Chapter 5
Gum-g-Copolymers: Synthesis, Properties, and Applications

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Abstract With the increasing concerns on environmental problems, the petroleum-based synthetic polymers gradually highlight their disadvantages and threats to the modern world from the perspective of energy source, resource, and environment. So the naturally renewable polymers have received great developments by virtue of their unique environmental and commercial advantages. The commonly cognitive natural polymers are mainly cellulose, starch, and chitosan, which were intensively researched and got extensive applications in food, fine chemicals, soft-tissue and pharmaceutical engineering, biomedical engineering, artificial sensors, etc. as a substitution of synthetic polymers. But these natural polymers fail to meet all requirements in modern industrial application because their boundedness in structure, solubility, colloidal properties, machinability, and so on. Gums have showed variety of structure and property due to their abundant sources and have gained enormous attention as new families of natural polymers. The original forms of gums have excellent suspension, viscosity, rheological properties, stimuli responsivity, flocculation, and adsorption performance besides the common renewable, biodegradable, nontoxic, and biocompatible characteristics. The usability can be further enhanced through the simple derivatization or graft copolymerization, and the drawbacks of gums such as poor rotting resistance can be improved. Compared with conventional derivatization reaction, graft copolymerization is especially important and effective because it can introduce various functional groups and increase the molecular weight of polymers. The graft copolymerization of gums with various monomers can enhance the intrinsic properties and can also bring new properties that raw gums do not have. The gum-g-copolymers usually

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showed better thermo- and degradation-resistant properties, high-viscous and shear-resistant properties, stimuli-responsive properties, electric properties, etc. and have been widely applied in many areas, such as drilling additives, flocculating agent, drug delivery carriers, adsorption of toxic heavy metals and dyes, water-saving materials, sand-binding materials, daily chemicals, thickener, electrical biomaterials, and macromolecular surfactants. Thus, this chapter detailedly introduced the types, structure, and derivatives of gums; the synthesis method of graft copolymer; the properties of graft copolymer; and their application domains.

Keywords Gum • Graft copolymers • Biopolymers • Initiator • Modification • Synthesis • Applications

Abbreviations

AG	Acacia gum
AMPS	2-Acrylamido-2-methyl-1-propane sulfonic acid
APS	Ammonium persulfate
CAN	Cerium(IV) ammonium nitrate
CAS	Ceric ammonium sulfate
CG	Cashew gum
CGG	Cationic guar gum
CHPTAC	3-Chloro-2-hydroxypropyltrimethylammonium chloride
CRSG	Cassia reticulata seed gum
CTG	Cassia tora gum
DDMC	Diallyldimethylammonium chloride
FET	Final decomposition temperature
GG	Guar gum
GGT	Gum ghatti
H_2O_2	Hydrogen peroxide
IDSG	*Ipomoea dasysperma* seed gum
IHSG	*Ipomoea hederacea* seed gum
IPSG	*Ipomoea palmata* seed gum
k-CGN	*k*-Carrageenan
KG	Konjac gum
KGM	Konjac glucomannan
KPS	Potassium persulfate
LBG	Locust bean gum
LGSG	Leucaena glauca seed gum
MW	Microwave
P4V	Poly(4-vinylpyridine)
PAA	Poly(acrylic acid)
PACA	Poly(2-acrylamidoglycolic acid)
PAM	Poly(acrylamide)

PAN	Poly(acrylonitrile)
PANI	Poly(aniline)
PCMGG	Partially carboxymethylated guar gum
PDAM	Poly(N,N-dimethylacrylamide)
PEA	Poly(ethylacrylate)
PEMA	Poly(ethyl methacrylate)
PEO	Poly(ethylene oxide)
PGMA	Poly(glycidyl methacrylate)
PIA	Poly(itaconic acid)
PMA	Poly(methacrylic acid)
PMAD	Poly(methacrylamide)
PMMA	Poly(methyl methacrylate)
PNVF	Poly(N-vinyl formamide)
PNVP	Poly(N-vinyl-2-pyrrolidone)
PPO	Poly(propylene oxide)
PSY	Psyllium
SA	Sodium alginate
SD	Sodium disulfite
TGG	Tragacanth gum
TK	Tamarind kernel
UV	Ultraviolet
XG	Xanthan gum
XGC	Xyloglucan

5.1   Introduction

Gums are important families of natural polymers derived from the seeds or tubers of plants and seaweed and are one of the most fast developed environmentally friendly polymers [1–3]. The different sources of gums endow them with different molecular structure and properties, but their common advantages such as renewable, biodegradable, nontoxic, biocompatibility, etc. make them found extensive applications as a commercial polymer in many areas such as thickening agent [4, 5], suspending agents [6], coagulant [7], drilling additives [8, 9], textile and dyeing [10], food [11], pharmaceuticals [12], cosmetic [13], matrix of nanomaterials [14], and papermaking [15]. However, the performance and applicability of raw gums are still limited due to their fixed structure and functional groups as well as the poor resistance to enzyme corrosion. Thus, many efforts have been engaged to develop the derivatives of gums by their reaction with active modification agents for introducing various or more functional groups [i.e., $-NH_2$, $-COOH$, $-NH_4^+Cl^-$, $-SO_3^{2-}$, $-OC_2H_5$, $-OCH_3$, $-CH=CH_2$, $-C=O(NH_2)$]. The introduction of new functional groups changed the charges, aggregation state

of molecular chains, hydrophilic–hydrophobic capability, complexing capacity, stimuli-responsive ability, and rheological behavior of gums, and so the application domain of gums was greatly extended. But, the derivatization of gum can only improve the properties to a finite degree because the number of introduced functional groups is less and the molecular weight of gum fails to be increased by the simple modification with small molecules. Graft polymerization is anticipated to be a quite promising technique for modifying the properties of a polymer, and the modification of natural polymer materials by graft copolymerization offers the opportunity to tailor their physical and chemical properties, functionalize biopolymers to impart desirable properties onto them, and combine the advantages of both natural and synthetic polymers [16–19]. Several grafting modification techniques have been reported, involving with "grafting-from" (growth of polymer chains from initiating sites on the polysaccharide backbone) and "grafting-to" methods (coupling of preformed polymer chains to the polysaccharide) [20]. "Grafting-from" is the most common procedure with the initiating sites generated by various chemical or high-energy irradiation methods. Different from the derivative modification by active small molecules, the graft reaction may introduce polymer chains with large amounts of functional groups to form a "brush-like" structure around the main chains. Correspondingly, the properties of gums, such as flocculation efficiency, complexing, stimuli-responsive, viscosity, controlled biodegradation, and shear resistance characteristics, were greatly changed by the new functional groups for extending the application domains of gums [21–23]. The results of graft polymerization are to improve the intrinsic properties of gums or bring gums with new properties. For example, *Cassia javahikai* seed gum is a better coagulant, but the graft of PAM chains onto the gum can further enhance its coagulant properties [24]. The graft of PAN onto *Ipomoea seed* gum may clearly enhance its viscosity (the maximum value reaches 10.56 folds of the gum) and stability [25]. The AG does not have conducting capability, but the graft of PANI results in good processability along with the electrical conductivity, and used to develop biopolymer-based electronic materials for the environmental favorable technologies [26]. By virtue of the excellent intrinsic properties and the adjustable character of the structure and properties of gums, their graft copolymers play vital role in almost each chemical industrial field, especially in wastewater treatment, controlled release of agricultural chemicals or pharmaceutics, petroleum industry, papermaking, daily chemicals, dyeing, thickener, smart materials and biomaterials, etc.

The properties of a gum-g-copolymer are highly dependent on the intrinsic structure and nature of gums, the sort of grafted monomer, grafting ratio, and efficiency. Over the past decades, researchers devoted many efforts to explore the graft mechanism, the structure-activity relation of graft copolymer, and the key influence factors of graft ratio and efficiency, and greater progress was made. So, the introduction about the types, structure, and derivatives of gums, the synthesis method, properties, and applications of gum-g-copolymer will be attractive.

5.2 Sorts, Structures, and Properties of Natural Gums

To understand the sorts, structure, and properties of gums is essential to develop their new derivatives or graft copolymers because the charge and polarity of functional groups, the molecular weight, and the viscosity of gum solution may affect the reaction activity and modification efficiency. According to the difference of the functional groups attached on the macromolecular chains, the gums are mainly sorted as nonionic and anionic gums, and their properties are different due to the discrepant structure.

5.2.1 Nonionic Gums

Most of natural gums are neutral polysaccharides with numerous hydroxyl groups and without charges. These hydroxyl groups are distributed in both main chains and side chains and form hydrogen bonding with each other. These bonding interactions among molecular chains render the gums higher viscosity, and so they are widely used as food additives or industrial thickening agents. However, the raw nonionic gums have no charge and cannot be ionized, and so they are usually used in the form of derivatives or graft copolymers for extending the application domains. The commonly concerned and representative nonionic gums are guar gum, locust bean gum (LBG), cassia gum, konjac glucomannan (KGM), *Ipomoea* seed gum, and so on.

5.2.1.1 Guar Gum

Guar gum (GG) is a nonionic edible carbohydrate polymer derived from the seeds of *Cyamopsis tetragonolobus* [1, 2, 27]. GG is consisted of a straight chain of mannose units joined by β-D-(1–4) linkages having α-D-galactopyranose units attached to this linear chain by (1–6) linkages, with a galactose-to-mannose ratio of about 1:2 (Fig. 5.1). GG could dissolve in cold water to form a highly viscous solution even at very low concentration and is one of the highly efficient water-thickening agents, dispersion agents, and water binders used in industry fields such as mining, textile and dyeing, explosive, papermaking, and drilling muds for petroleum industry, food, controlled drug release, etc. [28–32]. The viscosity of GG solution increases when heated for shorter periods of time, but decreases for longer periods of time. Also, the viscosity of such a solution is not very stable and is difficult to be controlled because of its drawback like easier susceptibility of microbial attack, which restricts its application and the gum is rarely used in its natural form [33, 34]. So, the derivative products are the main usage style of GG, and the direct derivatization and graft copolymerization of GG represent the main modification methods, which results in the retention of intrinsic properties and the introduction of desirable properties [22, 35–37].
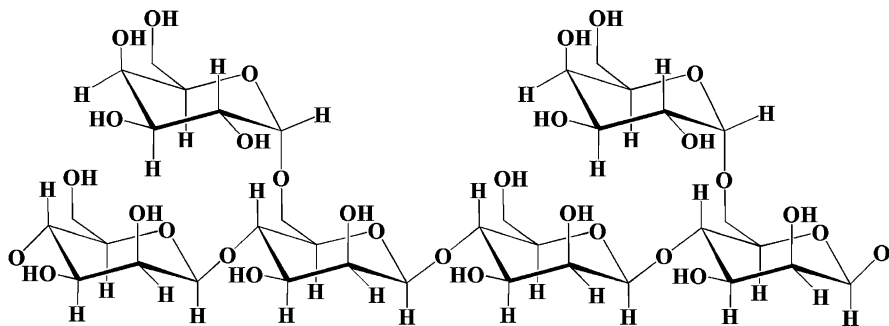
Fig. 5.1 Structure unit of guar gum [38]

The purification of guar gum is the basis of developing its derivatives and graft copolymers as well as studying the corresponding mechanism. Singh groups [39] reported a purification method of gum as follows: the 2.5 % (w/v) solution of GG was prepared by continuous stirring for 12 h at 60 °C and then precipitated with a standard barium hydroxide solution. The formed complex was separated and taken in 1 M acetic acid and stirred for 8 h and precipitated with ethanol. After washed with 70 %, 80 %, 90 %, and 95 % ethanol, the sample was purified by dialysis and filtration through 0.45 μm Millipore membranes (Millipore, Milford, MA).

5.2.1.2 Locust Bean Gum

LBG is a commercially available water-soluble β-1,4-polysaccharide obtained from the seed of the carob tree (*Ceratonia siliqua L.*) and is a galactomannan consisting of a mannose backbone with single side chain galactose units (Fig. 5.2) [40–42]. It can dissolve in water at 85 °C to form a viscous solution with the pH values of 5.4–7.0, and the solution can further form gel by adding sodium tetraborate. LBG is also soluble in LiCl-DMSO solutions. The viscosity is stable in the pH range of 3.5–9.0 and is not affected by Ca^{2+} and Mg^{2+} ions. But the acid or oxidizer will make the LBG salting out and reduce the viscosity. LBG can be used as emulsifier, thickener, stabilizer, and gelling agent [43, 44]. It can create a cream form, and so usually used for cream structure nature and usually used for dairy products and ice cream, jams, jellies, and cream cheese to improve the smear performance.

The typical preparation method of LBG is as follows: the endosperm of the legume beans was crushed after being roasted, and then extracted with hot water to remove the insoluble matters. After the extraction solution was concentrated, 95 % ethanol solution was added and the white floc was obtained. The solid was separated, dried, and smashed to obtain the product.
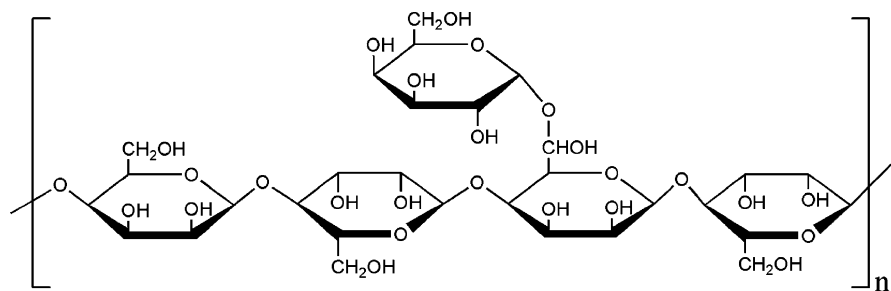
Fig. 5.2 Chemical structure of locust bean gum

5.2.1.3 Cassia Gum

Cassia is a common annual plant grown in tropical countries and is abundantly available in India. The plants of genus *cassia* are known to possess medicinal value and are a good source of mucilages, flavonoids, anthraquinones, and polysaccharides [45, 46]. *C. javahikai* (N.O. leguminosease) is a tree cultivated in gardens as ornamental plant. The seed gum of *C. javahikai* was investigated extensively for its potential as a coagulant in textile wastewater treatment [24, 35]. *Cassia* gum is a nonionic water soluble galactomannan isolated from endosperm of the *C. javahikai* seeds, with a molar ratio of galactose to mannose, 1:2. Seed gum has a branched structure consisting of a linear chain of β-(1–4)-linked mannopyranosyl units with D-galactose side chains attached through α-(1–6) linkage to the main chain [47]. It is very similar with LBG and GG in structure and chemical characteristics. Cinnamon gum is suitable to form gel with other colloid production and show potential applications in foods as a thickener, emulsifier, foam stabilizer, and insurance agent [48, 49]. The usage amount is the same as LBG and GG. Cassia gum is a yellowish gray powder-like substance with a unique fruit-like flavor, which can dissolve in cold water to form a colloid solution and form a hydrocolloid after boiling. The pH value of 5 % solution is 6.5–7.5.

Cassia gum was isolated by extracting the dried crushed seeds with light petroleum and ethanol to defat and decolorize, respectively. Then, the seed was extracted with 1 % aqueous acetic acid and the solution was added slowly to large excess of ethanol. The crude gum was collected, washed with ethanol, and dried (yield 3.2 g/100 g). The crude gum was purified through the method similar with the GG [50].

