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Structural engineering of polyurethane coatings for high performance applications ☆

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Abstract

This review addresses trends in the development of high performance polyurethane (PU) and its subclass coatings. Changes in the understanding the technical requirements and properties, along with novel approaches in creating high performance PU films are discussed. Some discussion of developments leading to the current status is provided, along with opportunities for the development of architectural, domestic and automotive coatings from carbamate chemistry. The review also focuses on the chemistry of PU, the importance of side products such as biuret, allophanate formation, as well as different low VOC PU coatings such as moisture-cured PU-urea, polyurea, PU-imide, UV cure and waterborne PU coatings. A brief description of functionalized dendritic/hyperbranched polymers, different monomers and synthetic approaches, and their use in the PU coating sector is addressed. In the context of nanostructuring, sol–gel chemistry to formulate ceramer coatings and use of functionalized nanomaterials in PU coatings is described. This portion also includes silica grafting and functionalization of nanosilica particles, polyhedral oligomeric silsesquioxane and the use of bridged polysilsesquioxanes in PU coatings. A wide variety of fillers, whiskers and fibers as well as clay and wollastonites with structural modification is described for use in nanocomposite PU coatings, with special emphasis on the latest development in PU-layered silicate nanocomposites.The use of different reactive-type organophosphorus compounds, aziridinyl curing agents in aqueous PU dispersions, phosphazenes, organo-boranes such as different carboranes for use in the formulation of flame retardant coatings is described. Since surface properties determine the resistivity of coatings towards corrosive chemicals, moisture and dirt repellency, a portion of the review will also be devoted towards modification of surface properties using fluoropolymer, and the synthesis and a brief description of the available fluorinated diols is given.
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Keywords: Polyurethane; Coatings; Hyperbranched; Nanostructuring; High performance

Contents

1. Introduction

Economic competitiveness and environmental concerns have driven the coating technologist to explore newer chemistry and approaches to improve the efficiency of organic coatings at a minimum volatile organic component (VOC). Organic coatings or paints on a substrate give aesthetic appearance as well as protection from the destructive phenomenon known as corrosion. Coatings can provide materials with the desired aesthetical properties such as color and gloss, but are of vital importance in the protection against environmental influences, including moisture, radiation, biological deterioration or damage from mechanical or chemical origin. This applies to both interior and exterior applications. The effectiveness of protection of a substrate against natural deterioration depends on factors such as the quality of the coating, the substrate characteristics, the properties of the coating/substrate interface, and the corrosiveness of the environment. Typical corrosion-resistant coatings protect the metallic surfaces primarily by two mechanisms: by acting as a physical barrier to isolate the substrate from corrosive environment, and by containing reactive materials (usually pigments or inhibitors) that interact with a component of the vehicle and inhibit corrosion. The increased demands for improved technical performance and/or minimized VOC level have motivated research on the development of new coating systems by both industrial and academic organizations. The challenge within the industry is to maintain or improve properties at a reasonable cost, while at the same time meeting the need for environmentally friendly coatings. Several new technologies, such as radiation curable, waterborne and powder coatings have obtained an increased market share since they address some of these issues. On the other hand, solvent-borne coatings have had particular prominence in the area of industrial coatings, where performance is essential. Therefore, some researchers have focused on methods to improve the solid content of the binder by utilizing relatively low molecular weight polymer that build in properties during cure through the formation of crosslink networks. The presence of crosslinks provides thermoset coatings with enhanced tensile strength, good abrasion and mar resistance as well as acid, alkali and solvent resistance, which are lacking in thermoplastic coatings. During the development of new systems, numerous aspects must be considered: the production of the coating formulation, storage of the coating, application and film formation must work with the techniques intended.

Current research on coatings has led two very active frontiers: the discovery of a new class of macromolecular architecture, called dendritic/hyperbranched polymers (HBPs) and the nanotechnology revolution. The presence of a minimum quantity of a reactive dendritic/HBP in a coating can improve the property profile, and at a reasonable cost, but success requires an understanding of the physical issues and careful planning. The possibility of gaining improved performance by combining the properties of organic and inorganic components in coatings has a long history, with examples from the beginning in the industrial era. Some of the earliest and most well known organic–inorganic mixtures are derived from the paint and polymer industries, where inorganic pigments or fillers are dispersed in organic components or binders (solvents, surfactants, polymers, etc.) to improve optical, mechanical and thermal properties. However, the concept of hybrid organic–inorganic materials exploded with development of the soft inorganic chemistry approach, where mild synthetic conditions allow versatile access to chemically tailor hybrid organic–inorganic networks. Subsequent research shifted towards more sophisticated nanocomposite coatings with higher value-added products. Other major coating research and developments include the improvement in flame retardancy and surface properties. Latest developments in improving the surface properties of coatings exposed to a highly corrosive environment has led to structural engineering in the macromolecular binder with high fluorine content at the surface. Due to the small size and high charge density of fluorine, such coatings have high resistivity towards corrosive chemicals, and are gaining importance as binders for exterior coatings. In this review, the major developments will be discussed with an emphasis to PU and its subgroup coatings in an effort to convey a unified concept, and to provide a basis for future developments.

1.1. Polyurethane (PU)

Otto Bayer and coworkers at I.G. Ferbenindustri, Germany in 1937 were the first to discover PUs in response to the competive challenge [1] arising from Carother's work on polyamides, or nylons, at E.I.

Dupont. The successful development of high molecular weight polyamides at E.I. Dupont stimulated Bayer to investigate similar materials not covered by Dupont's patent. The initial work was the reaction of aliphatic isocyanate with a diamine to form polyurea which was infusible and hydrophilic. Further research on this subject demonstrated the reaction of an aliphatic isocyanate with a glycol produces new materials with interesting properties. Dupont and ICI soon recognized the desirable elastic properties of PUs. The industrial scale production of PU started in 1940, but market growth of PU was seriously impacted by World War II. A noticeable improvement in the elastomeric properties PU waited until 1952, when polyisocyanate, especially toluene diisocyanate (TDI), become commercially available. In 1952–1954, Bayer developed different polyester–polyisocyanate system. In 1958, Schollenberger of BF Goodrich introduced a new virtually crosslinked thermoplastic PU elastomer. At approximately the same time, Dupont introduced a Spandex fibre called Lycra, which is a PU based on polytetramethylene glycol (PTMG), 4,4′-diphenylmethylene diisocyanate (MDI) and ethylene diamine. By the early 1960s, BF Goodrich produced Estane, Mobay marketed Texin, and Upjohn marketed Pallethane in the USA. Bayer and Elastgran marketed Desmopan and Elastollan, respectively in Europe [2]. With the development of low-cost polyether polyols, PU coatings opened the door for automotive applications. Formulations and processing techniques continuously developed as one- and two-pack systems were developed. The PU coating industry has entered a stage of stable progress and advanced technological exploitation. Today, PU coatings can be found on many different materials, to improve their appearance and lifespan. On automobiles, PU coatings give the demanded exterior high gloss, improved color retention, improved scratch and corrosion resistance. Different types of PU coatings are used in construction, where building floors, steel trusses and concrete supports are spray coated to make them more durable against environmental deterioration and less costly to maintain.

The wide applicability of PU coatings is due to versatility in selection of monomeric materials from a huge list of macrodiols, diisocyanates and chain extender (CE). The chemistry involved in the synthesis of PU is centered on the isocyanate reactions. The three important components of PUs are macrodiol, diisocyanate and CE. The synthesis

of PU involves a simple reaction between a di- or polyisocyanate with a di- and/or polyol.

1.2. Reactions of isocyanate

Isocyanates are highly reactive chemicals and create several chemically different products when combined with –OH and –NH functional substances. Desired products and side products are formed in different amounts. The basic reactions of isocyanate with different reagents are shown in Scheme 1. The high reactivity of isocyanate groups toward nucleophilic reagents is mainly due to the pronounced positive character of the C atom in the cumulative double bond sequence consisting of nitrogen, carbon and oxygen, especially in aromatic systems. The electronegativity of the oxygen and nitrogen imparts a large electrophilic character to the carbon in the isocyanate group. The common reactions of isocyanates can be divided into two main classes: (1) the reaction of isocyanates with compounds containing reactive hydrogen to give addition products, and (2) the polymerization of isocyanates, i.e., self-addition reaction. Isocyanates react with hydroxyl compounds to give urethanes (a) and with amines to give ureas (b). For primary and secondary alcohols, the uncatalysed reaction proceeds readily at 50–100 °C, tertiary alcohols and phenols react more slowly. Typical primary and secondary aliphatic amines and primary aromatic amines react rapidly with isocyanate at 0–25 °C to form urea functional substances. Similarly, water reacts with a diisocyanate and initially forms of an unstable carbamic acid, which decomposes and produces an amine (c). Amine is a nucleophilic reagent and further reacts with an isocyanate function to produces urea linkage (d). The availability of a lone pair of electrons on the nitrogen atom of urea group makes them nucleophilic centers, which upon reaction and fruitful collision with one molecule of isocyanate produces biuret (e). Similarly, isocyanates react with urethanes and produce allophanates (f).

Different secondary reactions shown in Scheme 1 occur to a lesser extent than the primary reactions. Reactions leading to the formation of allophanates and biurets are influenced by the reaction condition such as temperature, humidity level and the type of isocyanate used. The self-condensation of isocyanate results in uretidione rings (dimer-, g), isocyanurate (trimer-, h) or carbodiimide (j). The formation of carbodiimides is not usually
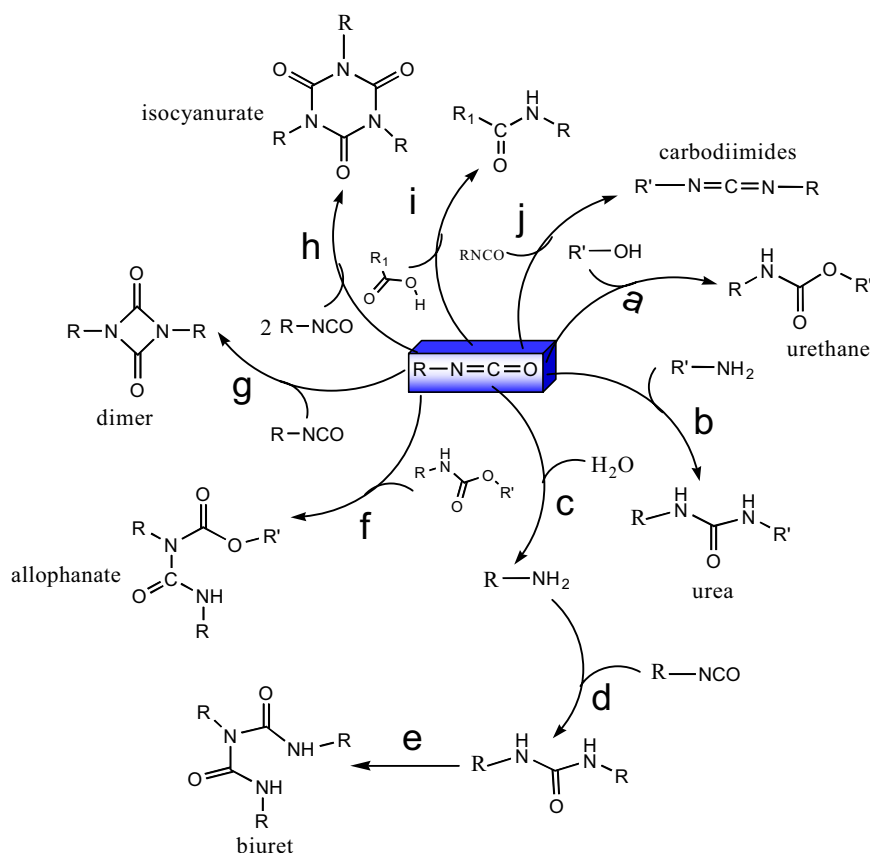
Scheme 1. Basic reactions of isocyanate with different reactants [178].

considered a polymerization reaction, but it could be classified as a condensation polymerization between isocyanate molecules with elimination of CO_2. This is due to degradation of isocyanates taking place at high temperatures [3]. When isocyanate reacts with carboxylic acids, the mixed anhydrides break down and form amide groups (i). The trimer isocyanurate rings, unlike uretidione rings, are exceptionally stable. The high reactivity of isocyanates may cause detrimental secondary reactions and uncontrolled condensations leading to the formation of unworkable crosslinked materials that are difficult to process. Therefore, blocking of isocyanate capped material or monomer may sometimes helps for improving the stability [4]. The blocked isocyanate can be converted to the active isocyanate form when required. More recently, commercial availability of blocked isocyanates has increased greatly. In particular, these reagents are suitable for light-stable two-component and single-package blocked adduct urethane coatings in which high temperatures ($> 100\,^{\circ}C$) are used to regenerate

the isocyanate and the blocking agent. The regenerated isocyanates react with hydroxyl or amine functionalized co-reactants to form thermally stable urethane or urea bonds, respectively [5–7]. Blocked isocyanates used in the literature were phenol, oxime [5], caprolactam [8], imidazoline [9], tetrahydropyrimidine, imidazole [10], pyrazole [11], etc. In order to avoid the release of volatile isocyanate blocking agents, a self-blocked concept has also applied [12].

1.3. Isocyanates

The polyfunctional isocyanate used to prepare PU coatings can be aromatic, aliphatic, cycloaliphatic or polycyclic in structure. The commonly used isocyanates in the manufacture of PUs are TDI, MDI, 4,4′-dicyclohexylmethane diisocyanate (H_{12}MDI), xylene diisocyanate (XDI), tetramethylxylylene diisocyanate (TMXDI), hydrogenated xylene diisocyanate (HXDI), naphthalene 1,5-diisocyanate (NDI), *p*-phenylene diisocyanate (PPDI),

3,3′-dimethyldiphenyl-4, 4′-diisocyanate (DDDI), hexamethylene diisocyanate (HDI), 2,2,4-trimethyl-hexamethylene diisocyanate (TMDI), isophorone diisocyanate (IPDI), norbornane diisocyanate (NDI), 4,4′-dibenzyl diisocyanate (DBDI), etc. Aromatic isocyanates have high reactivity than aliphatic or cycloaliphatic diisocyanates. Different diisocyanates contribute to the PU properties in different ways. For example, aromatic diisocyanates give more rigid PUs than do aliphatic ones, but their oxidative and ultraviolet stabilities are lower [13]. Triisocyanates used for synthesis of PU coatings will be addressed later.

1.4. Diols/polyols

The polyol component of the PUs can be a polyfunctional polyether (e.g., polyethylene glycol, polypropylene glycol, PTMG or polycaprolactone diol), polyester polyol (PEPO), acrylic polyol (ACPO), polycarbonate polyol, castor oil or a mixture of these. A wide variety of branched or crosslinked polymers can be formed since the functionality of the hydroxyl-containing reactant or isocyanate can be adjusted. The simplest polyols are glycols, such as ethylene glycol, 1,4-butane diol (BDO) and 1,6-hexane diol. The low molecular weight reactants result in hard and stiff polymers because of a high concentration of urethane groups. On the other hand, the use of high molecular weight polyols as the main reactants produces polymer chains with fewer urethane groups and more flexible alkyl chains. Long-chain polyols with low functionality (1.8–3.0) give soft, elastomeric PU while short-chain polyols of high functionality (greater than 3) give more rigid, crosslinked product.

Polyether polyols are produced by the addition of either ethylene oxide or propylene oxide to a polyhydroxy 'starter' molecule in the presence of a catalyst (Scheme 2a). Typical starter molecules include glycerol, ethylene glycol, propylene glycol and trimethylolpropane. PEPOs are produced by the condensation reaction of polyfunctional carboxylic acids or anhydrides with polyfunctional alcohols (Scheme 2b). ACPOs are produced by free radical polymerization of hydroxyethyl acrylate (HEA)/methacrylate with other acrylic precursors [14] (Scheme 2c). Depending on the field of application, PEPO, ACPO or polyether polyols have generally been chosen. In commercial applications, it is common to find polyesters prepared from a mixture of two or more diacids reacted with two or more glycols, which gives ample scope for a range of very complex products [15,16]. Though PEPO- and ACPO-based PUs are vulnerable to the gradual hydrolysis of the ester group but they are sufficiently stable against natural weathering. The hydrolysis takes place at the ester groups, which reverts to the carboxylic acid and alcohol. Additionally, the *in situ* formation of carboxylic acid catalyzes further ester hydrolysis, thus accounting for an autocatalytic effect [17] and therefore a significant reduction of average molar mass and, consequently, deterioration of mechanical properties occur on prolong exposure to humid atmosphere. To slow down the hydrolysis of polyester groups, polycarboimides can be added to poly(ester urethanes) that act as acid scavengers and suppress the autocatalytic effect
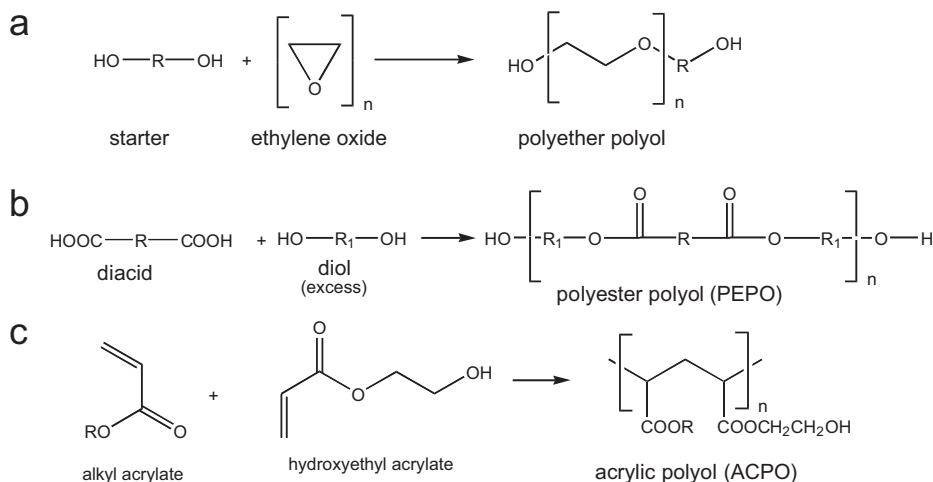
Scheme 2. Synthetic methods for the preparation of polyether polyol, PEPO and ACPO.
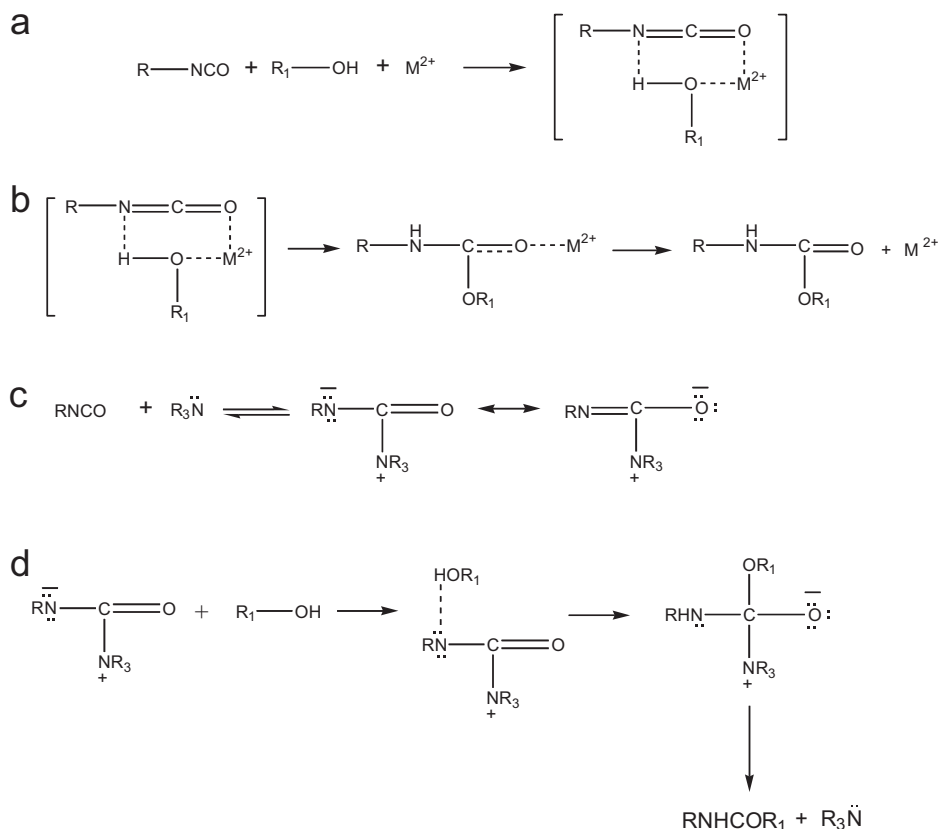
Scheme 3. Reaction mechanism for the NCO/OH reaction due to: (a) and (b) organometallic catalysis [23], and (c) and (d) tertiary amine catalysis [24,27].

[17,18]. PU coatings derived from PEPO have excellent heat stability, adhesive properties and oil resistance. Additionally, the lower manufacturing cost has made widespread application of polyester-type PU coatings.

1.5. Catalysts

Catalysts are added to allow the reaction to take place at a rapid rate, and at lower temperatures. For the reaction of an isocyanate with an alcohol, many effective urethane catalysts are available. Most often used catalysts are tertiary amines [19], especially 1,4-diazabicyclo [2.2.2] octane (DABCO), triethyl amine (TEA), and organo tin compounds [20], especially dibutyltin dilaurate (DBTDL), stannous octoate and THORCAT. Tetravalent tin compounds of the type $R_nS_nX_{(4-n)}$ with R being a hydrocarbon group (alkyl, aryl, cycloalkyl, etc.) and X being a halogen atom or a carboxylate group (acetate, laurate, etc.) have shown catalytic effect in urethane reaction [21]. The catalytic effect of

organometallic compounds is due to their complex forming ability with both isocyanate and hydroxyl groups [22,23]. The mechanism proposed by Britain and Gemeinhardt [24] is shown in Scheme 3. The interation of metal cation with isocyanate, alcohol molecule results an intermediate complex (Scheme 3a), which may then readily rearrange to yield the urethane product (Scheme 3b). Lenz [25] suggested that the catalysis mechanism of tertiary amines (NR_3) for urethane reaction involve complexation of the amine and isocyanate groups (Scheme 3c) followed by reaction of the complex with alcohol to form urethane product (Scheme 3d) [26]. The mercury catalyst THORCAT, however, is less efficient than either catalyst, perhaps due to a higher stability constant for the latter compound. Furthermore, mercury salt catalysts are thought to possess delayed action properties [27], which may also account for their reduced performance compared with other metal compounds [28]. Cyclic phosphine oxide catalyzes carbodiimide formation [3]. In the absence of a strong catalyst, allophanate

Table 1
Different types of coatings by ASTM classification

ASTM description	Type I one-package (pre-reacted)	Type II one-package (moisture cured)	Type III one-package (heat cured)	Type IV two-package (catalyst)	Type V two-package (polyol)	Type VI one-package (non-reactive lacquer)
Characteristics	Unsaturated drying oil modified; no free isocyanate	Contains free isocyanate	Blocked isocyanate	Isocyanate prepolymer and catalyst	Part A: isocyanate rich, Part B: polyols or amines	Fully polymerized PUs dissolved in solvents
Curing mechanism	Oxidation of drying oil; solvent evaporation	Reaction with atmospheric moisture	Thermal release of blocking agent and then reaction	Reaction of isocyanate with moisture and or/components in catalysts	Reaction between Parts A and B; instant curing is possible	Solvent evaporation
Polymer	Alcoholysis products of drying oils reacted with isocyanate	Higher molecular weight diols and triols	Prepolymer forms an adduct with blocking agents	Prepolymer similar to type II, but catalyst could contain polyol/amine	Relatively lower molecular weight	Thermoplastic polymer with relatively high molecular weight

and biurets formation do not take place for aliphatic isocyanates.

1.6. PU coating classification

ASTM has grouped six different PU coating types in the ASTM D16 Standard [29]. Table 1 summarizes the characteristics of six ASTM PU coating types. Most high solids and solventless PU coatings for high performance application and corrosion protection are designed using the plural component format of the ASTM D16-type V.

1.7. Thermoplastic PU coatings

Thermoplastic PU may be described as the linear structural block copolymer of $(SH)_n$ type, where S is soft and H is hard segment (HS). Due to the wide variety of properties between S and H segment, phase separation may be observed in the final material. Phase separation occurs due to the intrinsic incompatibility or thermodynamic immiscibility between the hard and soft segments (SSs). The HSs, composed of polar materials, can form carbonyl to amino hydrogen bonds and thus tend to cluster or aggregate into ordered hard domains [30], whereas SSs form amorphous domains. The HS acts as filler particle as well as crosslinker to restrain the motion of SS chains. Such a structure was first proposed by Cooper and Tobolsky in 1966 [31]. The early work of Schollenberger [32] as well as Cooper

and Tobolsky [31] established that segmented PUs consist of high glass transition temperature (T_g) or high melting temperature (T_m) HS microphase separated from relatively low T_g SS. The degree to which the hard and SSs phase separate, plays a vital role in determining the solid-state properties of these multi-block coatings.

Properties of thermoplastic PU coatings depend upon several factors such as the composition of soft and HSs, lengths of soft and HSs and the sequence of length distribution, chemical nature of the units composing the polymer, anomalous linkages (branching, crosslinking), molecular weight and the morphology in the solid state. At room temperature, soft macroglycol segments are above their T_g and have easy segmental rotations, which therefore impart the material its rubber-like behavior or elastomeric properties. On the other hand, hard domains are below their glassy or melt transition temperature and are thought to govern the hysteresis, permanent deformation, high modulus, and tensile strength and provide dimensional stability [33]. Compositional variables and processing conditions such as structure of soft and HSs [34], symmetry of diisocyanate, type of CE (diol or diamine) [35,36], number of carbons in linear low molecular weight CE [36], the type (polyester or polyether) and chain lengths of SSs [36–39], crystallizability of either segment [40], thermal history of the PUs [38,41,42] and the method of synthesis [34] are known to affect the degree of phase segregation,

phase mixing, HS domain organization, and subsequent PU coating properties.

1.7.1. Effects of SS

The chemical composition and molecular weight distribution (MWD) of the incorporated soft block influence the macroscopic properties of the resulting coatings. For example, Yoo et al. [43] claimed that the deformation and thermal properties of the PUs were strongly affected by the molecular weight of SS. Additionally, varying the chemical structure of SS changes its solubility parameter and hence the compatibility between soft and HSs in PU coatings. Investigations by Van Bogart et al. [44] and Hartmann et al. [45] revealed that increasing the SS molar mass at a fixed HS length gave rise to an increased tendency for the HS domains to be isolated in the SS matrix. A similar conclusion was reached in PU based on MDI and polycaprolactone using various instrumental techniques [46]. This phenomenon resulted in a higher degree of phase separation between hard and soft blocks, which produced a lower T_g value. In addition, increasing SS prepolymer molar mass at constant functionality (i.e., increasing the molar mass per functional group or equivalent weight, E_n) result [47–50] in a higher degree of phase separation again, owing to increased thermodynamic incompatibility between the two copolymer segments, resulting from the higher Flory–Huggins interaction parameter (χ) [51] and/or the higher crystallizability [39]. Stanford et al. [52] showed that increasing SS functionality significantly increases the strength of PU and reduces the overall degree of phase separation developed in these materials due to increased domain boundary mixing.

