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Review paper

Hydroxyl Terminated Polybutadiene: Chemical Modification and Application of these Modifiers in Propellants and Explosives

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Abstract: Hydroxyl terminated polybutadiene (HTPB) as a telechelic liquid polymer has been widely used in propellants and explosives and many modified-HTPBs have been reported in the literature. As a binder or additive in propellants and explosives, the chemical modification of HTPB for improving certain properties of propellants has been summarized in detail in this article. According to the application drawbacks of HTPB, modified-HTPB can be classified differently. Furthermore, there are polymers that have been modified on their energetic properties, such as GAP-PB-GAP, BAMO-PB-BAMO, AMMO-PB-AMMO, Nitro-HTPB, HTPB-DNB and NHTPB. Pre-polymers modified on their combustion properties include Butacene[®], FPDS-g-HTPB, Fc-HTPB, BiFc-g-HTPB, HTPB→[Fe(CO)₅]_x, PPA-HTPB-PPA and PNBE-HTPB-PNBE. HTPBs are also modified in curing systems containing, for example ETPB, PTPB, PrTPB, AzTPB, and PUPB, and other modification results are reviewed. Additionally, this overview is expected to provide an outlook for further studies in these fields.

Keywords: hydroxyl terminated polybutadiene, HTPB, telechelic polymer, CSP, PBX

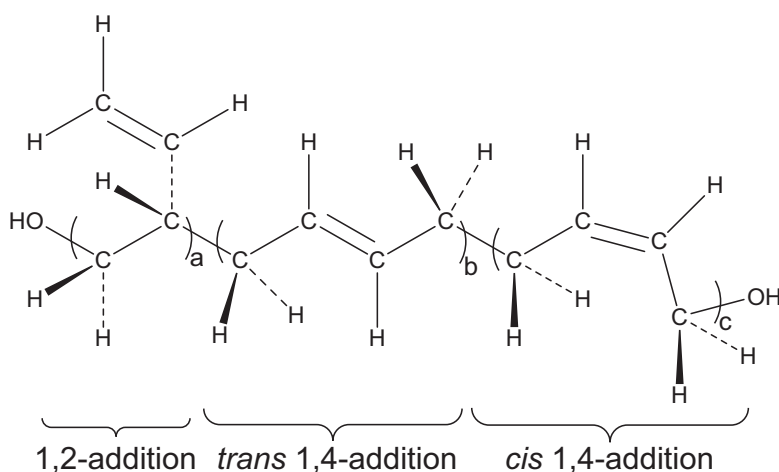
Nomenclature:

ACPC	4,4'-Azobis(4-cyanopentanoyl chloride)
ACPA	4,4'-Azobis(4-cyanopentanoic acid)
AdCl	Adipoyl chloride
ADN	Ammonium dinitramide
AIBN	Azobisisobutyronitrile
AMMO	3-Azidomethyl-3-methyl oxetane
AP	Ammonium perchlorate
BAMO	3,3-Bis(azidomethyl) oxetane
BR	Burning rate [mm/s]
CSPs	Composite solid propellants
CuCh	Copper chromite
DT	3,5-Diazido-2,4,6-triazin-1-yl
GAP	Glycidyl azide polymer
HDI	Hexamethylene diisocyanate
HNF	Hydrazinium nitroformate
HTPB	Hydroxyl terminated polybutadiene
IPDI	Isophorone diisocyanate
MW	Molecular weight
PBXs	Polymer bonded explosives
PO	Propylene oxide
PB	Polibutadiene
PU(s)	Poliuretane(s)
PVF	Poly(vinyl ferrocene)
T_c	Critical temperature [°C]
T_g	Glass transition temperature [°C]
TDI	Toluene diisocyanate
TMOs	Transition metal oxides
η	Viscosity [Pa·s]

1 Introduction

Since hydroxyl terminated polybutadiene (HTPB) (Scheme 1 [1]) emerged as a new type of telechelic liquid polymer in the 1960s [2], it has shown versatile applications in many fields, such as aerospace, biology, pharmaceuticals and agriculture [3-9]. One of the most important applications of HTPB is its use as a polymeric binder for both propellants and explosives. For example, HTPB acts as the matrix which binder together the organic oxidizer, metallic fuel, burning rate

catalyst and other additives in many composite solid propellants (CSPs) [10-18]. It has a similar role in binding together explosive powders in many polymer bonded explosives (PBXs) [19-23]. Furthermore, it possesses many positive features, such as excellent flow characteristics, low glass transition temperature ($T_g = -78\text{ }^\circ\text{C}$), high solid loading, good low temperature properties and ballistic performance. Usually, the characteristics of the pre-polymer and the elastomeric system have a great influence on the general energetic, combustion and mechanical properties of propellants and explosives. Therefore, HTPB is particularly important as a strong binder pre-polymer for building a three-dimensional network structure.



Scheme 1. Structure of HTPB

The literature [10, 24-27] reveals that some factors, including the contents of *cis*-, *trans*-, *vinyl*-isomers, the molecular weight and molecular weight distribution have a great influence on the physicochemical properties of HTPB. Certainly, through a proper choice of the polymerization methods and careful adjustment of the reaction conditions, the chain microstructure can be controlled in order to obtain a HTPB binder pre-polymer with better properties [28-30]. However, due to the inert and non-polar nature of HTPB, some drawbacks exist in HTPB, such as its low energy and poor compatibility with highly energetic components, which limit its further application in propellants or explosives. As for new weapon systems, ordinary methods, such as changing the cross-linker, chain extender [31] and curing agent [32-34], controlling the molecular weight (MW), or adjusting the curing parameters, cannot meet the needs of the increasing performance of CSPs and PBXs.

Modifications on the long chain of HTPB can be a convenient approach for improving the properties of HTPB-based propellants or explosives. There are two general methods for modifying HTPB: one is to modify the chain structure directly by introducing some functional groups, the other is to produce a hybrid between HTPB and other repeat units. Many studies have been done in this field, but no professional reviews are available. Based on the special properties of the resulting polymers, this article presents an overview of the modification of the chemical structure and progress of the applications of modified-HTPBs in the military field.

2 Modification of Energy

With the development of energetic materials [35-38] (*e.g.* energetic compounds, energetic plasticizers), energetic binders [39-42] have emerged in order to meet the increasing energetic needs of propellants [43]. However, these polymers show some limitations in mechanical properties after curing, or processability at higher solid loading. Therefore, HTPB is still the first and best choice for propellant formulations despite the availability of some new energetic binders. Some efforts have also been made on blends [44-46] and energetic interpenetrating polymer networks [47] between HTPB and GAP in order to improve the energy density of propellants based on HTPB. Unfortunately, the overall improvements of the performance for propellants and explosives have been greatly limited because of the poor compatibility between the two polymer ingredients.

It is therefore necessary to take full advantage of the superiority of HTPB in order to obtain energetically modified-HTPBs. Meanwhile, it is evident that there is tremendous scope to develop energetic HTPBs by introducing energetic functionality without destroying its excellent physicochemical properties. A considerable number of efforts have been proposed in the literature to modify HTPB by attaching energetic functionality onto its backbone.

2.1 Azido groups

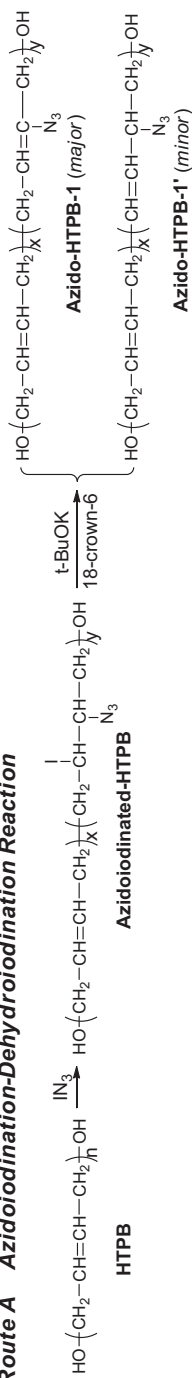
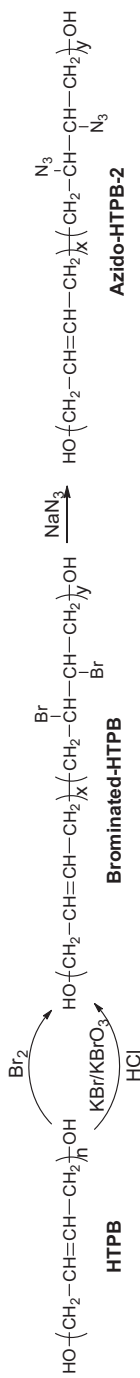
The azido group is an important energetic group in materials for military applications. It seems that the introduction of azido groups directly onto HTPB is the simplest approach for enhancing its energetic properties. Earlier in 1982, HTPB-derived polymers containing azido groups were prepared by Lillya *et al.* [48] through azido iodination followed by dehydroiodination (Scheme 2: Route A). This method itself has drawbacks during the dehydroiodination

stage, such as the loss of nitrogen, less directed elimination and byproducts. More importantly, vinyl azides are substantially less stable than alkyl azides. Therefore, the low thermal stability of HTPB derivatives containing vinyl or allylic azides and poor mechanical properties limit the further application of these derivatives as elastomers or binders.

More than 30 years later, Shekhar Pant *et al.* [49] synthesized azido-HTPB-2 via two established methods (Scheme 2: Route B and C). Although the Mn(III) acetate-catalyzed azidation reaction as a single-step synthesis seems more convenient, the bromination-azidation reaction can give better consistency in the azide content of the resultant pre-polymer. With regard to the determination of important physical and thermal properties, the improvement in viscosity and the glass transition temperature (T_g) of azido-HTPB-2 can be expected, and azido-HTPB-2 with 10% azidation ($\eta(30\text{ }^\circ\text{C}) = 11\text{ Pa}\cdot\text{s}$, $T_g = -66\text{ }^\circ\text{C}$) still gives acceptable properties for potential applications in composite propellants.

