10

POLYMER MODIFICATION: FUNCTIONALIZATION AND GRAFTING

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10.1 GENERAL CONCEPTS

The techniques for polymer functionalization and grafting are closely related. In many cases in which grafting is the ultimate goal, the generation of a reactive or functionalized polymer substrate is a preliminary step preceding the reaction of the functional groups along the polymer chain with other chemical entities (monomers or other polymers) in order to grow or attach side chains (grafts) along the primary polymer backbone. Therefore, the techniques for the generation of functionalized or functional polymers are analyzed first.

10.1.1 Methods for the Synthesis of Functional Polymers

The synthesis or modification of polymeric substrates in order to produce polymers with polar or functional groups can be carried out by several synthetic pathways. When the process starts from a previously existing nonfunctional polymer, and functional groups are introduced to the chain, the term *functionalization* is used. The techniques employed for the generation of a functionalized or functional polymer are as follows:

Direct copolymerization [1, 2]. In this case, two types of monomers react, one of them having a functional or pendant functional group; for instance, the copolymerization of maleic anhydride (MA) and styrene (St) generates the alternating copolymer poly (St-*alt*-MA) [1]. Another example is the direct copolymerization of α-olefins (polypropylene, PP, and polyethylene,

PE) with functional monomers such as MA or glycidyl methacrylate (GM); this goal remains as one of the challenges in synthetic polymer science [3]. In the latter example, the difficulty lies in the fact that the majority of this kind of polyolefins are produced by Ziegler–Natta or metallocene coordination chemistry, and both exhibit intolerance to Lewis bases because of their high oxophilic nature, which leads to deactivation of the catalysts [3b]. The most important mechanism in the catalyst deactivation is the formation of very stable complexes between the catalyst and the heteroatoms (N, O, halogens) present in the functional polar monomers [3c]. In spite of this, some advances in this field have been recently reported [4]. As a consequence, the postmodification of polyolefins with polar or functional groups, as opposed to the direct synthesis, offers the highest viability for the production of polyolefins with functional or reactive grafts.

End-functionalization [5]. Possible routes are (i) modification of the chain end of preexisting polymers; (ii) break of the growth of a polymeric chain or, (iii) break of the chain growth followed by its end-functionalization. In all cases, it is common to perform the indicated action using agents or chemical groups that contain the desirable functional group.

Functionalization-grafting [6, 7]. It consists of one of the following techniques: (i) synthesis *in situ* of grafts of homopolymers or copolymers (small or long chains) containing functional groups, starting from units located along an existing polymer backbone

(a form of the "grafting-from" technique, see next section); (ii) reaction or interchange of labile atoms of the polymeric backbone by functional monomers or reactive species; (iii) use of preexisting polymers possessing functional species and chain ends with chemical affinity to the backbone of the polymer (a form of the "grafting-onto" technique, see next section).

In several of the previous techniques, postmodification of polymers with functional groups or by grafting of polymeric chains with functional groups (polymer functionalization) is necessary. These can be generally carried out by abstraction of hydrogen atoms from the polymeric backbone by chemical methods using processes in bulk [8], solution [9], emulsion [10], or miniemulsion [11], via borane compounds [12] and in supercritical conditions (CO_2), [13] by gamma irradiations (γ) [14], ultraviolet (UV) irradiation [15], electron beam [16], or plasma [17], and by mechanical methods using high shear rate: reactive extrusion and mixing chamber [18], in the presence or absence of a peroxide-type initiator or azo-compounds; and using diverse commercial monomers or macromonomers previously synthesized. When the polymeric substrate has been previously modified, then the grafts or groups can be synthesized or attached by "grafting-from" or "grafting-onto" techniques, respectively.

10.1.2 Grafting-onto, Grafting-through, and Grafting-from

There are several ways in which structures having functional chemical groups or chains of homopolymers or copolymers grafted onto a polymeric backbone can be generated. In general, there are three common methods for the synthesis of this type of copolymers [6, 7]: "grafting-onto," "grafting-from," and "grafting-through." Figure 10.1 schematically shows the synthesis of graft copolymers.

The first technique, "grafting-onto" (also called *grafting-to*), involves the reaction of an end-functional structure previously synthesized with a complementary functional monomeric unit present in the polymer backbone. Thus, grafting-onto is widely used for the synthesis of comb polymers. The "grafting-through" method uses macromonomers (polymer chains of very low molecular weight or oligomers) containing groups at their end that are capable of carrying out polymerization, particularly vinyl groups. The addition of a second monomer (comonomer) in the presence or absence (in the case of auto-initiation) of an initiator, leads to the construction of several complex topologies of graft copolymers. Indeed, depending of the reactivity ratios and the distance between adjacent grafts, brushes, regular grafts, centipede, barbwire, etc., structures can be produced [7a]. Finally, "grafting-from" is the most popular method used
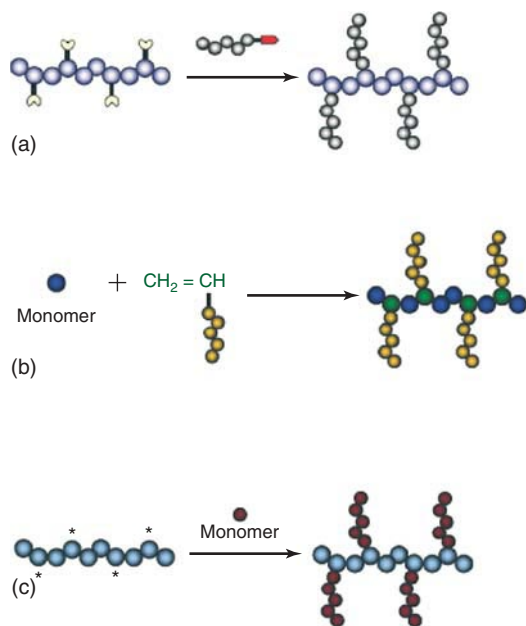

Figure 10.1 Schematic representation of (a) grafting-onto, (b) grafting-through, and (c) grafting-from methods. (*See insert for the color representation of the figure*.)

to obtain graft polymers, and requires a polymer containing reactive groups, functional species or initiator moieties along its backbone, which, in the presence of monomers, produce the growth of grafts from the surface of the substrate [7c–e]. Thus, the number of grafts can be controlled by the number of actives sites present along the backbone.

10.1.3 Grafting on Polymeric and Inorganic Surfaces

Some applications demand only the grafting or functionalization of the surface of the polymer instead of the bulk polymer as mentioned in the previous section. In those cases some of the techniques previously discussed, such as grafting-to or grafting-from, can be applied to the surface of the polymer only, but other surface-specific techniques can be used as well. Recently, a variety of techniques have been proposed for improving or modifying surface properties of polymers, among which are graft polymerization, direct chemical modification [12], ozone and UV irradiation [15], corona and glow discharge, γ-rays [14], and electron beam [16]. Polymer surface grafting offers a versatile means for providing existing polymers with new characteristics such as hydrophilicity, adhesion, biocompatibility, conductivity, antifogging and antifouling properties, and lubrication [19].

As an illustration of the application of these techniques, the surface of poly(ethylene terephthalate) (PET) films has been modified via the grafting of polyacrylamide (PAM) by surface-initiated atom transfer radical polymerization (ATRP) and UV-initiated grafting in order to obtain a film of PET with a hydrophilic surface [15c].

On the other hand, the synthesis of hybrid materials involving polymer–inorganic interfaces has nowadays attracted much attention from the academic and industrial points of view. These materials include composites made by the dispersion of micro or nanoparticles, nanowires, or nanotubes in a polymer matrix, as well as those involving a flat interface between a polymeric and an inorganic layer. Examples of the latter are polymers grafted on flat surfaces of silicon dioxide, titanium dioxide, magnetite, carbon derivatives, ZnO, etc. In all these hybrid materials, the inorganic surface is typically modified using anchoring groups or chains of polymers, as illustrated in Figure 10.2.

In the case of composites, the surface modification leads to a good dispersion of the inorganic material in polymers matrices and, depending on the nature of the dispersed phase, imparts improved chemical and physical properties such as mechanical properties, UV attenuation, flame retardancy, thermal stability, thermal and electrical conductivity, gas barrier properties, superhydrophobicity, antimicrobial properties, etc.

Physisorption, electrostatic absorption, and covalent bonding are the most important techniques used to obtain these hybrid materials [20]. Covalent bonding offers better thermal stability between the attached group and the particle or surface than the others. Two principal approaches are widely used to produce polymer grafts covalently attached from the surface: "grafting-from" and "grafting-to." "Grafting-to" produces a low grafting density (no. of chains/area) as a result of the diffusional effects (restriction of mobility by an increase of viscosity) of the chains into the reaction system. This problem can be overcome by the use of a solvent; however, the reaction time can increase considerably with this approach. Meanwhile, the "grafting-from" technique produces hybrid materials with high grafting density, and, similar to the polymer grafting case, it is possible to control the grafting density by controlling the number of active sites attached to the surface.