5.2.1.4 Konjac Glucomannan

KGM is a type of neutral heteropolysaccharide extracted from tubers of *Amorphophallus konjac C. Koch*. Chemically, KGM has β-(1→4)-linked D-mannose and D-glucose units in a molar ratio of 1.6:1 as the main chain, with branches joined through C-3 of the D-glucosyl and D-mannosyl residues and a low number of
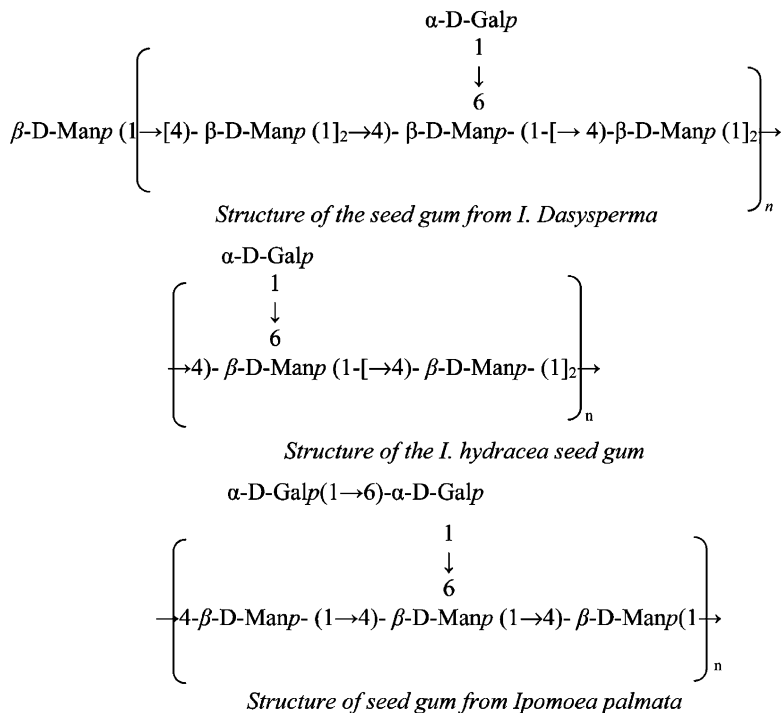
$$\alpha\text{-D-Gal}p$$
$$1$$
$$\downarrow$$
$$6$$

β-D-Man$p$ (1—[4)- β-D-Man$p$ (1]$_2$→4)- β-D-Man$p$- (1-[→ 4)-β-D-Man$p$ (1]$_2$→ $\Big]_n$

Structure of the seed gum from I. Dasysperma

$$\alpha\text{-D-Gal}p$$
$$1$$
$$\downarrow$$
$$6$$

→4)- β-D-Man$p$ (1-[→4)- β-D-Man$p$- (1]$_2$→ $\Big]_n$

Structure of the I. hydracea seed gum

$$\alpha\text{-D-Gal}p(1{\rightarrow}6)\text{-}\alpha\text{-D-Gal}p$$
$$1$$
$$\downarrow$$
$$6$$

→4-β-D-Man$p$- (1→4)- β-D-Man$p$ (1→4)- β-D-Man$p$(1→ $\Big]_n$

Structure of seed gum from Ipomoea palmata

Fig. 5.3 Structure of *Ipomoea seed gums* [25]

acetyl groups (approximately one acetyl group per 17 residues) at the C-6 position [51–54]. It has the characteristics of low cost, high viscosity, excellent film-forming ability, good biocompatibility and biodegradability, as well as gel-forming properties, and KGM and its derivatives have been used widely in various fields, such as food and food additives, and the pharmaceutical, biotechnology and fine chemical industries [55].

5.2.1.5 Ipomoea Seed Gums

Seed gum from *Ipomoea* plants is a nonionic water-soluble galactomannan with a branched side chains like GG (Fig. 5.1). The ratio of the galactose to mannose and degree of branching is found to vary from species to species and was 1:6, 1:3, and 2:3 for *Ipomoea dasysperma*, *Ipomoea hederacea*, and *Ipomoea palmata*, respectively (Fig. 5.3) [25, 56]. The seed gum was isolated from endosperm of the seeds and has a branched structure consisting of a linear chain of β-(1–4)-linked mannopyranosyl units with D-galactose side chains attached through α-(1–6) linkage to the main chain, a fundamental structural pattern found in other seed galactomannans like GG, carob gum, and LBG commercial gums, and the solution of gum showed similar behavior to the GG and was found to be stable over a wide

range of pH [39, 57]. The seed gum can be isolated by the following procedure: dried crushed seeds were extracted successively with light petroleum and ethanol to defat and decolorize, respectively, then extracted with 1 % aqueous acetic acid and extract was added slowly, with stirring to large excess of ethanol. The crude gum was collected, washed with ethanol, and dried (yield 2.3 g/100 g) [39]. The seed gum can be purified by barium complexing method [58].

5.2.2 Anionic Gums

A sort of gum contains anionic functional groups, such as –COOH, $-SO_3^{2-}$, etc. attached on its backbone and carries negative charges. Different from the nonionic gum without charges, the negatively charged functional groups of anionic gums may bring better hydrophilicity, complexing capability to cations, responsive behaviors to external stimulus, and higher reactive activity resulting from the polar functional groups. Thus, the anionic gums were also developed as valuable commercial polymer materials and found more expensive application in chemical and industrial fields. Xanthan gum, *k*-carrageenan, psyllium, alginate, and acacia gum are the representative sorts.

5.2.2.1 Xanthan Gum

Xanthan gum (XG) is an extracellular heteropolysaccharide of *Xanthomonas campestris*. Structural unit of xanthan gum consists of β-(1–4)-D-glucopyranose glucan (as cellulose) backbone with side chains of β-(3-1)-α-linked D-mannopyranose-(2-1)-β-D-glucuronic acid-(4-1)-β-D-mannopyranose on alternating residues (Fig. 5.4) [59, 60]. It was the first fermentative biopolymer product based on corn sugar and has attained commercial status. It can be used in food and pharmaceutical industry because of the properties like thickening, emulsion stabilization, water binding, suspending, and oil recovery [61–64]. Beside these usages, it has a drawback: it is susceptible to microbial attack, which limits its use. Modification of XG by graft copolymerization technique allows one to chemically change the polysaccharide chain by introducing polymer chain that configures different structural characteristics to the initial polymer.

5.2.2.2 k-Carrageenan (Also Called as Antlers Gum)

k-Carrageenan is one of the nontoxic linear sulfated polysaccharides that are obtained commercially by alkaline extraction of certain species of red seaweeds (algae). The structure of *k*-carrageenan is made up of α-(1–4) D-galactose-4-sulfate and β-(1–3) 3,6-anhydro-D-galactose (Fig. 5.5) [65–67]. It is widely used as a thickening, gelling, and stabilizing agent in food industry [68] as well as has applications in pharmaceutical [69] and biotechnology sectors [70]. *k*-Carrageenan
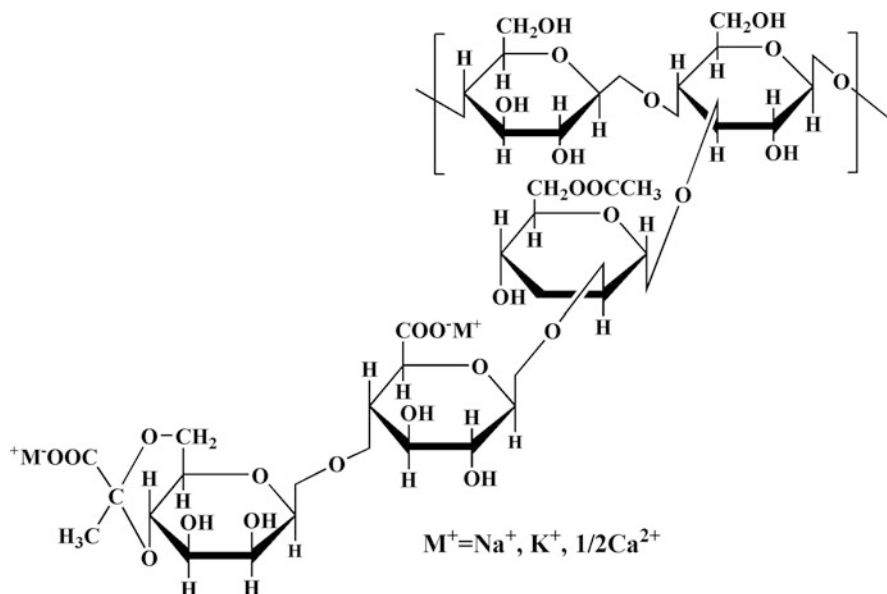
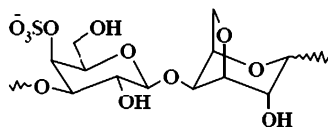**Fig. 5.4** Chemical structure of xanthan gum [60]

Fig. 5.5 Repeating disaccharide units of kappa-carrageenan (κC) [73]

has also been subjected to play an important role as free radical scavengers in vitro and antioxidants for prevention of oxidative damage in living organisms [71, 72]. Although k-carrageenan has wide application range, it suffers from certain drawback like biodegradability, which limits its use considerably. The presence of hydrophilic sulfate groups endows k-carrageenan with higher reactive activity, ionization tendency, and less sensitivity to salt solution [73].

5.2.2.3 Alginate

Alginate is an anionic linear polysaccharide extracted from the cell walls of brown algae or produced by bacteria, and so it is a renewable, water soluble, odorless, nontoxic, and biodegradable natural polymer. Alginate is a linear copolymer with homopolymeric blocks of (1–4)-linked β-D-mannuronate (M), and its C-5 epimer α-L-guluronate (G) residues, respectively, covalently linked together in different sequences or blocks. The monomers can appear in homopolymeric blocks of consecutive G-residues (G-blocks), consecutive M-residues (M-blocks), or alternating

Fig. 5.6 Chemical structure of sodium alginate [77]
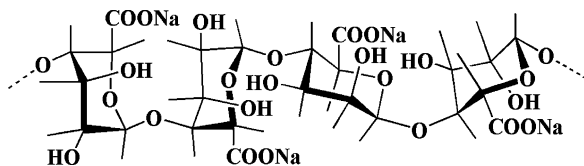
M and G-residues (MG-blocks) [74]. Due to the existence of –COOH or –COO⁻ groups, alginate is capable of absorbing 200–300 times its own weight in water to form a viscous solution, and it is widely used as thickening agent, emulsifier, sizing agents, and stabilizing agent of dye printing. The molecular chains of alginate could be modified by ionic cross-linking [75], grafting copolymerization [76, 77] to derive new hydrogel materials. It shows great application potentials in drug delivery carriers, especially for the target delivery of gastrointestinal tract drug. Chemical structure of sodium alginate is shown in Fig. 5.6 [77].

5.2.2.4 Acacia Gum

Acacia gum (AG) is a water-soluble chemically modified natural gum which is susceptible to easy biodegradation [78, 79]. AG is a complex arabinogalactan which contains a small proportion of proteinaceous materials and has been classified as arabinogalactan–protein complex [80]. Due to the existence of acacia acid (X-COOH) in the gum, the AG can be ascribed as an anionic gum. The gum is composed of D-galactose, L-arabinose, L-rhamnose, D-glucuronic acid, and 4-O-methyl-D-glucuronic acid [81]. It can easily dissolve in water to form viscous, weakly acidic solution (the solubility reaches 50 %), but does not dissolve in ethanol and most organic solvents. AG can be used as thickening agent, suspending agent, and stability agent and enjoys a wide range of applications in industries such as paper, textiles, pharmaceuticals, drink, and food. It has been reported that inorganic salt complexes of AG can behave as a superionic electrical conductor [82]. AG was produced from *Acacia senegal* or the cut flow effusion of stem and branch of tree *A. seyal*. After removing the impurities, the effusion was dried and smashed to form AG. The former is brittle than the latter. The AG can be used in the form of raw gum, derivatives, and graft copolymers.

5.3 Derivatives of Natural Gums

As described above, the intrinsic structure and properties of nonionic, anionic, and cationic gums make them found extensive application in various areas, but the raw gum also emerges some drawbacks and cannot meet all application requirements for some special purpose. Thus, the modification of gums with acrive small molecules was conducted because the derivatives can not only bring the favorable properties due to the introduction of functional groups, but also keep the intrinsic advantages of gums to the greatest degree [83]. And so the chemical modification

always plays a dominant role to improve gums and open prospects for extending the application of raw gums. Generally, the chemical functionalization of gums mainly includes the esterification, etherification, and cross-linking reactions of hydroxyl groups.

5.3.1 Carboxyl Derivatives

The reactive –OH functional groups of gum endow it with great potentials to be modified to meet various applications. In the presence of reactive carboxyl or carboxymethyl reagents (i.e., chloroacetic acid, maleic anhydride, and succinic anhydride), the –OH groups of gum may occur nucleophilic substitution reaction with the HOOC···Cl or (C=O)O(C=O) groups to form an ether or ester under the alkali condition [84]. The reaction can introduce –COOH or –COONa groups on the macromolecular backbone and transform a nonionic gum into an anionic gum. For one thing, the hydratability and solubility of gum was clearly improved due to the introduction of strong hydrophilic –COOH or –COONa groups; for another, the –COOH groups make gum having responsive capability to external stimuli such as pH value, electrolytes, or electronic field, which extended its application domain in biomedical or sensor fields. For instance, the carboxymethyl derivative of cashew gum has negative charges, and can form physical complex with the cationic polymer such as chitosan. The complex can generate insoluble cross-linked materials that can swell and realize the intelligent delivery and release of drugs [85]. The substitution degree of gum may be controlled by adjusting the reaction condition and recipe, and it determined the usage properties of the derivatives. Usually, the gum was partially carboxymethylated by controlling the reaction prescription and only a part of –OH groups were reacted. The residual active –OH groups can still graft with various monomers or react with other modifier to form derivatives with various groups (Fig. 5.7).

5.3.2 Hydroxyethyl Derivatives

Like cellulose, the hydroxyethyl derivatives of gum have better solubility and thermal stability in solution, good dispersibility in water, and high compatibility with anionic, cationic, and nonionic surfactants. So, they show more extensive application in many industrial sectors such as oil recovery, fabric printing, fracture fluids, food system, paints, mineral industry, and personal care [86]. The hydroxyethyl derivatives of gum could be prepared from natural gum via an irreversible nucleophilic substitution, and the derivatives show better colloid properties than the raw gums [87–89]. The chemical and functional properties of gum are mainly dependent on the distribution of molecular weight, the amount of hydroxyethyl substituents, the pattern of substitution, and the distribution of substituents.
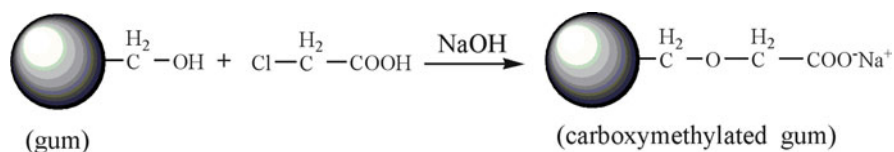
(gum)   (carboxymethylated gum)

Fig. 5.7 Carboxymethyl modification of gum

5.3.3   Vinyl-Functioned Derivatives

Many gums show poor reactive activity, and so it is difficult to derive new materials by the direct graft reaction with vinyl monomers. The modification of such gums by highly active small molecules with both vinyl groups and reactive end functional groups (i.e., acyl chloride and epoxy groups) may introduce reactive vinyl groups on the gum backbone. The vinyl-functionalized gum was denoted as macromonomers, which can graft with vinyl monomers to form a grafting copolymer with cross-linker network structure. The most frequently used modifying agent is glycidyl methacrylate (GMA), acrylic acid, acryloyl chloride, and maleic anhydride. Thus far, the vinyl-functionalized arabic gum [90], guar gum [91], cashew gum [92], xanthan gum [93], and pectin [94] were prepared under basic condition. At basic condition, the nucleophilic substitution reaction occurred. The –OH groups of gums tend to lose hydrogen under basic condition and generate some negative electrical property, which can attack the carbon atom in epoxy or the carbon atom connected with ester groups to form vinyl-functionalized gum (Figs. 5.8 and 5.9). At acidic condition, the oxygen atom in epoxy group may be protonated, which makes the nucleophilic occurring more easily [95]. The suggested pH values are in the range of 8–10 (basic condition) and 3.5–3.8 (acidic condition).