Alternatively, since energetic binders that already contain azido groups attracted the attention of many researchers, glycidyl azide polymer (GAP) is used as an energetic binder or plasticizer in propellant systems because of its positive heat of formation and high density [50]. With extended research, it also exhibits some poor low temperature properties (*e.g.* $T_g = -48\text{ }^\circ\text{C}$; $T_c = 6\text{ }^\circ\text{C}$ [51]) and poor processability due to its high chain stiffness. One of the solutions to obviate these problems may be the block copolymerization approach, in which the energetic segment is chemically linked to a rubbery segment such as HTPB in a single chain. Consequently, this method may not only resolve the application limitations of GAP, but also improve the energetic properties and some other drawbacks of HTPB. The copolymer is a designed hybrid combining the energetic properties of GAP and the physicochemical properties of HTPB, and it is also expected to have promising applications as a new energetic binder in rocket propellants. In the extensive literature, there are two main resolutions to obtain a copolymer between GAP and HTPB. One is free radical polymerization, the other is cationic ring-opening polymerization.

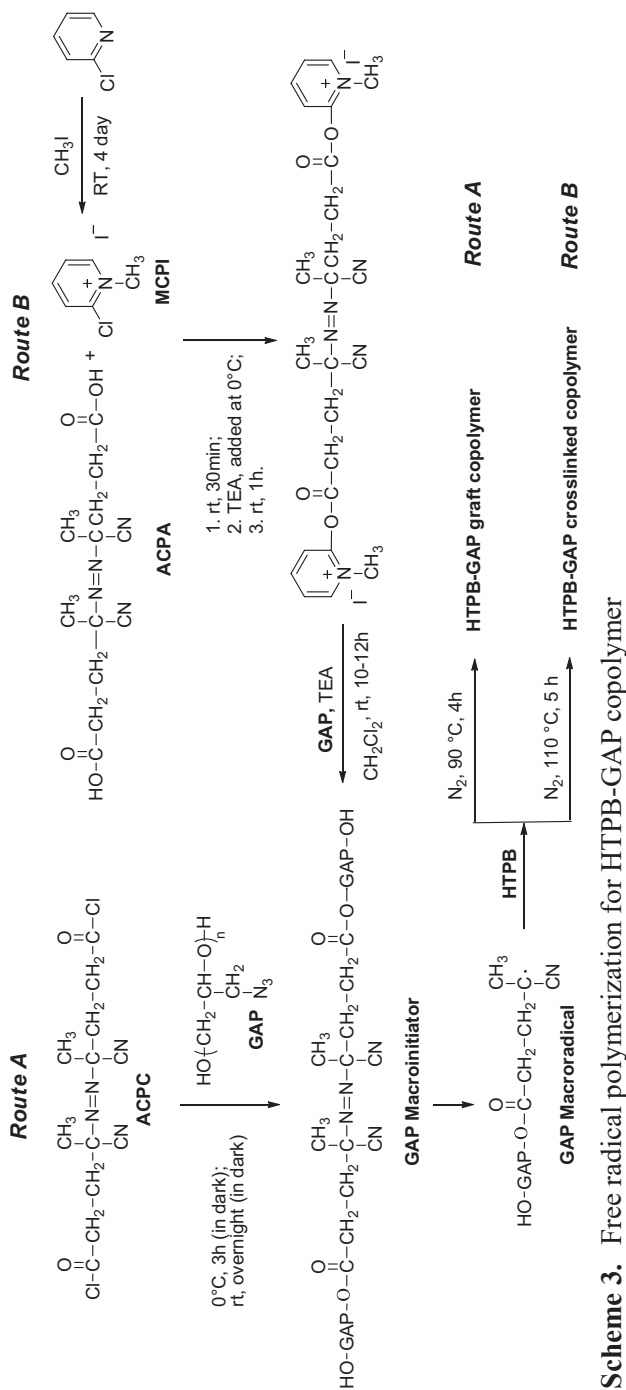
In the method of free radical polymerization, macro azo-radical initiators such as polyesters and polyamides are always employed for the preparation of block or graft copolymers. These macro-initiators can be readily prepared in high yields, by reacting 4,4'-azobis(4-cyanopentanoyl chloride) (ACPC) with diols or diamines, according to traditional methods [52]. Erođlu *et al.* [53] first described the grafting of GAP onto HTPB through the free radical polymerization route; the GAP macro-initiators used in this route were produced by the reaction between ACPC and GAP (Scheme 3: Route A). However, there were some difficulties in obtaining ACPC in high yield by reacting 4,4'-azobis(4-cyanopentanoic acid)

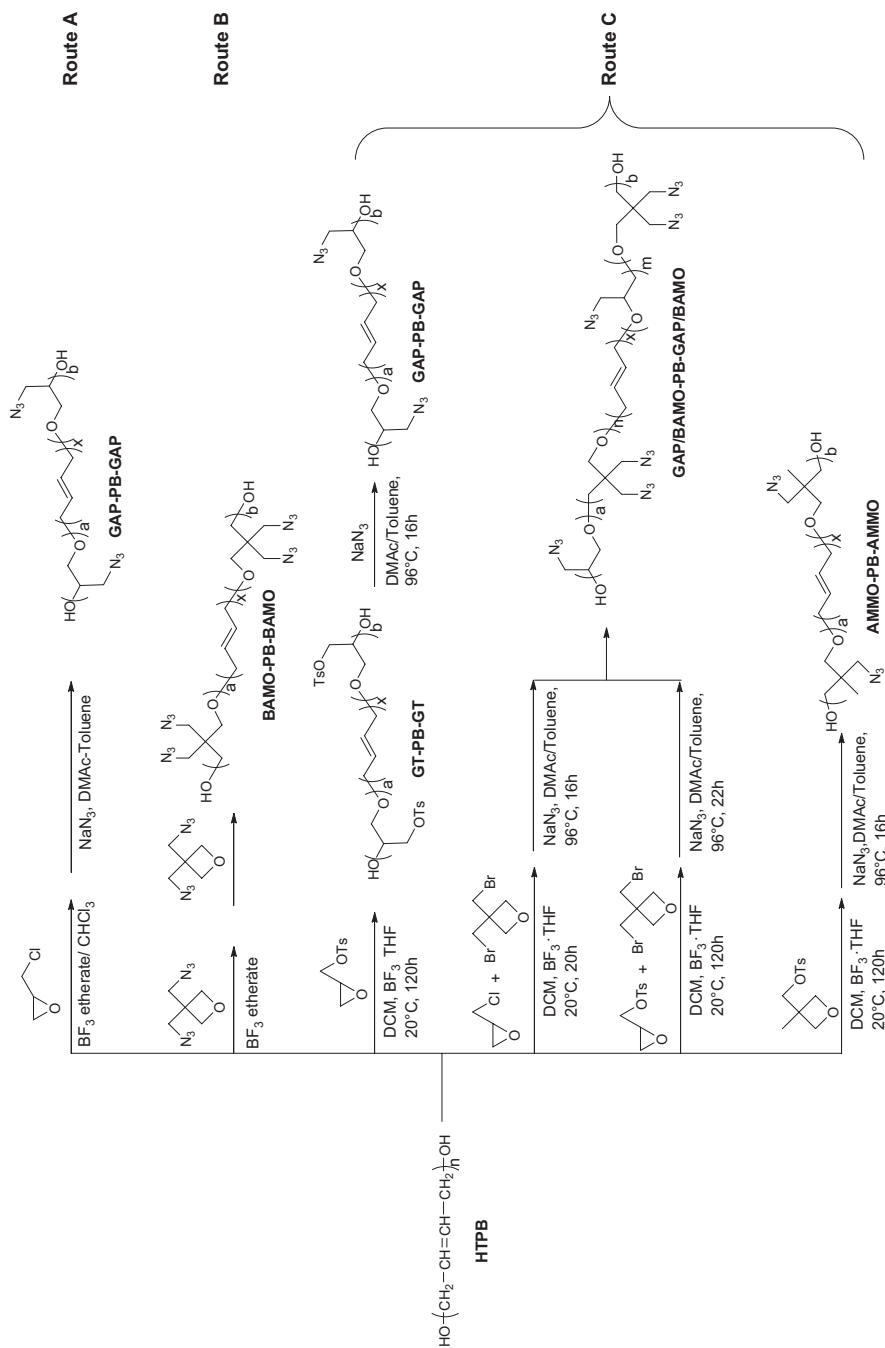
Route A Azidoiodination-Dehydroiodination Reaction**Route B Bromination-Azidation Reaction****Route C Azidation Reaction****Scheme 2. Routes for the direct introduction of azido groups**

(ACPA) with thionyl chloride or phosphorous pentachloride. In order to obtain the GAP macro-initiators in good yields, Mohan *et al.* [54] employed ACPA as the starting material, reacting it with GAP using N-methyl-2-chloropyridinium iodide as a condensation reagent without converting the carboxylic acid (ACPA) to the corresponding acid chloride (ACPC) (Scheme 3: Route B), thus generating the HTPB-GAP copolymer. In contrast to the micro-phase separation phenomenon of GAP-g-HTPB obtained at 90 °C, the HTPB-GAP cross-linked copolymer that was prepared at higher temperature was more homogeneous and could see potential applications in propellants as a binder pre-polymer or additive because of its thermal properties. Thus, it was shown that the phase separation can be solved not only at the macroscopic level but also at the microscopic level *via* a cross-linker copolymer between two polymer segments with different polarities.