1.7.2. Effects of HS

HS structure, length and distribution are very important parameters and largely affect morphology, thermal behavior as well as performance of segmented PU coatings [53–55]. Wang and Cooper [39] observed that the mechanical properties of polyether PUs depend primarily on the HS content. The presence of three-dimensional hydrogen bonding within hard domains leads to usually strong hard domain cohesion. On increasing the HS content, a morphological change occurs from interconnecting to isolated hard domains. The effect of HS content on the phase separation in PU based on MDI was studied by measuring the T_g of the SS [56]. The SS T_g was influenced by the restricted

movement imposed at the HS junctions and at phase boundaries, where the hard domain acts as a filler particle [57]. Bengston et al. [58] explained the variation in mechanical properties with increasing the HS content as due to morphology change. Models containing MDI/BDO repeating units have been described and investigated; and these studies pointed out that the melting of model compounds increases with the number of MDI units, and an extrapolated value for homopolymer, accounting for the chain end defects, was also achieved [34,59–64]. Tonelli et al. [65] used the model compounds R-(MDI–HQE)$_{p-1}$–MDI–R′ [where $p = 1$, 2, 3; R, R′ is ethanol and/or 2-phenoxyethanol; and HQE is bis(2-hydroxyethyl) ether] and shown that the melting point increases with increasing the oligomer length and quickly reaches an asymptotic values. They also calculated the limiting value of melting points for infinite molecular weight calculated by group contribution [66].

1.7.3. Type, position and structure of isocyanate groups

The type, position and structure of isocyanate group affect the reactivity with nucleophile and the macromolecular properties of the derived PU coatings [67]. The reactivity of primary and secondary isocyanate groups in IPDI are different due to stereoelectronic configuration and their reactivity depends on the reaction environment such as type and nature of catalyst, solvent, etc. Similarly, 2,4 and 2,6 TDI isomers differ markedly with respect to their structure as well as reactivity [68]. The 2,6 isomer is symmetric (Scheme 4b) as compared with the 2,4 isomer (Scheme 4a) and is therefore expected to form HSs with better packing characteristics. Again, the reactivity of the *ortho* position in the 2,4 isomer is approximately 12% of the reactivity of the isocyanate group in the *para* position because of the steric hindrance caused by the methyl group. However, when the reaction temperature approaches 100 °C, steric hindrance effects are overcome, and both positions react at nearly the same rate. In comparison, the isocyanate groups on the 2,6 isomer have equal reactivities when both groups are unreacted. However, after one of the isocyanate groups reacts, the reactivity of the second group drops by a factor of about 3 [69,70].

Sung and Schneider [71] reported that the strength of hydrogen bonds in PUs prepared from 2,6 TDI exceed those in 2,4 TDI-based PUs. Nierzwicki and Walczynski [72] investigated
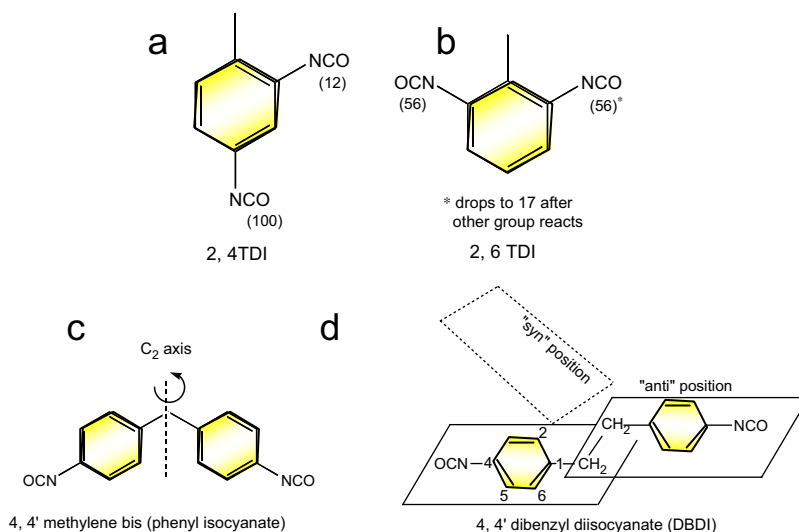
Scheme 4. Schematic of (a) 2, 4 TDI, (b) 2, 6 TDI (The numbers indicate relative rates of reaction of the isocyanate groups at the different positions.) [69], (c) MDI and (d) DBDI [77]. Structure of DBDI was reproduced with permission from Elsevier.

PTMG/BDO-based PU elastomers synthesized from different amount of 2,4 and 2,6 TDI isomers and showed that increasing content of the 2,6 TDI isomer resulted in a systematic increase in tensile strength, modulus and microphase separation. It was suggested that the symmetric nature of the 2,6 TDI isomer enhanced the stiffness of the hard domains. Barbeau et al. [73] observed strong hard–hard interurethane associations in 2,6-TDI-based prepolymers; these led to microphase segregation between polyether chains and urethane groups. Different studies [74,75] showed that the MDI-based TPUs in contrast to TDI-based materials possess a more perfect domain organization due to long-range order and show a higher extent of segregation between soft and HSs. Generally symmetric isocyanates form crystallizing HSs with good packing ability, producing higher strength materials. However, from a kinetic point of view, phase separation becomes more complete with aliphatic HSs because of increased mobility. Rogulska et al. [76] reported that the PUs prepared from HDI had higher ability to crystallize than the MDI-based PURs.

The structure of MDI and DBDI (Scheme 4c & d) differ only in the number of the methylene (CH_2) groups situated between the two aromatic rings bearing the isocyanate (NCO) groups in the *para* position. PUs prepared from DBDI (i.e., even number of CH_2 groups situated between the aromatic rings) is considerably higher melting than MDI-based PUs (i.e., odd-number of CH_2 groups situated between the aromatic rings) [77]. The MDI molecule introduces the rigid –Ph–CH_2–Ph– moiety in the elastomeric PU HSs. In contrast when using DBDI, the specific –Ph–CH_2–CH_2–Ph– moiety introduces a variable geometry into the HSs due to the possibility of internal rotation of this isocyanate around the –CH_2–CH_2– ethylene bridge. This leads to the appearance of both *syn* and *anti* rotational conformations, of which the *anti* conformation is most stable. Therefore, PUs prepared from DBDI can adopt compact packing due to the *anti* conformation of DBDI, which significantly enhance ordering and HS–HS hydrogen bonding [77].

1.7.4. Effect of CE

The effect of different CEs on morphology and properties of PUs were reported by various authors [60,78,79]. The chain length, molecular volume, functionality of the CE and its conformation can influence HS packing and crystallinity in the hard domains [80–82]. Blackwell and Nagarajan [83] and Blackwell et al. [60,84] suggested that for chain-extended PUs, CEs containing an even number of carbons produced polymers with a more phase separated structure than those containing an odd numbers of carbons. Auten and Petrovic [85] reported the effect of unsaturation in the CE on the structure and properties of derived PUs. They utilized CEs of the BDO series with increasing bond

order at the 2,3 carbons such as BDO, *cis*-2-butene-1,4-diol (BED) and 2-butyne-1,4-diol (BYD) and showed that increasing bond order progressively limit backbone chain flexibility. Consequently, HS size may increase, but hydrogen bonding groups may be forced into positions that do not allow effective interchain bonding, resulting in poor physicochemical properties. In addition, the relative acidity of the terminal alcoholic protons is expected to increase with increasing CE bond order because electron density at the oxygen atoms would be progressively shifted toward the π bonds. As the acidity of the CE O–H group increases, the reaction rates during polymer synthesis, polymer molecular weight, and thermal stability of the urethane groups formed could all be adversely affected.

It has also been shown that the physicochemical properties of thermoplastic elastomers are increased using diols with higher molecular weight as CEs [86]. While working with hydroxyl-terminated polybutadiene (HTPB)-based PUs, Zawadski and Akcelrud [87] observed that the mechanical properties increased with decreasing number of carbon atoms in the CE and their findings disagrees with previous results, which showed a zigzag pattern [88], or an increase in property with diol chain length [89]. Yen et al. [90] observed a higher tensile strength for diamine chain extended PUs in comparison to BDO chain extended PUs. They [90] also observed that ethylenediamine chain extended PU showed better tensile strength than diethyltriamine chain-extended PU. Earlier studies [35,36,39,91] compared urea with urethane by their influence on polymer properties and found that an increase in the urea group content would enhance the extent of hydrogen bonding between HSs.

1.8. Hydrogen bonding effect

Hydrogen bonding in PUs plays a vital role in determining their macroscopic properties. The high electronegativity of nitrogen atom in the urethane or urea moiety withdraws N–H bonded electrons and develops partial positive charge on the hydrogen, which thereby forms hydrogen bonding with the neighboring oxygen atom. In all cases, the hydrogen atom of the N–H group in the urethane or urea linkages is the donor proton, while the acceptor group can be the carbonyl of the imide groups, urethane's $C=O$, urea's $C=O$ or the oxygen atom of the ester or ether linkage when polyester or a polyether are present as the SS.

The hydrogen bonding interaction produces physical crosslinks, and thereby reinforces the PU matrix; increase strength and stiffness [92–94].

Fourier transform infrared spectroscopy (FT-IR) is well established as an analytical technique for functional group analysis and to study the hydrogen bonding and phase separation behavior in PUs. Pimentel and Sederholm [95] suggested a linear relationship between the length of the hydrogen bond (R) and the frequency shift (Δv) of the N–H absorption band caused by hydrogen bonding, as expressed in

$$R = 3.21 - \Delta v/(0.548 \times 10^3).\qquad(1)$$

The shorter the hydrogen bonding, the stronger the bonding.

In most cases, the degree of PU microphase separation as observed from FTIR study has been found to be incomplete. That is, the microphase is not pure due to the intersegmental mixing. Mixing within the soft microphase is reflected by an elevation in its T_g compared to the pure component value. The more SS domains are contaminated with the dissolved HS of high glass transition temperature, the higher the SS T_g. The degree of HS–SS mixing depends on HS length, SS length, overall HS content and the affinity of one segment toward the other [96].

1.9. Thermoset PU coatings

The major drawbacks of thermoplastic PU coatings are their poor resistance towards mechanical strains and high temperatures deformation and/or degradation. Generally, their acceptable mechanical properties vanish above 80 °C and thermal degradation takes place above 200 °C [97]. The presence of crosslinks provides thermoset coatings with enhanced tensile strength, abrasion and mar resistance as well as acid, alkali, and solvent resistance, which is lacking in thermoplastic PU coatings. These performance criteria are essential for most industrial coatings. Therefore, with the aim to further increase final performances and working temperature range, the introduction of chemical crosslinker in the PU structure was also evaluated. Normal crosslinking in the urethane elastomer is reported to occur by reaction of terminal isocyanate groups with urethane groups to form allophanate linkage. Chemical crosslinking was also obtained and controlled by substitution of a trifunctional hydroxyl compound in place of the normal glycol CE.

Increasing the functionality of the polyether or polyester SS also increase the crosslinking concentration. Coatings may contain triols or higher-functional polyols [98–103], isocyanates with functionalities greater than two [104,105], NCO/OH ratios greater than one [101–103,106] or combinations thereof [101–103]. Peroxides and tri-functional CEs have also been utilized to chemically modify the hard domain cohesiveness using chemical crosslinks [98]. The introduction of crosslinker into the HS, SS or CE would reduce the mobility of HSs and cause a steric hindrance that reduces the ability of HSs to form hydrogen bonding [99,107]. Crosslinked PUs have shown great potential in the coatings sector due to their high T_g's, ability to form high quality films, good solvent resistance and ease of synthesis and processing. In general, higher crosslinking promotes phase mixing [108–111]. For example, Thomas et al. [108] altered the level of crosslinking by changing the functionality of the polyol (2.56–2.76) by adjusting the mix of the mono-functional polyether with multifunctional components. They suggested that increasing the polyol functionality increased the phase mixing. Therefore, in order to modify the properties of a segmented PU for a high performance coatings application, a calculated amount of crosslinker is needed. The presence of crosslinks by deliberate addition of a crosslinker or *in situ* generation due to the side product formation seriously hampers the phase separation and produces a polymer which shows both the phase-mixed and phase-separated behavior, depending on the concentration of crosslinker.

1.9.1. High solid coatings

Since the 1980s, the main challenge for solvent-borne coatings was to improve the solid content. One way to achieve this objective is to reduce the quantity of organic solvents so as to increase solid substances to obtain high solid coatings. The approach adapted so far has been to lower the viscosity of the binder, add reactive diluents or lower the viscosity of the polyisocyanate crosslinking agent [112]. Hydroxy-terminated polyester and hydroxy-functional acrylic resins are the most common polyols. They are crosslinked through the isocyanate group in 2K high solid coatings. Generally, polyesters can achieve higher solids, greater solvent resistance and better adhesion to metals than acrylic resins [113,114]. Approaches to obtain low VOC for traditional polyesters in the polyester–urethane 2K coatings include: (1) controlling molecular weight and MWD, (2) selecting the number of functional groups, (3) using hydrogen bond acceptor solvents, and (4) reducing the ratio of aromatic/aliphatic diacids [115,116].
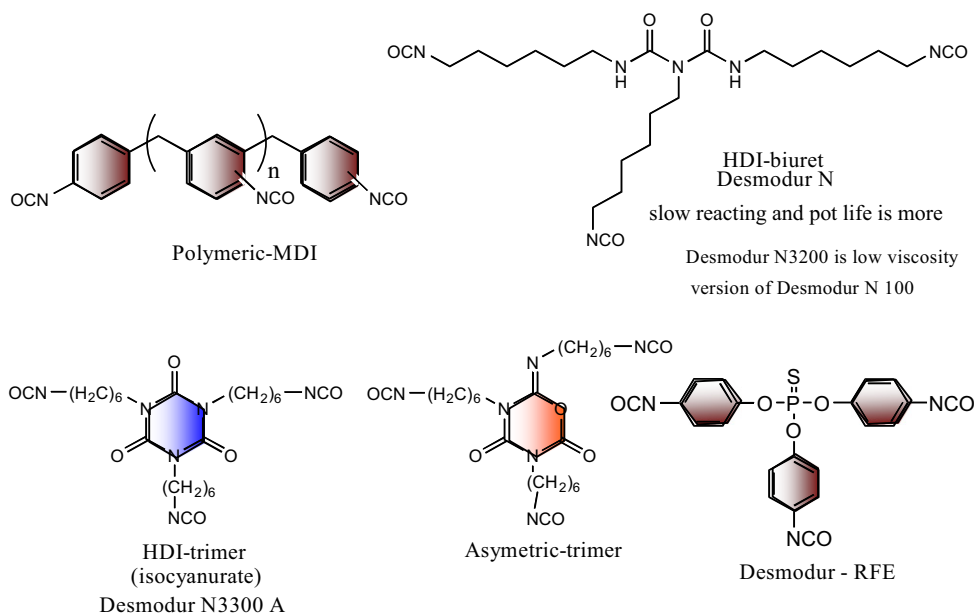
Some of the industrially important low viscous polyisocyanate crosslinker for making themoset high solid PU coatings are shown in Scheme 5. Ludewig et al. [117] reported the preparation of low viscosity allophanates by reacting compounds containing urethane groups with monoisocyanates. Most of the aliphatic polyisocyanates are made either from HDI or IPDI by catalytic routes yielding uretdiones (isocyanate dimers), isocyanurates (isocyanate trimers), and iminooxadiazinediones (asym. isocyanate trimers) [118,119]. Richter et al. [120] used trialkylphosphines and polyfluorides as dimerization and trimerization catalysts, respectively.

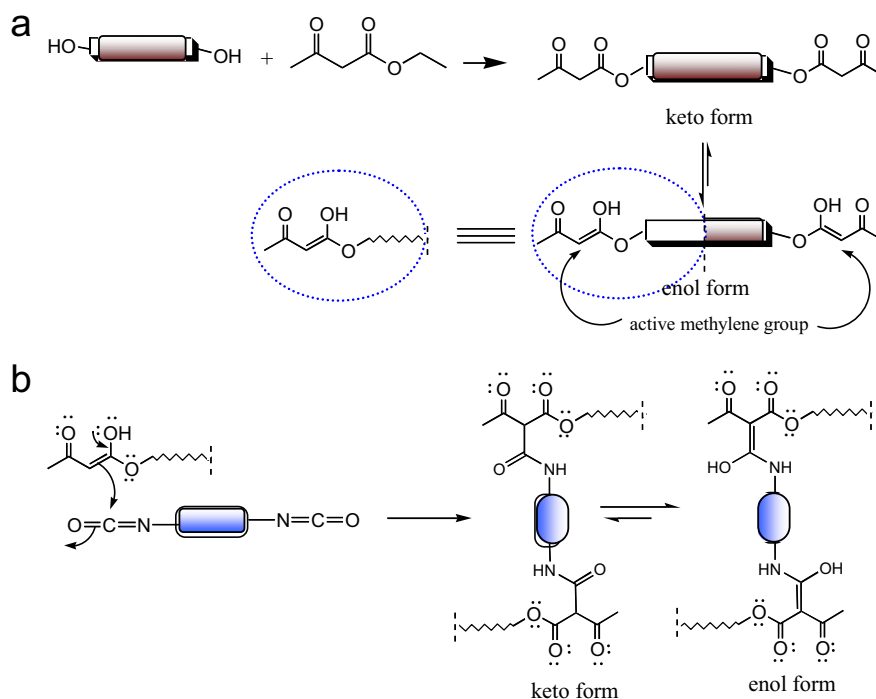### 1.9.2. Acetoacetylation and crosslinking with acetoacetate groups

In recent years, several studies have been carried out on the acetoacetylation of hydroxyl group containing polymers. Partial replacement of the hydroxyl groups in polyols (say polyester or acrylic polyols) with the less polar acetoacetate groups leads to an increase in solid content at the application viscosity as well as increase in adhesion due to chelate effect. Acetoacetylated or β-ketoester-incorporated polymers offer versatile crosslinking mechanism. This versatility results from the presence of two sites available for crosslinking reactions. These sites are the active methylene group and the ketone carbonyl group. β-ketoester groups are amphoteric and can participate in a variety of chemical transformations, which might be used to modify, or crosslink polymers. There are several routes by which acetoacetylated materials can be prepared of which transesterification route is preferred for the coating application [121–124]. Crosslinking reaction of the active methylene group in acetoacetylated polyols with diisocyanate (Scheme 6) produces additional crosslink with superior properties and weathering stability [125–128].

1.9.3. Moisture-cured polyurethanes (MCPUs)

MCPUs contains NCO-terminated PU prepolymer [129], which on cure with atmospheric moisture produce highly crosslinked networks. The cure reaction (Scheme 7) advances with time and

Scheme 5. Industrially important low viscous polyisocyanate crosslinker.

Scheme 6. (a) Acetoacetylation reaction of hydroxylated polyols and (b) crosslinking reaction of the active methylene groups in acetoacetylated polyols with diisocyanate.

produces crosslink networks by the diffusion of moisture and the nucleophilic attack and generation of primary amine that further react to produce urea bonds. Recently, 2,2′-different morpholino-containing substances such as dimorpholinodiethyl ether (DMDEE) as well as reactive amine catalysts were used as catalysts to speed up the moisture cure reaction [130].
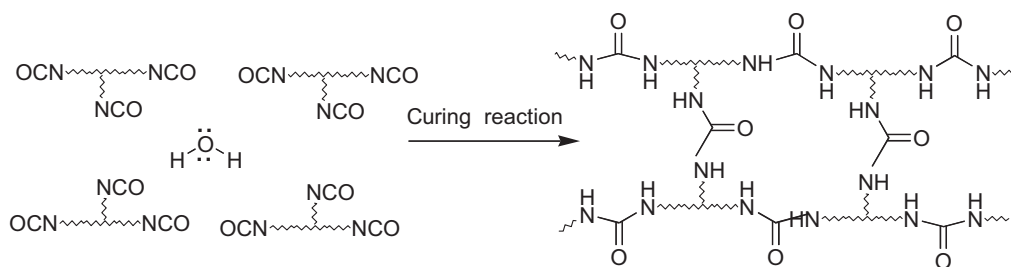
Scheme 7. The moisture curing reaction and film formation of NCO-terminated PU prepolymer [135, 138].

The major drawback of MCPU coatings is the formation of side products on storage and, if these reactions are significant, both pot stability and shelf life are expected to be dramatically affected. The presence of side products, for example allophanate and isocyanurate add branch points, increases the viscosity of the NCO-capped prepolymer and changes the onset of gelation during cure and thereby lower the storage stability of the product. The presence of additional HS material due to biuret and allophanate changes the hard domain volume fraction, and hence the interconnectivity of the HSs, to alter the thermal properties as well as adhesive behavior [131–138]. The advantages of MCPU coatings are their superior hardness, strength, stiffness and flexibility. Additionally, surface moisture completes the chemical reaction in MCPUs, and these materials adhere well to visibly damp surfaces as they penetrate into pores and tight crevices where moisture is usually present, to form strong chemical bonds. Since moisture is consumed in the process, the risk of blisters or a weak boundary layer caused by water trapped under the coating is greatly reduced.

A moisture scavenger is used to increase the stability of NCO-capped PU prepolymer. Monomeric monoisocyanates such as p-toluene sulfonyl isocyanate, a Zoldine MS Plus product based on oxazalidone, an Incozol 2-based oxazolane, an orthoformate-based additive known as OF, trimethyl orthoformate (TMOF), trimethyl orthoacetate (TMOC) and molecular sieves are commercially available moisture scavengers [139].

1.9.4. Polyurethane imide

Thermoplastic PU is well known to exhibit poor heat resistance that largely limits its use as engineering material. The thermal stability of PU depends on the chemical structure of its backbone, which consists of various HSs and SSs. For example, PUs produced from monomers with different diisocyanate structures present different thermal stabilities. There have been extensive research efforts on improving the thermal stability of PU, which led to great progress on its processing and application. A very effective way to improve the thermal stability of PUs is through chemical modification of their structures or introduction of chemical crosslinks. Chemical crosslinking produces a three-dimensional network structure and reduces macromolecular degradation to a negligible amount, even upto 300 °C. The other way of improving thermal stability or thermomechanical properties is to incorporate heterocyclic structures, such an imide, into the PU backbone by a one-shot technique or via a sequential method. Reaction of the isocyanate-capped PU prepolymer with an acid dianhydride is the method most often used to introduce an imide function into the PU backbone (Scheme 8) [97,140–143]. Pyromellitic dianhydride (PMDA), 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA), 3,3′,4,4′-sulphonyldiphthalic anhydride (DSDA) are widely used commercially available acid dianhydrides. A number of other methods have also been utilized:

1. An acid dianhyhydride was reacted with aminoethonal to give a hydroxyl-terminated imide monomer, which was then reacted with isocyanate-terminated PU prepolymer.
2. Reaction of isocyanate-terminated PU prepolymer with aromatic diamines and dianhydride to prepare PU-containing imide groups in the backbone.
3. Intermolecular Diels–Alder reaction of 4-methyl-1,3-phenylenebis (2-furanylcarbamate) with various bismaleimides is also reported to give PU-imides [144,145].
4. Additional methods include the use of polyamide acid [146], diimide-dinaphthols [147], and imidization of blocked PU prepolymer [148,149].
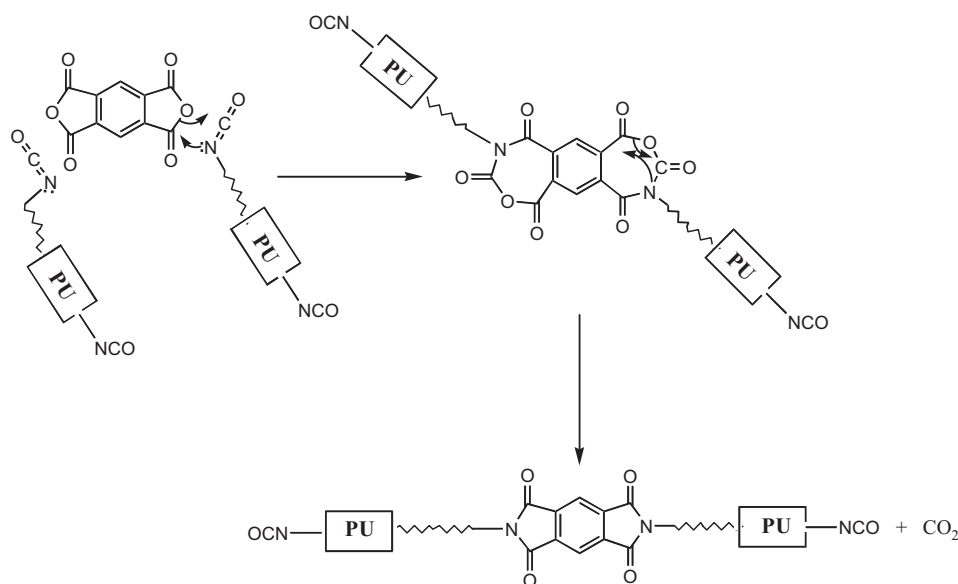
Scheme 8. PU-imide formation by the reaction of isocyanate-terminated PU prepolymer with PMDA.

1.9.5. Polyurea coatings

Polyurea coatings cure rapidly and therefore may be used in an aggressive environment, where high curing speed is required (e.g., an oil pipeline). The basic chemistry of polyurea coatings is the reaction of amine-functional reactants with an isocyanate-functional compound to produce a polymer with urea links. In many ways, a polyurea is very similar to a two-component PU. The usual procedure for manufacturing two-component PU coating is to have a polyol as the A side of a formulation. The B side, sometimes called the hardener or curing agent, is a diisocyanate or oligomeric isocyanate. On the other hand for polyurea coatings, the A side is an oligomerised amine or blend and B side is an isocyanate oligomer(s) or quasi-prepolymer. Polyurea coatings are manufactured by reacting a large excess of isocyanate capped oligomer with an amine or amine blend, and more usually with an amine-capped oligomer. The disadvantage of polyurea coatings is their high reactivity, and therefore a short pot life [150–152]. In order to increase the pot life of polyurea coatings, Wicks and Yeske [153,154] developed a methodology to slow down or reduce the reactivity and remove the need for plural spray equipment. It requires making the amines secondary rather than primary, sterically hindering them and generally making the molecule more bulky, thus altering the kinetics [155]. This can be achieved by making a polyaspartic ester by means of the Michael addition reaction. The reaction is shown

schematically in Scheme 9(a). The hindered amine species has a higher viscosity than the amine. One way to reduce the viscosity is to utilize a low-viscosity oxazolidine. Oxazolidines are useful species that may be used in both one and two-component PUs as moisture scavengers, reactive diluents and latent hardeners. Hydroxyethyl oxazolidine shown in Scheme 9(b) can be converted to a urethane bis-oxazolidine (high viscous) or a carbonate-bridged low viscous product [156].

1.9.6. Glycidyl carbamate resin in PU coatings

Resins containing glycidyl carbamate group have the potential to provide PU performance combined with epoxide reactivity. The synthesis and properties of difunctional glycidyl carbamates-based PU coatings have been reported [157–161]. Glycidyl carbamate functional oligomers such as biuret glycidyl carbamate (BGC), isocyanurate glycidyl carbamate (IGC), hexamethylene glycidyl carbamate (HGC) were synthesized from different polyfunctional isocyanate oligomers and glycidol. The oligomers were mixed with different amine crosslinkers at varying stoichiometric ratios and cured at different temperatures.

