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# Energetic Nitrate-Based Polymer-Bonded Explosives Derived from Sustainable Aza-Michael Reactions

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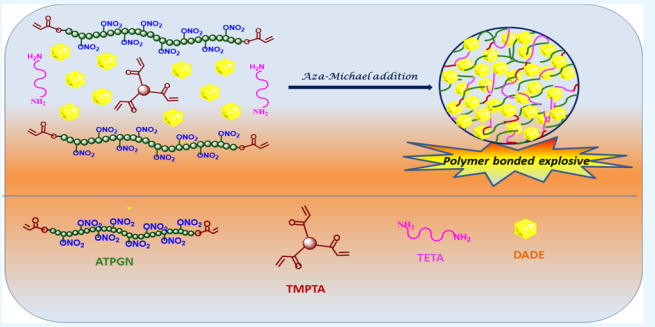
**ABSTRACT:** A novel nontoxic method for processing energetic binder, namely, polyglycidyl nitrate (PGN), using Aza-Michael reactions for deriving high-performance explosive formulations is being reported. The polyol binders used in polymer-bonded explosives (PBX) including PGN are usually cross-linked using isocyanate leading to polyurethane (PU)-based cured solid networks. These reactions require mild reaction conditions and yield good mechanical properties for the PBX but remain challenging due to extraneous reactions of isocyanate resulting in defects in the cured blocks. In addition, the presence of nitrato groups in the vicinity of terminal hydroxyl groups of PGN results in the decuring of cross-linked urethane that affects the storage life of PBX, though PGN-based binder can provide an 18% improvement in the velocity of detonation of PBX at lower solid loadings of 70%. This prevents researchers from exploiting the major performance advantage of using PGN for PBX compositions. This article herein features a green and mild aza-Michael reaction for functional modification of PGN using readily available substrates and triethylene tetramine to form a cross-linked *β*-aminocarbonyl network. The methodology ensures a void-free, stable, cured network and offers an effective replacement for toxic cure chemistry currently employed for processing of PBX.




## 1. INTRODUCTION

Polymer-bonded explosives (PBX), mainly composed of high-density energetic materials and polymer binders, are indispensable components of explosives used for weapons and civil use. The cross-linked network of the binder embedded with high explosive materials provides structural integrity and reduces its vulnerability.[1−5] Nitrato polymers are a prominent category of energetic polymers having nitrato groups (−$ONO_2$) in their polymeric backbone, which are known for their high oxygen balance and for use in energetic propellants as well as explosives. Polynitratomethylmethyl oxetane (PolyNIMMO), nitrated hydroxyl-terminated polybutadiene (NHTPB), polyglycidyl nitrate (PGN), etc, are the most known nitrato binders. Among these binders, PGN possesses high oxygen balance and heat of formation. The polymer was synthesized for the first time by Thelen and coworkers at the Naval Ordnance Test Station (NOTS) by the polymerization of the monomer, glycidyl nitrate.[1] Realizing the potential application of the binder in energetic formulations,[2] many researchers attempted to optimize the synthesis procedure of PGN by improving the purity of glycidyl nitrate and thereby improving the molecular weight of the polymer.[3−5] Propellant and explosive formulations were developed using PGN in combination with different oxidizers and energetic additives such as ammonium nitrate, octahydro-1,3,5,7- tetranitro-1,3,5,7-tetrazocine (HMX), 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), etc.[6−9] Usually, in PBX, an explosive loading above 80% is used to obtain the required performance. Unlike HTPB, polyether binders such as PGN require suitable plasticizers for improving the processability at high explosive loadings. The compatibility of PGN with different energetic binders was studied using thermal analysis, rheology studies, and DFT techniques by Shee et al. wherein plasticizers such as BuNENA and DEGDN were found to be more compatible binders for PGN.[10] Similar investigation on the compatibility of the energetic plasticizer, namely, 2,4-dinitro-2,4-diazapentane (DNDA-5) with different energetic binders, such as PGN, poly(3-nitratomethyl-3-methyloxetane) (PNIMMO), glycidyl azide polymer (GAP), and tetra functional glycidyl azide polymer (t-GAP), was done by Vijayalakshmi et al. The compatibility was evaluated using STANAG 4147 and theoretical computations using Gaussian 09.[11]

The hydroxyl-terminated polymer is usually cured using di & polyisocyanates, such as Desmodur N100, hexamethylene diisocyanate (HMDI), isophorone diisocyanate (IPDI), etc.

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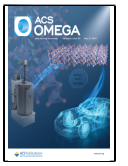
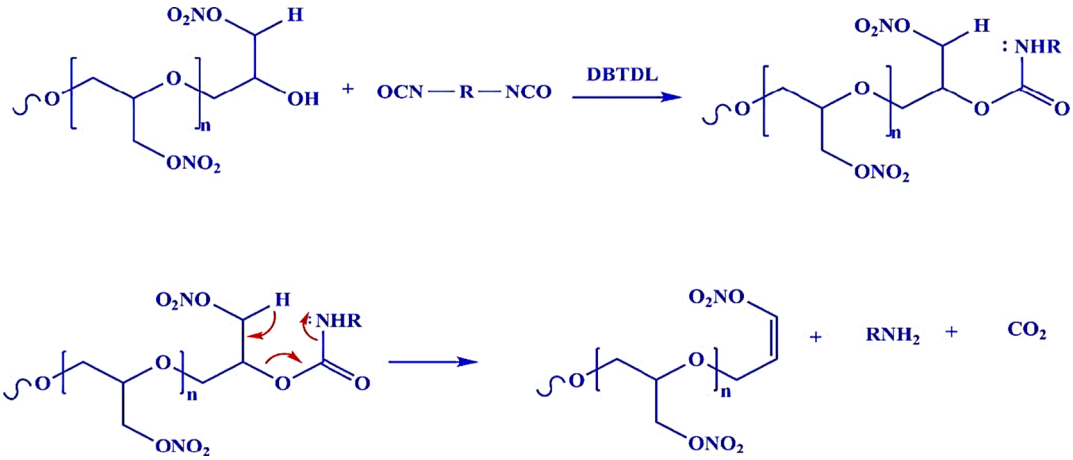
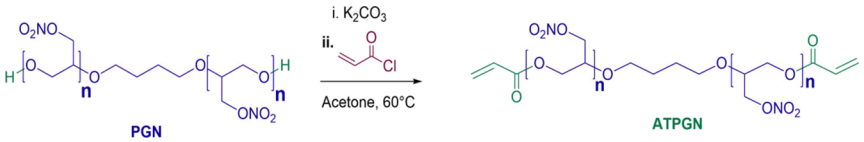


