

## GAP pre-polymer, as an energetic binder and high performance additive for propellants and explosives: A review

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**Abstract :** In preparation of energetic composite formulations, functionally terminated pre-polymers have been used as binder. After physically mixing the pre-polymers with oxidizing components, metallic fuel, burning rate modifier and other minor ingredients, they are cured with a suitable curing agent to provide physical and chemical stability. These pre-polymers could be functionalized with carboxyl, epoxide or hydroxyl groups at varying average chain functionalities. For carboxyl-terminated pre-polymers, an epoxy functional curing agents could be used. If the pre-polymer possesses hydroxyl groups, isocyanate functional curing agents are the most suitable curing agents in terms of easy and efficient processing. Glycidyl azide polymer (GAP) is one of the well-known low-molecular weight energetic liquid pre-polymer, which was developed to use as energetic binder, high performance additive and gas generator for high performance smokeless composite propellant and explosive formulations. Linear or branched GAP can be synthesized by nucleophilic substitution reaction of corresponding poly(epichlorohydrin) (PECH) with sodium azide through replacement of chloromethyl groups of PECH with pendant energetic azido-methyl groups on the polyether main chain. Positive heat of formation (+957 kJ/kg) enables exothermic and rapid decomposition of GAP producing fuel rich gases. Its polyether main chain provides GAP with relatively low glass transition temperature ( $T_g = -48^\circ\text{C}$ ) and presence of hydroxyl functional groups allows it to have easy processing in curing with isocyanate curing agents to form covalently crosslinked polyurethane structure. These outstanding properties of GAP enable it to be used as energetic polymeric binder and high performance additive in preparation of energetic materials and low vulnerable explosives.

**Keywords:** GAP; glycidyl azide polymer; PGA; polyglycidyl azide; energetic materials. ©2017 ACG Publications. All rights reserved.

### 1. Introduction

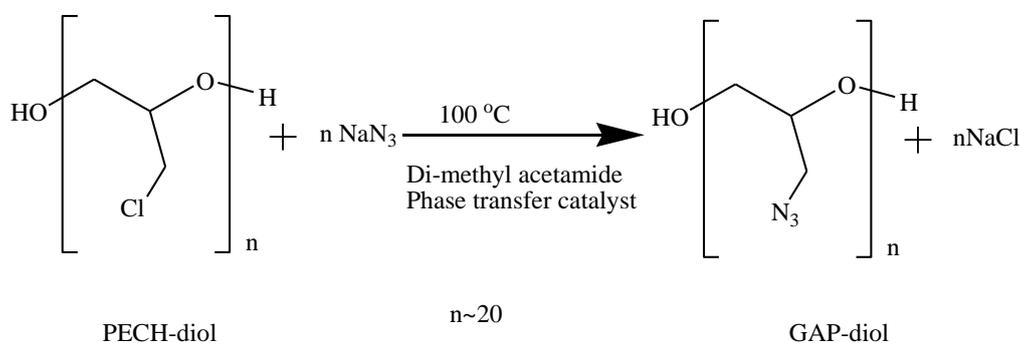
GAP was first achieved by Vandenburg<sup>1</sup> in 1972 by the reaction of sodium azide with PECH-triol in dimethyl formamide. Frenkel and co-workers synthesized PECH-triol, through a cationic ring opening polymerization of epichlorohydrin using glycerol as an initiator, which was further used for the synthesis of branched GAP. PECH-diol was later synthesized using ethylene

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glycol as an initiator and it was converted to linear GAP<sup>2-4</sup>. Ampleman reported a method for the preparation of linear GAP having increasing hydroxyl functionality<sup>5</sup>.

## 2. Synthesis of GAP

The synthesis of GAP is more specific than other energetic materials since, unlike other energetic materials, GAP is obtained by a small modification of its precursor polymer, PECH. Thus, it is obtained by the azidation of PECH having number average molecular weight ( $\bar{M}_n$ ) between 500-5000 g/mol which is synthesized by cationic ring opening polymerization of epichlorohydrin (ECH) in the presence of Lewis acids as a catalyst<sup>1, 2, 6</sup>. The azidation reaction is performed in an amphiphilic organic solvents such as dimethyl acetamide, dimethyl formamide etc., at 100 °C in the presence of quaternary ammonium salts as phase transfer catalyst (Figure 1)



**Figure 1.** Synthesis of GAP-diol

Synthesis of GAP is followed by spectroscopic and thermal analysis techniques. Kubota and Sonobe<sup>7</sup> showed that the thermal decomposition of GAP has two weight-loss steps. The first weight-loss step is due to the exothermic decomposition of azide groups resulting in acrylonitrile-like structure. The second weight-loss step corresponds to degradation of the remaining polyether main chain. Considering the characteristic two step degradation behavior of GAP, Eroglu et al. real-time followed the conversion of azidation reaction using thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) as well as Fourier transform infrared (FTIR) and UV-VIS spectroscopy techniques. Conversion of the reaction was ascertained from changes in characteristic IR peak intensities and thermal behavior of reaction products as a function of time which was found to be a first order reaction with a rate constant of  $k=0.74 \text{ h}^{-1}$ <sup>8</sup>.