1.9.7. UV-curable PU coatings

UV-curable PU coatings represent a class with no or little VOCs. This technique is based on the polymerization of an unsaturated resin system, induced by incident radiation, to obtain a
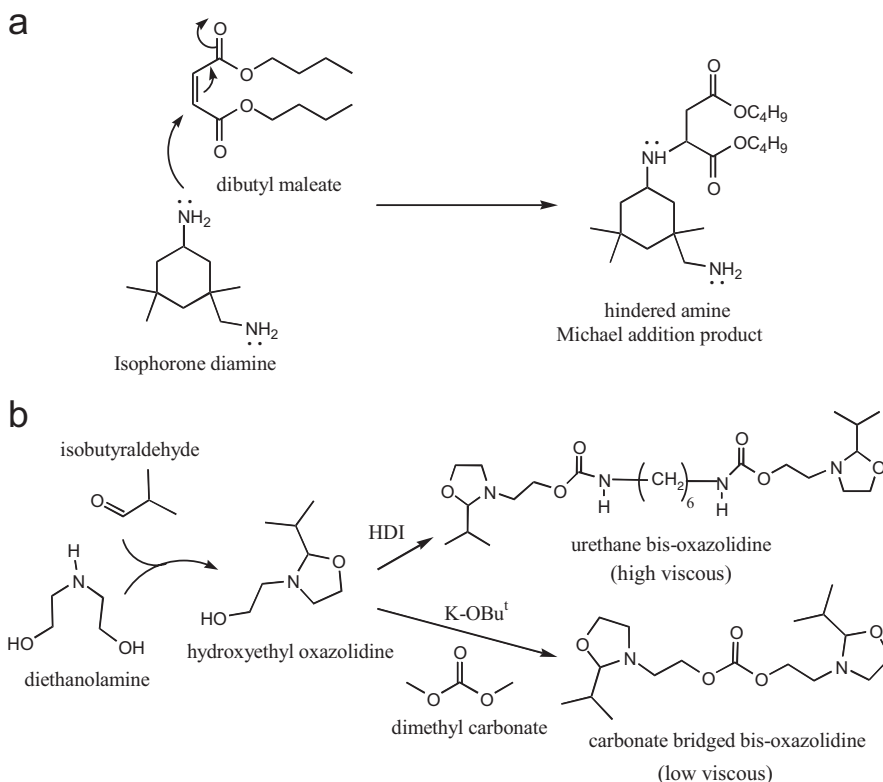
Scheme 9. Preparation of hindered amine and oxazolidine derivative for polyurea coatings [156].

three-dimensional network. During the cure reaction, the liquid polymer transforms within few seconds into a solid having rubbery or glassy properties at room temperatures. It has been widely applied in many industrial fields for manufacturing, decoration, and protection of different materials. In fact, there are many advantages to produce coatings by UV-curing, such as: (i) low energy requirement; (ii) very fast and efficient polymerization; (iii) cure selectively limited to the irradiated area; and (iv) no environmental pollution by VOC. The disadvantages are the oxygen inhibition and the needs for a UV source. Molecular oxygen at the coating surface is effective at terminating polymerization, which results in low molecular weight, tacky films. A number of methods e.g., use of oxygen scavenger (e.g., tannin, carbohydrazide, etc.), high radiation intensity or initiator concentration, etc., have been used in the recent past to overcome the oxygen inhibition effect [162]. Sometimes, the addition of a free amine such as methyl diethanol amine (MDEA) has a beneficial effect on the UV cure process, as they are able to donate a proton to hydrogen abstracting photoinitiators, such as benzophenone.

The resultant amine free radicals initiate polymerization in the UV cure process. In addition, amines can scavenge atmospheric oxygen at the coating surface.

The main components of UV curable formulations are an oligomer (e.g., acrylated PU as shown in Scheme 10), a reactive diluent and a photoinitiator [163]. The reactive diluent used not only to control the formulation viscosity, but also to control the cure speed and extent of polymerization, as well as the properties of the cured film. Multifunctional acrylates are the preferred reactive diluents in radiation-cured systems because of their rapid curing rates and low prices. The nature of the resultant cured films depends not only on the properties of the components, but also on the photopolymerization kinetics, i.e., the photopolymerization rate and final unsaturation conversion. The irradiation flux, temperature, sample thickness, photoinitiator concentration, and reactive diluent content for a given resin affect the photopolymerization kinetics to a large extent and, therefore, the physical and mechanical properties of the cured films. Cationic photopolymerization provides
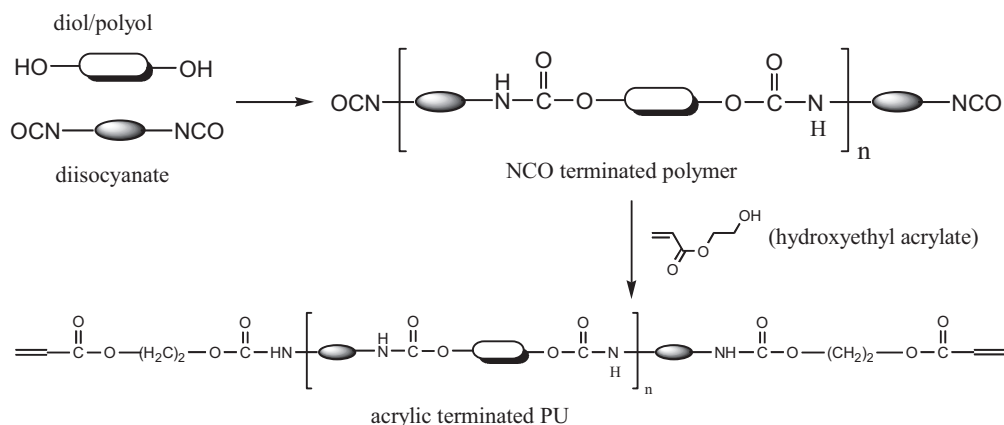
Scheme 10. Preparation of acrylic-terminated PU prepolymer for UV cure coatings.

coatings with lower shrinkage, better flexibility, lower VOC and less sensitivity to oxygen [164] than is usual with free radical photopolymerization.

1.9.8. Waterborne coatings

The increase interest in waterborne coatings is due to its low VOC content. Waterborne coating technologies require new types of resins for binder dispersions and additives to fulfill high quality requirements [165,166]. An aqueous PU dispersion (PUD) is a binary colloidal system in which the particles of PU are dispersed in continuous water phase. The particle size tends to be about 20–200 nm, and the particles have a high surface energy. This results in a strong driving force for film formation after water evaporation. Usually, PU polymers are not soluble in water and the degree of hydrophilicity is one of the key factors determining the particle size distributions in the PUD. The shelf life colloidal stability of PUDs is influenced by their particle size distribution. Therefore, a special treatment or structural modification is necessary for the polymer to be dispersible in water. Generally, aqueous PUDs can be prepared by incorporating hydrophilic groups into the polymer backbone or by adding a surfactant. The former material known as a PU ionomer in which the ionic groups act as internal emulsifiers. Therefore, waterborne PU ionomers consist of PU backbones with a minority of pendant acid or tertiary nitrogen groups, which are completely or partially neutralized or quaternized, respectively, to form salts.

Various processes have been developed for the preparation of aqueous PUDs. In all of these processes, a medium molecular weight polymer (the prepolymer) is formed by the reaction of suitable diols or polyols (usually macrodiols such as polyethers or polyesters) with a molar excess of diisocyanates or polyisocyanates in the presence of an internal emulsifier as first step. The emulsifier is a diol with an ionic group (carboxylate, sulfonate, or quaternary ammonium salt) or a non-ionic group [poly(ethylene oxide)] is usually added to allow the dispersion of the polymer in water. The critical step in which the various synthetic pathways differ is the dispersion of the prepolymer in water and the molecular weight buildup. The most important processes are the acetone process, pre-polymer mixing process, melts dispersion process and ketimine process [167–172].

Aqueous PUDs are of three types; non-ionic, cationic and anionic depending upon the type of hydrophilic segments present in the PU backbone. Depending on the type of ionic species, a minimum ionic content is required for the formation of a stable PU ionomer. The interaction between ions and their counter ions is responsible for the formation of stable dispersion. The ion-dipole interaction between the ionomer and dispersing media (e.g., water) results in the formation of a salvation sheath, where the ionomer properties depends on the degree of neutralization and content of ionic component.

1.9.8.1. Cationic PU.
According to Lorenz et al. [173] Lorenz and Hick [174], cationic PU ionomers in water are stabilized because of the formation of electric double layer. The SS of cationic PU is hydrophobic and the HS with NHR_2^+ is hydrophilic. Therefore, the molecular chains of cationic PU can self-organize to micelles when dispersed in water, with positively charged hydrophilic groups at

the surface and hydrophobic groups concentrated in the micelle interior. A electric double layer forms around the micelles, which undergo Brownian motion, stabilized against intermicelle aggregation by electrostatic forces. At the same time, there are hydrogen bonds between the hydrophilic groups and water molecules, and then the particles are surrounded by a layer of water molecules making a solvation sheath. This phenomena hinder the aggregation of particles [175]. For the preparation of a cationic PUD, 3-dimethylamino-1,2-propane-diol can be used to disperse the medium after neutralizing with a weak protonic acid in water.

1.9.8.2. Anionic PU. Dimethylol propionic acid (DMPA) is commonly incorporated into PU back-bones because it is very effective for water disper-sion in the subsequent neutralization reaction with triethylamine (TEA) [176–178]. The carboxylic ion of DMPA in the polymer is hydrophilic and serves as an anionic center as well as internal emulsifier. Carboxylic ions not only stabilizes aqueous PUDs, but may also become the curing site. The carboxyl groups in PUDs provide charges to the surfaces of PU micelles (particles), thereby causing repulsion between PU particles resulting in uniform PU particle size distribution in the water phase. Sche-matic diagrams of micelles formed by (a) cationic and (b) anionic PU ionomers in water are shown in Fig. 1. Because of the hydrophilic properties of the carboxyl group, these PUs become self-emulsified (or water-reducible) in the water phase. Such conventional aqueous-based PUs have a disadvan-tage similar to that of a polymer surfactant, in that

they exhibit high hydrophilicity after drying into a film. Therefore, the weight percent of DMPA used in the prepolymer not only influences the particle size and stability of the dispersion, but also the hydrophobicity of the coatings. For example, the use of higher amount of DMPA results in a smaller average particle size and high hydrophilicity in the film, which reduces the water resistance of the coating. Therefore an optimum amount of DMPA should be used for making a high performance coating.

Improvements in aqueous-based PUs are nor-mally achieved with post-curing reactions or poly-mer hybridization, which enhances the molecular weight, crosslinking density, and performance properties. A convenient post-curing reaction of aqueous-based PUs is mainly based on the carboxyl groups reacting with an aziridinyl curing agent when the pH drops below 6.0 or upon air drying [179,180]. The reaction of carboxyl group with a multi-aziridinyl curing agent results in amino ester linkage formation between polymers [167,180,181]. The carboxylic ion containing aqueous PUD and a multi-aziridinyl latent curing agent may be formu-lated as a self-curing PU system. Its self-curing reaction takes place at ambient temperature during the drying process or when its pH value dropped below 6 [180]. Ethyleneimine, also called aziridine, reacts not only with carboxylic or hydroxyl group containing compounds, but also reacts to form its homopolymers under an acidic condition at ambi-ent temperature. However, it remains stable in an alkaline solution system. During the past years, aziridinyl compounds have been used for several
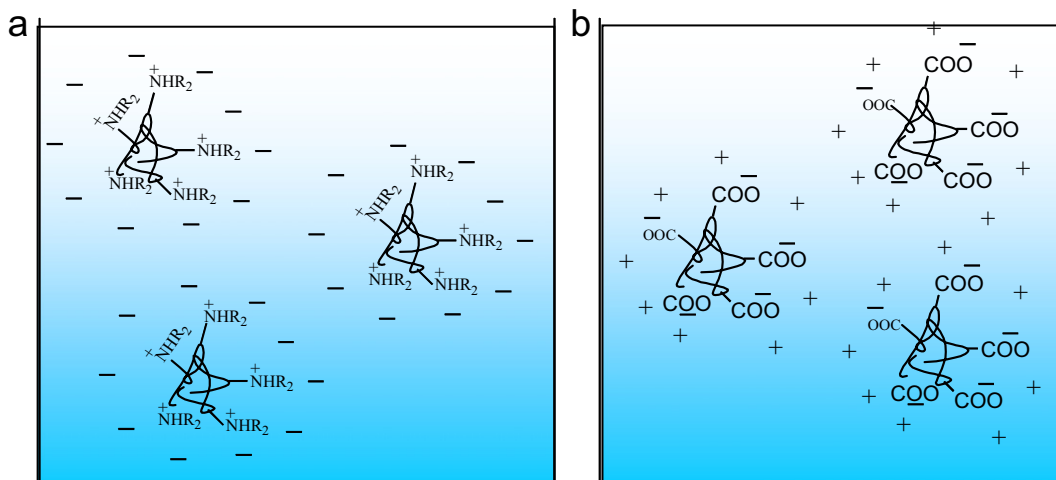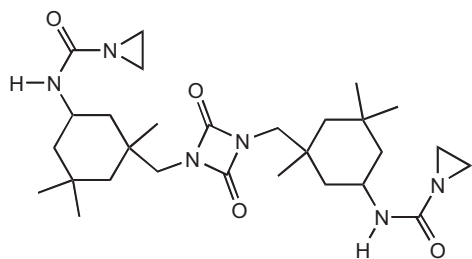

Fig. 1. Schematic diagram of micelles formed by (a) cationic and (b) anionic polyurethane ionomers in water [178].

Scheme 11. IPDI/uretedione aziridinyl derivative [183].

reported applications in coatings [167,182] because of their unique properties. Di- or triaziridinyl compounds are water soluble and readily mix with anionic aqueous-based PUDs in various ratios. The resultant single-pack dispersion is stable in a tightly sealed container for more than 3 months, without any sedimentation [180,181]. A new curing agent, IPDI/uretedione aziridinyl derivative (UAD) (Scheme 11) was prepared by Lai et al. [183]. Initially, the authors prepared dimer of IPDI, and later on the NCO groups of the dimer were reacted with aziridine. A more discussion on aziridinyl curing agent will be found in Section 4.2.

The ionic content, degree of neutralization [184–188], type of ionic component [184], counter ion used [177,184,188], molecular weight of SS [187,189] and the amount of cosolvent [170] used have considerable effect on the particle size of PU emulsion for both cationic and anionic PUs.

1.9.9. PU non-aqueous dispersion

Polymerization in a non-aqueous dispersion was found to be an effective alternative route for the preparation of uniform polymeric particles in the 1–10 μm size range [190]. Typically, polymerization in a dispersed medium starts with the monomers partially or totally soluble in the organic phase, and results in the formation of an insoluble polymer in the form of stable colloidal dispersion. Polymer microspheres with very narrow size distribution can be prepared in appropriate conditions. The role of the steric stabilizer is crucial in this procedure as it not only provides stability to the resultant particles, but also affects the final particle size and size distribution as well as the polymer molar mass. Usually, amphipathic polymers—block or graft copolymers—are effective stabilizers [191,192]. These stabilizers strongly adsorb onto the forming particle surface by virtue of the insolubility of one of their block units (also called the anchor part), and stabilizer desorption from the final material may

cause irreversible changes, such as the loss of the stabilization of the particles. One possibility to avoid this major drawback is to use reactive stabilizers or macromonomers that remain attached to the final particle. PU particles formed by suspension polymerization in a non-aqueous medium have been reported by Yabuuchi et al. [193]. According to their work, PU microspheres in the 5–50 μm size range were obtained by condensing oligomeric glycols with diisocyanates or isocyanate-terminated prepolymer in an organic medium, using poly(ethylene oxide)-b-poly(dimethylsiloxane) block copolymer as the steric stabilizer.

1.10. Selection and modification of PU coatings

In modifying the backbone structure of PU coatings, it is necessary to consider the end use for the coating and the cost of modification. The following factors must be considered while selecting a material in a specified environment:

1. The properties of the modified PU coating such as hardness, strength, stiffness, thermal stability and expansion coefficient.
2. The resistance of the coating towards mechanical, thermal and chemical stress during service.
3. The compatibility of the coating and the substrate over the temperature range of expected application. This includes minimizing thermal stresses (by matching thermal coefficients) and providing good coating–substrate adhesion.
4. Ultimately, whether or not a particular coating will be used depends on the trade-off between the benefits to be gained and the additional cost to be incurred. When the application is critical and the consequences of failure are disastrous, higher costs are justified, particularly when there is no other alternative.

Additionally, for a better protection of the substrate, knowledge of the following parameters is of paramount importance: coating application method, composition, thickness, hardness, coating–substrate adhesion, friction coefficient, wear resistance, Young's modulus, thermal expansion coefficient, heat conductivity, density, specific heat of both coating and substrate and information on residual stresses to assess the overall stress level exhibited by the coated body [194].

2. Dendrimers and HBPs

The most robust way to improve the mechanical properties of PUs is the chemical bonding of the PU chain with functionalized dendritic polymers through crosslinking. Even in small amount of such a molecular architecture is sufficient for manifold increase in tensile strength, with only a reasonable increase in cost. These types of polymers are among the most exciting ones developed in the recent past, and have shown a new dimension in coating research and development. The driving force behind the coatings R&D research in functionalized dendritic polymers is the differences in the properties of branched structure compared with their linear analogs. Dendritic polymers exhibit lower viscosities, are non-entangled globular structures, and often have increased solubility in various solvents and good rheological behavior. Their high functionality provide multiple covalent branching sites for crosslinking reaction and results in increasing the film's structural integrity, with excellent chemical resistance, durability and good mechanical properties, while maintaining low VOC in the coating formulation. For example, the presence of hydroxyl or amino functionality at the terminal unit can be used in small proportion to crosslink an NCO-terminated PU prepolymer [195,196]. Dendritic polymers comprise monodisperse dendrimers and polydisperse HBPs. The special macromolecular structures of dendritic polymers, such as, manifold of end-groups, compact molecular shape, and decreasing chain entanglement has resulted unique and widely different physical and chemical properties compared to the conventional linear counterparts. The nature, structure and concentration of these end-groups have a large influence on the properties. The possibility to produce specific end-groups or modify the structure of the end-groups can be used as a tool to adjust or modify the properties of the polymer with tailored crosslink densities and hydrophobicity for specific coating applications [197–201]. In recent years, a number of excellent reviews [197,202–205] have been published that describe the preparative methods, properties and difference between dendrimers and HBPs. Dendrimers are made in sophisticated fashion by the multiple replication of a sequence of two steps, and therefore are monodisperse, symmetrical, layered macromolecules and perfectly built onto a core molecule with a high degree of branching (DB). Dendrimers consists of three distinct areas: the polyfunctional central core or focal point, which represents the center of symmetry, various well-defined radial-symmetrical layers of repeating units (also called generations), and end-standing groups known terminal groups [206].

Dendrimers can be synthesized according to several distinct synthetic approaches such as divergent or convergent synthesis using AB_2 or AB_3 building blocks and multistep, time-consuming procedures involving protection, coupling and deprotection cycles resulting in low yields, leading to difficulties and a tendency for high cost in large-scale preparation [207]. These factors make dendrimers less attractive for large volume coatings applications. On the other hand, HBPs are polydisperse, not fully reacted at every repeating unit, have lower DB, an irregular structure with a mixture of branched and linear repeat units, but possess many similar properties of dendrimers and can be produced in large scale at a reasonable cost. The physical nature of HBPs depends on their glass transition temperature (T_g), e.g., brittle or soft for a high or low T_g, respectively, as usual [208,209].

In order to generate such highly branched structures, two distinct synthetic strategies have been widely employed. The first one is a step-wise process, in which the macromolecules are built-up one layer at a time, either using a convergent or divergent strategy to generate highly branched structures like dendrimers or starburst polymers and the other is the self-condensation of an AB_x type monomer (where $x \geqslant 2$), which produces incomplete branching. The one-step synthetic approach of HBPs using AB_x type multifunctional monomers is the most convenient way to improve coating properties, since structural perfection is not a strict prerequisite for most coating applications. A detailed structural investigation of HBPs reveals three different types of repeating units as illustrated in Scheme 12. The constituents are dendritic units (D) having all the groups reacted, terminal units (T) having the two B-groups unreacted, and linear units (L) having one B group unreacted. The linear segments are generally described as defects. The DB in AB_2 systems is given by DB = (2D + L)/(2D + L) [210].

2.1. Convergent and divergent synthetic methods

The core first (divergent) or core last (convergent) synthetic strategy of protection, condensation and deprotection cycles of AB_n-type monomers
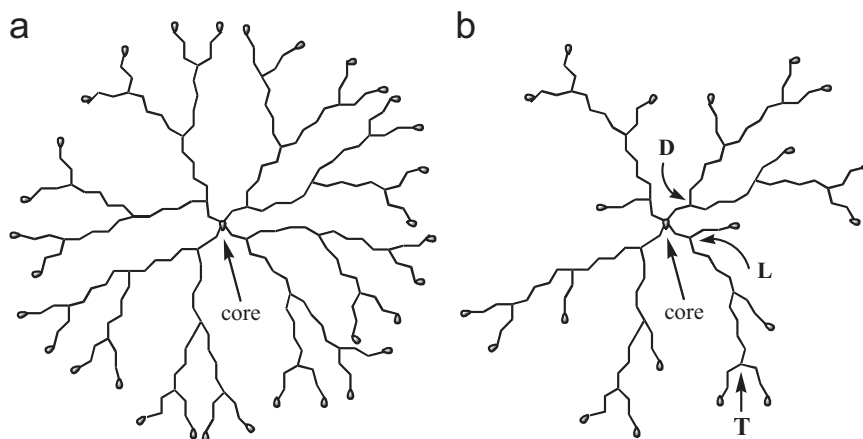
Scheme 12. Schematic structures of (a) dendrimers, and (b) hyperbranched polymers.

generates dendritic structures. The divergent methodology involves *in situ* branch-cell construction in stepwise, iterative stages around a desired core to produce mathematically defined core-shell structures with core molecule is allowed to grow outword. On the other hand, the convergent method use the inward growth of the periphery of the molecule to afford building blocks (dendrons) that are subsequently coupled to a branching monomer through reaction of a single reactive group located at its focal point. Outstanding control over growth, structure and functionality can be produced by convergent methodology [211]. Scheme 13 illustrates dendrimer growth by both the divergent and the convergent methodologies.

Dendrigraft polymers are one more class of dendritic polymers that combines the features of dendrimers and HBPs, and their synthesis follows a generation-based growth scheme similar to dendrimers, but use polymeric chains as building blocks. Since this review is focused on cost-effective eco-friendly methods of improving the performance characteristics of PU coatings, and that involves the use of HBPs with terminal functionality; further discussion of dendrimers and dendrigrafts is beyond the scope of interest here, and readers can refer to Refs. [197,212,213] for a detailed discussion on dendritic polymers and Refs. [214,215] for dendrigrafts.

2.2. Synthetic approaches of HBPs

Despite the numerous recent developments in the field of HBPs, the main challenge lies in the
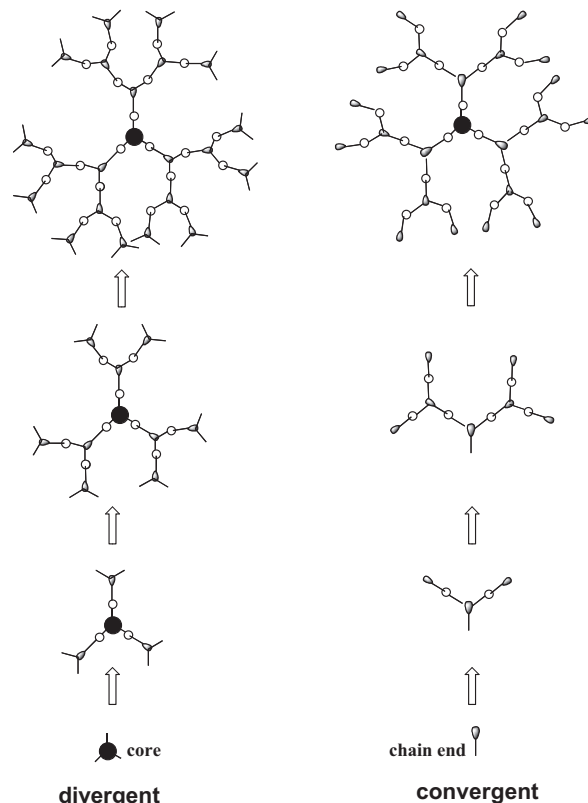
Scheme 13. Representation of dendrimer growth by the divergent and convergent methods [211].

development of synthetic strategies to prepare cost-effective, functionalized HBPs using available commercial monomers. The general HBP synthesis involves the self-polycondensation of AB_n-type

monomers, which have one A and n B functional groups, where A group of a monomer may react with B group of another monomer, but neither A nor B may react with themselves, so that the HBP will have B endgroups. In the statistical case, the DB is 50% as calculated, for example, according to Hawker et al. [216]. The commercial unavailability of most of the AB_x-type monomers or synthesis of these monomers sometimes requires a multistep organic methodology that takes longer time have made difficulties for large scale industrial applications. To meet the challenge, novel alternative approaches were developed and are based on the following design considerations:

1. $AB_2 + B_x$,
2. A_2 and B_3,
3. $A_2 + B_2B^*$,
4. $A_2 + CB_n$ {when a diisocyanate having large reactivity difference (say, IPDI) between two functional groups toward hydroxyl groups, then this method should be designated $AA^* + CB_n$ [217]},
5. $AA^* + CB_2$,
6. $AB + CD_n$.

