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The impact of 1,2,3-triazoles in the design of functional coatings

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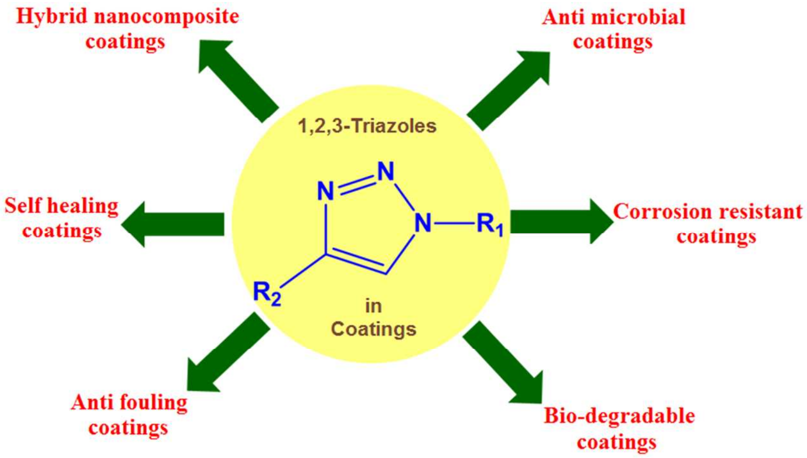
Abstract

In recent times 1,2,3-triazole rich molecules have gained much importance in the field of polymer and material science because of their excellent properties like strong anti-microbial and anti fouling nature of the triazole ring along with easy synthetic procedures and exceptionally high yield of end product. Generally these molecules are synthesized by azide-alkyne click reaction and this chemistry has gained potential application in the functionalization of wide range of inorganic moieties like metal oxide nanoparticles, carbon nanotubes etc. to develop hybrid nanocomposites for high performance materials. Based on the previous reports, this particular review article provides a comprehensive overview of the application of 1,2,3-triazoles in the design of various high performance organic coatings such as anti-corrosive, anti-microbial, self-healing, hybrid nanocomposite, bio degradable etc.

Graphical abstract



Introduction

Organic coatings are normally applied on surfaces for decorative, protective or functional purposes, but in most cases it is a combination of these[1]. If the coating shows an additional functionality (e.g., anti-corrosive, anti-microbial, self-healing, self-cleaning, flame-retardancy etc.), along with the conventional properties (i.e., decoration and protection), they will be termed as functional coatings[2]. This additional functionality can be achieved by modifying the structure of the macromolecule with heteroatoms[3,4] or by improving cross-linkings in the polymer structure[5] or by addition of some organic additives[6] or by the addition of some inorganic nanomaterials[7,8] etc. In general, the concepts of synthetic organic chemistry are highly helpful in development of new polymeric architectures with functional properties for the design of functional polymer coatings and allied products.[9,10] For a synthetic organic concept to be applicable in the design of macromolecules, the reactions must i) result in a stable linkage, ii) exhibit minimal cross-reactivity with other functional groups, iii) react to completion, iv) be free of appreciable amounts of side products, and v) proceed under gentle reaction conditions.[11] In this regard, the 1,3-dipolar cycloaddition reaction between azide and alkyne has been attracted by many material science research groups all over the world because of versatile properties of triazoles. In the historical prospective, the reaction mechanism of 1,3-dipolar cycloaddition between azide and alkyne for the formation of 1,2,3-triazole proposed for the first time by Rolf Huisgen in early 1960s. [12,13] In that procedure, two regioisomers of 1,4 and 1,5-substituted 1,2,3-triazoles were formed, and this reaction became famous as Huisgen 1,3-dipolar cycloaddition. After long time in 2001, Prof. K.B.Sharpless in Scripps research laboratory has developed 1,4-regio isomer selectively in the presence of Cu (I) catalyst at room temperature and this reaction became popular as Click reaction. In addition, Fokin and Jia *et al.*, demonstrated that 1,5-regio isomer can be selectively synthesized in presence of ruthenium (II) catalyst[14] (Fig.1a). Thereafter, Sharpless introduced the concept of click chemistry and defined it as "*A click reaction must be modular, wide in scope, high yielding, create only inoffensive by-products (that can be removed without chromatography), are stereo specific, simple to perform and that require benign or easily removed solvent*".[15] The click chemistry involves some specific reactions along with the copper catalyzed azide-alkyne cycloaddition reaction such as thiol-ene reaction (addition reaction between thiols and olefins), Diels-alder reaction (cycloaddition reaction between diene and dienophile), nucleophilic ring opening reactions (e.g., opening of epoxides with amines and thilos), addition of carbon-carbon multiple bonds and non-Aldol type reactions of carbonyl compounds (e.g., the formation of oxime ethers, hydrazones) etc.[16,17]. In short, the concept of click chemistry involves those reactions with high atom economy and simple reaction conditions. In case of 1,2,3-triazole formation the rate of reaction between azide and alkyne cycloaddition reaction is enhanced by 10^7 times in presence of Cu (I) catalyst than the non catalyzed reaction.[18] The reaction mechanism was given in the Fig.1b. Moreover, the Cu (I) catalyzed azide-alkyne cycloaddition reaction is regiospecific, chemoselective; thermodynamically and kinetically favourable (50 and 26 kcal/mol, respectively).[19] Apart from the azide-alkyne cycloaddition reaction, 1,2,3-triazole compounds can also be synthesized by other routes like diazotization of aromatic orthodiamines[20], C-H activation of aryl triazine compounds in presence of lead acetate catalyst[21], reaction of organic azides with ethylacetoacetate[22] in presence of sodium methoxide catalyst etc. (Fig.2).

The azide-alkyne click chemistry has already made revolutionary advancements in many research fields like organic synthesis, bio-chemistry, drug discovery, nanotechnology, supramolecular chemistry, pharmaceutical chemistry, bio-conjugation, peptide modifications.[23-26] However, the present review is restricted to the azide-alkyne click reaction (AAC) for the fabrication of functional polymer coatings. Since, the 1,2,3-triazoles are highly stable towards oxidation and acid hydrolysis[27], coating formulations with such type of materials are highly helpful in the design of exterior applications. Since each 1,2,3-triazole ring contributes the enthalpy of formation up to 168 kJ mol^{-1}. Hence, their inclusion in the polymer matrix improves the overall thermal and moisture resistance of the polymer hybrid, which could be utilized for the development of high-enthalpy modifiers in energetic binders and heat-resistant polymeric resins in advanced composite materials.[28,29] The large dipole moment of 1,2,3-triazole ring transforms N-2 and N-3 nitrogen atoms present in the triazole ring as good H-bond acceptors.[30] This hydrogen bonded triazole act as a biologically active site which shields the material from various bacterial and fungal attacks, which can find its application in coatings for biomedical applications.[31] Due to these interesting properties, 1,2,3-triazoles can extensively be used to attain better properties in various fields of polymer & material science such as corrosion protection[32], fabric coatings[33], anti-microbial coatings[34], biodegradable polymers[35], energetic binders[36], biomedical applications[37] and so on.

Applications of 1,2,3-triazole compounds in functional coatings

In this section, the applications of 1,2,3-triazoles are discussed briefly in the development of various coating technologies like anti-corrosive coatings, anti-microbial coatings, foul resistant coatings, self-healing coatings, bio-degradable coatings, nano composite coatings and other smart coating applications like UV resistance, self-cleaning, coatings for bio-medical applications, fire retardant materials, functionalization of various polymers etc.

Corrosion resistant coatings

Corrosion of metal substrate causes economic losses and environmental pollution.[38] The use of polymer coating with an organic inhibitor is one of the most practical, economic and eco-friendly way to stop the corrosion.[39] Organic inhibitors usually have hetero atoms like O, N, and S in their chemical structure. Such structures are found to have higher basicity and electron density and thus act as corrosion inhibitors.[40] In this regard, heterocyclic organic compounds with delocalized set of electrons are known to be good corrosion inhibitors. Since, 1,2,3- triazole compounds are heterocyclic compounds having three nitrogen atoms, having a planar delocalized conjugated system, when these moieties are adsorbed on the surface of the metal, each molecule covers large surface area and they can block the active sites by forming a co-ordinate covalent bond with the metal substrate, which leads to the decrease in the rate of corrosion of the metal.[41] And also, the polarity of the triazoles induces an electrostatic attraction on the metal surface so as to protect the metal substrate from corrosive medium. For example, the work of B. Hammouti *et al.*, showed that 3-amino-1,2,3-triazole as an excellent corrosion inhibitor even in aggressive acidic media containing phosphoric acid.[42] Similarly, Guillermo EN *et al.*, synthesized some novel 1,2,3-Triazole derivatives of Uracil and Thymine and have proved that these materials have potential inhibitory activity against acidic corrosion of steels.[43] Another important aromatic triazole compound is tolyltriazole; since the work of M.A. Migahed showed a feasible path to synthesize environmental friendly non-ionic surfactants based on tolyl triazole and then proved them as effective inhibitors for oil tubing steel during production process.[44] In detail, they have synthesized the inhibitors by reacting tolyl triazole with citric acid in 1:1 molar ratio to get a di acid terminated tolyl triazole product and which was further treated with polyethylene glycol in order to form the corrosion inhibitor and also observed that the inhibition efficiency of surfactants increased by increasing both the number of ethylene oxide units and molecular size of the molecule. Here the inhibition mechanism was again due to the strong adsorption ability of triazole groups onto the surface of the metal, which leads to the formation of protective layer on the surface and protects from the aggressive environments. Further, Michael T. Kocsik *et al.*, have patented that the composition of tolyl triazole treated carbonyl iron particles (0.1 to 10 microns size) with the polyurethane matrix. Here, tolyl triazole stabilizes the surface of the carbonyl iron particles against atmospheric oxidation (prevent rusting), which results corrosion resistant, electrically non-conductive, ferromagnetic metallic filler. The stabilized metallic fillers were then incorporated into a polyurethane matrix. The final composite material exhibits excellent corrosion resistance property. Due to the ferromagnetism of the metallic fillers, the hybrid coatings also useful as microwave absorbing materials.[45]

More particularly, these triazole compounds have attracted application in the corrosion inhibition of the copper and many of its alloys.[46] Copper development association (CDA), USA also approved that 1,2,3-benzotriazole as an efficient corrosion inhibitor for copper metal.[47] The corrosion protection mechanism on copper metal is via the formation of polymeric 5- and 6-membered copper-inhibitor ring complex on the copper surface by reaction between the triazole ring and the metal surface.[48] Further, the addition of little amount of benzotriazole to water, have been effective in preventing galvanic corrosion in mixed metal systems such as copper-steel, copper-zinc, and copper-aluminium.[49] However, triazole compounds lose its inhibition efficiency over copper metal, in environments polluted with sulfide ions. In sulfide polluted environments, sulfide ions compete for Cu (I) ions under a much stronger driving force than triazole units, consequently, sulfide ions can extract the Cu (I) ions from the Cu (I)-triazole complex. This leads to the breakdown of the protective film and occurrence of corrosion on the bare areas.[50] To overcome this problem, Faiza M. Al Kharafi *et al.*, have developed a method of vacuum pyrolysis of triazole derivatives (like benzotriazole) on the surface of copper which leads to the deposition of a compact layer of the inhibitor and this could resist the poisoning effect of sulfide ions.[51] The chemical structures of some of these triazoles were given in Fig.3.

