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Energetic Polymeric Network Prepared via a Solvent- and Catalyst-Free Thermal Cycloaddition of Azide-Bearing Polymer with Alkynes and Hydroxyl-isocyanate Addition Reactions

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Polymeric networks were prepared through a 1,3-dipolar cycloaddition of azide-bearing polymers with a variety of compounds having two or three terminal alkynes without solvents and catalysts. Dipolarophiles with an α-carbonyl underwent a very rapid Huisgen reaction within a few minutes to afford networks that were side-linked with triazole moieties. The reactivities of dipolarophiles were estimated by using frontier molecular orbital energies. To avoid the formation of defects in elastically ineffective networks, all polymer chain-ends were linked with urethane moieties, and very small quantities of azides were reacted with the dipolarophiles to link the pendent groups with the triazoles. Because the crosslinking densities of the energetic networks were inversely proportional to the reactivity of the dipolarophiles to the azides, the less reactive alkynes conveyed better mechanical properties to the networks prepared using the Huisgen cycloaddition reaction compared to the more reactive alkynes.

Introduction

Triazoles are heterocyclic compounds having high chemical and thermal stability, strong dipole moment, and hydrogen bond accepting capability.[1] Triazole derivatives have been extensively studied in the field of pharmaceuticals, biomolecules, and polymers.[2] N-heterocycles containing 1,2,3-triazole and 1,2,4-triazole have been used in the field of explosives and propellants because of their high nitrogen content and thermal stability, coupled with a low sensitivity to stimuli such as friction or impact.[3] The cycloaddition of azides and alkynes offers direct access to 1,2,3-triazoles. The Huisgen 1,3-dipolar cycloaddition between 1,3-dipoles azides and dipolarophile alkynes recently have been termed as a *click* reactions (modular-type reactions with a high selectivity and a quantitative yield but without by-products).[4] Huisgen cycloaddition processes can be accelerated tremendously by introducing metals species, such as Ru, Pd, Pt, or Ni, and most commonly copper (Cu).[5] Cu(I)-catalyzed azide–alkyne cycloadditions (CuAAC) that yield triazoles have been used extensively in organic and polymer syntheses. However, the

use of copper in click reactions has presented a significant problem in organic synthesis, especially in biological applications, due to the cytotoxicity of copper.[6] Efforts to avoid copper catalysts have focused on the development of non-catalyzed click reactions as an alternative to CuAAC.[7] In addition to catalyst-free (CF) reactions, solvent-free (SF) reactions have received significant attention among green chemists, because it can avoid the use of toxic (chlorinated) solvents.[8] Interestingly, the three-dimensional polymeric networks for solid propellants can be obtained under SF conditions. Homogeneous polymer network formation through specific crosslinking reaction without any volatile side products is an ideal characteristics for the preparation of solid propellants.

Urethane crosslinking systems have been widely used in solid propellants and the catalysts for urethane crosslinking system such as triphenyl bismuth and dibutyltin-dilaurate are miscible with both hydroxyl-terminated polymers, such as polybutadiene or polyether, and isocyanate curatives, such as isophorone diisocyanate or toluene diisocyanate, under SF conditions. The use of these catalysts in the urethane crosslinking systems for solid propellants has been systemically examined.[9] Demand for new non-urethane crosslinking systems has recently increased among solid propellant formulators who seek a propellant that is less sensitive to moisture and avoids the use of isocyanate compounds prepared through hazardous manufacturing processes involving phosgene. Isocyanate is incompatible with eco-friendly oxidizers such as ammonium dinitramide (ADN) and hydrazium nitroformate (HNF). A promising next-generation crosslinking system can be obtained by crosslinking of polymer chains through triazole moieties via a Huisgen 1, 3-dipolar

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cycloaddition of an azide-bearing polymer with an alkyne-type dipolarophile.[10] The azides used in explosives and propellants tend to perform well due to their high positive formation energy. The most widely used azide-bearing energetic polymer is glycidyl azide polymer (GAP), obtained through the azidation of polyepichlorohydrin. The cycloaddition reactions of GAP with dipolarophiles produce energetic networks that are crosslinked *via* triazole moieties.[11] While the catalysts used in urethane crosslinking system tend to be miscible with the hydroxyl-terminated polymers, the metal catalysts (especially Cu (I)) that are typically used to facilitate 1,3-dipolar cycloadditions could not be used with GAP because of their immiscibility. So it is desirable to make homogeneous GAP-based networks via the Huisgen cycloaddition under SF conditions at mild temperatures.