Desbrieres groups [93] also prepared vinyl-functionalized xanthan gum by esterification reaction of –OH groups with acrylic acid and by nucleophilic reaction with acryloyl chloride and maleic anhydride under different reaction conditions.

5.3.4   Cationic Derivatives

The cationic derivatives of gum have positive charges due to the introduction of cationic functional groups such as amino, ammonium, imino, sulfonium, or quaternary phosphonium groups. The cationic modification of gum is usually an etherification process, and the modifier is a reactive molecule with the end R–Cl or R-epoxy as well as the cationic functional groups. Specifically, the R–Cl or R-epoxy active groups may react with –OH groups to form ether, and the cationic groups were simultaneously introduced. The existence of these substituents and numerous hydroxyl groups in their structure may allow the establishment of different types of interactions with the anionic matters including anionic drugs, anionic dyes, and numerous negatively charged particles and can be used as
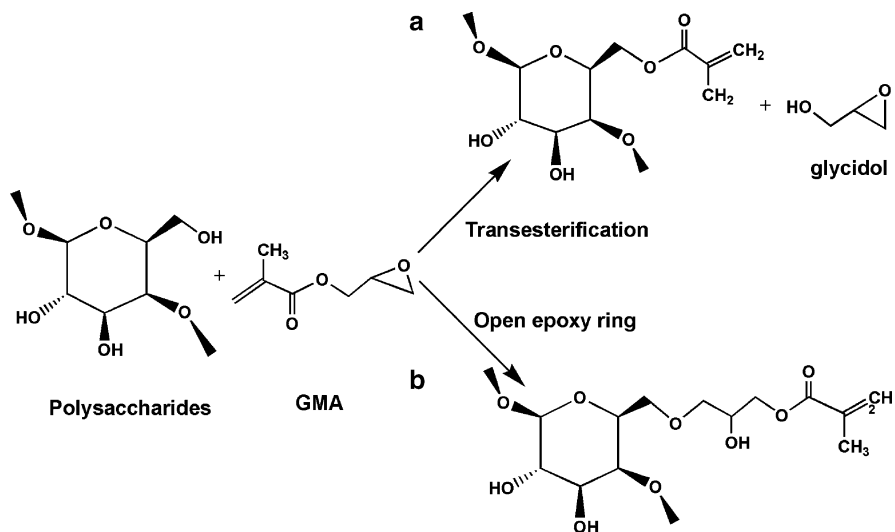
Fig. 5.8 The feasible pathways of modification of polysaccharides with GMA: (**a**) transesterification and (**b**) open epoxy ring mechanism [92]
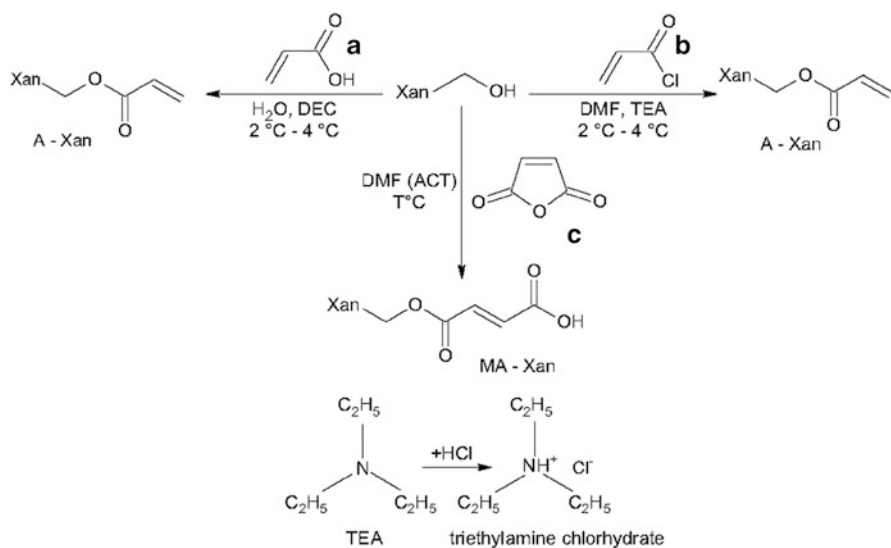
Fig. 5.9 Strategies for modification of xanthan: (**a**) acrylic acid, (**b**) acryloyl chloride, and (**c**) maleic anhydride [93]

effective carriers, filter aid agents, cationic flocculant, and additives of fine chemicals [96, 97]. Compared with the natural cationic polysaccharide chitosan, the ionization degree of cationic derivatives of gum is almost independent of pH owing to the presence of cationic substituents that cannot be protonated. Currently,
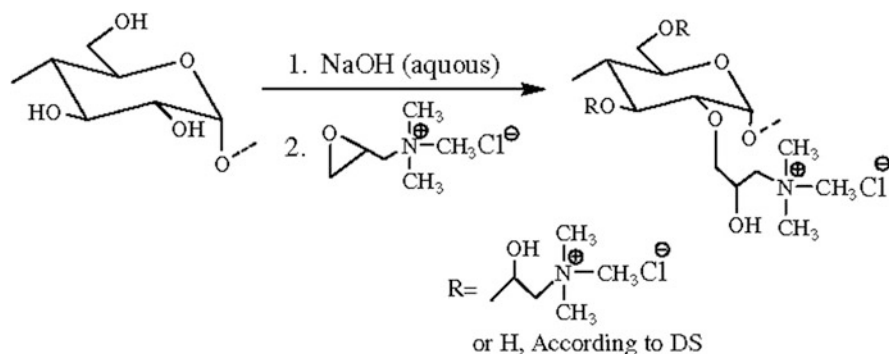
Fig. 5.10 Cationic derivatization mechanism of guar gum [99]

the quaternary ammonium derivatives of gum were focused, and the most common used modifier is 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC) [98, 99]. The quaternization of gum using CHPTAC as an etherifying agent under the catalytic action of NaOH may undergo several reaction steps (Fig. 5.10). Under the action of strong alkali, the –OH groups may generate O^- with stronger nucleophilic capability, which may attack the R–Cl end of CHPTAC and form –C–O–C ether. The $-NH_4^+ Cl^-$ group was also simultaneously introduced and the gums carried some positive charges.

5.3.5 *Amphoteric Derivatives*

Amphoteric natural polymer contains both anionic and cationic substituents on its structure, which exhibits distinct properties in contrast to the individual anionic or cationic polymer and receives extensive applications in fine chemicals, papermaking, dyeing, and package materials [100–102]. The common methods to prepare amphoteric derivatives of gum include the following: (1) simultaneously modifying gum with anionic and cationic modifiers [103] and (2) modifying gum with an amphoteric modifier [104]. The former was frequently used because it is simple, but the content of anionic and cationic groups of resultant derivative is difficult to be controlled. The latter is relatively complex because it needs to design an amphoteric modifier, but the ratio of anionic and cationic ions can be controlled at 1:1. Xiong et al. [104] synthesized an amphoteric modifier *N*-(3-chloro-2-hydropropyl)-*N*-(carboxymethyl)-*N*,*N*-dimethyllammonium-hydroxide (CCDH) and used for modifying guar gum to obtain an amphoteric guar gum with the positive–negative charge ratio of 1:1.
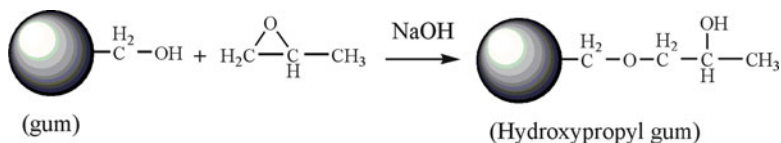
Fig. 5.11 Preparation procedure of hydroxypropyl gum

5.3.6 Hydrophobic Derivatives

The natural gums are mainly hydrophilic and soluble in aqueous medium, but it cannot meet the requirements for the application in organic solvent system. Other polysaccharide (i.e., starch, cellulose, chitosan) may form hydrophobic derivatives by introducing short chain hydrocarbon substituents through etherification reaction and show solubility in organic solvents. Similarly, the reactive groups of gum may be etherized by RO–X, phO–X (X = Cl or Br) to produce the derivatives with hydrophilic and hydrophobic characters. The hydrophobic modification of gums can form hydrophilic–hydrophobic gums with the characteristics similar to surfactants and can form a micelle in solution. For instance, the modification of gum under alkaline catalyst may form hydroxypropyl gum [105], which could trigger and accelerate the sol−gel transition of tetraethoxy-silicone in water and induce rapid formation of homogeneous gel matrix without the addition of any organic solvents or catalysts, and can modulate the gel strength of the silica matrix by the amount of hydroxypropyl gum (Fig. 5.11) [106]. The substitution and the average length of the hydroxypropyl substituents usually affect the properties of products [107].

5.4 Synthesis of Gum-g-Copolymers

5.4.1 Gum-g-Copolymers via Conventional Radical Grafting Methods

The conventional grafting method of gum was involved with the direct grafting reaction and the ring-opening reaction of macromolecular chains of gum. The direct grafting reaction usually occurred on the –OH groups of gum by a radical polymerization reaction process, and the used initiators are usually thermal initiator or redox initiator. In this process, the radicals were generated from the decomposition of thermal initiator (i.e., ammonium persulfate, sodium persulfate, potassium persulfate, azodiisobutyronitrile) or the oxide–redox action of redox initiation pairs (i.e., H_2O_2/Fe^{2+}, $K_2S_2O_4/Fe^{2+}$, $K_2S_2O_4$/ascorbic acid, benzoyl peroxide/dimethylaniline). The formed anionic radicals may strip down the H atom of –OH groups and initiate the macromolecular chains of gums to generate macroradicals, and these radical reactive sites may initiate the vinyl groups of monomers to process the chain propagation.

Comparatively, the most commonly used initiation system is redox system because activation energy for the redox initiation is quite low and it can initiate the reaction under ambient condition, and the reaction rate is faster and the energy consumption is low [108]. The type and activity of initiator usually decide the grafting reaction efficiency and rate, and the development of new initiator has long been the subject of great interests. Because of the different types of oxidants and reductants, the formation mechanism of free radicals in redox system is distinct, and the sorts of redox initiators are important factor to decide the graft efficiency. Figure 5.12 depicts the most frequently used redox initiation system and depicts the reaction and formation mechanism of radicals [34, 58, 59, 62, 67, 109–123]. For instance, in the $KHSO_5/Fe^{2+}$ redox system, the divalent Fe^{2+} may lose one electron under the action of oxidant $KHSO_5$ to form Fe^{3+}, and simultaneously the S–O or O–H bonds of $KHSO_5$ were broken to form $–OH^{\bullet}$ and $–SO_4^{\bullet-}$ radicals. In the potassium chromate/malonic acid initiation system, the CrO_4^{2-} ions may transform with H_2CrO_4 each other at acidic condition. The oxidant H_2CrO_4 may react with reductant $CH_2(COOH)_2$ to form Cr^{4+} midbody with higher activity. The Cr^{4+} may capture the active H atom of $CH_2(COOH)_2$ (the strong electron withdrawing capability of –COOH render the conjoint $–CH_2–$ higher reactivity) to form $^{\bullet}CH(COOH)_2$ radicals, and the Cr^{4+} ion was reduced as Cr^{3+} ion. In a word, the formation process of radicals is an electron transport process induced by a redox reaction.

As discussed above, although the formation mechanism of radicals for various initiation systems is different, the radicals have the same effect when they initiate the gum to perform a graft reaction and form a graft copolymer. Figure 5.13 gives the typical grafting mechanism of vinyl monomers onto gum backbone. Firstly, the primary radicals were generated by the decomposition of thermal initiator or the reaction of redox initiators (Fig. 5.12). These radicals striped down the hydrogen atoms of the –OH groups on gum chains to form macro-radicals. After added vinyl monomers, the active radical sites on gum chains may initiate vinyl groups of the monomers to process chain propagation. This is a typical "graft from" reaction. In the grafting process, the type and activity of initiators, the concentration, viscosity and activity of gum solution, the concentration of monomers, the reaction temperature, and time may greatly affect the graft ratio and efficiency. Table 5.1 shows the different gum-g-copolymers prepared by using various redox initiator systems as well as the grafting efficiency.

Besides the direct grafting reaction of –OH groups, the saccharide ring of gum may be opened. Typically, when the initiator is multivalent metal ions such as Ce^{4+} ion, the metal ions may interact with the C2–C3 glycol and the C6 hydroxyl of the anhydro-D-glucose unit of saccharide ring to form a gum–Ce^{4+} complex [134]. The Ce^{4+} ion in the complex can then be reduced as Ce^{3+} ion with the release of a proton and a subsequent formation of a free radical on the backbone of gum. These free radicals could then react with the end vinyl groups of monomer to initiate graft copolymerization (Fig. 5.14) [135]. Termination of the graft copolymer was carried out through the

Potassium bromate/ Fe^{2+}

$Fe^{2+} + BrO_3^- + H_2O \longrightarrow Fe^{3+} + BrO_2^- + \overset{\bullet}{O}H + OH^-$

$Fe^{2+} + BrO_2^- + H_2O \longrightarrow Fe^{3+} + BrO^- + \overset{\bullet}{O}H + OH^-$

$Fe^{2+} + BrO^- + H_2O \longrightarrow Fe^{3+} + Br^- + \overset{\bullet}{O}H + OH^-$

$Fe^{2+} + BrO^- + H_2O \longrightarrow Fe^{3+} + \overset{\bullet}{B}r + 2OH^-$

Potassiumperoxydiphosphate/ Ag^+

$H_2P_2O_8^{2-} + Ag^+ \longrightarrow H_2AgP_2O_8^-$

$H_2AgP_2O_8^- + XOH \longrightarrow$

$\quad X\overset{\bullet}{O} + HPO_4^{\bullet-} + Ag^+ + H_2PO_4^-$

Potassium Chromate/Malonic Acid

$H_2CrO_4 + CH_2(COOH)_2 + 4H^+ \longrightarrow$

$Cr^{+4} + HO\text{-}CH(COOH)_2 + 3H_2O$

$Cr^{+4} + CH_2(COOH)_2 \longrightarrow$

$\quad \bullet CH(COOH)_2 + H^+ + Cr^{+3}$

Peroxymonosulphate/Ascorbic Acid

Peroxymonosulfate/ Glycolic acid

$CH_2(OH)COOH + HSO_5^- \rightleftharpoons Complex$

$Complex \longrightarrow$
$\overset{\bullet}{C}H(OH)COOH + H_2O + SO_4^{\bullet-}$
$CH_2(OH)CO\overset{\bullet}{O} + H_2O + SO_4^{\bullet-}$
$CH_2(OH) + CO_2 + H_2O + SO_4^{\bullet-}$

