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Review / Praca przeglądowa

Development of new energetic polymers – analysis of potentially useful systems and the viability of their production

Opracowanie nowych polimerów wysokoenergetycznych – analiza potencjalnie korzystnych układów i możliwości ich otrzymywania

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Abstract: *The paper briefly presents the subject of energetic polymers and their application in energetic material formulations. Individual groups of energetic polymers are discussed and the latest literature reports are summarized. Based on the analysis of potential chemical structures and synthesis paths, chemical reactions which will be useful in obtaining new energetic polymers, have been selected.*

Streszczenie: *W pracy przedstawiono pokrótce problematykę polimerów wysokoenergetycznych i ich zastosowania w formulacjach materiałów wysokoenergetycznych. Omówiono poszczególne grupy polimerów wysokoenergetycznych i podsumowano najnowsze doniesienia literaturowe. W oparciu o analizę potencjalnych struktur chemicznych i ścieżek syntezy, wytypowano reakcje chemiczne, których wykorzystanie będzie użyteczne dla otrzymywania nowych polimerów wysokoenergetycznych.*

Keywords: *binder, energetic polymer, synthesis*
Słowa kluczowe: *lepiszcze, polimer wysokoenergetyczny, synteza*

1. Introduction

Polymers have found an extremely broad and large volume of application (approx. 368 mln tons in 2019), be they synthetic or natural [1, 2]. This success is due to the broad range of their properties, most of which can be readily adjusted through repeat unit modification or copolymerisation. This tailoring of properties determines the specific field in which a polymer can be applied. These applications can be as broad as packaging, textiles or construction materials, or as specialised as biomedical implants, drug delivery systems or flexible electronics [1, 3].

Literature reports show that only a single polymer, i.e. cellulose nitrate (commonly referred to as "nitrocellulose") is known to be able to sustain detonation. [4] Consequently, in the field of energetic materials (EMs), polymers are used as binders for the reactive species, which are typically low-molecular solid substances (e.g. 1,3,5-trinitro-1,3,5-triazinane (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX), 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20)) [5, 6]. This function translates to the desirability of such properties as high adhesion to various types of materials, high cohesion, low susceptibility to chemical agents, low reactivity, high thermal stability and low glass transition temperature. Depending on the specific type of EM formulation, other properties may be desirable, such as high elasticity in the case of polymer-bonded explosive (PBX) formulations or the ability to undergo curing in the case of composite propellants [7, 8].

Regardless of the type of EM formulation that a binder is used in, during an energetic event (deflagration or detonation), the polymer acts as a fuel (primary or auxiliary) and undergoes oxidation, primarily yielding gaseous decomposition products. Depending on the chemical composition of the polymer, these may be limited to carbon oxides and water, but commonly also include nitrogen and as well as other chemical species (e.g. SiO_2 in the case of polysiloxane binders) [9]. The chemical composition of the polymer determines both its oxygen balance (strongly negative for traditional polymers) and its heat of combustion (Table 1).

Table 1. Selected polymers used as binders in energetic materials: chemical composition, oxygen balance, and heat of combustion

Polymer binder	Representative chemical formula	Main decomposition products	Oxygen balance [%]	Heat of combustion [kJ/g]
Hydroxyl-terminated polybutadiene (HTPB)	$(C_4H_6)_n$ with terminal –OH groups	CO, CO_2, H_2O	–77.9	43-45
Polybutadiene acrylonitrile (PBAN)	$(C_4H_6–C_3H_3N)_n$	CO, CO_2, H_2O, N_2	approx. –60	32-36
Glycidyl azide polymer (GAP)	$(C_4H_6N_8O_2)_n$	CO, N_2, H_2O, HCN	–10 to –20	25-28
Polysiloxane	$(R_2SiO)_n$	CO, CO_2, H_2O, SiO_2	Strongly negative	18-22
Polyurethane (from HTPB + Isocyanate)	Crosslinked C, H, N, O network	CO, CO_2, H_2O, traces of NO_x	–55 to –65	25-35
Nitrocellulose	$(C_6H_7(NO_2)_3O_5)_n$	CO, CO_2, H_2O, NO_x	–25 to –30	17-20

In terms of the choice of binders for EM formulations, classic polymers, such as hydroxyl-terminated polybutadiene (HTPB) [10], fluoropolymers [11], polyurethanes [12] and the aforementioned polysiloxanes, have found significant application. Currently, however, research efforts are focused on a relatively new class of polymers, referred to as "energetic". These energetic polymers, while unable to sustain detonation by themselves, typically involve lower carbon content (in favour of increased nitrogen and oxygen content) than the abovementioned, traditional binders.

The most important advantage of this change stems from the increased (less negative than for traditional binders) oxygen balance values, which translates into decreased oxidising agent consumption. The ability to reduce the amount of utilised oxidising agent not only allows it to be replaced with substances increasing the performance of the EM formulation, but also allows an increase in the amount of energy available for the energetic event (due to oxidising agents typically exhibiting endoenergetic decomposition). The choice of energetic binder is not limited to the above, but also influences a broad set of properties, specific to

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the developed EM formulation, such as mechanical strength, thermal stability, crystal–binder adhesion, resistance to void formation during ageing, and sensitivity to impact and shock [13, 14].