Most of the HBPs studied were obtained through polycondensation of AB_2 and B_x monomers, that is, with equal reactivity of B functions. However, there are an increased interest in $A_2 + B_3$ systems [218–220] because a number of A_2 and B_3 monomers are commercially available at reasonable cost. Recently, Jikei et al. [219], Emrick et al. [220] and Fang et al. [221] and coworkers independently developed an approach to produce HBPs from commercially available A_2 and B_3 monomers. However, direct polycondensation of A_2 and B_3 monomers would generally result in gelation. The critical conversion of the A functional group for gelation can be calculated to be 0.87 when equimolar amounts of A_2 and B_3 monomers are reacted [219]. In the early 1950s, Flory [222] pointed out that the polymerization of AB_x monomers proceeds without gelation. He proposed $A_2 + B_3$ systems without any chemical selectivity between the reaction partners, for synthesizing HBPs [223]. For this system, a AB_2 molecule would be formed as an intermediate and accumulated in the system if the first condensation step of A_2 and B_3 molecules is faster than the following propagation steps. Careful controlled reaction condition and monomer concentration may result in soluble HB polymers from

the condensation of AB_2 molecules, but otherwise the system gels [222,224]. The $A_2 + B_2B^*$ or $AA^* + B_2B^*$ approaches (also reported as $A_2 + CB_2$ approach) have recently been explored where the selectivity and reactivity of one A^* function toward a selective B^* function was enhanced. Now one may ask the question: what is the difference between A_2 and AA^* monomers? The answer definitely comes from the concept of symmetry and asymmetry in structures. For example, diisocyanates like monomeric MDI, having a center or plane of symmetry (C_{2V}-symmetry) can be considered as A_2-type monomer. This type of structure having no selectivity in reaction with any diols and the reactivity of both the NCO groups in monomeric MDI is the same. On the other hand, asymmetric diisocyanate IPDI, which contains one primary and a secondary NCO groups with unequal reactivity is a AA^*-type monomer. An $A_2 + CB_n$ approach from a diisocyanate (A_2) and a dihydroxy amine monomers (CB_2: where C is more reactive than B) was used as an improved method for the preparation of HBPs by Gao and Yan [225,226]. The reaction produces $A(AC)B_n$, i.e., an AB_n-type intermediate *in situ*. Another important example includes the formation of hyperbranched poly(urea-urethane)s, as reported by Bruchmann et al. [217], Bruchmann and Schrepp [227]. For $AA^* + CB_n$ approaches, though the method works without protection of groups and opens up the use of a versatile and simple approach toward HBPs, it has some drawbacks. For example, the reaction of a diisocyanates (AA^* type) with alkanolamine (CB_n) is sensitive to different reaction conditions and gelation may take place when the concentration of the reagents is high in the reaction solution, as well as when the temperature is raised significantly above 60 °C. In order to overcome these demerits, Gao and Yan [225,226] applied long reaction times (5–10 h at low temperature, and as long as 1440 h for some aliphatic isocyanates) and Bruchmann and Schrepp [227] kept the starting mixture for about 1 h at −5 °C, and then the temperature was raised and when necessary a catalyst was added to speed up the reaction. Abdelrehim et al. [228] worked on the dependence of the polymer properties of hyperbranched poly(urea-urethane) by the $AA^* + CB_2$ approach on changes in reaction conditions. A slightly different approach, starting from two molecules of diisocyanate (B_2) and one molecule of a triol (A_3), the $A_3 + (B_2)_2$ leads to an AB_2-type building block, which bears two isocyanate and one

hydroxyl group [217]. The serious limitation for producing HBPs from isocyanates is its self-reactivity and reactivity towards water to form side products. To overcome these limitations, researchers used a protection/deprotection methodology and the choice of protecting group and, consequently, the speed of deprotection need to be chosen carefully to minimize side reactions. Side reactions can be avoided by the use of modified self-crosslinking isocyanates. While the isocyanate group is blocked with an isocyanate blocking agent, e.g. - a ketoxime, it is possible to deprotect the alcohol functionalities completely without any risk of a side reaction between isocyanate and water. Upon heating, the isocyanate group is regenerated and reacts to yield a hyperbranched structure. Scheme 14 shows the structure of different monomers for the preparation of HBPs [112,229,230].
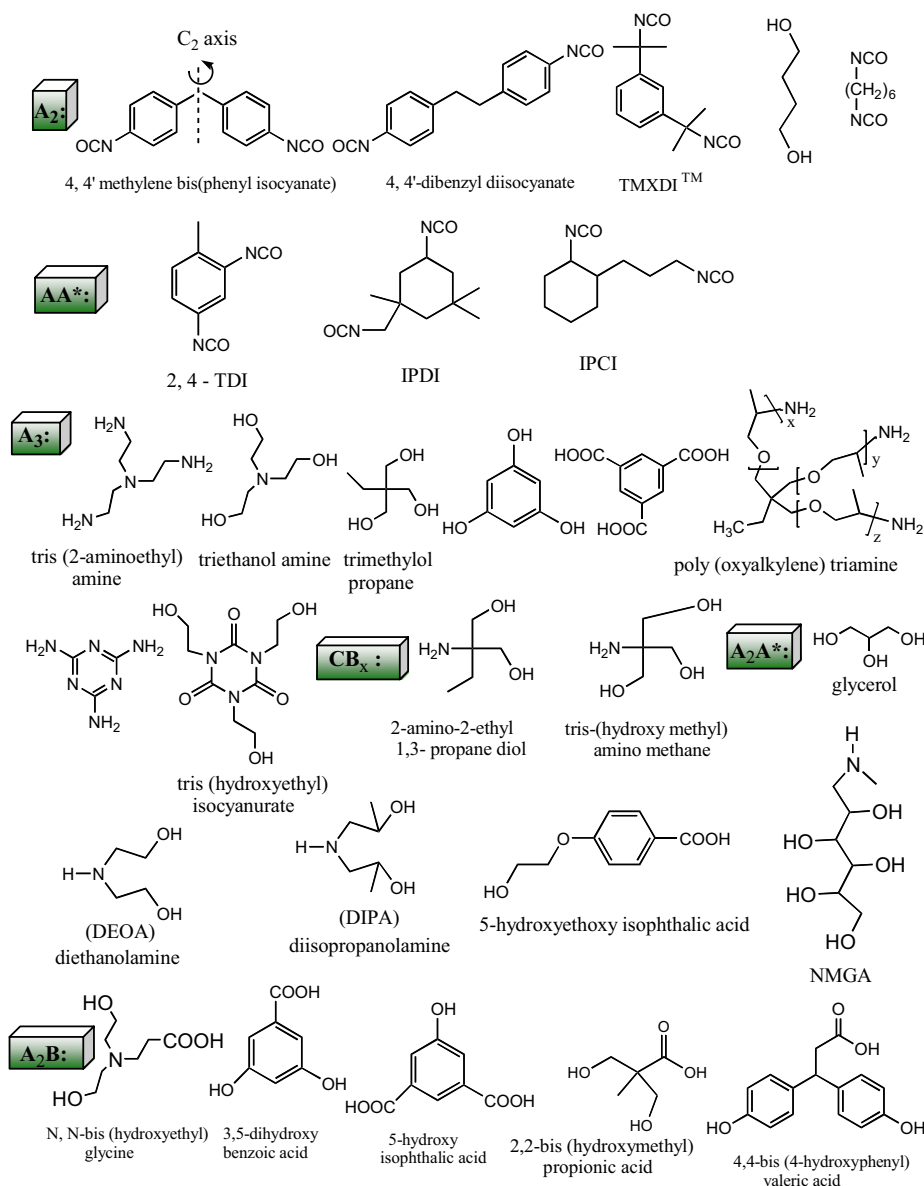
2.3. Hyperbranched polyols

A wide range of methodologies for constructing HB polyester polyols from AB_x monomers ($x \geqslant 2$) have been explored, where A and B are hydroxyl and carboxylic acid moieties, respectively. The routes involve thermally driven homo-polymerization or activation of either A or B functionalities. Thermally driven polycondensation of AB_2 monomers is a common method that uses *p*-toluene sulfonic acid (*p*-TSA) or an organometallic reagent as a trans-esterification catalyst. It has been reported that the properties of low VOC-coating formulations containing HB polyol are superior to linear polyols [231]. A systematic investigation of HB polyesters as curing agents has been developed in Sweden [232,233]. Several dendritic/HB polyester polyols are commercially available from Perstorp Polyols Inc. Perstorp AB, Sweden, with the trade name 'Boltorn', and are easy to synthesize [234]. For example, HB aliphatic polyester prepared from 2, 2-bis(methylol) propionic acid and 2-ethyl-2-(hydroxymethyl) 1,3-propanediol was used as crosslinking agent in a resin coating formulation. Ziemer et al. [235] prepared HB polyester from 4,4-bis (4-hydroxyphenyl) valeric acid in an A_2B approach (Scheme 15a). Others have proposed the batch copolymerization of a B_n core molecule with a AB_2 monomer as an improved method to control the polycondensation reaction [198]. Examples of such an AB_2-monomer/B_n-core approach include the preparation of aliphatic HB polyester synthesized from 2, 2-bis(methylol) propionic acid as A_2B

monomer and pentaerythritol [236] (Scheme 15b), triethanol amine (Scheme 15c) and trimethylolpropane [237,238] as core molecule. The HB polyester prepared from 4,4-bis-(4'-hydroxyphenyl)pentanoic acid and trimethylolpropane as core molecule was used by Pavlova et al. [239] for PU coatings preparation. The commercially available (Perstorp Polyols Inc.) hydroxyl-functional HB polyester of the third generation (G3) prepared from 2,2-bis(methylol) propionic acid (A_2B) and ethoxylated pentaerythritol (core) is shown in Scheme 16a. An $A_2 + B_3$ approach includes the synthesis of HB aliphatic polyester polyol from adipic acid and glycerol [240]. A number of synthetic routes recently developed that emerge from the combination of the multi-branching polymerization of glycidol with well-established epoxide polymerization techniques, leading to unprecedented polymer architectures is shown by Frey and Haag [241] and Sunder et al. [242] and Xinling et al. [243] and Xiaoying et al. [244]. The synthesis of hyperbranched polyglycidol (HPG) involves the cationic ring-opening polymerization of glycidol, by glycerol in the presence of boron trifluoride diethyl etherate catalyst in chloroform and the reaction was carried out in nitrogen atmosphere at 25 °C for more than 3 h (Scheme 16b).

The disadvantage of HB polyester polyols is their limited solubility. In order to make them soluble and processable, chemical modification of the hyperbranched cores by substituting a controlled fraction of the terminal hydroxyl groups with hydrophobic alkyl chains is shown as an effective method for controlling the amphiphilic balance [245]. For example, Ming et al. [246] have replaced 50 percent of the available –OH groups of partially soluble HB polyester prepared from 2,2-bis(hydroxymethyl) propionic acid (AB_2 monomer) and pentaerythritol (core molecule) with $C_7H_{15}COO$– groups. The modified product was a viscous liquid at room temperature and completely soluble in organic solvents like THF, etc.

2.4. Hyperbranched polyamides
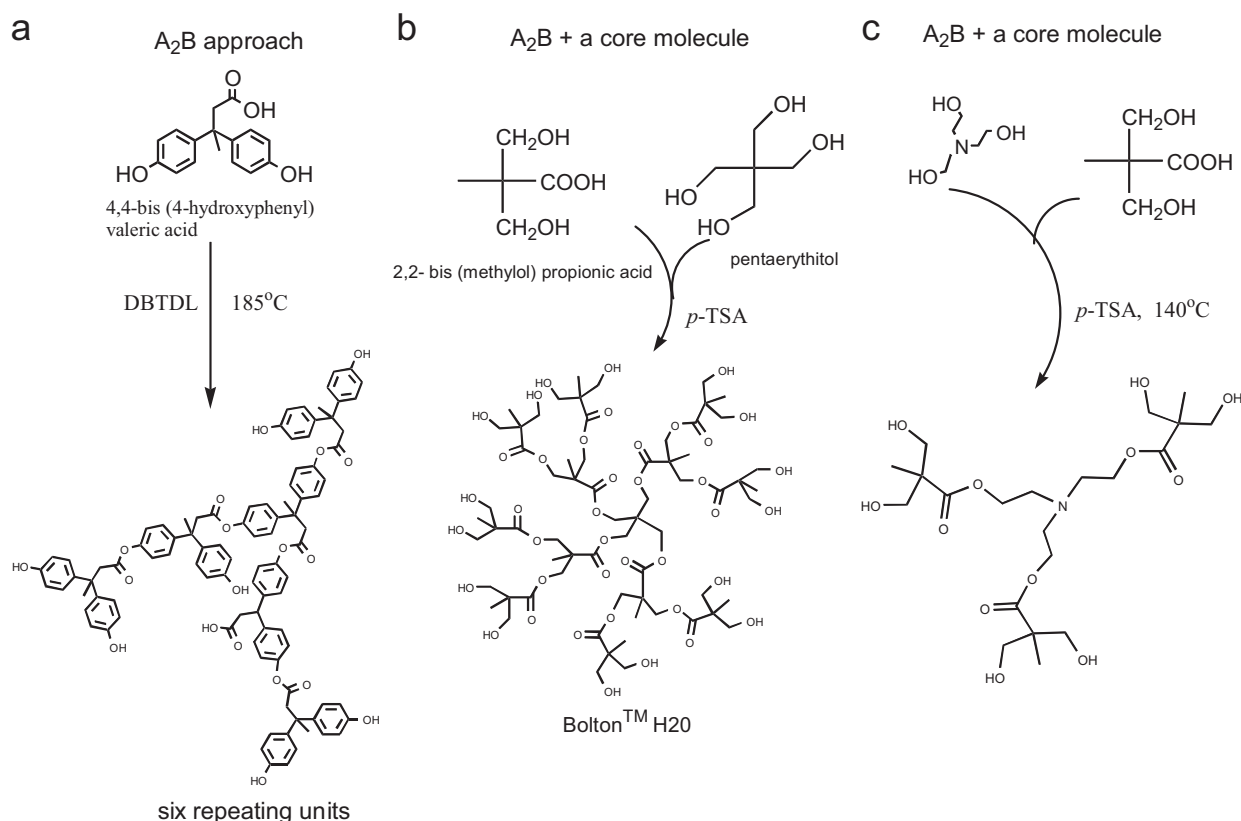
Use of hyperbranched polyamides having a large number of amine functional groups as crosslinking agents will result in polymers containing both urethane and urea groups. It is envisaged that such crosslinked polymers will show novel properties because the crosslinking agent used is in a polymeric form [247–249]. Yang et al. [249] reported the preparation of HB polyamide based on novel AB_2

Scheme 14. Different monomers for the synthesis of HBPs.

monomer. Nasar et al. [247] prepared hyperbranched polyamides having a low molecular weight and narrow MWD and used them as crosslinking agent in making crosslinked PUs. They showed that amine-terminated HBP of low molecular weight derived from 3,5-bis-(4-aminophenoxy) benzoic acid can be used in additive quantity (0.01 equivalent of HBP to 1.0 equivalent of PU prepolymer) to improve the tensile properties of PU significantly without compromising other properties. However the problem may arise from the high reactivity of aromatic hyperbranched

polyamides, which reduces the pot life of the coating. On the other hand, HB polyethylenimine (PEI) (Scheme 17), an aliphatic and therefore with low reactivity, is a readily available material that was initially developed as an additive for use in paper production, and has since found use in many other applications, e.g., as complexation agents, surface coatings, etc. A major drawback for large-scale production of PEI for many high-end applications is the relatively broad MWD and low DB of some such products. Some hyperbranched PEIs are commercially available from BASF AG.

a A$_2$B approach

b A$_2$B + a core molecule

c A$_2$B + a core molecule

4,4-bis (4-hydroxyphenyl) valeric acid

2,2- bis (methylol) propionic acid

pentaerythitol

Bolton^{TM} H20

six repeating units

Scheme 15. Different synthetic approaches for the preparation of hyperbranched polyols [235–238].

2.5. HBPs in UV cure systems

As a class of UV-curable oligomers, HB-acrylated systems have attracted increasing attention from a fundamental viewpoint and for the great variety of expected applications. Several groups are working with these materials for use as oligomers in UV-curable systems [250–252]. The resin could be UV-cured, and the T_g of the cured films can be correlated with the terminal group concentration in the HB acrylate [232]. HB acrylates have low viscosity compared to conventional polyester acrylates of similar molecular weight. HB acrylates exhibit rapid cure rate and lower shrinkage than conventional polyester acrylates. The cured films have excellent physical and mechanical properties such as good adhesion, flexibility, impact strength, hardness, chemical resistance, scratch resistance and the presence of small amount of low extractable residual unsaturation. The use of acrylated aliphatic HB polyesters based on 2, 2-bis(methylol) propionic acid in UV-curable application has been described in several papers [195,232,253–255]. Recently,

Dzunuzovic et al. [256] and Dunjic et al. [257] described the synthesis and properties of urethane acrylates based on aliphatic HB polyesters, but the products have rather high viscosity, especially those with higher functionality. In order to reduce the viscosity of the product, urethane acrylates were obtained from an HB polyester partially modified by a soybean fatty acid, IPDI and 2-HEA. The additional double bonds from the soybean fatty acids enhance its crosslink density [258]. Alkyds based on HB polyesters and unsaturated fatty acids exhibited a substantially lower viscosity compared to a similar mixture with conventional curing agent. Also they had excellent curing properties with amazingly short curing times, which is beneficial from UV cure point of view [233,259,260]. Shi and Xu [261] synthesized three UV-curable HB PU acrylates possessing different double-bond density and partially chain structures, which made the difference in their photo-polymerization behaviors and dynamic mechanical and thermal properties. The synthesis of hyperbranched PU acrylate by Shi and Xu [261] involves a three-step procedure.

a
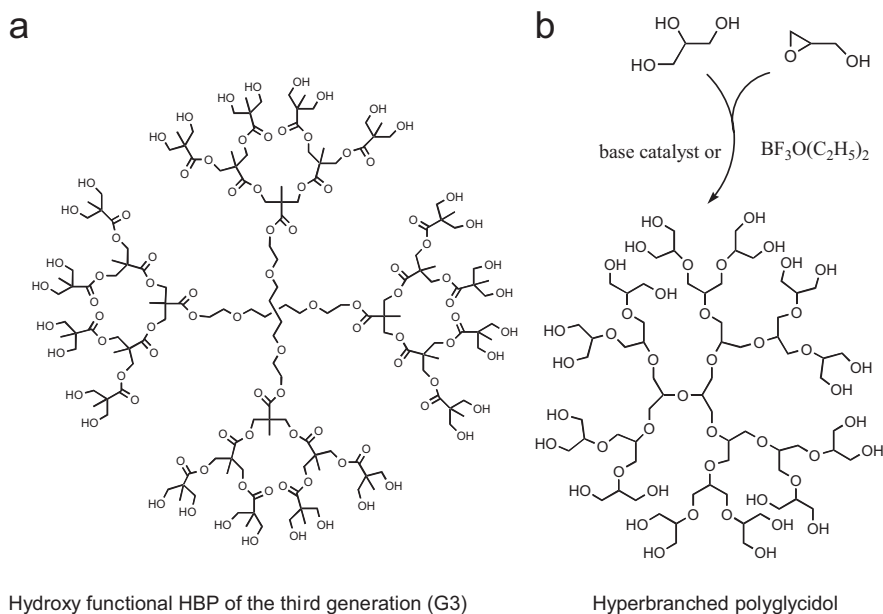
Hydroxy functional HBP of the third generation (G3)

b

Hyperbranched polyglycidol

Scheme 16. A third generation hyperbranched polyol (a) and hyperbranched polyglycidol (b).
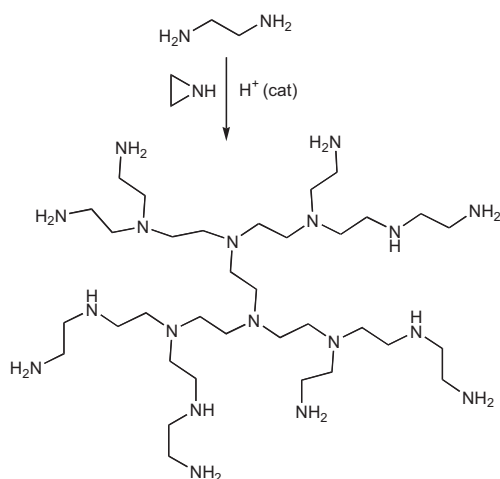
Scheme 17. Hyperbranched polyethylenimine (PEI).

The authors modified HBPE-OH with succinic anhydride or phthalic anhydride and then further reacted with epoxy propane and TDI-HEA; the photo-polymerization and the dynamic mechanical thermal properties of the resultant materials were studied (Scheme 18a). In another report from the same group [262], hyperbranched D-1-OH from HBPE-COOH was prepared (Scheme 18b). D-1-OH is a translucent viscous liquid and possesses eight double bonds at the periphery. They also prepared dendritic polyester with about 12 and 16 end-double

bonds by reacting hydroxyl group of D-1-OH with methacrylic anhydride. Tasic et al. [263] synthesized and evaluated new HB urethane acrylates having high functionalities and molecular weights, with acceptable viscosities. Their results show that the cured coatings have excellent mechanical properties due to high molecular weights and acrylate functionality.

HB acrylated aromatic polyester based on 5-hydroxyisophthalic acid as an AB_2 monomer, ethylenediamine tetra-acetic (EDTA) acid as a core molecule, and HEA as an end-group modifier (Scheme 19) [252] can also be used along with PU acrylated in UV cure coatings. In another report, Wei et al. [264] synthesized an acrylated HB polyester designated as HBP20-A from Boltorn[TM] H20. The synthesized HBP20-A was UV-cured with a linear aromatic PU acrylate resin.

2.6. HBPs in waterborne UV cure systems

In recent excellent studies by Asif et al. [265,267], and Asif and Shi [266], Boltorn[TM] H20 was modified with succinic anhydride, and then with glycidyl methacrylate (GMA). The modified acrylic-terminated Boltorn[TM] H20 was then dispersed in water in the presence of TEA and this dispersion was used for making waterborne UV-cured PU acrylates (Scheme 20).
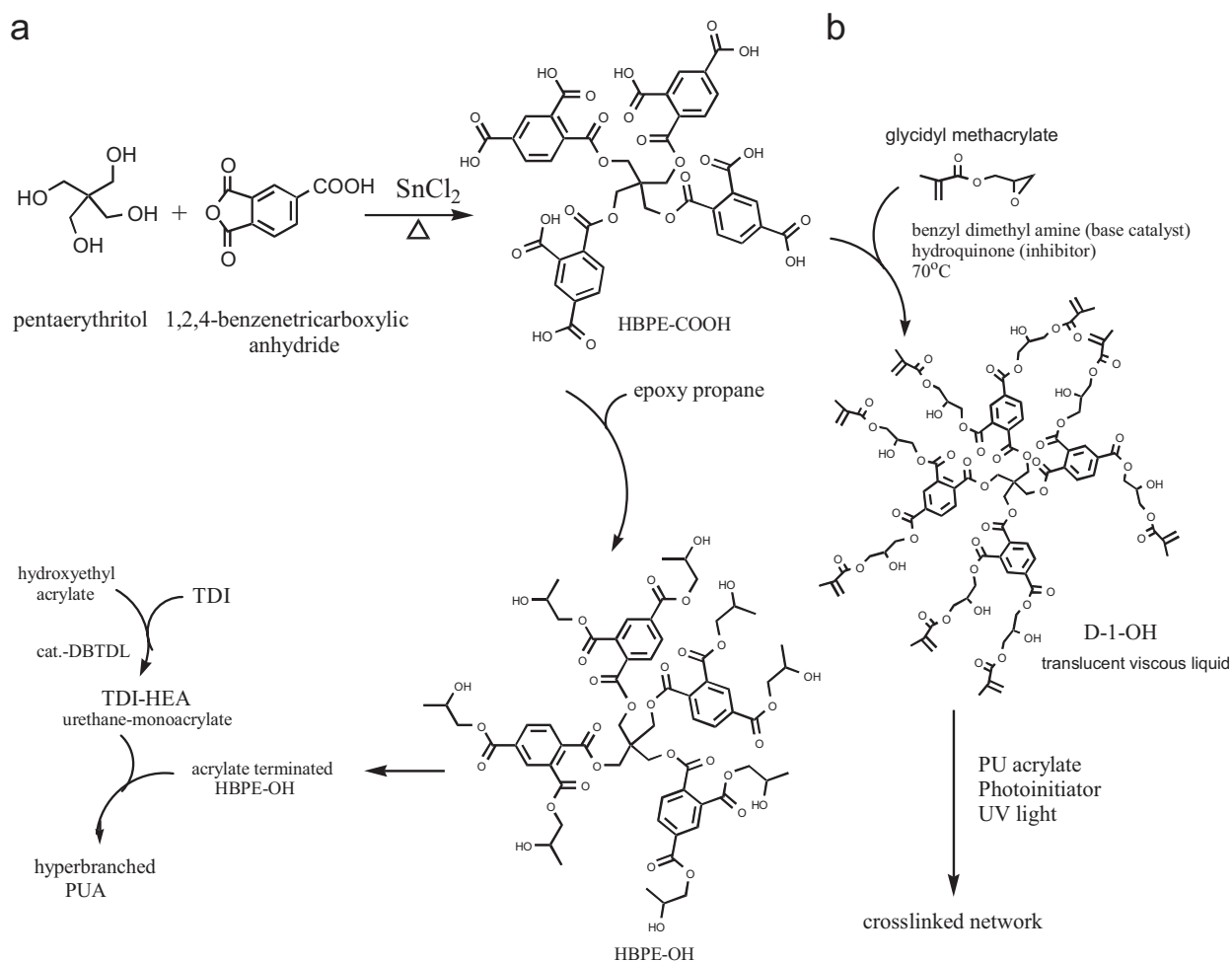
Scheme 18. Preparation of UV-cured PU coatings using hyperbranched polymers [261].

3. Hybrid sol–gel coatings

The basic idea behind the development of inorganic–organic hybrid materials is the combination of inorganic and organic moieties on a molecular scale to achieve a synergetic combination of the properties typical of each of the constituents. Modification of the kind and proportions of the organic and inorganic components allows a deliberate tailoring of properties, combining those of the inorganic and organic components. Therefore, processing sol–gel hybrid inorganic–organic materials, produces scratch and abrasive-resistant hard nanocomposite coatings with unique property combinations of the inorganic counterpart {hard, brittle, excellent heat, UV-radiation stability and solvent resistance due to stable $-(Si-O)_n-Si-$ backbone} and the organic counterpart (soft, flexible and

possess good mechanical properties) while maintaining optical transparency. The process can be used for the synthesis of well-controlled organic–inorganic hybrid coatings through the incorporation of low molecular weight and oligomeric/polymeric organic molecules with appropriate inorganic moieties [268–270]. The sol–gel synthetic method is based on inorganic polymerization reactions and is widely used for the preparation of inorganic materials in glass and ceramic industries. The organic–inorganic hybrid materials made in this way was named "CERAMERS" by Wilkes et al. [271] and "ORMOSILS" or "ORMOCERS" by Schmidt [272] are normally nanocomposites and have the potential for providing unique combinations of properties, which cannot be achieved by other methods. Organic–inorganic hybrid coating compositions may be applied by traditional coating
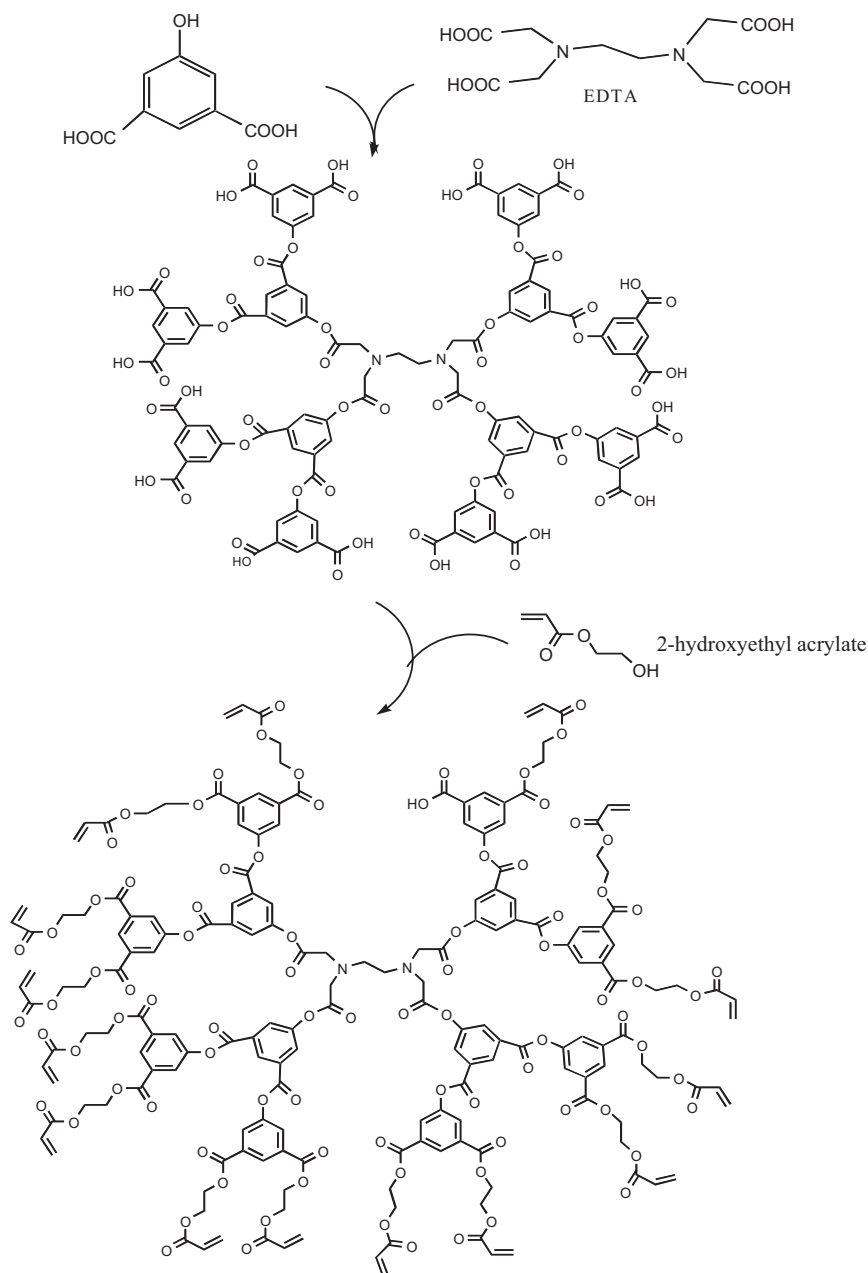
Scheme 19. Preparation of acrylate-terminated hyperbranched polymers for UV cure coatings.

processes such as dip coating, spin coating, flow coating, etc.