Dicumyl peroxide/ Fe^{2+}

Vanadium (V)/mercaptosuccinic acid

Potassium Persulfate/ Ascorbic Acid

$S_2O_8^{2-} \longrightarrow 2SO_4^{\bullet-}$

$SO_4^{\bullet-} + H_2O \longrightarrow SO_4^{-} + \overset{\bullet}{O}H + H^+$

$\overset{\bullet}{O}H + AH^- \longrightarrow \overset{\bullet}{A}H + OH^-$

$\overset{\bullet}{A}H + S_2O_8^{2-} \longrightarrow A + SO_4^{2-} + SO_4^{\bullet} + H^+$

AH represents Ascorbic Acid

Thioacetamide/Potassium monopersulfate

(Thioacetamide)   (RSH)

$RSH + HSO_5^- \longrightarrow RS^{\bullet} + SO_4^- + H_2O$

Peroxymonosulphate/Ascorbic Acid

Peroxymonosulfate/ Glycolic acid

$CH_2(OH)COOH + HSO_5^- \rightleftharpoons Complex$

$Complex \longrightarrow$
$\overset{\bullet}{C}H(OH)COOH + H_2O + SO_4^{\bullet-}$
$CH_2(OH)CO\overset{\bullet}{O} + H_2O + SO_4^{\bullet-}$
$CH_2(OH) + CO_2 + H_2O + SO_4^{\bullet-}$

Cu^{+2}/Mandelic Acid

(R•)

Vanadium (V)/mercaptosuccinic acid

Potassium Persulfate/ Ascorbic Acid

$S_2O_8^{2-} \longrightarrow 2SO_4^{\bullet-}$

$SO_4^{\bullet-} + H_2O \longrightarrow SO_4^- + \overset{\bullet}{O}H + H^+$

$\overset{\bullet}{O}H + AH^- \longrightarrow \overset{\bullet}{A}H + OH^-$

$\overset{\bullet}{A}H + S_2O_8^{2-} \longrightarrow A + SO_4^{2-} + SO_4^{\bullet} + H^+$

AH represents Ascorbic Acid

Potassium Monopersulfate/Ag(I)

$Ag^+ + HSO_5^- \longrightarrow Ag^{2+} + OH^- + SO_4^{\bullet-}$

$Ag^+ + HSO_5^- \longrightarrow Ag^{2+} + \overset{\bullet}{O}H2 + SO_4^{2-}$

Potassium Chromate/Malonic Acid

$H_2CrO_4 + CH_2(COOH)_2 + 4H^+ \longrightarrow$

$Cr^{+4} + HO\text{-}CH(COOH)_2 + 3H_2O$

$Cr^{+4} + CH_2(COOH)_2 \longrightarrow$

$\quad \bullet CH(COOH)_2 + H^+ + Cr^{+3}$

Bromate/Thiourea

$6HS\text{-}C(NH_2)(\overset{+}{N}H_2) + BrO_3^- \longrightarrow 6S\text{-}C(NH_2)(\overset{+}{N}H_2) + Br^- + 3H_2O$

Potassium Monopersulfate/ Fe^{2+}

$Fe^{2+} + HSO_5^- \longrightarrow Fe^{3+} + \overset{\bullet}{O}H + SO_4^{2-}$

$Fe^{2+} + HSO_5^- \longrightarrow Fe^{3+} + OH^- + SO_4^{\bullet-}$

Potassium Peroxymonosulphate/Ascorbic Acid

$\cdots \overset{\overline{HSO_5^-}}{\longrightarrow} \cdots + \overset{\bullet}{O}H + HSO_4^-$
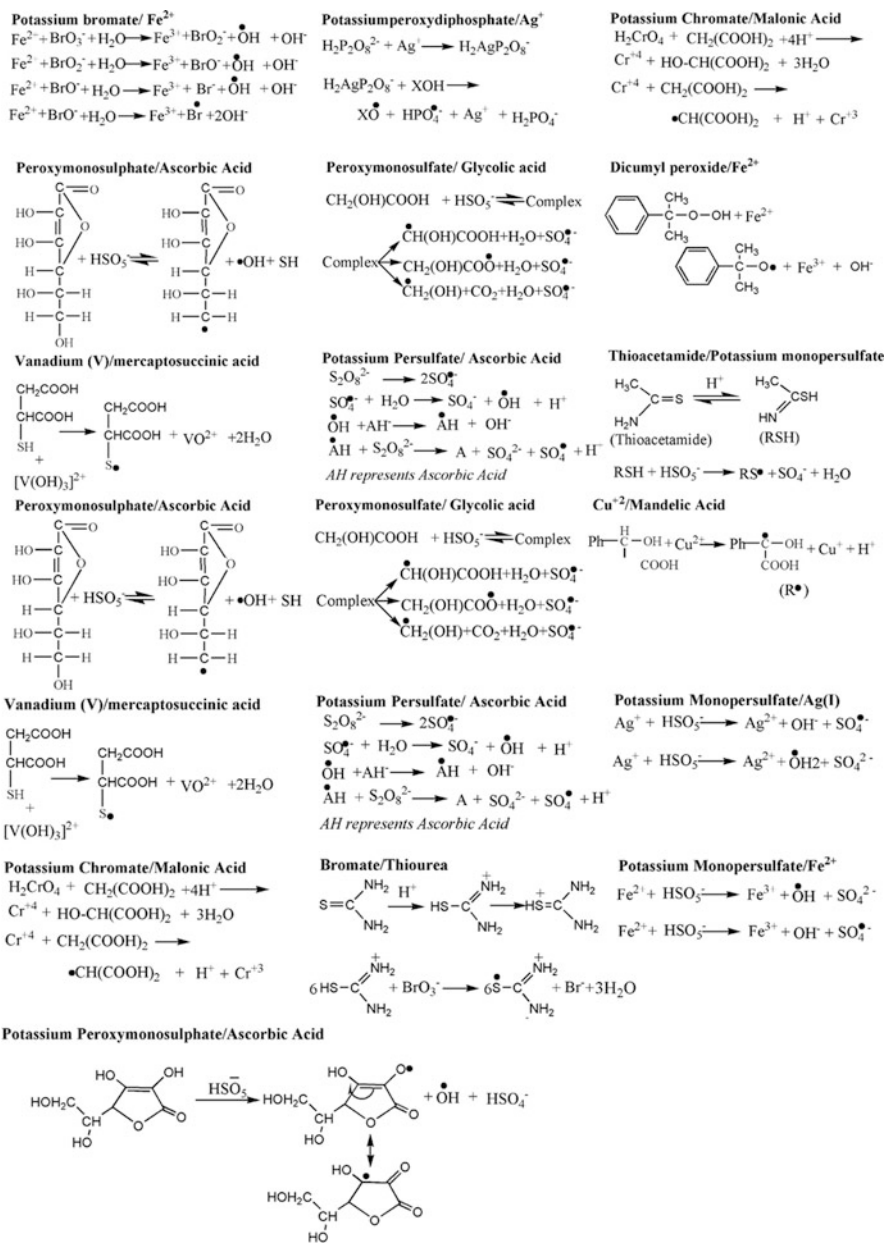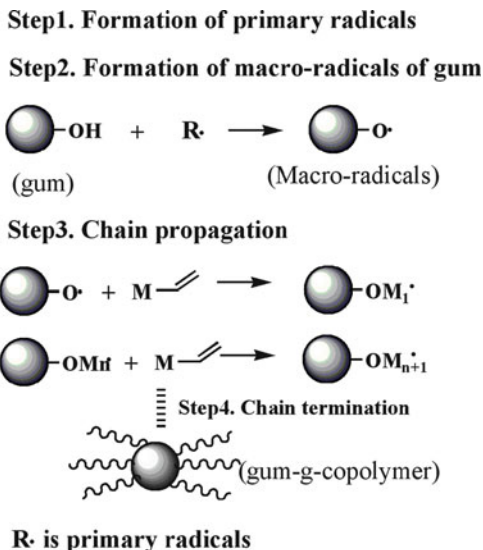
Fig. 5.12 Illustration of the conventional redox initiation systems [34, 58, 59, 62, 67, 109–123]

combination of radicals [135, 136]. In this system, the pH value of reaction system is important to the initiation efficiency of Ce^{4+} ion [78]. In contrast to the persulfate initiators or peroxide initiator, the Ce^{3+} initiators usually have higher grafting

Fig. 5.13 The common
mechanism for the graft
copolymerization of gum

Step1. Formation of primary radicals

Step2. Formation of macro-radicals of gum

Step3. Chain propagation

Step4. Chain termination

(gum-g-copolymer)

R· is primary radicals

efficiency. Compared with other transition metal ions (i.e., Fe^{3+}, Cu^{2+}, Co^{3+}, Cr^{6+}) [137, 138], the Ce^{4+} ion has the advantage that it produces a minimum amount of homopolymer [139, 140]. The representative graft-copolymer synthesized by the initiation of Ce^{4+} ions is listed in Table 5.2. Despite the Ce^{4+} ion initiator shows better efficiency, but it is not industrially feasible due to the undesirable toxicity and the higher cost.

5.4.2 Gum-g-Copolymers via Macromonomer Radical Methods

For the gum with lower reactive activity, its modification for forming a macromonomer-like structure is essential and becomes an effective approach to prepare gum-g-copolymer. The synthesis of macromonomers is the key factors affecting the grafting reaction and the properties of product. For general free radical graft reaction, the vinyl-functionalized gums were usually considered as a macromonomer because it contains many active vinyl groups that are similar with vinyl monomers. Desbrieres et al. [93] synthesized a vinyl-functionalized xanthan gum and used as a macromonomer to prepare new graft polymer. Tiwari et al. [157] modified guar gum with GMA to obtain guar gum–methacrylate (GG–MA) macromonomers and then polymerize them to form a hydrogel material. Guilherme et al. [92] synthesized cashew gum-based macromonomers with vinyl groups and used to react with vinyl monomer acrylamide. The monomer acrylamide was reacted with the vinyl groups of gum to form a graft copolymer, and the molecular chains of gum were connected with each other by the polymerization of monomers to form a network structure. The grafting and cross-linking reaction was simultaneously conducted.

Table 5.1 Examples of gum-g-copolymers formed by direct grafting reaction

Initiation system	Gum-g-copolymers	GE%[a]	GR%[b]	References
H_2O_2	GG-g-PMMA	61.50	–	[109]
$KMnO_4$/oxalic acid	GG-g-PAM	29.00	102.80	[124]
Potassium bromate/thiomalic acid	GG-g-PAM	81.00	–	[110]
KPS/ascorbic acid	GG-g-PAN	76.00	123.00	[111]
Cu^{+2}/mandelic acid	GG-g-PAM	93.70	129.77	[112]
Peroxydiphosphate/silver(I)	GG-g-PAA	87.00	1237.83	[125]
Peroxydiphosphate/metabisulphite	GG-g-PAM	97.70	277.80	[126]
Potassium chromate/malonic acid	GG-g-PMAD	88.30	151.20	[113]
Potassiummonopersulfate/thioacetamide	GG-g-P4V	75.80	504.29	[127]
KPS	GG-g-PMA	24.20	241.60	[114]
Bromate/ascorbic acid	GG-g-PNVF	96.90	358.70	[128]
Vanadium (V)/mercaptosuccinic acid	GG-g-PAA	63.60	160.40	[115]
Peroxymonosulfate/ascorbic acid	GG-g-P4V	52.90	560.90	[34]
Cu^{2+}/$Na_2S_2O_5$	GG-g-PAM	25.35	60.0	[129]
KPS/ferrous ammonium sulfate	GG-g-PNVP	77.90	168.00	[130]
Peroxymonosulfate/glycolic acid	GG-g-PNVP	76.92	200.00	[116]
Peroxymonosulfate/thiourea	PCMGG-g-PACA	70.60	292.80	[117]
H_2O_2	LGSG-g-PAN	100.00	167.60	[131]
KPS/ascorbic acid	IDSG-g-PAN	97.20	360.00	[58]
KPS/ascorbic acid	IDSG-g-PAN	–	80.00	[25]
KPS/ascorbic acid	IHSG-g-PAN	–	124.00	[25]
KPS/ascorbic acid	IPSG-g-PAN	–	149.00	[25]
Potassium monopersulfate/Fe^{2+}	XG-g-PAA	–	192.30	[118]
Potassium bromate/Fe^{2+}	XG-g-PAM	84.90	145.60	[119]
Fe^{2+}/H_2O_2	XG-g-PMA	93.33	168.00	[62]
Bromate/thiourea redox	XG-g-PAMPS	–	160.00	[59]
Potassium monopersulfate/Ag(I)	XG-g-PNVF	97.59	324.00	[120]
Potassium bromate/ascorbic acid	XG-g-PAMPS	–	433.00	[121]
Potassium peroxydiphosphate/Ag^+	XG-g-PNVP	78.90	300.00	[122]
Peroxymonosulfate/ascorbic acid	XG-g-P4V	87.80	400.00	[123]
Peroxymonosulfate/glycolic acid	k-CGN-g-PDAM	81.30	509.90	[67]
KPS	CG-g-PAM	96.30	144.40	[132]
APS	AG-g-PAM	73.50	459.00	[133]

[a]Graft efficiency
[b]Graft ratio

5.4.3 *Gum-g-Copolymers via High-Energy Initiation Grafting Method*

The synthesis of gum-g-copolymers by conventional chemical initiation methods was described above. These methods were intensively developed and used to derive numerous graft polymer materials. However, these methods are highly depended on the chemical initiator and can only be used for the liquid-phase reaction. For one thing, the usage of chemical initiators may inevitably introduce undesirable
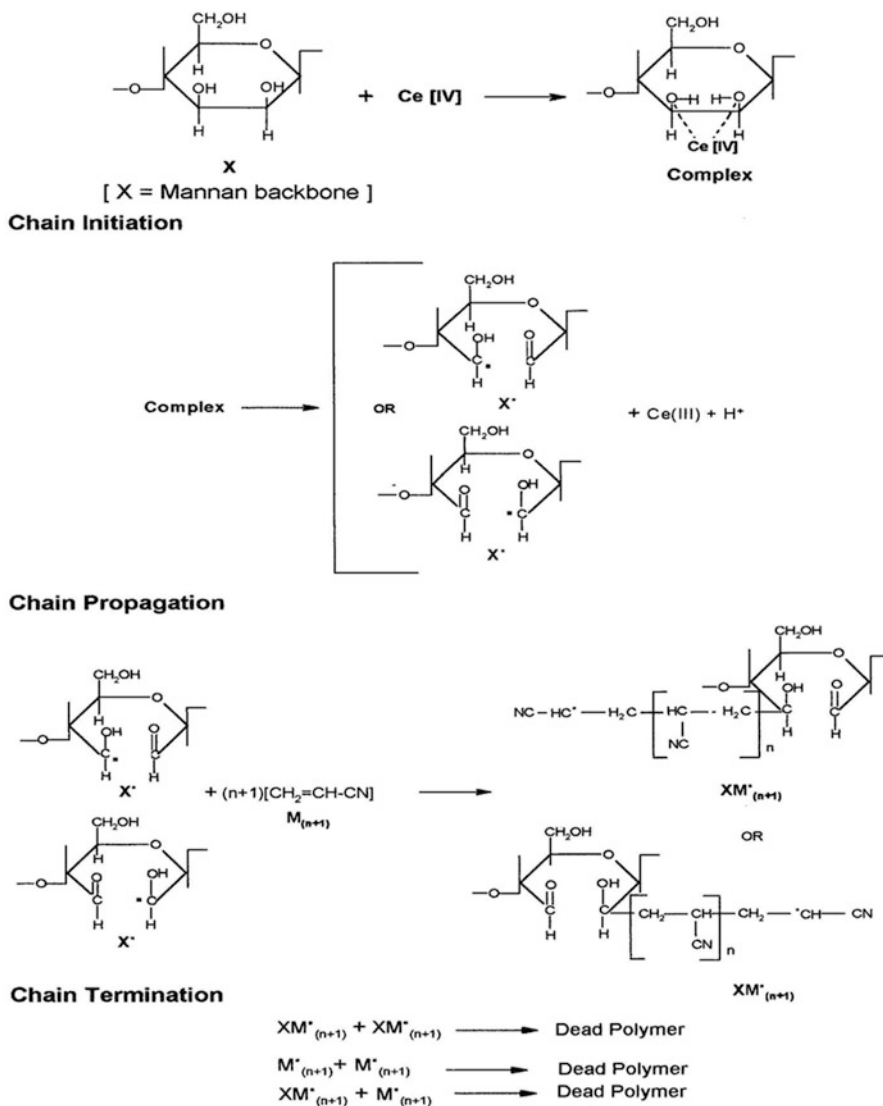
Fig. 5.14 Grafting mechanism of AN onto cassia tora gum initiated with CAN [135]

chemical matters, which affected the safety of graft copolymer in many application fields, especially in food, daily chemicals, and drug carrier areas; for another, the grafting reaction in solution may increase the cost and generate secondary pollution, and the conventional method is not suitable to treat solid sample. Thus, the high-energy initiation technologies have recently received increasing concerns because they are simple and can be done in both solution and dry medium.