The energetic polymers used as binders for EMs include such substances as cellulose nitrate, glycidyl azide polymer (GAP), poly(glycidyl nitrate) (polyGLYN), poly(3-nitratomethyl-3-methyloxetane) (polyNIMMO), polyvinyl nitrate (PVN), and novel printable energetic polymers like vinylimidazolium chlorates(VII). These polymers are designed to enhance the performance characteristics of EM formulations by contributing additional energy and improving mechanical properties [15-17].

Despite the multiple classes of energetic binders and even more numerous materials within them, as well as the favourable properties of those materials, the replacement of traditional binders with energetic polymers is at an early stage, with most applications relying on traditional systems. The main reasons for this appear to be the comparatively high unit costs and highly limited availability of energetic polymers compared to traditional polymer binders. In light of the above, in this work, an extensive analysis of new energetic polymers that are expected to exhibit properties favourable for application in EM formulations, was conducted as well as potential pathways for cost-efficient synthesis of those macromolecules.

2. Summary of reported energetic polymer structures

The primary approach to designing energetic polymers is to introduce explosophoric groups e.g. nitro or azido functionalities, into the hydrocarbon backbone of traditional polymers [18]. This can be achieved either via synthesis of an energetic monomer and its subsequent polymerisation or through the chemical modification of a polymer (Figure 1).

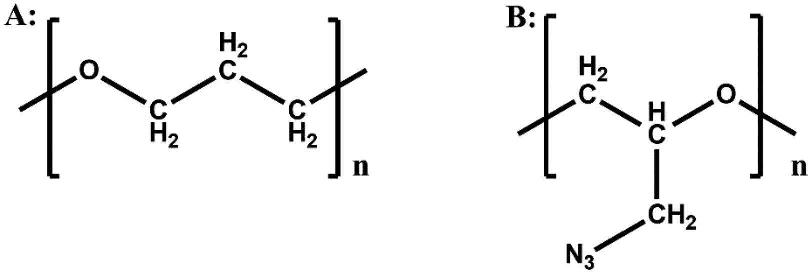

Figure 1. Structure comparison of an unsubstituted polyoxetane (A) and GAP (B)

Where the former approach typically yields well-defined energetic polymers, the latter often produces copolymers, due to the reactions used for modifying the polymer taking place with a < 100% yield. A prime example of this is the synthesis of GAP from polyepichlorohydrin via the azidation reaction, where only part of the chloride functionalities are replaced by azido groups, unless long reaction times are employed [19]. The reason for the use of this approach originates from the fact that for many promising energetic monomers, it is difficult to induce polymerization, as has been the case for glycidyl azide [20].

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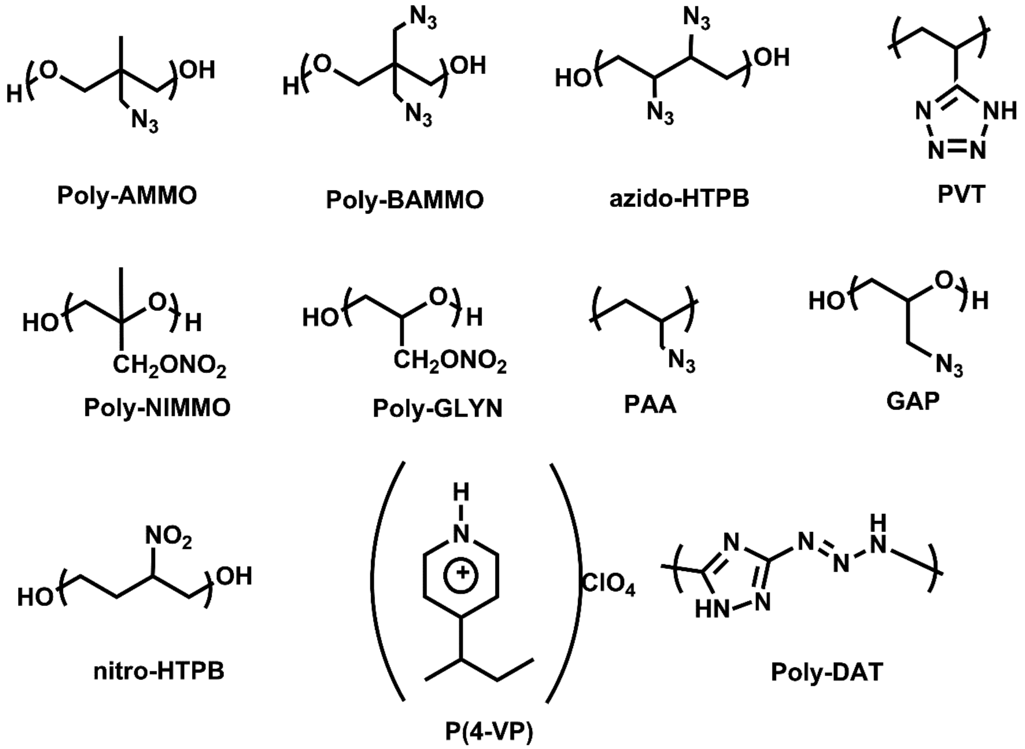

Figure 2. Sample structure of known energetic polymers

The energetic polymers reported in literature can be organised into several groups, following traditional polymer division schemes. These groups include: polyethers (polyoxetanes and polyoxiranes), polyolefins (polybutadienes and vinyl polymers) and polysaccharides (esp. cellulose nitrate).

