properties of filled triazole polymers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

second reaction stayed the same. NMR results suggested that no side reaction occurred for the second reaction. Unfortunately, the solid from the first reaction was insoluble in any organic solvent thus unanalyzable. However, the reaction of pure acetylene clearly indicates that side reactions may occur in the case of excess acetylene, which could result in unstable triazole polymers. Therefore, the ratio of acetylene to azide groups was kept at 1 : 1 to avoid any potential side reactions in the following experiments.

Effect of crosslinker concentration on the mechanical properties of triazole polymers

The effect of increasing concentration of crosslinker (3) on the strain and modulus of the resulting polymers was studied in both unfilled and filled systems having end groups in the ratio of 1 : 1 [(diacetylene + tetrapropiolate):diazide, Scheme 5]. It should be noted that this stoichiometry also optimized tack in the reacting system, and with it, the ability to maximize filler loading as well as avoiding potential side reactions. The properties of more highly filled systems will be the subject of a future article. Strain and modulus of the polymers were first tested man-

ually and then tested by Instron tensile testing machine.

The variation trend of strain and modulus values with increasing crosslinker concentration in unfilled triazole polymers is shown in Figure 5. The data in Figure 5 are from tests on dogbone samples by Instron tensile tester and listed in Table II.

As shown in Figure 5 and Table II, as crosslinker concentration was increased from 4 to 12 mol %, the modulus increased from 0.18 to 1.0 Mpa, whereas the strain decreased from 400 to 70%. This trend is due to increasing crosslink density. As the amount of crosslinker was increased, crosslink density was also increased, which means more crosslinks to restrict the individual chain mobility. This fivefold modulus increase and correlated stiffness increase occurs over a convenient range of crosslinker concentration and gives a facile method to control mechanical properties in these systems.

Because aluminum is commonly used as a fuel in rocket propellants,³¹ to simulate real filled binder systems, 43 wt % of aluminum powder was added to the crosslinked binder as a filler. With 43 wt % aluminum filler, the polymer has good processability, which facilitated the study of the crosslinker

TABLE II
Strain and Modulus of Unfilled Triazole Polymers

Entry	Crosslinker concentration (mol %)	Strain (%)	Modulus (Mpa)
1	4	400	0.18
2	6	200	0.38
3	8	120	0.62
4	10	88	0.93
5	12	70	1.0

TABLE III
Strain and Modulus of Filled (43% Al) Triazole Polymers

Entry	Crosslinker concentration (mol %)	Strain (%)	Modulus (Mpa)
1	4	310	0.5
2	6	180	1.1
3	8	120	1.2
4	10	95	2.2
5	12	50	3.9

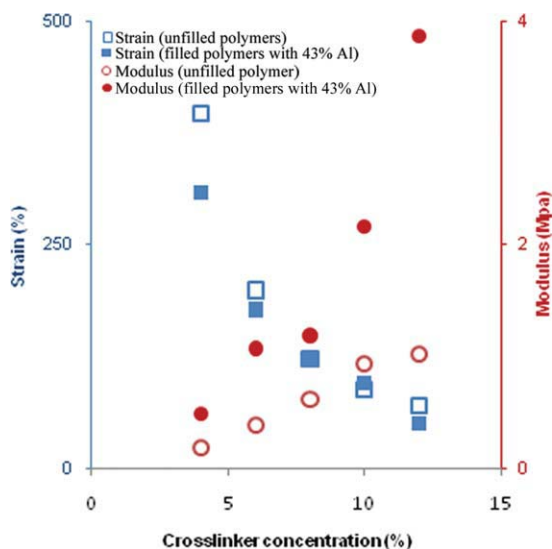


Figure 7 Comparison of mechanical properties of unfilled and filled (43 wt % Al) triazole polymers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

effect on the mechanical properties of filled triazole polymers. Mechanical tested data are plotted in Figure 6. Table III gives the specific values of strain and modulus corresponding to the data points in Figure 6. For unfilled and filled triazole polymers, crosslinker has the same effect on their strain and modulus: with increasing crosslinker concentration, the modulus increases whereas the strain decreases. For triazole polymers with 43% aluminum filler, with increasing crosslinker from 4 to 12 mol %, the modulus increased from 0.5 to 3.9 Mpa, an eightfold change, whereas the strain decreased from 310 to 50% (Table III). Because the strain and modulus for potential propellant binders should be at least 50% and 1.4 Mpa, respectively, the ideal range of crosslinker concentration to achieve the goal is around 9–12 mol %.