Anti microbial coatings

Antimicrobial coatings are useful in the development of hygienic surfaces. These are having some antimicrobial agent in their composition that either can kill or inhibit the growth of microorganisms.[52] These types of coatings have immense applications in the design of materials and devices in health care sector, hospital surfaces, surgery equipment, health-care products, water purification systems, textiles, food packaging and storage, domestic appliances etc.[53] Commonly used antimicrobial surfaces contain some antibiotics, silver ions, quaternary ammonium cations, halogens or some heterocyclic compounds.[54] Since 1,2,3-triazoles consist of excellent biocidal activity, and in most of the cases, this nature mainly due to the formation of hydrogen bonds by triazole rings with other moieties. In detail, the large dipole moment of 1,2,3-triazole modulates N-2 and N-3 nitrogen atoms present in the triazole ring as good H-bond acceptors.[8,55,56] This hydrogen bonded triazole acts as a biologically active site, that shields the material from various bacterial and fungal attacks, which can find its application in anti-bacterial coatings and biomedical applications.[9,57] And also these triazoles have excellent ability to bind effectively with various sterols present within the fungal membrane, such type of property useful in the development of anti-fungal coatings.[58]

The azide-alkyne click reaction also useful for incorporating effectively various other anti-bacterial compounds covalently into the coating formulation. For example, Kitty K.K. Ho *et al.*, have successfully attached a quorum sensing and antibacterial fimbrolides like dihydropyrrolones (DHPs) and various furanone derivatives covalently onto the coating surface using this azide-alkyne click reaction[59] (Fig.4). This shows that covalently bound DHP compounds are effective in reducing the adhesion by up to 97% for both Pseudomonas aeruginosa and Staphylococcus aureus and also these compounds inhibits the quorum sensing (QS), which shows a possible route to development of membrane based QS inhibition. Similarly, Lin Wang *etal.*, successfully attached a short antimicrobial peptide Tet-213 onto the silicon surface by Cu(I)-catalyzed azide–alkyne cycloaddition (Fig.5) and showed that the resultant surfaces inhibited 99.3% of *S. aureus* and 95.0% of *E. coli* bacteria in 2.5 h, and destroyed the walls of the bacteria with low cytotoxicity to rat bone mesenchymal stem cells.[60] Recently, our research group also synthesized triazole rich hyperbranched polyester and polyether polyols and were converted into polyurethanes. These polyurethane coatings exhibited a remarkable stability towards various bacterial and fungal stains. In order to incorporate the 1,2,3-triazole units into the polyurethanes, initially a hydroxy terminated triazole core molecule was synthesized by reacting ethylenediazide with 2-butyne-1,4-diol, which was then reacted with 2,2-bis (hydroxymethyl) propionic acid in order to develop a triazole rich hyperbranched polyester polyol(Fig.6) for the development of polyurethane coating applications.[61] Further, we have also shown a feasible path for the design of 1,2,3-triazole rich hyperbranched polyether polyols for the development of antimicrobial and anti-corrosive polyurethane coatings with high yields. The synthetic paths for the design of these polyols were given in Fig.7a. In order to synthesize these polyols, initially chlorinated polyols were prepared by reacting trimethylolpropane with epichlorohydrin and these polyols on further treatment with sodium azide and propargyl alcohol results triazole rich polyether polyols.[62] In another article, similar type of polyether polyol was synthesized by ring opening of trimethylolpropane triglycidyl ether with sodium azide, which on treatment with propargyl alcohol gives triazole rich polyols (Fig.7b). These polyols are reacted with 1-isocyanato-4-[(4-isocyanatocyclohexyl) methyl] cyclohexane (Fig.7c) to synthesize triazole rich polyurethanes[63], which are showing excellent stability towards various bacterial and fungal attacks (Fig. 7d). This activity is mainly due to the more possibility for the formation of active biocide unit by forming hydrogen bonding between triazole ring and urethane groups.

Foul resistant coatings

Shipping industry has been facing problems with fouling of marine organisms, such as algae, mussels, and barnacles on ship hulls.[64] It is reported that more than 4000 marine organisms have been identified in fouling structures worldwide.[65] Marine biofouling produces high frictional resistance, leading to increased fuel expenditure, maintenance costs and green-house gases emissions.[66] Additionally, marine biofouling causes pitting corrosion in metals and such environments results degradation and failure of materials and structures.[67] In 1970's tributyltin self-polishing coating (TBT-SPC) was developed, which is composed of acrylic co-polymers with an active substance TBT.[68, 69] But due to the usage of hazardous TBT in the formulation, wakens the fish immune system and causes imposex and sterility in female mammels.[70, 71] Due to the restrictive legislation regarding TBT paints, number of tin free SPC were developed in 1990's by replacing tin with copper.[72, 49] Even though, copper ions are showing good antifouling nature, unlike, TBT these are not showing long term foul resistance due to conversion of Cu^{+2} to Cu^0. In order to get long-term fouling protection, it is now essential to add other biocides, so called *boosters*, in combination with copper.[73] After a lot of research, it is found that triazoles and imidazole based molecules are boosting anti-fouling nature of SPC paint towards a wide spectrum of antifungals. These units make co-ordination bonds with copper ion and make them stable and causes controlled release.

From literature, Koichi Kamijima *et al*., have patented several long lasting antifouling polyester based coating and varnish formulations which contain copper compounds along with 1,2,3-triazoles like derivatives of benzotriazole, alkyl or aryl substituted triazoles as antifouling additives. The resultant eco-friendly coating compositions have excellent long lasting antifouling properties which equals organotin copolymers.[74] Another strategy proposed by Christopher J. Ochs *et al.*, in which they have successfully attached poly(L-lysine) (PLL) and poly(L-glutamic acid) using azide-alkyne click reaction and the capsules were post functionalized by depositing a monolayer of hetero bifunctional poly(ethylene glycol) (PEG). The resultant coating films showed excellent antifouling property along with bio-degradable nature[75] (Fig.8). Simone Ciampi *et al.*, have integrated biological molecules on the surface of silicon wafers with azide-alkyne click reaction. The surface of the silicon wafer was first modified with alkyne groups by hydro silylation reaction. These acetylene terminated silicon wafers were further reacted with an anti biofouling moiety 2-{2-[2-(2-azidoethoxy)ethoxy]ethoxy}ethanol groups (Fig.9). These silicon wafers have excellent antifouling nature and can be used for applications as diverse as biosensors and molecular electronics.[76]

In recent times, polymer bush coatings synthesized by using controlled radical polymerization and click chemistry strategies have gained much interest in the design of antifouling polymer coating formulations.[77] The polymer brush coatings can prevent marine biofouling with the integration of functional groups with specific anti-adhesion, microbial resistant and corrosion resistant properties, to provide a non-biocide releasing, eco-friendly antifouling coatings.[78] Recently, Wan JY et al., have developed several antimicrobial and foul resistant coatings by using barnacle cement with the help of azide-alkyne click chemistry.[79,80] Barnacle cement is an eco-friendly biological adhesive from barnacles, which has strong adhesion to metal substrates due to its high chemical reactivity.[80] The authors first coated the stainless steel surface with barnacle cement, which results surface with amine and hydroxy functional groups. The surface on treatment with azidoethyl carbonyl imidazole results azide terminal surface (SS-Azide). To this surface, a highly antifouling alkyne-functionalized poly(N-hydroxyethyl acrylamide) and antibacterial alkyne-functionalized poly(2-(methacryloyloxy)ethyl trimethyl ammonium chloride) polymers were attached by using azide-alkyne click reaction (Fig.10a). The resultant bifunctional polymer brush coatings are showing excellent antifouling and antibacterial properties, especially on gram-negative *Escherichia coli* (*E.coli*) and gram-positive *Staphylococcus epidermidis* (*S.epidermidis*). The same research group reported another approach to develop antifouling and antimicrobial multi-layer polymer coatings by using azide-alkyne click chemistry.[81] In this approach, initially the surface of the stainless steel was terminated with alkyne functional groups by treating with propargyl amine. To this, Fouling-resistant azido-functionalized poly(ethylene glycol) methyl ether methacrylate-based polymer chains (azido-poly(PEGMA)) were attached through click reaction. The azide terminal surface was made to react with antimicrobial alkynyl-functionalized 2-(methacryloyloxy)ethyltrimethyl ammonium chloride-based polymer chains (alkynyl-poly(META)). The process was continued several times to create layer by layer assembly of antifouling and antibacterial surfaces (Fig.10b). The resulted multilayer polymer coatings are showing high resistance to bacterial adhesion and excellent bacterial resistance towards *Pseudomonas* sp. NCIMB 2021 and also the settlement of barnacle *B.amphitritecyprids* on the multilayer coatings was reduced by up to 80%. The antifouling efficiency of the coating increases with number of deposited polymer layers on the stainless steel surface.

Self-healing coatings

In modern years, self-healable polymeric materials are gaining much consideration in the field of coatings and associated fields. Self-repairable polymers can be categorized into two categories. One being an autonomic self-repair process that requires no external stimulus except the damage whereas; the other is a non-autonomic process, which is responsive to a specific external stimulus like heat and light.[82] The irreversible formation of 1,2,3-triazole ring from 1,3-dipolar cycloaddition reaction between azide and alkyne has investigated its application in the development of self healingmechanisms.[83] However, there are very less number of reports available on self-healing coatings based on azide-alkyne click chemistry. Earlier reports by Maria Gragert *et al.,* [84] proposed an encapsulated azide and alkyne monomers into nanocapsules, which were then incorporated into a variety of liquid polymers (Fig.11). When damage occurs, the capsules will break the healing agent leaks into the damage and then polymerizes. It was reported that these polymers showed excellent self-healing property in presence of Cu (I) catalyst at room temperature along with considerable improvement in the storage modulus after healing because of improved cross-linking. Another interesting strategy was made by Qiang Wei *et al.,* [85] in which they have reported a hyperbranched poly(aryl triazole) system with terminal azide and alkyne functional groups for self-healing coatings. In this approach, the healing of the damaged area happened by heating the damaged area at 60-70°C. Upon heating, the terminal unreacted azide and alkyne groups react each other by 1,3-dipoalr cycloaddition reaction without any Cu(I) catalyst in order to repair the damaged area. Here, the healing was done by simple heating because the azide and alkyne groups can react with each other above 60°C temperature (Fig.12).

Hybrid nanocomposite coatings

Nanoparticles are the particles with size ranging from 10 nm to 1000 nm.[86] Metal and metal oxide nanoparticles are grasping much attention in various industrial applications and research fields due to their unique properties like large surface to volume ratio, high thermal and mechanical stability.[87] Nanoparticles have made revolutionary advancements in many fields like drug delivery[88], catalysis[89], biological sensors[90], textiles[91], cosmetics[92], sports goods[93] etc. In the past decade, several academic and industrial research groups from all over the world have enlarged this field to develop various polymer coatings for high performance applications. The integration of nanomaterials gives superior and advanced properties to the polymer coatings like hydrophobicity[94], thermal stability[95], mechanical strength[96], antimicrobial nature[97] etc. However, the direct incorporation by physical methods is difficult in most of the cases.[98-100] So, the surface modification of the nanoparticles is essential for attaining desirable properties.[101] The surface modification stabilizes the nanoparticles against agglomeration, renders them compatible with another phase and enables their self-organization.[102] A plethora of different methodologies have been used for surface modifications of nanoparticles. In most of the cases, a uniform self-assembled monolayer was formed around the nanoparticle surface by organosilanes, phosphonates and carboxylates etc.[103] Along with these techniques, the surface can be further efficiently modified with organic molecules, polymers, complex ligands, biological elements etc in order to achieve desirable properties by utilizing the concept of azide-alkyne click chemistry.[104] In order to connect the nanomaterials to the polymeric structures using click reaction, initially the surface of the nanoparticles was modified using azide or alkyne functional groups and then reacts with alkyne or azide functional polymers.[105]

Since silica nanoparticles have potential applications in the field of coatings in order to enhance hardness, hydrophobicity, temperature and weather resistance of the coatings.[106,107] But due to high surface energy the nano-silica aggregates easily, which limits its application large extend.[108] Azide-alkyne click chemistry offers a better solution to overcome such problem by surface modifications. For example, Daoxing Sun *et al.*, have successfully modified the surface of the silica nanoparticles with azide moieties and then reacted with alkyne terminated water borne polyurethane in presence of Cu(I) catalyst at room temperature. They have obtained upon loading of 3 weight percentage of silica content, the water contact angle was increased from 61° to 91° and the hardness of the coating improved from HB to 2H[109] (Fig.13). Further, azide-alkyne click reaction discovers its application in the fabrication of cactus-like hierarchical structures around the silica nano-wafers with controllable size.[110] The surface roughness of the particles biomimics the surface topology of sticky super hydrophobic gecko feet. These hierarchical silica particles were produced by self assembly of azide- and alkyne- modified silica in a series of sequential cycles. In final stage, the surface was modified with hydrophobic fluorinated azo-molecule by click reaction. Various steps involved in the synthesis of these particles were given in Fig.14a. It was demonstrated that the surfaces were super hydrophobic with a contact angle that increased from 134° to 152° with increasing silica coupling cycles.