As mentioned above, cationic ring opening polymerization by the activated monomer initiation mechanism can also be applied in the synthesis of the GAP-HTPB co-polymer, thus more directly giving a tri-block copolymer with polybutadiene (PB) as the central block. Subramanian *et al.* [55] (Scheme 4: Route A) obtained GAP-PB-GAP tri-block copolymer by means of cationic ring opening polymerization as the first stage, with azidation as the second stage. Research on the copolymer used in non-aluminized propellant strands, with and without a burning rate (BR) catalyst, and other properties was also carried out. The results showed that it is possible to achieve the required BR of a propellant without a BR catalyst and the enhanced energy output of a propellant by chemically linking a rigid energetic GAP segment of suitable size onto the ends of HTPB. Similarly, Vasudevan *et al.* [56] prepared GAP-PB-GAP by the same route and used it in an ammonium perchlorate (AP)/HTPB propellant, partially replacing the HTPB. Compared with the original AP/HTPB propellant, the GAP-triblock modified system showed improved interfacial properties and better ballistic properties.

Recently, polybutadiene/poly(glycidyl azide) block copolymers were also synthesized by Cappello *et al.* [57] *via* a one pot strategy starting from the homopolymers and using two different chain extenders: hexamethylene diisocyanate (HDI) and adipoyl chloride (AdCl). The reagent quantities were chosen based on the stoichiometry of the GAP-PB-GAP tri-block copolymer. Although this method is faster and easier compared to the cationic copolymerization abovementioned route, the resulting copolymers cannot be purified and the final mixture is supposed to contain many other side products derived from the random combination of GAP and PB blocks as well as the un-reacted homopolymers. However, the mixture





Scheme 4. Cationic ring opening polymerization for HTPB-GAP copolymer

exhibited homogeneous and stable morphologies without macroseparation. More importantly, the sample prepared with AdCl may be the best candidate as a binder for application in propellants or as a compatibilizer in GAP-HTPB mechanical blends. The latter had been verified by the investigation of the phase stability *via* fluorescence microscopy.

With regard to other energetic repeating units containing azide groups, 3,3-bis(azidomethyl) oxetane (BAMO) with a higher N content (50 wt.%) and 3-azidomethyl-3-methyl-oxetane (AMMO) could also be considered. However, unlike AMMO, a homopolymer of BAMO cannot be directly used as an energetic binder because of its crystalline properties arising from the symmetric nature of the monomer [58-60]. Alternatively, it could be applied in polymerization with HTPB to prepare a copolymer in order to improve the energy performance. In 2007, a BAMO-HTPB copolymer with different monomer ratios was successfully synthesized by Reddy *et al.* [61] *via* an activated monomer mechanism through the polymerization-azidation route (Scheme 4: Route B). Considering the safety and compatibility of the process, Cappello *et al.* [62] employed an alternative procedure for the preparation of 3 ether-butadiene-ether copolymers using four similar routes: GAP-PB-GAP, GAP/BAMO-PB-GAP/BAMO and AMMO-PB-AMMO (Scheme 4: Route C). Since the first GAP-HTPB copolymer had been prepared from different precursors, the other two copolymers were described for the first time. Based on their studies, they clearly described the side reactions between the azidic functionalities and the unsaturated bonds. Then, they also described a good resolution of this problem *via* the application of a toluene/DMAc mixture as the solvent in combination with small quantities of Vulkanox BKF as an anti-ageing compound for polymer preparation, and the use of the same anti-ageing compound for prolonging storage in an inert and dark atmosphere. Compared with the monomers with substituted halogen, their researches also revealed that the azide strategies starting from highly sterically hindered tosyl groups in long polymer chains would give lower azide contents.

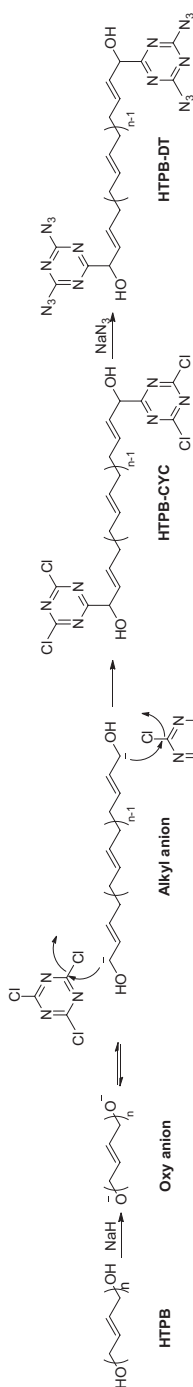
There is a further strategy for terminal modification without perturbation of the backbone of HTPB. Jana *et al.* [63] reported a novel approach for the covalent attachment of a polyazido nitrogen rich molecule onto the terminal carbon atoms of the HTPB through a two-step nucleophilic substitution mechanism (Scheme 5). Despite the increased viscosity, the resulting polymer HTPB-DT (DT: 3,5-diazido-2,4,6-triazin-1-yl) exhibits additional energy because of the introduction of the DT group as a superior energetic moiety. The role of the terminal DT groups on the structure-property relationship of HTPB based polyurethanes has been extensively investigated by the same research team [64]. The polar substituents

located at the meta-positions of the triazine ring on the terminal carbons of HTPB-DT promotes electrostatic interactions with the urethane backbone and results in the formation of nanometer-sized mass fractals of hard segment domains (HAD) in the PUs. Hence, these modified PUs exhibit significant improvements in the static and dynamic mechanical properties. For example, the tensile strengths of HTPB-DT based PUs, which were cured by IPDI, 2,4-TDI and 2,6-TDI, were 1.97, 4.55 and 6.36 MPa and their Young's modulus values were 0.020, 0.052 and 0.069 MPa, respectively. However the tensile strength and Young's modulus values of the reference HTPB based PUs were 0.922, 2.85, and 4.49 MPa, and 0.0058, 0.012, and 0.063 MPa, respectively.

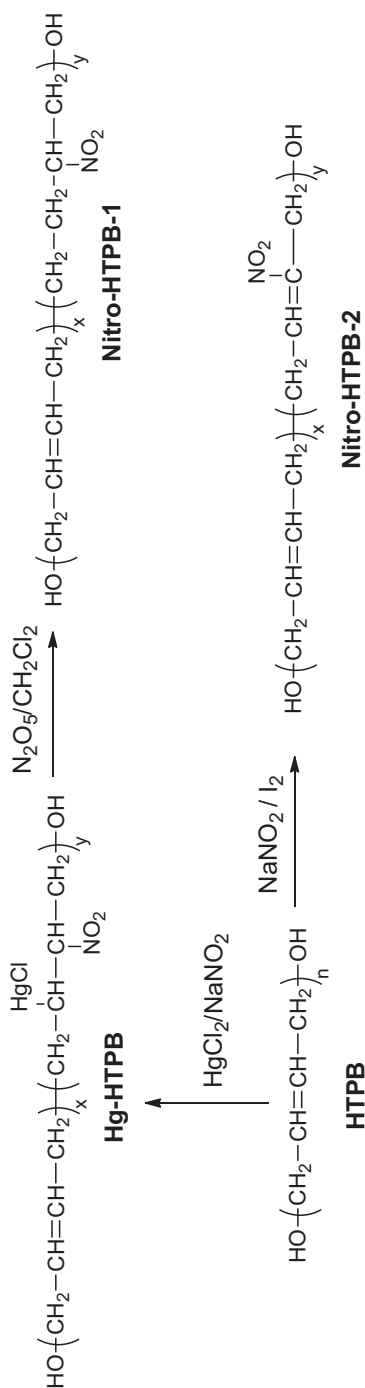
2.2 Nitro groups

Another common method for making molecules or polymers energetic is to introduce nitro groups, as a general energetic group, onto their structures. Taking this into consideration, some scientists have modified HTPB by employing nitro groups to obtain an energetic binder. Early in the 1980s [65], the nitration of poly(*cis*-butadiene) was successfully achieved and gave a possible route to nitro-HTPB-1 through a nitromecuration-demercuration route (Scheme 6: nitro-HTPB-1). However, some drawbacks to this method still exist, such as selectivity, solubility and stability. Considering other methods in the literature for the nitration of alkenes to give conjugated nitroalkenes, Shekhar Pant *et al.* [66] employed nitryl iodide (NO_2I) generated *in situ* as the active reagent for nitration, to synthesize nitro-HTPB by an addition-elimination reaction process. In this reaction, NO_2I can be generated *in situ* by reaction of sodium nitrite (NaNO_2) and iodine (I_2) (Scheme 6: nitro-HTPB-2). Recently, an investigation of the reaction operation and conditions for nitro-HTPB-2 was given for its optimization by Ghayeni *et al.* [67].

