

Nitroxide-Mediated Polymerization from Surfaces

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Abstract The current chapter gives a general overview on surface-initiated nitroxide-mediated polymerization (SI-NMP). More particularly, the developed strategies to perform an SI-NMP process, the various type of substrates including inorganic and organic supports, and the potential of SI-NMP to prepared advanced materials are discussed. Based on a selected number of literature examples it appears that SI-NMP is a versatile and powerful approach to introduce polymer brushes on surfaces and/or tune polymer surface properties.

Keywords Grafted or brush polymers • Nitroxide-mediated polymerization • Planar, spherical, and porous surfaces

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Abbreviations

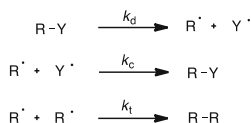
3-MPS	3-Methacryloxypropyltrimethoxysilane
AFM	Atomic force microscopy
AIBN	Azobisisobutyronitrile
APTES	3-Aminopropyl triethoxysilane
ATRP	Atom transfer radical polymerization
BlocBuilder MA	2-Methyl-2-[<i>N-tert</i> -butyl- <i>N</i> -(1-diethoxyphosphoryl)-2,2-dimethylpropyl]aminoxy]propionic acid
BPO	Benzoyl peroxide
CNT	Carbon nanotube
DLS	Dynamic light scattering
DMAC	Dimethylacetamide
DMF	<i>N,N</i> -Dimethylformamide
DPPC	<i>L</i> -Adipalmytoyl-phosphatidylcholine
HEMA	2-Hydroxyethyl methacrylate
LB	Langmuir–Blodgett
MAMA-NHS	2-Methyl-2-[<i>N-tert</i> -butyl- <i>N</i> -(1-diethoxyphosphoryl)-2,2-dimethylpropyl]aminoxy]- <i>N</i> -propionyloxysuccinimide
MMA	Methyl methacrylate
MMT	Montmorillonite
MWNT	Multiwalled carbon nanotube
NEXAFS	Near-edge X-ray absorption fine structure
NMP	Nitroxide-mediated polymerization
OMS	Ordered mesoporous silica
P3VP	Poly(3-vinylpyridine)
P4VP	Poly(4-vinylpyridine)
PAA	Poly(acrylic acid)
PBA	Poly(<i>n</i> -butyl acrylate)
<i>Pt</i> BA	Poly(<i>tert</i> -butyl acrylate)
PDMAEA	Poly(2-dimethylamino ethyl acrylate)
PHPMA	Poly(2-hydroxypropyl methacrylamide)
PNIPAM	Poly(<i>N</i> -isopropylacrylamide)
PPTEA	Poly[2-phenyl-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)ethyl acrylate]
PS	Polystyrene
PS- <i>b</i> -PCL	Polystyrene- <i>block</i> -polycaprolactone
PSMA	Poly[styrene- <i>co</i> -(maleic anhydride)]
RAFT	Reversible–addition fragmentation chain transfer
SANS	Small-angle neutron scattering
SAXS	Small-angle X-ray scattering
SG1	<i>N-tert</i> -Butyl- <i>N</i> -[1-diethylphosphono-(2-2-dimethylpropyl) nitroxide]
SI-NMP	Surface-initiated nitroxide-mediated polymerization
SWNT	Single-walled carbon nanotube

TEM	Transmission electron microscopy
TEMPO	2,2,6,6-Tetramethylpiperidinyl-1-oxy
TEMPO-Br	1-Oxo-2,2,6,6-tetramethylpiperidinium bromide
TIPNO	2,2,5-Trimethyl-4-phenyl-3-azaheptane-3-oxyl
TSPMA	3-(Trimethoxysilyl)propyl methacrylate
VBC	4-Vinylbenzyl chloride
XPS	X-ray photoelectron spectroscopy

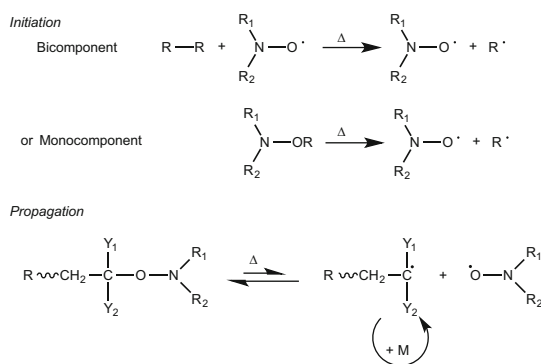
1 Introduction

Surface modification with thin polymer films is considered one of the most attractive ways of obtaining “smart” surfaces in response to external stimuli such as solvent, temperature, pH, and ions. This modification imparts new surface properties such as wettability, biocompatibility, corrosion resistance, and friction. Thin polymer films can either be prepared by spin-coating with a polymeric solution or by covalent attachment of one end of a polymer chain to the surface. The latter technique gives rise to polymer brushes [1]. The “grafting-from” approach is one of two strategies commonly used to attach polymers to a substrate surface. This approach has been largely developed thanks to controlled or “living” polymerization techniques (CLRP), because they allow accurate control over polymer thickness, density, composition, and architecture [2]. Polymerizations can be performed on substrates exhibiting different topologies, such as planar wafers, spherical particles, or a confined environment, and are compatible with a broad range of monomers. Different controlled radical polymerization (CRP) techniques such as atom transfer radical polymerization (ATRP), reversible–addition fragmentation chain transfer (RAFT), and nitroxide-mediated polymerization (NMP) have been used for the preparation of functionalized surfaces [2–4]. However compared with other CRP techniques, NMP is underexploited and has so far been the subject of only a few review articles. Indeed, initially, NMP was limited to a small range of polymerizable monomers (i.e., only styrene and its derivatives). Meanwhile, the development of more potent nitroxides has greatly expanded the number of monomers (acrylates and acrylamides) compatible with the NMP process [5]. An important advantage of surface-initiated NMP (SI-NMP) is that no further addition of metals or metal complexes is necessary. Hence, no extra purification steps are required and the likelihood of introducing impurities is also strongly limited. This specific feature is particularly attractive for applications where the purity of polymer-based materials is of high importance, such as in biomedical and electronic fields.