The anchoring groups covalently bonded to the surface typically are: di- or tri-(ethoxy, methoxy, chloro, etc.) silane, thiol, phospono, and nitroxide groups [20–22]. The second moiety could be practically any chemical species, such as methyl, ethyl, vinyl, epoxy, acrylate groups, or hydrocarbon chains, as well as peroxide and azo-compounds and chemical species that, in the presence of a monomer or monomers, are capable of producing grafts on the surface by free-radical polymerization (FRP) or controlled radical polymerization (CRP) [22]. In the last case, the chemical species will be those agents used by nitroxide-mediated radical polymerization (NMRP), reversible addition-fragmentation transfer (RAFT), or ATRP.

The functionalization or modification of the particle surface with chemical groups or polymer grafts is the key to achieve excellent dispersion in polymer matrices and to enhance the physical and chemical properties of the resulting composite; of course, in order to reach these goals the grafts must be compatible with the matrix in which the particles are dispersed.

10.1.4 Polymer Coupling Reactions

The modification of polymers can be readily conducted by chemical coupling reactions when the chain to be modified possesses groups such as vinyl, hydroxyl, or azide [23], etc. The Diels–Alder reaction between a diene and a dienophile, discovered by Otto Diels and Kurt Alder in 1928 [24], is the most important example of click chemistry.[1] These robust and efficient click coupling reactions have been widely exploited in the construction of tailor-made functional polymeric materials with complex molecular architectures [26]. Copper-catalyzed [3+2] cycloaddition reactions of azide–alkyne have also been used [23]; however, the main focus of several polymer research groups during the second half of the last decade has been the development of novel coupling reactions conducted in the absence of metal catalysts and under friendly ambient conditions [21], such as (i) metal-free [3+2] cycloaddition reaction of azide and activated alkynes, (ii) [4+2] Diels–Alder reactions, and (iii) thiol-based "click" reactions.

10.2 GRAFT COPOLYMERS

10.2.1 Commercial Polymer Grafting

The production of thermoplastics by polymer grafting synthesis techniques is widely used in the industry today. Large amounts of commercial thermoplastics, especially styrenic polymers, are nowadays produced by diverse grafting techniques, but other graft polymers are also produced commercially. Some of the most relevant examples are discussed below.

10.2.1.1 High Impact Polystyrene (HIPS) HIPS is a heterogeneous material produced by continuous bulk or bulk-suspension processes, in which a butadiene-based elastomer (polybutadiene (PB), or a block copolymer of styrene-butadiene) is first dissolved in styrene monomer (St) and the resulting mixture is then heated so that the polymerization proceeds either thermally or with the aid of a chemical initiator. At the molecular level, the product is a mixture of free polystyrene (PSt) chains and elastomer chains grafted with PSt side chains. The process yields a continuous (free) PSt matrix containing

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[1]The term *click chemistry* was introduced by Sharpless et al. 25 in 2001 and denotes the development of a set of powerful, highly reliable, versatile, and selective reactions for the rapid synthesis of useful new compounds and combinatorial libraries through heteroatom links.
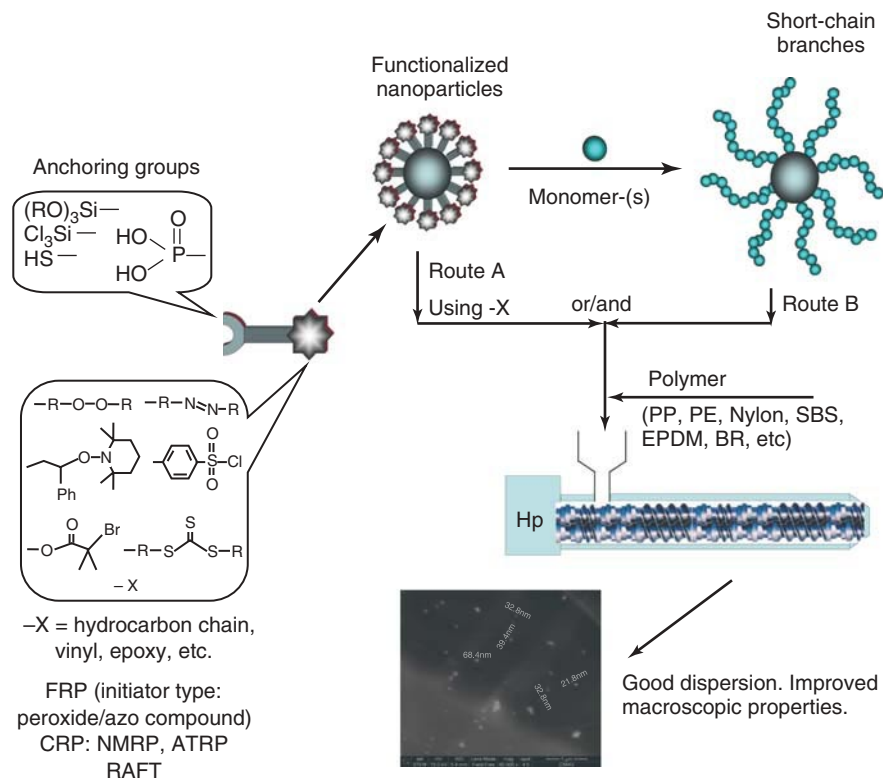
Figure 10.2   Grafting on surfaces and their dispersion in polymer matrices.

dispersed grafted PB particles of 0.5–6 μm, stabilized in the PSt matrix by the grafts of PSt which act as a compatibilizer between the matrix and the, in principle, incompatible elastomer. HIPS was born back in the 1920s when it was obvious that the versatile general-purpose polystyrene (GPPS) was too brittle for many applications. As early as 1927, Ostromislensky [27] invented HIPS by the polymerization of St in the presence of natural rubber in order to impart impact resistance to the resulting material; physical blends of rubber and PSt were also included in that pioneering patent. Later, around 1954, other companies (Shell [28], Dow [29], and Monsanto [30]) obtained patents for different versions of the synthesis process, such as the suspension and the mass-suspension processes. HIPS has become a commodity thermoplastic mainly produced by the continuous bulk process and ranks among the world's top five families of thermoplastic polymeric materials in terms of the volume of production. The world production of HIPS together with GPPS amounts to nearly 15,000,000 metric tons per year.

Technical Aspects   The reaction mechanism in the synthesis of HIPS involves the basic reactions present in any FRP: initiation (thermal and chemical), propagation, transfer to monomer, and termination, mainly by combination (see Chapter 4 for the basic FRP mechanism). In addition
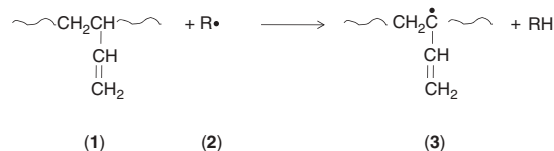
Scheme 10.1   Grafting mechanism by hydrogen abstraction illustrated on a 1-2 butadiene unit (**1**) of a PB chain. R• can be either a primary radical from the initiator or a polystyryl radical. A side chain (PSt graft) grows from (**3**) by the addition of styrene to the radical center.

to the basic scheme, some other specific reactions that lead to the grafting structures occur in the presence of PB (or butadiene units if styrene-butadiene rubber (SBR) is used); hydrogen abstraction from the PB backbone by primary or polystyril radicals create radical centers along the PB chain from which PSt grafts (trifunctional branches in Flory's terminology) grow by propagation of the radical center with styrene monomer. Hydrogen abstraction especially occurs at the labile allylic hydrogen atoms next to unreacted double bonds of the butadiene units in the elastomer. Scheme 10.1 illustrates the grafting reaction mechanism.

Another reaction that can create grafts is addition to the double bond. Instead of abstracting the hydrogen atom in (**1**), species (**2**) can add to the double bond creating also

a radical center (tetrafunctional branch) that can propagate, but leaving R covalently bonded to the PB backbone. HIPS recipes typically consist of rubber contents of 4–8 wt% with respect to the total charge to the reactor, the rest being essentially monomer and small amounts of initiator and additives. If the process is carried out in the batch mode, the chronology of events occurring during the reaction is well known. In early stages of the process, the continuous phase is a solution of rubber in styrene and the dispersed phase is made of PSt particles swollen with monomer that precipitate out of the solution; however, at relatively low monomer conversions (15–30%), there is a phase inversion and the PSt/St solution becomes the continuous phase while the dispersed phase consists of rubber particles stabilized by the poly(butadiene-*g*-styrene) chains formed *in situ* during the polymerization. A complex interaction of process conditions, thermodynamic factors, and the kinetics of grafting leads to the formation of a particular rubber particle morphology known as the *salami morphology*, in which the dispersed rubber particles contain occlusions of PSt (Fig. 10.3).