**Scheme 1. Decuring Mechanism of PGN Cured by the Urethane Route**




**Scheme 2. Synthesis of ATPGN**




The major problem of this methodology is that urethanes formed with aliphatic isocyanates are highly susceptible to decuring as depicted in Scheme 1,[9] which restricts the use of PGN in many applications. The affinity of the polyether backbone of the polymer to moisture and the subsequent reaction of isocyanate with moisture will also affect the quality of the cured specimens, leading to porosity and voids.

Though a few methods for end-group modification have been reported to address the decuring phenomenon, it is at the expense of a few nitrato groups that result in the reduction of its energy content.[12−14] Recently, curing of PGN using polyisocyanate, namely, polyaryl polyisocyanate (PAPI), was reported, which could improve the cross-linking network in the polymer.[15] Nevertheless, the realization of a void-free cured specimen by urethane cross-linking is very difficult as reported.

Energetic propellant and explosive formulations are being developed for specific applications using energetic additives, such as dinitramides, triazoles, tetrazoles, etc, along with PGN.[15,16] Certain isocyanates are found to be incompatible with these additives since they are susceptible to reaction with amino groups present in them to form urea derivatives imparting inferior mechanical properties to the propellant.[17,18]

An isocyanate-free curing methodology is warranted for the realization of defect-free energetic propellant/explosive formulations using PGN in combination with energetic materials. Wang et al. reported epoxy-terminated PGN that is cured with phthallic anhydride resulting in a stable elastomeric network.[19] Copolymerization of PGN with polyols terminated with primary hydroxyl groups that are cured with a co-isocyanate curing method using a mixture of IPDI and Desmodur N100 was also reported as a viable method to arrest decuring.[20] However, this method needs a moisture-free condition for the realization of void-free specimens due to the hydrophilicity of the terminal hydroxyl groups and the polar backbone of polyols leading to process constraints.

Aza-Michael addition has been widely pursued recently due to numerous advantages, such as high atom economy, mild reaction conditions, etc.[21] It refers to the addition reaction between an activated alkene and a primary or secondary amine resulting in a $\beta$-amino carbonyl linkage.[22] The advantage of this reaction is that, unlike other variants of Michael addition reactions, aza-Michael addition does not require a base or catalyst,[23] which is of significance in realizing PBX compositions.

The $\beta$-aminocarbonyl linked polymers are widely used in biomedical applications.[24] Furthermore, the reaction is utilized for the development of several thermosets.[25−28] It is the first time that this reaction is being explored for explosive applications. This work reports the cure chemistry of PGN using aza-Michael addition for the development of PBX. The major advantage of choosing the aza-Michael addition is that the decuring observed in the polyurethane cross-linked polymer can be eliminated. As shown in Scheme 1, the decuring of urethane happens due to the C−N bond dissociation. The bond dissociation energy of C−C (348 kJ/mol) is higher compared to that of the C−N bond (305 kJ/mol), and since the cure reaction is executed in solventless medium under mild temperature, the retro-aza-Michael addition is unlikely to occur. Therefore, the adduct, namely, $\beta$-amino carbonyl moiety, formed is stable.

In this work, the aza-Michael addition reaction is effected in PGN by the esterification of its hydroxyl groups to form acryloyloxy-terminated PGN (ATPGN). The curing or cross-linking of ATPGN is accomplished using triethylenetetramine (TETA) to achieve defect-free specimens. This can be used for PBX for space or military applications in combination with energetic additives, such as 1,1-diamino-2,2-dinitroethene (DADE or FOX 7), 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), l,3,5-trinitro-1,3,5-triazacyclohexane (RDX), pentaerythritol tetranitrate (PETN), guanyl urea dinitramide (GUDN or FOX 12), etc.



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## 2. RESULTS AND DISCUSSION

**2.1. Characterization of ATPGN.** ATPGN was synthesized by the functional modification of the hydroxyl groups of PGN, as shown in Scheme 2.

The conversion of the hydroxyl to acryloyl group was achieved with a product yield of 60%. The polymer was characterized by FTIR spectroscopy to confirm the functionalization. The hydroxyl value of PGN reduced to 40.8 mgKOH/g in ATPGN from 54.4 mgKOH/g.