NMP is controlled by the persistent radical effect (PRE) [6] that can be described as follows: If we consider a diamagnetic compound (RY) that decomposes homolytically to generate two radical species at both the same time and the same rate, the PRE occurs when one of the radical species (Y[•]) is more persistent than the other (R[•]). Typically, at the early stages of the reaction, the concentrations of the



Scheme 1 Homolytic decomposition of a diamagnetic compound RY, with R[·] being transient and Y[·] persistent



Scheme 2 Mechanism of nitroxide-mediated polymerization

two radical species are strictly equivalent. However, after a short period of time some self-termination reactions of the transient radical (R[·]) are unavoidable, leading to a decrease in its concentration relative to that of the more persistent radical species. Therefore, recombination of the transient and persistent radicals becomes progressively favored, rather than self-reaction of the transient radical (Scheme 1). This specific feature of the PRE explains many highly selective radical cross-coupling processes, including the NMP process.

Hence, NMP is grounded on a reversible termination equilibrium between the propagating (macro)radical and the nitroxide (Scheme 2) [5]. Typically, the nitroxide plays the role of controlling agent and, thanks to the PRE, the growing polymer chains mainly have a (macro)alkoxyamine-based chemical structure. These (macro)alkoxyamines (the so-called dormant species) are able to cleave homolytically to yield the propagating radical and the nitroxide once again. Interestingly, this equilibrium is only ruled by a thermal process.

Initially, NMP was conducted using a bicomponent initiating system (i.e., a conventional radical initiator in the presence of a nitroxide). Obviously, this system is attractive from an economic and practical point of view. However, with a bicomponent initiating system, the polymerization kinetics and the molecular weight of the polymer chains are difficult to control. Indeed, with conventional radical initiators it is difficult to exactly determine the number of generated radicals. Moreover, compared with the radical initiator concentration, a large excess of nitroxide decreases the polymerization rate by shifting the equilibrium

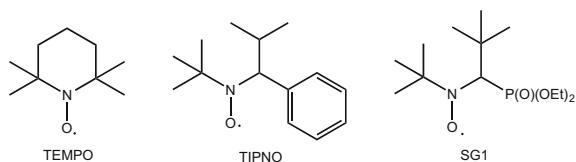


Fig. 1 Structure of nitroxides frequently used for SI-NMP. *TEMPO* 2,2,6,6-tetramethylpiperidinyl-1-oxyl; *TIPNO* 2,2,5-trimethyl-4-phenyl-3-azahexane-3-oxyl; and *SG1* *N*-tert-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide

of the propagating step towards the dormant species. To overcome these drawbacks, the use of a monocomponent initiating system is preferred. This approach consists in using an alkoxyamine that decomposes homolytically, under heating, to afford the corresponding alkyl radical as initiator and nitroxide as controller. The dissociation rate constant of the alkoxyamine is of major importance in ensuring efficient establishment of the PRE and, therefore, an efficient CRP process [5].

Typically, surface-initiated NMP is achieved by following one of two main strategies. As an example of the first strategy, a conventional radical initiator is anchored to the surface and then the polymerization reaction is performed in the presence of free nitroxide, which allows the in situ formation of (macro) alkoxyamine. In the second strategy, a preformed alkoxyamine is first attached to surface; in this case, the initiation and polymerization control proceeds from a monocomponent system. Depending on the chemical nature of the surface substrate, various strategies can be envisioned for grafting the initiator to the surface. For instance, initiator anchoring can be achieved using covalent bonding, electrostatic interaction, or even hydrogen bonding. The nitroxides frequently used for SI-NMP are TEMPO, TIPNO, and SG1 (see Fig. 1 for structures).

This review focuses on NMP initiated from the surface of different substrates such as silicon, metal oxide, carbon, and polymer. The possible architecture and composition of polymer chains grown from the surface is also discussed. Application of surfaces modified with polymer films prepared by NMP is briefly described.

2 Variation of Substrates

SI-NMP has proven efficient for the growing of polymer chains from various substrates. To reach this goal, the surface is usually modified with a suitable initiator or mediator, introduced in either a single step or via a multistep procedure.

In this section, the preparation of grafted polymer via SI-NMP from different substrates such as silicon oxide, metal oxide, metal and semiconductor, mineral clay, carbon-based materials, and polymer surfaces is discussed. For each class of substrate, the discussion focuses on the surface chemistry available for introducing functional groups that allow SI-NMP.