2.1. Energetic polyethers and recent progress in the field

Currently, research on energetic polyethers focuses on polyoxetanes, produced via the ring opening polymerisaiton of oxetanes equipped with various functionalities (Table 2).

Table 2. Oxetane-based energetic monomers and their abbreviations [21]

Abbreviation	Full chemical name
AMMO	3-Azidomethyl-3-methyloxetane
AMNMO	3-Azidomethyl-3-nitratomethyloxetane
BAMO	3,3-Bis(azidomethyl)oxetane
MNAMMO	3-Nitraminomethyl-3-methyloxetane
NIMMO	3-Nitratomethyl-3-methyloxetane
PAMCMO	Poly(3-azidomethyl-3-cyanoethoxymethyloxetane)
PAMMO	Poly(3-azidomethyl-3-methyloxetane)
PAMNMO	Poly(3-azidomethyl-3-nitratomethyloxetane)
PBAMO	Poly(3,3-bis(azidomethyl)oxetane)
PNIMMO	Poly(3-nitratomethyl-3-methyloxetane)

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The methods for producing homopolymers of energetic oxetanes have already been well-investigated and were the subject of multiple review articles. Consequently, current research has moved on to the fine-tuning of the properties of energetic polyoxetane binders, primarily through the synthesis of their copolymers with other polymer systems [22].

An interesting development in this regard is the use of click chemistry methods to produce well-defined polyoxetane copolymers [23]. In this case, alternating copolymers of BAMO (repeat units acting as hard segments) and one of five diols (acting as soft segments) were obtained via end-functionalisation of poly(BAMO) with tosylate groups and treating them with alkoxides obtained from these diols. The diols used in the work were both small molecules and polymers, i.e. diethylene glycol (DEG), triethylene glycol (TEG), 1,4-butanediol (BDO), pol(ethylene glycol) (M_W = 200 g/mol) and polytetrahydrofuran (M_N = 250 g/mol). Based on the choice of diol and the synthesis conditions of poly(BAMO), it was shown that the properties of the resultant copolymers could be controlled to a significant extent, as exemplified by the range of achieved glass transition temperatures, i.e. –47.5 to 63.3 °C. This click chemistry approach was also applied to the synthesis of AMMO copolymers, showing that the method can be considered universal to the preparation of well-defined polyoxetanes [24].

Copolymers of BAMO and THF [25] have also been applied to composite propellants containing ammonium chlorate(VII), aluminium and HMX. Not only was relatively high density (1.79 g/cm^3) reported, but the stress relaxation of these propellants and influence of the use of chain extenders on their low-temperature performance was detailed.

The choice of co-monomers for energetic oxetanes does not have to be limited to diols, as shown by the reported copolymers of BAMO and GAP [26]. The copolymers not only exhibited favourable properties but were also found to offer high compatibility with commonly used EMs, such as RDX, HMX and CL-20.

The copolymers may also be produced traditionally, i.e. via treating multiple hydroxyl-terminated polyethers with a multifunctional isocyanate curing agent [27]. In this case, a GAP oligomer fraction was used as one co-monomer, which was used either to produce reference homopolymers or was cured alongside one of three energetic oxetane oligomers (MNAMMO, AMMO, BAMO). Interestingly, both homopolymers and all copolymers showed similar glass transition temperatures (–20.4 to –30.1 °C, with both extremes being recorded for GAP homopolymers) with the exception of the copolymer with MNAMMO (–6.0 °C). All investigated samples were reported to show a high degree of phase mixing, signifying favourable adhesion properties, making them potentially interesting binders for EM formulations.

Although polyoxetanes and GAP are the most commonly researched energetic polyethers, the class is not limited to those two building blocks, as shown by the recently reported energetic polymer originating from a dioxolane ring [28]. The reported advantages of this new system are: maintaining a nitrogen content comparable to poly(AMMO) (32.6% vs 33.1%), while achieving an increased oxygen content (24.8% vs 12.6%); removing the non-energetic methyl group present in AMMO; being prepared via a more efficient and less complex synthetic route than poly(AMMO). Although this new polyether is also reported to exhibit favourable thermal and mechanical properties, it is yet to be tested for compatibility with common EMs or investigated as a binder for any EM formulation.