We reported previously the preparation of triazole-crosslinked polymeric networks under SF-CF conditions using two dipolarophiles.[11b] Here we used a variety of novel dipolarophiles (bivalent and trivalent) to make homogeneous GAP-based networks under SF conditions. In an effort to predict the cyclization reaction rate of GAP with the dipolarophiles, we estimated the highly occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies associated with the dipole and dipolarophiles by computational methods. The nature of the substituents adjacent to the terminal alkyne groups were found to affect the reaction kinetics as well as the swelling and mechanical characteristics of the resulting polymeric networks.

Experimental

Materials and methods

The azide-bearing polymer used in this study was a hydroxyl functionalized GAP with a molecular weight and hydroxyl index of 2,400 g/mol and 0.74 eq/kg, respectively. The GAP was purchased from 3M under the trade names GAP diol (L9961). An isophorone diisocyanate (IPDI) urethane curative with a molecular weight/isocyanate index of 222 g·mol^{-1}/8.86 eq·kg^{-1}, was purchased from Mobay. Triphenyl bismuth (TPB) was obtained from Samchun Pure Chemical. All solvents for the swelling tests of the networks crosslinked through triazoles were used as received. All solvents used to synthesize the terminal alkynes were purchased from Aldrich and used as received. FT-IR spectral measurements were carried out using a Nicolet NEXUS model ATR system. ^{1}H-NMR (400MHz) and ^{13}C-NMR (100MHz) spectra were recorded using an ADRIAN spectrometer. CDCl$_3$ was used as a solvent for all Nuclear Magnetic Resonance (NMR) studies. Glass transition temperature was measured by using Differential Scanning Calorimeter (DSC, model : TA Q20) with a heating rate of 10°C/min. All networks formed through triazole moieties were cut into dumbbell-shaped specimens (33×4.0×3.5 mm), and the mechanical properties of these specimens were measured using a universal testing machine (Model 5567, Instron, USA) at a crosshead rate of 50 mm/min at room temperature. The

swelling tests were carried out using a series of organic solvents with solubility parameters in the range of 14.0–30.0MPa$^{1/2}$. The crosslinking densities of all networks crosslinked via triazoles were determined in dimethyl acetamide (DMA$_C$, δ_{DMAC} = 22.1 MPa$^{1/2}$) at room temperature. The swelling ratio (Q) was calculated according to the equation (1),

$$Q = 1 + (w_2/w_1 - 1)\,\rho_2/\rho_1 \qquad (1)$$

where w_1 and w_2 are the weights of the unswollen and swollen specimens, and ρ_1 and ρ_2 are the densities of the solvent and GAP.

Preparation of the elastomeric networks

All reagents were dried overnight in a vacuum oven at 60°C prior to use. The polymeric networks were prepared by mixing GAP and a dipolarophile in a rotary evaporator, followed by degassing at 50°C. The solid-type dipolarophiles were dissolved in acetone. The mixture was poured into a Teflon-coated mold and cured at 50°C for 7 days. A dual crosslinking system consisting of both an IPDI curative and a dipolarophile was used to prepare the networks. The isocyanate curative/GAP (NCO/OH) equivalent ratio was 1.1, and TPB (0.1%) was essentially introduced into the binder to accelerate the urethane reaction.
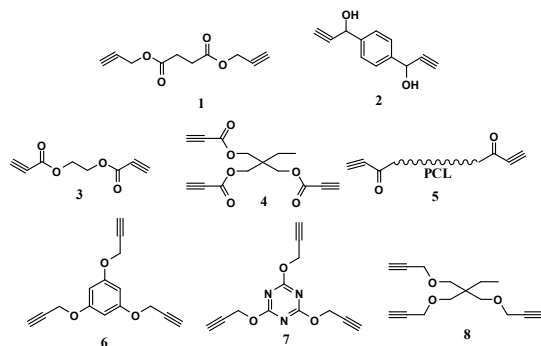
Results and discussion

The triazole curing systems based on polymers containing azido pendent groups undergo cycloaddition reactions between azides and alkynes to yield a highly crosslinked network. The preparation of solid-filled plasticized elastomers is thereby complicated as the highly crosslinked side chains reduces the plasticizer levels and prevents large quantities of solid particles from being loaded into the elastomers. The networks tend to form rigid elastomers that yield poor mechanical properties and a low resistance to fracture and rupture.

Good mechanical properties and a high formation energy may be achieved ideally by promoting the reaction of only one of azide groups in each polymer chain with one alkyne of a divalent dipolarophile to form a side-crosslinked network. A single linkage between polymer chains can be obtained by introducing one molecule of a divalent dipolarophile into each azide polymer molecule. An equivalent ratio exceeding 0.07 (C≡CH/-N$_3$) was needed for the formation of a GAP network in the presence of divalent alkynes. However, formation of a network having good mechanical properties from an end-functionalized polymer also requires that essentially all of the terminal functional groups should be reacted with the corresponding groups of the crosslinking agent as designed.

