1 Polymers as Binders and Plasticizers – Historical Perspective

Ever since the introduction of nitrocellulose (NC) as an explosive fill in the 1850s, polymers have contributed considerably to advancements in the technology of both propellants and explosives. In addition to the specific instance of the use of NC polymer in explosive fills, applications of polymers have been most extensive in binders and plasticizers. Over the years, with the maturity of composite propellant and polymer bonded explosive technology, diverse classes of polymers have been developed for binder applications, in order to meet the dual objectives of insensitivity and high performance. This chapter focuses on the historical development of polymers for propellant and explosive formulations, particularly as binders and plasticizers.

1.1 Nitrocellulose

Nitrocellulose (NC) (Figure 1.1), a nitrated carbohydrate, was the first polymer to be used in energetic material formulations, particularly in smokeless propellants. NC was discovered by Christian Friedrich Schönbein in Basel and Rudolf Christian Bottger in Frankfurt-am-Main around 1845–1847 [1]. Henri Braconnot and Theophile Jules Pelouze had unknowingly prepared NC in 1833 and 1838, respectively, in France. They named these combustible materials

![Chemical structure of nitrocellulose](attachment:chemical_structure_of_nitrocellulose.png)

**Figure 1.1** Chemical structure of nitrocellulose.
xyloidine and nitramidine. The announcements from Schonbein and Bottger in 1846 that NC had been prepared, meant that their names have since been associated with the discovery and utilization of NC. Schonbein’s process became known through the publication of an English patent to John Taylor British Patent 11407, (1846). NC was prepared by immersing cotton in a 1 : 3 mixture of nitric and sulfuric acids, which was washed in a large amount of water to remove the free acids, and then pressed to remove as much water as possible. However, NC produced by Schonbein’s process was unstable, due to the rapid decomposition of the material, which was promoted by the free acid generated during the process. In 1865, Sir Frederick Abel’s patent British Patent 1102, (1865). On improvements to the preparation and treatment of NC demonstrated that a pulping process could greatly increase the stability of the NC. Pulping breaks up the long fiber into shorter pieces so that the remaining acids can then be easily washed out of it. In 1868, Abel’s assistant, E.A. Brown, demonstrated the first application of NC as an explosive fill, which was later employed extensively in naval mines and shells during World War II.

The application of NC as a binder was exploited when it was used for propulsion purposes in homogenous propellants, with the invention of the smokeless powder, Poudre B, by Paul Vieille in 1884 [2]. It was made by treating a mixture of soluble and insoluble NC with a 2 : 1 ether–alcohol mixture, kneading it to form a thick jelly, and rolling into thin sheets. The NC binder provided the necessary structural integrity for the propellant, which could be molded to conform to a wide range of motor geometries and be used to deliver long duration thrust. NC has been used as a single-base propellant, but only to a limited extent due its negative oxygen balance (−28.6). This was followed by the development of Ballistite (a gelatinous mixture of nitroglycerin (NG) and soluble NC in varying proportions with a small amount of aniline or diphenylamine stabilizer) invented by Alfred Nobel in 1888 and Cordite (a combination of 58% NG, 37% NC, and 5% Vaseline) by Abel and James Dewar. A mixture of NC with NG results in a higher energy propellant, not only because of the energetic nature of the NG, but also the positive oxygen balance of NG (+3.5) results in complete oxidation of the NC. Ballistite and Cordite are used as double and triple base propellants, which are still in widespread use [3].

1.2
Polysulfides

Polysulfide (Figure 1.2) was the first polymer to be used as a binder in the heterogeneous (composite) family of propellants in 1942 [4]. It was invented by Dr. Joseph C. Patrick in 1928 as a condensation product of ethylene dichloride

\[
\text{Polysulfide} = \left[\text{CH}_2\right]_m \text{S}_x \right]_n
\]

Figure 1.2. Chemical structure of polysulfide.
with sodium polysulfide. He named this polymer Thiokol and formed the Thiokol Corporation to commercialize the product. In 1945, JPL engineer Charles Bartley used polysulfide polymer (known commercially as LP-3) to formulate a new type of composite solid propellant [5, 6].