Since Titanium dioxide nanoparticles are one of the mostly used nanoparticles in the coating formulation in order to develop self-cleaning, high refractive index and anti-corrosive coatings.[111,112] The strong absorption of the UV rays by these nanoparticles helps in the development of UV resistance of coatings.[113] Due to their large surface-area/particle-size ratio, TiO_2nano-particles tend to agglomerate easily, hence reduces the resultant mechanical properties of the nanocomposite materials.[114] Thus, in order to produce suitable nanocomposite coatings it is necessary to disperse the nanoparticles without aggregation in organic binders. For instance, Peng Tao *et al.*, developed a transparent TiO_2 polymer nanocomposite coating with high refractive index by grafting poly(glycidyl methacrylate) chains onto the surfaces of TiO_2 nanoparticles via phosphate coupling and triazole formation.[115] This grafting leads to overcome the agglomeration of the nanoparticles and the refractive index of the composites increased by 0.3 with 60 wt% loading of TiO_2 fillers, while maintaining more than 90% transparency (Fig.14b) in the overall visible light range.

In the field of nanotechnology, carbon nanotubes (CNTs) are gaining much attention because of their unique properties in electronics, solar cells, optical devices, and biomedical devices.[116] Recently the carbon nanotubes also can effectively modified with different moieties using the click reaction. By using this strategy, the surface of the CNT surface can be covalently attached to other substrates effectively. For example, Santosh KY *et al.,* have modified the CNT surface with alkyne groups and have attached a hyperbranched azide polymer and observed the uniform dispersion of CNTs in the polymer matrix(Fig.15).This polymer composite has superior mechanical properties along with excellent anti microbial properties.[117] Another potential application by using polyurethane-CNT composite materials was reported by Sasidhar K *et al.*, [118] where the surface of CNT was modified using a hyperbranched polyol through azide-alkyne click chemistry (Fig.16). Upon incorporation of 2 wt% of the modified CNT into a polyether based polyurethane matrix, the tensile strength of the polyurethane hybrid composite improved from 1.25 to 6.25 N/mm^2; water contact angle improved from 54 to 108^o and also the rate of corrosion reduced from 0.047 to 0.0019 mm/year. It is also observed that these hybrids possess remarkable shape recovery properties, which is attributed to the excellent mechanical stability of the CNT and high thermal conductivity coefficient. The above works demonstrate that the decorated CNT can be used as high performance additive for improving various properties of polyurethane hybrids in cost effective and eco-friendly ways.

Since polymer/clay nanocomposites are also an attractive research area in the development of coatings for engineering applications because of the excellent barrier properties of the nano clay particles.[119] In general exfoliated clay structures are more useful to prepare polymer composites with advanced properties like flame resistance and barrier, mechanical, electronic, and optical properties.[120] Again in the development of these composite materials, the most important challenge is the effective dispersion of clay particles in the polymer matrix. Azide-alkyne click chemistry is one of the interesting tools to exfoliate the clay nano particles and to synthesize functional coatings. Yun-Sheng Ye *et.al.*, have prepared an alkyne modified montmorillonite clay particles and then synthesized a polytriazole-clay nanocomposite using *insitu* polymerization (Fig.17). In this approach, the clay layers completely exfoliated and well dispersed with polymer matrix, which results a highly thermally stable nanocomposite.[121] Further, the application of click chemistry extends to develop protein resistant coatings using nanodiamonds. From literature, it is observed that Ivan Rehor *et al.*, have constructed a biocompatible fluorescent bioimaging probes for targeting cancer cells (Fig.18) and they are also useful as Protein-Resistant Polymeric Coatings by modifying the surface of the nanodiamonds with polypeptides using click reaction.[122]

Green biodegradable coatings

Vegetable oils based products are highly useful in the development of eco-friendly polymers for coatings and allied products.[123,124] Most importantly, polymer coatings derived from the naturally available oils are prime alternatives to coatings derived from petroleum based polymers.[125,126] The polymerization of these oils can be achieved by introducing polymerizable functional groups in their structural backbone.[127] Most of the established approaches like transesterification of triglycerides, hydroformylation of double bonds etc. suffered with some disadvantages like cumbersome conversion and often require expensive reactants or catalysts. To the best of our knowledge, there are very less reports available on polymers from triazole modified vegetable oils. For example, Hadi Bakhshi *et al.*,[128] have developed a 1,2,3-triazole ring incorporated soybean oil polyols. They have synthesized azidated soybean oil by nucleophilic ring opening of epoxidized oil with sodium azide. In the next stage, this azide terminated soybean oil was treated with various alkynes like propargyl alcohol, phenyl styrene and N,N-dimethylpropargyl amine (Fig.19). The resultant triazole rich polyols were treated with isophorone diisocyanate to synthesize corresponding polyurethanes. They have reported that thermal stability, glass transition temperature, hardness and mechanical strength of the coating improved along with superior biocidal activity. Among these, polyurethane derived from the N,N-dimethylpropargyl amine has a tertiary nitrogen atom, which are useful to create quaternary ammonium salt by reaction with methyl iodide and the authors reported that this particular polyurethane was showing excellent biocidal activity against various microorganisms especially on E. coli, S. aureus, and C. Albicans. Jian Hong *et al.,* have developed a wide range of biopolymers by coupling various oils through azide-alkyne coupling reaction. They have reacted alkyne terminated soybean oil with azidated vegetable oils such as soybean, castor, linseed, canola, corn oils with simple heating at 100^{o}C, in catalyst and solvent free conditions. The cross-linked networks shows good thermal stability, such as it takes 500^{o}C temperature for complete degradation. Tensile strength and glass transition temperature of the coating films are high in case of canola oil based polyurethanes.[129] Again, the same research group reported another approach in which, cross-linked vegetable oils by reacting azidated vegetable oils with a di-alkyne molecule through click chemistry for designing various coatings[130] (Fig.20). This type of triazole cross-linked polymers is better alternatives to the conventional polymeric coatings.

Other smart coating applications

Along with the above mentioned applications, 1,2,3-triazoles proved their efficiency in the development of other functional coatings like UV resistant coatings, hydrophobic coatings, highly cross-linked polymer coatings, powder coatings, fire resistant materials and coatings for bio-medical applications etc. In this section, some miscellaneous applications of the triazole materials are discussed.

One of the main problems of exterior coatings is their stability to UV exposure as the white paint will turns into light yellow, whereas dark paints will get shaded. To avoid such problems, some of the 1,2,3-triazole compounds are extremely useful. For example, with addition of small amount of additive like 2-hydroxy 4-methyl benzotriazole into the coating formulation, acts as UV absorbers and hence prevent the paint from deteriorating.[131] There are some reports available in which, 1,2,3-triazole based compounds were used to improve the cross-linkings in the coating formulations. For instance, Priyanka KG *et al.,* have synthesized a triazole based pentol cross-linker using click chemistry and then incorporated into NCO terminated polyurethane matrix (Fig.21a) in order to improve thermo-mechanical properties of the polyurethane coatings; with loading of 10% cross-linker and it is observed that the tensile strength of the polyurethane was improved from 27 MPa to 43 MPa.[132] Dean C. Webster and co-workers have synthesized novel dihydroxy functional 3-arm star polymers by combining three techniques such as atom transfer radical polymerization (ATRP), ring opening polymerization and click chemistry and then incorporated into a polyurethane matrix. Here the role of click chemistry is to couple the alkyne-functional polycaprolactone diol and the azide-functional ATRP polymers to form the novel diols with pendant polymer chains. Due to the presence of acrylate and styrenic units in the polymer chain, the diol chain extender shows biocompatible and hydrophobic nature. After incorporation into the polyurethane matrix (Fig.21b), the hybrid coatings were showing superior properties like improved contact angle and glass transition temperature.[133]

Further the application of the azide-alkyne reaction was extended in the development of bio-medical coating applications by immobilization of various bio-molecules on various surfaces.

For example, Canalle LA used the strain promoted azide-alkyne click reaction to modify the surface of the glass by direct polymer deposition (Fig.22). Initially they have modified the surface of the glass with alkyne functional groups using silane coupling reaction. In the next stage, an azide containing polymer was coated on the surface and cured at 120^{o}C to couple azide and alkyne groups. Later the unreacted azide groups were functionalized with alkyne containing coumarone derivatives. As a result of the transparent and bio-orthogonal nature of this functionalization step, bio-molecules are expected to retain their activity after immobilization on these clickable coatings. Omitting copper during both the synthesis and functionalization of the coatings makes this procedure highly suitable for biomedical applications.[134] On the other hand, Xiaopei Deng *et al.,* and Himabindu N *et al.,* have used two step click chemistry procedure for sequential immobilization of different bio-molecules on separate areas of the same surface using chemical vapour deposition coating process (Fig.23). The authors have immobilized Oregon 488 and biotin bio-molecules on same substrate. These types of substrates have great applications in the developments of bio-functional surfaces for diagnostics (e.g. microarrays), biosensors, and biomedical device coatings.[135, 136]

Since, fluorine rich polymers are interesting in coating technologies because of their high thermal and oxidative stability, chemical resistance and superior electrical insulating abilities. Recently azide-alkyne click chemistry also afforded in the synthesis of these polymers. For example, Xing-Jian Li *et al.,* have reported fluorinated waterborne polyurethane by coupling alkyne terminated waterborne polyurethane with azide terminated fluoro compound. The resultant polyurethane has good thermal stability up to 300^{o}C and has high hydrophobicity (water contact angle 82^{o}) with self-cleaning and fire retardant properties.[137] F.L.Qing and co-workers prepared addition polymers by Cu-AAC which possessed perfluoro-cyclobutyl (PFCB) groups along the main chain.[138] The same research group also synthesized a novel class of linear aromatic polyethers polymers containing per-fluorocyclobutyl and triazole unites from the click chemistry of 1,2-bis(4-azidomethylphenoxy) per-fluorocyclobutane and bisethynyl compounds[139] (Fig.24a and 24b). The resultant polymers were thermally stable up to 400^{o}C and were soluble in organic solvents making them attractive candidates for low dielectric and other high performance coating applications. Recently, the click reaction proved its importance in the development of materials for flame retardant applications as well. Generally the flame retardancy can be achieved by employing organophosphates as additives in the coatings. Borreguero AM *et al.*, have succeeded in the covalent attachment of organophosphates to the polyurethane foam using azide-alkyne click reaction.[140] Initially, they have prepared a linear polyol by the ring opening polymerization of propylene oxide and glycidyl propargyl ether in order to create an alkyne terminated polyether (Fig.25a). To this already synthesized azido alkyl-phosphonate molecule was attached by the click reaction. Even after thermal treatment at 400°C, the polyurethane foam material displayed enhanced flame resistant properties by forming a char layer on the surface of the polymer. Such technologies are also highly useful in the development of flame retardant functional coatings as well.