Mohan et al. synthesized GAP polymers with different diol structures via azidation of the corresponding precursor, PECH. The stability and glass-transition temperature were found to be dependent on the diol unit present on the polymer chains<sup>9</sup>. As a new energetic plasticizer, acyl terminated GAP was synthesized through the reaction of 2,4,6-trinitrobenzoyl (TNB) chloride with GAP. Detailed characterization studies were performed<sup>10</sup>. To obtain a more safe energetic material with better mechanical properties methyl glycidyl azide polymer was synthesized and detailed characterization was performed<sup>11, 12</sup>.

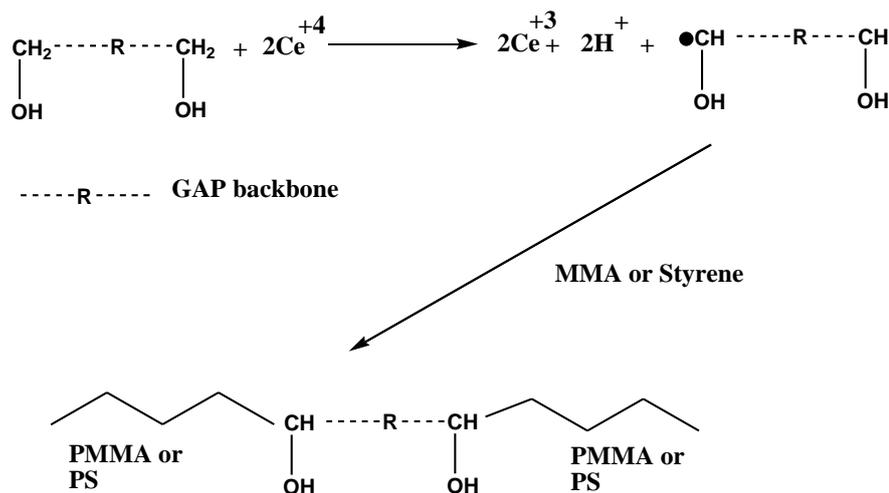
The nature of the terminal hydroxyl groups of GAP influences its mechanical properties. In the course of curing with isocyanates. As the primary hydroxy groups are more reactive than secondary hydroxy groups primary hydroxyl terminated GAP was synthesized to improve the mechanical properties<sup>13</sup>. Kshirsagar et al. performed a microwave assisted synthesis of GAP with different diol units, for which the PECH precursors containing different diol units were reacted

with sodium azide under microwave irradiation (600W) at 80 °C for 12 min. The detailed thermal and spectroscopic characterization was performed<sup>14</sup>. In addition to GAP, aiming to develop less sensitive and highly energetic propellant formulations, various energetic azido polymers such as 3,3-bis(azidomethyl)oxetane polymer (BAMO), 3-azidomethyl 3-methyl oxetane polymer (AMMO) and their copolymers have been synthesized<sup>15-20</sup>.