The sulfur in the polymer backbone functioned as an oxidizer in the combustion process contributing towards higher specific impulses. The polymer could be cross-linked by oxidative coupling with curatives such as \( p \)-quinonedioxime or manganese dioxide to form disulfide (\(-\mathrm{S-S-}\)) bonds. The cured elastomers have good elongation properties for wider operating temperature ranges.

### 1.3 Polybutadienes (PBAA, PBAN, and CTPB)

In early 1955, the role of aluminum as a high-performance ingredient in propellant formulations was demonstrated by Charles B. Henderson’s group at the Atlantic Research Corporation, USA. The polysulfide propellant developed by Thiokol could not be adapted to the use of aluminum, because chemical reactions during storage led to explosions. Therefore a new series of binders based on butadienes were developed by Thiokol. Furthermore, a polybutadiene chain polymer was found to be more favorable than a polysulfide chain to provide higher elasticity [7]. The first of the butadiene polymers to be used in a propellant was the liquid copolymer of butadiene and acrylic acid, PBAA (Figure 1.3) developed in 1954 in Huntsville, Alabama, USA.

The PBAA is prepared by the emulsion radical copolymerization of butadiene and acrylic acid. The very low viscosity of these polymers permitted the development of propellants with higher solids. However, owing to the method of preparation, the functional groups are distributed randomly over the chain. Hence, propellants prepared with PBAA show poor reproducibility of mechanical properties [8].

The mechanical behavior and storage characteristics of butadiene polymers were improved by using terpolymers based on butadiene, acrylonitrile, and acrylic acid (PBAN) (Figure 1.4) developed by Thiokol in 1954. The introduction of an acrylonitrile group improves the spacing of the carboxyl species.

This polymer has a low viscosity and low production costs. The curing systems for PBAN are based on di- or tri-functional epoxides (commercial name: Epon X-801) or aziridines (commercial name: MAPO). PBAN propellants can provide a better specific impulse, but require elevated curing temperatures [9]. The PBAN polymer was soon used in propellant formulations such as TP-H-1011, which is

\[
\begin{align*}
\text{H}_2\text{C-CH=CH-CH}_2 \quad & \quad \text{CH}_2=\text{CH} \quad \text{COOH} \\
\end{align*}
\]

**Figure 1.3** Chemical structure of PBAA.
used in space transportation system solid rocket motors, with total production exceeding that of all other binder compositions [10].

In late 1950s, carboxyl terminated polybutadiene (CTPB) (Figure 1.5) with the trade name HC-434, which took full advantage of the entire length of the polymer chain, was developed by Thiokol [11].

HC-434 was prepared by the free-radical polymerization using azo-bis-cyanopentanoic acid initiator. In parallel to the Thiokol polymer work, Phillips Petroleum Company developed another brand of CTPB known as Butarez CTL, which was prepared by lithium initiated anionic polymerization. CTPB propellants offer significantly better mechanical properties particularly at lower temperatures in preference to PBAA or PBAN binders, without affecting the specific impulse, density, or solids loading [12]. The curatives for CTPB prepolymer are the same as that for PBAA and PBAN. CTPB formulations were used in propellants from the 1960s. In 1966, the CTPB based propellant TP-H-3062 was used in the surveyor retro motor for the first landing on the moon [13].

1.4 Polyurethanes

Almost concurrently with the development of polybutadiene polymers, Aerojet, who were a competitor to Thiokol, developed the polyurethane branch of binders, in the mid-1950s. Polyurethane binder, the general structure of which is shown in Figure 1.6,
is formed by the reaction of a high molecular weight di-functional glycol with a diisocyanate forming a urethane linked polymer.