Abusaidi *et al.* [68] synthesized nitro-HTPB-2 by using the aforementioned reaction and reported research on the thermal stability and decomposition kinetics of nitro-HTPB-2 containing different amounts of nitro groups. The results showed that the thermal stability of nitro-HTPB-2 is higher than nitrated-HTPB (NHTPB) and slightly lower than nitrocellulose. The thermal behaviour and decomposition kinetics of an HMX-based nitro-HTPB-2 polymer-bonded explosive (PBX) were also studied by the same group [69]. The TG/DSC curve of the nitro-HTPB-2 based PBX showed a single decomposition process. The maximum peak temperature was shifted to higher temperatures as the DSC heating rate was increased. The thermal stability of the PBX samples decreased with increasing nitro-content in nitro-HTPB-2. Furthermore, compared with the results for nitro-HTPB-2, the PBX explosive samples with 80% solid loading (80 wt.%)



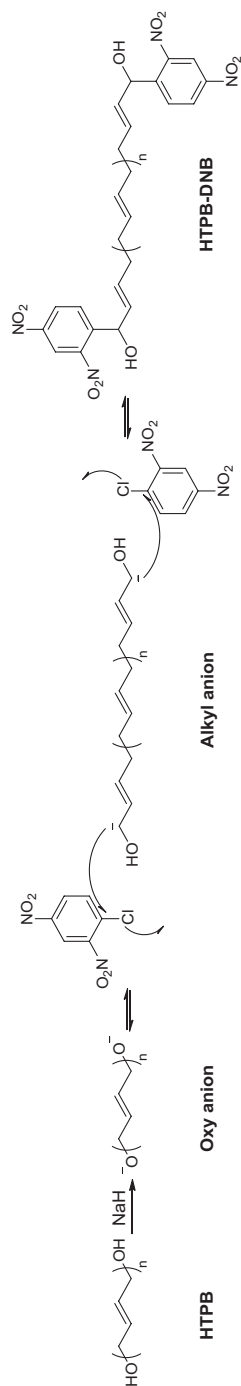
Scheme 5. Terminal modification for introducing azido groups



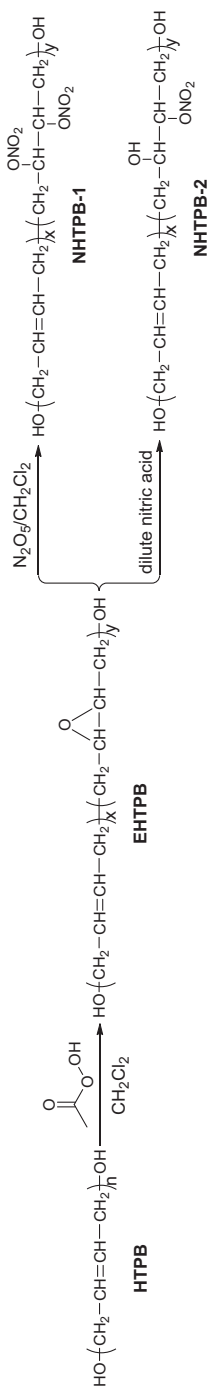
Scheme 6. The introduction of nitro groups onto the HTPB polymer chain

HMX/15 wt.% nitro-HTPB-2/5 wt.% Bu-NENA) were more stable. They recently revealed further research on nitro-HTPB-2 used as an energetic binder in an AP/Al-based propellant [70] and the essential properties were also investigated. As a result, both nitro-HTPB-2 based PBXs, with and without the energetic plasticizer Bu-NENA, give good mechanical properties and further improvement of the T_g , elongation and viscosity. Meanwhile, nitro-HTPB-2 based propellants just gave a small increase, but still remained in the safety range according to the tests for impact and friction sensitivity. Additionally, another application of cured and unfilled nitro-HTPB-2 based elastomer, using nitro-polybutadiene as an energetic plasticizer, was reported by Ashrafi *et al.* [71]. Compared with the HTPB/DOA system, nitro-HTPB-2/nitro-polybutadiene exhibited lower migration rates because of the similarity in structure between these two polybutadiene based polymers, and this new binder system can not only enhance the energetic properties but also possess good mechanical properties.

Unlike co-polymerizing with HTPB or introducing energetic groups onto the backbone of HTPB, which would more or less have an influence on the thermal or rheology properties, such as the T_g and viscosity, the terminal modification of HTPB by energetic moieties may have a reduced influence. Based on this idea, Jana *et al.* [72] employed 1-chloro-2,4-dinitrobenzene (DNCB) as a covalent modifier attached to the terminal carbons of HTPB by a nucleophilic substitution mechanism (Scheme 7: HTPB-DNB). As expected, the resulting polymer HTPB-DNB could be a promising energetic binder, according theoretical calculations, while this kind of modification did not destroy the unique physicochemical properties of the parent HTPB. Importantly, the $-\text{NO}_2$ groups in the dinitrobenzene units can not only form intermolecular hydrogen bonds with the terminal $-\text{OH}$ groups of HTPB-DNB, but also provide strong interactions between the $-\text{NO}_2$ of the soft segment and HTPB-DNB based PU backbone. Furthermore, the unique supramolecular hydrogen bonding network in HTPB-DNB based PU matrix can accelerate a higher cross-linking density and simultaneously improve the tensile strength and elongation at break, which was rarely accomplished in earlier research [73]. Four years later, in 2014, the formation of an AP/Al propellant with HTPB-DNB as the binder was carried out by Abdullah *et al.* [74]. Based on the same formulation with 88% solid loading, the HTPB-DNB based propellant had similar friction and impact sensitivity to the HTPB based system. At the same time, the former also has a higher burning rate and lower pressure exponent than the HTPB propellant. With regard to the small motor test, the HTPB-DNB motor exhibited a higher burning rate and density impulse, but almost no obvious improvement in specific impulse. Hence, the propellant applications of HTPB-DNB as a binder need further investigation.



Scheme 7. Terminal modification for introducing nitro groups



Scheme 8. The introduction of nitrate groups onto the HTPB polymer chain

2.3 Nitrate groups

As an energetic group, the nitrate group is also worth considering for the modification of the energy output of HTPB. Differing from the previously mentioned nitration method for HTPB, another green approach was employed by Colclough *et al.* [75] to synthesize nitrated HTPB (NHTPB-1). This polymer modification route relies on the reaction of N_2O_5 with epoxide groups to produce vicinal dinitrate esters (Scheme 8: NHTPB-1). The nitrate group content has a significant influence on some important physical properties of NHTPB-1. Based on many small-scale tests and research, they found that NHTPB-1 with 10% double bonds converted to dinitrate ester groups would give a good balance between energy output and mechanical properties. Furthermore, it can be a good energetic binder because of its lower viscosity for not only processability but also a high solids loading and better miscibility with other energetic ingredients in propellants when compared with HTPB. According to Colclough *et al.* [76] research on the miscibility with different energetic plasticizers hinted that the overall energy output of propellants and PBXs can be further improved by using energetic plasticizers with NHTPB-1. More recently, Wang *et al.* [77] studied in detailed the thermal decomposition kinetics of the 10% NHTPB-1. They also estimated the half-life at 50 °C and the critical explosion temperature for NHTPB-1, which were about 20 years and 154 °C, respectively. Compared to the poor compatibility of HTPB, the compatibility of NHTPB-1 has been improved because of the introduction of $-ONO_2$ as polar groups. Additionally, the facile and low cost preparative process cannot be neglected. In the view of its advantages, NHTPB-1 has persuaded the Royal Armament Research and Development Establishment (RARDE) in England to study this topic further [78].

Additionally, NHTPB-2, which contains nitrate groups with hydroxyl groups attached to two adjacent carbon atoms respectively in one repeat unit, was also synthesized by Wang *et al.* [79] by nitrating epoxy hydroxyl-terminated polybutadiene (EHTPB) with dilute nitric acid (Scheme 8: NHTPB-2). Orthogonal experiments were also carried out for the optimization of the reaction conditions. With regard to its performance, such as its thermal properties, safety evaluation and usability, NHTPB-2 shows a higher decomposition temperature than NHTPB-1 and good safety arising from its thermal properties and low impact sensitivity. Additionally, the BR of NHTPB-2 based propellants had been improved by 2 mm/s. However, more hydroxyl groups in the backbone perhaps limit its further application, because of poor reproducibility during the curing process.