Further, 1,2,3-triazoles are used in powder coating technologies up to some extent. Very few reports are available on this particular application. Generally, during the development of the powder coating formulations, due to low glass transition temperature of the coating composition results agglomeration of the particles. To overcome such problems, Kamlesh PP *et al.*, have patented a low temperature curable powder coating formulation, in which they have used a triazole blocked polyisocyanate and a branched polyester polyols. The triazoles used for the blocking isocyanates are 1H-1,2,3-triazole and 1H-1,2,3-triazolo[4,5-b]pyridine. Initially, these triazoles were reacted with diisocyanates like hexamethylene diisocyanate, 2,4-diisocyanato toluene, 2,6-diisocyanato toluene,1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane, 4,4-diisocyanatodiphenyl methane, 2,4'-diisocyanatodiphenyl methane. In the next stage, these blocked isocyanates were made to react with a branched oligoester at 145°C (usually for a powder coatings cure above 250°C) for providing cross linked powder coating. The resultant composition was showing good desirable hardness, flexibility, solvent resistance, corrosion resistance, weatherability and gloss.[141]

Recently various polymer systems were also modified with desirable moieties through the azide-alkyne cycloaddition. Filip duprez and co-workers extensively worked on this area and showed some feasible paths to functionalize polyurethane chain with various moieties.[142] In one report, they have prepared various alkyne terminated polyurethane by treating hexamethylene diisocyanate with combination of 1,4-butane diol and 3,5-bis(hydroxymethyl)-1-propargyloxybenzene (mono alkyne diol) or 2,2-di(prop-2-ynyl)propane-1,3-diol (dialkynediol). Later this alkyne functional polyurethane was treated with various azide molecules like benzyl azide (BzN_3), N-(azidoethyl)phthalimide ($PHT-N_3$),tridecafluoro-8-azidooctane ($TDFO-N_3$) or

Zonyl-N_3. The property of the polyurethane was directed by the azide functional molecule (Fig.25b). In another article[143], they have functionalized both polyurethane films and foams, in which the alkyne terminated polyurethane was modified with the above mentioned azide molecules. Among these, zonyl group attached polyurethane film was showing good hydrophobicity (contact angle ~ 109^o). Finally the authors showed a path to functionalize the polyurethane with desirable molecules (Fig.25c). In this way, azide-alkyne click chemistry offers on demand functionalization of the polymer chains with desirable moieties.

In addition to the above applications, recently 4 or 5-vinyl substituted 1,2,3-triazole compounds become valuable and versatile building blocks in the construction and functionalization of various well-defined macromolecules, because this particular structure combine the features found in classical monomers, such as aromaticity, polarity, and structural diversity inherent to styrenics, vinylpyridines and acrylates respectively.[144,145] These molecules can be polymerized or co-polymerized easily by the free radical polymerization technique. Inspection of these 1,2,3-triazole-based polymers showed unique physical properties, indicating increased stability due to the aromatic triazole ring, a large dipole moment, and significant hydrogen-bonding character. For example, Hawker CJ *et.al.*,[146] developed various isomeric, substituted 5-vinyl-1,2,3-triazoles and 4-vinyl-1,2,3-triazoles monomers under regiospecific conditions by taking advantage of Cu(I)- and Ru(I)-catalyzed "click" chemistry methodologies (Fig.26). These monomers were subjected to controlled polymerization to give a library of isomeric homopolymers, copolymers, and block copolymers. It was observed that 1,5-isomers had significantly higher glass transition temperatures, up to 220°C for the cyclohexyl derivative and decreased solubility when compared to the corresponding1,4-isomers. These studies are highly helpful in the development of various polymers with tunable properties. In addition to this, David KH has patented that 4- or 5-vinyl substituted regioisomers of 1,2,3-triazoles (1-octyl-4-(prop-l-en-2-yl)-IH-l,2,3-triazole) are potential monomers to develop coating solutions to printing inks, screen printing etc. They have reported that this coating is UV curable and conductive; it can be applied on metal, plastic, glass and textile surfaces.[147]

Conclusions

The current review is an attempt to showcase the recent trends in the development of high performance functional coatings through azide-alkyne click chemistry. In this review, the application of 1,2,3-triazoles were discussed elaborately in the development of functional coatings such as corrosion resistant coatings, anti-bacterial, antifungal coatings and nanocomposite coatings are primarily dealt with. Considerable attention is also laid on self healing coatings, bio-degradable coatings and other smart coatings. Though triazole is found to be the most desirable group in the design of functional coatings, but not much of these molecules have been commercialized. Further research and development to provide sufficient evidence for the function of triazole in coatings is essential.

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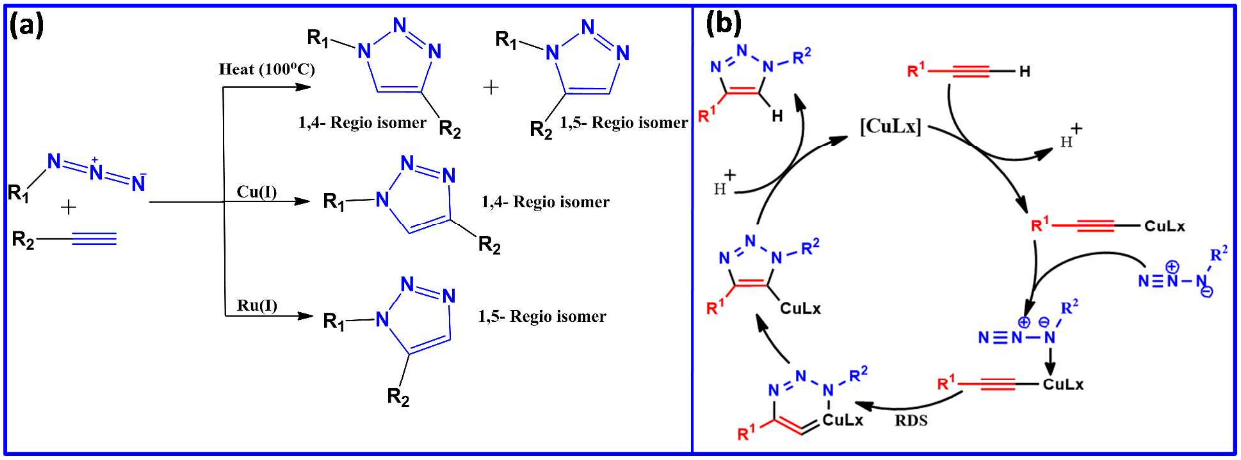


Fig. 1 (a) 1,3-dipolar cycloaddition reaction between azide and alkyne in presence of various catalysts. (b) Mechanism for Cu(I) catalyzed azide-alkyne cycloaddition.

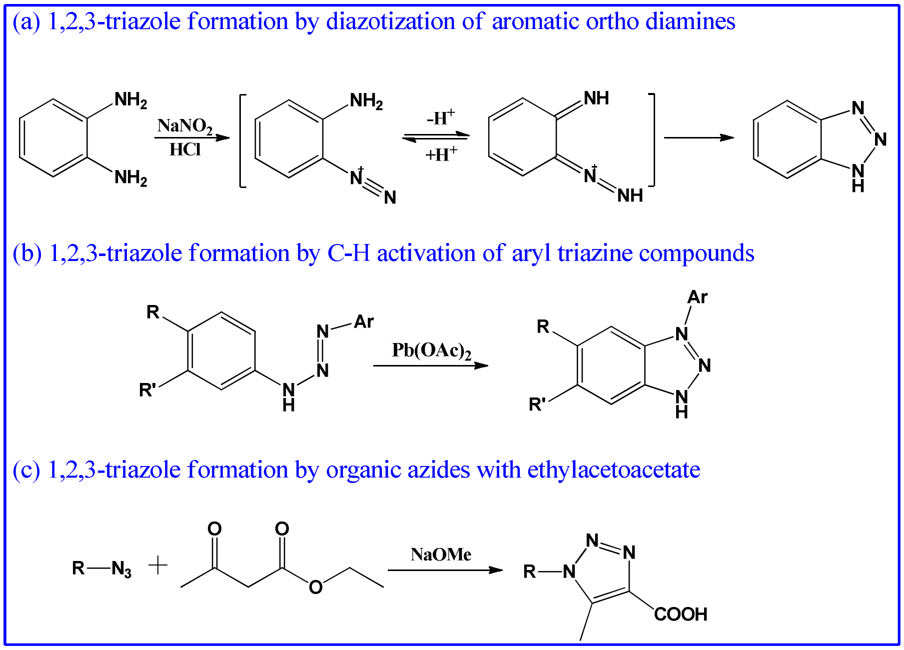
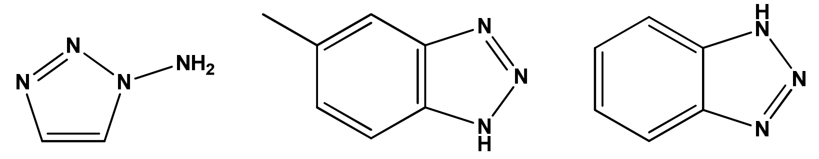


Fig. 2 Other possible routes to synthesize 1,2,3-triazole compounds.



3-amino-1,2,3-triazole **tolyl triazole** **1,2,3-benztriazole**

Fig. 3 Chemical structures of some 1,2,3-triazole corrosion inhibitors.

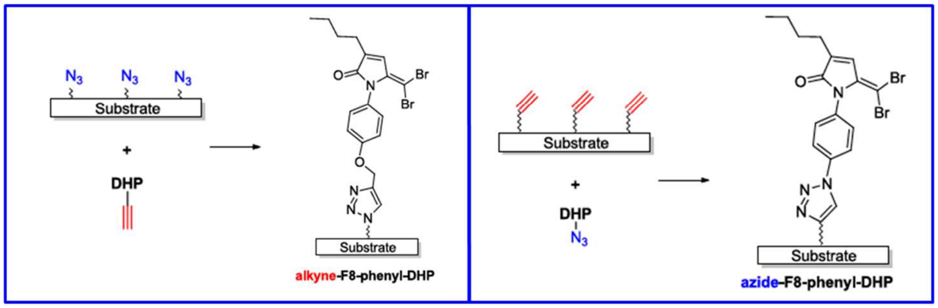


Fig. 4 Schematic representation of the immobilization of alkyne/azide functionalized DHP onto azide/alkyne-terminated surfaces via click reaction. (Reproduced with permission from ref. 59, copyright 2014, Elsevier)

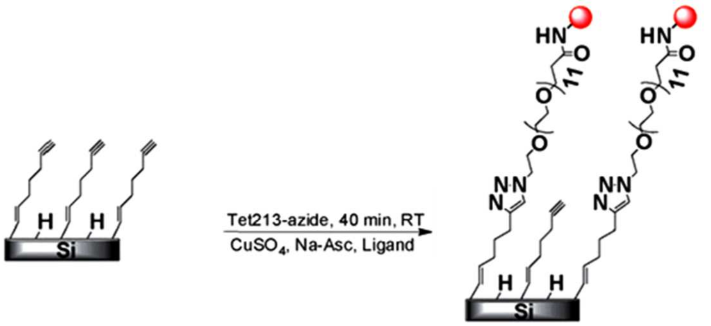


Fig. 5 Preparation of the surface clicked with antimicrobial peptide Tet 213. (Reproduced with permission from ref. 60, copyright 2014, Royal Society of Chemistry)

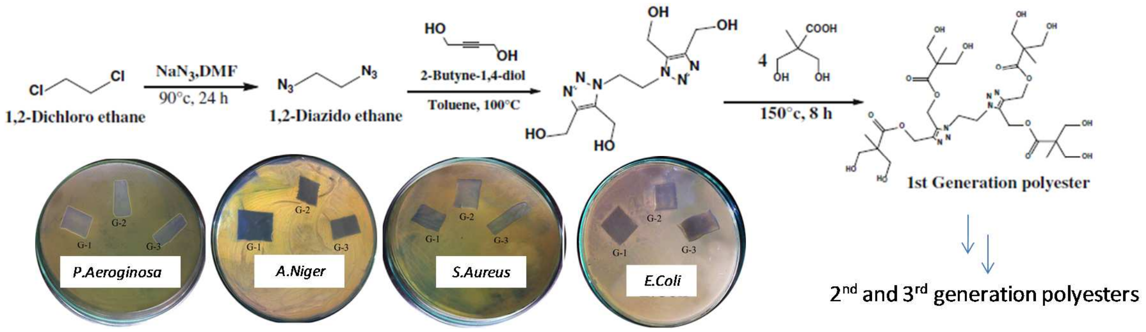


Fig. 6 Synthesis of triazole core hyperbranched polyester polyol resins and the antimicrobial activity of the corresponding polyurethane coatings. (Reproduced with permission from ref. 61, copyright 2013, Springer)