The third building block in a polyurethane binder is a triol such as Trimethylol Propane (TMP) causing cross-linking of polymer chains. Polyurethane binder systems provide shrink-free, low-temperature, and clean cure. An additional benefit of polyurethane binders is that the backbone polymer contains substantial amounts of oxygen [14]. It is not necessary, therefore, to use a high percentage of oxidizer in the formulation of the propellant to achieve comparable energies. Also, several of the urethane polymers are known for their thermal stability [6]. A commonly used polyurethane binder material is ESTANE, a product of the B.F. Goodrich Chemical Company. However, in spite of the advantages of polyurethane binders, polybutadiene formulations still remain more popular.

1.5 Hydroxy Terminated Polybutadiene

The applicability of hydroxy terminated polybutadiene (HTPB) polymer as a binder was demonstrated by Karl Klager of Aerojet in 1961 [4]. HTPB (Figure 1.7) was prepared by the free radical polymerization of butadiene using hydrogen peroxide as the initiator.

Even though the development of HTPB began in 1961, it was not proposed to NASA until 1969 due to the popularity of PBAN and CTPB formulations. HTPB binder was first tested in a rocket motor only in 1972 [4]. It was commercialized with the trade name R-45M by ARCO chemicals. Isocyanates are used as cross-linking agents for HTPB polymers to form urethane linkages, thereby reuniting the polyurethane family of binders with the polybutadiene family. HTPB binders exhibit superior elongation capacity at low temperature and better ageing properties over CTPB [15]. It has since become the most widely-used binder in solid propellant formulations with excellent mechanical properties and enhanced insensitive munition (IM) characteristics [10].

1.6 Explosive Binders

Concurrent with the research on polymers as binders in solid propellants, they were also explored as binders for high explosives, mainly intended for

\[
\text{HO} \quad \text{H}_2\text{C} \quad \text{H}_2\text{C} \quad \text{CH} \quad \text{CH} \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{OH}
\]

Figure 1.7 Chemical structure of HTPB.
desensitization. At that time, natural and synthetic waxes were used for desensitization of explosives [16–18]. A more successful method for desensitization was devised through the use of polymer bonded explosives (PBX), in which, the explosive crystals are embedded in a rubber like polymer matrix. The first PBX composition was developed at the Los Alamos Scientific Laboratory, USA, in 1952 [10]. The composition, designated as PBX 9205, consisted of Royal Demolition Explosive (RDX) crystals embedded in a polystyrene matrix plasticized with dioctyl phthalate. It has been found that PBX formulations offer processability and insensitivity advantages over the standard “waxed” explosives [19].

The rubber like polymer binders originally developed for solid propellant applications were successfully applied for PBX formulations also.

With the development of more insensitive explosive fillers (e.g., triaminotrinitrobenzene, TATB), the function of the polymer binder shifted from that of a desensitizer to the one that imparts structural integrity to the PBX formulation. In this context, soft rubbery binders were replaced by the use of hard and high modulus polymers as binders. Epoxy resins, phenolic resins, fluoropolymers (Teflon, Kel-F 3700) (Figure 1.8), and polyamides (Nylon) are examples of hard polymers that are used in PBX formulations.

1.7 Thermoplastic Elastomers

In the early 1980s, screw extrusion technology was envisaged for processing of energetic material formulations, particularly PBX, with the core objective of reducing the cost of production [20]. For its effective implementation, thermoplastic elastomers (TPE) began to be used as binders. TPEs consist of alternate hard and soft segments of crystalline and amorphous polymers, possessing the combined properties of glassy or semi-crystalline thermoplastics and soft elastomers. TPE technology enabled rubbers to be processed as thermoplastics. This feature makes TPEs suitable for high-throughput thermoplastic processes, such as screw extrusion and injection molding, which allow the development and production of

\[ \begin{array}{c}
\text{Kel-F 3700} \\
\begin{array}{c}
\text{CF}_2 \\
\text{CF}_2
\end{array}
\end{array} \]

\[ \begin{array}{c}
\text{Teflon} \\
\begin{array}{c}
\text{CF}_{2} \quad \text{CF}_{2} \\
\text{n}
\end{array}
\end{array} \]

\[ \begin{array}{c}
\text{Viton} \\
\begin{array}{c}
\text{CF}_{3} \\
\text{F}
\end{array}
\end{array} \]