Fisher and Hellmann [31], Leal and Asua [32], and Díaz de León et al. [33], among others, have published works that propose explanations for the formation of the particle morphology. Other particle morphologies are possible depending on the type of rubber used and other reaction conditions (reactor agitation, use of chain transfer agents, etc.) [34]. The particle morphology is a determining factor in the final properties of HIPS, in particular, its impact resistance and optical appearance. Fracture in HIPS occurs by the mechanism of formation of crazes, which are microcracks that propagate through the PSt matrix but initiate and terminate at rubber particles where impact energy is dissipated by particle deformation. Typical HIPS is an opaque material, but some translucent grades can be obtained by the use of styrene-butadiene block copolymers as the rubber phase.

The kinetic mechanisms [35, 36] in the HIPS polymerization process and the complete process [37–41] have been mathematically modeled to a detailed level by different groups. Diverse aspects of the HIPS technology have been extensively studied in the past by many authors; works that review several of these aspects are the texts of Scheirs and Priddy [42] (properties, applications, modeling, and later technologies), Echte [34] (particle morphology), Simon and Chappelear (industrial processes) [43], and Meira et al. [39] (process modeling and control).

10.2.1.2 Acrylonitrile-Butadiene-Styrene (ABS) Polymers

Another family of important styrenic materials that are synthesized by grafting techniques, is that of acrylonitrile-butadiene-styrene (ABS) polymers. These are also thermoplastic materials like HIPS, but they exhibit improved impact and chemical resistance as well as better appearance (gloss) than HIPS. Some grades are considered engineering polymers because of their superior properties. Worldwide production of ABS together with SAN (styrene-acrylonitrile) copolymers lies in the range of 4,000,000–5,000,000 metric tons per year during the decade 2000–2010. ABS resins show higher tensile strength and toughness as well as better solvent and heat resistance than HIPS resins. They are widely used in electrical and electronic appliances, such as telephones, radio, TV and printer cabinets, as well as automobile components [44].

ABS can be produced either by emulsion or by a bulk process. The emulsion process is more complicated but provides better flexibility than the bulk process. In the emulsion process, the first step is to generate rubber particles in a latex (aqueous dispersion) by emulsion polymerization of butadiene; since the particles produced in this way are too small, they may require an agglomeration step in order to increase their size. Next, styrene and acrylonitrile are copolymerized in the presence of the rubber latex. Part of the SAN copolymer is grafted on the rubber. Additional blending steps with SAN copolymer, either in latex form or in solid form (in an extruder), complete the synthesis process [45]. On the other hand, the continuous bulk process requires a more specialized reactor design and special pumping equipment (gear pumps) to propel the material through several reaction steps; however, the process is more cost-efficient and less contaminating, and produces a cleaner polymer than the emulsion process; so it is becoming the dominant process for massive production. In some technologies, a small amount of solvent may be used to facilitate the flow of the material.

The structure of ABS is similar to that of HIPS but with a SAN matrix instead of the PSt matrix in HIPS. PB grafted with SAN acts as a compatibilizer between the rubber particles and the SAN matrix. The rubber particle morphology in ABS can be similar to that in HIPS, with salami-type particles, but ABS particles can also be of the core–shell type, with a core of solid PB and a shell of graft copolymer, especially if the ABS is produced by the emulsion process [34]. In addition to craze formation, an important fracture mechanism in ABS polymers is shear yielding, which leads to tougher materials [46].

10.2.1.3 Other Impact-Modified Commercial Grafting-Based Polymers

Typical HIPS and ABS polymers are opaque materials; however, MABS (methyl methacrylate-acrylonitrile-butadiene-styrene) polymers, which are produced by processes similar to those used in the production of ABS, are transparent materials. This property is obtained by the addition of methyl methacrylate (MMA) to the recipe in order to impart transparency to the polymer by equalizing the refracting index of the rubber particles to that of the matrix. These materials find applications
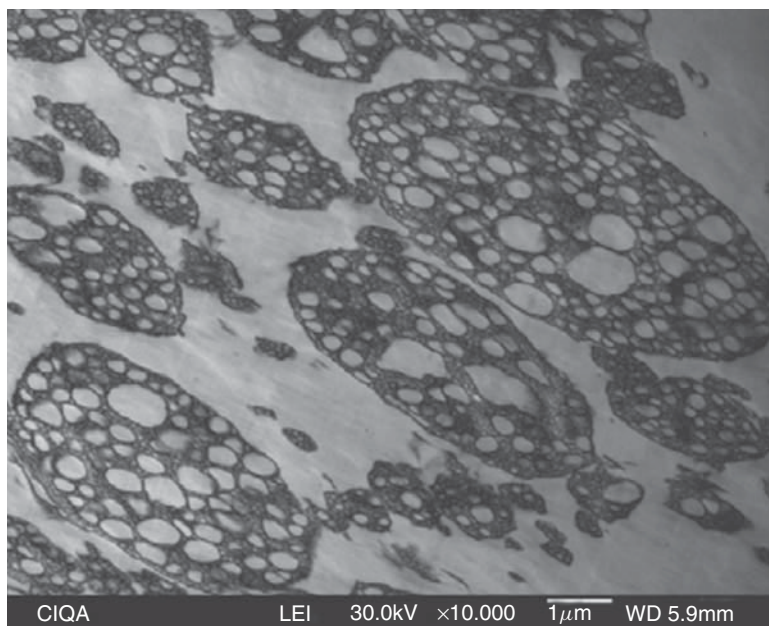
Figure 10.3   Typical salami morphology in a HIPS sample. Amplification ×10,000. The sample was treated with OsO$_4$. Dark areas correspond to PB segments and clear areas to PSt. Picture kindly provided by Dr. R. Díaz de León, CIQA.

in some household appliances and in electronic devices where both impact resistance and transparency are needed. A closely related family of polymers is known as *MBS* (*methyl methacrylate-butadiene-styrene*), which are based on a PB-rich backbone grafted with a copolymer of St-MMA. They can be produced by an emulsion process, and in this case they possess a core–shell morphology with a core rich in partially crosslinked elastomeric PB and a rigid shell of St-MMA copolymer. The main application of MBS is as an impact modifier for PVC resins.

Acrylonitrile-styrene-acrylate (ASA) copolymers is another family of graft-copolymer-based materials in which the rubber phase is really a copolymer of butyl acrylate (BuA) and butadiene (at least in some recipes) [47, 48], and the matrix is made of a SAN copolymer. Originally, butadiene was not present in the rubber phase [49] and perhaps those were not really graft-copolymer-based materials. The main advantage of ASA over ABS is its increased UV stability and long-term heat resistance due to the lack of residual double bonds in the acrylate part of the rubber.

10.2.1.4 Graft-Polyols   Polyurethane foams are synthesized from the polycondensation reaction between a polyol and a diisocyanate. Polyols can be of two types: conventional ones (polyethers) and graft-polyols [50]. The latter are obtained by the copolymerization of SAN in the presence of a polyol polyether using a free-radical initiator. Some of the SAN chains are grafted to the polyol backbone, while others remain free. The grafting is promoted by adding to the recipe a macromer formed by polyol polyethers functionalized with a vinyl monomer. The final result is a dispersion of SAN particles in a continuous phase of polyol polyether with the graft copolymer acting as a stabilizer. The foams formed from graft-polyols exhibit better physical and processing properties than their conventional counterparts, especially increased hardness.

10.2.2   Polyolefins

10.2.2.1 Borane Compounds   A pioneering work in this field was that due to Chung and Jiang [51], who introduced a novel method to synthesize grafts along the polyolefin backbone. The chemistry is based on a "grafting-from" reaction using a borane-containing polymer. Under oxidation conditions, the borane group becomes a reactive site for FRP. With the appropriate choice of borane group and reaction conditions, the free-radical-polymerized polymers are chemically bonded to the side chains of the polyolefin with controllable compositions and molecular structures [12, 51]. The graft copolymerization of α-olefins with the monomer proceeds stepwise. The first step typically is a Ziegler–Natta or metallocene direct copolymerization of an α-olefin with a borane compound (alkyl-9-BBN, borabicyclononane); or the hydroboration [51d] of poly(ethylene-*co*-propylene-*co*-dienic monomer) (EPDM) with 9-BBN. In the next step, grafts of the polymer are produced when the copolymer is placed in the presence of monomer in THF under oxygen feed. Many grafted polyolefins have been synthesized following this novel

route [51]: for example, PE-*g*-PMMA, PP-*g*-PMMA, PP-*g*-PMA, EPDM-*g*-PMMA.

10.2.2.2 Ziegler–Natta and Metallocenes Henschke et al. [52] synthesized graft copolymers of poly(propene-*g*-styrene) by the copolymerization of propene with PSt macromonomers using the catalyst system [Me$_2$Si(2-Me-Benzind)$_2$]ZrCl$_2$ and methylaluminoxane (MAO). Because of the high reactivity of allyl-terminated PSt in the metallocene-catalyzed copolymerization with propene, the application of the grafting-through method for the synthesis of polyolefin graft copolymers was possible. On the other hand, PE-*g*-silane was also synthesized by a grafting-through approach [53], copolymerizing 7-octenyldimethylphenylsilane with ethylene via Et(Ind)$_2$ZrCl$_2$ methylaluminoxane catalyst system without loss of catalyst activity or decrease in molar mass. Finally, syndiotactic PSt-*g*-polydimethylsiloxane copolymers have also been synthesized stepwise [54].