Table 5.2 Examples of gum-g-copolymers formed by Ce^{4+}-initiated reaction

Initiation system	Graft copolymer	GE%	GR%	References
CAS/dextrose	GG-g-PMMA	65.34	–	[141]
CAN	GG-g-PAN	94.00	295.00	[142]
CAS	AG-g-PMMA	82.45	–	[78]
CAN	PCMGG-g-PAN	98.50	291.75	[143]
CAS	CGG-g-PAM	98.20	–	[144]
CAS	AG-g-PEMA	86.64	1629.00	[145]
CAS	CGG-g-PAM	95.00	1200.00	[146]
CAN	TGG-g-PAN	–	543.00	[147]
CAS/SD	CRSG-g-PAM	91.20	142.60	[148]
CAN	TK-g-PAM	93.66	231.45	[149]
CAN	*k*-CGN-g-PAN	95.00	125.00	[150]
CAN	SA-g-PIA	87.87	635.28	[151]
CAN	KG-g-PAM	98.60	–	[152]
CAN	TK-g-PAN	64.00	86.00	[153]
CAN	GG-g-PGMA	–	730.00	[154]
CAN/MW	GGT-g-PAM	168.6	843.00	[155]
CAN	CTG-g-PAN	98.50	211.57	[135]
CAN	XGC-g-PMMA	94.78	84.70	[156]

5.4.3.1 Microwave-Assisted Grafting Copolymerization

As an efficient thermal energy, microwave (MW) irradiation technology is becoming the standard and high-efficient synthesis technique in various fields of chemistry or engineering [158, 159]. Microwaves generate electromagnetic radiation in the frequency of 300 MHz to 300 GHz, and the energy can be rapidly transferred in the bulk of the reaction mixture. Usage of microwave initiation for preparing the grafting copolymers of polysaccharides has recently been developed [158, 160–162]. By comparison with conventional method, the relatively higher yields and grafting efficiency could be achieved within a very short time with no or little addition of any radical initiators or catalyst, and the extent of grafting could be adjusted by controlling the microwave conditions [163–166]. Microwave radiations cause "selective excitation" of the polar bonds only, which in turn leads to their rupture/cleavage. This cleavage of bonds creates many free radical sites on the polymer backbone. The "C−C" sequence of the backbone polymer remains unaltered by the microwave radiation since it is relatively nonpolar [167]. Figure 5.15 depicts the graft polymerization mechanism initiated by individual microwave and based on free radical mechanism. Typically, the polar O−H bond can easily be broken under the action of microwave radiation, while the C−C bond (practically nonpolar) has not been affected. The cleavage of the O−H bonds leads to the formation of free radical "active" sites on the backbone of gum. These active sites can react with vinyl monomers to achieve the growth of chains, and the graft copolymer could be formed [167–169].
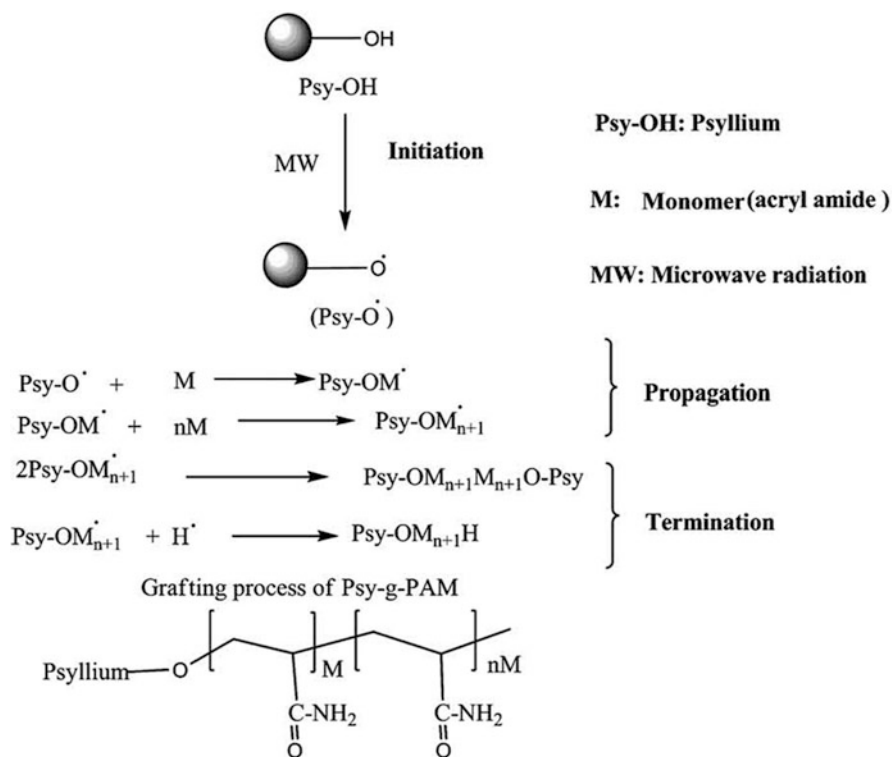
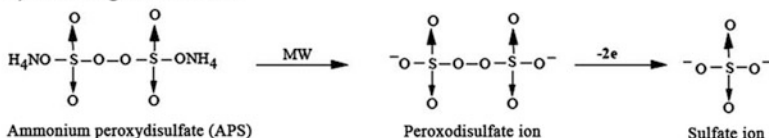Fig. 5.15 Mechanism for "microwave-initiated synthesis of PSY-g-PAM" [167]

The microwave-assisted graft copolymerization in the presence of little (or catalytic amount of) chemical initiator is another important reaction styles [26, 162, 163, 166, 170]. The main initiator is persulfate and ceric salts. The primary radical can be formed more effectively under the action of microwave, and the graft efficiency can be improved to a certain degree. The active radicals formed on the hydroxyl groups of gum may react with vinyl monomers (i.e., acrylic acid, acrylamide, acrynitrile, 4-vinylpyridine) or non-vinyl monomers (i.e., aniline) to form graft polymers. Figure 5.16 shows the graft mechanism of aniline onto the AG using APS and MW as the associated initiation approach. The radical initiator APS was decomposed under microwave radiation to form a sulfate ion radical, and then the radical stripped down the H atom of the –OH groups of gum to generate a macroradical. The macroradical may react with the active PANI chains [26] to form the graft copolymer.

5.4.3.2   Radiation-Initiated Grafting Copolymerization

Gamma ray is electromagnetic radiation of high frequency and therefore energy. Gamma rays are ionizing radiation and are classically produced by the decay from high-energy states of atomic nuclei (gamma decay) but also in many other ways.

Step1: Generation of primary radicals

1) Oxidizing action of APS

Ammonium peroxydisulfate (APS)   Peroxodisulfate ion   Sulfate ion

2) APS act as initiator

Peroxodisulfate ion   Sulfate ion   Sulfate ion radical
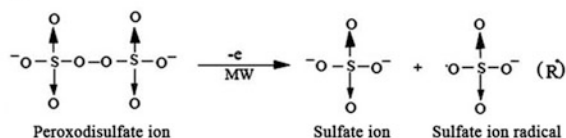
Step2: Polymerization of aniline to form polyaniline ion radical

Step3: Graft of PANI onto acacia gum
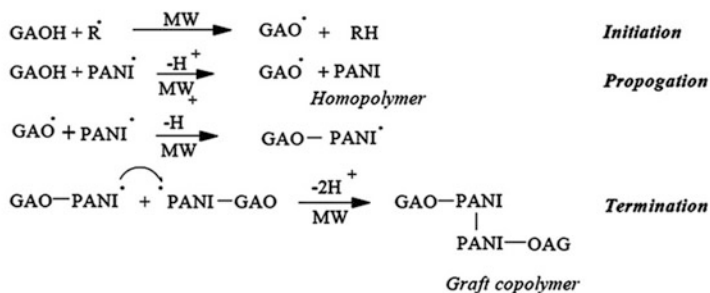
Fig. 5.16 The grafting mechanism of AG with aniline initiated by MW and APS [26]

Recently, gamma irradiation-initiated graft polymerization was developed as a preferred method for commercial synthesis and exhibits a great potential to synthesize the graft copolymers by virtue of its higher efficiency, low cost, and convenient to modify polymer [171, 172]. The utilization of gamma irradiation for the synthesis of gum-g-copolymers has been intensively concerned. For example, Lokhande et al. [173] and Biswal et al. [174] prepared guar gum-g-copolymer by using γ-radiation as the initiation approach. It was found that ideal graft efficiency was obtained, and the graft efficiency is dependent on the dose of radiation. The increase of radiation dose can enhance the graft ratio and decrease the content of homopolymers, but the viscosity or molecular weight was decreased due to the depolymerization effect of radiation to gum. Besides, the graft copolymer of other gums such as XG [175] and KG [54] was reported. However, the problems associated with radiation initiation involve lack of distinction between the different bonds of the backbone polymer because there is always a strong probability of radiation damage (radiolysis) to the gum backbone, and undesirable breakage of bonds may occur under the action of strong radiation [176]. In addition, this method

has required a complex instrument and equipment and exists with safety problem resulting from the radiation. This limited the extensive application of radiation technology in the synthesis of gum-g-copolymer. Figure 5.17 depicts the graft mechanism of the PSY-g-PAA initiated by gamma-radiation [177]. The −OH groups of arabinoxylan on PSY chains act as active sites for the graft copolymerization reaction, and the formed radical sites may initiate the monomers to form grafted side chains.

5.4.3.3 UV Radiation-Initiated Grafting Copolymerization

Due to the advantages of low operation cost and mild reaction conditions, UV has been extensively applied for surface graft polymerization with the aid of a photoinitiator or photosensitizer, such as benzophenone (BP) [178, 179]. UV radiation is usually used for the purpose of surficial grafting [178], and various surface functional groups were grafted on the substrate surface by UV irradiation with various sources [180]. In the process of grafting reaction in solution, UV radiation has usually been used along with a photo-initiator. For example, the graft copolymer of PCGG with methyl acrylate was synthesized by using ultraviolet radiation (generated by a 125-W medium-pressure mercury lamp) as an assisted initiation approach and CAN as a photo-initiator [181]. The UV-initiation method shows higher graft ratio and graft efficiency than that without UV-initiation [181].

5.4.3.4 Electron Beam-Initiated Grafting Copolymerization

High-energy electron beams have usually been used to graft vinyl monomers to solid-state natural polymers in order to make plastic composite materials and modify the properties of solid surface [182–184]. The product prepared by high-energy electron beams can be free from impurities such as chemical residues from initiators for no or less catalysts or additives are needed to initiate the reaction in radiation processing, and the degree of cross-linking and grafting can be controlled by the change of radiation dose [185]. For the graft reaction of natural polymers to form a dispersible or soluble graft copolymer, only less works were made [186, 187], and this greatly extended the application domain of electron beam. Different from conventional initiation method, the electron beam may break the C−C bonds of gum chains and degrade the gum at room temperature to a predetermined molecular weight and polydispersity, and so the viscosity, flow property, suspending, and stability of gum-g-copolymers can be controlled. In addition, the impurities in the final product were reduced. For example, the vinyl monomer may be grafted onto the XG or GG chains when they are exposed to a high-energy electron beam irradiation. In this process, GG with molecular weight of 2,000,000 Da can be depolymerized to a lower preselected molecular weight that is about 700,000 or 500,000 or 300,000 Da, and this provides possibility that the molecular weight of graft-copolymer is lower than the original gum [187].
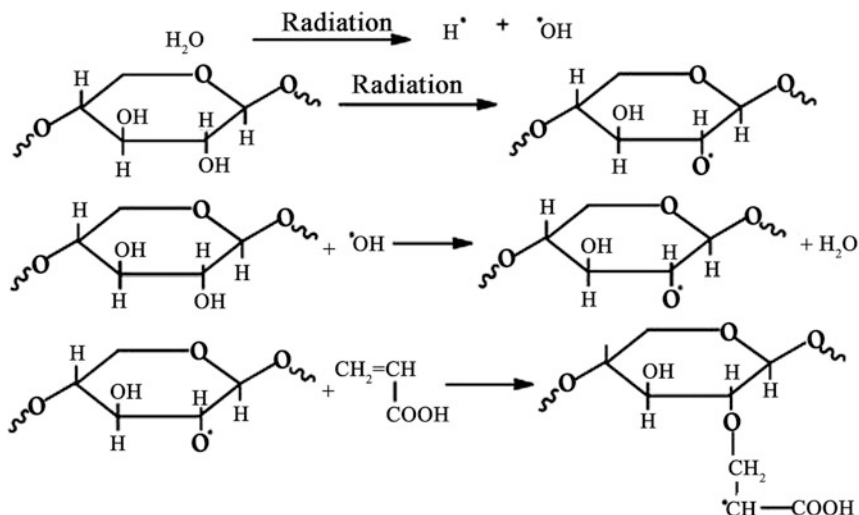
Fig. 5.17 The mechanism of gamma-radiation-initiated graft copolymerization [177]