Figure 1.8 Chemical structures of fluoropolymers used as explosive binders.
energetic material composites without solvent emissions. Furthermore, TPE binders permit recovery and recycling of energetic material ingredients resulting in additional pollution prevention. TPE binders based on segmented polyurethanes (Estane 5703) and block copolymers of styrene and ethylene/butylene (Kraton G-6500) are widely used as binders in a variety of energetic material formulations including rocket propellants, explosives, and pyrotechnics.

Estane 5703 (Figure 1.9) is a multiblock copolymer obtained by the polymerization of 4,4′-diphenylmethane diisocyanate (MDI) and poly(butylene adipate) (PBA) with 1,4-butanediol as the chain extender. The hard and soft segments of Estane 5703 are polyurethane (MDI) and polyester (PBA), respectively.

Kraton G-6500 (Figure 1.10) is a triblock copolymer of styrene–ethylene/butylene–styrene (SEBS) prepared by anionic polymerization using alkyl lithium initiators.

The polystyrene block is the hard segment and the polyethylene/butylene block constitutes the soft segment. At room temperature, the flexible rubbery polyethylene/butylene blocks ($T_g \sim -100 \, ^\circ C$) are anchored on both sides by the glassy polystyrene blocks ($T_g \sim 100 \, ^\circ C$). Therefore, they behave as cross-linked rubber at ambient temperature and allow thermoplastic processing at higher temperatures.

Figure 1.9  Chemical structure of Estane 5703.

Figure 1.10  Chemical structure of Kraton.
Energetic Polymers (Other Than NC) as Binders

Strength and sensitivity problems of propellants and explosive formulations were addressed to a larger extent by the success of composite propellant and PBX technologies. However, with the addition of non-energetic or inert binders into formulations, a high level of energetic solid loading is required to meet the given performance requirements, as the explosive energy is diluted. Furthermore, processing technology would also have to be altered in order to cast these highly filled compositions into the required shapes [21].

Hence, in the 1950s, scientists realized the need to develop energetic binders derived from energetic polymers for energetic material formulations. Energetic polymers are obtained through the substitution of energetic functional groups, such as azido and nitrato moieties, as pendent groups to the polymer backbone. The presence of energetic functional groups on the polymer allows the composition to have comparatively less explosive filler, thereby rendering the formulation less sensitive to external stimuli. It is also possible to obtain enhanced performance by using energetic binders instead of the inert ones.

The immediate choice of an energetic polymer for binder application was NC. However, NC suffers from undesirable mechanical properties, particularly very low elongation at sub-ambient temperatures. In order to improve the mechanical/energetic properties of NC formulations, two routes were employed. These were: (i) inert binders in combination with energetic plasticizers, nitroglycerin (NG), or butanetriol trinitrate (BTTN); and (ii) NC binder employed with energetic/non-energetic plasticizers [22]. However, neither of these routes led to formulations with acceptable performance. Therefore, a new series of polyether-based energetic polymers were developed targeted specifically at binder applications.

1.8.1 Polyglycidyl Nitrate

Polyglycidyl nitrate (PGN) (Figure 1.11) was the first energetic prepolymer to be investigated for binder applications. Initial work was done on PGN by Thelen and coworkers [23] in the 1950s at the Naval Surface Warfare Center (NSWC). This was later evaluated as a propellant at the Jet Propulsion Laboratory (JPL) [24].