A number of routes are available for the synthesis of hybrid sol–gel materials and some of these are:

(a) Low molecular weight organo alkoxysilanes can be used as one or more of the precursors for the sol–gel reaction in which organic groups are introduced within an inorganic network through the $\equiv$Si–C bond.

(b) Functionalized oligomers or polymers can be co-condensed with the metal alkoxides, which results in chemical bonding between organic and inorganic phase.

(c) *In situ* formation of inorganic species within a polymer matrix.
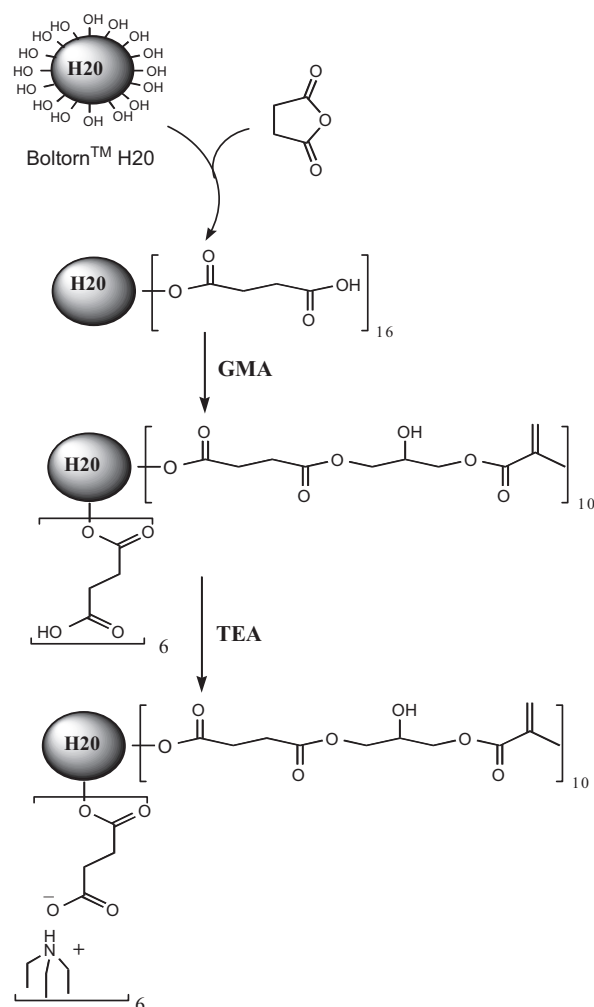
Scheme 20. Schematic description of the synthesis of waterborne hyperbranched polymer [267]. Reproduced from Asif A, Huang C and Shi W by permission from Springer.

(d) Interpenetrating networks and simultaneous formation of inorganic and organic phases.
(e) Using trialkoxysliane $R'Si(OR)_3$ as the precursor with R' being a polymerizable group such as an epoxy group. An organic network can be formed within the inorganic network by either photochemical or thermal curing.
(f) Use of polymerizable monomers as the co-solvent such that all mixture components contribute either to the silica network or to the organic polymer to avoid large-scale shrinkage [273].

3.1. Class I and II materials

The nanostructure and their arrangements, degree of organization and properties of hybrid sol–gel material depends on the chemical nature and ratio of the components, and the synergetic effect between these components. Therefore, the tailored design of products includes the tuning of the nature, extent and accessibility of the inner interfaces. The nature of the interface or of the links and interactions between the organic and inorganic components has been used to categorize these hybrids into two main classes [274,275].

Class I: Systems where no covalent or iono-covalent bonds are present between the organic and inorganic components. In such materials, the various components exchange only weak interactions (at least in terms of orbital overlap) such as hydrogen bonding, vander Waals, London or electrostatic forces.

Class II: At least a fraction of the organic and inorganic components are linked through strong chemical bonds (covalent, iono–covalent, or Lewis acid–base bonds) [276]. Desirable bulk properties of the coatings, such as superior hardness, thermal and mechanical properties, as well as reduced permeability, can be achieved through the covalent attachment together with the higher network density in hybrid Class II polymeric materials.

3.2. Sol–gel reaction

The reaction is generally divided into two steps: hydrolysis of metal alkoxides to produce hydroxyl groups in the presence of stoichiometric water (usually in the presence of acid or base catalyst), followed by polycondensation of the resulting hydroxyl groups and residual alkoxyl groups to form a three-dimensional network (Scheme 21). Different metal alkoxides based on silicon, aluminum, transition metal alkoxides such as titanium and zirconium also have been used as sol–gel precursors in combination with a variety of organic components. For non-silicate metal alkoxides, generally no catalyst is needed for hydrolysis and condensation because they are very reactive. The sequence of reactivity is expressed as follows:

$$Zr(OR)_4, Al(OR)_3 > Ti(OR)_4 > Sn(OR)_4 \gg Si(OR)_4.$$

However, owing to the loss of volatile by-products formed in the hydrolysis–condensation reactions, it is difficult to control sample shrinkage during three-dimensional network formation [273,277–280].

Factors such as the nature of the alkyl group, solvent, temperature, water to alkoxide molar ratio,

Hydrolysis Reaction:

alkyl alkoxy silane (when M = Si)
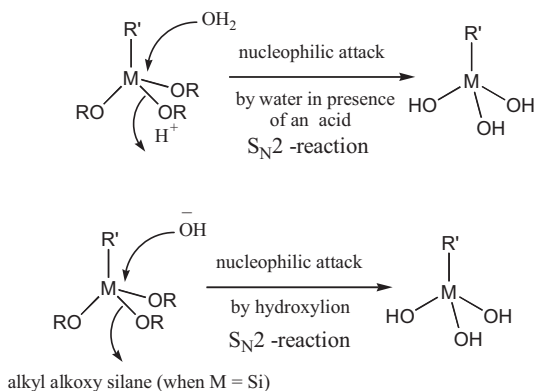
Condensation Reaction:
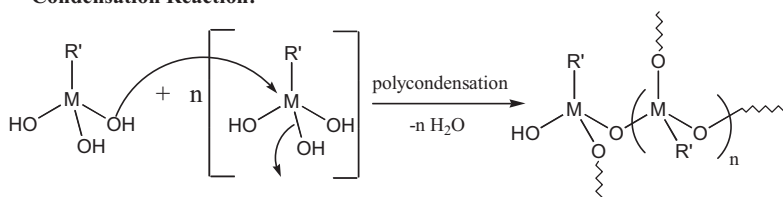
Scheme 21. The sol–gel hydrolysis and condensation polymerization reaction [273].

presence of acid or base catalysts, etc., are known to effect the hydrolysis reaction [281]. For example, in the presence of base catalyst, the rate of condensation is fast compared to hydrolysis and results in the formation of dense, colloidal particles. On the other hand, the rate of condensation is slow relative to the rate of hydrolysis under acid catalysis and the resultant silica has a highly ramified, low fractal-dimensional structure with many silanol groups on the silica surface [282].

The precursors of these compounds are organo-substituted silicic acid esters of general formula $R'_nSi(OR)_{4-n}$ and bridged precursors of silsesquioxanes $X_3Si-R'-SiX_3$ (X = Cl, Br, OR); where R' can be any organo functional group and n is usually 1 or 2. If R' bears any reactive group that can, for example, polymerize or copolymerize (e.g., methacryloyl, epoxy, amino, isocyanate, vinyl or styryl groups) or undergo hydrolysis-condensation (trialkoxysilyl groups), it will act as a network former. Therefore, siloxane Class II hybrids can be easily synthesized as the $Si-C_{sp}^3$ bonds are covalent and stable towards nucleophilic attack by water, alcohols, hydroxylated ligands, etc. They can be used, for example, as building blocks for the formation of highly ordered polyhedral oligomeric silsesquioxane

(POSS) clusters [283,284] and as organosilane coupling agents for ceramic particle coatings [285,286]. A limited selection of sol–gel precursors is shown in Scheme 22 [287].

Functional silane coupling reagents such as 3-glycidoxypropyltrimethoxysilane (GPTMS) and 3-amino-propyltrimethoxysilane are most popular trialkoxysilane-type precursors often used as a modifier of organic polymer precursors. In acid-catalyzed reaction of GPTMS, polymerization of oxirane moiety is also simultaneously achieved in addition to the formation of inorganic network, yielding transparent hybrid coatings in which organic and inorganic units are linked together by covalent bonds. The reactions and behavior of GPTMS in the presence of colloidal silica particles have been studied by Daniels et al. [288]. The reaction mechanism is very complex, and the morphology and properties of the resulting coatings are considerably influenced by the method of their preparation. The best properties of these ceramic-particle-based coatings were achieved when the acidic hydrolysis and alkaline polycondensation of GPTMS in the presence of low molecular weight polyamine was used (see Scheme 23) [289,290].
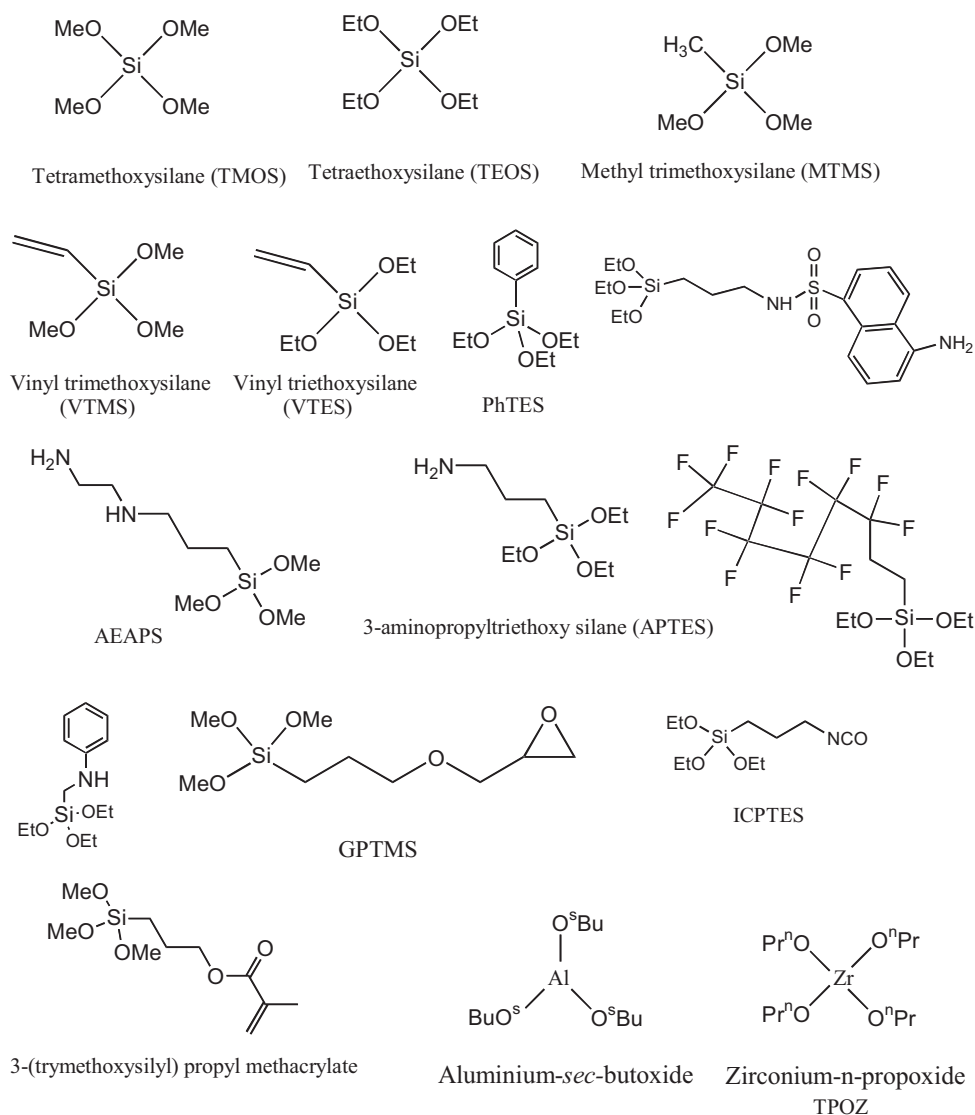
Scheme 22. Different sol–gel precursors used in coating application [276].

3.3. Hydroxyl functional alkoxysilane

In general, hydroxyl functional alkoxysilanes such as 3-hydroxypropyl triethoxysilane are not commercially available because they polymerize due to intermolecular trans-esterification reaction. Stable hydroxyl functional alkoxysilane can only exist in alcoholic solutions. These silanes can be obtained by hydrolyzing epoxy functional trialkoxysilanes such as GPTMS and 2-(3,4-epoxycyclohexyl) ethyl-trimethoxy-silane (ECHETMS) (Scheme 24a and b). Alternatively, they can be prepared by the reaction of 3-isocyanato propyltriethoxysilane (ICPTES) with polyols or amino alcohols. Scheme 24c shows the

preparation of N, N'-bis (2-hydroxyethyl) ureido-propyl triethoxysilane (BHEUPTES). The hydroxyl functional alkoxysilane obtained can then be reacted with an NCO-terminated PU prepolymer, which on hydrolysis and condensation produces sol–gel coatings [291].

3.4. Application of sol–gel process in coatings

Thin sol–gel-derived silica coatings show considerable potential in modifying the surface and bulk properties of polymers and finds applications in different domains, particularly as abrasive or scratch resistant coatings [292,293]. The mechanical,

Scheme 23. Use of GPTMS in the development of creamer coatings.
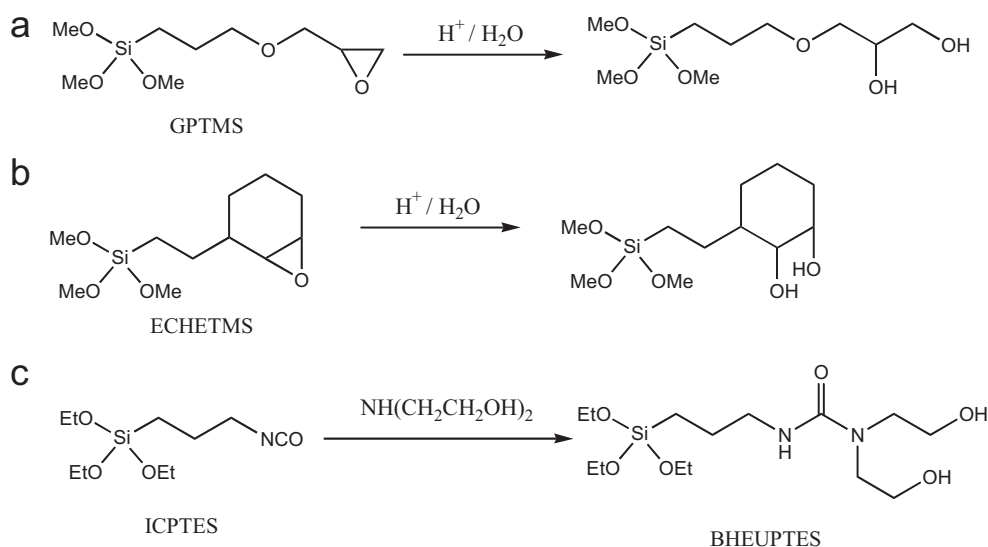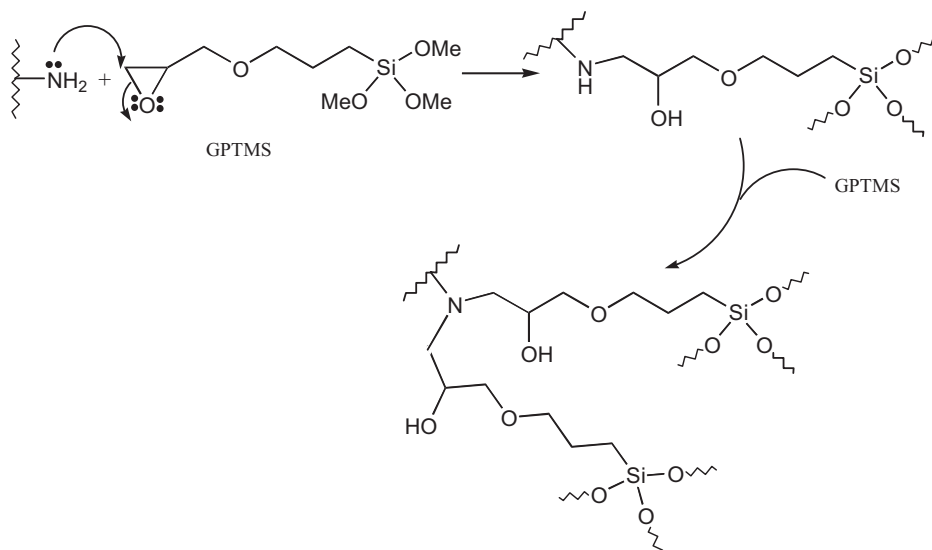
Scheme 24. Formation of hydroxyl functional alkoxysilanes [291].

optical, permeability, corrosion resistance properties are largely influenced by the intrinsic properties of the coating and adhesion characteristics with the substrate material. These properties are controlled by the sol–gel processing parameters i.e., a judicious control of the chemistry and processing variables, including the ratio and nature of the organic and inorganic structural units, solution pH, hydrolysis ratio, drying and heating temperatures produce tunable properties [287,294–296]. Up to now, several inorganic–organic, optically clear abrasion-resistant coating materials have been reported in the literature [297,298]. In these networks, the Si–O–Si inorganic backbone structure in combination with the level of crosslinking provides high abrasion resistance and the organic part of the network contributes to properties such as impact, toughness, and adhesion improvement.

A wide range of applications for these hybrid materials with structure controlled at the molecular level are envisaged or already exploited. These include semipermeable, heat and fire resistant hybrid films for packaging and coating applications [299], as conversion coatings and primers on metal

for corrosion protection [300] or even as high performance coating binders or pigments [279,301]. Therefore, sol–gel coatings with improved hardness [302,303], toughness [304], elasticity, low surface energy [305], chemical, radiation and heat resistance [306], enhanced corrosion protection or substrate passivation in corrosive environments [307,308], availability of reactive functional, can be produced by different approaches [309–317]. Additional advantages are related to the possibility of controlling shape, morphology and topology of phase-separated domains or pore structure, from the macroscopic to the nanometer-size. Therefore, the superior synthetic versatility ensues from the availability of many synthetic routes to independently modify the two components or to build-up a hybrid superstructure.

Atanacio et al. [287] studied the mechanical properties of various hybrid sol–gel films on copper substrates using nanoindentation and tensile testing and observed the dramatic change in indentation response and interfacial adhesion with the change in organic alkyl substituents (R′) to the inorganic sol–gel network. Goda and Frank [282] observed that even though silica component may destroy the ordered hydrogen bonded structure of HS in the PU, at appropriate concentration of silica the derived material showed improved mechanical and thermal properties. Zhang et al. [318] synthesized self-crosslinkable PU-urea formulations extended with different contents of aminoethyl-aminopropyl-trimethoxysilane (AEAPS). Two routes for the synthesis of sol–gel PU coatings from the reaction of NCO-capped PU prepolymer with triethoxy silane precursor (aminophenyl) triethoxysilane (APTES) and AEAPS are shown in Scheme 25.

Most inorganic–organic hybrid network materials reported in literature are thermally cured [275,306,319–321], often with high transparency [322]. Alternatively, hybrid network materials can also be prepared by the use of radiation curing using an UV curable binder system.

3.5. PU acrylate

Sol–gel precursors such as 3-(trimethoxysilyl) propyl methacrylate (TMSPM; Scheme 26) can be reacted with an acrylated terminated PU by UV as well as thermal curing.

The other way is to chemically modify nanosized silica particles and make it nanosilica with terminated unsaturation that can be reacted with an acrylic-terminated PU. For example, Yu et al. [323] used TMSPM to modify the silica surface and Liu et al. [324,325] used allylglycidylether as surface modifier for silica nanoparticles (Scheme 27).

3.6. Silica grafting

Silica is incorporated into the PU polymer by utilization of an organo-silica linking component. The linking component is a silicon-based material of the type including silanes and siloxanes. The linking component includes two different functional groups. The first functional group is an organo functional group that is effective in reacting with and binding to organic compounds e.g., amine, thiol, hydroxyl and carboxyl groups. The second functional group of the linking component must be capable of reacting with exposed hydroxyl groups on the surface of the silica in order to form a bond between the linking component and the silica i.e., methoxy or ethoxy groups [326]. Chen et al. [327] grafted 3-aminopropyl triethoxysilane (APTES) on fumed spherical nanoparticles and produced APTES modified silica nanopowder by refluxing the mixture for 12 h at 120 °C (Scheme 28).

3.7. Polyhedral oligomeric silsesquioxane (POSS)

Silsesquioxane is the term for compounds with the formula $(RSiO_{1.5})_n$; they may form cage, ladder, and sheet like oligomers and polymers. Their synthesis is based on the hydrolysis-condensation of $R′SiX_3$ derivatives (X = Cl, OMe, OEt, etc.). The hydrolysis reaction of different trifunctional silane may produce the diverse structure shown in Scheme 29. The hyrdrolysis in acid catalysis produces loose, coil-like polysilsesquioxanes (SSQO) structures, whereas basic catalysts promotes fast polycondensation, leading to compact, cagelike products [328]. Silsesquioxanes nanobricks correspond to cage compounds, where n is an even number ranging from 6 to 18 [329,330]. The most common nanobrick is a cubic-shaped octamer (n = 8) with one silicon atom at each corner. This oligomer has a size of ca. 10 Å, and can be thought as the smallest existing part of silica [329]. Changing the nature and/or the size of the outer functional group allows the generation of an enormous number of POSS-based molecules with a wide range of tailored properties. For example, surface properties and the miscibility behavior can be altered by proper choice of hydrophobic or hydrophilic
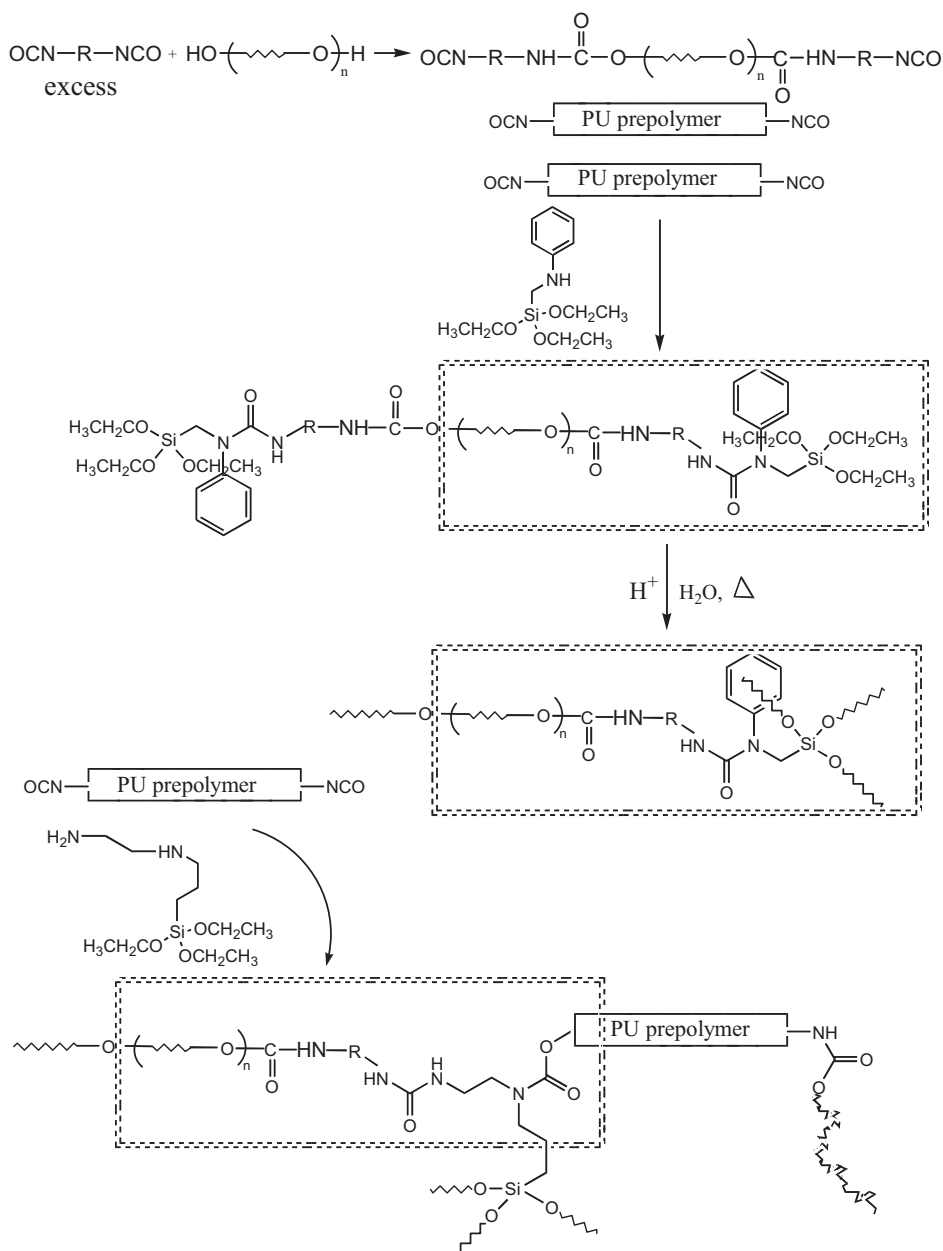
Scheme 25. Preparation of polymer sol–gel precursors and the sol–gel process to form organic–inorganic hybrid coatings.

attachments [331]. Hybrids may be produced by (1) blending POSS into a polymer matrix, (2) covalently bonding POSS into a polymer backbone and (3) reacting POSS macromer possessing one polymerizable functional group with a suitable function in the polymer [332]. Polymers incorporating POSS are becoming the focus of many studies due to the simplicity of processing and the excellent comprehensive properties of this class of hybrid materials. The hybrid polymers show improved

properties such as higher T_g and modulus, a large increase in heat distortion, reduced flammability and enhanced mechanical strength [333].