The functionalization of ATPGN was confirmed from the FTIR and $^1$H NMR spectra as shown in Figures 1 and S1

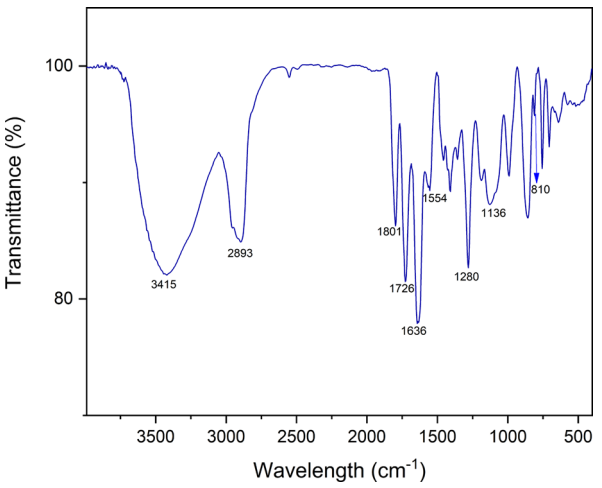



**Figure 1.** FTIR spectrum of ATPGN.

respectively. Characteristic peaks at 1726 and 810 cm$^{-1}$ for the acryloyl carbonyl peak, 3415 cm$^{-1}$ for the hydroxyl (−O−H), 2893 cm$^{-1}$ for the −CH stretch, 1636 and 1280 cm$^{-1}$ for the $-ONO_2$, 1554 cm$^{-1}$ for the N−O nitro stretch, and 1136 cm$^{-1}$ for the −C−O−C stretch on the polymer backbone were observed in the FTIR spectrum. The characteristic signals of acryloyl protons were observed in the $^1$H NMR spectrum at 6.2, 6.4, and 6.7 ppm.

**2.2. Curing Studies.** *2.2.1. FTIR Studies.* The cross-linking of ATPGN by aza-Michael addition was achieved using a tetrafunctional amine, namely, triethylene tetramine (TETA), along with a trifunctional acrylate cross-linker. The *β*-aminocarbonyl cross-linked network of the cured system is depicted in Scheme 3.

The cure reaction of ATPGN using the amine, namely, TETA, evaluated by FTIR spectroscopy is shown in Figure 2.

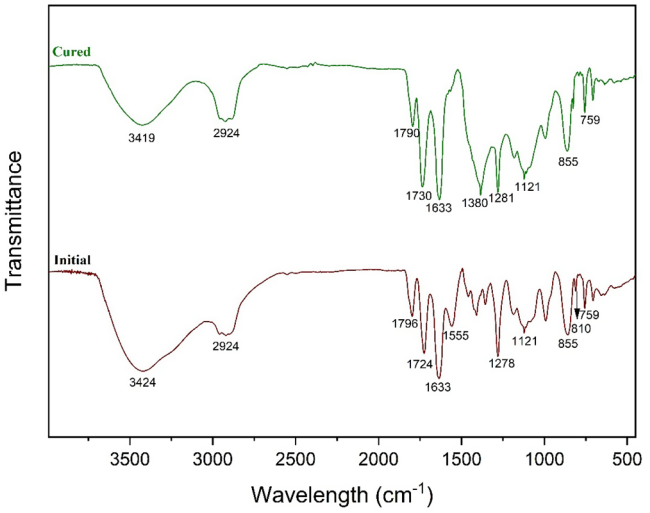
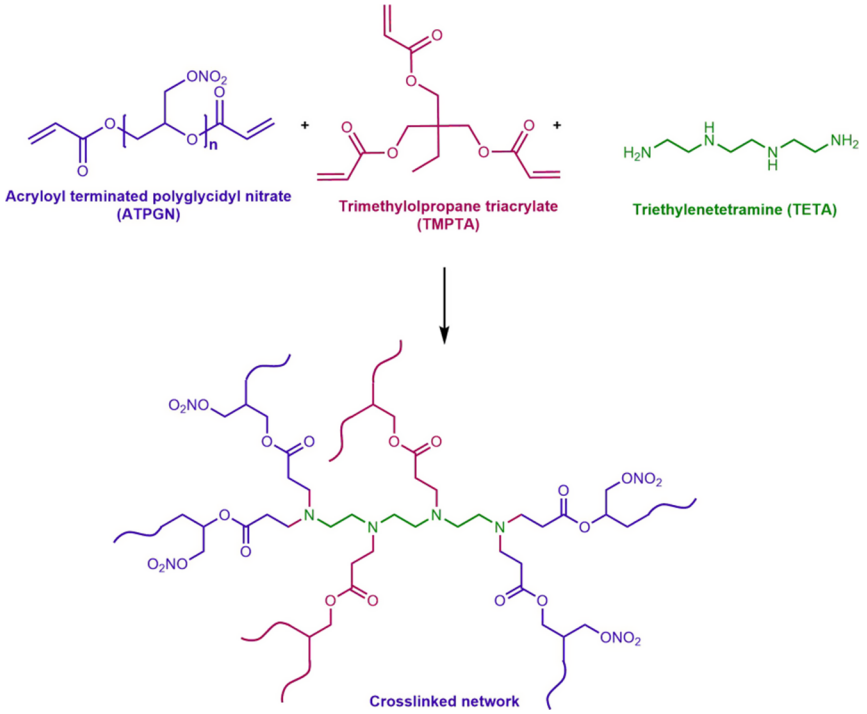



**Figure 2.** FTIR spectra of ATPGN, TMPTA, and TETA formulations (initial and cured samples).

**Scheme 3. Cure Reaction of ATPGN**



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The confirmation of cure reaction was ascertained by the disappearance of the peaks corresponding to the N−H bending arising from TETA at 1557 $cm^{-1}$ and the acryloyl C═C in the cured sample at 810 $cm^{-1}$. The shift in the carbonyl peak from 1724 to 1730 $cm^{-1}$ upon curing substantiates the addition reaction taking place in the conjugate alkenyl group. The peaks observed at 1633 and 1278 $cm^{-1}$ in the uncured sample correspond to the nitrato ($-ONO_2$) group in the polymer chain which is not altered in the cured sample. The peak observed at 1122 $cm^{-1}$ shows that the ether group in the polymer backbone also remains unaltered after curing.