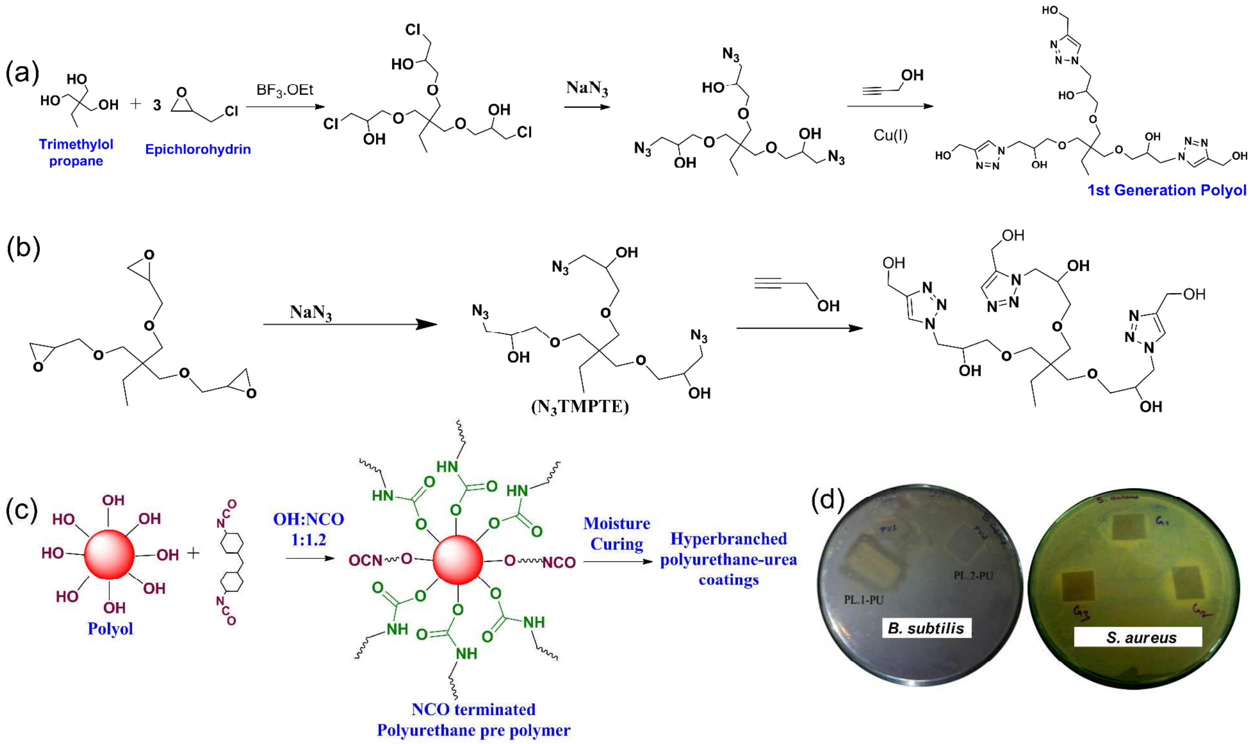


Fig. 7 (a) and (b) Development of highly branched polyurethanes based on triazole rich polyether polyols (c) schematic representation for the hyperbranched polyurethane-urea coatings (d) Antibacterial activity of the coating free films on different bacteria. (Reproduced with permission from ref. 62, copyright 2014, American Chemical Society and ref.63, copyright 2013, Elsevier)

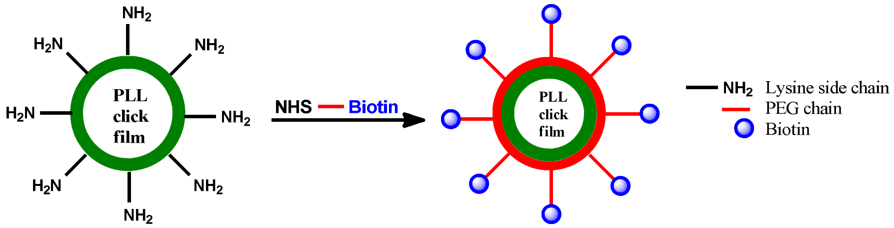


Fig. 8 A biotin-PEG-terminated film will lead to an increase in SA_{FITC} binding because of the specific interaction with biotin. At the same time, the low-fouling properties of the underlying PEG layer regarding non-specific adhesion will be maintained. (Reproduced with permission from ref. 75, copyright 2008, American Chemical Society)

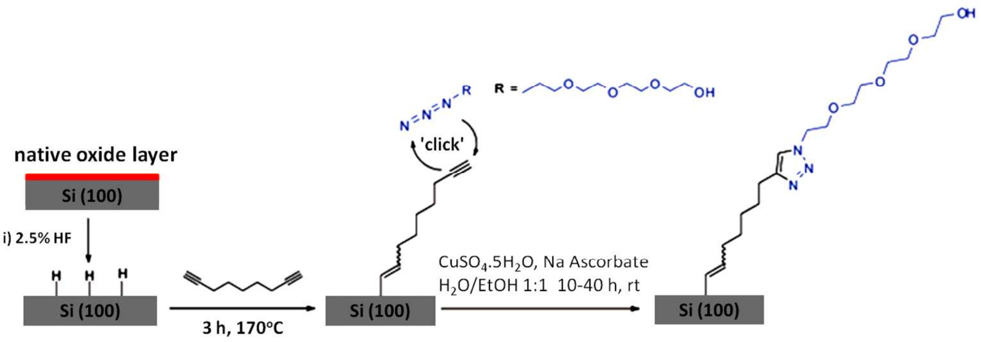


Fig. 9 Azide-Alkyne Cycloaddition Reactions on Acetylene-Terminated Si(100) Surfaces. (Reproduced with permission from ref. 76, copyright 2007, American Chemical Society)

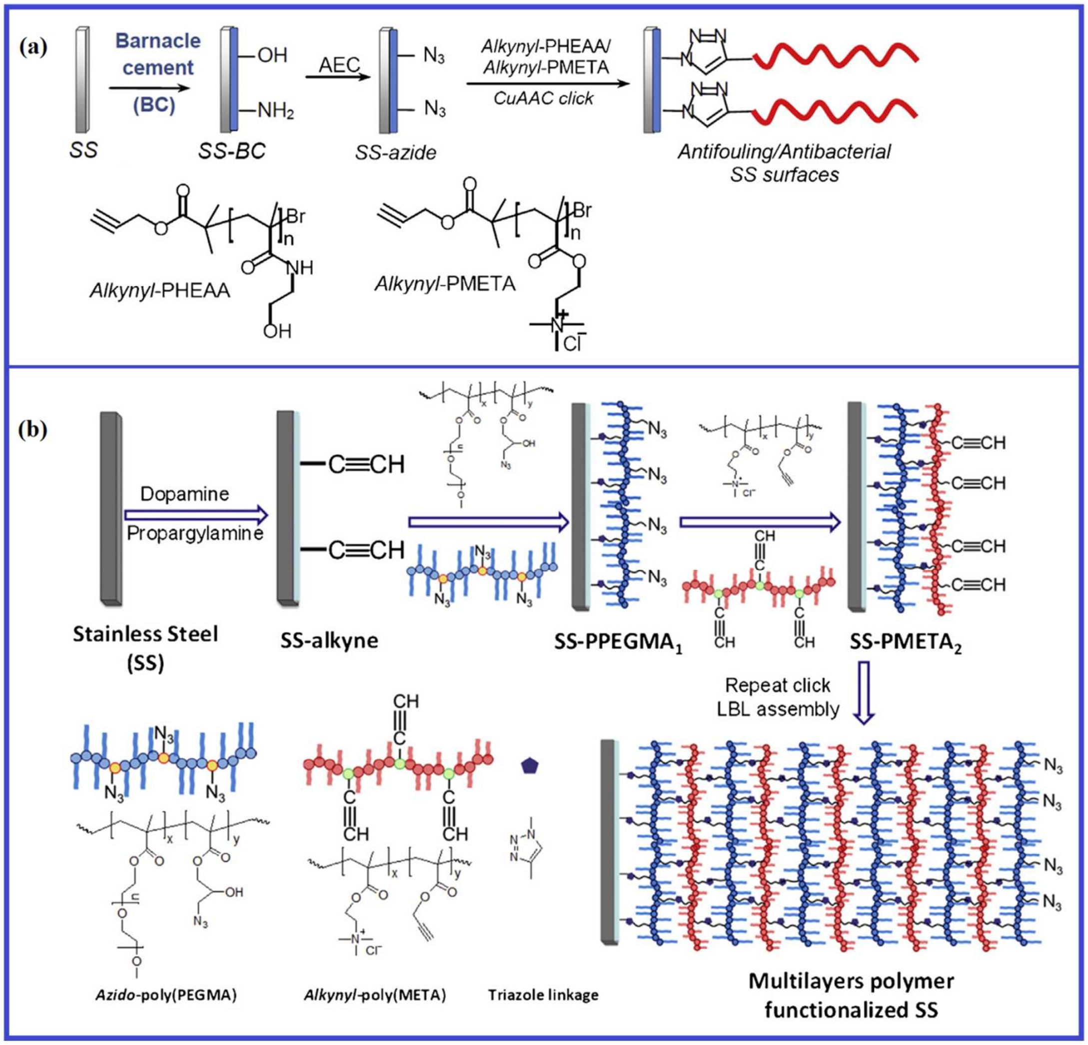


Fig. 10 (a) Barnacle cement based antifouling and antibacterial polymer brush coatings using click chemistry on stainless steel. (b) Schematic illustration of the preparation of antifouling and antibacterial polymer multilayer coatings via layer-by-layer click deposition. (Reproduced with permission from ref. 81, copyright 2012, American Chemical Society)

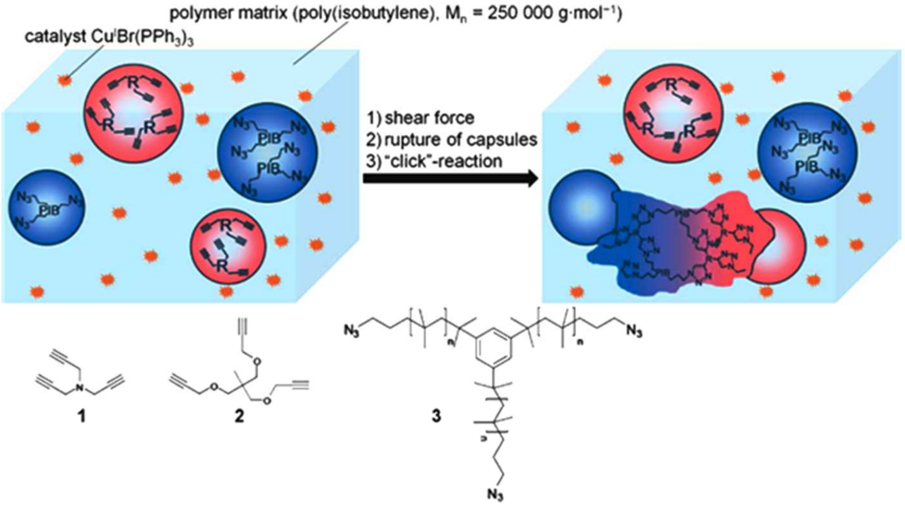


Fig. 11 Representative picture of encapsulated low molecular weight alkynes and polymeric azides along with Cu(I) catalyst in high molecular weight poly isobutylene matrix. The induction of the shear force leads to rupture of the capsules and releasing the reactive components and for the network formation via azide-alkyne click reaction at room temperature. (Reproduced with permission from ref. 84, copyright 2011, Wiley)