3 Modification of Burning Rate

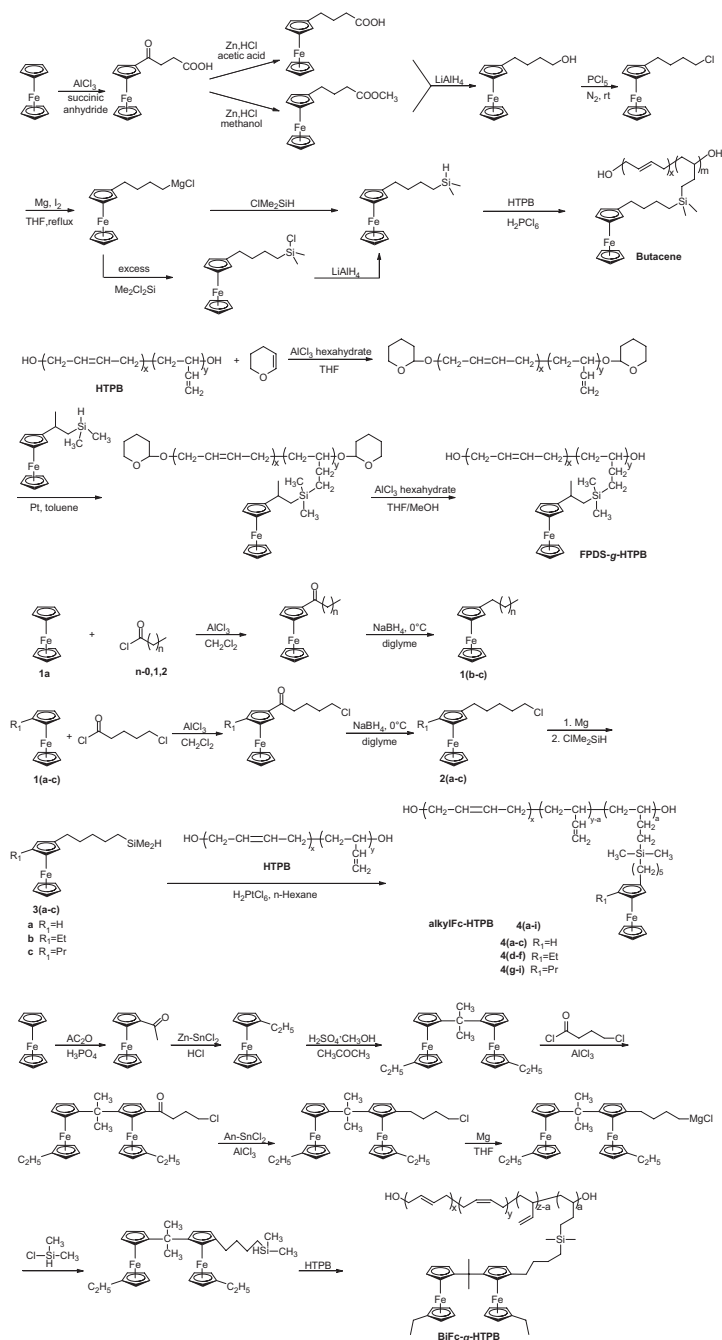
Solid propellants play an important role as a power source for rocket motors, relying on their combustion processes [80]. The BR has a significant effect on the gas output and the power of the motor in CSPs, while the burning rate-pressure exponent is also an important parameter for measuring the sensitivity and stability of the propellant during its combustion process. Ideally, the perennial goal for solid propellant designers is to obtain a solid propellant with well-tailored BR properties. There are also many methods for controlling the BR, such as changing the oxidizer particle size, using novel oxidizers or highly energetic additives, changing the propellant core shape and adding BR catalysts [81]. As a convenient method, the BR can be enhanced and the pressure exponent can be decreased by the direct introduction of a BR catalyst, such as ferrocene derivatives [82] and transition metal oxides (TMOs) [83], to the propellant mixture. However, an ingredient introduced physically to an HTPB-based propellant will cause some unavoidable problems, such as compatibility or migration. Therefore, much work has been done on changing the manner in which BR catalysts are incorporated to give better combustion performance and lifetime to the HTPB-based propellant. In these studies, some small moieties, such as BR catalytic groups, have been chemically connected to HTPB to give a modified HTPB with some new properties, including anti-migration, anti-volatilization and anti-agglomeration.

Ferrocene and its derivatives are commonly applied as BR catalysts, mainly due to their particular advantages, such as compatibility, dispersibility and fluidity. However, some inherent drawbacks, such as migration during storage, sensitivity and safety arising from evaporation or sublimation during processing [84], stability in low-temperature applications or storage because of crystallization [85, 86], cannot be overlooked. Compared with the introduction of ferrocene-modified polymers [87, 88] or functionalized ferrocene [89], it is still much more facile and important to covalently link an appropriate ferrocene derivative onto the structure of HTPB in order to improve the performance of propellants, such as compatibility, safety, stability and BR. In addition, this method can also address the migration problem to some extent.

The former SNPE in France leads the world in the field of chemical and civil products, including solid and liquid rocket propellants, rocket charges, and explosives [90]. Early in the 1980s, a new type of pre-polymer named Butacene[®] was successfully developed at SNPE and achieved bulk industrial production, while the migration problem arising from ferrocenyl derivatives as catalysts in propellants was well resolved. In 1991, batch

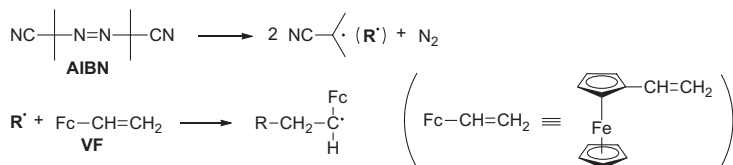
production of Butacene[®] reached to 200-300 kg and its annual production capacity was more than 10,000 kg [91]. This pre-polymer is a grafted polymer obtained by hydrosilylation of a ferrocenyl organo silicon derivative, Fe-R-SiH(CH₃)₂, and the vinyl groups of HTPB (Scheme 9: Butacene[®]). Many studies of Butacene[®], such as application, [92, 93] rheological behavior [94-97] and characterization [98] of Butacene[®]-based polyurethanes have been thoroughly executed. Kurva *et al.* [99] envisaged an application for high BR composite propellants with Butacene[®] as a BR modifier by partially (10% to 50%) replacing HTPB using a TDI/IPDI bi-curing system in the ratio of 65/35. Compared to the base composition, the introduction of Butacene[®] will cause the end of mix viscosity and impact and friction sensitivity to increase to different extents. However, studies on the ballistic properties revealed that the introduction of 50% Butacene[®] as a replacement enhances the BR by up to nearly 53%, and the pressure exponent value can also be lower.

Inspired by Butacene[®], Cho *et al.* [100] employed 2-(ferrocenylpropyl) dimethylsilane (FPDS) as a ferrocenyl organo silicon catalyst to synthesize FPDS-grafted HTPB (FPDS-g-HTPB) by hydrosilylation with Pt as a catalyst (Scheme 9: FPDS-g-HTPB). As expected, the polyurethane networks based on FPDS-g-HTPB had a similar structure to Butacene[®] and exhibited a higher T_g than the one based on HTPB. Furthermore, the former also had a faster decomposition process because of the grafted FPDS. Similarly, Teimurimofrad *et al.* [101] also used the hydrosilylation strategy to give three kinds of 5-(dimethylsilyl)pentylalkylferrocene-grafted HTPBs (alkylFc-HTPB) with HTPB in the presence of hexachloroplatinic acid catalyst (Scheme 9: alkylFc-HTPB). Each kind of the three alkylFc-HTPB samples, with different iron contents and physical properties, such as viscosity, glass transition temperature and iron percentage as important parameters, were investigated. The viscosity and the glass temperature increased with increasing iron content due to the greater number of ferrocene units grafted onto the polymer. However, it is worth noting that the viscosity of the alkylFc-HTPBs with similar iron contents decreased as the length of the alkyl branch on the ferrocene ring was increased. This interesting phenomenon will benefit the processability of the pre-polymer in the manufacture of propellants.

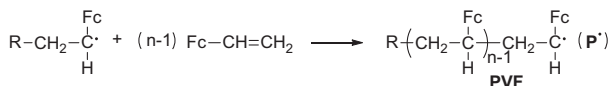


Scheme 9. The introduction of ferrocene groups onto HTPB via hydrosilylation

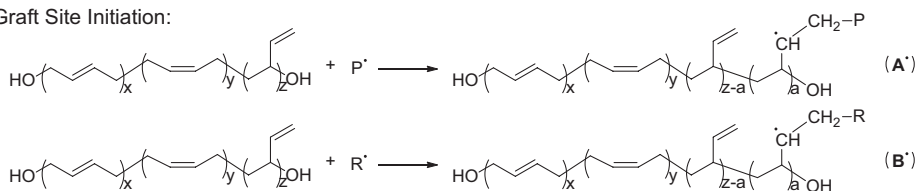
Monomer Initiation:



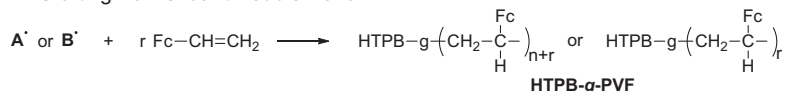
Propagation for PVF:



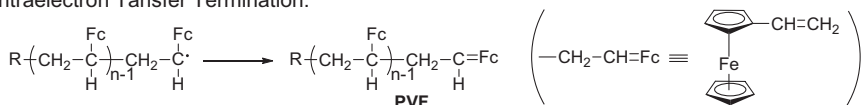
Graft Site Initiation:



PVF Grafting via Pendant Double Bond:



Intraelectron Transfer Termination:



Scheme 10. Introduction of ferrocene groups onto HTPB *via* free radical polymerization

Subramanian *et al.* [102] grafted poly(vinylferrocene) (PVF) onto HTPB by employing azobisisobutyronitrile (AIBN) as an initiator through a free-radical polymerization mechanism (Scheme 10: HTPB-g-PVF). The maximum weight percent of Fe in HTPB-g-PVF can only achieve 0.43 wt.%. To a certain extent, this is because of the presence of un-grafted HTPB in the resulting resin and also the low grafting efficiency. The AIBN-initiated grafting efficiency cannot be easily improved by simply increasing the VF concentration due to a significant chain transfer to monomer. However, it is noteworthy that, with regard to the non-aluminized propellant BR studies, the propellant strand based on the grafted HTPB as a binder shows better catalytic efficiency than not only the binder-dissolved free VF but also binder-distributed solid catalysts such as copper chromite (CuCh) and ferric oxide (Fe₂O₃) at the same weight percent level.

Moreover, its BR value could be maintained for at least 1 year under ambient conditions. Without the previously mentioned problems of polymerization, Fc-HTPB with four different iron contents, from 0.02 to 1.05 wt.%, were synthesized by Saravanakumar *et al.* [103] *via* Friedel-Crafts alkylation grafting of ferrocene onto the vinyl groups of HTPB (Scheme 11: Fc-HTPB). A comparative study on the gumstock based on Fc-HTPB systems cured by IPDI and TDI revealed that both of these had nearly the same mechanical properties and better processability was obtained when IPDI was used as the curing agent. With regard to the BR analysis of the aluminized AP propellants with Fc-HTPB as the binder, not only the Fc-HTPB propellant but also the diluted one with HTPB show higher BRs than the normal HTPB propellant.