2.2. Energetic polyolefins and recent progress in the field

Interestingly, polyvinyltetrazoles, one of the earliest reported groups of energetic polyolefins were not initially perceived as such, merely as general polymeric binders for composite propellants and other EM formulations [29]. Although this class of polymers has long since been taken up by other applications (e.g. use in solid electrolytes) [30], the use of tetrazole moieties in energetic polymers remains a current trend [31], giving rise to e.g. tetrazole-substituted polybutadienes. Although azole-substituted HTPBs have been shown to exhibit interesting material properties, as of now they appear not to have been tested as binders, despite the claims contained in the cited work.

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Poly(allyl azide) is another, more recently reported example of energetic polyolefins [32]. An interesting feature of this polymer is its ability to produce intra- and inter-molecular crosslinks via decomposition to polymeric imine and reactions between the formed imine groups.

3. Prospective chemical reactions for the synthesis of energetic polymers

3.1. Hydrosilylation and its application in the synthesis of organosilicon polymers

In the mid-1950s, specifically in 1957, John L. Speier discovered hexachloroplatinic acid, which proved to be a highly efficient precursor for platinum catalysts. This discovery marked a significant breakthrough in the industrial synthesis of organosilicon compounds and organic silicon derivatives. The hydrosilylation reaction itself was first described by Leo Sommer in 1947, who conducted the addition of trichlorosilane to 1-octene, catalysed by acetyl peroxide.

Growing interest in hydrosilylation subsequently led the Polish researcher, Professor Bogdan Marciniec, to publish the *Comprehensive Handbook on Hydrosilylation* in 1992. In this work, he substantially extended the scope of hydrosilylation reactions to include a broad range of unsaturated substrates and highlighted its potential applications not only in special materials chemistry but also in organic synthesis.

In general, the hydrosilylation reaction involves the addition of inorganic or organic silicon hydrides to carbon–carbon multiple bonds, carbon–heteroatom bonds, and heteroatom–heteroatom bonds, resulting in the formation of carbon–silicon bonds. Owing to its high industrial relevance, hydrosilylation is widely applied in the synthesis of silanes and the functionalization of polysiloxanes.

Hydrosilylative polymerization is a catalytic hydrosilylation reaction involving bifunctional organosilicon monomers containing silicon–hydrogen bonds, alkenyl groups, or alkynyl bonds. This process yields both saturated and unsaturated organosilicon polymers featuring carbon–silicon bonds within their structures. There are two principal approaches for obtaining polymers with carbon–silicon bonds in the backbone. The first involves intermolecular hydrosilylative polymerization of alkenyl hydrosilanes, while the second is based on the polyhydrosilylation of dienes or α,ω-dienes using dihydro-substituted organosilicon compounds.

Anti-Markovnikov addition of silanes to alkenes and alkynes offers numerous opportunities for the synthesis of polymeric materials with high efficiency and stereoselectivity. The industrial application of this reaction primarily involves the synthesis of functional siloxanes and silanes. In general, most industrial hydrosilylation processes are carried out in the presence of Speier's or Karstedt's catalysts, due to their high activity and selectivity. Furthermore, the use of these platinum-based catalysts determines the proposed reaction mechanism of hydrosilylation, as described earlier by the Chalk-Harrod mechanism and its modifications (Figure 3) [33].

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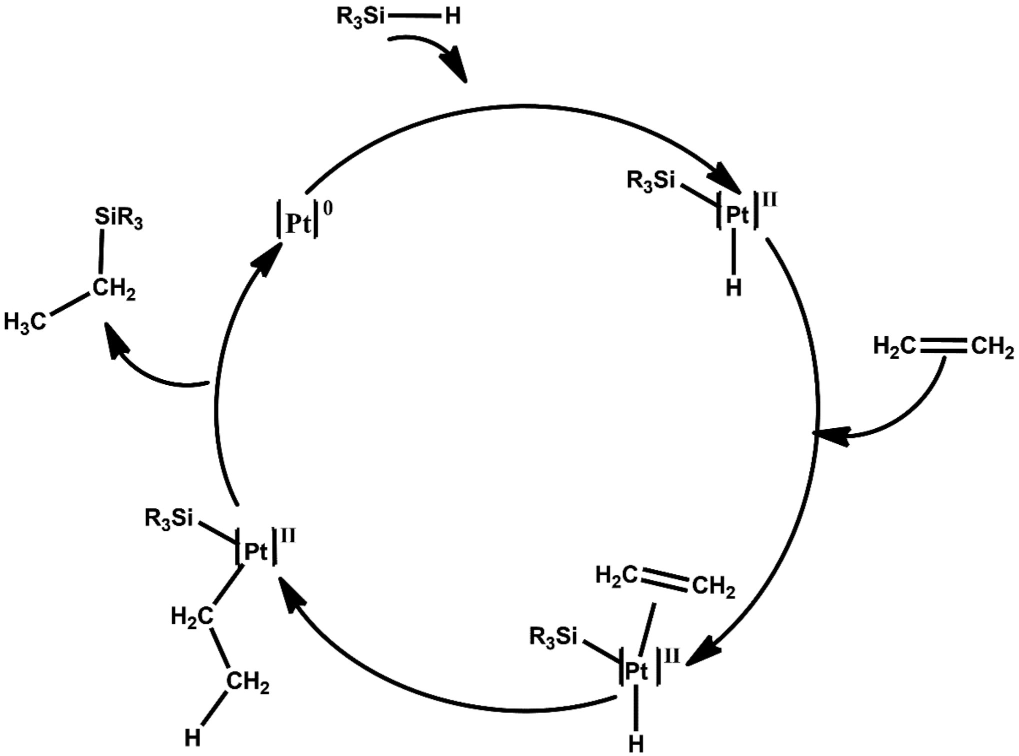