*2.2.2. Molecular Modeling Studies.* The activation energy for the cure reaction via aza-Michael addition was determined using density functional theory (DFT) calculations using Gaussian 09[29] with the b3lyp functional and 6-31g(d)basis set. During geometry optimization, no symmetry constraints were imposed. The activation energy of the reaction of the amino groups in TETA with the acryloyl groups in PGN for aza-Michael addition was computed using a model compound viz 3-(nitrooxy) propane-1,2-diyl diacrylate (Figure 3). The reactions of the model compound with the primary and secondary amino groups of TETA are listed in Scheme 4.

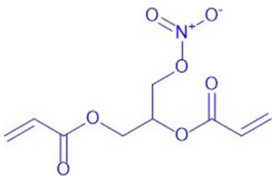


**Figure 3.** 3-(Nitrooxy) Propane-1,2-diyl Diacrylate.

Figure 4a,b shows the minimum energy structures of transition state geometry identified in the computation for reactions involving primary and secondary amino groups, respectively. The transition state of the aza-Michael adduct of the primary amino group of TETA with acryloyl group is characterized by a bond-breaking N−H bond distance of 1.25 Å and C−N and C−H formation bond distance at 1.55 and 1.58 Å, respectively. The activation energy of this reaction was 134.4 $kJmol^{-1}$. The transition state of the aza-Michael adduct of the secondary amino group of TETA with acryloyl group possesses a bond-breaking N−H distance of 1.26 Å and bond formation distances of 1.55 and 1.56 Å for C−N and C−H bonds. The activation energy for this reaction was 123.7 $kJmol^{-1}$. The optimized geometries, *xyz* coordinates, and the corresponding energies of the reactants and transition states are given in the Supporting Information (SI) (Figures S2−S5 and Tables S1−S4). The secondary amino group was found to

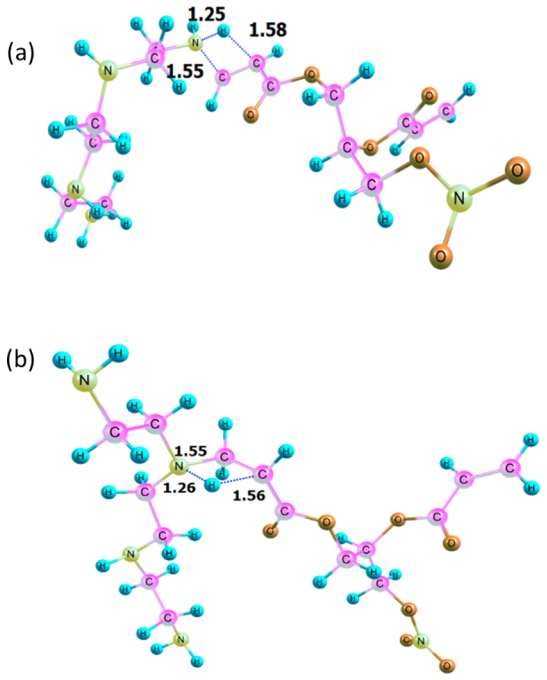
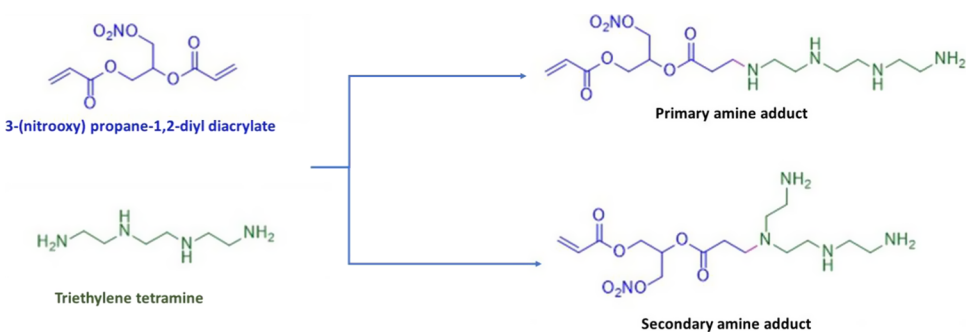



**Figure 4.** (a) Transition state of aza-Michael adduct of primary amino group of TETA with acryloyl group. (b) Transition state of aza-Michael adduct of secondary amino group of TETA with acryloyl group.

be slightly more reactive than the primary amino group which is evident as reported in the literature.[19] This gives a basic insight into the reaction which is further studied experimentally in a catalyzed system using acrylate functional cross-linkers.

*2.2.3. Differential Scanning Calorimetric Studies.* The activation energy of curing was calculated by differential scanning calorimetric (DSC) studies. Due to the low heat of the reaction, the uncatalyzed reaction could not be monitored by DSC. Hence, the kinetics of curing was studied in a catalyzed system with 0.1% of cuprous iodide ($Cu_2I_2$) as a curing catalyst. The mixture of ATPGN, 3% trimethylolpropane triacrylate (TMPTA) and stoichiometric quantity of TETA were mixed and subjected to dynamic DSC analysis at variable heating rates, namely, 5, 7, 10, and 12 °C/min. The heat flow was measured at temperatures from 25 to 150 °C. The DSC thermogram of curing at 12 °C/min is given in Figure 5a. The cure exotherm was observed in the temperature range of 36−95.6 °C with an enthalpy change of 40.9 J/g. The activation energy was calculated using the Kissinger[30] method