Compared with a typical polyurethane, elastomeric liner matrix for rocket propellants having strain 150–900% and 0.05–1.9 MPa,²⁵ triazole polymers have much improved modulus (0.5–3.9 MPa). For more highly filled triazole-based systems, the modulus can be expected to show further increases.

The mechanical properties of unfilled and filled triazole polymers are compared in Figure 7. The modulus of filled polymers is at least two times that of the unfilled polymers due to the addition of much stiffer aluminum powder to the polymer matrix. Generally, the strain of the filled polymers decreased slightly compared with the unfilled polymers, and this is in accordance with literature, which states that the filler restricts the mobility of polymer chains leading to decrease of strain.³² The decrease in strain is not drastic, and this may be due to the good tack of

these materials noted above and adhesion of binder to the filler.

Figure 8 compares the stress–strain curves of the polymers with different crosslinker concentration measured on the dogbone samples at controlled strain rate. The change of mechanical properties of the polymers with different crosslinker concentrations can be clearly seen from these stress–strain curves. With lower crosslinker concentration, the polymer is softer and more elastic. Likewise the samples become stiffer and more prone to elongational failure as the crosslinker concentration was increased.

CONCLUSIONS

The reaction of E300 dipropiolate (1) with diazide obtained from tetraethylene glycol (2) was selected from 13 reactions of various organic diazides and diacetylenes as a model reaction to study effects of crosslinker concentration on the mechanical properties of triazole polymers. The modulus of both unfilled and filled polymers increased, whereas the elasticity decreased with increasing percentage of crosslinker. Thus, the triazole polymers with desired mechanical properties as potential rocket propellant can be obtained by adjusting the crosslinker concentration during the polymerization. Compared with unfilled polymers, the addition of 43 wt % aluminum filler greatly improved modulus of triazole polymers, which could reach nearly 4 Mpa. Compared with urethane-cured rocket propellants, these unoptimized triazole polymers have comparable modulus that can be further increased in highly filled system. The filler also had minimal effect on elongational strain at failure.

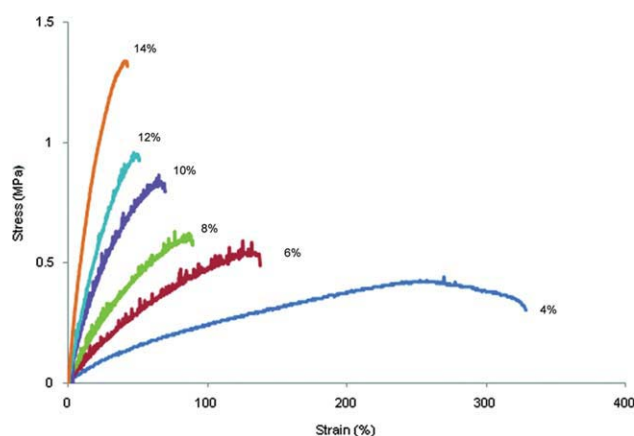


Figure 8 Stress–strain curves of filled triazole polymers (43 wt % Al) with increasing crosslinker concentration (4 mol %–14 mol %). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