FMO energies and kinetics of the 1, 3-dipolar cycloaddition reaction

The purely thermal azide-alkyne Huisgen cycloaddition produced 1, 4- and 1, 5-triazole regioisomers due to interactions between the $HOMO_{dipole}$-$LUMO_{dipolarophile}$ and $HOMO_{dipolarophile}$-$LUMO_{dipole}$ frontier molecular orbitals (FMOs). A small HOMO-LUMO gap was favored and resulted in a greater fraction of the regioisomer than other HOMO-LUMO interactions. The HOMO-LUMO gap (or reactivity) associated with the thermal cycloaddition depended strongly on the identity of the substituent adjacent to the dipole and dipolarophile. An electron-withdrawing group (EWG) adjacent to the alkyne reduced the frontier energies of the LUMO and HOMO of the dipolarophile and promoted the formation of a 1, 4-regioisomer ($HOMO_{dipole}$-$LUMO_{dipolarophile}$). On the other hand, an electron-donating group increased the energies of the LUMO and HOMO of the dipolarophile to create a dominant $HOMO_{dipolarophile}$-$LUMO_{dipole}$ interaction that promoted the formation of the 1, 5-regioisomer in excess. In this work, the FMO energies were calculated using the Gaussian-3 program. We characterized the reaction type and rate between eight novel and distinct alkyne-terminal dipolarophiles (four bivalent compounds and four trivalent compounds) with an energetic dipolar polymer bearing azide pendent groups. The FMO energies of the azide group in the GAP were modeled based on 1-azido-2-methoxypropane.

Scheme 1 shows the structures of the bivalent dipolarophiles **1** (bis(propargyl) succinate, BPS) and **2** (1,4-bis(1-hydroxypropargyl)benzene, BHPB), bearing an EWG (-OC(=)O- or –OH, respectively) at the beta-position to the terminal alkyne. The oxygen group was located at the beta-position to the alkyne in the trivalent dipolarophiles (**6**, **7**, and **8**). The bivalent (**3**, **5**) and trivalent (**4**) dipolarophiles bore an ester (-C(=O)-O-) group adjacent to the alkyne. Table 1 lists the interaction energies of the $HOMO_{dipole}$-$LUMO_{dipolarophile}$ and $HOMO_{dipolarophile}$-$LUMO_{dipole}$. The calculation results predicted that the cycloaddition of the azide with **1** would display a marginal preference for the 1, 5-regioisomer over the 1, 4-regioisomer. This result was consistent with the density functional theory (DFT) results reported by Reshmi et al.[11c] A strong $HOMO_{dipolarophile}$-$LUMO_{dipole}$ interaction was observed in BHPB, which led to the formation of an excess of the 1,5-regioisomer. By contrast, the electronically activated (electron-deficient) dipolarophiles possessing an α-carbonyl (**3** and **4**) provided much smaller $HOMO_{dipole}$- $LUMO_{dipolarophile}$ energy gaps than any of the other dipolarophiles.

Table 1 Calculated energies and gel times for the reactions of the dipolarophiles with the azide-bearing GAP

Dipolarophile	$HOMO_{dipole}$-$LUMO_{dipolarophile}$	$HOMO_{dipolarophile}$-$LUMO_{dipole}$	Gel time(hrs)@50°C
1	-158.12	-155.02	9
2	-150.29	-132.17	7
3	-126.25	-163.4	<10min @20°C
4	-122.95	-161.37	0.5
5			4
6	-167.58	-119.82	3
7	-146.64	-154.26	5
8	-143.11	-139.72	