Polyhedral silsesquioxane molecules are easy to prepare in high yield and standard organic manipulations can be applied to functionalize the exterior of the molecules, generally in high yield with retention of the silsesquioxane structure intact. Examples of reactions of POSS species can be found in a review by Lichtenhan [335], and references
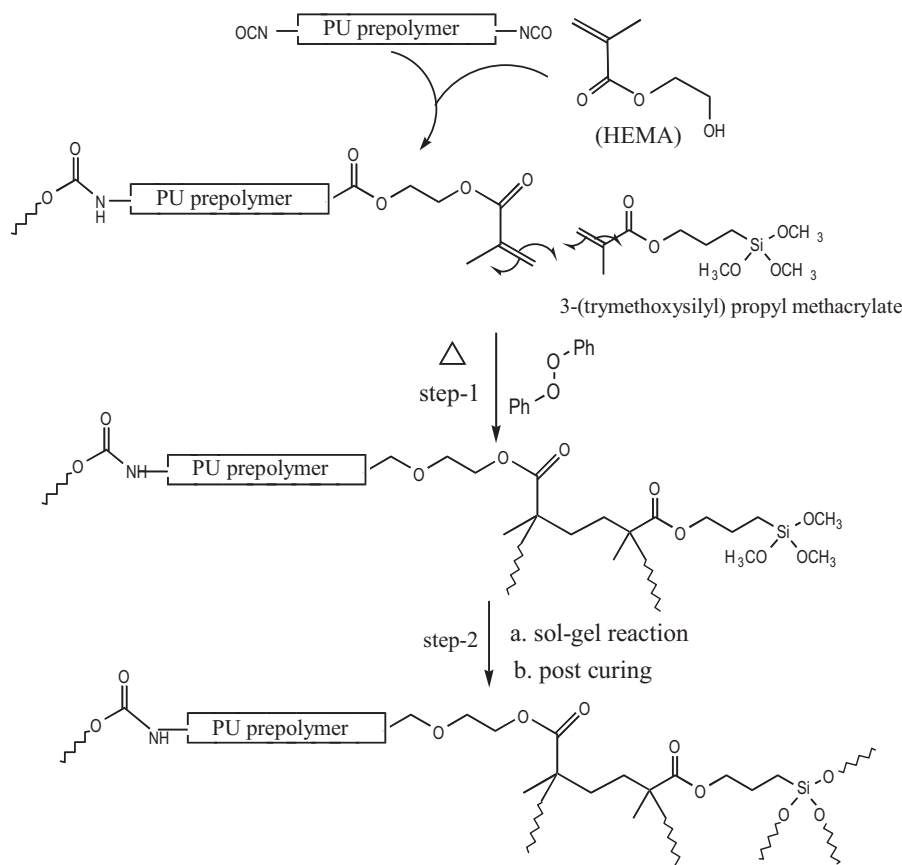
Scheme 26. Synthesis of polyurethane-acrylate sol–gel coatings.
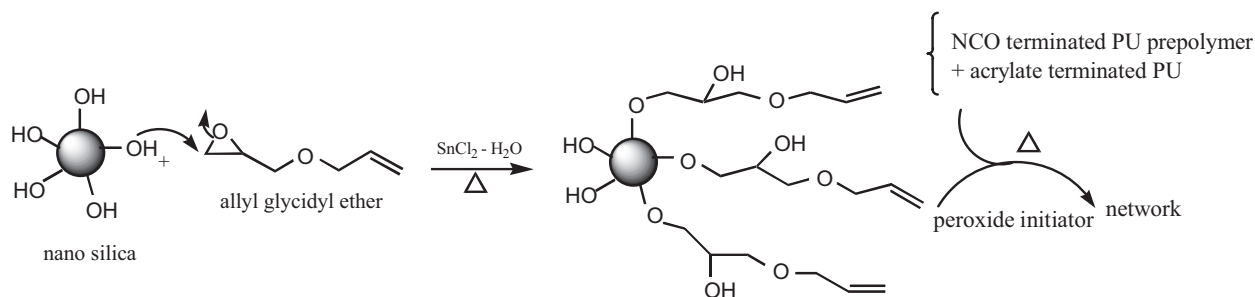
Scheme 27. Surface functionalization of nanosilica particles and the formation of crosslinked networks [324, 325].

therein. An efficient method for preparing functionalized POSS involves the corner-capping of incompletely condensed POSS trisilanols $R_7T_7(OH)_3$ (Scheme 30). Corner-capping of the POSS trisilanol can be carried out using a variety of trichlorosilane coupling agents to produce fully condensed T_8-POSS silicon-oxygen frameworks [336,337]. In addition to corner-capping, POSS trisilanol reacts with a wide range of main group, transition metal, and lanthanide elements to afford fully condensed metal-silsesquioxanes [338].

Pendant POSS can be introduced into the PU structure through polycondensation reactions [339–341]. For example, the nanobrick $(HMe_2–SiO)$ $(c\text{-}C_6H_{11})_7Si_8O_{12}$ was reacted with 3,3′-diallyl-bisphenol A and produces BPA-POSS, which then co-polycondensed with PTMG and MDI [333,339]. BPA-POSS can be used as diol CE to produce PU hybrid (Scheme 31). Devaus et al. [342] reported
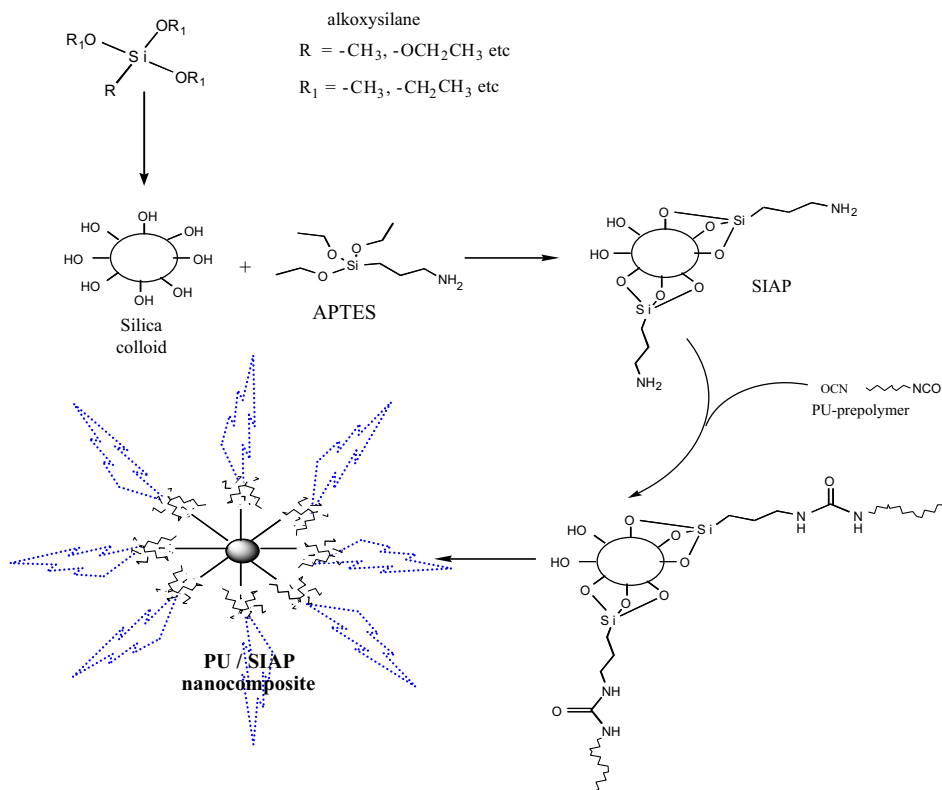
Scheme 28. Schematic formation of 3-aminopropyl triethoxysilane (APTES)-modified silica (SIAP) by grafting APTES into the silica nanoparticles surface and PU/SIAP hybrid nanocomposites. Scheme for the preparation of SIAP was reproduced with permission from Springer [327].

that the incorporation of POSS into PU gave materials with improved flame retardance. More recently, Liu and Zheng [343] used octa aminophenyl polyhedral oligomeric silsesquioxane (Oap-POSS) to replace part of the aromatic amine crosslinking agent, and thus the POSS cages act as nanostructured crosslinking sites and produced improved thermal stability (Scheme 32).

POSS may also be used as a nanocrosslinker in PU systems. This is accomplished through the functionalization of POSS with eight identical groups that may be reacted to form materials with a high crosslink density. Neumann et al. [332] reported the synthesis of a new type of POSS macromer with eight reactive isocyanate groups suitable for the synthesis of hybrid organic–inorganic urethane nanomaterials with discrete POSS molecules dispersed within the polymer matrix (Scheme 33).

3.8. Bridged polysilsesquioxanes

Bridged polysilsesquioxanes are a family of hybrid organic–inorganic materials prepared by

sol–gel polymerization of molecular building blocks that contain a variable organic bridging group and at least two trialkoxysilyl groups. Trialkoxysilyl groups are the most common silyl functionality, although other groups, such as silyl chlorides, have served as precursors as well. The molecular building blocks used for their synthesis are comprised of a variable organic component and an inorganic oxide precursor. A small change in the variable organic component results in profound changes in the final properties (e.g., surface area, thermal stability, etc.).

Shea and Loy [344] reviewed the preparation and application of bridged polysilsesquioxane as a class of hybrid organic–inorganic hybrid materials. Sol–gel polymerization of bridged trialkoxysilanes proceeds by a series of hydrolysis and condensation reactions. The high level of functionality of these monomers may result in their rapid gelation, even in dilute solution. The bridging group can be varied as well as the ethoxy group can be replaced in varying degree with an organic R group that may or may not have any functionality to
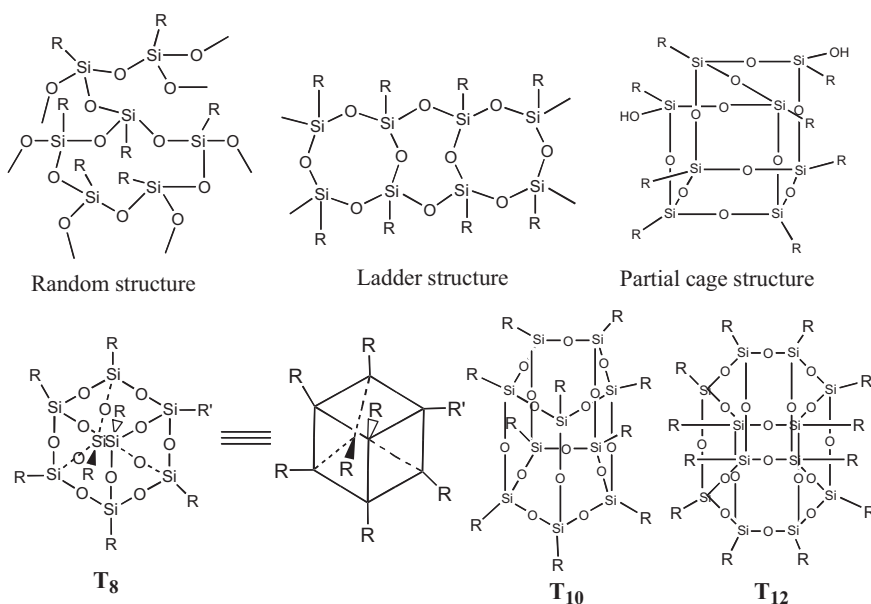
Scheme 29. Generation of different structure during hydrolysis of trifunctional silane [334].
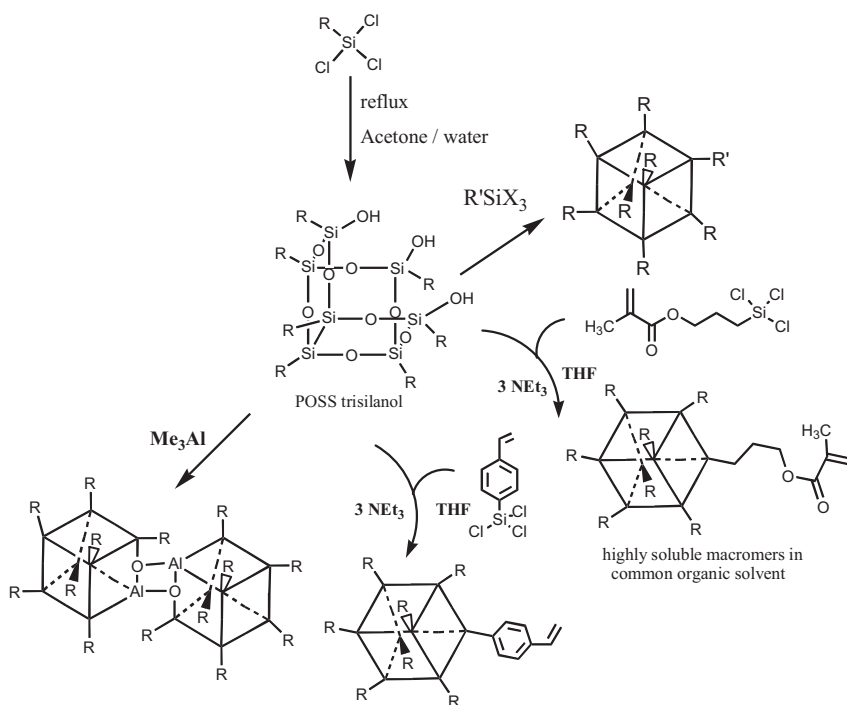
Scheme 30. Preparation of functionalized POSS [336,338].

decrease the crosslinking and making a soluble product that can be used to react with NCO-terminated PU prepolymer or to make nano-powder, which can then be used as reinforcing fillers to tailor make the products. Schemes 34a and b show the preparation of PU-bridged poly-silsesquioxanes from isocyanate silane [344,345]. Ether- and urea-bridged polysilsesquioxanes used
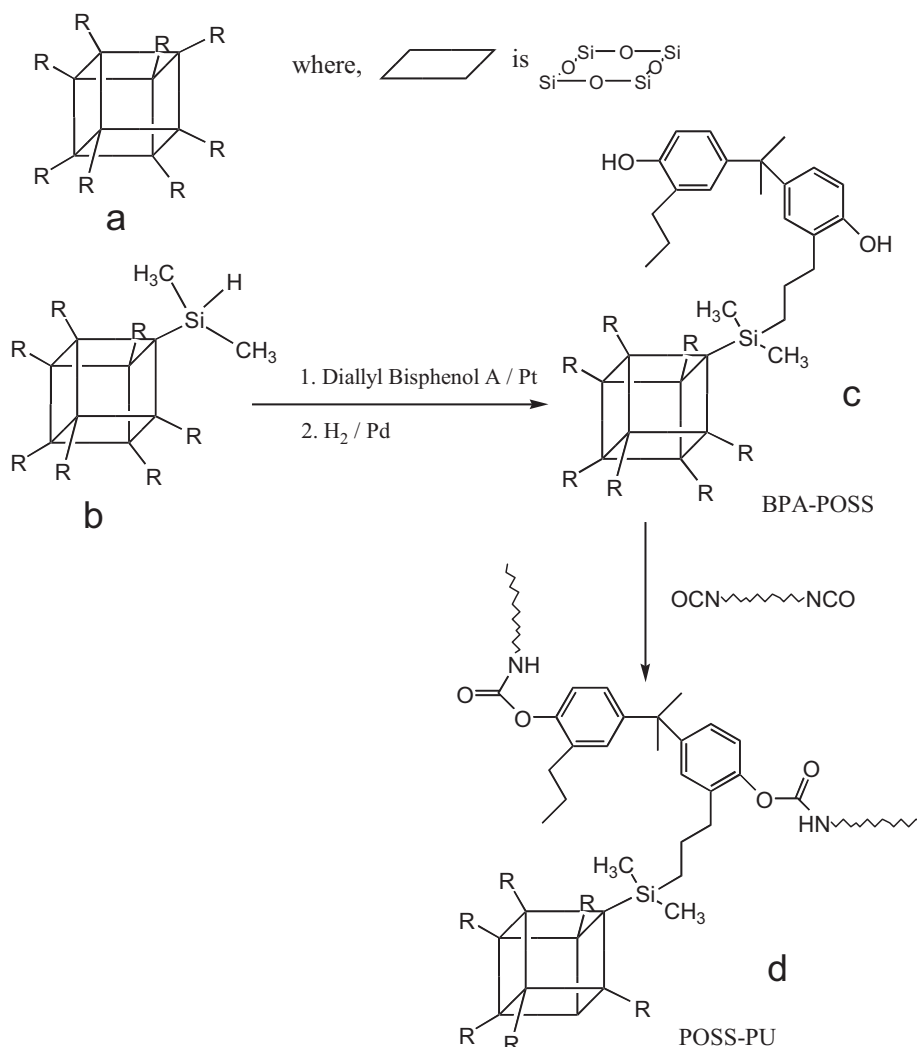
Scheme 31. Schematic diagram of the synthetic route for POSS-PU: (a) octaalkyl-POSS, (R group enhance solubilizing in organic matrix), (b) one corner group substituted by hydridomethylsiloxy group: hydrido-POSS; and (c) one corner group substituted by 3-(allybisphenol-A) propyldimethylsiloxy group: BPA-POSS; and (D) POSS-PU [333].
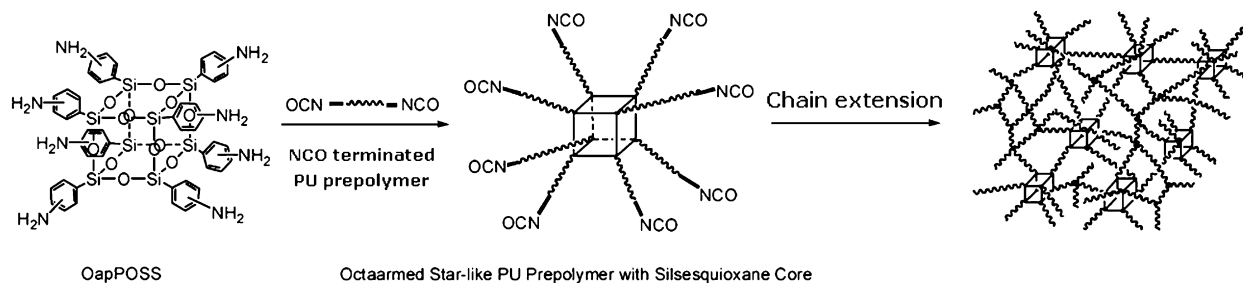
Scheme 32. Polyurethane hybrid network containing POSS [343]. Reproduced from Liu H. and Zheng S. by permission from Wiley–VCH.

in tough coatings are shown in Schemes 34c and d, respectively. Materials with alkylene, ether and urea functionalized bridging groups can result in the formation of tough and relatively hard films as well as protective layers for metals [344].
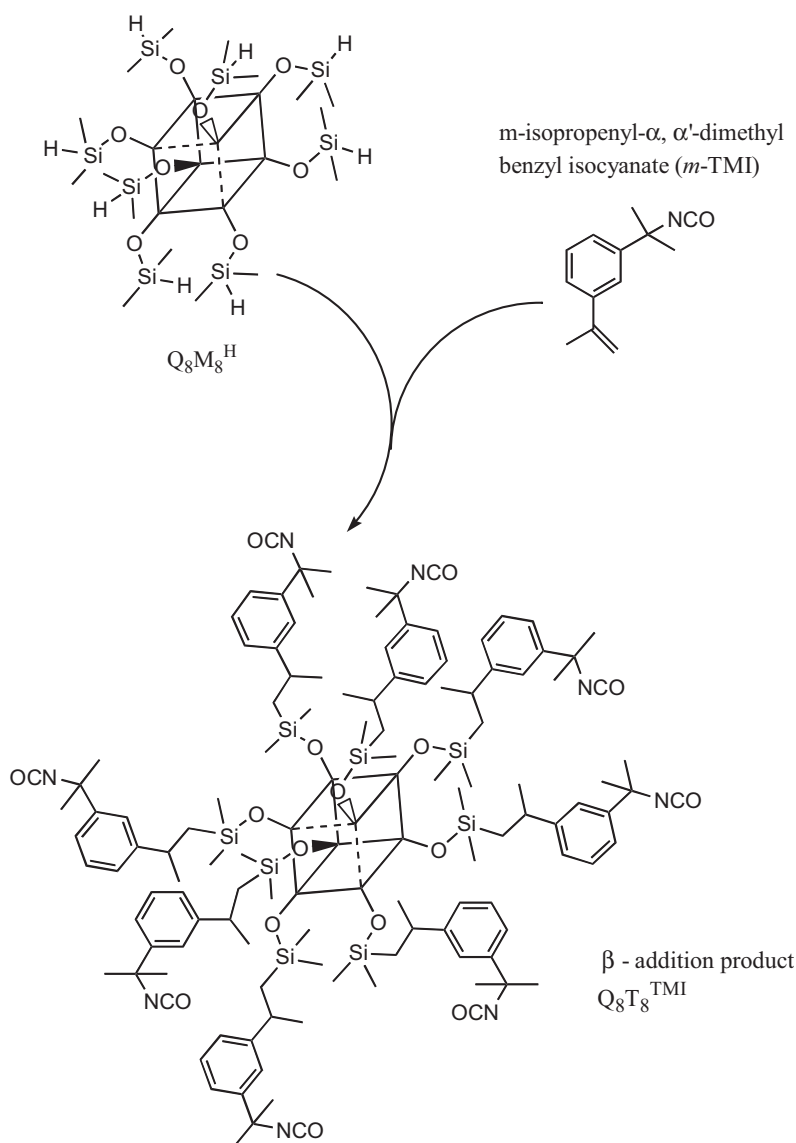
Scheme 33. Synthesis of octakis [*m*-isopropenyl-α,α′-dimethyl-benzyl isocyanate dimethylsiloxy] octasilsesquioxane ($Q_8T_8^{TMI}$) from octakis (dimethyl-siloxy) octasilsesquioxane ($Q_8T_8^H$) in presence of Karstedt's catalyst and in dry tetrahydrofuran solvent [332]. Reproduced with permission from J. Am. Chem. Soc. 2002; 124: 13998–13999. Copyright 2002, American Chemical Society.

3.9. Applications of nanomaterials in PU coatings

3.9.1. Fillers

A wide variety of fillers, whiskers and fibers as well as clay and wollastonites, are being used in PU formulations to reinforce the PU matrix for improved hardness, strength and stiffness. In general, the properties of filled PUs depend on filler shape, average diameter and interfacial coupling. To meet modern technological demands in this arena, the size of the materials should be reduced to the nanometer scale though high specific surface area of nanomaterials, which results in high reactivity and a strong tendency towards agglomeration and rapid grain growth. Nanomaterials can be classified into nanocrystalline materials and nanoparticles. The former are polycrystalline bulk materials with grain sizes in the nanometer range (less than 100 nm), while the latter refers to ultrafine dispersive particles with diameters below 100 nm. Nanoparticles are generally considered as the building blocks of bulk nanocrystalline materials.
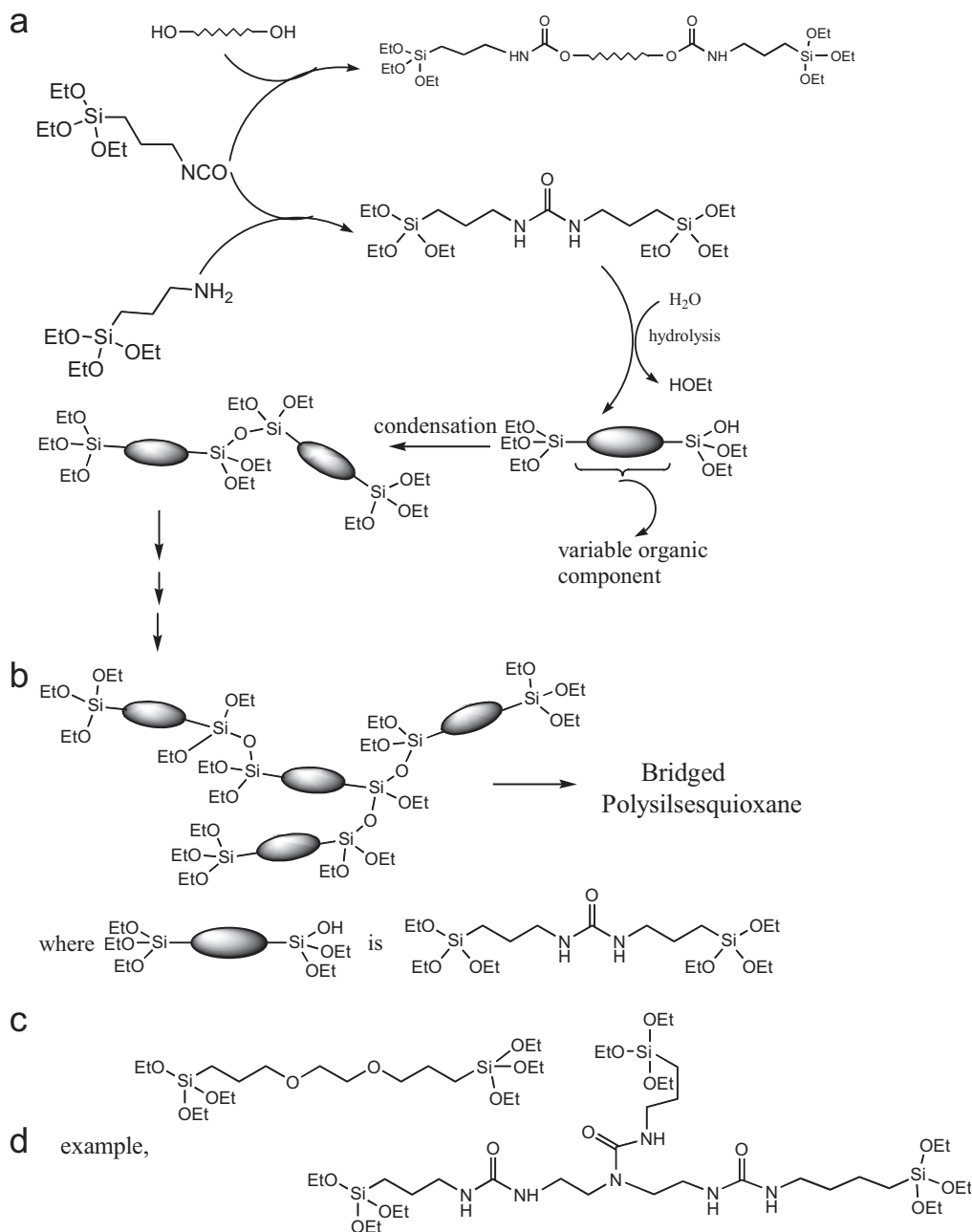
Scheme 34. Synthesis of bridged polysilsesquioxanes. Part of the scheme was reproduced with permission from Chem. Mater. 2001; 13: 3306–3319 [344]. Copyright 2001, American Chemical Society.

Nanoparticles synthesized from several routes may have different internal structures that would affect the properties of materials consolidated from them. As unique properties of nanocrystalline materials derived from their fine grain size, it is of crucial importance to retain the microstructure at a nanometer scale during consolidation to form the bulk materials [346].

The search for nanostructured coatings with unique physico-chemical properties is driven by the improvement in coating technologies and the availability of various kinds of synthesized

nanopowders, which results on incorporation to the PU matrix an interface with high cohesive strength; good mechanical, thermal, barrier and flame-retardant properties; higher specific heat and electrical resistivity; improved hardness and fracture toughness [347,348]. In the past decade, favorable applications have been found for hard and wear-resistant ceramic coatings in industrial sectors [281,349–352].