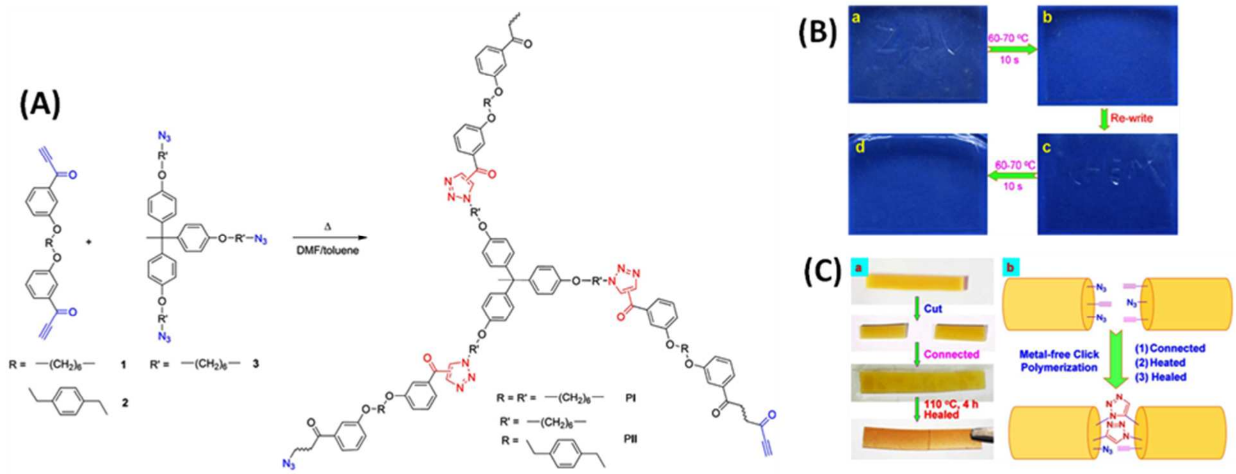


Fig. 12 (A) Synthetic routes to hyperbranched poly(arolytriazole)s, (B) Self-repairing of the scratched surface of PI film. (a) Curved ''ZJU'' on the surface, (b) after heating the film (c) re-inscribed ''CHEM'' on the same place of the surface, and (e) recovered surface of the film again by the same method. To better visualize the process, a blue background was used. The film is in the size of 19.9 mm 3 26.3 mm. (C) (a) The self-healing process of the PI sticks, and (b) the proposed mechanism of self-healing of polymer sticks. (Reproduced with permission from ref. 85, copyright 2013, Nature)

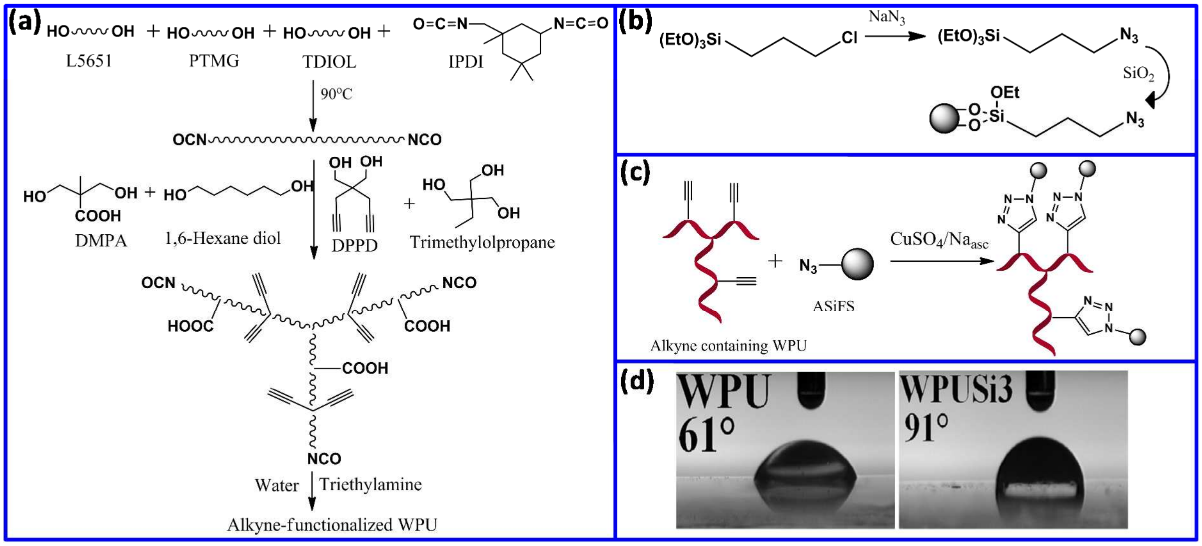


Fig. 13 (a) Synthesis of alkyne-functionalized Waterborne Polyurethane, (b) Synthesis of azide-functionalization of nano-silica particles, (c) Synthesis of Triazole-forming waterborne polyurethane composites using azide-alkyne click chemistry, (d) Water contact angle results. (Reproduced with permission from ref. 109, copyright 2011, Elsevier)

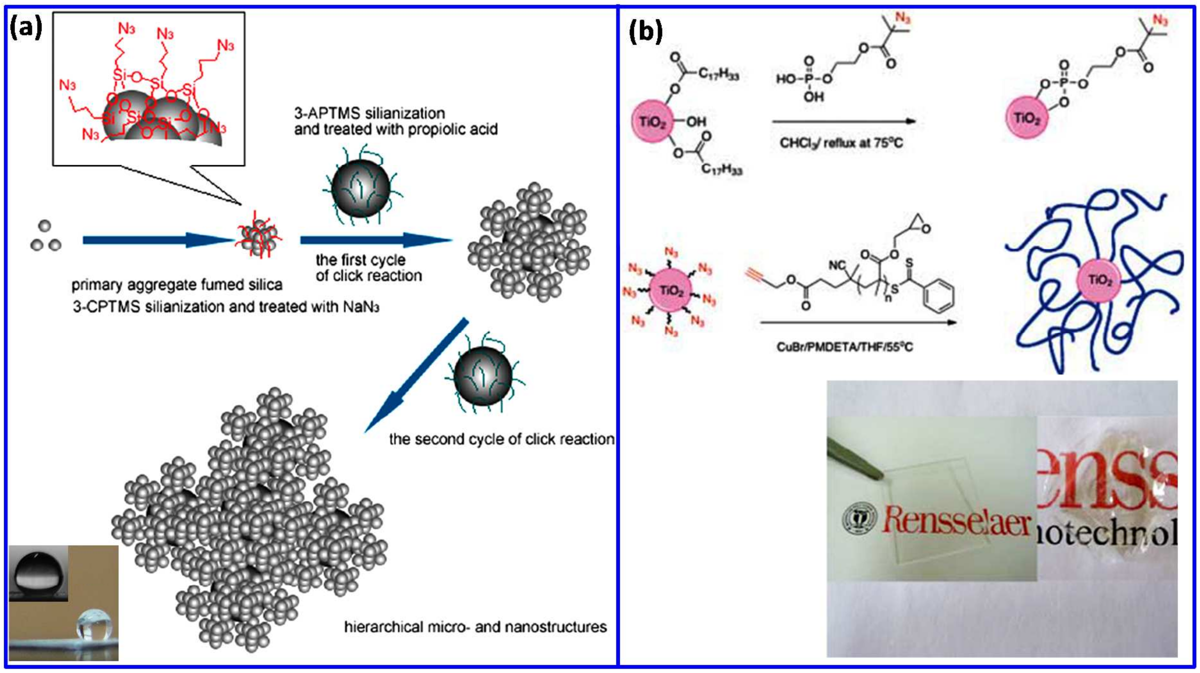
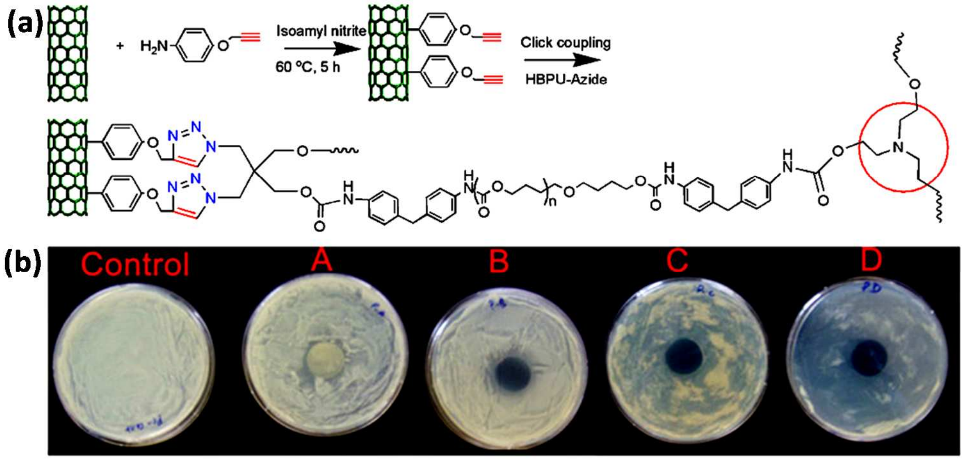


Fig. 14 (a) Fabrication of the Cactus-Like Hierarchical Particulate with an Alkyne-Functionalized Particle as Core and Azide-Functionalized Aggregates Clicked on to the Surface and the inset of image of water contact angle on the as-prepared surface with a value of about 146± 2.2°. (Reproduced with permission from ref. 110, copyright 2010, American Chemical Society) (b)Surface ligand exchange with phosphate-azide ligand and subsequent grafting of PGMA polymer chains via alkyne-azide ''click'' chemistry. Photograph of coating of TiO2-PGMA (55 wt%) on glass slides (with a thickness of 20 mm) and transparent self-standing film.