Figure 3. Chalk-Harrod mechanism for hydrosilylation reaction [33]

This reaction enables large-scale production of various materials, including medical coatings [34]; antifouling coatings, such as those obtained by hydrosilylation grafting of allylcarboxy-betaine onto polydimethylsiloxane, catalysed by Karstedt's elastomeric complex [35]; and functionalized packaging materials for electronic applications. In microelectronics, epoxy-silicone resins, which do not yellow under UV exposure, are used as electronic sealants and LED encapsulants [36]. Hydrosilylation also allows for the fabrication of hybrid organic–inorganic semiconductors [37].

Additionally, anti-graffiti films can be produced by introducing poly(methylhydrosiloxane) grafted with hexafluorobutyl acrylate into polyurethane matrices [38]. Superhydrophobic and highly transparent coatings can also be prepared via hydrosilylation, making them suitable for automotive glass and related applications [39]. Overall, hydrosilylation provides versatile synthetic routes to functional organosilicon substrates, which explains the broad applicability of this reaction. As a result, the polymeric materials obtained through hydrosilylation are employed extensively in the coatings industry as well as in electronics.

3.2. Huisgen cycloaddition and applications of 1,2,3-triazole derivatives

The azide–alkyne Huisgen cycloaddition (Figure 4) was first reported in 1961 by Rolf Huisgen. It is a 1,3-dipolar cycloaddition between an azide and either an internal or terminal alkyne, resulting in the formation of a 1,2,3-triazole [40]. This reaction can proceed thermally or be catalysed by ruthenium or copper complexes and is widely applied in organic chemistry. Copper-catalysed cycloaddition reactions are often classified as "click" reactions, whereas the classical 1,3-dipolar cycloaddition cannot be strictly defined as such due to the formation of regioisomeric mixtures when asymmetric alkynes are employed as substrates.

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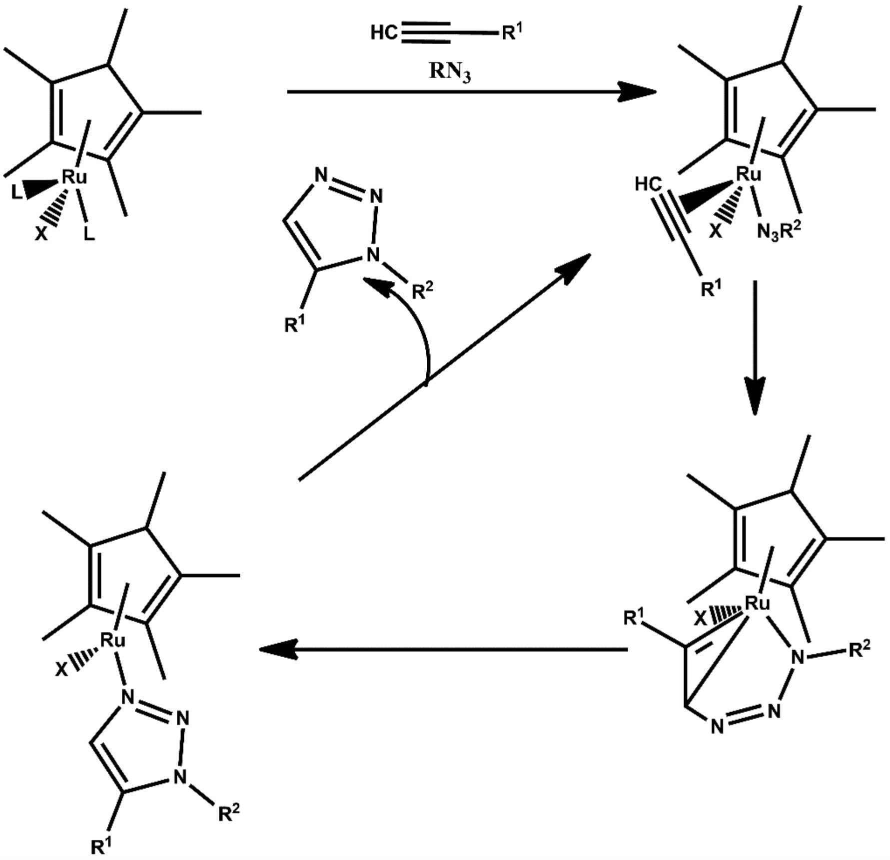

Figure 4. Huisgen reaction mechanism based on ruthenium catalyst

The reaction can be conducted at elevated temperatures, as both alkynes and azides are kinetically stable under such conditions. However, both thermal and catalytic approaches have certain limitations. The thermal method, as noted, leads to regioisomeric mixtures and requires high reaction temperatures. On the other hand, the catalytic method cannot be applied in the synthesis of biological compounds due to the presence of transition metals, which are unsuitable for the preparation of polysaccharides or oligonucleotides.