3.9.2. Nanosilica, Fe_2O_3 and TiO_2 particles

Nanoscale silica particles do not have the narrow gallery structure of layered clay, but possess a large interfacial area as long as the diameter of the particles is in the range of nanometers, and they are well dispersed in the polymer. The improvement in physical properties [353–356] and thermal stability [357] by the addition of nanoscale silica particles to polymers were reported. The addition of mesoscale silica particles to various polymers significantly reduces the heat release rate of the polymers [358,359]. It was reported that polymers filled with nanoscale size silica particles exhibit a second, apparent glass transition at a much higher temperature than that of the polymer resins. This phenomenon was attributed to the formation of tightly bound and loosely bond polymer chains around the particles, which might improve the thermal stability and flammability of the polymer [360].

In the coating industry, the vibratory mechanical milling process is used to prepare nanocrystalline Fe_2O_3 and TiO_2 powders. In this process, raw powder particles with a size of several microns experience severe plastic deformation, i.e., undergo a repetitive cold welding and fracturing mechanism [361]. The disadvantage of ball milling for making nanocrystalline Fe_2O_3 powders is the contamination of products from the milling media (balls and vial) and the atmosphere. For example, the powders may be contaminated with Fe if steel balls and containers are used [281].

3.9.3. Clay

Talc, mica and montmorillonite, hectorite, laponite and saponite belongs to the general family of 2:1 layered- or phyllosilicates and are characterized by a moderate negative surface charge (known as the cation exchange capacity, CEC and expressed in meq/100 g). Montmorillonite is an expandable dioctahedral smectite with a mean layer charge density of 0.25–0.50 equiv/mol and consisted of disc-like shaped layers of 100 nm in diameter and

1-nm thick with a regular van Der Waals gap between the interlayer. They are made up of two-silicate tetrahedron fused to an edge-shared octahedral sheet of either aluminum or magnesium hydroxide. Isomorphic substitution within the layers generates negative charges, which are compensated by alkaline earth or hydrated alkali-metal cations (Na^+, Ca^{2+}, Mg^{2+} or K^+) residing in the gallery space [362]. The layers swell in water and the 1-nm-thick layers can be easily exfoliated by shearing, giving platelets with high aspect ratio. The ion exchange reactions of montmorillonite with various organic cations such as alkyl ammonium cations or with cationic surfactant produce hydrophobic and organically modified montmorillonite. The organic cations lowered the surface energy of silicate layers and increase the basal-plane spacing (*d* spacing). This improves wetting, swelling, miscibility between the silicate layers and the polymer and exfoliation of the aluminosilicate in the polymer matrix [363–366]. Additionally, the organic cations may contain various functional groups that react with the polymer to improve adhesion between the inorganic phase and the matrix.

It is the absorption and swelling characteristics that makes montmorillonite so useful for industrial and commercial applications. The theoretical formula and structure for montmorillonite is shown in Fig. 2.

3.9.4. Nanocomposite coatings

Polymer–clay nanocomposites are a new class of filled polymers in which clay platelets at the nanometer scale are dispersed in a polymer matrix. These silicate nanocomposite coatings possess several advantages, such as (i) lighter weight due to the low clay content (between 2 and 5 wt%), which is economically interesting; (ii) enhanced mechanical behavior i.e., higher stiffness and strength [367,368]; (iii) higher permeation-barrier properties due to reduction in straightway movement of water and oxygen molecule [362]; (iv) improved thermal properties, such as fire retardance and heat distortion temperature (HDT) [362,369–378].

Several routes were developed to achieve a high degree of dispersion of the clay nanoplatelets: (i) *in situ* polymerization of monomers which were initially intercalated between silicate layers, (ii) melt intercalation and further exfoliation for thermoplastic polymers and (iii) combination with a polymer solution [379].

$$M^+_y(Al_{2-y}\,Mg_y)(Si_4)\,O_{10}(OH)_2,\,nH_2O$$
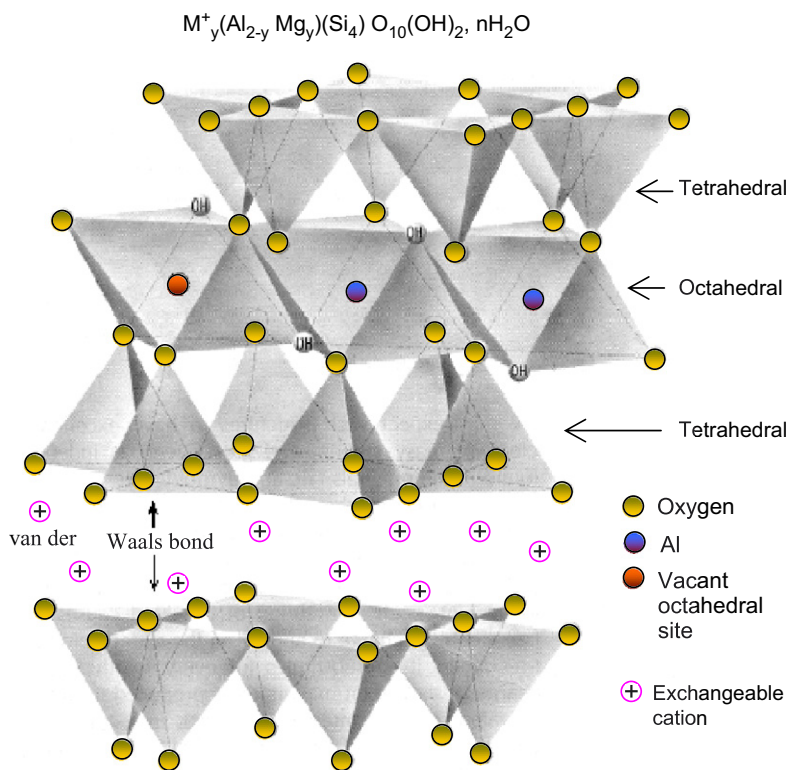
Fig. 2. Structure of montmorillonite [362].

Depending on the nature of the components used (layered silicate, organic cation and polymer matrix) and the method of preparation, three main types of composites may be obtained when layered clay is associated with a polymer. When the polymer is unable to intercalate between silicate sheets, a phase-separated composite (Fig. 3a) is obtained, whose properties are in the same range as traditional microcomposites. Therefore, any physical mixture of a polymer and silicate (or inorganic material in general), however, does not form a nanocomposite. There are two possible types of nanocomposites with ultrafine dispersion at the nanometer level. Fig. 3b shows the intercalated structure, where a single (and sometimes more than one) extended polymer chain is intercalated between the silicate layers resulting in a well ordered multilayer morphology built up with alternating polymeric and inorganic layers. When polymers intercalate layered silicates, interlayer distance increases and the silicates are broken down into their nanoscale building blocks to afford dispersions of anisotropic inorganic–organic hybrid particles with high aspect ratios. When the silicate layers are completely and uniformly dispersed in a
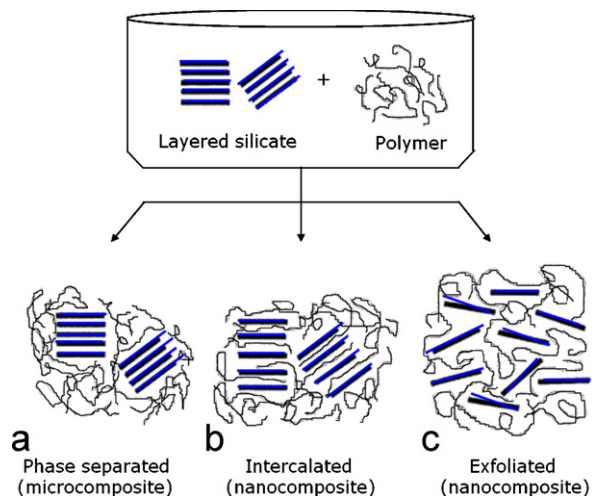
Fig. 3. Scheme of different types of composite arising from the interaction of layered silicates and polymers: (a) conventional composites (microcomposites)-phase separated, (b) Intercalated nanocomposites, and (c) exfoliated nanocomposites [379]. Reproduced with permission from Mater. Sci. Eng. R: Reports 2000; 28: 1–63. Copyright 2000, Elsevier B.V.

continuous polymer matrix, an exfoliated or delaminated structure is obtained (Fig. 3c) [365,367, 368,371,379–381]. The delaminated structure is of

particular interest because it makes the entire surface of clay layers available for the polymer, and maximizes polymer–clay interactions. In such an environment, the interfacial bonding between the polymer matrix and the reinforcing materials will be dramatically increased [382,383].

3.9.5. Effect of alkyl chain length, cation type and organoclay concentration

The longer chain length of the alkyl group in the ammonium ion produces better hydrophobicity and generates better compatibility between the hydrophobic polymer and the hydrophilic negatively charged montmorillonite layer [371]. The modified clays in the binder adopt a structure, where the carbon chains are fully extended and oriented perpendicularly to the silicate plane. Therefore, intercalated, partially exfoliated or totally exfoliated nanocomposite structure formation depends on the alkyl chain length of modified clays. For example, the protonated *n*-octylamine generates an intercalated and partially exfoliated structure, whereas the protonated *n*-octadecylamine gives a totally exfoliated structure [384]. In order to activate clay exfoliation, presence of acidic species in the intergallery is necessary. The decrease in layer exfoliation with decreasing Bronsted acidity of the exchange ion follows the order [385]:

$$CH_3(CH_2)_{17}NH_3^+ > CH_3(CH_2)_{17}N(CH_3)H_2^+$$
$$> CH_3(CH_2)_{17}N(CH_3)_2H^+ > CH_3(CH_2)_{17}N(CH_3)_3^+.$$
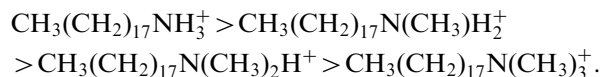
Chen et al. [380,386] studied the effect of organoclay concentration on the properties of PU/clay nanocomposite. Yao et al. [381] observed a decrease in thermal conductivity with an increase in the loading of layered clay to a polyether–urethane matrix.

In order to improve the tensile-mechanical properties [387] and thermal durability [388] of PU by silicates, Tien and Wei modified montmorillonite with reactive swelling agents containing one to three hydroxyl groups and then treated the swelling agent (such as tris-hydroxymethyl aminomethane) as a pseudo-CE along with the regular CE, 1,4-butanediol, for a reaction with the isocyanate groups of PU prepolymer to extend its chain length (Scheme 35). The reactive swelling agents used have dual functions: (1) the amine group in these reactive swelling agents was converted into an onium form to replace the metal ions in the gallery of the silicates for intercalation and (2) the available

hydroxyl functional groups can react with the isocyanate groups of the PU prepolymer. The intercalation force for attaining an exfoliated structure of silicates in PU apparently reached the maximum in the case of a trihydroxyl-group swelling agent.

4. Flame-retardant coatings

Flame-retardant coatings are non-combustible materials, which prevent or delay flashover from the coating surface of combustibles. The research on flame-retardant materials was spurred by an important finding of flame-retardant materials such as halogenated paraffin and antimony oxide in the course of research on flame-retardant military clothing used by the US during World War II. After that, the finding of a synergism between the halogen compound and antimony oxide made halogen compounds a typical organic flame-retardant compound. Halogenated additives work by suppressing ignition and by slowing flame spread. During incineration, the evolved halogen acids can act as irritants. Halogen acids are also potential corrosive agents for metals [389]. A growing demand to avoid these disadvantages have resulted in the development of non-halogen-containing flame retardant [390].

Two general approaches to achieve flame retardancy in polymers are known as the additive and the 'reactive' types. Additive-type flame retardants are incorporated into the polymer by physical means, and as a consequence poor compatibility, leaching and a reduction in mechanical properties takes place due to the reduction in hydrogen bond association in the PUs. Reactive flame retardants involves either the design of new intrinsically flame retarding polymers or the modification of existing polymers through copolymerization with a flame retarding unit(s), either in the chain or as pendent [391]. The incorporation of phosphorus-containing chemical units into the PU backbone or in the side chain is the most effective way to improve flame retardance, because a phosphorus group accelerates crosslinked phosphorus-carbonaceous char formation. Therefore, PUs containing reactive-type flame-retardants char more easily during combustion than that containing additive-type flame-retardants, and results in higher flame retardancy [392,393].

Based on the flame-retardant mechanism, these coatings can be classified into intumescent and non-intumescent, i.e., those that swell and char on exposure to a flame, and those that do not do so,
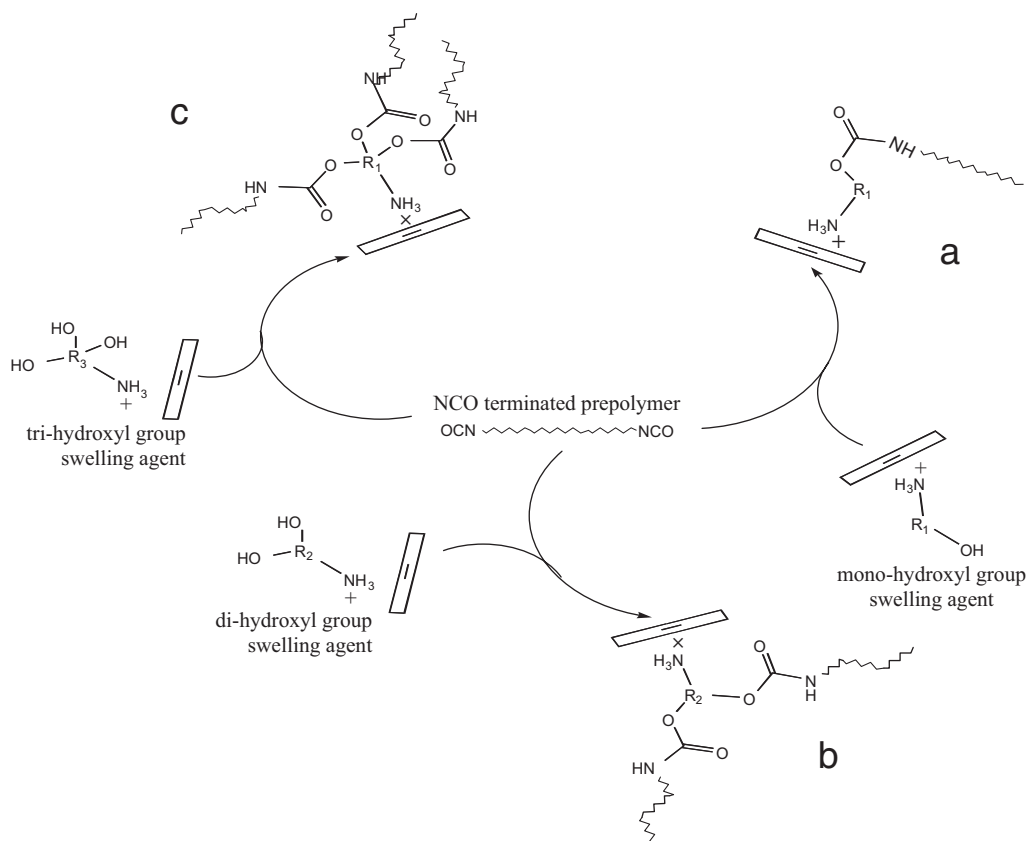
Scheme 35. Schematic drawings of the molecular architecture of PU/layered silicates nanocomposites through reactive swelling agents containing (a) monohydroxyl group, (b) dihydroxyl group, or (c) trihydroxyl group. Reproduced with permission from Macromolecules 2001; 34: 9045–9052 [387]. Copyright 2001, American Chemical Society.

respectively. Intumescent systems have attracted more and more attention from many researchers [394,395]. The porous foamed mass, usually carbonaceous produced by an intumescent material acts as a barrier to heat, air and pyrolysis product. A char forming agent, a catalyst for char formation and a foaming (spumific) agent are used in intumescent coatings. At high temperature, the formed charred layer on the coating surface provides resistance to both heat and mass transfer, giving good heat insulation to the underlying binder. Intumescent systems consist of three main substances: an acid source (e.g., phosphorus-containing substance), a carbon source (e.g., polybasic alcohol), and a gas source (nitrogen-containing substances).

4.1. Organophosphorus compounds

Many organophosphorus compounds of various types have been synthesized for use as flame retardants, and some of them are commercially available. Reactive phosphorus-containing compounds, mainly polyols, are the most suitable flame retardants for easy inclusion in the PU structure [396]. Unlike non-reactive additives, they do not diffuse toward the surface of the polymeric material and remain more resistant against combustion for longer periods [397]. Some basic structure, such as phenyl dichlorophosphate, phenyl phosphonic dichloride, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and spirocyclic pentaerythritol di (phosphoric acid monochlorides) (SPDPC) shown in Scheme 36 [398–403] have attracted unique attention due to the presence of an electrophilic phosphorus center in all these structures. An organo-modifier i.e., a nucleophile can modify these structures. For example, 1,3-dihydroxybenzene (resorcinol) reacts with phenyl dichlorophosphate and produces bis(3-hydroxyphenyl) phenyl phosphate (BHPP) [404], which can be reacted with an NCO-capped PU. Ma et al. [397]
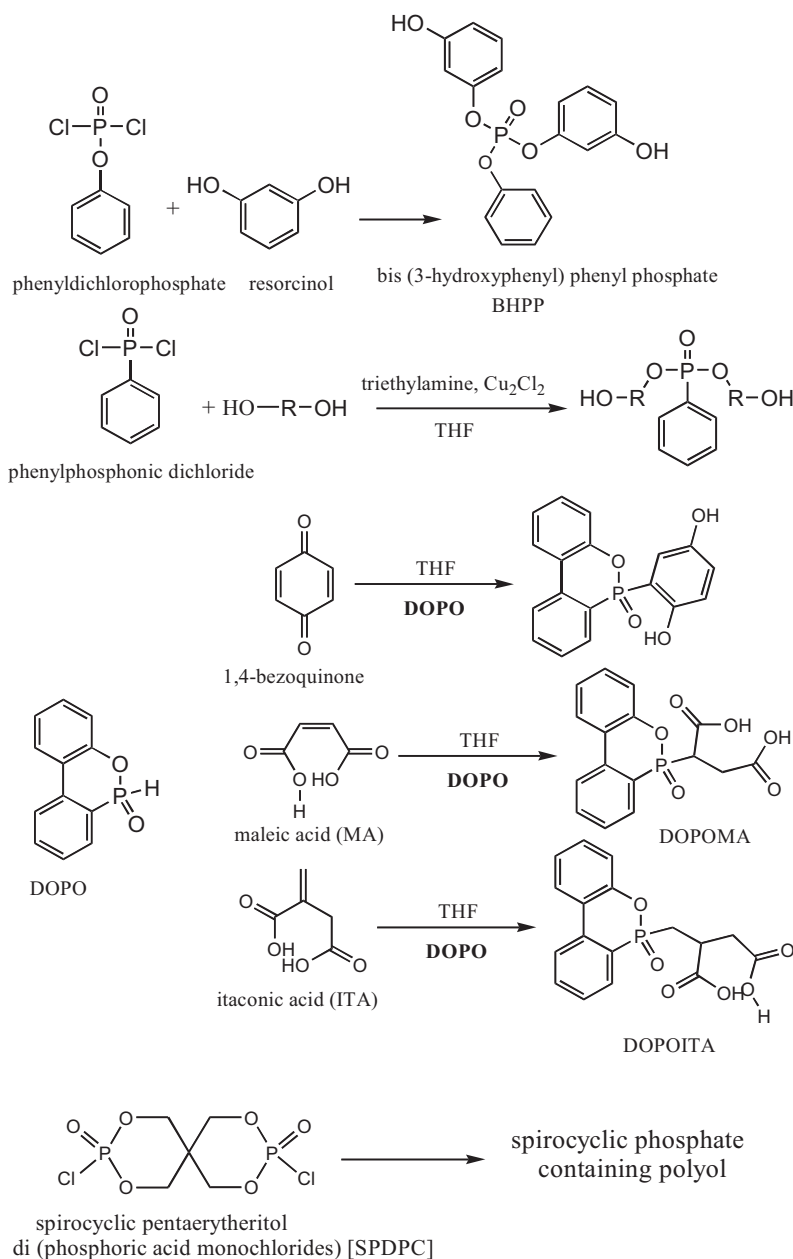
Scheme 36. Different organophosphorus reactive-type flame retardants [391, 397, 404].

used spirocyclic phosphate-containing polyols as reactive-type flame retardant material in PU coatings. Kuo et al. [405] synthesized oligomeric polyalkyl phosphate-type polyols from phosphorus oxychloride, ethylene glycol and 1,4-butanediol. These polyols were then reacted with TDI to form the corresponding flame retardant PUs. Chang et al. [406] prepared PUs from TDI, PPG and phenyl bis(hydroxyethyl)-phosphonate. Park et al. [407, 408] incorporated phosphorus functions in polyester

polyols and produced phosphorus-containing lactone-modified polyesters. Mequanint et al. [409] used a phosphate-containing carboxylic acid and a glycol to prepare phosphated polyester macroglycol.

In the UV cure technology, contributions have come from Zhu and Shi [410–412] and Wang et al. [413]. Different phosphorus-containing diols or triols were reacted with diisocyanates and produced NCO-capped monomers. These monomers were further reacted with hydroxyl group containing

acrylates e.g., HEMA or HEA to produce unsaturated reactive-type flame retardants. For example, methacrylated phosphate (MAP) and diphosphate (MADP) reactive flame retardant for UV-curable formulations were synthesized by Zhu and Shi [412]. In their study, phosphorus trichloride was reacted with ethanol and the resulting product $(C_2H_5O)_2$-POH was treated with sodium bicarbonate and potassium permanganate to get diethylphosphoric acid (DEPA). The reaction of DEPA with glycidyl methacrylate results in MAP, whereas treatment of MAP with TDI produce MADP (Scheme 37a). MADP contains terminal unsaturation and can be used for making PU-acrylate flame retardant formulation. Wang et al. [413] copolymerized DMPE (Scheme 37b) with different acrylic monomers and prepared acrylic co-polyols, which they reacted with MDI for the preparation of flame retardant PUs.

4.2. Phosphorous-containing aziridinyl curing agents

For aqueous-based PUs, the introduction of phosphorus-containing curing agents during the post-curing reaction is a very effective way to impart flame retardancy, improving thermal stability and tensile strength [414,415]. The carboxyl groups of the PU are the reactive sites toward aziridinyl compounds (Scheme 38). A synergistic effect was observed in the aziridinyl and phosphorus-containing compounds in cured PUs. Cured PUs exhibited better thermal stability and a higher oxygen limiting index value. Wang and Chen [415]
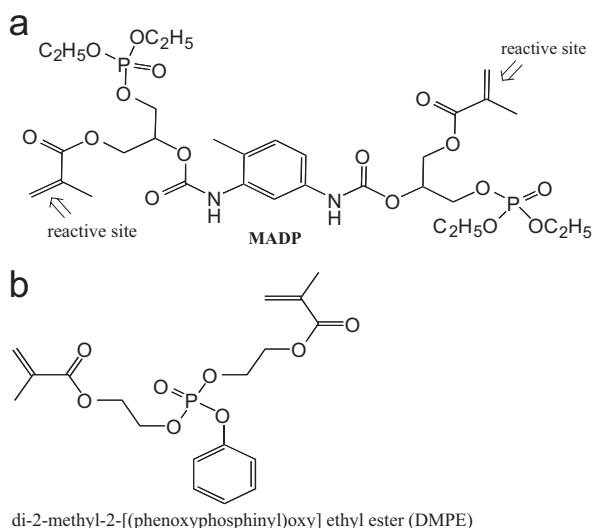
synthesized a series of phosphorus and multi-aziridinyl group containing post-curing agents. Huang et al. [416] introduced aziridinyl phosphazene (NPAZ) as a flame retardant into an anionic PUD and observed an increase in thermal and mechanical properties with a small dosage of the curing agent. NPAZ was prepared from the substitution reaction of hexachlorocyclotriphosphazene with aziridine in a similar mechanism similar to that with $POCl_3$. NPAZ served dual functions: (1) as a crosslinker a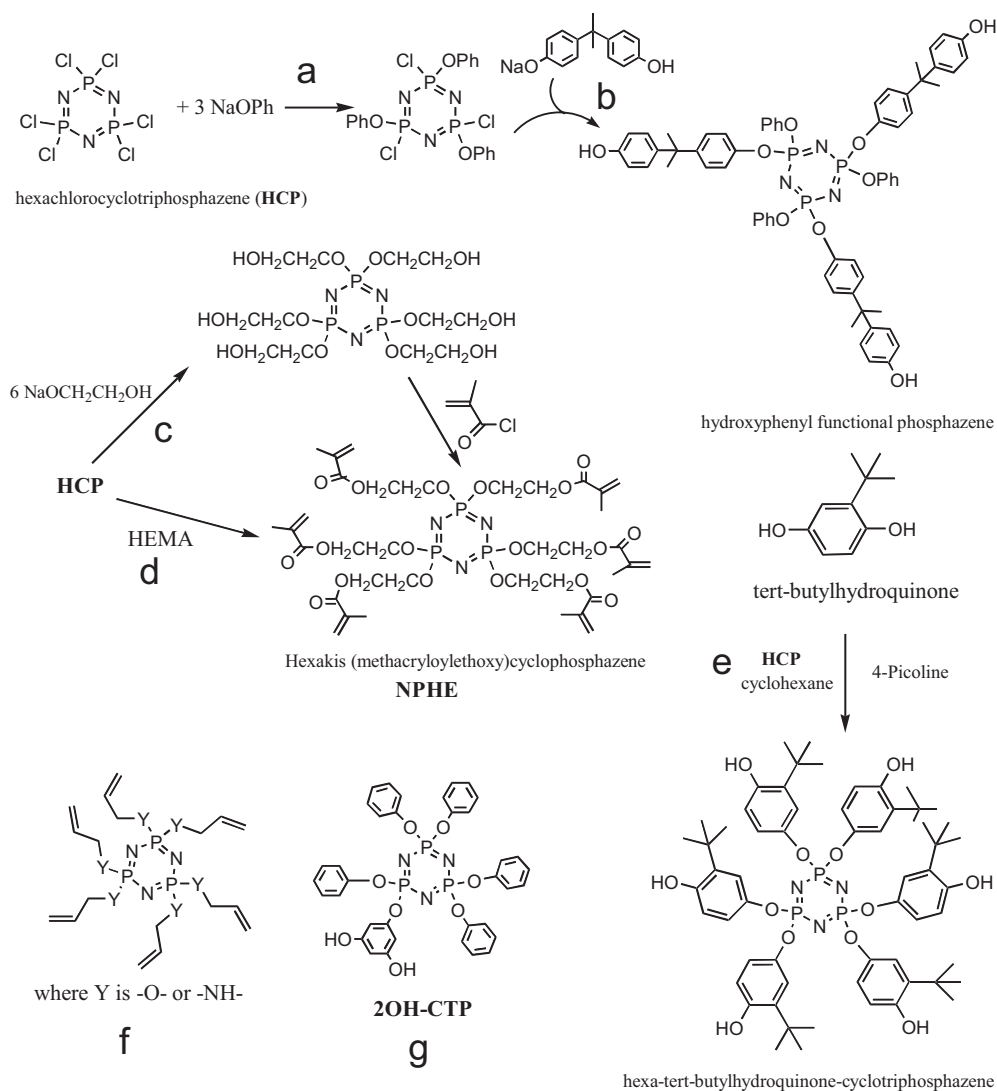nd (2) as a reactive flame retardant for the curing of aqueous-based PU. Therefore, this PU-curing system needs only a small phosphazene-curing dosage to achieve its improved performance.