Generally, the weight of Fe in a grafted-polymer has a large influence on the catalytic effect. The vinyl content of HTPB is about 20% [104], therefore, even if the grafting efficiency could reach 100%, the Fe content could still only achieve a low value. With the development of biferrocene derivatives, it seemed meaningful to graft them onto HTPB to improve the combustion performance. Recently, BiFc-g-HTPB with 8.24 wt.% iron content was obtained through HTPB grafted with biferrocene 2,2-di(ethylferrocene)propane-organo silicon. As described by Zhang *et al.* [105] the organo silicon was synthesized by a series of steps, such as Friedel-Crafts acylation, reduction reaction, coupling reaction (Scheme 9: BuFc-g-HTPB). As for the thermal analysis, 5% BiFc-g-HTPB had a better catalytic performance than 5% Butacene[®] on the decomposition of AP.

As a common and conventional way, TMOs (*e.g.* iron oxide [106], CuCh [107] and cobalt oxide [108]) could be easily used as BR catalysts in propellants and affect the BR by lowering the thermal decomposition of AP and the binder [109, 110]. However, since this kind of catalyst of high content may lead to poor processing, ageing and mechanical characteristics of the resultant propellants, it seems difficult to realize workable propellants with high BR requirements. Additionally, some other inherent disadvantages, such as agglomeration, in-homogeneity in distribution and particle size, diminished BR enhancement and settling with catalyst loadings, limit their further application as BR catalysts. Furthermore, their bad morphology and poor reproducibility, varying from batch to batch from a single manufacturer, also cannot be ignored.

Based on the literature [111] $\text{HTPB} \rightarrow [\text{Fe}(\text{CO})_3]_x$, in which Fe is linked to HTPB by linking the iron as $-\text{Fe}(\text{CO})_3$ to the HTPB backbone, was synthesized by Subramanian *et al.* [112] through either iron pentacarbonyl (IPC, $\text{Fe}(\text{CO})_5$) or tri-iron dodecacarbonyl (FDC, $\text{Fe}_3(\text{CO})_{12}$). The investigation revealed that this resin with an Fe content below or equal to 0.8 wt.% will have no significant

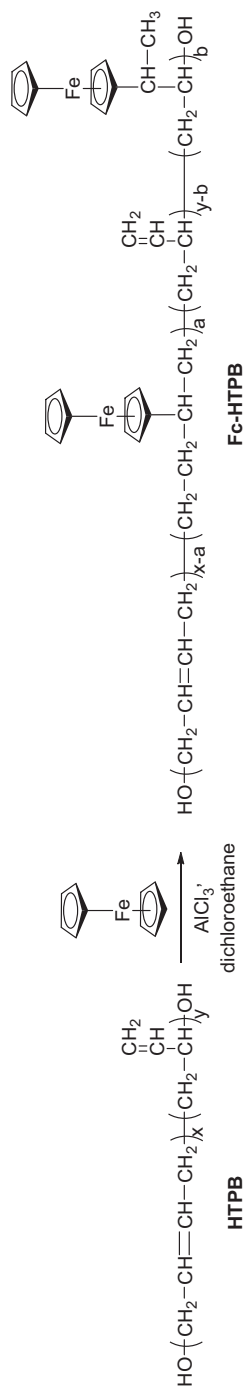
effect on the physical appearance and processability or castability of the propellant. Compared with the HTPB/free IPC or Fe_2O_3 containing the same weight percent of Fe, the modified-HTPB, which can be used either alone or blended with pure HTPB, has a greater BR enhancement.

PPA-PB-PPA and PNBE-PB-PNBE, as two tri-block copolymers, were reported by Vasudevan *et al.* [113] and they were polymerized with phenylacetylene (PA) or norbornene (NBE), with HTPB-anchored tungsten hexachloride as catalyst, *via* a metathesis polymerization (Scheme 12). Based on these investigations, both of these tri-block copolymers can be used as additives in propellants. Compared to the HTPB-based propellant, the addition of copper chromite along with the tri-block copolymers shows better performance, and the PNBE-PB-PNBE based samples gave lower pressure dependence. With regard to the BR studies, AP/HTPB propellants with the combination of polyNBE-HTPB and CuCh exhibit better burning characteristics.

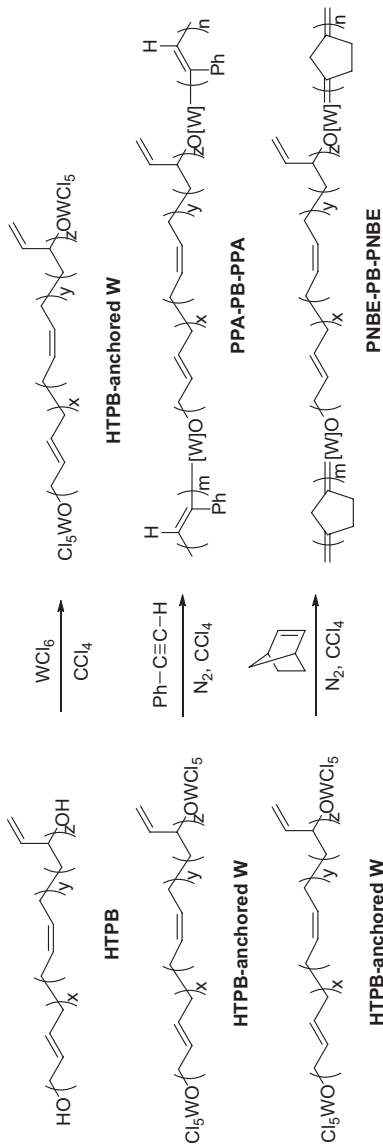
4 Modification of Cure Methodology

Polyurethane, as a conventional cross-linked curing system, has been widely used as a binder for the majority of solid rocket propellants in service or in research. This type of network structure comes from the reaction between hydroxyl groups on the binder pre-polymer and the isocyanate groups on the curing agent [114]. However, cross-linked polyurethanes suffer from being humidity sensitivity in the curing procedure, leading to a deterioration of the mechanical properties of the propellant grains [115, 116]. Additionally, this kind of curing system limits the overall energy output of the propellants due to the poor compatibility between polyurethane and highly energetic oxidizers like ammonium dinitramide (ADN) and hydrazinium nitroformate (HNF) [117-119]. Therefore, there is an urgent need to find a new binder methodology for high energy propellants or explosives. Furthermore, HTPB, as a widely used binder with good low temperature mechanical properties, which arise from its properly flexible long chain, urgently needs to be modified for further application in propellants to overcome the stability problems.

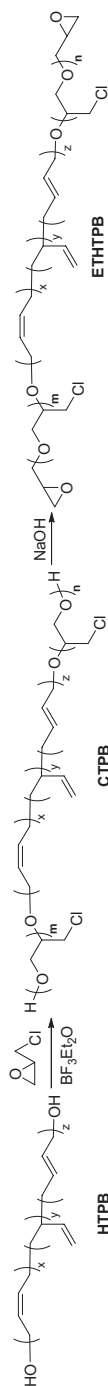
Generally, the terminal functional groups directly determine the curing mechanism, while the long chain structure in the telechelic binder pre-polymer have a great influence on its physical properties, such as T_g and rheological properties. In research on a new type of isocyanate-free curing system, Li *et al.* [120] modified HTPB to prepare a terminally-epoxidized block polymer, epoxy-terminated polybutadiene (ETHTPB), *via* cationic ring-



Scheme 11. Introduction of ferrocene groups onto HTPB via Friedel-Crafts reaction



Scheme 12. Metathesis polymerization catalyzed by HTPB-anchored W



Scheme 13. Preparation of ETHTPB

open polymerization using HTPB as an initiator and borontrifluoride etherate ($\text{BF}_3 \cdot \text{OEt}_2$) as catalyst for the first step, followed by a ring-closing reaction (Scheme 13). The preliminary results showed that polyamide 650 is good curing agent of ETHTPB.

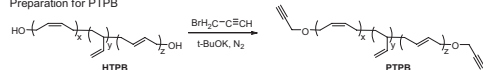
Additionally, Fu *et al.* [121] gave a detailed report on the surface-interfacial properties between epoxy-terminated polybutadiene (ETHTPB) as an adhesive and Al, AP, RDX and HMX as solid fillers. Because of the lower surface tension of ETHTPB, it can easily spread on the surfaces of the solid propellant components. This research provides a certain basis for further investigations on ETHTPB-based propellants. However, this isocyanate-free methodology, by using an amine as the curing agent may have an influence on the ageing characteristics of the propellants. Consequently, this inherent drawback limits its further application.

In the development of the classical click reaction, the Huisgen 1,3-dipolar cycloadditions based on azides and alkynes has earned considerable attention due to the fact that it is a virtually quantitative, very robust, insensitive, general, and orthogonal ligation reaction [122].

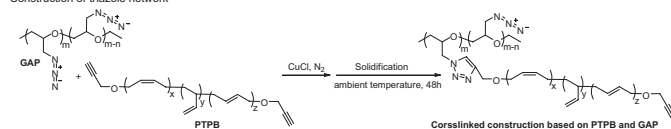
In 2014, Ding *et al.* [123] initially reported an alkynyl-functionalized PB (PTPB), which was synthesized by the alkynylation of HTPB and a series of triazole-linked composites based on GAP and PTPB (Scheme 14: Route A). Compared to the GAP-HTPB copolymer and the crosslinked GAP-HTPB network, PTPB itself and its triazole composites with GAP showed a single and lower T_g range $-(84.2-81.5)^\circ\text{C}$, which not only indicated really similar flexibility between the crosslinked network and its parent PTPB, but also showed little phase separation between the two segments GAP and PTPB. Although the authors did not give an analysis for the variation of T_g , the lower T_g of PTPB may be because of the absence of intermolecular hydrogen bonds that exist in HTPB. These investigations revealed a new type of composite regulated mechanical performance and its great potential application as a binder in solid propellants, because of its advantages, such as moisture insensitivity and compatibility with other high-energy components in propellants.