The FMO energies of the oligomeric dipolarophile **5** were not calculated due to structural restrictions; however, the interactions in this structure are expected to be similar to those present in **3** and **4** because the carbonyl groups are located adjacent to the terminal alkynes. A $LUMO_{dipole}$-controlled cycloaddition reaction was predicted to occur in the trivalent phenyl-type dipolarophile **6**. On the other hand, the $HOMO_{dipole}$-$LUMO_{dipolarophile}$ interaction was predicted to be slightly more dominant than the $HOMO_{dipolarophile}$-$LUMO_{dipole}$ interaction in the triazine-type dipolarophile **7**. The trivalent dipolarophile **8** was predicted to preferentially react with GAP via $HOMO_{dipolarophile}$-$LUMO_{dipole}$; however, the difference between the $HOMO_{dipole}$-$LUMO_{dipolarophile}$ and the $HOMO_{dipolarophile}$-$LUMO_{dipole}$ was not as large as in **7**. This reaction type was similar to that of BPS (**1**) and displayed a marginal preference for one regiospecific compound over the other. The calculated FMO energies confirmed that the HOMO and LUMO energies of the dipolarophiles **3** and **4** were reduced in the presence of an EWG adjacent to the alkyne, leading to a $HOMO_{dipole}$-controlled reaction.
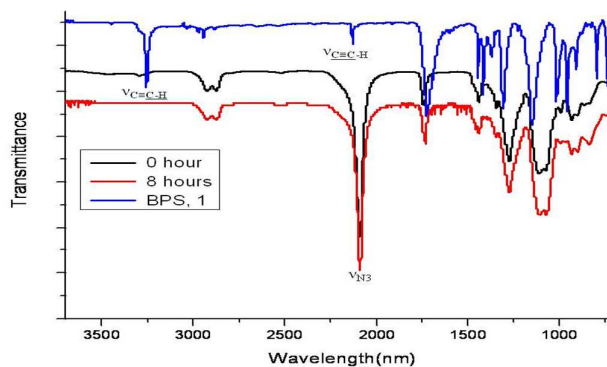

Fig. 1 FT-IR spectra of a dipolarophile (1) and its mixtures with GAP,over time.

Scheme 1 Structures of a variety of dipolarophiles bearing terminal alkynes.

The FMO energies of dipole and dipolarophiles were used to predict the kinetics of the triazole crosslinking reactions via the cycloaddition of GAP with each dipolarophile. As shown in Table 1, the lowest energy gap betweenthe HOMO and LUMO was found in the trivalent triazine **6**, which underwent a $HOMO_{dipolarophile}$–$LUMO_{dipole}$ reaction. The energies increased in the order of **6**, **4**, **3**, **2**, **8**, **7**, and **1**. As expected, the interaction energies in **3** and **4**, which included carbonyl groups adjacent to the alkynes, were much lower than those in other dipolarophiles, indicating an increase in the rate of network formation.

The kinetic predictions were validated by monitoring the triazole crosslinking reactions using FT-IR spectroscopy. As shown in Fig. 1, the ethynyl group peaks at 3260 and 2130cm^{-1} were very weak and overlapped with the strong azide peaks. The intensity of the ethynyl peak at 3260$cm^{-1}$was low in the initial mixture due to the very low −C≡CH/-N$_3$equivalent ratio (0.1, meaning that 10% of the azide groups reacted with a dipolarophile). The time-dependent intensity of the ethynyl (-C≡<u>CH</u>) peak was, therefore, difficult to monitor. Photographic images of the mixtures were collected during gelation at 50°C over time. Contrasting with the predictions obtained using the FMO calculations, the energetic networks formed the fastest in the presence of α-carbonyl dipolarophiles. The mixture involving the dipolarophile **3** gelled in less than 10 minutes at room temperature prior to heating in the oven. The compounds **4** and **5** displayed gel times of less than 10 and 30minutes, respectively. As shown in Fig. 2(a), the energetic networks prepared using the trivalent β-EWG dipolarophiles formed in the temporal order of **7**, **6**, and **8**. The dipolarophile **1** provided the slowest reaction rate, followed by the dipolarophile **2**. Nearly 10 hours were required to form the network, as shown in Fig. 2(b).The experimental results described here agreed well with the predicted reaction rate ordering among the various substituents adjacent to the terminal alkynes. A concentration exceeding 7 pph divalent dipolarophile (relative to GAP) (an equivalent ratio of 0.07) was required to form a side-linked network.[11b] The trivalent dipolarophiles, as shown in Fig. 2(c), formed a network at an equivalent ratio of less than 0.05.
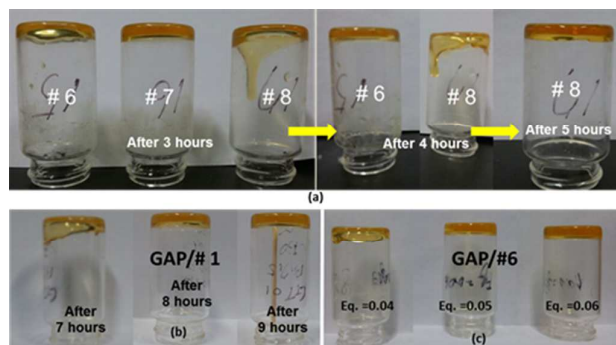