### 3. Copolymers and Other Derivatives of GAP

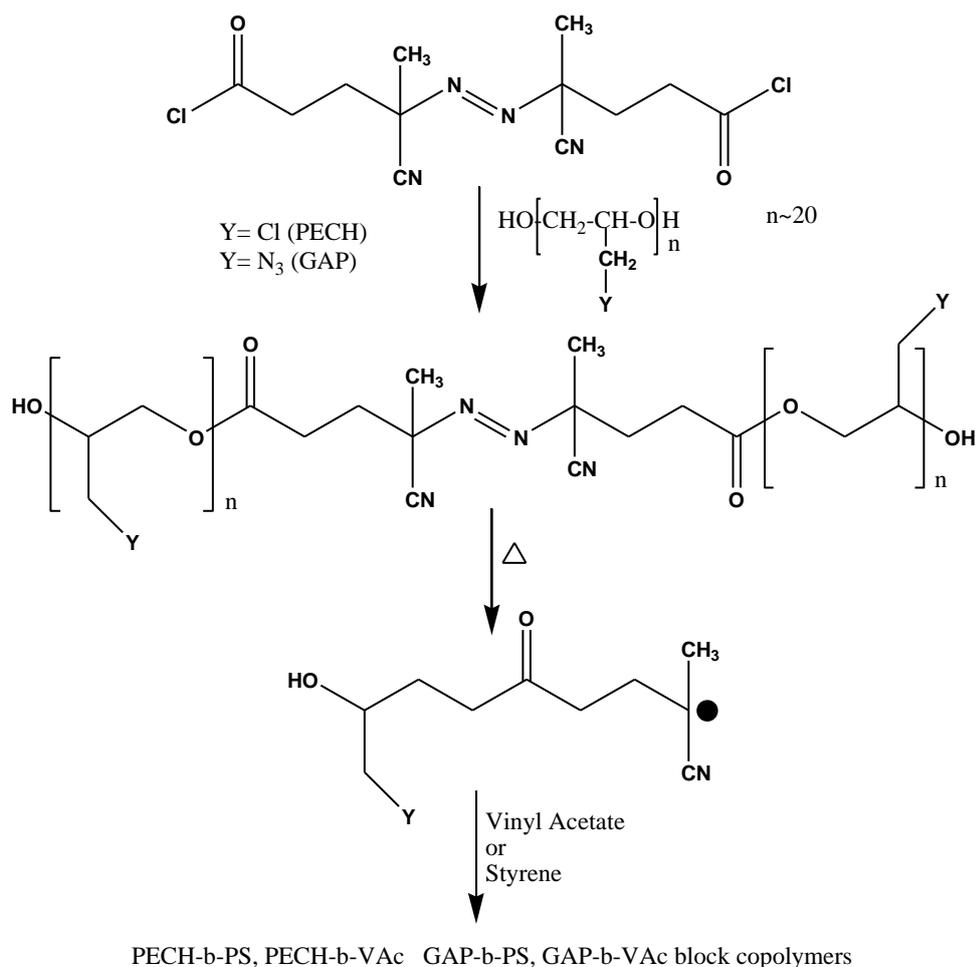
Although GAP-diol is a well known energetic pre-polymer, it has insufficient mechanical properties for composite propellant formulations relative to butadiene-based (PBD) pre-polymers. Therefore, its various copolymers were synthesized to improve the physical and chemical properties to expand its application area. Min, recently cured the GAP-diol with di-isocyanate and pluriisocyanate (containing more than two isocyanate groups) in the presence of poly(ethylene glycol), PEG, poly(caprolacton)-diol and PCL-diol. Incorporation capability of various energetic plasticizers into the networks was investigated<sup>21</sup>. Ampleman synthesized a di-azido terminated glycidyl azide polymer as an energetic plasticizer.<sup>22</sup>

Pisharath et al.<sup>23</sup> synthesized a copolymer of GAP-diol and another energetic azide polymer, poly(bis(azidomethyl)oxetane), Poly(BAMO), using borontrifluoride dimethyl ether complex/diol initiator system to study thermal decomposition behavior of the copolymer. DSC studies of the copolymer showed a main decomposition step arising from the azide groups as a broad exothermic peak at higher temperature than that of GAP-diol (298 °C). Subramanian<sup>24</sup> synthesized GAP-PBD-GAP energetic triblock copolymer by means of azidation of poly(chloromethyl ethylene oxide-b-butadiene-b-chloromethyl ethylene oxide) (PECH-PBD-PECH) using sodium azide in dimethyl acetamide-toluene mixture at 95 °C. In this study, the spectroscopic, thermal and chromatographic characterization studies of the copolymer were performed. Using this copolymer, Ammonium perchlorate (AP) based polyurethane propellant formulation was prepared and their ballistic parameters were determined. As another interesting method for the block copolymerization of GAP-diol with a vinyl monomer was oxidation of functional -CH<sub>2</sub>-OH groups of GAP-diol with transition metal ions. In this method, cerium (IV) was used as versatile oxidation reagent to produce radical sites on both ends of GAP-diol according to mechanism given in Figure 2.<sup>25</sup> The successful synthesis and characterization of GAP-PMMA-GAP type block copolymer by redox polymerization was reported.