**Scheme 4. Formation of Aza-Michael Adduct of Model Compound with TETA**



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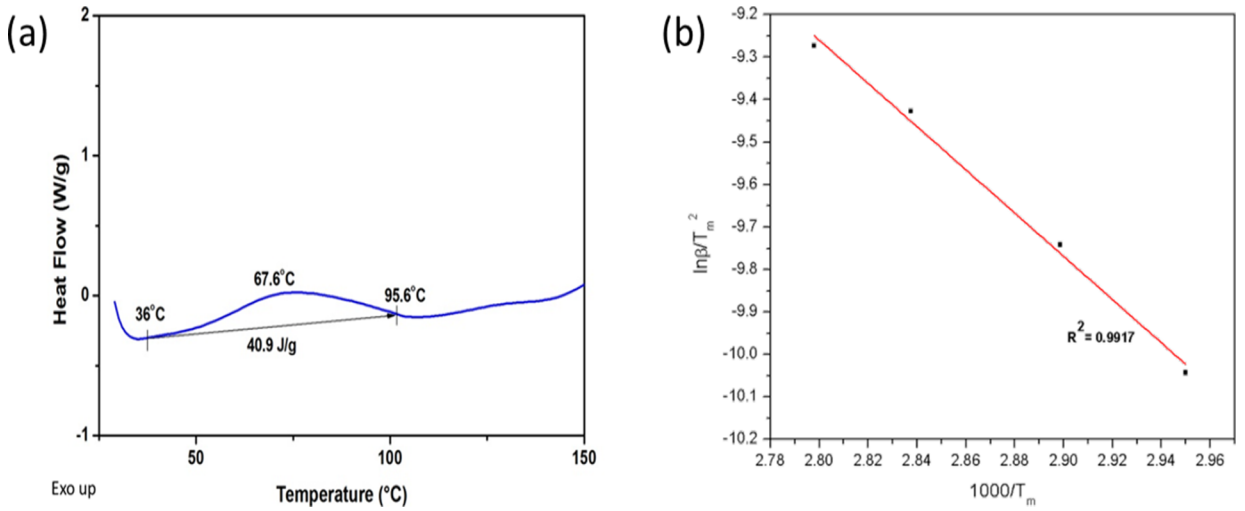