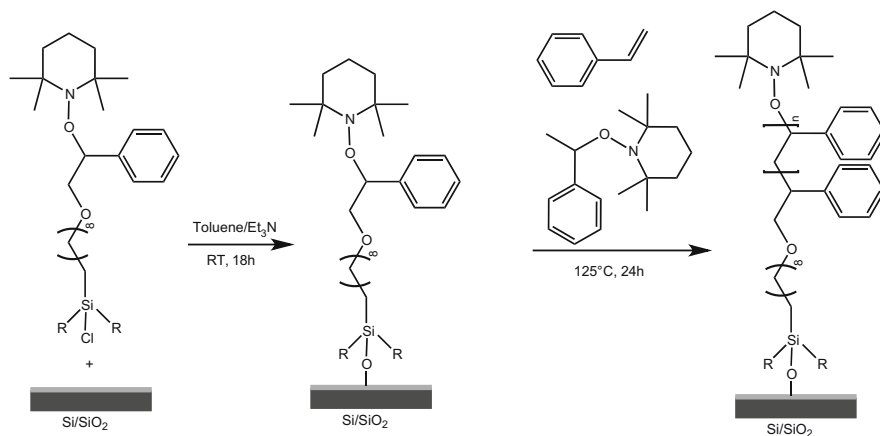
2.1 NMP from Silicon Oxide Surfaces

Silicon oxide is probably one of the most studied substrates used to graft polymer chains via NMP. Typically, silicon wafers, glass, quartz slides, porous and non-porous particles, as well as membranes are used in the SI-NMP process. To introduce a functional group that can initiate or mediate SI-NMP from silicon oxide surfaces, organosilane is often used. Prior to the grafting step, silicon oxide materials are first treated with a $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ mixture or oxygen plasma to clean the surface and optimize the number of silanol groups involved in further reaction. In this case, a thin layer of water is formed on the silicon oxide surface. The introduction of organosilane onto this surface is obtained after surface adsorption, hydration, and salinization steps. In this procedure, the silanol functions ($\text{Si}-\text{OH}$) present at the silicon oxide surface are able to undergo a condensation reaction with different types of organosilane reagents, such as $\text{R}-\text{SiMe}_2\text{Cl}$, $\text{R}-\text{SiCl}_3$, or $\text{R}-\text{Si}(\text{OMe})_3$, and $\text{R}-\text{Si}(\text{OEt})_3$, leading to siloxane bonds $\text{Si}-\text{O}-\text{Si}$ [7].

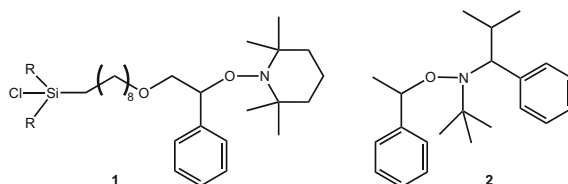
2.1.1 NMP from Silicon Oxide Planar Surfaces

The first example of polymer synthesis from SI-NMP was reported by Hawker's group [8]. The authors immobilized a TEMPO-based alkoxyamine on the surface of an oxidized silicon wafer via the reaction of chlorosilane groups present on the alkoxyamine with the silanol groups of the oxidized silicon wafer in the presence of triethylamine as catalyst. Then, polystyrene (PS) brushes were obtained from NMP of styrene. For planar substrates with low specific surface areas, such as silicon wafer in this example, the concentration of persistent radicals in the reaction medium is low because of the limited number of initiator molecules on the wafer surface. To overcome this drawback, a predetermined amount of free alkoxyamine (called sacrificial initiator) can be added to the reaction mixture to control the polymerization process (Scheme 3). Addition of this sacrificial alkoxyamine provides a sufficiently high concentration of free nitroxide in the polymerization mixture, which controls the polymer chain growth of both immobilized and soluble initiators. However, the addition of free alkoxyamine leads to the formation of non-surface-attached polymers, which have to be removed from the resulting polymer brushes. The authors found that the number-average molecular weight (M_n) and the dispersity of the grafted PS were similar to those of the free polymer chains in solution. Following this strategy, homopolymer and random copolymers grafted on surfaces were prepared with control of molar mass or thickness of the brushes (up to 80 nm), while maintaining low dispersities. The living nature of the polymerization was demonstrated by re-initiation of the end-capped chains to form the corresponding block copolymer brushes.

Following this strategy, Hawker and coworkers [9] successfully initiated the polymerization of *tert*-butyl acrylate from the surface of oxidized silicon wafer functionalized with **1** in the presence of the TIPNO-based alkoxyamine **2** and TIPNO (Scheme 4) [10]. The rapid exchange of free nitroxide between bound



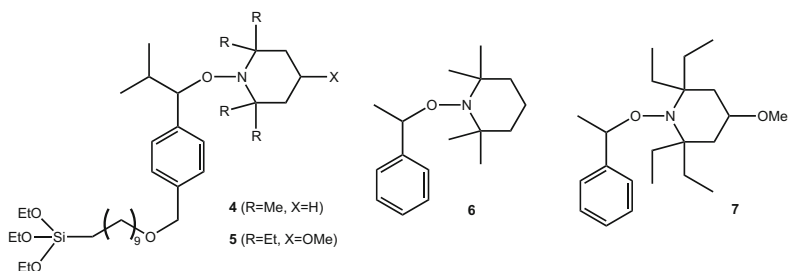
Scheme 3 Styrene SI-NMP from silicon wafer grafted with a TEMPO-based alkoxyamine