Recent studies on Huisgen cycloaddition have focused on developing metal-free approaches [41]. In 2010, Fokin's group reported a transition metal-free reaction involving the treatment of aryl azides with terminal alkynes at room temperature in the presence of catalytic amounts of hydroxide. This triazole synthesis method proved to be straightforward, with the additional advantage of being insensitive to moisture and oxygen [42].

The feasibility of this reaction is governed by the interaction of the participating highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), which depend on the relative orbital energies of the dipolarophile and the dipole. The interaction of the dipolarophile's LUMO with the dipole's HOMO is favoured by electron-withdrawing groups on the dipolarophile, whereas electron-donating groups on the dipolarophile promote the opposite interaction [43]. The reaction is highly exothermic and possesses a high activation barrier, which accounts for its relatively slow progress, even at elevated temperatures [44].

The products of the reaction 1,2,3-triazoles constitute an exceptionally interesting class of heterocyclic compounds with a wide range of applications. These compounds exhibit various biological properties,

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including antiviral, anticancer, antibacterial, and antitubercular activities. The triazole ring serves as a rigid linker in biologically relevant polymers due to its resistance to hydrolysis and metabolic degradation pathways [45, 46]. Additionally, 1,2,3-triazoles are employed in the production of mineral fertilizers, agrochemicals, dyes, photostabilizers, and corrosion inhibitors [47, 48].

The use of copper catalysts enables the synthesis of nucleotide analogues in nucleoside chemistry, allowing modifications within the nucleobase, the sugar moiety, as well as the preparation of bioconjugates [49]. The Huisgen cycloaddition can also be applied to the modification of glycidyl azide polymers. In this modification reaction, the azide groups of the polymer react with alkynes to form triazole moieties [50].

3.3. Ring-opening polymerization (ROP) and its applications

The first publications concerning ring-opening polymerization (ROP) appeared at the beginning of the 20th century; however, the mechanism and thermodynamics of the process were not described until 1950. That publication included estimated changes in enthalpy, free energy, and entropy calculated for the polymerization of unsubstituted liquid cycloparaffins and their methyl derivatives [51]. In 1977, the first report on the synthesis of high-molecular-weight polymers via ring-opening polymerization was published, with poly(2-hydro-2-oxo-1,3,2-dioxaphosphorinan) being the first polymer obtained by this method [52]. A year later, a study on the polymerization of cyclic phosphate esters was published [53].

According to the IUPAC definition, ring-opening polymerization is a type of polymerization in which “a cyclic monomer yields a monomeric unit that is acyclic or contains fewer rings than the monomer”; furthermore, “if the monomer is polycyclic, opening of a single ring is sufficient for the reaction to be classified as ring-opening polymerization” [54]. This process involves the reaction of unsaturated monomer molecules with polymer chains containing an active centre, leading to the growth of the macromolecular chain [55].

The driving force behind the ring-opening of cyclic monomers is the steric repulsion between atoms within the ring or the release of ring strain between bonds. According to thermodynamic principles, the enthalpy change for the ROP reaction is negative, similar to other types of polymerizations. An initiator is required to start the polymerization, which in most cases proceeds via a chain-growth mechanism. During the reaction, monomers sequentially add to the cationic or anionic active centres (Figure 5). However, ring-opening polymerization can also proceed via coordination or radical polymerization mechanisms. The exact ROP mechanism depends on the type of monomer, initiator, and the polymerization conditions used [55]. Moreover, ring-opening polymerization enables the synthesis of polymers which are difficult to prepare by other polymerization methods.

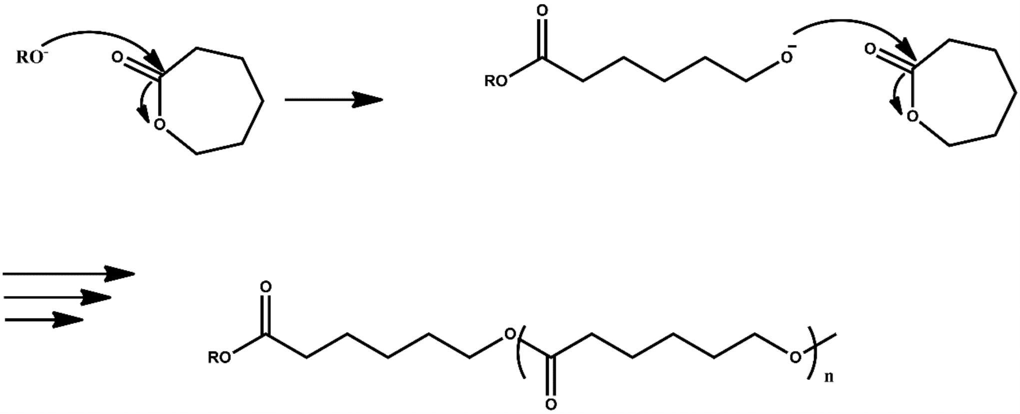

Figure 5. ROP mechanism based on anionic polymerization

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ROP leads to the synthesis of polymers with technologically significant properties which can be specifically tailored and controlled. Additionally, this method allows for the synthesis of polymers that occur naturally, as well as for the optimization of polymers used in medicine, pharmaceuticals and agriculture.