Route A: Triazole crosslinked network based PTPB and GAP

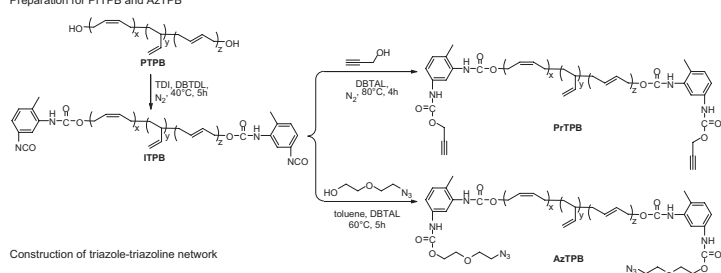
Preparation for PTPB



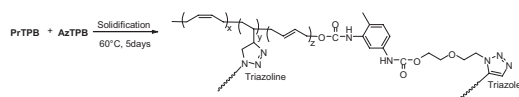
Construction of triazole network

**Route B: Triazole crosslinked network based PrTPB and AzTPB**

Preparation for PrTPB and AzTPB



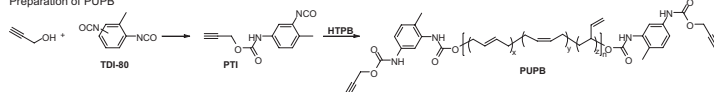
Construction of triazole-triazoline network



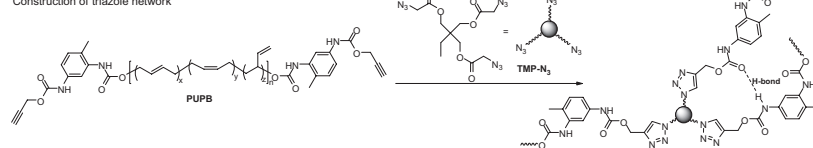
Crosslinked construction based on PrTPB and AzTPB

Route C: Triazole crosslinked network based PUPB and TMP-N₃

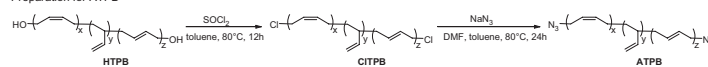
Preparation of PUPB



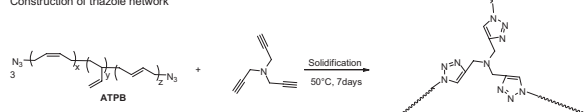
Construction of triazole network

**Route D: Triazole crosslinked network based ATPB and tripropargylamine**

Preparation for ATPB



Construction of triazole network

**Scheme 14. New curing systems based on classical click chemistry**

However, the numerous azido groups in GAP and the higher crosslink density make the reproducibility of the curing system poor. By comparison, Reshmi *et al.* [124] made a good use of the chain structure of HTPB and synthesized azide and alkyne terminated polybutadienes, which are azidoethoxycarbonylamine terminated polybutadiene (AzTPB) and propargyloxycarbonylamine terminated polybutadiene (PrTPB), respectively. A new cross-linked network based on the two polymers was then obtained also *via* a 1,3-dipolar addition reaction (Scheme 14: Route B). Although the propensity of azide groups for addition to the ethynyl groups is higher than to double bonds, the relative concentration of double bonds is much higher than that of triple bonds, so that triazoline moieties in the resultant network, arising from an azide-ethylenic reaction, can be observed in addition to the triazole moieties reported by Ding *et al.* [123]. Compared to HTPB-TDI, the PrTPB-AzTPB based network shows a slower cure rate at 60 °C (5 days), indicating a longer pot-life and superior properties, such as crosslink density, mechanical properties. As a result of the propellant's level studies, the novel binder based propellant, with AP as oxidizer and Al as metallic fuel, shows some particular advantages, such as enhanced pot-life and superior mechanical properties without effecting the BR. More recently, a comprehensive pyrolysis mechanism of this new triazole-triazoline network was investigated in detail and was rationalized through density functional theory (DFT) based computational analysis by the same group [125]. The results showed that the thermal decomposition occurs in two stages, the first stage, at 215-315 °C, involves urethane cleavage along with decomposition of the triazole-triazoline groups, and the second stage, at 315-500 °C, involves the polybutadiene backbone. Furthermore, analysis of the thermal decomposition pattern of the new binder based AP propellant, with low Al revealed better ballistics with higher BR at lower pressure ranges, 2.94-6.93 MPa, and a lower pressure exponent. The slightly high flame temperature and higher mass percentage of gaseous products, such as CO and N₂, suggest gas generator or pyrogen igniter applications.

Recently, an alkyne terminated polybutadiene with urethane segments (PUPB) was synthesized in a two-step routine by Li *et al.* [126] (Scheme 14: Route C). Importantly, this method avoids the unnecessary chain extension reaction and the undesirable mixture due to the direct reaction between HTPB and TDI-80. Therefore, this pre-polymer showed a well-controlled macromolecular structure *via* the reaction between an important intermediate, named propargyl(3-isocyanato-4-methylphenyl)carbamate (PTI) and HTPB. Polytriazole elastomers based on PUPB and PTPB were also studied. The elastomer based on PUPB, combined polytriazoles with urethane segments together, and showed improved performance, such as insensitivity to humidity

because of the polytriazoles and enhanced mechanical properties arising from the strongly hydrogen bonded urethane. Compared with the one based on PTPB, its tensile strength had increased from 0.62 to 4.2 MPa, and its elongation at break had increased from 47.0 to 81.5%. After plasticization with dioctyl sebacate, its T_g value can be lowered to -73.7 °C and the elongation at break increased to 293.3%.

Additionally, Dong *et al.* [127] synthesized an azido-terminated polybutadiene (ATPB) *via* a substitution-azidation reaction (Scheme 14: Route D). The cross-linked network based on ATPB as pre-polymer and tripropargylamine as the curing agent was studied in detail in the thesis [128]. However, the rigorous low temperature storage conditions required for ATPB may limit its further application, due to side reactions between the terminal azido groups and the large number of double bonds in HTPB.

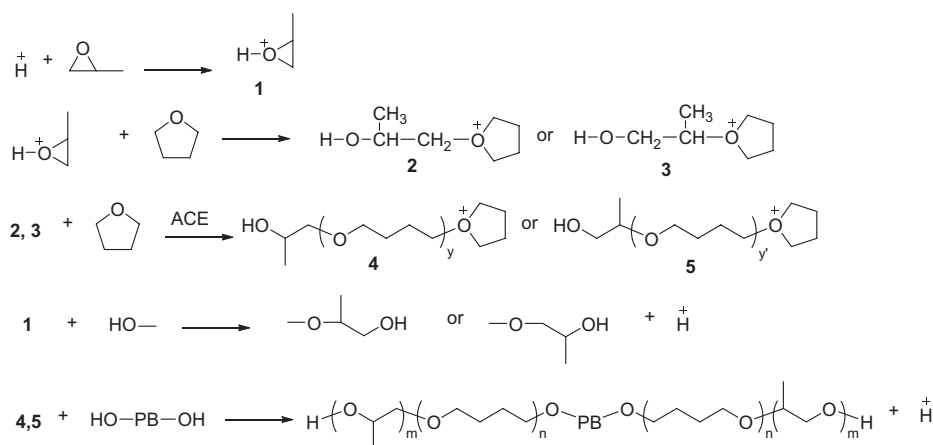
5 Other Modifications

As mentioned above, HTPB with its large number of unsaturated bonds in the backbone exhibits some fascinating chemical and physical properties, such as low temperature flexibility, low surface energy and low viscosity. However, the inert and non-polar backbone of HTPB will also have a negative influence on the mechanical properties of its elastomers due to the lack of interactions between segments. Meanwhile, its immiscible nature with polar components, especially with energetic materials, arises for the same reasons.

Although resolutions for improving the mechanical properties of HTPB are multiple, it is still essential to improve the polar nature of its backbone. Fortunately, binders with a polar backbone, such as polyesters or polyethers [129], retain nitrate ester plasticizers. Therefore, some effort has been made for improving the compatibility by preparing copolymers between HTPB and polyethers or polyesters. Earlier in 1989, Bennett *et al.* [130] prepared polycaprolactone-HTPB block copolymers (PCP-PB) from macro-initiator HTPB and caprolactone (CL) as monomer with stannous octanoate as catalyst. Compared with the T_g of PCP, the T_g value of PCP-PB was -71 °C, close to the T_g value of HTPB. The low T_g ensures that PCP-PB based propellants or explosives have good low temperature mechanical properties, *e.g.* the strain is greater than 300% at -53.8 °C. As expected, the tri-block copolymer also exhibits better compatibility with nitrate esters than the parent HTPB. Furthermore, this block copolymer, a hybrid of PCP and HTPB, can be tailored to provide more optimized characteristics for high energy compositions for particular

purposes, through balancing of the ratio of PCP and PB segments. Its thermal stability increases with increasing amounts of PCP units [131]. Additionally, the thermal decomposition of composite propellants based on PCP or PCP-PB-PCP pre-polymer as a binder was studied by Huang *et al.* [132]. They designed fifteen propellants with different contents of AP and a nitramine (RDX or HMX) as oxidants, aluminum as fuel, bis(2,2-dinitropropyl)acetal/formal (BDNPA/F) as plasticizer and N-100 as curing agent. The detailed research showed that the PCP-PB-PCP based ones were less stable than the PCP based ones.