5.4.4   Synthesis of Gum-g-Copolymers by Click Chemistry

Click chemistry, called as dynamic combinatorial chemistry, is a new synthetic concept proposed by chemist K. B. Sharpless in 2001. The characteristic of click chemistry is to rapidly synthesize various molecules by the montage of small molecular units, and this method emphasizes the synthesis pathways based on the construction of C–X–C bonds. The representative reaction is the copper-catalyzed azide-alkyne Huisgen cycloaddition and was usually used in the development of drugs and biomedical materials [188]. For gum-g-copolymers, the conventional synthesis methods are not quantitative and are sensitive to the molecular weight of the polysaccharide, and the gum may be degraded under some harsh reaction conditions and the yield is low. Thus, the click chemistry, a "graft to" approach, provided a new pathway to prepare special graft copolymers. For example, the thermo-responsive bio-hybrid grafted copolymers GG-g-(PEO-*co*-PPO) were prepared in aqueous medium by copper-catalyzed 1,3-dipolar Huisgen cycloaddition, and the structure and composition is tunable [189]. The detail synthesis procedure is depicted in Fig. 5.18. Typically, guar gum was firstly alkyne functionalized through the reaction of guar gum with propargyl bromide under basic condition using isopropanol as the solvents. Similarly, the methanesulfonyl chloride and triethylamine may react with α-butoxy-ω-hydroxy-PEO-co-PPO to generate α-butoxy-ω-azido-poly[(ethylene oxide)-co-(propylene oxide)] (ω-N_3-PEO-co-PPO) grafted chains. The alkyne-functionalized guar gum may react with ω-N_3-PEO-co-PPO under action of the catalysis copper(II) sulfate and ascorbate to form GG-g-(PEO-*co*-PPO) polymer. Using the similar method, the guar gum-based graft copolymer was also prepared by this workgroups [189, 190].
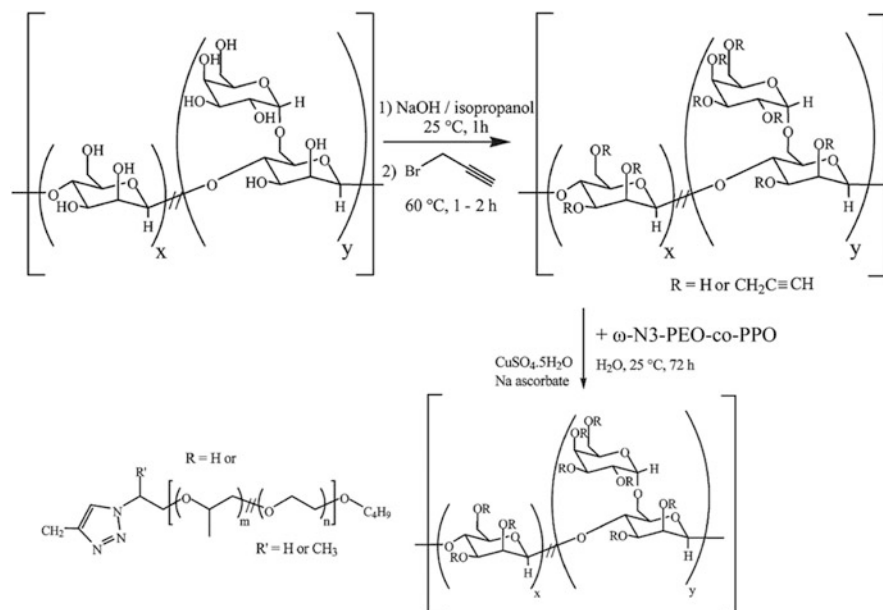
Fig. 5.18 Synthesis mechanism of GG-g-(PEO-co-PPO) copolymer by click chemistry [189]

5.4.5 *Atom Transfer Radical Grafting Copolymerization*

Atom transfer radical polymerization (ATRP) is a new type of active polymeriza-
tion reaction. Active radical polymerization is one of the most active research areas
in polymer science, and ATRP reaction is an effective way to achieve the con-
trolled/living polymerization. The character of ATRP is to use alkyl halide as
initiator, and to use the style of transition metal catalyst or degradation chain
transfer effectively inhibits double-base termination reaction of radicals. ATRP
can also be applied to both nonpolar and polar monomer and can be used to prepare
polymer with various, controlled, and clear structures [191]. With the development
of ATRP technology, it is possible to synthesize a gum-g-copolymer for some
special application. For example, Rannard workgroups [40] have synthesized a
series of locust bean gum-graft-copolymers by a "graft to" method using ambient
aqueous ATRP. The reaction mechanism was depicted in Fig. 5.19. Typically, the
hydroxyl groups of 2-bromoisobutyric acid (**2**, BIBA) or its acid bromide may react
with the coupling agent 1,1'-carbonyl diimidazole (**3**, CDI) to produce a tertiary
bromide capable of initiation. The CDI solution was added dropwise at ambient
temperature to 2 to form the acid imidazolide. Once the reaction was completed, **4**
was added to the LBG solution and then reacted for certain time. After being
precipitated with methanol and subsequent methanol washings and Soxhlet
extractions, the macroinitiator, **5**, was generated. The macroinitiator may further
react with the vinyl-monomers to form a series of graft copolymers with controlled
graft ratio. A similar mechanism for other polysaccharides was also proposed [192].
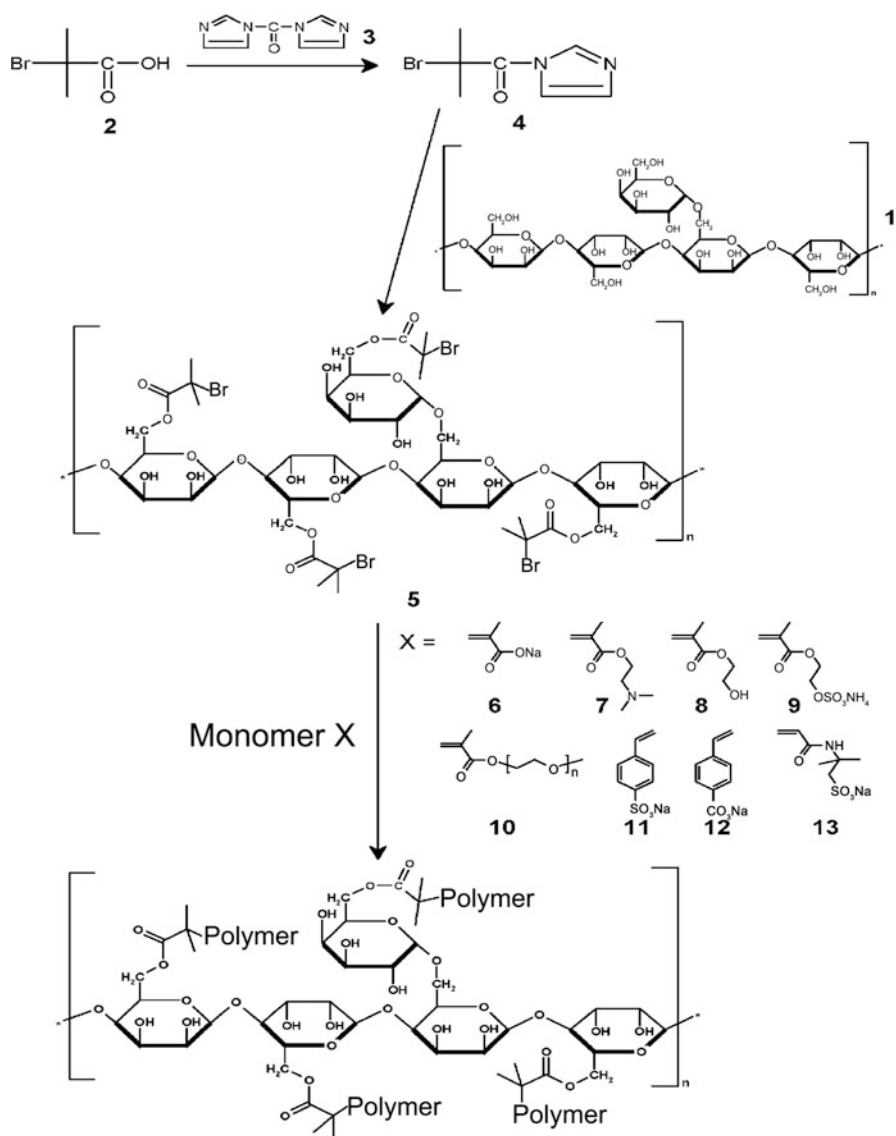
Fig. 5.19 ATRP reaction mechanism of locust bean gum-graft-copolymers. **1** is locust bean gum; **2** is 2-bromoisobutyric acid (BIBA); **3** is 1,1′-carbonyl diimidazole (CDI); **4** is acid imidazolide; **5** is water-soluble macroinitiator; **6** is sodium methacrylate (NaMA); **7** is 2-dimethylaminoethyl methacrylate (DMAEMA); **8** is 2-hydroxyethyl methacrylate (HEMA); **9** is 2-(sulfoxy)ethyl methacrylate (SEM); **10** is monomethoxy poly-(ethylene glycol methacrylate) (PEGMA); **11** is 4-styrene sulfonic acid sodium salt (SSA); **12** is 4-vinyl-benzoic acid sodium salt (VBA); **13** is 2-acrylamido-2-methyl-1-propanesulfonic acid sodium salt (AMPS) [40]

5.5 Evidence of Grafting Copolymerization

5.5.1 Infrared Spectra

Infrared spectroscopy is an important approach to identify the characteristic groups and prove the existence of a special chemical group. For the gum-g-copolymer, the FTIR spectra can be used as the evidence of forming a graft polymer. Typically, the spectrum of the gum-g-copolymer shows a set of strong absorption bands which is absent in the spectrum of raw gum, and the new characteristic bands are ascribed to the polymerization of monomers. The position of absorption bands is decided by the type of functional groups of monomers. The grafted product was usually washed by large amount of water and then soaked or extracted with ethanol (or methanol, acetone, etc.) to remove the unreacted gum and the formed homopolymers. After these treatments, the interference can be suppressed and the FTIR spectra are convincible and can be as an evidence for graft copolymers. For instance, Biswal et al. [174] proved the acrylamide was grafted onto guar gum backbone by FTIR spectra. The appearance of absorption bands of gum at 1,670 and 1,635 cm^{-1} (amide-I (C=O stretching) and amide-II (N–H bending)) indicated the graft of poly(acrylamide) chains onto the guar gum backbone. Another approach to prove the graft reaction by FTIR spectra is to remove the gum backbone through chemical reaction and to determine the FTIR spectra of the residual moiety. For example, Chowdhury et al. [78] hydrolyzed AG by acid in the grafted polymers and then determined the FTIR spectra of residues. Results indicate that the FTIR spectra of the residues are identical with the spectra of PMMA, but are different from the FTIR spectra of graft copolymer. It proved the occurrence of graft reaction between AG and MMA.

5.5.2 Thermogravimetric and Differential Scanning Calorimetric Analysis

Thermal analysis is also a conventional method to provide an evidence for graft reaction. Besides the gum backbone, the grafted polymer chains may generate various interactions with each other (such as condensation and cyclizing reaction) to affect the thermal behavior during the process of thermal decomposition [116, 120, 121]. So, different grafted monomers (or functional groups) and graft efficiency may cause different thermal stability of the corresponding graft copolymers. However, it is true that the thermal stability and endothermic–exothermic behaviors of graft copolymer are clearly better than the matrix gum due to the increase of molecular weight and number of functional groups. The raw gum may rapidly thermal decompose by a one-step process, but the graft copolymer enhances the thermal decomposition temperature and usually exhibited 2–4 steps thermal decomposition. For example, the graft
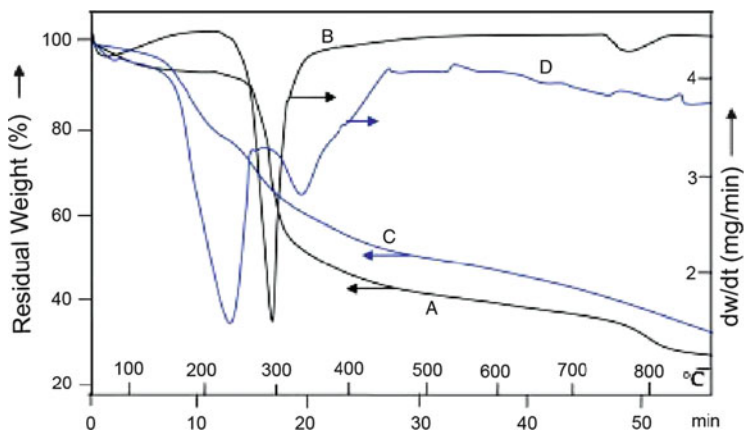
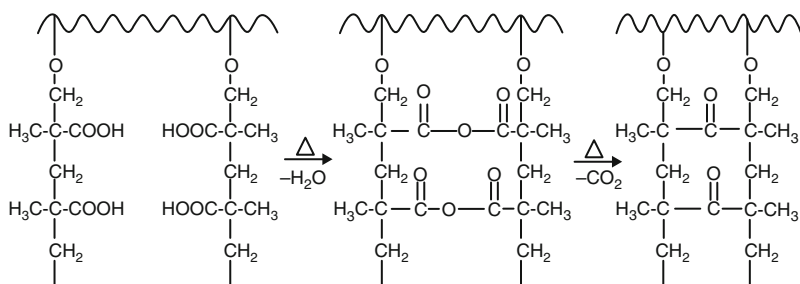**Fig. 5.20** TG (A) and DTG (B) curves of XG; TG (C) and DTG (D) curves of XG-g-PMA [62]

Fig. 5.21 Schematic representation of degradation of XG-g-PMA [62]

copolymer of XG with methacrylic acid shows different thermal behaviors from XG (Fig. 5.20) [62].

XG shows a single step thermal degradation process started at about 232 °C, and nearly 45 % weight loss occurred between 200 and 310 °C, and the final decomposition temperature (FDT) is 316 °C. The 60 % of XG was degraded at 600 °C. The weight loss rate of graft copolymer increased with increasing the temperature up to 250 °C, and two T_{max} are obtained at 243.9 and 343.58 °C. The FDT is 452 °C, which is much higher than XG. The weight loss in the range of 150–250 °C is due to the formation of anhydride with elimination of H_2O molecule from the two neighboring carboxylic group of the grafted chains. The second T_{max} is attributed to the decarboxylation of the anhydrides formed earlier (Fig. 5.21). The change of thermal behaviors confirmed the formation of grafted copolymer.

Differential scanning calorimetric analysis (DSC) is a useful technique to explain the formation of graft copolymers. The endothermic or exothermic peaks of the gum could be changed after grafting reaction due to the increased interaction between the main chains of gun and the grafted polymer chains.

5.5.3   UV–Vis Spectra

UV–vis spectra are simple and accurate approach to identify the existence of aromatic groups. In the families of gum-g-copolymers, many used monomers (such as styrene, aniline, sodium 4-vinylbenzenesulphonate) have benzene rings, and so the corresponding graft copolymers possess aromatic characteristic. Thus, UV–vis spectra were developed as an effective approach to prove the graft of these monomers onto the gum backbone. The the grafting copolymers of gum with aniline has focused much attention because it can introduce electrical properties into gum. In the UV–vis spectra of AG-g-PANI polymer [26], AG showed a broad absorption band at 298 nm due to the presence of arabinogalactan components in the AG. Furthermore, the characteristic peaks of both arabinogalactan components and PANI were observed in the graft copolymer, and it confirmed the grafting of PANI onto AG backbone. In addition, UV–vis spectra are effective for a hydrogel based on graft-copolymer of gum. Wang et al. [193] introduce styrene in the GG-g-PAA/muscovite hydrogel system and the properties were obviously improved. In the UV–vis spectra of the swollen gel, the E band absorption of phenyl rings was observed, but it is absent in the spectra of sample without addition of styrene. This proved styrene participates in graft copolymerization. The UV–vis spectra are suitable for solution, solid, film, and gel.