Development of PGN into an energetic binder was delayed due to the hazardous processes of monomer preparation, purification, and polymerization. The monomer, glycidyl nitrate (GN), was prepared by a single-step method consisting of

![Chemical structure of PGN](image-url)
reacting glycidol with a potentially dangerous nitrating mixture of 100% nitric acid and acetic anhydride, which is known to generate the unstable explosive acetyl nitrate in-situ. A further disadvantage of the method was the cumbersome purification process of the monomer to remove the dinitroacetate contaminants. Polymerization of GN to PGN was carried out by using entire monomer in the reaction, but this was considered too hazardous due to the exothermic nature of the process.

In the 1990s, the British Defense Research Agency (DRA) modified the monomer preparation by using dinitrogen pentoxide (N₂O₅) in a flow reactor to give dichloromethane solutions of GN in high yield and purity [25, 26]. This process does not require any further purification prior to polymerization. After establishing the method of monomer synthesis, di-functional PGN was safely and reproducibly prepared by the cationic ring opening polymerization of GN. This polymerization employed a tetrafluoroboric acid etherate initiator combined with a di-functional alcohol. The hydroxyl terminated polymers were subsequently cross-linked with isocyanate curing agents to give energetic polyurethanes with potential application as binders in explosives and propellants. Concurrently with the work in the UK on PGN, considerable success was achieved on the scale-up of PGN production and its evaluation as a propellant binder at the Naval Weapons Center, China Lake, USA [27].

### 1.8.2 GAP

In 1976, research work was initiated at Rocketdyne in the USA on the preparation of a hydroxy-terminated azido prepolymer (glycidyl azide prepolymer, GAP) as an energetic polymer (Figure 1.12), which takes advantage of the positive heat of formation of the azido chemical groups [28].

The logical starting point for GAP synthesis was glycidyl azide (GA), which was prepared by the reaction of epichlorohydrin (ECH) with hydrazoic acid, followed by cyclization with a base. However, attempts to polymerize GA were unsuccessful due to the lack of reactivity of the monomer. Emphasis shifted to polymerization of ECH to give polyepichlorohydrin (PECH), followed by conversion of PECH into GAP. GAP triol was successfully prepared in 1976 by the reaction of PECH triol with sodium azide in a dimethylformamide medium [28]. GAP is a unique high-density polymer with a positive heat of formation equal to +490.7 kJ/mol. Currently, GAP is the most readily available energetic polymer due to the low cost of

![Figure 1.12](image-url)  
**Figure 1.12** Chemical structure of GAP.
the synthetic route and its excellent binder properties [29]. The 3M Company has commercialized the GAP polymer under the name GAP 5527 polyol.

1.8.3 Energetic Polyoxetanes

Energetic polymers derived from oxetane monomers, namely 3,3-bis(azidomethyl) oxetane (BAMO), 3-azidomethyl 3-methyl oxetane (AMMO), and 3-nitratomethyl methyl oxetane (NIMMO), were sought for binder applications, because of their low viscosity and good mechanical properties after cross-linking. G.E. Manser discovered energetic polyoxetanes based on BAMO and AMMO at Aerojet in 1984 [30]. His group subsequently reported the preparation and polymerization of the nitrato alkyl oxetane monomer, NIMMO [31, 32]. The energetic polyoxetanes (Figure 1.13) were synthesized by the cationic ring opening polymerization of the respective monomers using boron trifluoride etherate catalyst [33–35].

The critical aspect of the preparation of energetic polyoxetanes is the ease of preparation and purity of monomers. NIMMO was first prepared by the nitration of 3-hydroxy methyl-3-methyl oxetane (HMMO) by acetyl nitrate [33]. Owing to the hazardous nature of the reaction, the synthesis was modified by selective nitration of HMMO using dinitrogen pentoxide nitrating agent in a flow nitration system at DRA [36], which provided excellent yields of pure NIMMO. Therefore, among the energetic polyoxetanes, Poly(NIMMO) gained popularity due to its scalable and safe procedure for preparation [37]. Poly(NIMMO) is a very promising binder for propellant and explosive applications. The manufacturing process for Poly(NIMMO) is licensed to ICI, UK, by the DRA.