Fig. 2 Photographic images showing the progress of the cycloaddition of GAP with the less electronically activated terminal alkynes. a: gelation over time, depending on the type of alkyne present; b: gelation using the alkynes 1 over time; c: gelation over time, depending on the equivalent ratio of −CC/N$_3$.
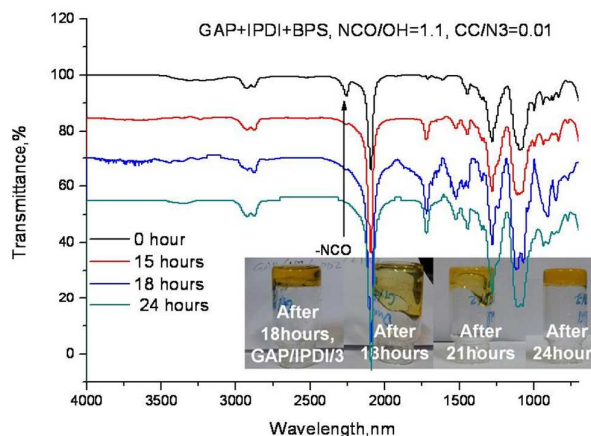

Fig. 3 FT-IR spectra and photographic images of the GAP mixtures during curing in the presence of both a dipolarophile and a diisocyanate, over time.

In addition to the formation of networks via 1,3-dipolar cycloaddition reactions, a urethane–diisocyanate reaction was used to link the polymer chain ends (-OH) to form a dual crosslinked network in which the polymer chain ends and side chains were linked through urethane and triazole moieties, respectively. It should be noted that GAP, which did not cure in the presence of a divalent isocyanate (IPDI) alone, formed a network upon the addition of small amounts of a dipolarophile (equivalent ratio, -C≡CH/-N$_3$= 0.01). The azide-bearing networks also formed upon the addition of small amounts of the dipolarophile, corresponding to an equivalent ratio of 0.005.

The network formation reaction using the dual curing system was monitored by FT-IR. The dipolarophiles **1** and **3** displayed the slowest and fastest cycloaddition reactions, respectively. The kinetics of the single (triazole) curing system could not be monitored using FTIR techniques.

On the other hand, as shown in Fig. 3, the kinetics of the dual curing system could be monitored according the disappearance of the FTIR isocyanate peak at 2270cm^{-1}over time. The isocyanate peaks in both mixtures disappeared within 18 hours.The mixture containing the dipolarophile **3** formed a gel. By contrast, several hours were needed for the mixture containing the dipolarophile **1** to form a gel (Fig. 3). The reactivity of the dipolarophile with the azide influenced the kinetics of the dual curing system.

Swelling characteristics

The solubility parameter is a measure of certain fundamental thermodynamic properties of polymers and may be used to describe the miscibility in a multi-component mixture that includes at least one polymer. The solubility parameters of the energetic networks prepared using various dipolarophiles were determined as measures of the crosslinking density (v_e) and molecular weight between crosslink points (M_c).[12] The physical and chemical properties of a propellant network crosslinked

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through triazole groups and containing energetic nitrate ester plasticizers were measured. Previous studies reported the solubility parameters of urethane-crosslinked networks prepared using GAP.[14] The conversion of azido groups in the repeating GAP units into triazole groups was expected to influence the solubility parameter of the polymeric network. Therefore, the solubility parameters of the side chain-linked networks prepared using a variety of dipolarophile curatives were calculated using Gee's theory according to the following Equation (2). The solubility parameters provided a measure of the effects of the triazole linkage on the physical properties of the network.[13]

$$Q/Q_{max} = \exp[-aQ \, (\delta_{solvent} - \delta_{polymer})^2] \quad (2)$$

Here, Q_{max} is the maximum swelling ratio and α is a constant. This equation may be rewritten as

$$[Q^{-1}\ln(Q_{max}/Q)]^{1/2} = |a^{1/2}(\delta_{solvent} - \delta_{polymer})| \quad (3)$$

A plot of $[Q^{-1}\ln(Q_{max}/Q)]^{1/2}$ against $\delta_{solvent}$ for a series of solvents may be used to determine $a^{1/2}$ and $\delta_{polymer}$, based on the slope and intersection with the horizontal axis, respectively. The swelling ratios obtained from the various solvents were linearly related to the solubility parameters, as predicted by eq. (2). The maximum swelling ratios for all networks were observed in pyridine, dimethylacetamide and epichlorohydin, in which solubility parameters are in the range of 21.7~ 22.5 MPa$^{1/2}$.