**Figure 2.** Synthesis of GAP-PMMA-GAP block copolymer initiated using Ce(IV) as initiator

Macro-azo-initiators provide a useful and versatile method for the synthesis of different block copolymers via radical process. Macroazo-initiators can be prepared by the condensation reaction of a prepolymer with azobis-isobutyronitrile, 4,4' azobis(4-cyanopentanoyl chloride) and 4,4' azobiscyanopentanol. Eroglu et al. synthesized block copolymers of GAP-diol and its precursor PECH-diol with styrene and methylmethacrylate according to the mechanism given in Figure 3.<sup>26</sup>



**Figure 3.** Synthesis of the block copolymers of GAP-diol and its precursor PECH-diol with styrene and vinyl

**Fig**

Zhang et al. synthesized chloroethyl methacrylate terminated PECH based macroinitiators to use in the synthesis of GAP-b-poly(azidoethyl methacrylate), GAP-b-PAEMA, copolymer<sup>27</sup>. Regarding the unique thermal properties of GAP-diol and physico-chemical properties of HTPB at relatively low temperatures, a HTPB-g-PGA copolymer was prepared and characterized. As this graft copolymer was expected to have promising polymeric binder in solid propellants, macro-azoinitiation of GAP-diol was synthesized and attached to pendant vinyl groups of HTPB via radical mechanism at 90 °C. DSC results showed the presence of two incompatible block segments on the copolymer structure resulting in immiscibility<sup>28</sup>. Al-Kaabi et al. synthesized GAP carrying pendant N, N-diethyl dithiocarbamate groups and used as macro-photoinitiator for grafting of methylmethacrylate onto the polyether main chain.<sup>29</sup>

Submarin reported the synthesis and characterization of an energetic triblock copolymer, hydroxyl-terminated poly (azidomethyl ethylene oxide-b-butadiene-b-azidomethyl ethylene oxide) (GAP-PBD-GAP). A detailed structural characterization was performed. its potential as a binder for ammonium perchlorate based polyurethane propellant formulation was evaluated<sup>24</sup>.

Jin et al. synthesized a series of poly(vinyl 2,4,6-trinitrophenylacetal)-*g*-polyglycidylazides, PVTNP-*g*-GAP, copolymers at different molecular weight. Two different glass transition temperature and excellent thermal decomposition resistance upto 200 °C were observed. Sensivity and compability tests showed that these copolymers could be used in TNT-based melt-cast explosive formulation<sup>30</sup>.

Using GAP and nitrocellulose fibers a double base propellant having a homogeneous structure was synthesized to replace nitroglycerin in double base propellant formulation. Rise of onset decomposition temperature up to 194.6 °C indicated a good thermal stability, safe storage and operation. NO, NO<sub>2</sub>, CO, CO<sub>2</sub>, NH<sub>3</sub>, CH<sub>4</sub>, HCN, N<sub>2</sub>, CH<sub>2</sub>O and C<sub>2</sub>H<sub>4</sub>O are the main gas decomposition products.<sup>31</sup>

Triazole type crosslinked GAP networks were prepared as an alternative to polyurethane networks which have been studied by different authors<sup>31-35</sup>. Click chemistry with bispropargyl succinate (BPS) via a 1,3-dipolar cycloaddition instead of isocyanates was performed and 1,2,3-triazole network was obtained by Reshmi et al. Characterization studies showed that the crosslink density and thus, tensile strength and modulus of elasticity could be controlled by the azide/propargyl ratio.<sup>36</sup> Another triazole curing system was used for GAP by Ding et al., which was prepared by blending propargyl-terminated polybutadiene (PTPB) with GAPs in the presence of cuprous chloride as catalysis. Various crosslinked systems were prepared at different azide/propargyl group ratios. Triazole crosslinked network resulted in a slight increase in glass transition and  $\alpha$ -transition temperatures, reflecting the hindered rotation of polymer chain, with increasing miscibility of GAP and PTBT<sup>37</sup>.

Dubois et al. investigated the reaction between azide groups bearing polymers and double, triple bonds of the light olefins which yielded triazole and aziridine cycles. They observed a higher burning rate at relatively lower pressure for triazole substituted GAPs. They described a safe production route with lower molecular weight GAP plasticizer and suggested the use of propargyl alcohol and a semibatch reactor to avoid sudden temperature raise in the reaction mixture<sup>38</sup>.