Synthesis of BAMO monomer involved treating 3,3-bis(chloromethyl) oxetane (BCMO) with sodium azide in dimethylformamide [38]. The monomer AMMO

![Chemical structures of polyoxetanes used as energetic binders.](image-url)
was prepared by azidation with sodium azide of the tosylate derivative of 
HMMO [39]. The symmetrically di-substituted Poly(BAMO) is too highly crystalline to be 
used as a homopolymer for binder applications. Hence it must be co-polymerized 
with the relatively less energetic AMMO or NIMMO to bring down the melting 
and glass transition temperatures. Poly(BAMO) is nearing commercialized pro-
duction by Aerojet and Thiokol.

Energetic polyoxetanes containing difluoroamine (–NF2) groups were success-
fully synthesized on the laboratory scale by the cationic ring opening poly-
merization of 3,3-bis(difluoroaminomethyl) oxetane or 3-difluoroaminomethyl 
3-methyl oxetane using borontrifluoride etherate catalyst [40]. However, the diffi-
cult synthetic steps in the monomer preparation have so far prevented their 
evaluation as binders in large-scale.

1.8.4 Polyphosphazenes

Recently, inorganic polymers based on polyphosphazenes have shown promise as 
energetic binders on account of their high densities, low glass transition tempera-
tures, potential synthetic flexibilities, and good chemical and thermal stabili-
ties. Polyphosphazenes, having the general structure (N═PR2)n, (Figure 1.14) are 
inorganic–organic polymers in which the side groups (R) can be halogeno, or 
organo units [41].

Phosphazene polymers are rendered energetic by the macromolecular replace-
ment of halogen/organo units by nitrato or azido groups. The synthetic pathway 
comprises the use of polymeric alkoxy substituted precursors of phosphazenes and 
its subsequent nucleophilic substitution of the alkoxy group with the energetic 
pendant group. Both nitrate ester and azide functionalized energetic phospha-
zenes have been successfully synthesized on a laboratory scale at the Atomic 
Weapons Establishment (AWE), UK, for potential binder applications [42].

1.8.5 Energetic Thermoplastic Elastomers

Energetic versions of TPE binders (energetic thermoplastic elastomers, ETPEs) 
have been developed by Thiokol Inc. USA, to be used as binders in melt cast 
explosive and propellant formulations [43]. ETPEs consist of alternate crystalline 
(hard) and amorphous (soft) segments of energetic polymer molecules. The hard

![Polyphosphazene](image)

**Figure 1.14** General chemical structure of polyphosphazene.
segment of ETPEs consist of Poly(BAMO) and the soft segment of Poly(NIMMO), Poly(AMMO) or GAP. Typical examples of ETPEs are illustrated in Figure 1.15.

ETPEs are prepared by either linking the blocks of individual energetic polymers with isocyanates [44] or by sequential polymerization [45], and have been used as binders in experimental formulations of new low-vulnerability (LOVA) propellants with success [46, 47]. They are environmentally friendly and recyclable. The utilization of ETPE as a binder is rapidly increasing with the emergence of twin-screw extrusion as a promising route for the manufacture of ETPE based formulations.