Cationic and Anionic Graft Copolymerization Anionic and cationic polymerizations have been used in the synthesis of functionalized polyolefins. Although it is well known that living cationic polymerization has often been used in the polymerization of styrene, vinyl ethers, or isobutylene, some examples have been reported in the literature on their graft polymerization. For instance, Martini et al. [55] synthesized a copolymer of polyethylene-*g*-polystyrene (PE-*g*-PSt) using an alkylation reaction with different amounts of aluminum chloride (AlCl$_3$) as catalyst under near-critical conditions of n-hexane. Anionic polymerization has also been used in the synthesis of functional polyolefin-*g*-copolymers. Lu et al. [56], synthesized amphiphilic graft copolymers of polyethylene-*g*-polyethylene oxide (PE-*g*-PEO) by a new approach using anionic polymerization. The graft structure, molecular weight, as well as the molecular weight distribution of the graft copolymer could easily be controlled. The molecular weight of the side-chain PEO was proportional to the reaction time and the monomer concentration, which indicates the "living" character of the anionic polymerization of the grafts of ethylene oxide. Gohy et al. [57] reported the synthesis of well-defined poly(butadiene-*g-tert*-butyl methacrylate) (PB-*g*-P*t*-BuMA) amphiphilic copolymers by reaction of P*t*-BuMA chains end-capped with a *tert*-butyl 4-vinylbenzoate anion with the selectively hydrosilylated 1,2-units of anionically synthesized PB.

10.2.3 Modern Grafting Techniques onto Polymers

10.2.3.1 NMRP, RAFT, and ATRP Grafting functional groups (i.e., reactive monomers) onto polyolefins by means of free-radical initiators has been intensively studied and is now an established industrial process. Different kinds of chemistry routes as well as polymerization processes have been developed to produce grafting polymers by traditional FRP. Nevertheless, FRP does not provide well-defined grafts of uniform length [58]. On the other hand, CRP has emerged as a powerful tool of synthesis in order to produce grafts of polymer with controlled architectures and narrow polydispersity for several practical applications. CRP combines the advantages of FRP—tolerance to impurities and moisture, capability of polymerization and copolymerization of a large range of monomers, smooth reaction conditions, and implementation in several polymerization process (bulk, suspension, emulsion, reactive extrusion, etc.)—with those characteristic of living polymerization chemistries (narrow polydispersities and capability for the synthesis of well-defined polymers and block copolymers). Thus, by combining the best of both worlds, CRP allows the polymerization of a large number of monomers with narrow polydispersity, as well as the synthesis of block copolymers, novel topologies, and functionalities [59]. Stable free-radical polymerization (SFRP), ATRP, and RAFT are the principal techniques employed to synthesize polymers and copolymers with controlled grafts. Refer to Chapter 4 for a brief description of CRP and each of these techniques.

10.2.3.2 Grafting and Functionalization of Polymers via CRP The synthesis of controlled grafts on polymers or the incorporation of functional/reactive entities in a controlled manner along the backbone of polymers, has been and still is one of the long-term challenges in the science and technology of polymers [58–60]. This is motivated by the potential applications of the resulting materials as compatibilizers in polymer blends with improved properties, as selective membranes to gases for food packaging, as novel polymer matrices, as nanodispersions for biomedical applications, as hybrid materials for applications in solar cells, etc. Grafting or controlled functionalization reactions have been performed or are possible in a variety of polymeric substrates such as PB, (6e, 7d,e, 13a), polyisoprene (PI) [7d], EPDM (6d, 13a), poly(styrene-*b*-isoprene-*b*-styrene) (SIS) [13a], poly(styrene-*b*-butadiene-*b*-styrene) (SBS) [61], butyl rubber (BR) (6d, 62), poly(ABS) [63], SBR [64], PP [65, 70, 80, 83, 84], PE [66, 81], and hydrogenated elastomers (SEBS) [67], among others.

Polydienes via NMRP The "grafting-from" methodology to modify polydienes by NMRP has been discussed in the patent literature; however, there are a few publications in the scientific literature that provide a deeper insight over the fundamental aspects of the modification of this kind of polymeric substrates in the presence of nitroxide groups. In the pioneering patents of Solomon et al. [68] controlled grafting of poly(methyl acrylate) along the PB backbone was described using two chemical steps. First, a multifunctional macroalkoxyamine was produced

on the basis of the functionalization of *cis*-polybutadiene (*cis*-PB, M_n = 400,000 Da) with nitroxide moieties (randomly distributed along the PB backbone) by using di-*tert*-butyl nitroxide and initiator (di-*t*-butylperoxyoxalate) at 50 °C in a solution process. Then, functionalized PB in the presence of tetrachloroethylene and methyl acrylate monomer at 95 °C led to well-defined grafts of poly(methyl acrylate) along the PB backbone. In 1997, Priddy and Li [69] reported the synthesis of block copolymers with controlled grafts in order to produce transparent impact polystyrene (TIPS) and HIPS. The first block copolymer (polydiene) was synthesized via anionic polymerization or by FR in the presence of peroxide or azo-type initiators and several kinds of persistent radicals (typical nitroxide radicals or initiators and comonomers previously modified with pendant nitroxide groups). The functionalized polydiene was then dissolved and heated in the presence of a vinyl monomer (bulk polymerization). The patent [69] covers the synthesis of the first block containing comonomer units with nitroxide pendant groups, which in the presence of the monomer can generate controlled grafts. Note that the dosing of comonomers with hanging nitroxide groups can produce a high density of grafting sites (brush type) in several places of the PB backbone. In 2003, Rhot et al. [70] from Ciba Spezialitätenchemie, extensively described the synthesis of controlled grafts at high temperatures (150–300 °C) by an extrusion process onto several polymeric substrates based on a variation of the strategy proposed by Solomon et al. [68] Some examples in the patent cover the functionalization of PP and SBS with nitroxide moieties and the possibility of producing compatibilizers of α-olefins-*g*-polar monomers or SBS-*g*-polar monomers. In a 2008 patent, Saldívar-Guerra et al. [13a] disclosed the synthesis of controlled grafts of PSt or poly(butyl acrylate) (PBuA) onto both PB and SIS backbones in supercritical CO_2 (scCO_2). In a first step a multifunctional macroalkoxyamine was produced using nitroxide, initiator, and scCO_2 (swelling agent instead of organic solvents) in the presence of PB or SIS at 135 °C. Afterwards, the macroalkoxyamine in the presence of monomer in scCO_2 at 125 °C led to well-defined grafts.

In the open literature, Howell et al. [71] in 1999 described the synthesis of PB with pendant nitroxide groups to produce HIPS with high graft density by combining di-*tert*-butylperoxalate and TEMPO (2,2,6,6,-tetramethyl-piperidinyl-1-oxy) in solution. The authors found that substrates possessing very high molecular weight in combination with the type of initiator used favored the formation of a gel, even in the presence of a TEMPO excess. This problem was overcome using a PB of 5000 Da. In a second step, functionalized PB was dissolved in the presence of St (5 wt%) and heated at 135 °C for 1 h to produce controlled grafts of PSt. In 2004 [64, 63], controlled grafts of PSt were synthesized

from brominated SBR [64] and brominated ABS [63], respectively, using the concept of Georges et al. [72] and the methodology developed by Hawker et al. [73] by reacting brominated sites with a functional nitroxy compound (hydroxyl derivative of 1-benzyloxy-2-phenyl-2-TEMPO-ethane, Bz-TEMPO). The resulting macroinitiator (SBR-TEMPO) was heated in the presence of St to obtain the desired graft copolymer.

In 2008, in a detailed study using a combination of nitroxide/initiator and a model PB (5000 Da, 80/20 cis,trans/vinyl portion), Bonilla-Cruz et al. [7e] provided evidence on the functionalization mechanisms of polydienes with nitroxide and the influence of the side reactions during this process. The authors also demonstrated the feasibility of functionalization of PB with nitroxide only (PB-*g*-TEMPO) using an excess of nitroxide in solution under mild conditions. Finally, they showed that PB-*g*-TEMPO in the presence of St at 125 °C led to well-defined grafts of PSt along the backbone of PB. This work was further extended to the functionalization of PB, PI [7d], and EPDM [6d] using several types of nitroxide radicals and high throughput experimentation techniques, in which the grafting kinetics of the alternating copolymer of poly(styrene-*co*-maleic anhydride) (SMA) was studied in detail. More recently, in 2011 [7c] a macroinitiator of TEMPO-terminated syndiotactic polystyrene (*s*PSt–TEMPO) was prepared by reacting chloroacetylated *s*PSt with sodium 4-oxy-TEMPO derived from TEMPO-OH, which was used in the NMRP of St and *p*-methyl styrene (*p*-MSt) to yield controlled graft copolymers of *s*PSt-*g*-(PSt-*co*-*p*MSt).