**Figure 5.** (a) DSC thermogram of curing of ATPGN. (b) Kissinger plot of curing of ATPGN.

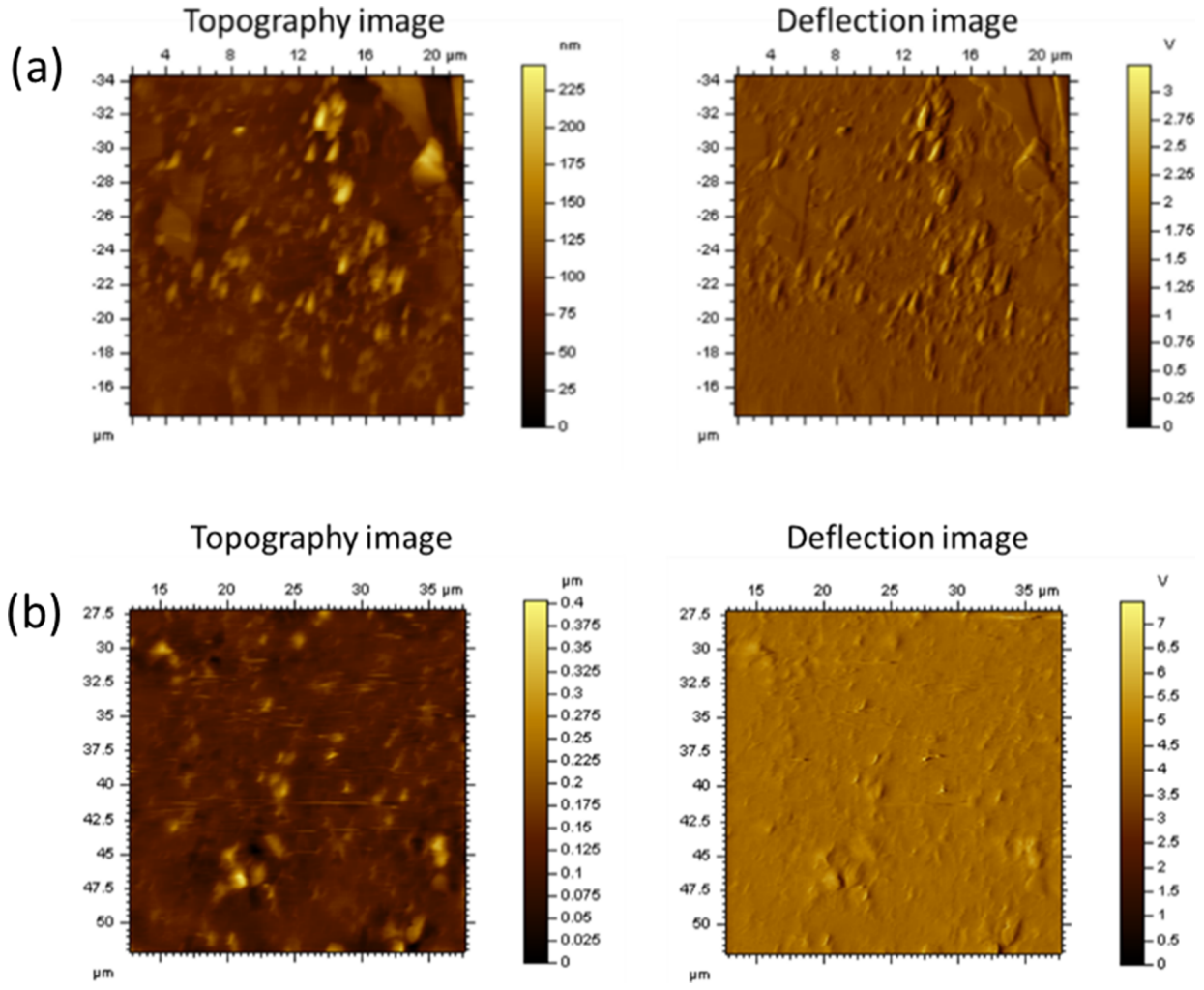


**Figure 6.** (a) AFM image of PGN cured with IPDI. (b) AFM image of ATPGN cured with TETA by Aza-Michael addition.

by plotting $\ln(\beta/T_m^2)$ against $1000/T_m$ where $\beta$ is the heating rate and $T_m$ is the peak temperature in the Kelvin scale in the curing exotherm (Figure 5b). Activation energy calculated from the slope of the plot was 42.4 kJ/mol. The rate constant of the reaction calculated from the Arrhenius equation, $k = Ae(-E_a/RT)$, was $3.99 \times 10^{-4}$ $s^{-1}$, and the pre-exponential factor, $A$, was $4.04 \times 10^{-4}$. The activation energy observed for aza-Michael addition was slightly lower when compared with the activation energy of 54.1 $kJmol^{-1}$ for the curing reaction between PGN and PAPI reported in the literature.[17] The activation energy for formation of $\beta$-amino networks using TMPTA and pentaerythritol tetraacrylate (PTA) in an



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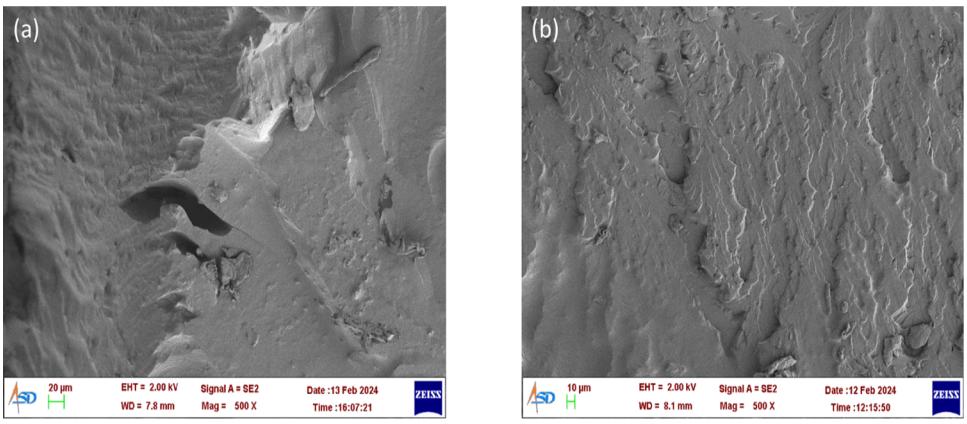


**Figure 7.** FESEM image of (a) PGN cured with IPDI and (b) ATPGN cured with TETA.

uncatalyzed medium using different multifunctional primary amines such as (4,4′-methylenebis(cyclohexylamine) (MBCA), Jeffamine D2000, and Priamine 1074 to form covalent adaptable networks (CANs) was in the range of 110−242 kJ/mol as reported by Taplan et al.[31] The lower activation energy observed by the Kissinger method than the theoretically predicted value is due to the catalytic action of $Cu_2I_2$ and also the simultaneous cross-linking reaction of TMPTA with TETA. The catalysis of aza-Michael reactions using cuprous halide was reported by Kantam et al. and Kang et al. separately.[32,33] The promising catalytic activity of CuI for aza-Micahel addition was reported by Asraf Ali et al., and a plausible mechanism was also suggested.[34,35]

*2.2.4. Morphology Studies.* The morphology of the cured sample was analyzed by atomic force microscopy (AFM) in noncontact mode. The AFM image of the samples of PGN cured by conventional urethane route and via aza-Michael addition is depicted in Figure 6a,b, respectively. The topography of the PGN cured by isocyanate, namely, IPDI, shows a heterogeneous pattern, and the deflection image shows distinct phase separation within the urethane network that may be due to the presence of microvoids. The topographic image of the cured ATPGN specimen indicates a similar pattern to the urethane-cured PGN, but the deflection image indicates a homogeneous phase. The homogeneity in the deflection image can be attributed to the void-free nature of the cured specimen. Furthermore, FESEM analysis of the cross-section of the cured samples was also compared, which gives a deeper insight into the integrity of the specimens. The voids formed in the urethane-cured polymer are visible in Figure 7a. Figure 7b indicates a comparatively uniform cross-section without any voids. Hence, aza-Michael addition provides defect-free morphology and is thus very effective for the curing of ATPGN.

*2.2.5. Evaluation of Mechanical Properties.* The typical values obtained for the mechanical properties of the cured polymer evaluated by uniaxial tensile tests are tabulated in Table 1.

**Table 1. Mechanical Properties of Cured ATPGN**

| Tensile strength (MPa) | Elongation (%) | Stress at 100% elongation (MPa) |
|---|---|---|
| 0.125 ± 0.007 | 121 ± 1.41 | 0.085 ± 0.007 |

The optimization of functional group conversion of the hydroxyl to acryloyl group can further improve the mechanical properties of the cured polymer.

*2.2.6. Swelling Studies of the Cured Polymer.* The cured polymer (0.4052 g) when immersed in dichloromethane (DCM) for 24 h, the soluble fraction of unreacted PGN dissolves in DCM forming a clear yellow solution, while the undissolved cross-linked fraction remained swollen in the solution. The swollen sample when removed and immersed in fresh DCM for another 48 h, no color change was observed in the solution, while the cross-linked polymer remained suspended as a swollen gel. The swollen fraction weighed 0.4665 g, while the deswollen sample weighed 0.0855 g. The gel fraction calculated using eq 1 was found to be 21.1%. This value is in good correlation with the conversion yield obtained for ATPGN.

## 3. ASSESSMENT FOR PBX APPLICATIONS

**3.1. Evaluation of Velocity of Detonation.** The velocity of detonation determines the performance of an explosive. A PBX formulation was developed using 1,1-diamino-2,2-dinitroethene (DADE) as an energetic filler with ATPGN. PBX formulations using inert binders employ higher solid loading in the range of 80−85% to achieve the required energetics. ATPGN, being an energetic binder, contributes to the overall energy content of the formulation.