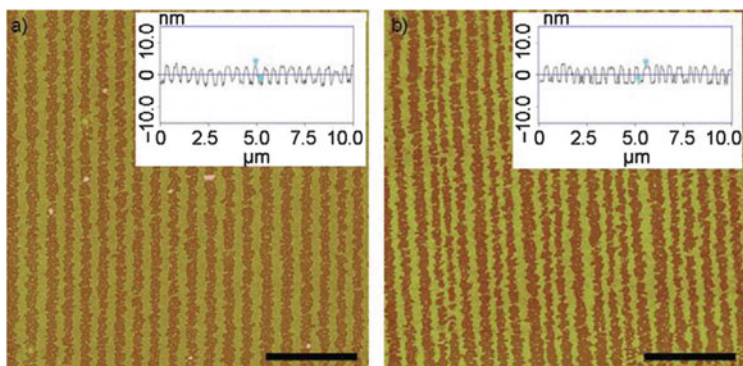
Scheme 4 Structure of alkoxyamines used for SI-NMP of *tert*-butyl acrylate on oxidized silicon wafer. Reported by Hawker and coworkers [9]

macroalkoxyamines on the surface and nitroxide in solution allowed the controlled formation of poly(*tert*-butyl acrylate) (PtBA) chains from surfaces. The thickness of polymer brushes (100–200 nm) could be controlled by varying the molar ratio of *tert*-butyl acrylate and alkoxyamine **2**. The PtBA brushes were then patterned using photolithographic techniques to yield original patterned poly(acrylic acid) chains, leading to discrete hydrophobic and hydrophilic domains.

TEMPO-functionalized silicon wafers or glass slides were also used to prepare SI-NMP-made polymer brushes on surfaces [11–19]. Chapel and colleagues employed a similar system, using an ester instead of ether linkage and triethoxysilane as reactive anchor group on a C₁₁ spacer [11, 17]. With this reactive system, molecules spread on water gradually become amphiphilic when triethoxysilane end groups are converted to trihydroxy groups. Taking advantage of this amphiphilic character, stable monolayers of various densities can be deposited by the Langmuir–Blodgett (LB) technique onto silicon wafers. Hydrolysis and/or condensation of the triethoxysilane end groups allows formation of a Si–O–Si covalent bond with the oxidized silicon wafer. Surface-initiated styrene polymerization was performed on a system with different initiator densities. In addition, immobilization of alkoxyamine initiators and subsequent surface-initiated styrene polymerization was performed on an atomic force microscopy (AFM) tip by LB transfer [12].



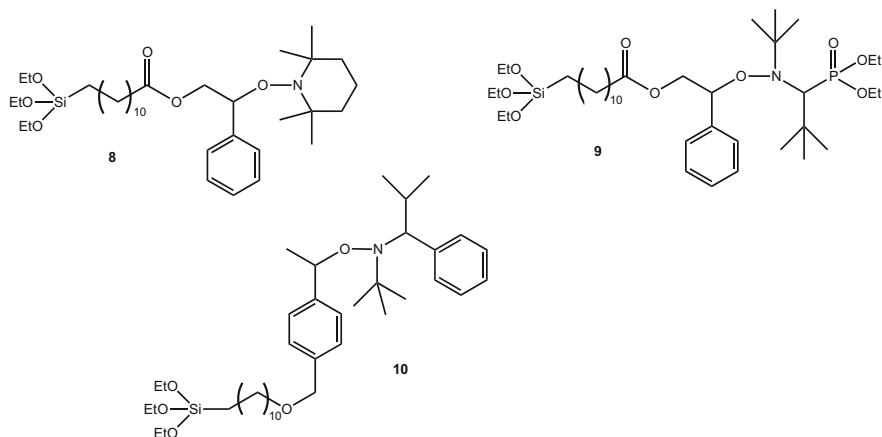
Scheme 5 Alkoxyamines and nitroxide used for SI-NMP of *tert*-butyl acrylate on oxidized silicon wafer. Reported by Studer and coworkers [16]



Scheme 6 (a) AFM image of surface after SI-NMP of styrene with **5**. (b) AFM image of surface after SI-NMPP of *n*-butyl acrylate with **5** (insets show cross-sections; scale bars: 2.5 μm). Reproduced from Brinks et al. [16] with permission from Wiley

LB lithography for spatially controlled attachment of initiator to form regular stripes of PS and poly(*n*-butyl-acrylate) (PBA) brushes was reported by Studer and coworkers [16]. Mixed monolayers of *L*-adipalmytoyl-phosphatidylcholine (DPPC) and TEMPO-derived alkoxyamines **4** or **5** (Scheme 5) were transferred by the LB technique onto oxidized silicon wafer in regular stripes with submicrometer lateral dimensions. Physisorbed DPPC was removed by washing, and NMP of styrene from the surface of silicon wafer covalently bonded to **4** was performed at 125°C for 24 h in the presence of **6** as sacrificial polymerization regulator. NMP of *n*-butyl acrylate was conducted with a surface modified with **5** in the presence of **7** at 105°C for 24 h. Polymer stripe width was controlled by the concentration of alkoxyamine in the mixed phase and adjusted from about 0.2 to 1.3 μm . The height of the stripes increased to 8 ± 0.2 nm for PS and 4.7 ± 0.2 nm for PBA (Scheme 6).