ROP enables the production of numerous polymers of industrial importance. Among these are polynorbornene, polyethylene oxide, polysiloxane, polyphosphazene, and polyethyleneimines obtained via cationic polymerization of aziridine or oxazoline. However, the most industrially significant polymers obtained through ring-opening polymerization are polyoxymethylene, synthesized from trioxane and diols, and nylon-6, produced via the anionic ring-opening polymerization of ε-caprolactam [56].

3.4. Suzuki cross-coupling reaction and its applications

In 1979, a publication appeared describing cross-coupling catalysed by a palladium complex. The reaction, in which a carbon–carbon bond is formed through the reaction of a boronic acid with an organic chloride in the presence of a palladium catalyst, was developed by Akira Suzuki, recipient of the 2010 Nobel Prize in Chemistry. The Nobel Prize was awarded jointly to three scientists for their work on “palladium-catalysed cross-couplings in organic synthesis” [57].

A deeper understanding of the reaction mechanism (Figure 6) and the broad possibilities offered by cross-coupling reactions have enabled the application of the Suzuki reaction in the synthesis of styrene’s, polyolefins and substituted biphenyls.

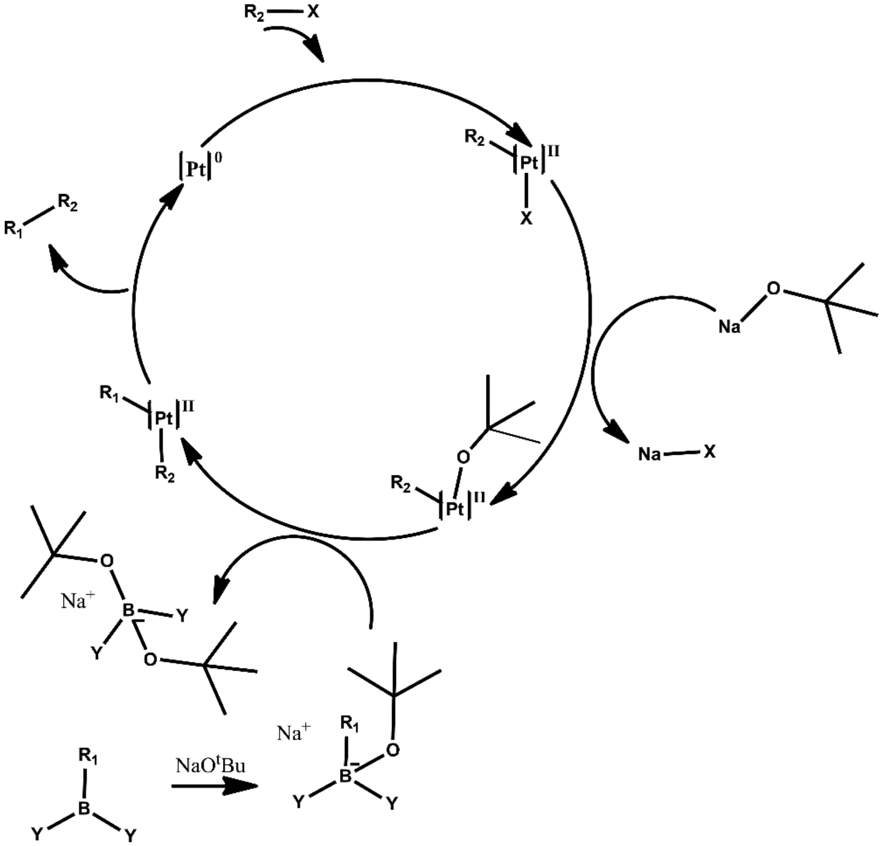

Figure 6. Suzuki mechanism

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The Suzuki coupling reaction is widely utilized due to the fact that the reagents used are relatively inexpensive, easy to store and exhibit low toxicity. With the expansion of the range of applicable reagents, the discovery of alternatives to the original substrates and the development of new catalysts, this reaction has found broad industrial application (Figure 7). In the pharmaceutical industry, the Suzuki coupling reaction is employed in the production of various chemical intermediates, biologically active compounds and pharmaceuticals [58]. Another important application of the reaction is in the synthesis of liquid crystals for electronic applications. When using bifunctional substrates, the reaction allows for the synthesis of oligomers and polymers for specialized applications [59]. Furthermore, the Suzuki polycondensation method enables the preparation of polymers with specific optical and electronic properties. Well-defined alternating copolymers obtained through this approach can be employed in solar cells [60].