The velocity of detonation (VoD) of the PBX formulations using ATPGN with varying percentages of DADE content, such as 70, 75, 80, and 85%, were computed using the thermochemical code, namely, EXPLO5,[36,37] at 90% of theoretical maximum density. The detonation velocity for each explosive formulation was calculated using a built-in nonlinear curve fitting program to fit relative volume-pressure data along the expansion of isentrope according to the Becker-Kistiakowsky-Wilson equation of state. The velocity of detonation was calculated at the equilibrium point of the Hugoniot adiabat known as the Chapman−Jouguet (C−J) point.

The VoD results of PBX formulations using ATPGN-DADE were compared with those of HTPB-DADE and HTPB-RDX systems and are tabulated in Table 2. The graph depicts the VoD values of these PBX systems in Figure 8. It is clear from the graph that ATPGN-DADE-based PBX possesses higher VoD even at 70% of explosive content than the HTPB-based PBX using DADE and RDX. At 80% solid loading, ATPGN-DADE and HTPB-RDX systems have equivalent performance.


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Table 2. Theoretical VoD of PBX Formulations

| | VoD (km/s) | | |
|---|---|---|---|
| DADE content (%) | ATPGN -DADE | HTPB-DADE | HTPB-RDX |
| 70 | 7.26 | 6.14 | 6.81 |
| 75 | 7.33 | 6.67 | 7.07 |
| 80 | 7.40 | 6.88 | 7.38 |
| 85 | 7.47 | 7.31 | 7.73 |

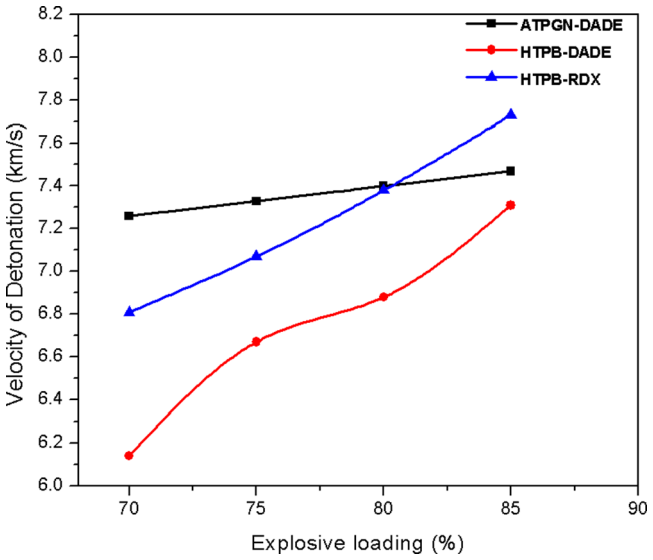


Figure 8. Comparison of VoD of PBX systems.

Hence, there is an advantage of improved processability and performance at lower solid loading for ATPGN-based PBX in comparison with HTPB-based PBX with an efficiency improvement of ∼18%.

## 4. CONCLUSIONS

A new method of PBX processing is established using a high-energy polymer, PGN via an aza-Michael addition reaction. This methodology enables the realization of void-free specimens using PGN. The curing reaction of aza-Michael addition was facilitated by the synthesis of acryloyl functionalized PGN and its reaction using TETA which was monitored by FTIR analysis and confirmed. The reactivity of the acryloyl functional model compound with TETA, computed by DFT, was comparable for both primary and secondary amino groups, and the corresponding activation energies were 134.4 and 123.7 kJmol$^{-1}$. However, the activation energy calculated by DSC experiments in the catalyzed system using the Kissinger equation was 42.4 kJ/mol, which is slightly lower compared to the activation energy of curing PGN using polyaryl polyisocyanate (PAPI) that validates the feasibility of the cure reaction in the polymer. The morphology of the cured polymer by AFM and FESEM analyses proved the void-free nature of the cured polymer with acceptable mechanical properties. The combination of ATPGN and DADE proves to be a promising PBX system concerning its detonating properties compared to polybutadiene-based explosive formulations. Velocity of detonation of the PBX at different solid loadings shows that a VoD in the range of 7200−7300 m/s is achievable at a lower solid loading of 70−75%, which is attributed to the energetic behavior of the binder. This eases the processability of the PBX without compromising its performance. Aza-Michael addition thus paves the way for eliminating the handling hazard of toxic isocyanates in PBX with desirable properties and energy density.

## 5. EXPERIMENTAL SECTION

**5.1. Materials.** PGN (hydroxyl value: 54.4 mgKOH/g, weight average molecular weight (Mw) of 2270g/mol) was purchased from M/s. Primodia Chemicals and Pharmaceuticals, Hyderabad. Potassium carbonate (99%, AR grade) and trimethylol propane triacrylate were purchased from M/s. Chemical Drug House, Mumbai, and benzyl triethylammonium chloride (98%, LR grade) were purchased from M/s. SRL Mumbai. Acryloyl chloride (stabilized with phenothiazine) was purchased from M/s. Alfa Aesar. Acetone (99%, AR grade) and triethylenetetramine (AR grade) were purchased from M/s. HPLC and used as received. The energetic filler, 1,1-diamino-2,2-dinitroethene (DADE), was synthesized in-house adopting a reported procedure.[38]

**5.2. Instrumentation and Methods.** The hydroxyl value of the polymers was evaluated by the acetylation method by titrating the acetylated polymer against standardized potassium hydroxide solution.