References

1. Lutz, J. F. *Angew Chem Int Ed* 2007, 46, 1018.
2. Takizawa, K.; Nulwala, H.; Thibault, R. J.; Lowenhielm, P.; Yoshinaga, K.; Wooley, K.; Hawker, C. J. *J Polym Sci Part A: Polym Chem* 2008, 46, 2897.
3. Nagal, A.; Kamel, Y.; Wang, X.; Omura, M.; Sudo, A.; Nishida, H.; Kawamoto, E.; Endo, T. *J Polym Sci Part A: Polym Chem* 2008, 46, 2316.
4. Evans, R. A. *Aust J Chem* 2007, 60, 384.
5. Wu, P.; Feldman, A. K.; Nugent, A. K.; Hawker, C. J.; Scheel, A.; Voit, B.; Pyun, J.; Frechet, J. M. J.; Sharpless, K. B.; Fokin, V. V. *Angew Chem Int Ed* 2004, 43, 3928.
6. Helms, B.; Mynar, J. L.; Hawker, C. J.; Frechet, J. M. J. *J Am Chem Soc* 2004, 126, 15020.
7. Dirks, A. J.; Van Berkel, S. S.; Hatzakis, N. S.; Opsteen, J. A.; Van Delft, F. L.; Cornelissen, J. J. L. M.; Rowan, A. E.; Van Hest, J. C. M.; Rutjes, F. P. J. T.; Nolte, R. J. M. *Chem Commun* 2005, 4172.
8. Parent, M.; Mongin, O.; Kamada, K.; Katan, C.; Blanchard-Desce, M. *Chem Commun* 2005, 2029.
9. Van Steenis, D. J. V. C.; David, O. R. P.; Van Strijdonck, G. P. F.; Van Maarseveen, J. H.; Reek, J. N. H. *Chem Commun* 2005, 4333.
10. Quemener, D.; Davis, T. P.; Barner-Kowollik, C.; Stenzel, M. H. *Chem Commun* 2006, 5051.
11. Zhou, Y.; Jiang, K.; Chen, Y.; Liu, S. *J Polym Sci Part A: Polym Chem* 2008, 46, 6518.
12. Joosten, J. A. F.; Tholen, N. T. H.; Ei Maate, F. A.; Brouwer, A. J.; Van Esse, G. W.; Rijkers, D. T. S.; Liskamp, R. M. J.; Pieters, R. J. *Eur J Org Chem* 2005, 3182.
13. Laurent, B. A.; Grayson, S. M. *J Am Chem Soc* 2006, 128, 4238.
14. Diaz, D. D.; Punna, S.; Holzer, P.; Mcpherson, A. K.; Sharpless, K. B.; Fokin, V. V.; Finn, M. G. *J Polym Sci Part A: Polym Chem* 2004, 42, 4392.
15. Katritzky, A. R.; Meher, N. K.; Hanci, S.; Gyanda, R.; Tala, S. R.; Mathai, S.; Duran, R. S.; Bernard, S.; Sabri, F.; Singh, S. K.; Doskocz, J.; Ciaramitaro, D. A. *J Polym Sci Part A: Polym Chem* 2008, 46, 238.
16. Thompson, C. M.; Hergenrother, P. M. *High Perform Polym* 2001, 13, 313.
17. Reed, R. U.S. Pat. 6,103,029 (2000).
18. Herder, G.; Weterings, F. P.; De Klerk, W. P. C. *J Therm Anal Calorimetry* 2003, 72, 921.
19. Tian, J.; Wan, L.; Huang, J.; Hu, Y.; Huang, F.; Du, L. *Polym Adv Technol* 2007, 18, 556.
20. Wan, L.; Luo, Y.; Xue, L.; Tian, J.; Hu, Y.; Qi, H.; Shen, X.; Huang, F.; Du, L.; Chen, X. *J Appl Polym Sci* 2007, 104, 1038.
21. Wan, L.; Tian, J.; Huang, J.; Hu, Y.; Huang, F.; Du, L. *J Macromol Sci, Part A: Pure Appl Chem* 2007, 44, 175.
22. Katritzky, A. R.; Singh, S. K.; Meher, N. K.; Doskocz, J.; Suzuki, K.; Jiang, R.; Sommen, G. L.; Ciaramitaro, D. A.; Steel, P. J. *Arkivoc* 2006, 5, 43.
23. Magrab E. B. *Integrated Product and Process Design and Development: The Product Realization Process*; CRC Press LLC: Boca Raton, FL, 1997.
24. Fan, R.; Zhang, Y.; Huang, C.; Zhang, Y.; Fan, Y.; Sun, K. *J Appl Polym Sci* 2001, 81, 710.
25. Haska, S. B.; Bayramli, E.; Pekel, F.; Ozkar, S. *J Appl Polym Sci* 1996, 64, 2347.
26. Zhang, Y.; Hu, B.; Xia, C.; Chen, Z.; Yin, Q. *Hecheng Huaxue* 2002, 10, 335.
27. Riser, D.; Hunter, J.; Rast, R. *AIAA/SAE/ASME/ASEE 28th Joint Propulsion Conference and Exhibit*; Nashville, TN, 1992, July 6–8.
28. Grant Cowie, J. M. *Polymers: Chemistry and Physics of Modern Materials*; CRC press: Boca Raton, FL, 1991.
29. Rosato, D. V. *Plastics Engineering, Manufacturing & Data Handbook*; Rosato, D. V., Schott, N. R., Rosata, M. G., Eds. Springer: New York, 2001, Vol 1, p 131.
30. Ramachandran, P. V.; Rudd, M. T.; Reddy, M. V. R. *Tet Lett* 2005, 46, 2547.
31. Sutton, G. P.; Biblarz, O. *Rocket Propulsion Elements*; Wiley: New York, 2001.
32. Unal, H. *Mater Des* 2004, 25, 483.