(Right). (Reproduced with permission from ref. 115, copyright 2011, Royal Society of Chemistry)



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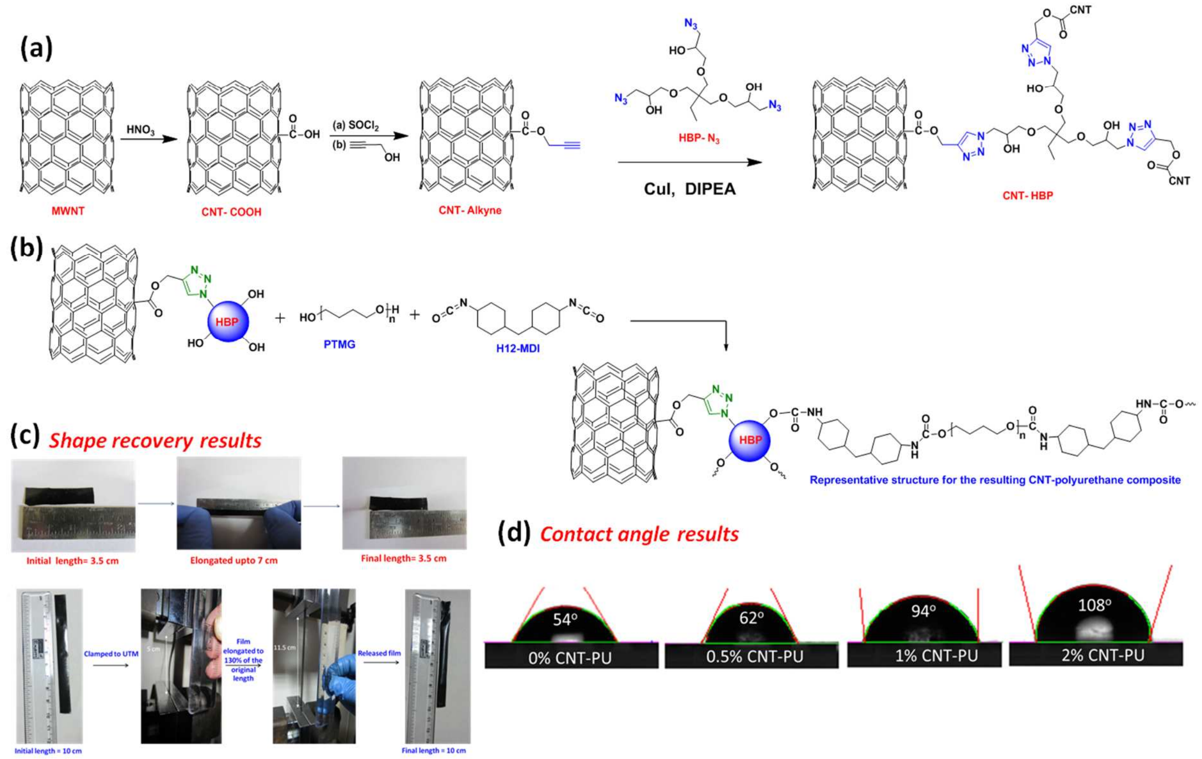

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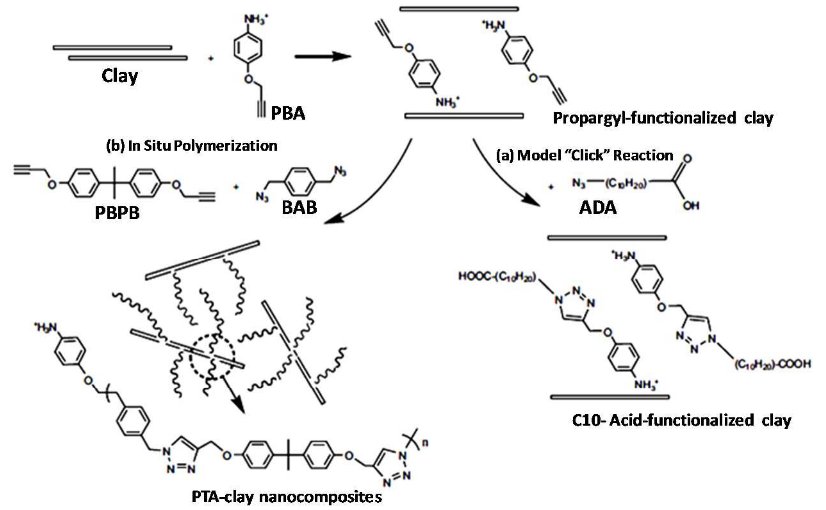

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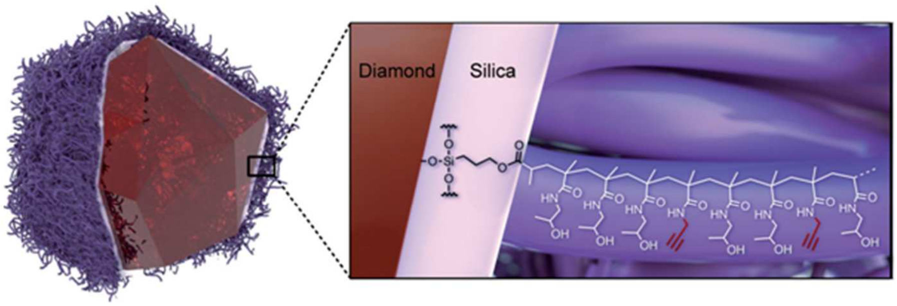


Fig. 18 Schematic structure of the polymer coating on a fluorescent nanodiamond crystal. (Reproduced with permission from ref. 122, copyright 2014, Wiley)

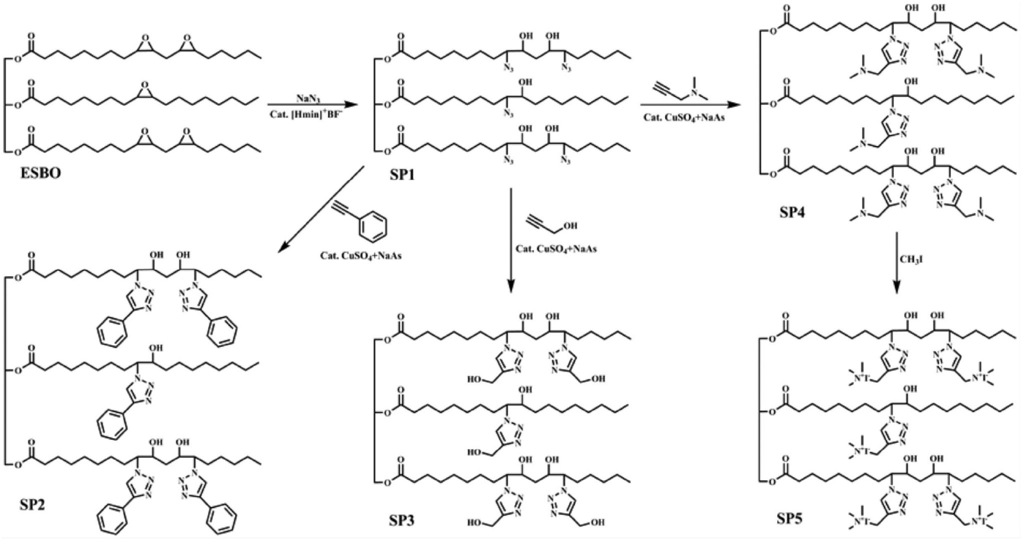


Fig. 19 Polyurethane Coatings Derived from 1,2,3-Triazole-FunctionalizedSoybean Oil-Based Polyols. (Reproduced with permission from ref. 128, copyright 2013, American Chemical Society)

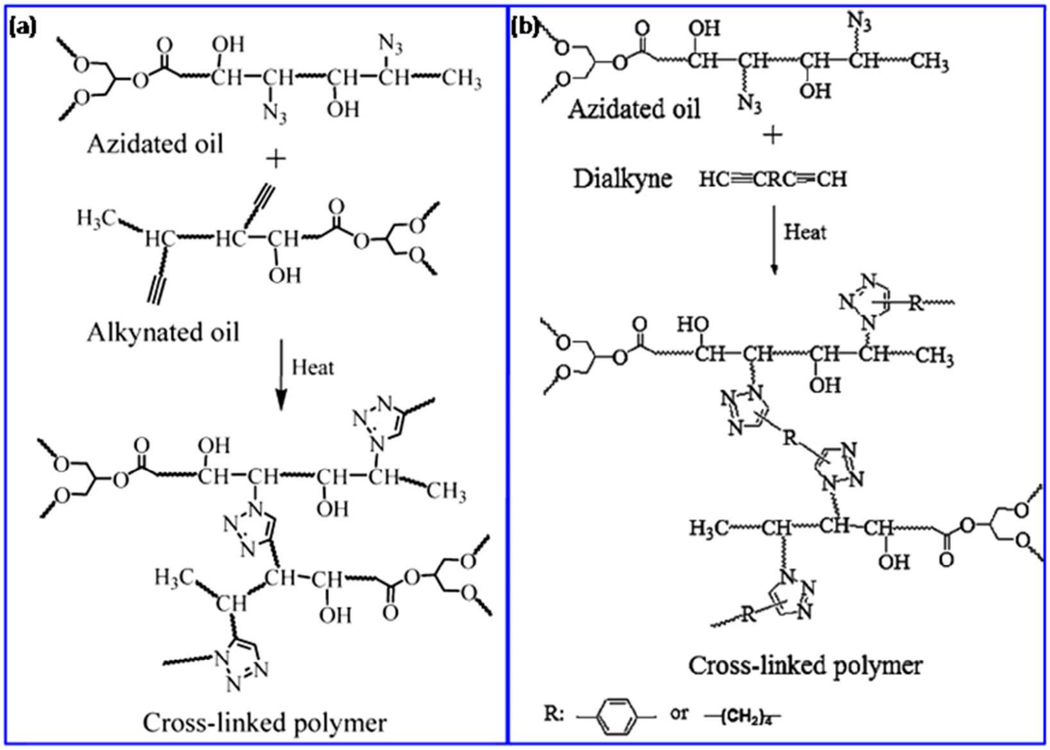


Fig. 20 Formation of cross-linked polymer via thermal click chemistry (Reproduced with permission from ref.129, copyright 2013, Wiley; ref. 130, copyright 2012, American Chemical Society)

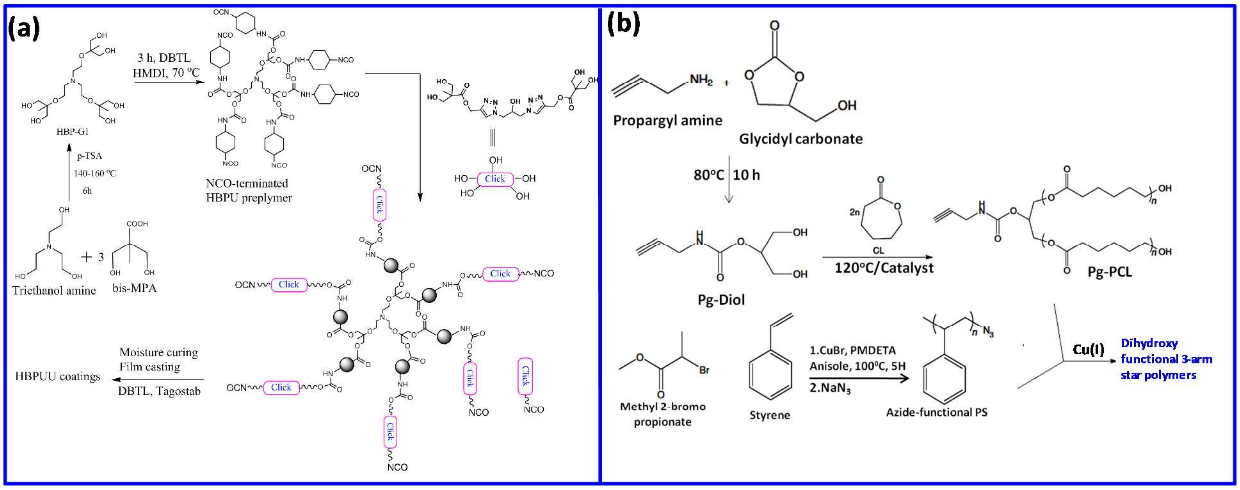


Fig. 21 (a) Hyperbranched polyurethane coating based on the triazole containing pentol chain extender. (Reproduced with permission from ref. 132, copyright 2012, Wiley)

(b) Synthesis of dihydroxy functional 3-arm star polymeric chain extender by utilizing ATRP, ring opening polymerization and click chemistry techniques. (Reproduced with permission from ref. 133, copyright 2010, Springer)

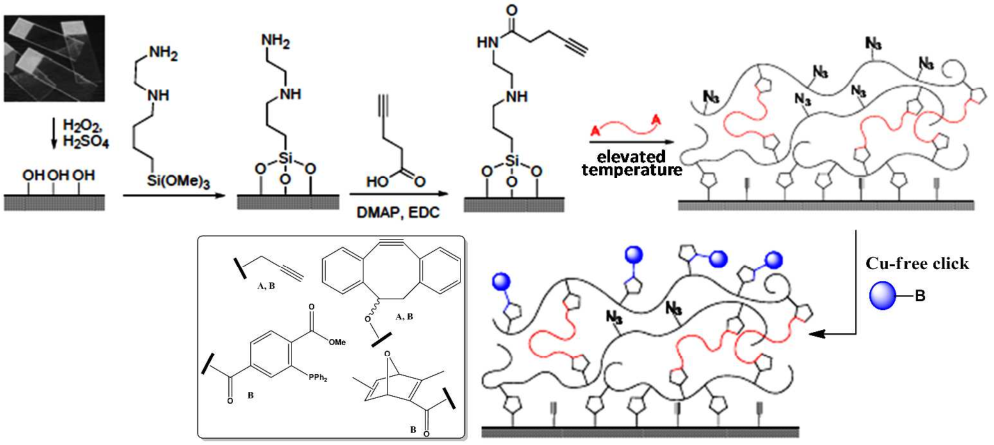


Fig. 22 Schematic overview of the construction of a clickable coating, where both coating formation and coating functionalization are performed using azido groups (Reproduced with permission from ref. 134, copyright 2009, Wiley)