Equation (3) indicates that the solubility parameters of the energetic networks cured through triazole moieties were δ_{GAP} = 21.83–22.40 MPa$^{1/2}$. This range of values was comparable to the value obtained from a urethane-crosslinked GAP network (22.506 MPa$^{1/2}$). Here, the networks prepared using the polycaprolactone (PCL)-structured dipolarophile **5** showed the lowest solubility parameters because the solubility parameters of the PCL-based networks were lower than those of the GAP networks.[14]

The solubility parameters v_e and M_c of the networks were determined using the Flory–Rehner equation. As shown in Table 2, a higher crosslink density was produced in the presence of the β-EWG dipolarophiles (**1**, **2**) than in the presence of the α-EWG dipolarophiles (**3**, **5**). The low crosslinking densities of the networks prepared using **3** or **5** were attributed to the fact that the initial crosslinking reactions mainly involved the short polymer chains due to the high reactivity of the dipolarophiles and azide. The trivalent-based networks displayed higher crosslinking densities compared to the bivalent-based networks, as expected. The crosslinking density of the network formed by **4** was higher than that formed by the β-EWG dipolarophiles (**6**, **7**, and **8**). Surprisingly, the crosslinking densities decreased significantly as the equivalent ratio was reduced from 0.1 to 0.08.

The energetic networks formed using a dual crosslinking system further corroborated the observation that highly crosslinked networks did not form in the presence of electron-deficient alkynes, as indicated in Table 3. BPS showed the slowest reactivity among bivalent dipolarophiles in the Huisgen cycloaddition and offered the highest crosslinking density. The other bivalent dipolarophiles provided the crosslinking densities in the order of BHPB > **5** > **3**. The polymer chains in the dual crosslinking system were apparently linked by the dipolarophile before all chain ends had been fully linked via urethane moieties (Fig. 4). The low reactivity of the dipolarophiles relative to the azide favored competition between the cycloaddition (triazole formation) and polycondensation (urethane formation). The energetic network, therefore, was homogeneous, and BPS and BHPB delivered higher crosslink densities compared to the other dipolarophiles. In the single (triazole-forming) crosslinking system using trivalent alkynes, large variations in crosslink density were observed depending on the type of trivalent alkyne used. In the dual crosslinking system, by contrast, no great differences were observed between the electron-deficient (**4**) and less electron-deficient (**6**, **7**, and **8**) dipolarophiles. This result may have arisen from the small differences between these dipolarophiles (in contrast to the large reactivity differences between BPS (or BHPB) and the other dipolarophiles).
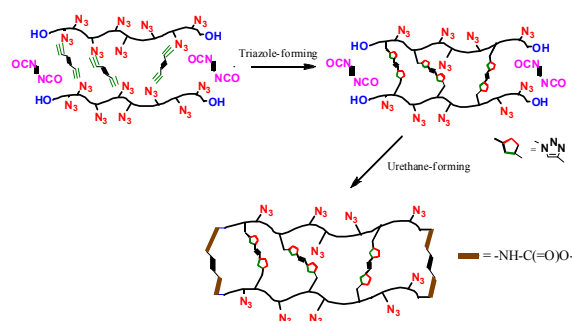

Fig. 4 Schematic diagram showing the construction of azide-bearing polymeric networks using a dipolarophile and a diisocyanate.

Mechanical characteristics

The characteristics of a polymeric network can significantly influence the structural integrity of a solid-filled application, such as an elastomeric composite propellant containing an oxidizer, metal particles, and rubber elastomers. The mechanical characteristics of solid-filled elastomers depend strongly on the properties of the networks. For example, solid propellants may be subject to a range of stresses and strains during the deformation of a composite motor under pressure during firing. A solid propellant with good elastomeric and viscoelastic properties can maintain its structural integrity without rupturing under strain. The viscoelasticity of a network matrix depends on the matrix's mechanical properties, which are, in turn, determined by the crosslinking density and the molecular length between two crosslinked points (M_c). Table 2

shows that a high triazole crosslinking density (i.e., a lower M_c) produced a high stress and a low elongation during deformation. BHPB and BPS provided good mechanical properties. The oligomeric dipolarophile **5** provided a higher elongation than the dipolarophile **3**, which showed a crosslink density comparable to that of **3**.The longer chain length between the azide linkages in the system based on **5** caused that network to have a higher M_c. The stress and strain values in the trivalent dipolarophiles were higher and lower, respectively, than the corresponding values of the divalent dipolarophiles. Interestingly, the stress decreased significantly as the equivalent ratio was decreased from 1.0 to 0.08.The stress in the networks formed using **8** was significantly smaller than the stress values obtained in the networks formed by **6** and **7**. These properties appeared to result from the unreactive dangling ethyl group in **8**, which functioned as a network defect. The use of BPS and BHPB yielded better mechanical properties than those obtained using the other dipolarophiles; however, none of the dipolarophiles studied afforded elastomeric mechanical properties.