1.9 Energetic Polymer Plasticizers

Generally, plasticizers are non-reactive liquid diluents used for improving the processability and low temperature mechanical properties of energetic material composites. Energetic plasticizers based on nitrateesters (e.g., BTTN) not only improve processing and low-temperature properties but also improve the overall energetic properties of the formulation. However, nitrate ester plasticizers suffer from migration problems, especially with energetic binder formulations, resulting in the loss of the plasticizer over a period of time. A promising recent approach is to use
low molecular weight oligomers of energetic polymers for plasticizer applications, which offer a number of advantages, including excellent miscibility with the new energetic binders, low volatility, low glass transition temperature, decreased plasticizer mobility, excellent combustion properties, and reduced hazard characteristics [48, 49]. Under this category, low molecular weight GAP [50] and GLYN (glycidyl nitrate) polymers [51] have gained importance as energetic polymer plasticizers.

In another important development [52], the molecular structure of the low molecular weight GAP polymer have been modified to convert the free hydroxyl moieties at the chain ends into azido functional groups (Figure 1.16). This will prevent unwanted reaction of the plasticizer with the isocyanate cross-linking agent, which results in the loss of plasticizing action. The 3M Company has commercialized this product as GAP-0700 plasticizer.

The timeline of the development of polymers for binder applications is illustrated in Scheme 1.1 and the details are given in Table 1.1.

![Figure 1.16](image_url)  
**Figure 1.16** Chemical structure of azido terminated GAP.

![Scheme 1.1](image_url)  
**Scheme 1.1** Time line of the development of different polymers as binder for propellant and explosive applications.
Table 1.1  Polymers used in binder applications.

<table>
<thead>
<tr>
<th>Polymer (abbreviation)</th>
<th>Preparation method</th>
<th>Trade name</th>
<th>Curing agent</th>
<th>Year of development</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrocellulose (NC)</td>
<td>Nitration of cellulosic materials (cotton, paper, wood)</td>
<td>Poudre B; Ballistite; Cordite</td>
<td>—</td>
<td>1888</td>
</tr>
<tr>
<td>Polysulfide elastomer</td>
<td>Condensation polymerization of ethylene dichloride and sodium polysulfide</td>
<td>Thiokol LP series</td>
<td>p-Quinonedioxide</td>
<td>1928</td>
</tr>
<tr>
<td>Polybutadiene–acrylic acid copolymer (PBAA)</td>
<td>Emulsion radical polymerization</td>
<td>HA series</td>
<td>Di- or tri-functional imine/epoxide</td>
<td>1954</td>
</tr>
<tr>
<td>Polybutadiene–acrylic acid–acrylonitrile copolymer (PBAN)</td>
<td>Emulsion radical polymerization</td>
<td>HB series</td>
<td>Di- or tri-functional imine/epoxide</td>
<td>1957</td>
</tr>
<tr>
<td>Carboxyl terminated polybutadiene (CTPB)</td>
<td>Free radical polymerization</td>
<td>HC-434; Butarez CTL</td>
<td>Di- or tri-functional imine/epoxide</td>
<td>Late 1950s</td>
</tr>
<tr>
<td>Polyurethane (PU)</td>
<td>Condensation polymerization of diols and isocyanates</td>
<td>Estane</td>
<td>Multifunctional alcohols</td>
<td>Mid-1950s</td>
</tr>
<tr>
<td>Hydroxyl terminated polybutadiene (HTTPB)</td>
<td>Free radical polymerization of butadiene</td>
<td>R-45M</td>
<td>Isocyanates</td>
<td>1961</td>
</tr>
<tr>
<td>Energetic polyglycidyl nitrate</td>
<td>Ring opening polymerization of glycidyl nitrate</td>
<td>PGN</td>
<td>Isocyanates</td>
<td>1950 Commercialized by DRA in 1990</td>
</tr>
<tr>
<td>Glycidyl azide polymer</td>
<td>Ring opening polymerization of epichlorohydrin followed by azidation</td>
<td>GAP 5527</td>
<td>Isocyanates</td>
<td>1971</td>
</tr>
<tr>
<td>Energetic polyoxetanes</td>
<td>Ring opening polymerization of oxetanes</td>
<td>Poly(oxetanes)</td>
<td>Isocyanates</td>
<td>1990</td>
</tr>
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References