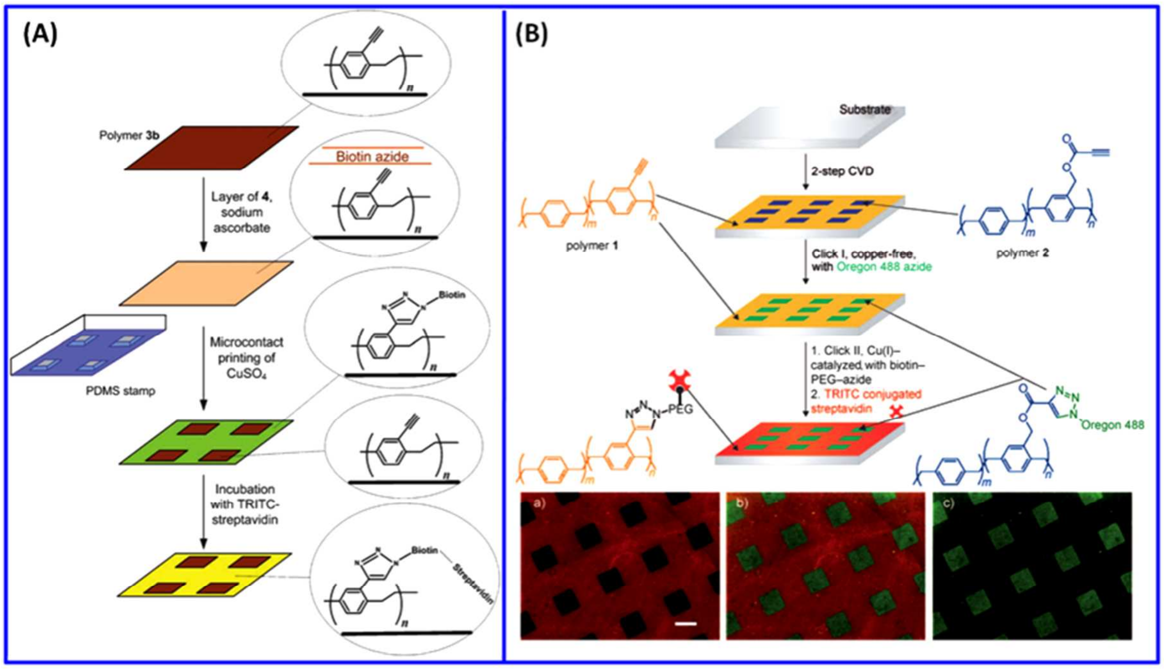
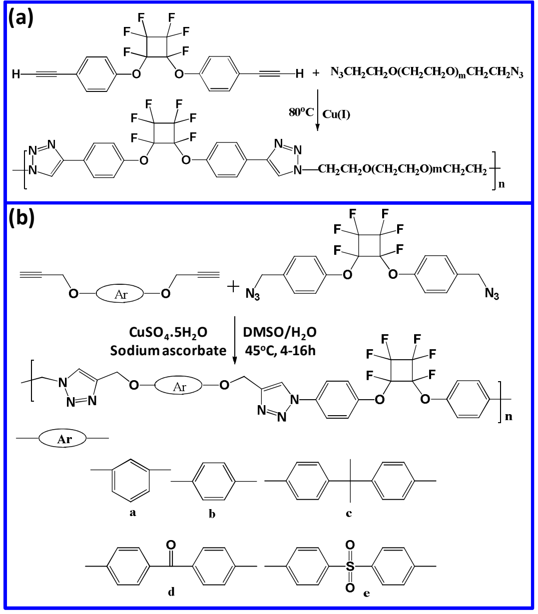


Fig. 23 (A) Immobilization of azide-containing ligand on the reactive polymer coating 3b Subsequently the $CuSO_4$ catalyst precursor is micro contact printed on a pre-adsorbed layer of biotin azide ligand 4 on the reactive polymer 3b (Reproduced with permission from ref. 136, copyright 2006, Wiley) (B) Scheme of two-step click reactions on surface coated with different polymers in different selected areas. The goal is to achieve sequential immobilization of

molecules on defined areas of the same surface by utilizing the different reactivity of activated and non activated alkynyl groups towards azide groups. a), b),c) Fluorescence images of samples prepared exactly as shown in the schematic representation. b) Overlay image of green and red channels shown in (a) and (c). Scale bar represents 200 mm. (Reproduced with permission from ref. 135, copyright 2011, Wiley)



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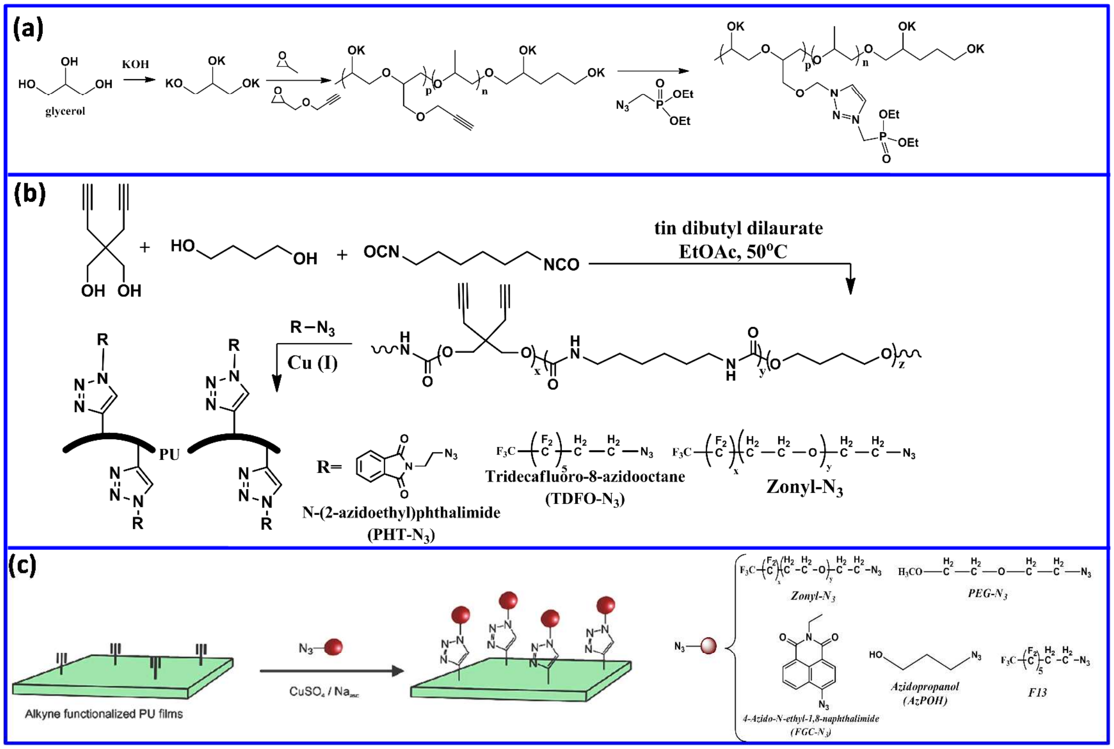

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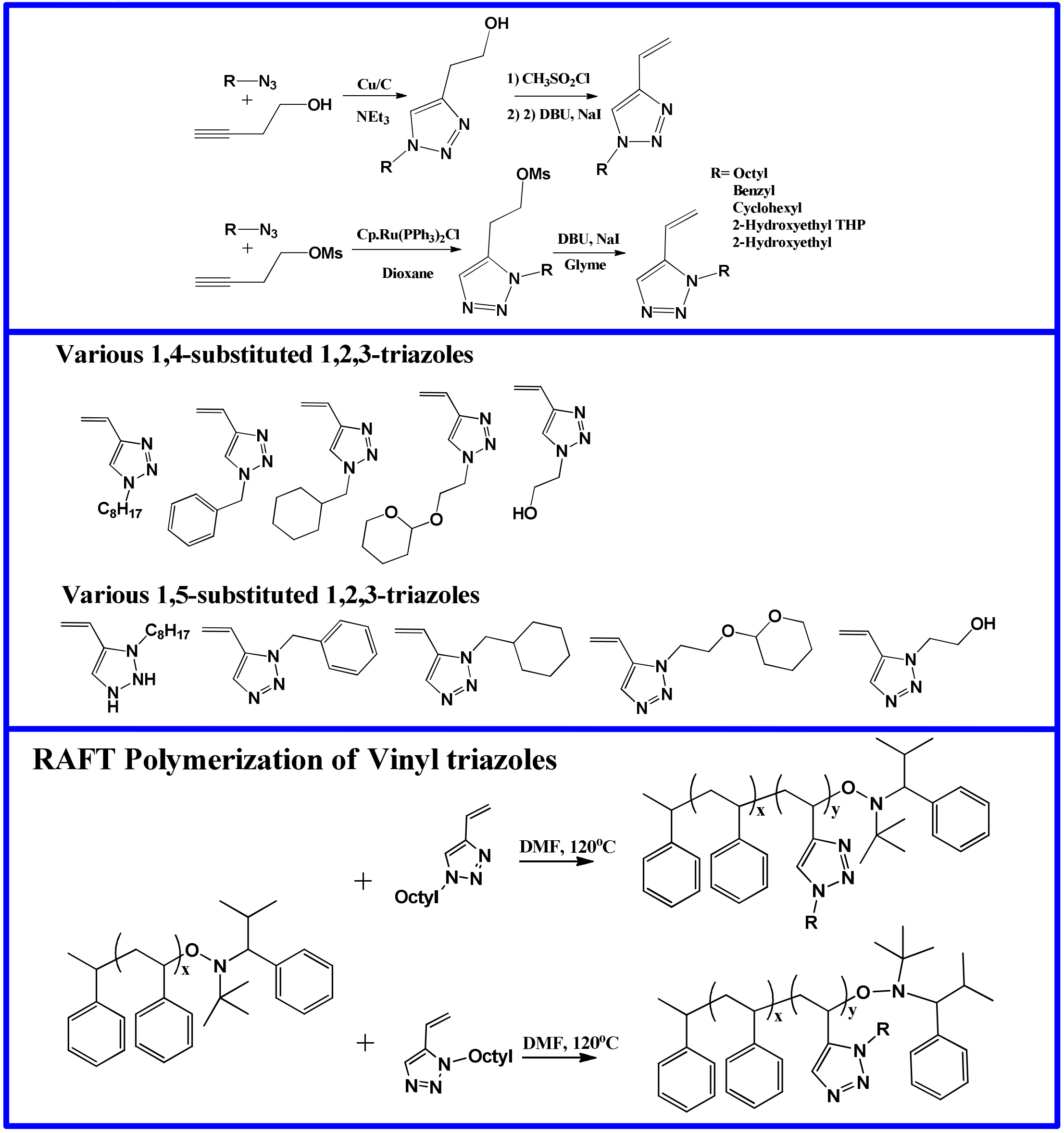

Fig. 26 Synthesis of various 1,4 and 1,5-substituted isomeric triazoles and polymerization of substituted vinyltriazoles with polystyrene. (Reproduced with permission from ref. 146, copyright 2009, Royal Society of Chemistry)

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Sasidhar Kantheti