Table 2 Swelling, mechanical and thermal characteristics of the azide-bearing networks crosslinked via the triazole moieties.

Alkynes (-C≡C/N^3 (EQ)=0.1)	Swelling			Mechanical				Thermal
	v_e, mol/cm^3 x 10^4	M_c^1, g/mol	δ MPa$^{1/2}$	S_m, bar	ε_m, %	E_o, bar	H_s	T_g(^{o}C)
1	2.03	6,357	22.02	3.4	61	8.1	24	-32.3
2	2.95	4,373	22.35	3.4	74	6.6	24	-32.1
3	1.69	7,639	22.26	2.2	50	5.8	19	-33.1
4	7.35	1,755		5.5	33	20.2	48	-31.1
5	1.21	10,646	21.83	2.4	80	4.6	21	-34.3
6	6.10	2,114	22.40	5.1	25	23	48	-30.8
7	6.31	2,044	22.06	4.9	35	35	49	-32.7
8	6.38	2,021	22.09	4.9	28	20	45	-31.7
6, EQ=0.08	3.78	3,411		2.3	30	9.4	11	-33.1
7, EQ=0.08	3.24	3,986		2.7	43	8.2	10	-34.4
8, EQ=0.08	3.27	3,941		1.4	16	9	10	-34.3

1 : Determined by $v_e=\rho/M_c$ (ρ : density of polymer)

Table 3 Swelling, mechanical and thermal characteristics of the azide-bearing networks crosslinked via both triazole moieties and urethane moieties.

Alkynes (-C≡C/N^3 (EQ)=0.1)	Swelling		Mechanical				Thermal
	v_e, mol/cm^3 x 10^4	M_c^1, g/mol	S_m, bar	ε_m, %	E_o, bar	H_s	T_g(^{o}C)
1	2.19	5,889	6.17	252	5.1	21	-31.1
2	0.86	15,010	5	138	5.8	23	-30.8
3	0.49	26,551	4.3	233	3.5	11	-30.0
4	0.54	23,927	3.7	260	2.6	8	-30.4
5	0.53	24,539	4.1	232	3.7	12	-29.5
6	0.46	28,135	2.4	328	1	10	-33.2
7	0.45	28,446	2.8	363	0.9	8	-33.1
8	0.53	24,458	3.3	279	1.9	7	-32.2
6, EQ=0.005	0.18	70,889	3.2	313	1.5	5	-31.0
7, EQ=0.005	0.20	65,903	2.2	694	0.5	0	-31.4
8, EQ=0.005	0.19	67,273	4.3	593	1.2	1	-30.2

As described previously, the poor mechanical properties of an energetic network formed by the Huisgen cycloaddition could be improved by introducing a urethane-formation reaction. As shown in Table 3, the mechanical properties of the networks improved remarkably. Above all, the elongation increased upon introduction of urethane crosslinks because all polymer chain ends were crosslinked by urethane moieties. No elastically ineffective chains, such as dangling free chains, remained present, although the networks were looser than networks formed via triazole crosslinks alone.

The dipolarophile type affected the mechanical properties of the networks. The mechanical properties of the β-EWG aliphatic alkyne (BPS)-based networks were much better than the properties of networks prepared using other bivalent dipolarophiles or trivalent dipolarophiles. The β-EWG aromatic alkyne, BHPB, also formed good elastomers with high strength and modulus values. The strain properties, however, were not as good as the properties obtained in other networks. The elongation value was comparable to the values obtained from urethane-crosslinked networks.

The crosslinking densities and H_s values in the dual crosslinked networks were similar, except for BPS and BHPB; however, the networks prepared using β-EWG trivalent aromatic dipolarophiles were weaker than networks prepared using other aliphatic trivalent dipolarophiles (**4** and **8**). Thus, the mechanical properties of the network obtained using **8** were comparable to those obtained from the dipolarophile **4**-based network, regardless of the reactivity toward the azide.

Thermal characteristics

T_g values of networks crosslinked via triazole moieties or both triazole and urethane moieties were shown in Table 2 and 3. It was interesting that the large difference between T_g values of all networks crosslinked via triazole moieties and T_g (about -33°C) of GAP urethane- crosslinked with only mutifunctional isocyanate (Desmodur N-100) was not observed.