LB reactive deposition was also employed for anchoring of triethoxysilyl alkoxyamine derivatives of TEMPO **8**, SG1 **9**, and TIPNO **10** nitroxides to silicon substrates (Scheme 7) [17]. The nitroxide polarity and, therefore, the behavior of the corresponding alkoxyamine at the air–water interface of the LB trough had a

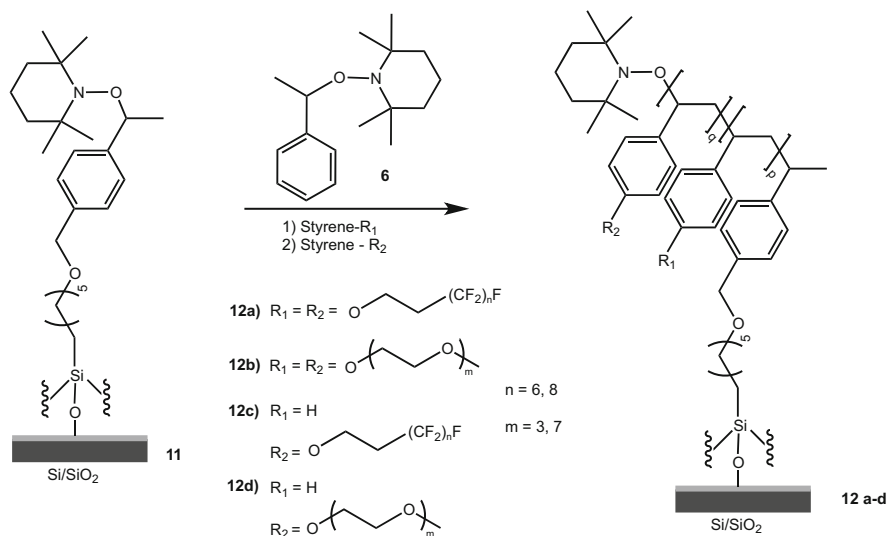


Scheme 7 Triethoxysilyl alkoxyamines derivatives of TEMPO **8**, SG1 **9**, and TIPNO **10** nitroxides

strong influence on the grafting density and the stretching of the resulting PS brushes. The TEMPO- and TIPNO-based alkoxyamines yielded relatively dense PS brushes, whereas the SG1-based alkoxyamine yielded brushes with low grafting densities and stretching as a consequence of the polar phosphorylated group.

Surface-tethered styrene-based homopolymer and diblock copolymers brushes bearing fluorinated alkyl side groups or ethylene glycol oligomers were produced with controlled chemical architecture and high coverage using SI-NMP on planar oxidized silicon surfaces [14, 15]. The silicon oxide surfaces were first modified with a chlorosilyl-functionalized TEMPO derivative (Scheme 8). In the case of diblock copolymer brushes, the second block was always detected at the polymer–air interface, as shown by angle-resolved X-ray photoelectron spectroscopy (XPS) and water contact angle measurements. Near-edge X-ray absorption fine structure (NEXAFS) analysis revealed an orientation of fluorinated side chains that could be correlated with surface stability upon exposure to water. Surface grafted with oligo (ethylene glycol)-containing polymer brushes possessed a superior ability to inhibit protein and cell adhesion compared with surface assemblies with deposited oligo (ethylene glycol).

Tethered alkoxyamines were also obtained in situ following a two-step procedure. First, 3-(trimethoxysilyl)propyl methacrylate (TSPMA) was attached to the surface. Then, the methacrylate function was allowed to react, under heating, with AIBN in the presence of TEMPO to afford the corresponding alkoxyamines. From this alkoxyamine-coated silicon, PS and poly(2-hydroxyethyl methacrylate) (HEMA) were then successfully prepared [20]. The novelty of this report is that micropatterning of the silicon surface was controlled by a combination of SI-NMP and SI-ATRP. The ATRP initiator was covalently immobilized via UV-induced hydrosilylation of 4-vinylbenzyl chloride (VBC) with the (hydrofluoric acid-etched) hydrogen-terminated silicon (Si–H) microdomains to produce a micropatterned and Si–C bonded VBC monolayer.

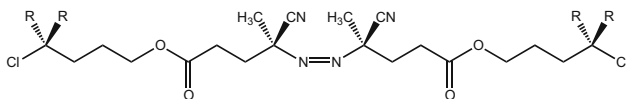


Scheme 8 Synthesis of surface-grown styrene-based homopolymer and diblock copolymer brushes bearing fluorinated alkyl side group and ethylene glycol oligomer

Recently, Studer and coworkers [19] prepared polymer brushes bearing α -hydroxyalkylphenylketone moieties as photoreactive polymer backbone using SI-NMP with **11**. Photoreactive polymer brushes (with thickness up to 60 nm) can undergo Norrish type I photoreaction upon irradiation to give surface-bound acyl radicals, which are trapped with functionalized nitroxides to give the corresponding acylalkoxyamines. This post-polymerization modification provided functionalized polymer brushes bearing cyano, poly(ethylene glycol), perfluoroalkyl, and biotin moieties.

Vapor phase polymerization from SI-NMP of various vinylic monomers resulted in polymer brushes with greater thicknesses than those formed by the solution phase process [21]. To explain this result, the authors supposed a more efficient reaction on the surface as a result of prolongation of the mean path of vaporized monomers in a vacuum, higher thermal energy of the monomer, and the possibility of adjusting the reaction parameters independently. Thin films of PS grafted polymer, poly(acrylic acid) (PAA), poly(2-hydroxypropyl methacrylamide) (PHPMA), and poly(*N*-isopropylacrylamide) (PNIPAM) were prepared with thicknesses of a few nanometers to submicrometers. This process was also used for the preparation of block copolymers (e.g., PS-*b*-PAA and PAA-*b*-PS-PHPMA). It is important to mention that solution phase polymerization of AA, HPMA, and NIPAM is impossible with TEMPO-based alkoxyamines.