Polyolefins and Other Commodities via NMRP   In a pioneer work, Stehling et al. [74] in 1998 reported the copolymerization of α-olefins (propylene or 4-methylpentene) with an alkene-substituted alkoxyamine using a cationic metallocene catalyst. The functional polyolefins were used as macroalkoxyamines in the NMRP of St at 123 °C under argon in the presence of acetic anhydride. In 2000, Wiyatno et al. [75] synthesized an alkoxyamine possessing pendant polymerizable vinyl groups, which, in the presence of ethylene and 1-butene, led to terpolymers of poly(ethylene-*co*-butene-*co*-vinyl-TEMPO) using a metallocene catalyst. The terpolymer, in the presence of butadiene at 125 °C, led by NMRP to well-defined branches of PB. On the other hand, Baumert et al. [76] synthesized a novel alkoxyamine-functionalized 1-alkene which was copolymerized with ethylene using a palladium catalyst. The resulting highly branched PE with alkoxyamine-functionalized short-chain branches was used as a macroinitiator to initiate the NMRP of St and St/acrylonitrile. Mohajery et al. [77] reported the synthesis of PE-*g*-PSt copolymers via NMRP, copolymerizing first ethylene with *m*,*p*-MSt employing a metallocene catalyst Et(Ind)$_2$ZrCl$_2$ followed by the introduction of bromine at the benzylic position through bromination.

Macroalkoxyamines were prepared by reacting brominated copolymer with hydroxylamine. PE graft copolymers (22.6 mol% of PSt) were obtained via NMRP of St initiated from the macroalkoxyamine.

The postmodification of polyolefins in solution was studied by Park et al. [65a] PE-*g*-TEMPO and PP-*g*-TEMPO were obtained by the dissolution of the polyolefins (LDPE, M_w = 482,000 Da; PP, M_w = 1,850,000 Da) in 1,2,4-trichlorobenzene (TCB) at 170 °C in the presence of benzoyl peroxide (BPO) and TEMPO. After that, PE-*g*-PSt and PP-*g*-PSt were obtained by heating St at 120 °C in the presence of the macroalkoxyamines. Polyolefins grafted with PSt were used as coupling agents in blends of PE/PSt and PSt/PP. This idea was extended by the same group in order to polymerize controlled grafts of SMA [65b]. Lopez et al. [78] reported the preparation of a macroalkoxyamine based on PE and PE-*b*-PBuA via the NMRP of *n*-BuA, initiated by alkoxyamine-terminated PE. Finally, PVC [79] containing side-chain TEMPO (PVC-TEMPO) was prepared by reacting arylated and then brominated PVC (PVC-Ph-Br) with hydroxylamine. The macroalkoxyamine in the presence of St at 125 °C reacting during 4 h led to graft copolymers of PVC-*g*-PSt.

The chemical surface modification of polyolefin films using γ-irradiations and TEMPO has been reported by Miwa et al. [80] in a study in which peroxide groups were formed along the PP backbone by exposing isotactic PP (*i*PP, M_v = 400,000 Da) to ^{60}Co γ-irradiation in the presence of air. The macroinitiator PP-peroxide in the presence of TEMPO and St leads to the graft copolymer PP-*g*-PSt. Also, the same idea was utilized out by Yamamoto et al. [81] using PE (M_n = 1.3 × 10^4 Da) instead of PP. In 2001, Miwa et al. [82] extended this approach to form copolymers from PP-peroxide in the presence of TEMPO, St, and a small amount of *n*-butyl methacrylate (BuMA) in order to obtain PP-*g*-poly(St-*r*-BuMA). Building upon the same approach, in 2003 Sugino et al. [83] added BPO in the copolymerization of St-BuMA under the hypothesis that, without free-radical initiators, the grafting process cannot be well controlled because of the considerably low concentration of peroxides along the polyolefin. On the other hand, polyolefins have been modified using UV irradiation. Yamamoto et al. [84] synthesized controlled grafts of MMA and BuMA onto films of *i*PP using benzophenone as initiator, toluene, and 2,2,6,6-tetramethyl-4-aminopiperidine-1-oxyl (4-amino-TEMPO) at 65 °C. Also, the synthesis of controlled grafts of PSt on silicon by NMRP atmospheric pressure plasma surface activation has been reported [85].

ATRP Techniques   The synthesis of controlled grafts onto polymers by ATRP has been extensively reported in the literature (66, 86, 59a). One approach is to introduce halogen atoms along the preexisting polymeric backbone to produce controlled grafts. For instance, Wang et al. [87] reported the synthesis of EPDM-*g*-PMMA in two steps. First, EPDM was brominated using an *N*-bromosuccinimide/azo-bis-isobutyronitrile system. The EPDM holding bromine groups, was then used as a macroinitiator to produce controlled grafts of MMA. Coiai et al. [88] synthesized well-defined core–shell structures polymerizing St, MMA, or ethylacrylate (EA) from brominated microparticles of ground tire rubber (GTR). On the other hand, 4-methyl-4-octene was used as a model compound of natural rubber [89], which was epoxydized to 4,5-epoxy-4-methyloctane. After that, the epoxydized compound in the presence of (a) 2-bromopropionic acid or (b) 2-bromo-2-methylpropionic acid resulted in ATRP macroinitiators, which, in the presence of MMA, produced controlled grafts of PMMA. Different kinds of graft copolymers, namely, SEBS-*g*-PMMA, SEBS-*g*-PSt, and SEBS-*g*-P*t*-BuA, were recently developed by Xu et al. [90] using a stepwise procedure: (i) immobilization of ATRP initiators on the side chains of SEBS via partial chloromethylation of phenyl groups, and (ii) graft polymerization via iron-mediated activators generated by electron transfer (AGET)–ATRP. Fónagy et al. [91] synthesized thermoplastic elastomers of polyisobutylene-*g*-polystyrene (PIB-*g*-PSt) via ATRP. Functional nanoporous polymers based on nanoporous 1,2-polybutadiene with gyroid morphology were obtained by Guo et al. [92] using surface-initiated ATRP and click chemistry. Also, well-defined PB-*g*-PMMA and PB-*g*-P*t*-BuA with low polydispersity and very high molecular weights were obtained by ATRP of MMA or *t*-BuA in the presence of brominated PB [93].

In the polyolefin field, controlled grafts of poly(*N*-vinyl-2-pyrrolidone) (PNVP) were synthesized onto non-woven membranes of PP [94]. In another work, using a functionalized macroinitiator derived from hydroxylated isotactic poly(1-butene), Shin et al. [95] synthesized a polar graft polyolefin, namely, isotactic poly(1-butene-*g*-poly(*tert*-butyl acrylate)) by ATRP, which was later hydrolyzed to generate some carboxylic acid functionality at the side chains. Also, an amphiphilic graft copolymer of poly((1-butene)-*g*-(acrylic acid)) was obtained from the hydrolysis of the *tert*-butoxy ester group of the graft copolymer synthesized earlier. Yamamoto et al. [96a] studied the graft polymerization of MMA from high density polyethylene (HDPE) films modified by 2,2,2-tribromoethanol or benzophenone. Also, in another approach of the same group, controlled grafts of MMA were synthesized onto PE via reverse ATRP [96b]. Liu and Sen [97] studied the synthesis of several linear PE-based copolymers with diblock grafts by ATRP. Finally, PBuA-*g*-branched PE was prepared stepwise: First, a branched PE macromonomer with a methacrylate-functionalized end group was prepared by Pd-mediated living olefin polymerization; the macromonomer was then copolymerized with *n*-BuA by ATRP [98].

RAFT Techniques Surface modification of PP microporous membranes was carried out by grafting block copolymers of poly(acrylic acid-*b*-acrylamide) using a combination of UV irradiation and the RAFT method with dibenzyl trithiocarbonate as a RAFT agent [99]. EPDM-*g*-PSt was synthesized by Joo et al. [100] stepwise. First, PSt was synthesized through the RAFT technique using trithiocarbonateas chain transfer agent. Then, a "grafting-onto" reaction of PSt onto EPDM was carried out using peroxide as a radical-generating agent. The peroxide created radical reactive sites on EPDM through hydrogen radical abstraction reaction, which were then transferred to trithiocarbonate units in PSt to afford EPDM-*g*-PSt. In another example, poly[*N*,*N*′-(1,4-phenylene)-3,3′, 4,4′-benzophenone tetracarboxylicamic acid] (PAmA) possessing controlled grafts of PMMA side chains (PAmA-*g*-PMMA) was synthesized by Fu et al. [101] via thermally induced graft copolymerization of MMA with ozone-pretreated PAmA using a RAFT process.