As shown in Table 2, T_g values of triazole crosslinked networks were a little dependent on the kind of the dipolarophiles. T_gs of networks prepared using trivalent dipolarophiles were slightly higher than those of others due to their higher crosslink densities. T_gs of divalent-based networks were also proportional to their crosslink densities. The network prepared using the oligomeric dipolarophile **5** exhibited the lowest T_g among dipolarphiles, which is attributable to its higher molecular mobility. Moreover, Tgs of networks prepared using trivalent dipolarophile (6, 7, & 8) were lowered with decreasing the equivalent ratio from 0.1 to 0.08.

In dual crosslinked networks (Table 3), networks obtained using β-EWG trivalent dipolarophiles exhibited slightly lower T_g, compared to others. Unlike the triazole crosslinked network prepared using the oligomeric dipolarophile **5**, the effect of molecular structure of **5** on T_g was not observed. This may be because the amount of 5 added into GAP is very small. Moreover, as expected, T_gs of dual crosslinked networks were

decreased with lowering the equivalent ratio of alkyne/azide from 0.01 to 0.005.

 Although the networks prepared in this study were not thermally characterized in high temperature, it has been known that the decomposition of azide-bearing networks crosslinked via triazole or urethane moieties starts beyond 200°C, which is attributable to the presence of residual azides.[11] Therefore, considering the processing temperature (less than 60°C) of solid propellants and explosives, azide-bearing networks cured via triazole moieties can be feasible for the defense applications.

Conclusions

 Eight dipolarophiles, classified as bivalent or trivalent compounds, were successfully synthesized in an effort to prepare energetic networks via triazole side-linkages formed by a Huisgen dipolar cycloaddition reaction. The relative rates and types of cycloaddition were predicted using FMO calculations. The predictive value of the calculations with respect to the kinetics was tested by monitoring the gelation time. Dipolarophiles carrying an EWG immediately adjacent to the alkyne reacted with GAP very rapidly, and the polymer chains gelled within a few minutes under SF and CF conditions without heat. The 1,4-regioisomer was expected to form much more selectively than the 1,5-regioisomer due to the very small FMO energies of the HOMO$_{dipole}$ and LUMO$_{dipolarophile}$. The Huisgen cycloaddition of trivalent dipolarophiles carrying an EWG such as oxygen at the β-position to the terminal alkynes also reacted readily with GAP leading to the formation of a network within a few hours under moderate heating. In addition, divalent dipolarophiles featuring an EWG at the β-position also facilely formed networks within 10 hours at 50°C without any prompters or medium. The FMO calculations for this type of dipolarophile (i.e., BPS), obtained using a model compound, predicted a marginal preference for the 1,4-regioisomer over the 1,5-regioisomer. Two of the trivalent dipolarophiles carrying β-oxygen groups did not show a significant preference for the 1,4- over the 1,5-regioisomer. A urethane-forming reaction was introduced alongside the cycloaddition to link the GAP chain ends and avoid the formation of defects, such as dangling chains. This dual crosslinking system formed energetic networks within a day. Although the reaction times were longer than those required for the single (triazole-forming) systems, the longer reaction times are desirable for manufacturing formulation-based elastomers and composites. Interestingly, the networks prepared using divalent-or less electron-deficient alkynes provided high crosslinking densities compared to the α-EWG dipolarophiles. The trivalent-based networks formed denser networks compared to those prepared using the bivalent dipolarophiles. The crosslinking densities of the dual crosslinked networks based on less electron-deficient divalent dipolarophiles exceeded those of the electron-deficient dipolarophiles and the trivalent alkynes. The mechanical properties of the networks prepared using β-EWG alkynes were much better than the properties of the other networks.

These mechanical characteristics were not as good as the properties of networks in which the chain ends were linked with urethane moieties. The poor elastomeric mechanical characteristics improved significantly through the use of a dual crosslinking system with small amounts of the dipolarophiles, regardless of the type of dipolarophile used; however, as observed in the single crosslinking system, the β-EWG aliphatic divalent terminal alkynes provided the best mechanical properties among all dipolarophiles tested.
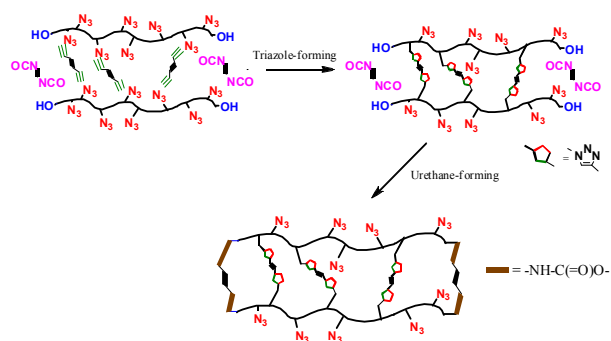
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The construction of azide-bearing polymeric networks using a dipolarophile and a diisocyanate.