Fourier transform infrared spectra and attenuated total reflectance (ATR) spectra of the samples were recorded using a Thermo Fischer Nicolet iS50 FTIR spectrometer in the wavelength region of 4000−500 cm$^{-1}$ with four scans and a resolution of 4 cm$^{-1}$. Cure reaction was monitored by smearing the admixture including the polymer, chain extender, and curing agent in a KBr pellet and recording the spectra initially and after heating the specimen for the predetermined duration in an oven at the specified temperature. The mechanical properties of the cured polymer were evaluated by uniaxial tensile tests using an Instron UTM Machine. DSC was used to experimentally evaluate the kinetics of the cure reaction by the Kissinger method. The heat flow of the reaction mixture was measured against temperatures ranging from 25 to 140 °C at heating rates of 5, 7, 10, and 12 °C per minute. The kinetic parameters, such as activation energy and pre-exponential factor, were calculated. The DFT computations for calculating the activation energy for cross-linking were performed using the b3lyp functional with a 6-31g(d) basis set as implemented in the Gaussian 09 package. The morphology of the cured specimens was studied by AFM in noncontact mode using an Agilent 5500 scanning probe microscope. FESEM analysis of the cured samples was undertaken using a Gemini SEM 500 field emission scanning electron microscope with Bruker Detector with a magnification of 500X. The velocity of detonation of the PBX formulations was theoretically computed using the thermochemical code, namely, EXPLO 5.

**5.3. Synthesis and Characterization of ATPGN.** PGN (10g,4.4 mmol) dissolved in acetone (25 mL) was reacted with potassium carbonate (1.66g,12 mmol), which was added to the PGN solution in small lots, in presence of benzyl triethylammonium chloride (0.4 g,1 mmol) as a phase transfer catalyst. The reaction was carried out in an inert atmosphere with continuous stirring at 60 °C for 8 h. Acryloyl chloride (1.1 g,12 mmol) was added to the reaction, and stirring continued for 24 h. The reaction mixture was cooled to room temperature and allowed to settle. The supernatant liquid was filtered, and the solvent was evaporated under vacuum to obtain the acryloyl-terminated polymer (ATPGN).


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**5.4. Curing Studies.** The cure reaction of ATPGN with a multifunctional amine, namely, TETA, was studied using FTIR in combination with a chain extender, namely, TMPTA. The weight percentage of the chain extender was optimized as 3% of the binder for the studies. 0.1% weight of Cuprous iodide ($Cu_2I_2$) solution in acetonitrile was used as a cure catalyst. The admixture of ATPGN, TMPTA, and $Cu_2I_2$ in acetonitrile was mixed thoroughly, and the solvent was evaporated under vacuum. TETA was further added and mixed uniformly with the mixture. The reaction mixture was smeared in a KBR pellet and the FTIR spectrum was recorded. The pellet was heated to 60 °C for a predetermined duration of 5 days, and the FTIR spectrum was again recorded.

The kinetic parameters of curing were measured by DSC in dynamic mode at heating rates of 5, 7,10, and 12 °C per minute. The activation energy for curing of the binder using TETA, without the chain extender, in a noncatalyzed system was studied by molecular modeling using a model compound, namely, 3-(nitrooxyl) propane-1,2-diyl diacrylate.

ATPGN was cured using TETA with 3% TMPTA as a cross-linker for a duration of 5 days at 60 °C in a TEFLON-coated aluminum mold as dumbbell-shaped specimens having a gauge length of 33 mm and a thickness of 2.5 mm as per ASTM D412.[39] The mechanical properties of the cured polymer were evaluated by uniaxial tensile measurements. The morphology of the cured polymer was compared to that of an isocyanate-cured PGN specimen by AFM analysis. The cross-linking of the polymer was proved by swelling studies in dichloromethane. The gel fraction of the cured polymer, which substantiates the cross-linking reaction, was calculated by swelling the cured sample in dichloromethane. A weighed specimen of cured polymer was immersed in dichloromethane for 24 h. The soluble part of the unreacted PGN, which formed a clear yellow solution, was decanted, and the insoluble fraction was again immersed in fresh dichloromethane for another 48 h. The cross-linked fraction of ATPGN was observed as a swollen gel in the clear solvent. The swollen polymer was weighed, and subsequently, the solvent was removed in a vacuum oven at 40 °C for 2 h. The sample after deswelling was again weighed. The gel fraction of the cured polymer was calculated using eq 1.

$$\text{Gel fraction} = \frac{\text{Weight of deswollen sample}}{\text{Initial weight of the cured sample}} \quad (1)$$

**5.5. Studies on Explosive Formulations.** PBX using ATPGN in combination with an insensitive additive, namely, DADE, was formulated. Theoretical evaluation of VoD of the explosive formulations processed using ATPGN and DADE at solid loadings of 70, 75, 80, and 85% were computed and compared with that for HTPB-based PBX using DADE and RDX using the thermochemical code, namely, EXPLO5, at 90% of theoretical maximum density (TMD). EXPLO5 uses the Becker-Kistiakowsky-Wilson equation of state at the C−J point.[31]

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.4c00349.

Figure S1. $^1$H NMR spectrum of ATPGN; Figure S2. 3-(nitrooxy) propane-1,2-diyl diacrylate-Reactant; Table S1. Cartesian coordinates of 3-(nitrooxy) propane-1,2-diyl diacrylate (Reactant); Figure S3. Triethylene tetramine (TETA) − Reactant; Table S2. Cartesian coordinates of Triethylene tetramine (TETA); Figure S4. Transition state of 3-(nitrooxy) propane-1,2-diyl diacrylate-TETA adduct with 1° amino group; Table S3. Cartesian coordinates of the transition state of primary amino adduct; Figure S5. Transition state of 3-(nitrooxy) propane-1,2-diyl diacrylate-TETA adduct with 2° amino group; and Table S4. Cartesian coordinates of the transition state of the secondary amino adduct (PDF)

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The manuscript was written through equal contributions of all authors. All authors have approved the final version of the manuscript.

### Notes

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