10.2.4 Functionalization and Grafting from Surfaces

10.2.4.1 Grafting from Nanoparticles The synthesis of grafts onto nanoparticles of silica (NPSiO₂), titanium dioxide (NPTiO₂), magnetite (NPFe₃O₄), and CdSe to obtain hybrid materials (nanoparticle-polymer) has been discussed in recent reviews and compilations [102]. As mentioned in Section 10.1.3, nanoparticle functionalization with chemical groups or grafts of polymer is the key to obtaining good dispersions of nanoparticles in polymer matrices, improving the physical and chemical properties of the resulting composite. NPSiO₂-*g*-polymer hybrids form the most studied system using FRP and CRP techniques. In general, the synthesis of grafts proceeds stepwise. In the first step, the nanoparticle surface is typically modified with organosilanes (Cl₃Si–, (**R**O)₃Si–; **R** = methyl or ethyl) or organophosphorus ((HO)₂PO-) derivative compounds used as anchoring groups containing: (i) initiating moieties (azo [103] or peroxide groups [104]), (ii) vinyl ends [105], (iii) alkoxyamines [106] (synthesized *in situ* or attached), or (iv) initiating species for ATRP [107] or RAFT [108] polymerization. In the second step, functionalized nanoparticles in the presence of monomer(s) in solution, or alternatively in bulk, led to nanoparticle-*g*-polymer composites. Prucker and Rühe [103a] were pioneers in modifying a NPSiO₂ surface with azo-chlorosilane through a base-catalyzed condensation reaction, in which PSt chains were synthesized by FRP using SiO₂-azo as a hybrid initiator at 60 °C during 6 h in the presence of St. Feng et al. [103b] introduced azo groups onto an NPSiO₂ surface via condensation between 4,4′-azobis-4-cyanopentanoic acid and alkyl-hydroxyl groups immobilized on the NPSiO₂ surface under ambient conditions. PSt chains were grafted

by FRP at 70 °C. Kasseh et al. [103c] introduced *tert*-butyl hydroperoxide onto fumed silica, which, in the presence of St and/or BuA monomers and N-*tert*-butyl-1-diethylphosphono 2,2-dimethyl propyl nitroxide (DEPN, also known as *SG1*) at 120 °C in bulk, led to controlled grafts of PSt, PBuA, or poly(St-*b*-BuA). Also, controlled graft polymerization [103d–f] of BuA or ethyl acrylate (EA) can be achieved by decomposition of azo groups from NPSiO₂ functionalized with azo-triethoxysilane in the presence of SG1 and monomer at 100–120 °C. Ni et al. [104] functionalized SiO₂ particles bearing a peroxo functionality, which were used as hybrid initiators in the NMRP of St with TEMPO.

On the other hand, organosilanes with vinyl ends have also been attached to NPSiO₂ by the polymerization of vinyl monomers; thus core–shell NPSiO₂–polyacrilamide (PAM) nanospheres were synthesized by Liu and Su in 2005 [105a]. By emulsion polymerization, the vinyl ends of functionalized NPSiO₂ with γ-methacryloxypropyltri(isopropoxy)-silane were polymerized with fluorinated acrylate–siloxane monomers to obtain an organic–inorganic composite latex with an irregular core–shell structure [105b]. NPTiO₂ anatase [105c] or rutile [105d] have also been functionalized with organosilanes possessing vinyl ends, which, in the presence of St, led to grafts of PSt by FRP. Recently, in 2011, Jaymand [105e] synthesized a novel-type poly(4-chloromethyl styrene-graft-4-vinylpyridine)-*g*-TiO₂nanocomposite. First, a poly(4-chloromethyl styrene)/TiO₂nanocomposite (**1**) was synthesized by *in situ* FRP of 4-chloromethyl styrene and 3-(trimethoxysilyl) propylmethacrylate (MPS) modified nano-TiO₂. Thereafter, hydroxylamine (H-TEMPO) was covalently attached to (**1**), replacing the chlorine atoms in the poly(4-chloromethyl styrene) chains. The controlled graft copolymerization of 4-vinylpyridine was initiated by (**1**) carrying TEMPO groups as macroinitiator. Wang et al. [105f] functionalized nanosilica with vinyl-trimethoxysilane by dispersing nanosilica in the presence of vinyl-trimethoxysilane in ethanol during 2 h under ultra-sonication. Functionalized nanosilica with vinyl groups in the presence of St, MA, TEMPO, and BPO led to controlled grafts of poly(SMA) at 130 °C. Magnetite (Fe₃O₄) nanoparticles with controlled grafts of 4-vinylpyridine have been obtained by polymerizing the alkoxysilane-functionalized nanomagnetite in the presence of hydroxy-TEMPO, 4-vinylpiridine, and BPO [105g].

Alkoxyamines can also be covalently bound to nanoparticles for subsequent NMRP. Thus, fumed nanosilica was functionalized with a trichlorosilane group containing an alkoxyamine initiator based on SG1 [106a]. The hybrid alkoxyamine, in the presence of BuA and sacrificial nitroxide (SG1) and *N-tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethyl)propyl nitroxide (MONAMS) at 120 °C during 5–6 h, led to well-defined grafts of PBuA. Also,

Bartholome et al. [106b–d] functionalized nanosilica (diameter = 13 nm) with triethoxysilane group containing an alkoxyamine initiator based on SG1. This hybrid alkoxyamine in the presence of St leads to controlled grafts of PSt covalently attached onto nanosilica. Recently, well-defined grafts of PSt attached to both the inner and outer surfaces of ordered mesoporous silica (OMS) particles have also been generated by an NMP polymerization of St initiated from an SG1-based alkoxyamine [106e]. Sill and Emrick [106f] in 2004 functionalized cadmium–selenide nanoparticles (CdSe, 3–4 nm) with a TEMPO-alkoxyamine modified with a phosphine oxide functionality. The alkoxyamine in the presence of St at 125 °C led to controlled grafts of PSt on the CdSe surface. Kobayashi et al. (106 g) chemically modified magnetite (diameter = 10 nm) and titanium oxide nanoparticles (diameter = 15 nm) with an alkoxyamine modified with a phosphoric acid group. These hybrid alkoxyamines, in the presence of St or 3-vinyl pyridine (3VP) at 125 °C, led to controlled grafts of PSt or P3VP by NMRP.

Nanoparticle functionalization to obtain hybrid alkoxyamines is often a complicated multistep process because of the fact that it is first necessary to synthesize sophisticated alkoxyamines possessing anchoring groups that can react with -OH groups on the particle surface; therefore, new methods of functionalization involving only one step of synthesis/functionalization are highly demanded. As an example: Bartholome et al. [106c,d] synthesized a unimolecular alkoxyamine initiator (**1**) carrying triethoxysilyl end groups reactive toward the silica. This alkoxyamine was formed on the surface *in situ* by the simultaneous reaction of a polymerizable acryloxy propyl trimethoxysilane (APTMS), azobisisobutyronitrile (AIBN), and SG1 at 70 °C during 26 h. After that, (**1**) in the presence of St, toluene and sacrificial alkoxyamine, styryl-SG1, at 110 °C during 72 h led to controlled grafts of PSt on the nanosilica surface. In another work, Bonilla et al. [20b] obtained a hybrid SiO_2-TEMPO by functionalization of SiO_2 particles with TEMPO using oxoammonium salts in the presence of solvent and triethylamine by a one-step synthesis. After that, well-defined grafts of poly(St-*co*-MA) were obtained by polymerizing St and MA in the presence of SiO_2-*g*-TEMPO.

On the other hand, double-hydrophilic cylindrical polymer brushes of *t*-BuMA and oligo(ethylene glycol) methacrylate were synthesized from magnetite immobilized with poly(2-(2-bromoisobutyryloxy)ethyl methacrylate) by ATRP [107a]. Brushes of high grafting density (0.9 chains/nm^2) were synthesized by combining NMRP to form PSt (8.7–8 kDa) and sequential ATRP to form P*t*-BuA (18.6 kDa) from functionalized silica particles with a novel asymmetric monochlorosilane-terminated difunctional initiator [107b]. Surface-initiated ATRP with high grafting density (2 chains/nm^2) of benzyl methacrylate,

MMA, and St from magnetite nanoparticles functionalized with an organophosphono initiator, was reported by Babu and Dhamodharan [107c]. Mesoporous hybrid materials made of mesoporous silica and a covalently grafted polymer with controlled chain length were successfully synthesized by surface-initiated ATRP of St and MMA [107d].