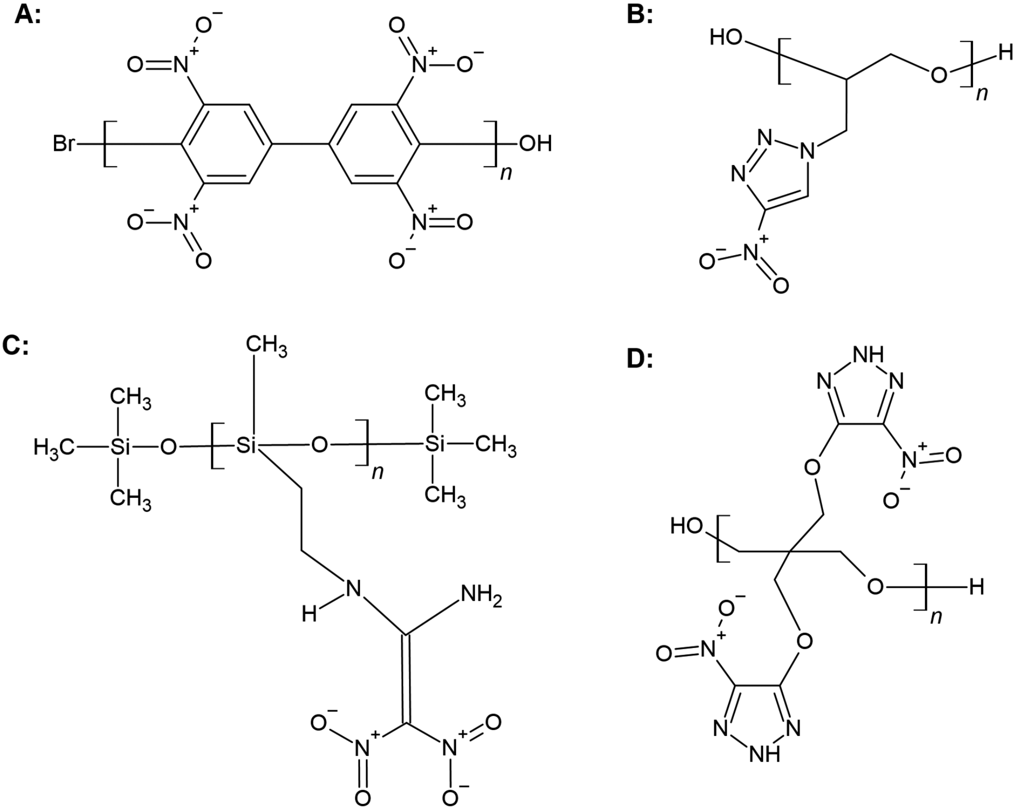

Figure 7. Sample structures of future high-energy polymers to be obtained via: Suzuki coupling reaction (A), Huisgen reaction (B), hydrosylilation (C), ROP (D)

3.5. Limitations of the reactions

One of the major limitations of hydrosilylation reaction is steric hindrance, which can prevent grafting of the high-energy monomers to the polysiloxane backbone. The Suzuki reaction is typically carried out in a biphasic system, which requires that the monomers used are soluble in organic solvents which do not mix with water. In the case of ROP, the reaction is limited to a specific group of monomers whose cyclic structures exhibit significant ring strain. This excludes many five- and six-membered rings, which are common among potential high-energy polymer precursors. Moreover, ROP can lead to undesired

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side reactions, such as cyclization or degradation. All of these reactions require the use of catalysts to ensure selectivity and to allow the reactions to proceed under milder conditions. However, removal of the catalyst after the reaction can be challenging and may necessitate additional purification steps, complicating the overall process. Additionally, each of the discussed reactions requires the presence of specific functional groups which can undergo the desired transformation. Monomers bearing the necessary functional groups for the synthesis of high-energy polymers may not be commercially available, which introduces the need for additional synthetic steps.

4. Summary and conclusions

- ♦ The synthesis methods proposed in this study are well-established and thoroughly characterized in the field of organic chemistry, with their reaction mechanisms comprehensively described in the literature. This mechanistic insight enables a rational modification of known energetic compounds by introducing appropriate functional groups, thereby expanding their applicability in synthetic pathways aimed at the development of novel energetic materials, including energetic polymers. As an example, picric acid, due to the presence of a reactive hydroxyl group, can undergo a variety of functionalization reactions, such as bromination, which serve as a basis for further structural modifications ultimately leading to polymer formation with tailored energetic properties.
- ♦ The key limitation for development in the subject lies in the trade-off between steric hindrance and atomic composition, that is, the energetic moieties (e.g. nitro groups) are rather voluminous and can limit the availability of active sites for binding to the polymer chain. This is typically alleviated through the use of linking groups, which in turn are primarily hydrocarbon in nature, contributing to the lowering of the oxygen balance and nitrogen content of the system. Consequently, there is significant breakthrough potential in the development of sterically-minimised energetic moieties which can be included in the structure of polymers, particularly via the reaction pathways discussed in this work.
- ♦ Replacing traditional polymer binders with energetic polymers is also reliant on their comparative cost effectiveness. As such, the choice of reagents and reaction pathways becomes crucial to obtaining a high-performing energetic polymer at sufficiently low unit cost to compete with traditional polymers.

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