4.3. Phosphazenes

Phosphazenes, $[NPR_2]$, are an important class of inorganic compounds. The most striking characteristic of phosphazenes is their ability to form high polymers, of which the properties can be tailored by the choice of appropriate R groups on phosphorus. The R group can be an organic, inorganic or organometallic unit. For an in-depth knowledge, readers may go through the review articles about the synthesis and use of functionalized poly(organophosphazenes) and related compounds written by Allcock [417,418] and De Jaeger and Gleria [419]. They are usually prepared by nucleophilic substitution reactions with an alkoxides, aryloxides, or amines containing functionality and by protection–deprotection steps of the respective functions. New additions to the flame retardant application include the blending of poly (bispropoxyphosphazene) with PU [420]. The cyclic trimer of phosphazene is known as cyclotriphosphazene. Cyclotriphosphazenes, one more important type of flame retardant agent, are usually made from the starting material hexachlorocyclotriphosphazene (HCP) with six reactive chlorine atoms. The extreme reactivity of the chlorine atoms towards nucleophilic substitution can be used to introduce a number of functional groups to convert into reactive intermediates. This conversion allows preparation of new monomers and polymers [421,422]. Hexakis (methacryloylethoxy) cyclophosphazene (NPHE) [423,424] can be prepared by direct reaction of HCP with HEMA (Scheme 39d). Reaction of HCP with ally1 alcohol or with ally1 amine can be used to produce allyl-group containing cyclophosphazenes (Scheme 39f). Among hydroxyl functional cyclophosphazene, hydroxyphenyl functional phosphazene [421],

di-2-methyl-2-[(phenoxyphosphinyl)oxy] ethyl ester (DMPE)

Scheme 37. Structure of (a) MADP and (b) DMPE [412, 413].

Scheme 38. Structure of aziridinyl curing agents used in aqueous PUDs and the curing reaction [391, 414, 415].

dihydroxyl cyclotriphosphazene (2OH-CTP) [425] and hexa-tert-butylhydroquinone-cyclotriphospha-zene [422] were synthesized in a similar fashion and can be used to prepare new cyclotriphospha-zene-containing PUs (Scheme 39b, e.g.). UV-curing reaction of phosphazene acrylate monomer e.g., NPHE with PU acrylate oligomer is a convenient

process to introduce covalent-bonded phosphorus into PU [424].

4.4. Silsesquioxanes and organo-boranes

Silsesquioxanes impart flame resistance on in-corporation to PU structure; these are discussed in

Scheme 39. Synthetic methods for the preparation of hydroxy-terminated and allyl group-containing cyclotriphosphazene [391, 421–425].

Section 3.7. The chemical modification of a polymer chain by boron-containing compounds leads to significant improvement in flame retardancy [426]. Tris(2-hydroxypropyl) borate (Scheme 40a) can be used in the PU formulation as a reactive flame retardant. It was prepared from boric acid and 1,2-propanediol [427,428]. Other example includes the reaction products of boric acid with 1,3-butanediol [3], monoethanolamine [429] and epichlorohydrin [430].

Icosahedral carboranes (dicarba-closo-dodecaboranes) are a class of carbon-containing boron-cluster compounds having remarkable thermal and chemical stability and exceptional hydrophobic character compared with other boron-containing compounds. These qualities have made possible the development of extensive derivative and substitution products. Most carborane derivatives of the icosahedral (C_2B_{10}) or small cage (C_2B_4) systems are formed by varying the groups on the cage carbon atoms. This is usually accomplished in the original carborane synthesis by treating substituted acetylenes with either the decaborane or pentaborane precursors to give directly carboranes that have adjacent carbon atoms in the cage (carbon atoms adjacent). The larger cages are obtained as closo-icosahedra. The three isomers of closo-dodecaborane are the *ortho*, *para* and *meta*-form. On heating at 470–600 °C in an inert atmosphere, *o*-carborane undergoes an irreversible thermal reaction resulting

a

b
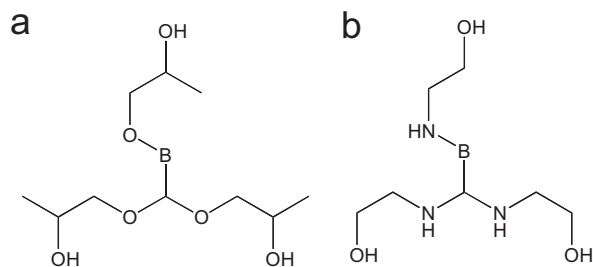
Scheme 40. Structure of boron-containing reactive-type flame retardant prepared from boric acid [391].

in the formation of the *meta*- isomer in quantitative yield. Further heating to about 650–700 °C in inert atmosphere results in another isomerization forming *p*-carborane.

The carborane cage is generally stable towards organic reactions and it is possible to carry out a variety of reactions on substituent groups attached to carborane while leaving the cage system intact. In carborane, the carbon-bound hydrogen atoms are acidic and can be easily deprotonated, allowing the formation of numerous derivatives, including a wide variety of organic substituents. On the other hand, substitution at boron atoms is relatively difficult. The acidic hydrogen atom can be easily removed using alkyllithiums, LDA or *t*-BuOK giving rise to a highly nucleophilic carbanion. Reaction of carbanion with electrophile organo-modifier provides a convenient route to C–C bonds formation (Scheme 41; [431]). For example, Cheung et al. [432] prepared hydroxyalkyl *o*-carboranes by a very simple method. Diaryl-*o*-carboranes with substituents at the *para*- or *meta*-position of aromatic rings are used as backbone structure in various fields of chemistry [433,434]. Vinyl and isopropenyl *o*-carboranes prepared from *o*-carboranes do not polymerize via a radical mechanism due to the high electronegativity of the carborane nucleus and steric hindrances. Whereas, acryloyl or methacryloyl derivatives of *o*-carborane are active and are used in homo- and copolymerization reactions [435].

Delman et al. [436] prepared carboranes-PU and studied the thermal behavior of structurally related polymers having a carborane nucleus in the recurring unit. Parrott et al. [437] prepared a third-generation hyperbranched polyester polyol (Scheme 42) from the functionalized *m*-carboranes. Though the application of this HBP was different in their study, but it can be used in low concentration as a crosslinker in 2 K NCO-capped PU formula-

tion for the preparation of thermally stable PU coatings. For a detailed knowledge of other kinds of flame-retardant additives used in PUs, readers may consult the recent reviews of Lu and Hamerton [391] and Levchik and Weil [3].

5. Application of fluoropolymer in PU coatings

The ever increasing demand of paints for outdoor durability and high resistance in aggressive environments has resulted in ongoing development of fluoropolymer coatings with interesting bulk and surface properties [438–445]. The C–F bonds in organic molecules are very strong and the intermolecular interactions of the fluorocarbons are weak due to the small size and high electronegativity of fluorine. So, the presence of, say the trifluoromethyl group, strongly affects chemical reactivity. For example, nucleophilic substitution at a trifluoromethyl-substituted carbon atom is not an easy process. The difficulty is attributed to destabilization of the transition state by fluorine and also to electrostatic repulsion between a nucleophile and the lone pair of electrons on the fluorine atoms. As a consequence, fluorine-containing polymeric materials exhibit unique property combinations of low surface energy; low friction; low refractive indices; dirt repellant; biological inertness (i.e., resistant to a harsh environment); good resistance to corrosive chemicals; good stability against hydrolysis; low water and ion permeability; low solubility in polar and non-polar organic solvents (being non-wettable and oleophobic, low interfacial free energy) due to substantial hydrophobicity. They also have remarkable resistance to flame, UV radiation, fouling agents like by marine organisms, chemicals, solvents, oxidative attack and possess excellent thermal stability [446–453]. The hydrophobic nature reflects low values of cohesive energy density and surface energy. In general, the strength of the C–F bond increases with the extent of adjacent carbon fluorination, and this means that the longer the fluoroalkyl group is, the higher its stability and hydrophobicity.

Out of the list of properties mentioned above, some are bulk properties, e.g., chemical inertness, thermal stability, and lubricity, and some are surface properties such as oil, dirt and water repellence and cleanability. In many coating applications, the bulk properties of fluoro polymers such as chemical and thermal resistance are the desired properties. In these cases, the use of large quantities
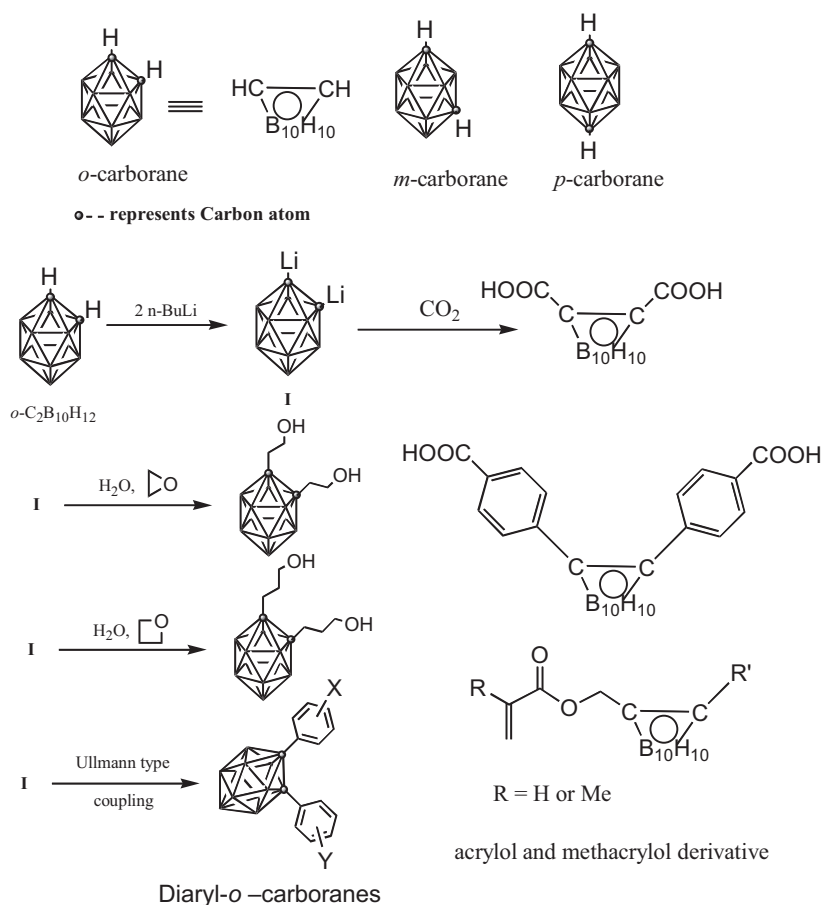
Scheme 41. Structure of caroranes and their derivatives [391,432,433,435].

of fluorine throughout the coating is necessary. However, thermoset PU coatings have adequate chemical and thermal resistance and the use of fluorine-containing monomers and polymers is not a cost-effective alternative approach for structural modification. Therefore, obtaining the repellency and cleanability of a fluoropolymer would be desired with a less cost. In these cases, the surface property improvement by introducing fluorine will tailor the coating for using in aggressive environment and formulator do not need to use systems that have fluorinated groups throughout the bulk of the film. In fact, excess fluorine content throughout the film decreases the adhesive strength at the metal/polymer interface [454].

Incorporation of fluorine into the polymer main chain or its side chains are well known methods that lead to large changes in the surface properties. This is due to the segregation of fluorinated chains toward the polymer–air interface, which results in a considerable decrease in the surface energy. PU is

one material that would benefit from the characteristic properties of fluorinated polymers, as mentioned above. The effect of fluorine-containing PUs on their properties has been described [455–459]. Fluorocarbon chains have been incorporated into PUs via fluoro-containing isocyanates [460], CEs [455–459] or SSs [461–463]. Yoon and Ratner [455–457] and Yoon et al. [458,459] synthesized a series of fluorine-containing aromatic PUs using various perfluoro CEs. They studied the surface and bulk structure of the synthesized PUs. Ho and Wynne [461] and Honeychuck et al. [462] prepared fluorinated PUs based on a series of fluorinated diols to obtain surfaces with minimum adhesion.

The largest part of the scientific contributions refers to the use of short fluorinated CEs. These diols, because of their low MW, do not show any tendency to self-segregate from the hydrogenated moiety. Consequently, these materials present neither improved elastomeric properties nor fluorine enrichment to the surface. Completely different
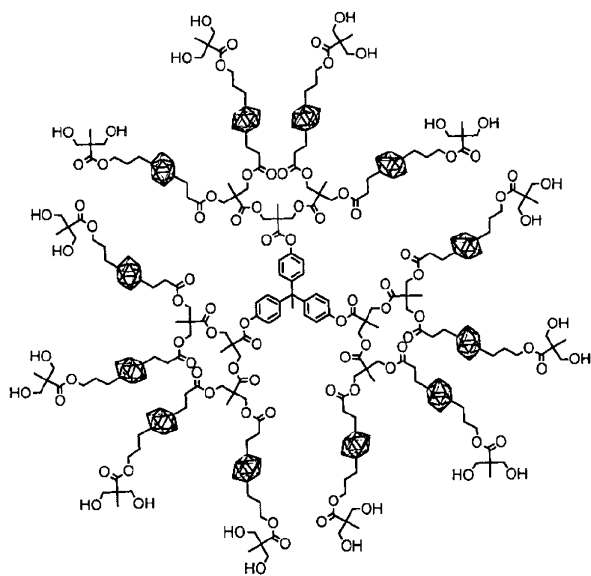
G-3 Polyester Dendrimer

Scheme 42. A third generation hyperbranched polyester polyol from the functionalized *m*-carboranes [437]. Reproduced from Parrott MC, Marchington EB, Valliant JF and Adronov A by permission from WILEY-VCH.

results can be achieved if a poly(fluoro-oxyalkylene) diol having a relatively high MW is used [464–468]. Functional perfluoropolyethers (PFPEs) are known as intermediates for the preparation of high performance coatings [447]. Due to the extremely low viscosity [469], PFPE reactive oligomers having molecular weight about 1000 allow the obtainment of really high solid formulations reaching 80–90 wt% of solid content.

In particular, Fomblin® ZDOL PFPE have a number of peculiar properties such as extremely low T_g, low viscosity, excellent thermal and UV-light stability, insolubility, minimum surface energy. Among them, a family of PFPE OH-functionalized oligomers is currently industrially available and are [470]:

$$HOCH_2CF_2(OCF_2CF_2)_p(OCF_2)_qOCF_2CH_2OH;$$
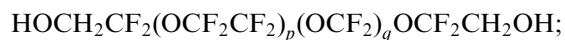
with $p/q = 1 - 2.2$, $Mn = 500 - 4000$.

ZDOL is produced in the oligomeric molecular weight range and it is a low viscosity, high density liquid at ambient temperature. While higher molecular weights are used for the preparation of thermoplastic or thermoset elastomers, lower oligomers (Mn around 1000) are suitable for the preparation of polyfunctional resins for coatings (commercial name Florobase® Z). Scheme 43 shows

the industrially used method for the preparation of Fomblin Z-functional derivatives.

Di and polyfunctional PFPE-based resins (Fluorobase® Z) were recently developed exploiting the above-mentioned positive features [447]. Several properties of this new class of materials have been described [447], including electrochemical impedance for TiO_2-pigmented coatings [472]. Studies have focused on both crosslinked and linear PUs obtained by a full replacement of the hydrogenated soft macromer by a PFPE segment. These studies demonstrated that PFPE-containing PUs offer a larger service temperature range than conventional PUs, combined with superior chemical resistance and surface characteristics [66,452]. Therefore, PFPE-based PUs offers significant advantages in applications where unusual bulk and surface properties are required. In fact, this approach allows one to design new structures depending on the extent of fluorine modification and can maintain most of the outstanding properties of the fluorinated macrodiols.

Delucchi et al. [473] compared the effect of the chain length of the fluoroether macromer on the properties of PUs prepared from HDI polyisocyanurate and IPDI polyisocyanurate. The use of more polydisperse fluoropolyether samples, or bimodal MWDs with significant tails of low oligomers, can give an optimized balance to the desired set of final performances. In another report, Delucchi et al. [474] used ZDOL of molecular weight 500 or 1000 and prepared NCO-terminated resins by reacting with HDI polyisocyanurates. The resins were crosslinked as moisture-cured formulations. Tonelli et al. [475] used a three-step process to reduce the homopolymerization tendency due to the strong incompatibility between the hydrogenated and fluorinated macrodiol. They prepared a hydrogenated –NCO-capped prepolymer from the conventional PTMG macrodiol and MDI, and thereafter a defined amount of fluorinated macrodiol $H(OCH_2CH_2)_nOCH_2CF_2O(CF_2CF_2O)_p(CF_2O)_qCF_2$ $CH_2O(CH_2CH_2O)_nH$ was added and continued the reaction. In the third step, 1,4-butanediol was added as a CE to complete the unreacted NCO reaction and shown that small amount of fluorine content in the range 3.3–15.8% w/w in the PUs produced unique characteristics. The surface properties were close to those expected for fluorine-rich materials, particularly in terms of improved chemical resistance, a reduced coefficient of friction and an easier phase segregation property than conventional PUs.
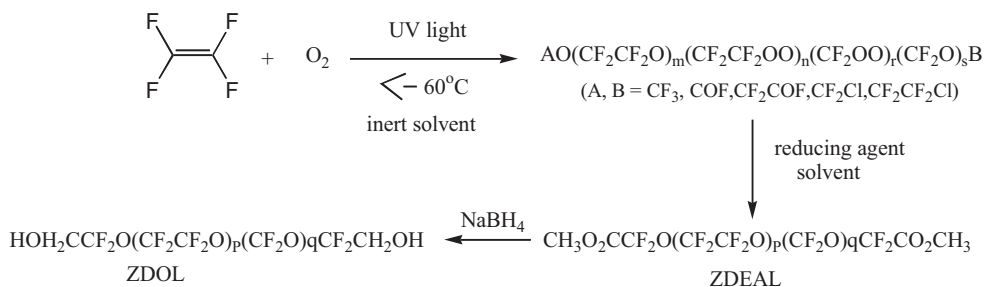
Scheme 43. Industrial synthesis of Fomblin Z functional derivatives [471]. Reproduced from Turri S, Scicchitano M, Simeone G and Tonelli C by permission from Elsevier.

The incompatibility of ZDOL with hydrogenated co-reagents and its reactivity difference with hydrogenated polyols motivated Turri et al. [471] to use a two-step synthesis, in which PFPE-NCO-capped oligomers from IPDI were prepared first, which subsequently chain extended with trimethylol propane (TMP). In their study polyester polyols were also synthesized from ZDOL, aliphatic anhydrides and TMP/neopentyl glycol.

Tonelli et al. [452] described the synthesis of model PFPE-based resins from the etherification reactions of ZDOL. The easiest way involves a base catalyzed etherification with glycidol to give a tetra-ol oligomer bearing both primary and secondary hydroxyls groups (TOL):

$$HOCH_2CH(OH)CH_2OCH_2CF_2O$$
$$(CF_2CF_2O)_p(CF_2O)_qCF_2CH_2OCH_2CH(OH)CH_2OH.$$
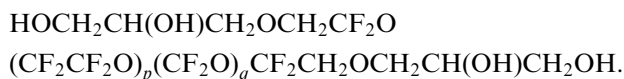
Mixtures of ZDOL and TOL give resins characterized by an OH functionality ranging from 2 to 4, thus allowing adjusting the crosslink density of the final film. Etherification of ZDOL with α,ω-dibromoalkanes followed by polyfunctionalization with diethyl malonate and final chemical reduction produce tetra-functional resins bearing primary hydroxyls (more reactive) exclusively. The reactivity of hydroxyl function in ZDOL is affected by neighboring perfluorinated electron-withdrawing chains, which causes an acidity of the O–H bond. Compatibility with free NCO-containing crosslinkers is achieved when urethane prepolymers like TMP-IPDI or TMP-TDI adducts are used instead of the less polar cyclic trimers of HDI or IPDI. Ho and Wynne [461] prepared a fluorinated diol shown in Scheme 44, which was reacted with equimolar portion of HDI for making PU coatings for preventing settlement of organisms.

Kim et al. [476] used fluorinated oxetane polyol (F-polyol: Scheme 45) for partial replacement of polyhexamethylene carbonate (PHMC) polyol SS in MDI-based PU-containing BDO CE. They examined the effect of fluorine content on the friction coefficient. The dependence of the surface fluorine concentration upon the friction coefficient is displayed in Fig. 4. The setup for evaluating friction behavior was based on the ASTM D1894 method and surface fluorine at% was obtained from XPS results.

Recent technological advances in polymer design have resulted in overcoming of traditional fluorocarbon polymers limitations, giving rise to a new generation of PFPE-based resins that are soluble in common organic solvents, curable at room as well high temperatures and have increased compatibility with curing agents.

At this point, we have described the design requirements for improving the surface properties of PU and as a summary, a few principal design rules are: (a) The fluorine should be in the form of CF_3-terminated fluoroalkyl groups as opposed to CF_2 chains. The surface energy of a CF_2 surface (PTFE: teflon) is 19 dyn/cm, whereas the surface energy of a close-packed fluoroalkyl surface can be less than 10 dyn/cm. The lower we can make the surface energy, the lower the work of adhesion of the contaminants; (b) Fluoroalkyl groups in the binder should be at the surface; if they are not at the surface then they cannot improve the surface properties; (c) The fluoroalkyl groups should be contained in the continuous phase in order to cover the entire surface of the coating. The contrasting case is the PTFE powder filled coating where the fluorochemical is in a separate phase and cannot modify the surface energy of the continuous resin phase. If fluoroalkyl groups phase-separate, then
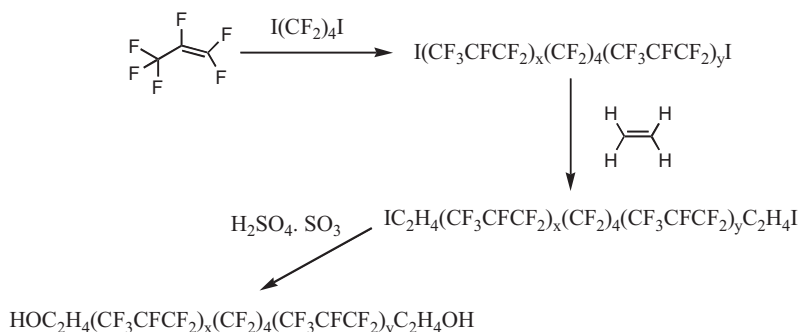
Scheme 44. Synthetic route of fluorinated diol used by Ho and Wynne [461]. Reproduced from Ho T. and Wynne K.J. by permission from American Chemical Society.
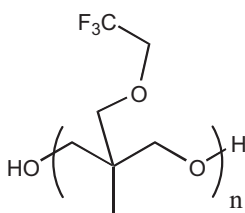
Scheme 45. Chemical structure of fluorinated oxetane polyol (F-polyol) [476].
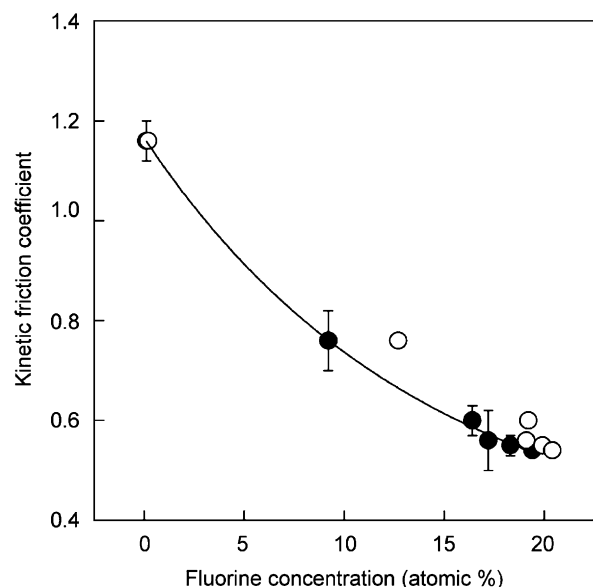
Fig. 4. Dependence of the surface fluorine content on kinetic friction coefficients of solution polymerized PU elastomer [476]. Reprinted with permission from Elsevier B.V., Copyright 2002.

should aim to create a binder where this migration is kinetically allowed, and should understand the mechanism of surface segregation behavior of fluoroalkyl groups and their attachment towards surface during cure reaction of the coating [454]. This behavior may indicate or generate a preferential enrichment of urethane groups at the primer/topcoat interphase and of fluorinated chains at the coating/air interphase.

6. Conclusions

In the past decade, novel ways of material design of PU coatings have grown rapidly from the contribution of polymer and coatings research in academic and industrial laboratories, product developers and corrosion engineers. The broadening in knowledge of materials derived from HBPs with reactive terminals and nanoscience/nanotechnology is already leading to useful products at the consumer level. The steps forward towards the structural engineering of coatings arises from the idea of being able control or enhance the coating durability and properties by tailoring the macromolecular architecture with specific recognition and binding sites (building block functionalization) that may lead to the enhancement in properties at a reasonable cost. In a new perspective, carefully controlled and highly localized structural variation can be considered as an important and useful element of system design. Low VOC coatings and films with previously non-achievable properties can now be produced due to the innovation of a new class of macromolecular architecture, called HBPs and nanotechnology revolution. These booms have created the ability to design and produce, model and surface functionalize nanosystems of many shapes and properties

different phase could introduce haze to the final film [454].

Keeping in mind the thermodynamic driving force for the fluoroalkyl groups promotes their migration to the surface of the coating, the designer

that will allow fabricating new types of coatings with novel properties.

Research efforts in the 1980s were devoted towards thermoset coatings to achieve high performance at a minimum VOC level. During the past decade, the desire to develop high performance eco-friendly coatings at a reasonable cost and competitive market has made the manufacturers of coatings and researchers to reinvent novel ways of designing macromolecular architecture by functionalization or modifying from the core to periphery of a hyperbranched structure by end capping, terminal grafting, surface growing and hypergrafting to achieve tailor-made properties. Research is now focused on the means to incorporate hyperbranched structure into a thermoset for further improvement in solid content, thermal stability and durability of the coatings. Though the aspect of functionalization and application of hyperbranched structure in coatings is still in its early stages, in the near future, more and more interesting materials and structures based on HBPs will be successfully developed for incorporation into coatings.

In the context of nanostructuring, it should be acknowledged that nanotechnology is not new. Unknowingly, nanoparticles have been used in coatings from the older methods using sol–gel processing. The research towards developing novel materials with nanostructures and the outcoming reports over the last decade has created the ability to re-think materials in new ways or to develop coatings with novel and highly desirable properties. Therefore, from an expanding knowledge about the chemistry at the molecular level from these new sciences, it is possible to create new types of functional systems that can take the best advantage of size-tunable properties of nanosized components. The developing ability to make uniform nanoscale components and to include them in complex macromolecular structures will allow technologists to have a new level of control on physical and chemical properties of the components that make up macroscopic materials.

This review provides an up-to-date summary of the syntheses, properties and applications of PU coatings for high performance applications. Various main routes have been successfully used to improve the performance characteristics have been discussed. This review hopefully will open up new possibilities from both practical and fundamental view points for paint formulator and researchers to improve the performance, durability and to understand the important role of design consideration on coating properties.

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