Using the RAFT technique, silica nanoparticles were functionalized by covalently attaching 3-methacryloxypropyldimethylchlorosilane on their surface. The functional group attached had a methacrylic group at one end, which served as the initiating moiety. Thus, the polymerization of MMA in the presence of 4-cyano-4-(dodecylsulfanylthiocarbonyl) sulfanylpentanoic acid as RAFT agent and AIBN, produced PMMA–SiO_2 nanocomposites [108a] Ngo et al. [108b] synthesized hybrid TiO_2 nanoparticles of TiO_2-*g*-PMMA and TiO_2-*g*-poly(*tert*-butyldimethylsilyl methacrylate) (TiO_2-*g*-PMASi) by RAFT polymerization. First, the nanoparticles were immobilized with 3-(trimethoxysilyl) propyl methacrylate (MPS). After that, the vinyl ends of MPS were polymerized with MMA or MASi in the presence of 2-cyanoprop-2-yl dithiobenzoate (as RAFT agent) and AIBN. In this approach, the amount of free homopolymer formed was higher than that of the polymer anchored onto the surface of titania particles. On the other hand, using DDAT (*S*-1-dodecyl-*S*′-(α,α'-dimethyl-α''-acetic acid) trithiocarbonate) as RAFT agent, Feng et al. [108c] prepared CdSe-*g*-poly(acrylonitrile) nanocomposites in the presence of a small amount of AIBN under ultrasonic radiation.

10.2.4.2 Carbon Derivatives A great number of carbon nanotube (CNT) applications are related to polymer nanocomposites. Much efforts has been focused to enhance the nanocomposite preparation methods aiming at the homogeneous dispersion of CNTs into diverse matrices to obtain novel composites with improved properties. CNT surface reactivity and polymer–nanotube interaction have been improved by functionalization [109] and surface polymer grafting [110]. The main methods to obtain hybrid CNT–polymers are (i) non-covalent attachment (i.e., polymer wrapping and absorption) and (ii) covalent attachment (i.e., "grafting-to," "grafting-from," and functionalization). In the case of covalent attachment, the resulting grafted polymer is usually named a polymer brush [111]. Thus, these kinds of hybrids have potential applications as cleaning, scrapping, and applying electronic contacts, among others [112]. The direct covalent functionalization of CNT preserves the nanotube structure and could favor a homogeneous and extended coverage of functionalized sites over the nanotube surface. In particular, radical reactions could be used to prepare further CNT derivatives, such as polymer-grafted nanotubes, and specifically the controlled radical polymer-grafted CNT. Several radical reactions have been performed with carbon structures (carbon black

(CB), fullerenes, and CNTs) with organic peroxides and nitroxides. Experimental results have reported the addition of radicals to carbon structures using electron spin resonance (ESR) [113]. Even more, polymer grafting has been carried out in several carbon structures, such as CB, fullerenes, CNTs, and graphene. Previous studies performed using CB and fullerenes constitute the pioneering work that evolved in the polymer grafting on CNT and graphene surfaces.

Carbon Black (CB)   A permanent radical concentration [114], as well as a strong radical trapping behavior has been observed in CB [115], and also both properties have been used to graft polymers onto its surface [116]. Polymer grafting with CB has been achieved using the "grafting-from" and "grafting-onto" techniques. Cationic and anionic polymerization by azo [117], peroxyester [118], acylium perchlorate [119], and potassium carboxylated [120] groups introduced on the CB surface are examples of the "grafting-from" technique. Also, by FRP of vinyl monomers in the presence of CB under the "grafting-to" method leads to grafts of polymer onto CB with low grafting density (<10%), due to the fact that CB preferentially traps low molecular weight initiator fragments rather than polymer radicals [121]. Furthermore, when CB is treated with conventional free-radical initiators (BPO or AIBN), the corresponding radicals are bound on the surface, forming polycondensed aromatic rings and quinonic oxygen groups (115b, 122), which act as strong radical trapping agents for polymer radicals. Using this behavior as an advantage, Hayashi et al. [116a] reported the "grafting-to" reaction of CB with PSt chains polymerizing St in the presence of CB and TEMPO at temperatures above $100\,^{\circ}$C. These experiments confirmed that CB preferentially traps more initiator fragments of low molecular weight than polymeric radicals. This behavior could be explained by the stability and the steric hindrance of the growing polymer radicals. Also, polymers having hydroxyl terminal groups could be grafted onto the CB surface in the presence of ceric ions. Complementary results by the same group determined that PEO could also be grafted onto CB without inducing gelation or crosslinking. This behavior revealed that radicals formed did not react with two CB particles.

Fullerenes   Early studies on FRP of vinyl monomers in the presence of C_{60} reported very low yields of polymer formed in solution, or even complete inhibition [123]. From these studies, it has been suggested that, in the case of St, the free radicals are trapped by fullerene, and the resulting fullerene radicals do not propagate but can terminate instead. Nevertheless, there are pieces of evidence suggesting that if the polymerization is carried out in the presence of a large excess of initiator, the radicals undergo multiple additions on the fullerene surface, changing their nature sufficiently not to inhibit polymerization [124]. Thus,

Krusic et al. [125] have shown that free-radical species can efficiently couple to the surface of C_{60}, resulting in highly functionalized fullerenes. Mehrotra et al. [123] reported that, in the presence of C_{60}, the polymerization of vinyl monomers (methyl acrylate, MMA, acrylonitrile, cyanovinyl acetate, vinyl acetate, 2-cyanoethyl acrylate, St, and *N*-vinylpyrrolidone) in solution was inhibited, yielding 15% or less of the polymer product. Therefore, it was concluded that the C_{60} intercepts the initiating radicals in the polymerization reaction. Furthermore, it was observed that monomers with high reactivity could form fullerene-based radicals by their addition to the fullerene surface and could continue the polymerization process. In fact, functionalization of fullerenes with well-defined polymers by living polymerization techniques (e.g., anionic polymerization, NMRP, ATRP) has been reported recently. With these living methods, both the architecture of the polymer grafting on fullerene surfaces and, even more, the architecture of the polymer chains can be well-controlled [126].

Recently, a functionalization of carbon nano-onions (CNO, multilayer fullerenes) was carried out by [2+1] cycloaddition of nitrenes. The grafted products were prepared by the "grafting-from" method combining *in situ* ring-opening polymerization (ROP) and ATRP [127].

Carbon Nanotubes   The first synthesis of polymer-grafted multiwalled carbon nanotubes (MWNTs) was reported by Jin et al. [110b] in 2000. Since then, the number of papers on this subject has increased enormously. In most of these papers, the polymer grafting of MWNTs has been achieved by one of the already mentioned techniques: "grafting-from," "grafting-to," and "polymer reactions with functional groups at the nanotube surface."

POLYMER GRAFTING OF ACID-FUNCTIONALIZED CARBON NANOTUBES   The first covalent attachment of PSt chains onto pretreated CNTs was reported by Shaffer in 2002 [110a]. PSt and some of their copolymers (such as poly(styrene-*co*-hydroxymethyl styrene) and poly(St-*co*-aminomethylSt) [128]) had been reported as being grafted on CNTs by one of the three previously discussed methods. In the case of acid-functionalized CNTs, the grafting of PSt could be achieved by several reactions, such as esterification [129], amidation [130], acylation [131], and Huisgen cycloaddition [132], among others. Nowadays, several polymers have been successfully grafted onto MWNTs using the "grafting-from" technique: PMMA grafted via emulsion polymerization [110c,d], sterification [133], and other methods [134]; polyethylenimine [135] and hyperbranched polyetherketones [136] via Friedel–Crafts acylation in polyphosphoric acid (PPA) [137]; PEO and PSt [138]; polyureas, polyurethanes, and poly(urea-urethane) [139]; polyethers [140], polyacetylene [141], and PSt

[142]. In all of these cases, the CNTs were chemically functionalized by acid treatment to introduce initiator molecules by chemical reaction using surface functional groups that could be used to carry out *in situ* polymerization of the different monomers.

POLYMER GRAFTING OF CARBON NANOTUBES BY CON-TROLLED/LIVING RADICAL POLYMERIZATION Polymer grafting techniques that use direct covalent functionalization methods, such as radical reactions, have been developed in order to avoid the problems associated with the functionalization of CNTs using acids. These grafting techniques eliminate the need for nanotube pretreatment before the functionalization and allow attachment of polymer molecules to pristine tubes without altering their original structure.

The grafting mechanism involves free radicals from a growing or terminated polymer chain that attach themselves to the defective, doped and/or oxidized sites [110a,b], or to an aromatic ring by the inherent radical trapping mechanisms [110e] of the CNT. Both, the polymer "grafting-from" and the "grafting-to" methods on CNTs could be performed by FRP or CRP. Living polymerization methods in addition to the previously mentioned CRP include: anionic, carbocationic, and ROMP. All these methods have been used in the synthesis of polymer brushes in a "grafting-from" approach, as detailed below.

Nap et al. [143] considered how the strength and distance of the minimal interaction could be controlled by the choice of polymer chain length, surface coverage, and type of functional end group, and also how the feed ratio of monomers controlled the quantity of the grafted polymer. Like these, many other factors need to be studied to reach an understanding of the formation of polymer brushes on nanotubes. Some of the studied systems involved PMMA grafting on CNTs. Park et al. [144] reported the polymerization of PMMA over CNTs using AIBN as initiator. In this system, the radicals induced by AIBN on the outer wall of the MWNTs were found to initiate the grafting of PMMA [145]. Other authors have reported that poly(4-vinylpyridine) grafts to SWNTs during the *in situ* FRP of 4-vinylpyridine [146].