SI-NMP can also be carried out using an initiator/nitroxide bimolecular system [22]. In this strategy, an azo-based initiator functionalized with chlorosilyl groups was first attached to the silicon wafer after immersion of the substrates in a toluene solution containing the azo derivatives. The formation of PBA brushes with thickness of 4–14 nm using two different azo initiators (AMCI and ATCI) was performed



Scheme 9 Chemical structure of the chlorosilyl derivatives of azo initiators ATCl ($R=Cl$) and AMCl ($R=CH_3$)

in the presence of SG1 as controlling agent (Scheme 9). Elaboration of block copolymers by re-initiation of PBA growth from macromolecular chains grafted on a flat substrate with different monomers was also achieved.

Recently, SI-NMP using a bimolecular system was applied to the preparation of PS brushes. In this study, the initiator sites were generated from the silicon wafer surfaces by treating the latter with hydrogen plasma at atmospheric pressure [18]. According to the authors, the dissociation of molecular hydrogen in gas phase collisions produces hydrogen plasma, which can react with surface sites and surface-adsorbed water to form surface-activated sites. Precise control of plasma treatment time and radio frequency power allows a dense surface coverage of radical initiators to be obtained, from which vinyl monomers can combine to form surface-grafted polymer chains. Growth of PS film was thus achieved in the presence of TEMPO and exhibited a linear increase with respect to time, resulting in a polymer layer thickness of 28 nm.

2.1.2 NMP from Silicon Oxide Particle Surfaces

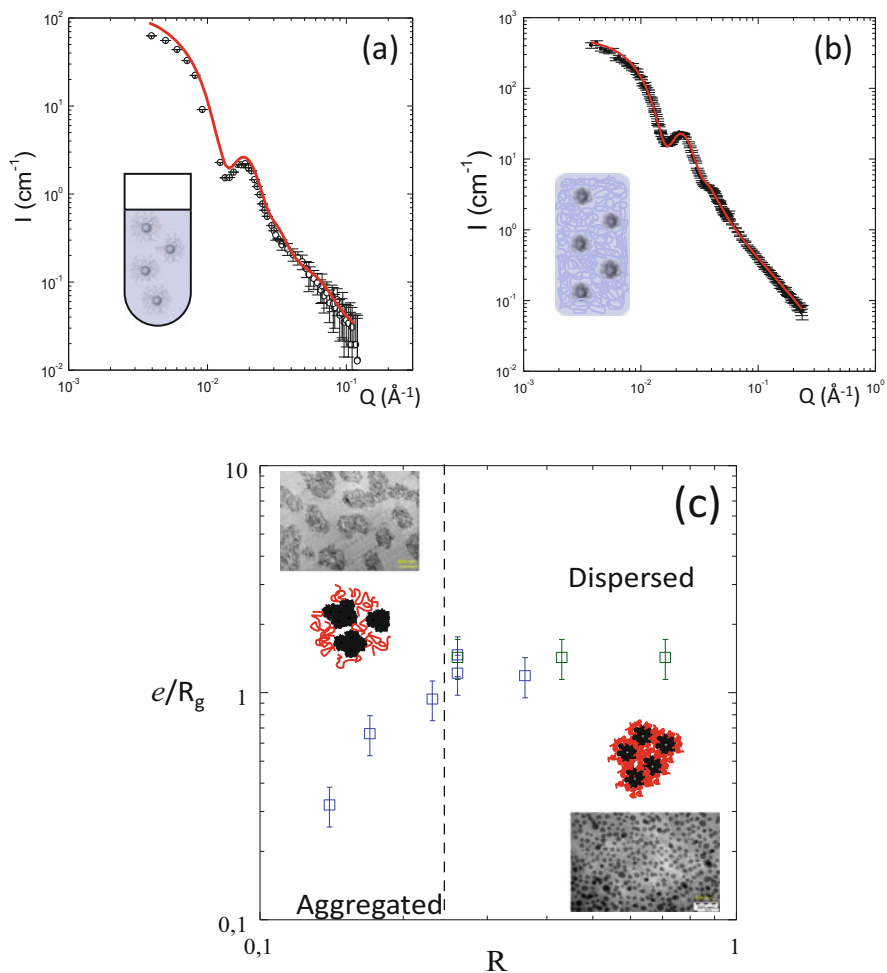
Synthesis

SI-NMP from silicon oxide surfaces has not been confined to planar surfaces, but has also been extended to colloidal supports as well as particle surfaces. As with silicon oxide planar surfaces, the most convenient strategy for introducing initiator onto the SiO_2 particle surfaces is to first graft functional alkoxyamines on their surfaces and then perform the polymerization reaction. A number of TEMPO, TEMPO-derivative, TIPNO, or SG1-based alkoxyamines bearing trichlorosilane ($-SiCl_3$), trimethoxysilane [$-Si(OMe)_3$], and triethoxysilane [$-Si(OEt)_3$] as the functional group have been prepared. A complete review of SI-NMP from SiO_2 particle surfaces has been recently published [5]. Chain conformation is a crucial factor in determining the macroscopic properties (solution, gel, composite, thin film, etc.) of the final grafted nanoparticle system. NMP enables the preparation of well-defined grafted silica nanoparticles. Therefore, control of polymerization opens the way to probe the conformation of the grafted chains at the surface of the nanoparticles and to analyze whether this conformation is affected by grafting as a function of various parameters such as the molecular mass of the grafted chains, grafting density, solvent quality, nature and shape of the surface (surface curvature), and interactions of nanoparticles in solution.