#### 4. Decomposition of GAP

Numerous studies have been performed to ascertain the thermal decomposition behavior of GAP using different methods since GAP decomposes very rapidly even at relatively low temperatures. It was observed from DSC and TGA measurements that GAP has two weight loss steps. The first weight loss step is exothermic process accompanying with the elimination of N<sub>2</sub> from the azide groups. The energy liberated at this stage was determined to be 1828 J/g by DSC<sup>7, 39</sup> and the activation energy of decomposition was determined as  $E_a = 176.4$  kJ/mol. The second weight loss step is due to the decomposition of remaining polyether structure.<sup>8, 40-42</sup>

Eroglu and Guven followed the azide group elimination by taking real time FTIR spectra of GAP at which the sample cell was heated from room temperature to 220 °C in a controllable manner. During decomposition, while the intensity of the azide absorption peak at 2100 cm<sup>-1</sup> started to decrease at 170 °C, new peaks were appeared. They proposed the formation of -C=N-C- type structure as a result of thermal decomposition and, thus, possible crosslinked structure<sup>39</sup>. The combustion and thermal decomposition characteristic and their kinetic parameters for cured and linear GAP were studied. The decomposition products of GAP were analysed by molecular beam mass-spectrometry (MBMS)<sup>43</sup>

Kumar and Lee<sup>44</sup>, Has et al.<sup>40</sup>, Tang et al.<sup>45</sup>, studied the photodecomposition of GAP using laser irradiation. CO, C<sub>2</sub>H<sub>2</sub> and HCN were major decomposition products, while minor products were C<sub>2</sub>H<sub>4</sub>, CH<sub>4</sub>, NH<sub>3</sub> and CO<sub>2</sub>.

In another study thermal analysis of branched GAP was investigated using DSC, TGA and accelerating rate calorimetry (ARC) at various heating rates and isothermal conditions. Results

showed that decomposition activation energy of branched GAP was lower than GAP-tiol indicating less stability of branched GAP than linear GAP<sup>46</sup>

## 5. Some Physico-chemical Properties and Network Characterization Studies

For a composite propellants, mechanical properties and solid loading capacity are two important properties. These properties are inversely proportional such that increasing the solid content results in weakening in mechanical properties while becoming more energetic. Mechanical properties, such as strength and elongation at break values are strongly influenced by number average molecular weight between cross-links ( $\bar{M}_c$ ) of a network. Low  $\bar{M}_c$  of a network results in high tensile stress and low elongation. Therefore, desired  $\bar{M}_c$ , tensile stress and elongation values can be optimized by reactive group ratios<sup>2,6</sup>. Eroglu and Guven calculated the  $\bar{M}_c$  values of the GAP networks from their equilibrium swelling values in tetrahydrofuran (THF) at 45 °C. The networks were prepared using different cross-linker systems at different cross-link densities. They reported important thermodynamic parameters of GAP which is polymer-solvent interaction parameter ( $\chi_1$ ) as 0.25 in THF at 45 °C<sup>47</sup>. In another study, Eroglu et al. determined the Hildebrandt solubility parameters of GAP and PECH as 11.0 (cal.cm<sup>-3</sup>)<sup>1/2</sup> and 11.2 (cal.cm<sup>-3</sup>)<sup>1/2</sup>, respectively<sup>48</sup>.

Mechanical and adhesive properties of propellants are directly related to interface interactions between binder and oxidizers. Therefore, the surface free energy of GAP networks and its change with type of cross-linker and cross-link density are of important. Doğan et al. determined the surface free energy of different GAP networks<sup>49</sup>. Since GAP is an energetic material and starts decomposition at relatively low temperature (~170 °C)<sup>39</sup>, the shelf time prediction of GAP and PECH at different temperatures is of great importance. Therefore, the thermo-analytical life time testing of PECH and GAP were performed. As a result of TGA studies, it was understood that if GAP is stored at room temperature, there will be no significant change in its ballistic and viscosity properties<sup>50</sup>

## 5. Conclusion

During the last two decades, due to increasing awareness and sensitivity on environmental problems, an increasing effort was performed to develop chlorine free, having high specific impulse and high burning rate and smokeless composites and double base propellant formulations. In formulations, nitro explosives and their derivatives have met these requirements in some extent but they are not as safe as they should be in handling and use. For an energetic material, a high degree of safety in handling and reduced sensitivity to detonation are primarily desired. Considering these requirements, various energetic polymers having azidomethyl groups were developed. GAP is a typical example to them. The hydroxyl terminated polyether main chain structure, having relatively low glass transition temperature (T<sub>g</sub>=-48 °C), low viscosity and relatively high density compared to other polymeric binders attracted the interest of scientists working in the related fields. A number of studies have focused on the synthesis and characterization of GAP and its derivatives, which have been found a wide area of use in explosive formulations. Depending our experience and the literature survey, it could be interesting and useful to release such a short review article for scientists working on this subject.

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