5.5.4   Elemental Analysis

Elemental analysis is an identification method based on the difference of elements between gum backbone and graft copolymers in a type or content of special elements. The main characteristic elements are N and S. The monomers containing N elements (i.e., acrylamide, *N*-vinyl-2-pyrrolidone, aniline, *N*-isopropyla-crylamide, 4-vinylpyridine) or containing S elements (i.e., 2-acrylamido-2-methyl propane sulfonic acid, sodium 4-vinylbenzenesulphonate) were grafted to the gum backbone; the elemental analysis may show the change of contents of N or S elements (for the gums containing N or S elements) or the appearance of N or S elements in the graft copolymer (for the gums without N or S elements). This provides direct evidence that these elements were grafted onto the gum backbone [132, 152, 155]. According to the change of elemental contents, the graft amount of monomers may also be roughly calculated, and this is also the advantages of elemental analysis method.

5.5.5   NMR Analysis

The ^{1}H-NMR and ^{13}C-NMR analyses are accurate approach to identify the molecular structure. By comparing with the change of special groups before and after grafting reaction, the occurrence of graft copolymerization reaction can be

confirmed. In the literature [58], the ^{1}H-NMR of the pure gum showed a peak at δ 4.65 (s) for anomeric protons and at δ 3.5–3.9 (m) and 2.05–2.06 (d) due to sugar protons, while the gum-g-copolymer showed an additional peak at δ 2.5 (due to protons of methylene groups at grafted chains of PAN on the guar gum backbone), indicating the presence of PAN in the graft copolymer and the grafting reaction occurred.

5.6 Properties of Gum-g-Copolymers

5.6.1 Thermo- and Degradation-Resistance Properties

Thermal stability is important to the application of a polymer material. The raw gums are mainly saccharides-type carbohydrate backbone, and so they can be easily thermally decomposed and carbonized. The graft copolymerization of gum can introduce new polymer chains and functional groups. The polymer chains may increase the molecular weight of gum, and the functional groups may form a cross-linking or cyclization structure to delay the thermal degradation. For instance, the value for ΔH in case of xyloglucan is found to be 258.5 J/g, but the xyloglucan-g-PMMA increased this value to 265.8 J/g. An endothermic peak is observed at 132.5 °C in XG-g-PMMA and another exothermic peak above 227 °C. This supports that the grafting of PMMA onto xyloglucan improved the thermal stability [156].

Similarly, the degradation-resistance capability can be improved by the graft copolymerization. Samui et al. [145] improved the degradation-resistance properties of acacia gum by grafting ethyl methacrylate onto its molecular chains. The acacia gum may be biodegraded about 37.5 % after 150 days, but the graft copolymer only degraded 5.4 % and the degradation degree can be controlled by the grafting ratio.

5.6.2 Viscous and Rheological Properties

The grafting reaction of gum may alter its molecular weight and charge and thus affect the viscosity of graft copolymers. The viscosity of graft copolymer is closely related to the graft ratio and graft efficiency which is mainly decided by the type and concentrations of gums, structure and concentration of monomers, initiation efficiency, and so on. Singh workgroups [25] investigated the effect of structure of *Ipomoea* seed gums on the graft efficiency and viscosity. It was concluded that the extent of grafting was dependent on the galactose-to-mannose ratio and the degree of the branching in the galactomannans. After grafting with acrylonitrile, the viscosity of gum was clearly enhanced from 3.87 cP to 40.9 cP (galactose-to-

mannose ratio, 1:6), 47.1 to 168.5 cP (galactose-to-mannose ratio, 1:2), and 129.6 to 193 cP (galactose-to-mannose ratio, 1:1.5). In addition, the graft of acrylonitrile obviously enhanced the stability of viscosity. The viscosity of raw gum decreased from 3.87 cP to 2 cP (galactose-to-mannose ratio, 1:6), 129.6 to 1.9 cP (galactose-to-mannose ratio, 1:2), and 47.1 to 2.54 cP (galactose-to-mannose ratio, 1:1.5) after 254 h, but the graft copolymers have no change of viscosity. The absolute viscosity of cashew gum-g-acrylamide at 2.5 % concentration (w/v) up to 33 and 3.3 times of the CG and PAM values, respectively [132].

5.6.3 Complexing Capacity

The nonionic gum may complex with metal ions by the –C–OH groups, and the anionic gum may complex with ions through –COOH or $-SO_3^{2-}$ groups. However, most of the natural gum has poor complexing capacity to metal ions because of the lack of functional groups with strong chelating capability. As described above, the simple graft of gum with functional monomers such as AMPS, AA, AM, AN, N-vinyl-2-pyrrolidone, 4-vinylpyridine, etc. may introduce numerous chelating groups (i.e., –COOH, –COO⁻, –C=O(NH$_2$), –CN, –SO$_3^{2-}$) in the gum backbone. Based on this, the gum was changed as a "bush" with numerous "hand," and it can easily fetch metal ions from aqueous medium with a higher adsorption amount. The main mechanism is the chelating action of functional groups with metal ions. Because the functional groups are mainly from the grafted chains, the type of gum backbone has only small influence on the complexing capacity, and it mainly takes a supporting action. The adsorption capacity is related with the grafting ratio, molecular weight of graft copolymer, and the type of functional groups.

5.6.4 Mechanical Property

The mechanical property of polymer materials is mainly derived from the strength of molecular chains and the interaction among chains. The graft copolymers have usually higher molecular weight than raw gum and have branched graft chains and the functional groups that can easily generate hydrogen-bonding or ionic interaction. Thus, the mechanical property can be adjusted by controlling the graft ratio and the type functional groups. For example, Samui et al. [145] prepared the AG-g-PEMA copolymer and compared its mechanical properties with that of AG. It was concluded that the tensile strength (N/nm^2) and elongation at break (%) were enhanced by 140 % and 650 %, respectively, in contrast to raw AG. The improvement of mechanical properties is extremely favorable to prepare high-strength film materials.

5.6.5 Flocculating and Decoloring Properties

The flocculating or decoloring mechanism of a flocculating agent is to change the electric potential of the suspended matter or dyes in water body through the interaction of flocculating agent having positive or negative charges with these matters and then make the suspended matter precipitating [194–196]. Due to the molecular weight and molecular charges, some gums have intrinsic flocculating and decoloring properties. After moderate modification, these properties can be enhanced, but the usage properties are still not satisfactory due to the limited charges. The graft copolymerization of gum may introduce numerous functional groups and increase the molecular weight and so can greatly enhance the flocculating or decoloring effect [144]. The type (positive or negative) and number of charges on the chains of gum can be controlled by the grafting technology, and so the graft-copolymer can be designed to be suitable for various water bodies. For instance, the introduction of $-COO^-$ may increase the flocculating and decoloring capability to positively charges particle or dyes, and the introduction of $NH_4^+Cl^-$ may enhance the flocculating and decoloring capability to negatively charged particle or dyes.

5.6.6 Amphiphilic Properties

Most of the gums are hydrophilic and water-swellable polymers. The graft copolymerization of gum with hydrophobic monomer may introduce moderate hydrophobic groups and make the gum having amphiphilic properties. The hydrophilic or hydrophobic capability can be controlled by the selection of functional groups and the graft ratio [197].

5.6.7 Electrical Property

Generally, the raw gums have usually no electrical properties due to their structure characteristics, but the graft copolymers of gums may generate electric conduction. The electric characteristics are mainly derived from the grafted chains and are dependent on the type and graft efficiency of monomers, and the commonly used monomer is aniline. Polyaniline (PANI) is considered as one of the most promising conducting polymer materials [198], but the synthesized PANI has low molecular weight and mechanical strength, poor solubility in common solvents, and infusibility at traditional melt-processing temperatures, which limited its application in the fabrication of electronic devices [199–202]. The graft of PANI with gum may not only improve the mechanical strength of graft copolymer but also endow the gum with electrical properties, and so the desirable hybrid properties of biopolymer and

PANI can be obtained. Tiwari et al. [203] prepared an electrical conducting guar gum-based polymer through the graft copolymerization reaction of guar gum with aniline using APS as the initiator. The features of gum were kept and an electrical conductivity of 1.6×10^{-2} S/cm was reached at room temperature. This work group also synthesized AG-g-PANI copolymer, and its cyclic voltammogram showed three anodic peaks at 0.20 V, 0.58 V, and 0.64 V along with two cathodic peaks at 0.50 V and 0.40 V, and the electrical conductivity is dependent on the ratio of aniline to AG, temperature, and pH value. Besides, the other monomer such as pyrrole was also grafted onto biopolymer collagen and shows better electrical properties [204, 205], but rare research is regarded on its graft reaction with gum.

5.6.8   Stimuli-Responsive Property

Many natural gums, such as PSY and XG, have stimuli-responsive capability when it suffers external stimuli such as pH value and electrolyte because they have functional groups –COOH or $-SO_3^{2-}$. The responsive mechanism is the transform between –COOH and $-COO^-$ groups with the change of external pH values. When the pH value is lower (acidic condition), the $-COO^-$ was changed as –COOH groups, and the gum may generate volume change and a responsive behavior occurred. Based on these characters, many stimuli-responsive materials were designed, such as cross-linked XG [206, 207], PSY [208], CG [209], and SA [210]. But the stimuli-responsive capacity is weak because of the limited functional groups. The graft copolymerization of gum may introduce various types and numbers of functional groups, and the intrinsic responsive property can be enhanced or new responsive properties were introduced. For example, the introduction of temperature-sensitive groups such as isopropyl acrylamide, dimethyl formamide may bring the gum with temperature-responsive properties.

5.7   Applications of Gum-g-Copolymers

Graft copolymerization of gums with vinyl monomers or other functional monomers may introduce new groups on the gum backbone to form a comb-type structure or form a three-dimensional network structure by adding slight cross-linker. The introduced groups or branch chains on the gum backbone may alter its charges, mobility, flexibility, hydrophilic or hydrophobic properties, molecular weight, and so on, and thus, the colloidal properties, complexing capacity for metal ions, and water absorbing were obviously improved, or the new function derived from the grafted chains was presented.

5.7.1   Drilling Additives

With the increasing concerns on the environmental impact of oil-based drilling fluids in oil-field applications, the water-based drilling additive systems have been extensively used as shale inhibition, viscosity building, and filtration control for enhancing oil recovery [211, 212]. As the most important environmentally friendly polymers, the modified natural polymers show great potentials in oil-field application due to their renewable, low cost, nontoxicity, and biodegradability [213]. Currently, the modified cellulose such as carboxymethylcellulose, polyanionic cellulose, and cellulose graft copolymers was mainly focused and frequently used. Recently, with the increasing concerns on plant gum, gum-based polymers begin to be concerned because they have excellent viscosity and can be easily modified to form new materials. XG or its graft polymer was considered as a potential drilling additive because it has anionic characteristic with side-chain structure, higher molecular weight, excellent viscosity, good shear stability, and salt-resistance capability [214, 215].

5.7.2   Thickener

Currently, the commercial thickeners mainly include four categories: inorganic thickeners, cellulose, polyacrylate, and associative polyurethane thickener. The cellulose thickener has long usage history and various types, such as methylcellulose, carboxymethyl cellulose, hydroxyethyl cellulose, and hydroxypropyl methyl cellulose. With the progress of modern industry, the development of novel thicker with higher thickening efficiency and nontoxic characteristic becomes the subject of great interest. As described above, the aqueous solution of almost all the gums has gained great viscosity due to the interactions between polymer chains, and so gums are the important thickener in manufacture, distribution, storage, and consumption of water-based products, particularly formulations of surface coatings, drugs, cosmetics, and foods [216, 217]. Compared with the raw gums, the gum-g-copolymer usually showed higher viscosity due to the change of molecular weight, chain–chain interaction, and structure charges. Nickzare et al. modified acacia gum by its graft copolymerization with acrylic monomers for a thickening purpose, and it was found that the thickening properties were highly improved to form non-Newtonian fluids in water at concentrations below 2 % [218].

5.7.3   Adsorption of Toxic Heavy Metals

As discussed above, the gum-g-copolymer has strong complexing capability, and so it showed great prospect in the adsorption of toxic heavy metals. Sharma and Lalita [130] prepared GG-g-PNVP polymer and used for the sorption of Fe^{2+} and Cr^{6+} ions. It was found that the adsorption amount increased with increasing percent
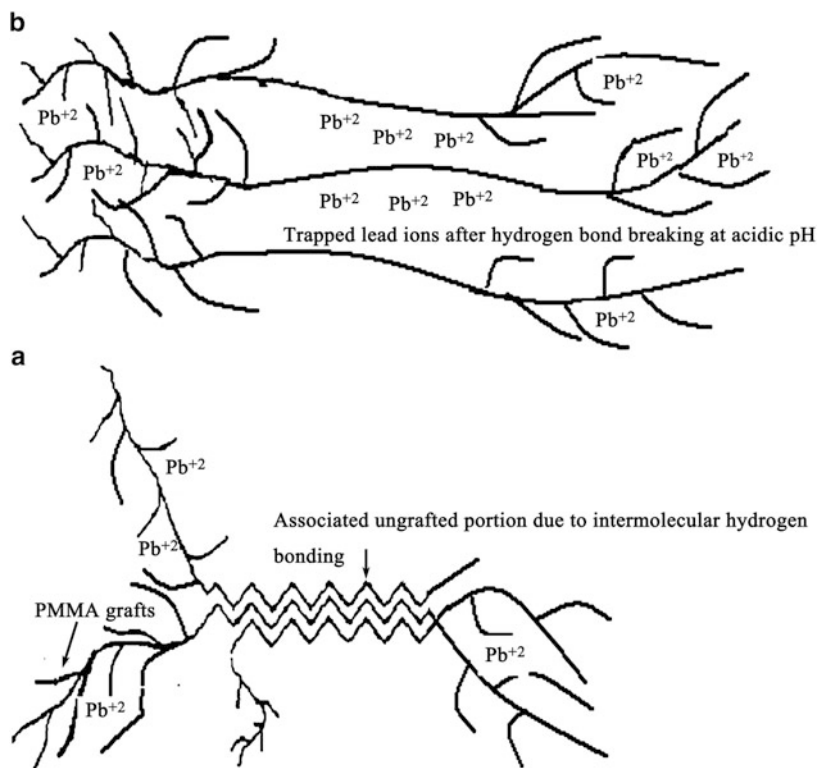
Fig. 5.22 Model for interaction between the Pb(II) and graft copolymer: (A) at normal pH, (B) at highly acidic pH [219]

grafting. Srivastava and Behari [116] synthesized GG-g-PNVP and evaluated its adsorption on heavy metal ions Cu^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+}, and Hg^{2+}; it was concluded that the graft copolymers enhanced the adsorption amount by 279.4 % (Cu^{2+}), 240.7 % (Ni^{2+}), 207.1 % (Zn^{2+}), 367.2 % (Pb^{2+}), and 433.3 % (Hg^{2+}) in contrast to GG. Behari and coworkers [59] prepared XG-g-PAMPS graft copolymer, and its adsorption capacity on Cu^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+}, and Hg^{2+} ions was enhanced by 382.2 %, 353.9 %, 356.8 %, 292.0 %, and 262.3 %, respectively, and the retention capability was improved. The adsorption capacity is proportional to the graft ratio. The grafting ratio may be controlled by altering the graft reaction condition and the dosage of monomers, and the type of gum has obvious effect on it. For a gum with low reaction activity such as cashew gum or higher viscosity, the grafting ratio usually is low. By controlling the graft parameter, the solubility of the graft copolymer was decreased, and this is favorable to its application for wastewater treatment [138]. The GG-g-PEA graft copolymers shows ideal adsorption properties to Cd^{2+} ions than guar gum [165], and the adsorption capability can be adjusted by the grafting ratio. Singh et al. also proved the *Cassia grandis* seed gum-graft-poly(methylmethacrylate) has stronger combination action with the Pb(II) ions than the gum (Fig. 5.22) [219].