Conformation of Grafted Polymer Chains

Numerous works have been carried out on spherical grafted brushes to predict the conformation of grafted chains using theory [23, 24] and/or numerical simulations [25, 26]. Experimental validation is limited to a small number of techniques for evaluating the typical size of the grafted chain: rheology for the viscosimetric radius R_η , dynamic light scattering (DLS) for the hydrodynamic radius R_h [27, 28], and small angle X-ray or neutron scattering (SAXS or SANS) for the radius of gyration R_g . Viscosimetric or DLS measurements give a total value (including the nanoparticle size) that can be affected by nanoparticle concentration or nanoparticle aggregation and/or percolation. The accuracy of such determinations can be improved using SANS combined with neutron contrast variation, enabling direct determination of the radius of gyration of the grafted chains by matching the scattering of the core particles while controlling the colloidal stability of the solution by determination of interparticle structure factors. In solution, contrast variation is simply performed by adjusting the ratio of hydrogenated and deuterated solvent to obtain the desired values of neutron scattering length density for both the particle and the grafted polymer. This was first described by Chevigny et al. [29] for silica nanoparticles grafted with PS chains. The efficiency of the polymerization was improved by adding free initiator at the beginning of the reaction. At the final stage, free polymer chains were removed by ultrafiltration. The grafted brushes were finely characterized by fitting the SANS curves with different models (core-shell and Gaussian chain mode) to extract the physical parameters of the grafted brushes: number of chains per particle, molecular mass, and radius of gyration of the grafted chains. An example of such a curve is given in Scheme 10a.

A significant feature of the curve is the decrease in intensity as a function of scattering vector (Q^{-2}) for the high Q region, indicating that the grafted chains are still Gaussian. The extension of the grafted layer $h = 2R_{g \text{ grafted}}$ was ~ 1.30 times larger than the corresponding Gaussian chain in theta solvent ($2R_{g \text{ bulk}}$, with $R_{g \text{ bulk}} = 0.275 M_w^{0.5}$), as determined by size-exclusion chromatography (SEC) after the cleaving process. This indicates stretching of the chain at the surface of the particle. Such a stretching, which can be explained by excluded volume interactions with lateral neighboring chains, has been described by Alexander in terms of scaling laws of the grafting density [24]. For a layer grafted on a planar surface, the extension of the grafted layer is expected to be $h = a_0 N^{1/3}$ for a good solvent and $h = a_0 N^{1/2}$ for a theta solvent, where a_0 is the monomer length and N the number of monomers. In addition, the effect of surface curvature $r_0^{2/5}$ has to be taken into account; it reduces the extension of the grafted layer to $h = N^{1/2} \sigma^{1/2} r_0^{2/5}$ for the case of theta solvent [26]. Replacing free initiator by controller (SG1) in the reaction enables variation of the molecular mass of the grafted chain in the range 5–50 kg. mol⁻¹ [32]. Whatever the N value, a systematic agreement is found between the extension of the grafted brush deduced from the fitting analysis $h = 2R_{g \text{ grafted}}$ and the theoretical prediction derived from the scaling law $h = N^{1/2} \sigma^{1/2} r_0^{2/5}$. Genevaz and colleagues (unpublished results) have recently adapted the previous NMP protocol to the grafting of a diblock copolymer P*t*BA-*b*-PS at the surface of silica



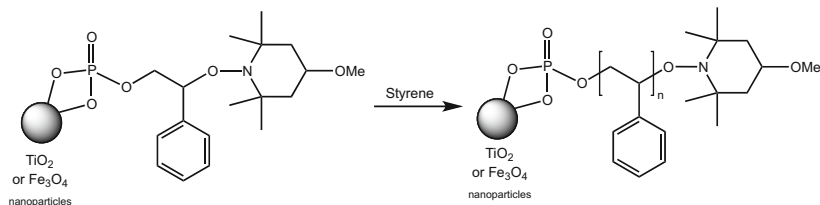
Scheme 10 (a) SANS curve of silica nanoparticles with PS-grafted brush in solution (*black dots*) and the corresponding fitting calculation (*red line*). From Chevigny et al. [29]. (b) SANS curve of silica nanoparticles with PS-grafted brush in melt (*black dots*) and the corresponding fitting calculation (*red line*). From Chevigny et al. [30]. (c) Variation of the grafted brush conformation as a function of the nanoparticle dispersion in the host polymer matrix. From Chevigny et al. [31]

particles by associating dynamic light scattering (DLS) and SANS. The motivation of this work was to make spherical brushes with an interface of tunable dynamics using a combination of a block (PtBA) with low glass transition temperature (T_g) and a block (PS) with high T_g . They showed that the diblock conformation behaved in the same way as the homopolymer chain and that the grafting had no influence on the chain extension when the chain is close to the Kuhn length. Robbes et al. [33] grafted PS chains on magnetic nanoparticles (maghemites, $\gamma\text{-Fe}_2\text{O}_3$) using NMP. In contrast to the silica “single sphere” particles, in solution maghemites form linear

clusters of three to four primary particles from which the PS chains grow under controlled polymerization. It is possible to directly probe the influence of surface curvature on the extension of the grafted chains for a given grafting density and under theta solvent conditions; indeed, the extension of the grafted chain ($h = 18$ nm) was found to be intermediate between the pure spherical case ($h = 11$ nm) and the pure plan geometry ($h = 44$ nm). Regarding the question of the conformation of grafted chains in solution, it is interesting to look at the corresponding conformation in nanocomposites when spherical brushes are mixed with identical free chains. This was probed by Chevigny et al. [30] using a statistical hydrogenated–deuterated PS matrix that matched the particle scattering in SANS experiments; the silica becomes invisible to neutrons in the matrix, and only the deuterated corona contributes to the signal. The resulting curve (presented in Scheme 10b) was perfectly fitted by a Gaussian model and showed partial collapse of the grafted brushes from solution (12 nm) to film (6 nm), corresponding to a wet–dry transition driven by entropy mixing between the grafted and free chains. By varying the dispersion state of the nanoparticles inside the matrix, the same authors [31] demonstrated a second transition from partial to complete collapse of the spherical brushes, associated with the formation of compact aggregates inside the film (Scheme 10c).