POLYMER GRAFTING OF CARBON NANOTUBES BY LIVING POLYMERIZATIONS Anionic and cationic polymerization techniques can be used to graft polymer chains on CNT surfaces. Mylvaganam et al. [147] reported, using density functional theory (DFT), that ethylene and epoxide functional groups can be grafted to CNTs using methoxy radicals and *sec*-butyl anion as initiators, leading to PE- and polyepoxide-grafted nanotubes, respectively. The theoretical study predicts that both the free-radical and the anionic functionalization methods are energetically favorable, that the resulting CNT radical and the CNT anion can react with ethylene and epoxide functionalities, respectively, and that the resulting products have free electrons and negative charges on the carbon and oxygen atoms at the free ends of ethylene and epoxide, respectively. Hence, the *in situ* free-radical and anionic polymerizations can propagate to produce polymer-grafted CNTs. The cationic functionalization of CNTs using BF_3 as an initiator was found to be infeasible. In addition, PSt chains were grafted onto SWNTs via anionic polymerization techniques [148]. Particularly, the *in situ* surface-initiated CRP from the surface of CNT was reported by several authors using RAFT [149], ATRP [150], and NMRP [151], among others. There are only a limited number of experimental evidences of these radical polymerization techniques for the polymer grafting of CNT even after several years of work in this field. Hong et al. [149a] reported the poly(N-isopropylacrylamide) grafting of MWNTs via RAFT polymerization using RAFT agent-functionalized MWNT as chain transfer agents. Using the same technique, PSt chains were grafted from the surface of MWNTs [149b]. Additional examples involved the preparation of core–shell hybrid nanostructures using a RAFT agent immobilized on MWNTs. The hard phase was composed by MWNTs and the soft was a brush of poly(methacrylate) wherein the content of the polymer around carbon nanotubes could be modulated by the feed ratio [149c]. On the other hand, ATRP procedures proposed for nanotube surface polymerization are of two types: (i) the attachment of polymerization initiators via a cycloaddition reaction or the ROMP [152] and (ii) the attachment of initiator by the carboxy group generated by chemical oxidation [153]. The polymers growing over nanotubes using these techniques reported so far are principally PSt [150, 154], PMMA [155], Pt-BuA [156], PNIPAM [157], and PAA [158], as well as their copolymers [159]. Recently, a summary of the developments in nanostructured materials prepared by CRP has been given by several researchers [160]. Some advances in the understanding of the ATRP technique for the attachment of polymer on the CNT have been documented. Among these studies, Chun-Hua and Cai-Yuan [161] reported an increase in the molecular weight and a reduction of the reaction time when the *in situ* ATRP polymerization of St in the presence of silica nanoparticles and carbon nanotubes was carried out with an amount of PSt. In addition, using AGET–ATRP several amphiphilic polymers have been attached to nanoparticles forming self-assembling conjugates. Among these results, Hermant et al. [162] reported the preparation of poly(2-hydroxyethyl methacrylate)-grafted CNT. The result was an amphiphilic nanostructure. In addition, PMMA and PSt were successfully grafted over large-size pore silica under activator regenerated by electron transfer (ARGET)-ATRP conditions with control of the polymer loading and molecular weight of the grafted polymer [163]. The authors discovered that the capacity (in number, form: cylindrical or

spherical, and size) of the nanopores in the mesoporous silica defines the width of the polymer distribution. This approach, in which the polymers are degraded to convert them to carbon and the silica template is dissolved, permits the preparation of ordered arrays of hollow nanospheres and nanotubes.

Furthermore, the preparation of nanostructured carbon materials was proposed by McGann et al. [164] using the pyrolysis of films of PBuA-*b*-polyacrylonitrile copolymers previously prepared by ATRP. Modifications of molecular weight induced changes in the final mass of the graphitic carbon films. Lee et al. [165] proposed a self-organization of aqueous droplets upon a volatile solution in order to yield macroporous polymer/carbon nanomaterial films. The materials prepared by the calcination of the polymer phase presented high conductivity and large surface area with potential applications innanoelectronics (supercapacitors, catalytic supports) and energy storage materials (solar/fuel cell electrodes).

Recently, several authors have proposed the preparation of nanostructured materials by the use of conductive polymers and organically derived nanostructures [166]. In particular, Matyjaszewski et al. [160] have explored the use of polyaniline and polypyrrole, ionically conductive polymers, cationic poly(ethylene oxide), and various carbon nanostructures (such as graphenes), in order to generate polymers for dielectric applications. CNTs have been coated with covalently bonded polyelectrolyte brushes. Llarena et al. [167] have used poly(3-sulfopropylamino methacrylate) (PSPM) as coating by *in situ* polymerization via ATRP from initiating silanes previously attached to the CNTs. This led to the formation of hybrid nanocomposites of CNTs coated by PSPM with CdS and FeO embedded particles. The synthesis method for the hybrid nanostructures was ion exchange using sulfonate groups followed by precipitation. The reaction was followed by zeta potential measurements and TEM. Examples of metal-loaded polymer materials were developed by several researchers such as Kallitsis et al. [168] in order to add optoelectric properties to the inherent polymer properties through the presence of certain metal ions. This type of materials prepared by the use of bipyridine- and terpyridine-based ruthenium containing monomers, resulted in homo and copolymers with high Ru contents. The combination of these materials with others with electron–hole transporting properties or semiconducting properties, such as conjugated polymers or CNTs, could lead to multifunctional advanced materials (see also Chapter 29). Finally, the polymer grafting of boron nitride nanotubes (BNNT) using PSt and PMMA via ATRP has also been reported [169].

NMRP has been demonstrated on surfaces, nanoparticles and amphiphiles, and as well as very recently on CNTs by Ramirez et al. [151b]. This technique has been used in both "grafting-to" and "grafting-from" methods. In the first case, NMRP produces well-defined polymers that are end-capped with thermally labile nitroxide functionalities; thus, this method could result in the controlled formation of polymer-centered radicals that could be utilized in the functionalization of CNT (151a, 170). In the second case, the pair initiator nitroxide could be attached to the nanotube to form a "macroinitiator," which is susceptible to thermal initiation. The opening and closing mechanism for the free radical–controller pair favors the polymer chain growth, as described after an extensive characterization by Dehonor et al. [171] The advantage of this functionalization is that the CNTs could be used as received and the reaction proceeds to a good extent. The available literature on the grafting of PSt to CNTs using NMRP invariably includes the functionalization of the nanotubes using strong acids to attach the initiator to the nanotube ends and defective sites. Particularly, Ramirez et al. [151a] attached an NMP initiator through carbodiimide or acid chloride chemistry to acid-functionalized nanotubes. Adronov et al. [152] proposed that the polymers could be covalently attached to SWNTs through the radical coupling of the polymer to the nanotube walls. Datsyuk et al. [151b] synthesized DWCT-polymer brushes by *in situ* nitroxide-mediated polymerization. Recently, the self-assembly of amphiphilic block copolymers of (poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide)) on MWNTs was studied. The polymer grafting proceeded using a nitroxide labeled Pluronic™. The presence of MWNTs changed the temperature and the dynamic behavior of the polymer and a different behavior were obtained depending on the type of CNTs used. SWNTs induced the formation of hybrid polymer–SWNT micelles, whereas the MWNTs induced the assembly of polymer aggregates at the surface of the MWNTs [172]. NMRP is the less reported CRP technique to graft polymer chains on CNT; however, the technique is promising because of the following: (i) successful functionalization is possible without any carbon nanotube surface damage like in acid-functionalized CNT and (ii) purification and separation problems are minimal (when compared to a technique such as ATRP).

10.2.5 Concluding Remarks

The development and applications of graft polymers and nano-objects (nanoparticles, carbon derivatives, etc.) possessing polymer grafts, is a scientific and technological field in continuous growth. Specifically, the CRP techniques in the synthesis of controlled grafts, have become a powerful tool to obtain new and novel materials with sophisticated architectures. As illustrated in this chapter, there are several approaches to carry out the polymer grafting of both nanoparticles and carbon nanostructures by "grafting-to" and "grafting-from" techniques. In our experience, the chemical modification (functionalization) of the surface of the nanoparticles or carbon derivatives

with grafts of polymer is the best way to achieve excellent dispersions of these nano-objects in a polymer matrix. As a consequence, the preparation of hybrid structures based on polymer grafting over solid nanostructures, is a useful tool for the design, fabrication, optimization, and eventual application of more functional nanomaterials.

In this section, a short review of the "state of the art" in the fields of synthesis of grafts over existing polymers and grafting onto different kind of nanoparticles and carbon derivatives has been presented.

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