In the process of graft reaction, if the cross-linker was introduced, the cross-linked three-dimensional network structure can be formed, and the resultant adsorbents show better adsorption capability [130].

5.7.4 Flocculating Agent

Flocculating agent is important in the fields of wastewater treatment. The frequently used flocculating agents are inorganic polyhydroxyl metal salts (i.e., poly (aluminum sulfate), poly(ferric sulfate), poly(aluminum silicate), poly(ferric silicate), poly(aluminum phosphate), poly(iron phosphate), poly(silicic ferric sulfate) (PFSS), poly(phosphorus aluminum chloride) and synthetic polymers (i.e., poly (acrylamide), poly(sodium acrylate), poly(2-methyl acryloxyethyl trimethyl ammonium chloride), and poly(diallyldimethylammonium chloride)). These flocculating agents have found extensive application, but they are not eco-friendly. With the increasing attention on the safety of materials, natural polymer-based flocculating was focused. Many gums, such as xanthan gum, *C. javahikai* seed gum, etc. have intrinsic flocculating properties, and so they gained wide application in wastewater treatment as a commercial polymer material, and were honored as the green materials in twenty-first century. However, the flocculating properties of raw gums are limited due to their finite charges, functional groups, and molecular weight. Also, the fungus resistance ability of raw gums is low. Thus, the gum-g-copolymers show great application prospect as a flocculating agent because they combined the advantages of synthetic polymers and natural gum. For example, Sanghi groups [24] synthesized *C. javahikai* seed gum-g-polyacrylamide and used as coagulant for the removal of dyes from wastewater. The graft copolymer shows better coagulant effect than the raw gums. The graft of poly(acrylamide) onto the gum ghatti may decrease the turbidity from 200 NTU to about 45 NTU, but the raw gum can only decrease it to about 160 NTU [155]. The flocculating efficiency is increased with enhancing the graft ratio. The coagulants based on psyllium [167], tamarind kernel polysaccharide [220], *Ipomoea* seed gums [221], tamarind kernel polysaccharide, sodium alginate [222], *C. javahikai* seed gum [24], cationic guar gum [96], etc. have been developed.

5.7.5 Pitch Control Agents in Papermaking Industry

Papermaking plays an important role in modern chemical industries. The key process of papermaking is pulping. The aggregation and deposition of hydrophobic wood resins in the papermaking process has a problem for the pulp and paper industry. The sticky wood resins tend to deposit on the surface and result in downtime of the paper machine. The traditional alum is futile at neutral and alkaline pH when it was used as a pitch control agent. Thus, the water-soluble cationic

polymers have received great attention because they can act as bridging agents, attaching the wood resin particles onto papermaking fibers besides neutralizing the anionic matters. The commonly used cationic polymers are synthetic homopolymer or block copolymer based on petroleum monomers, which is not environmental friendly [223]. The natural polymer may resolve the environmental problem resulting from synthetic polymers, but it is hardly to reach an ideal effect. The graft copolymer of natural polymers with cationic monomers may integrate the advantages of natural polymers and synthetic polymers, especially was used as a pitch control agent. For example, the GG-g-P(AM-co-DDMC) was synthesized; it was proved that the graft copolymer is a good fixative as well as a good colloidal stabilizer with the combination of properties shared only by high molar mass P(AM-co-DDMC) and GG. And the wood pitch fixative properties of the graft-copolymer are effective over the entire pH range as compared to the other fixatives evaluated [224].

5.7.6 Macromolecular Surfactants

As known, most of the chemical surfactants such as cetyltrimethyl ammonium bromide, sodium dodecyl sulfate, and dodecyltrimethylammonium bromide are toxic and extremely harmful to the environment, but they are indispensable in modern industry. Thus, to seek for a substitution of chemical surfactants, the natural polymers, such as cellulose, starch, and gums were introduced. The surfactants are usually composed of hydrophobic end and hydrophilic chain end. Because the gum is usually hydrophilic, the moderate hydrophobic modification of gum may form a surfactant-like structure. For example, Daly groups [197] synthesized a graft copolymer of guar gum with polyalkoxyalkyleneamide. The introduction of hydrophobic monomers provides a facile approach to introduce hydrophobic region on the gum chains, and the hydrophobic degree can be controlled by adjusting grafting conditions. The graft copolymer has water-soluble characteristic, but can form micelle structure in water or oil (Fig. 5.23), and can be used for the emulsion polymerization or the others. Currently, the corresponding research is less, but it shows great application prospect in the modern industrial fields.

5.7.7 Electrical Biomaterials

Conducting biopolymer hybrids are widely adoptable materials for the fabrication of artificial nerves and muscles, sensors and actuators, blood vessels, etc. [225, 226]. For biomedical application, the safety and durability of materials are extremely important, and so the biopolymer-based materials are attractive and promising. Compared with other material derived from natural polymers, the graft copolymers of biopolymers with PANI have controlled electrical
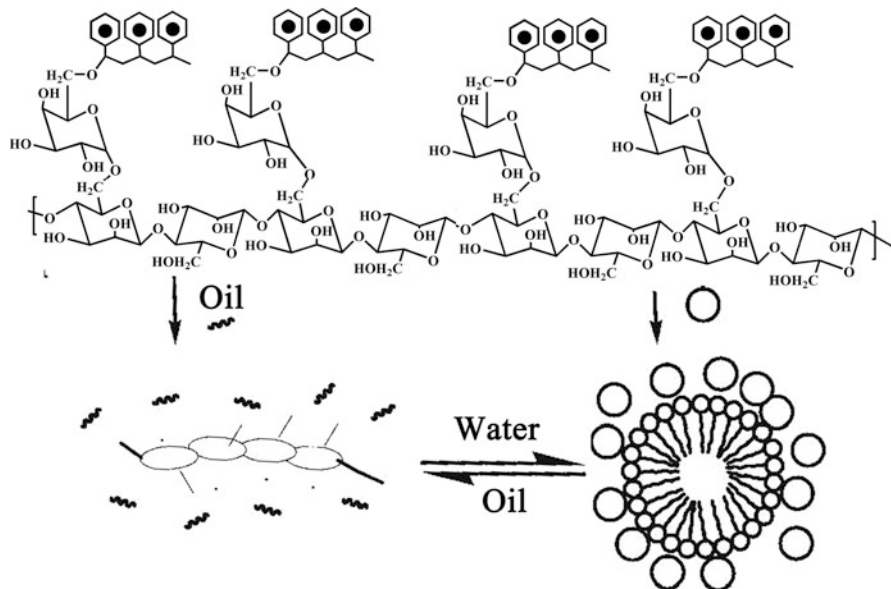
Fig. 5.23 Introduction of hydrophobic grafts may facilitate reversible micelle formation [197]

conductivity, good adhesion properties, high mechanical strength, and sandwich properties of component polymers [227–229]. Tiwari workgroups [227, 230, 231] developed the graft copolymer of AG with PANI, studied its electrical properties, and evaluated the application prospect of the graft copolymer in semiconductor, biomaterial for the fabrication of various sensor field. In addition, the conductive graft polymer of guar gum [203] was developed and evaluated for its practical application.

5.7.8 Drug Delivery Carriers

Natural gums have been used as drug delivery carrier for the controlled release of oral drug by virtue of their non-toxic, biodegradable, and biocompatible advantages. The gums were made as nanoparticles, beads, or tablet to load, deliver, and release the target drugs [232, 233], and the usage of gums fully resolved the safety problem of drug delivery carriers. For reducing the by-side effect of drugs resulting from the improper release and enhancing the efficiency of drugs, the smart drug carriers with ideal loading capability were highly concerned. The smart characteristics of carriers are mainly their responsive capability to external stimuli such as pH, temperature, electrolyte, electrical field, and photo. The nonionic gum has no responsive ability to external stimuli due to the absence of functional groups. The anionic gums (i.e., XG, PSY, k-CGN) may response to pH, electrical field, and
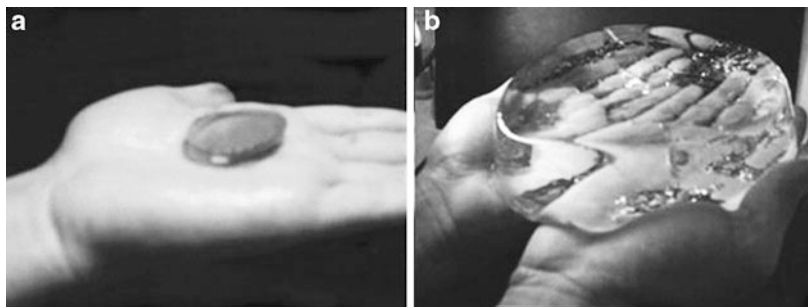
Fig. 5.24 Digital photo of superabsorbent hydrogel before (**a**) and after (**b**) swelling [238]

electrolytes because of the existence of functional –COOH or –SO$_3{}^{2-}$ groups in their structure, and they have been developed as pH-sensitive drug carriers [234–236]. However, the loading efficiency of natural gums on drugs is lower and can only be used for pH- and saline-sensitive carriers. Thus, the gum-g-copolymers exhibit greater advantages as drug delivery carriers because the introduction of more functional groups enhance the loading of drug and responsive functionality. Toti et al. synthesized AG-g-PAM copolymer and used as a delivery tablet of two antihypertensive drugs diltiazem hydrochloride and nifedipine [133]. The graft of PAM chains may prolong the release time to 6 and 14 h for diltiazem hydrochloride and nifedipine, respectively. The graft of *N*-isopropylacrylamide onto guar gum makes it sensitive to temperature [129], which can be used to deliver and control the release of drug by the change of temperature.

5.7.9 Superabsorbent Materials

Superabsorbent materials are moderately cross-linked hydrophilic polymer materials with three-dimensional network structure and water-swellable characteristics (Fig. 5.24) [237, 238]. Traditional superabsorbent materials are mainly synthetic polymers based on petroleum monomers, which cannot be biodegraded and are easy to induce secondary pollution [239]. So the biopolymer-based superabsorbents have attracted great attention in recent years. The raw natural polymer or its derivative has relatively lower water uptake capability, and so the developed superabsorbents are mainly graft copolymers of biopolymers. Grafting of hydrophilic monomer on the gum backbone usually introduces many hydrophilic graft chains, which can enhance the water-holding capability of gums. The graft copolymer can be directly used in soil to improve the water-retention capability, but its water-absorption and retention capability is poor. Thus, the utilization of gum-g-copolymer as water-saving materials (named as superabsorbent) usually involved with the fabrication of three-dimensional network structure by the addition of cross-linker. In the preparation process of superabsorbent, the graft reaction and cross-linking reaction simultaneously occurred. In the presence

of initiator, the hydrophilic monomers (i.e., acrylic acid, acrylamide, AMPS, acryloni-trile) may graft onto the gum backbone to form a chain structure. In the process of chain propagation, the cross-linker with double end vinyl groups may react with the radical on the graft chains and connect these chains to form a network structure. When the superabsorbent was contacted with water, the hydrophilic groups can be ionized and form an osmotic difference between interior network and external solution. The water molecules may penetrate into the network by diffusion or hydrogen-bonding attractive action and hold in the network structure. When the swollen superabsorbent was placed in a dry condition, the water molecules absorbed can release slowly to reach a water-saving effect. The superabsorbent product was mainly applied in agriculture, physiologic hygiene livings, drug delivery, and fine chemicals. Among most of these applications, the safety and biodegradability of materials are highly concerned, and correspondingly the research on gum-g-copolymers-type superabsor-bent has been focused. Thus far, the superabsorbent based on the graft copolymer of GG [77, 240–243], XG [244], artemisia seed gum [245], PSY [246], tara gum [247], cashew gum [92, 248], AG [249], gum ghatti [250], and k-carrageenan [251–253] has been developed and applied.

5.7.10 Sand-Binding Materials

With the aggravation of global aridity and desertation of lands, the ecological recovery of sand lands becomes exigent. The mobility of sands increases the difficulty of planting in sandy land, and the fixation of sand is the key. It is expected that the sand binder can not only fix the mobile sand but can also retain and hold water. The traditional sand-bonding materials are mainly petroleum-based syn-thetic polymer. Although it has better corrosion-resistance properties, it is expen-sive and nonbiodegradable. Gums are hydrophilic natural polymer with viscosity and water-holding capability and have shown greater potentials as environmental friendly ecological recovery materials [254, 255]. The usage efficiency of such materials is dependent on the viscosity and water-absorbing capability. The natural gums have relatively better viscosity and water-swelling capability, but they are easily attacked by bacterial and the water-absorbing capability is limited. As a result, the binding capability and water-holding capability is poor when it was used for longer period of time. Therefore, the gum-g-copolymer was widely developed as sand-binding materials because it overcomes the drawbacks of both petroleum-based polymers and natural gums. The incorporation of more hydrophilic groups also improved the water-absorbing and retention properties.

5.7.11 Micro-reactor of Preparing Nanomaterials

With the boost of application field of nanomaterials, the synthesis method of nanomaterials tends to be diverse. As a formation template of nanomaterials (called as micro-reactor of nanomaterials), the gum-g-copolymer shows great potential due

to the various molecular structure and functional groups. The gum-based micro-reactor was usually used as two forms: the direct usage of gum-g-copolymer and the construction of a three-dimensional network structure based on graft copolymer. Abdel-Halim groups [256] prepared GG-g-PAM graft copolymer and used for the synthesis of Ag nanoparticles through the reduction of silver nitrate at pH 12.5. It was confirmed that the graft copolymer contributes to form a nanoparticle with better dispersion, small particle size, and narrow particle distribution. This provides possibility of using gum-g-copolymer to synthesize various nanoparticles with desirable morphology and property.

5.8 Conclusions

The increasing global resource and environment crisis continuously propels the development of eco-friendly materials as a succedaneum of petroleum-based products. The naturally occurring raw materials have recently raised a research upsurge owing to their unique "green" characteristics, and considerable efforts have been engaged. On the one hand, the new natural polymers were explored; on the other hand, the chemical or material researchers devoted to modify or utilize these polymers to derive new eco-friendly materials with desirable applicability. Gum is one of the rapidly developed natural polymers by virtue of its abundance, biodegradability, processibility, and structural diversity, and so the gums play irreplaceable role in modern industry. With the extension of application domains, the drawbacks of raw gum were increasingly highlighted, and the modification and derivatization of gum especially significant, and becomes the hot research subject. The derivatization of gum may tailor the properties of gum by introducing additional functional groups, and the application domains were greatly deepen. But the general derivatization can only introduce limited number of functional groups, and the congenital drawbacks of gums such as poor fungus resistance and heat-resistance capability have no evident improvement. Therefore, graft copolymerization of gum shows its advantages over general derivatization because it can improve the properties to a great degree or bring additional properties in the premise of keeping the intrinsic superiorities. The structure and properties of the graft copolymers could be easily tailored, and so the applications of gum were greatly extended. The influence factors of graft reaction are complex, and the exploration of the optimal reaction condition suitable for various gums and monomers is concerned. Thus, based on the latest efforts to the graft copolymerization of gum, this chapter demonstrated the sorts, structure, and sources of gums; the derivatives of gums; as well as the synthesis, properties, and applications of representative gum-g-copolymers. The development of new graft copolymer will provide a new approach for the utilization of gums. In addition, the work has also paved the way for enhancing the commercial importance and values of gums.

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