Polytetrahydrofuran, with a large number of polar ether bonds, has good cryogenic properties and it is also used to prepared copolymers in order to improve mechanical properties. A novel triblock copolymer poly(tetrahydrofuran-*co*-propylene oxide)-*b*-polybutadiene-*b*-poly(tetrahydrofuran-*co*-propylene oxide) [P(THF-*co*-PO)-*b*-PB-*b*-P(THF-*co*-PO)] was reported by Fan *et al.* [133, 134]. P(THF-*co*-PO)-*b*-PB-*b*-P(THF-*co*-PO) was synthesized by covalently attaching copolyether segments onto the terminals of HTPB *via* cationic ring-opening copolymerization of THF and propylene oxide (PO) in the presence of HTPB as a macroinitiator and $\text{BF}_3 \cdot \text{OEt}_2$. In this system, PO acted as a co-monomer and a promoters of THF polymerization. As a result, the synthesized triblock copolymer exhibited excellent cryogenic properties ($T_g = -81.7 \text{ }^\circ\text{C}$), viscosity (lower than HTPB) and thermal stability similar to HTPB. Additionally, the introduction of copolyether segments had a significant effect on the dynamic and static mechanical properties of the elastomers. Compared with the HTPB-TDI based elastomer, this copolymer based elastomer had a lower T_g ($-74.1 \text{ }^\circ\text{C}$ from DSC), higher $\tan\delta$, and higher elongation at break (232%).



Scheme 15. Ring opening copolymerization for HTPB-THF copolymer

The introduction of epoxy functional groups into nonpolar HTPB chains can also improve the polarity of the final polymers. The conventional methods for epoxidizing HTPB mostly use a stoichiometric mixture of peracids, such as *m*-chloroperbenzoic acid (*m*CPBA) [135], peroxyacetic acid [136], and *tert*-butylhydroperoxide, with vanadium(IV) acetyl acetonate as an oxidant [137]. However, these methods usually have many drawbacks, such as several undesired side reactions (*e.g.* degradation, opening of the oxirane ring, further oxidation, gelation at high epoxidation levels), and the stability of the epoxidized HTPB (EHTPB) because of the residual acid and environmental pollution from waste acid disposal. Therefore, epoxidation with a method free of peracid would be very advantageous in view of the chemical technology and synthesis. In 1996, Fan *et al.* [138] reported the epoxidation of HTPB using hydrogen peroxide as the oxidant in the presence of sodium tungstate, *o*-phosphoric acid and quaternary ammonium salts as catalysts. Subsequently, a method based on ammonium tungstate hydrate instead of sodium tungstate with different phase transfer catalysts (PTCs) was investigated in detail by Wang *et al.* [139, 140]. The formation of the active catalyst $Q_3\{PO_4[W(O)_nO_4]_4\}$ is responsible for the epoxidation. Particular single factor tests and kinetic studies showed that this system hinted at a mild and selective epoxidation of the three configurations of double bonds in HTPB and the reactivity towards epoxidation decreased in the following order: 1,4-*cis* > 1,4-*trans* > 1,2-*vinyl*. Additionally, Alavi Nikje *et al.* [141-146] extensively studied the process of HTPB to EHTPB conversion by employing *in situ*-generated dimethyldioxirane (DMD) as the active oxidant and different transition metal oxide/salt complexes as catalysts with/without PTC at room temperature. The *in situ*-generated DMDs in this system are cyclic peroxides known as powerful, reactive and efficient oxidizing agents, which are usually prepared from the reaction of acetone and aqueous Oxone[®] (2KHSO₅, KHSO₄, K₂SO₄). These systems show chemoselectivity for the double bonds in comparison with the hydroxyl groups towards oxidation, as well as no formation of side-products. Generally, the polyurethane based on EHTPB will exhibit a significantly improved tensile strength and a rapidly decreased elongation with increasing epoxide content [147-149]. However, according to Jie *et al.* [150] well-tailored EHTPBs with high *cis*-1,4 content (>95%) may be prepared based on the selective oxidolysis process starting from butadiene rubber, which show low glass transition temperatures ($T_g < -90$ °C). The mechanical properties of PUs based on this high *cis*-HTPB by the same method are better, possessing 4.34 MPa of tensile strength, 3.56 MPa of Young's modulus and 649 ±46% of elongation at break. Additionally, its T_g can be about 25 °C lower than the PU based on the free-radical polymerized HTPB (FHTPB).

Therefore, we can expect that the PU based on high *cis*-1,4 content EHTPB reported Jie *et al.* [150] will possess better mechanical properties than traditional EHTPB. Disappointedly, there has been no specific research on EHTPB used as a binder in the propellant field. However, Fu *et al.* [151] gave a possible prospect for EHTPB use with particular formulations for different applications in propellants.

As with general unsaturated materials, some irreversible chemical reactions, such as oxidation, may occur at the double bonds of HTPB, which not only affects its ageing characteristics but also has a further effect on the mechanical properties and combustion stability of the propellant. In addition to the introduction of inhibitors, it is also feasible to control the double bond content in HTPB in order to improve the thermal and ageing stability. Theoretically, hydrogenated hydroxyl-terminated polybutadiene (HHTPB) is likely to be stiffer than HTPB because the activation energy for rotation about an sp^3 - sp^3 C-C single bond is higher (3 kcal/mol) than an sp^2 - sp^2 C-C single bond. Improved mechanical properties, such as tensile strength, can also be realized through hydrogenation. Early in 1953, the hydrogenation of non-functionalized polybutadiene and its copolymers was studied by Jones *et al.* [152]. The investigations revealed that the hydrogenated polybutadiene and its copolymers exhibited excellent low temperature properties. Furthermore, when the unsaturation values of the resultant polymers were lower than 50%, the parent polymers changed to become a class of thermoplastics with outstanding freeze points, oil resistance and tensile strength. While nearly all hydrogenated linear polybutadienes with high fractions of *trans*- and *cis*-microstructures would form inelastic polybutadiene, even at room temperature, the almost fully hydrogenated hydroxyl terminated polybutadiene (1,2-HHTPB) [153] with a high vinyl group content showed better fluidity, processability and lower T_g because of the pendant vinyl groups from every monomer. Scariah *et al.* [154] studied the thermal degradation of HHTPB and its copolyurethanes with varying compositions of HHTPB. HHTPB decomposes by a two stages mechanism. The initial stage involves the cleavage of pendant ethyl groups followed by cyclization reactions and the main second stage involves further degradation of the cyclized products, with an activation energy of $216 \pm 6 \text{ kJ}\cdot\text{mol}^{-1}$. The HHTPB-HTPB based copolyurethanes decompose in a two stage decomposition. The first stage may be attributed to a combination of the initial stage losses of HTPB and HHTPB and the loss of TDI, since the urethane linkages undergo reversible cleavage at high temperature to give the alcohol and isocyanate base. The main second stage may decompose by two different mechanisms related to the formation of butadiene (PB). The mechanical properties of copolyurethanes with different

HHTPB contents was investigated by Sekkar *et al.* [155] The results showed that the addition of HHTPB to HTPB generally increased its ultimate tensile strength, modulus and hardness, with a marginal decline in the elongation values. Specifically, compared with the HTPB based polyurethane, the tensile strength and modulus of the one based on 25% HHTPB can increase from 5.8 to 10.8 ksc and 2.8 to 7.4 ksc, respectively, with an elongation decrease from 345% to an acceptable level of 200%. The CSPs based on copolyurethanes containing HHTPB and HTPB were also investigated. The tensile strength and modulus both increase with the HHTPB content in the binder. Whilst the elongation, hardness and BR are relatively less affected.

6 Conclusions

The effects of chemical modification of HTPB on energy, burning rate, curing methodology and other characteristics have been summarized in this review. The general methods contain two parts: one concerns changes to the main chain structure *via* copolymerization, azidation or nitration, and the other concerns modification of the terminal atoms or functional groups *via* coupling or substitution. Consequently, the resulting modifications exhibit some special properties compared with pure HTPB, and there are also some star products for further scale-production and research such as NHTPB-1 and Butacene[®]. With regard to cure methodology, this still needs further study before its further application, because of the excellent mechanical properties and more mature systems of polyurethanes.

Since there is no absolute advantage for the modified systems compared to that of HTPB, few of them may be able to entirely replace the use of HTPB in propellants. Although most of the modified HTPBs have special improvements in some properties, defects still exist:

- a) Some unique merits of HTPB itself have been lost along with changes to the main chain structure. Therefore, modification of HTPB needs to be designed carefully.
- b) The method for the introduction of azido groups onto HTPB is not mild enough, because of the possible side reactions between azido groups and double bonds influencing the preparation and storage of modified-HTPBs with azido groups.
- c) There is also a lack of modifying groups for modification and effective reactions for the synthesis or curing mechanisms.
- d) Many studies are limited to the laboratory-scale without further detailed

investigation for the manufacture of propellants.

Research on the modified cure methodology based on the click reaction, especially the Huisgen 1,3-dipolar cycloaddition, will ensure a much milder, convenient and feasible strategy for further applications in propellants or explosives in the future. Furthermore, if the urethane group (–NHCOO–) can be ingeniously introduced into this system, PUs based on modified HTPBs will not only possess an appropriate and facile processability for manufacture but will also exhibit improved and satisfactory mechanical properties for applications. Meanwhile, the improved PUs can also realize higher energy formulations in order to meet the needs in the field of propellants and explosives. Of course, more innovative modifiers will still be required for investigation and application in propellants or explosives in the future, due to the merits of HTPB, including excellent mechanical properties, being more feasible and easy to modify than other binders that can be obtained, but have few practical applications.

Acknowledgement

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