2.1.3 NMP from Porous Silicon Oxide

In comparison with colloidal particles such as silica or planar surfaces such as silicon wafer, SI-NMP from ordered mesoporous silica (OMS) has been much less investigated. Alongside the usual issues of SI-CRP from dense substrates, such as initiator and deactivator concentration or initiator efficiency, the porous nature of OMS (high specific surface area, high porous volume, pore morphology, pore diameter, and pore connectivity) brings to the system new complexity, such as diffusion of reactants in a confined space. The first SI-NMP from OMS was performed by Lenarda et al. at the inner surface of MCM-41 mesoporous silica [34]. Typically, the MCM-41 silica was modified following a three-step grafting procedure: first, reaction with 3-aminopropyltriethoxysilane, then terephthaloyl chloride, and finally 1-hydroxy-2-phenyl-2-TEMPO-ethane. The styrene polymerization was shown to occur inside the mesoporous silica channels. It should be mentioned that partial filling of the pores decreased the surface area of the MCM-41 silica without destroying its structural and morphological characteristics. More recently, the SI-NMP of styrene was performed from various types of ordered mesoporous silica particles with different morphologies and pore sizes, using an SG1-based alkoxyamine derived from BlocBuilder MA initiator [35]. Whatever the pore morphology and pore size, the polymerization kinetics were similar in all cases, but with important differences in the molar mass distribution. The authors showed that for good diffusion of the reactants, large pore sizes of 5 nm were adequate and that the porous morphology of the particles is of high importance, particularly pore connectivity.



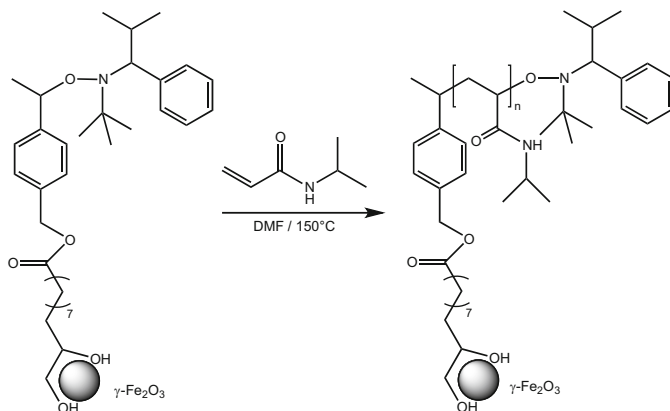
Scheme 11 Polymerization of styrene on metal oxide nanoparticles

2.2 NMP from Metal Oxide Surfaces

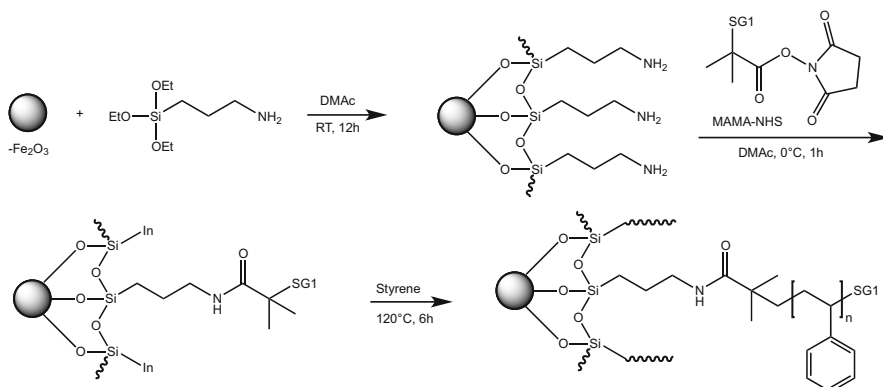
SI-NMP from metal oxide surfaces is mainly performed from previously modified titanium or iron oxide substrates. Titanium oxide (TiO_2 , $d = 15$ nm) and magnetite (Fe_3O_4 , $d = 10$ nm) nanoparticles chemically modified with 4-methoxy-TEMPO-based alkoxyamine by a phosphonic acid group were utilized by Takahara and coworkers for the preparation of PS (Scheme 11) and poly(3-vinylpyridine) (P3VP) brushes [36–40]. The grafting densities of PS chains on TiO_2 particles were estimated to be 0.04–0.28 chains nm^{-2} whereas those on Fe_3O_4 particles were 0.12–0.2 chains nm^{-2} . Functionalized nanoparticles showed stable dispersibility in good solvents of PS without losing their physical properties. In the case of P3VP-modified magnetite, the particles gave a stable dispersion in good solvents thanks to pyridinium formation through either protonation of the pyridine rings with an acidic solution or quaternization with an aqueous solution of iodomethane [40].

In a similar procedure, Binder et al. used a TIPNO-based alkoxyamine bearing a 1,2-diol function for its attachment onto iron oxide. This system was used for the preparation of core-shell Fe_2O_3 nanoparticles with a well-defined PNIPAM shell (Scheme 12) [41]. The polymerization reaction was performed in *N,N*-dimethylformamide (DMF) at 150°C . Under these conditions, monomer conversion reached 90% and experimental M_n was $5,600 \text{ g mol}^{-1}$. Poly (4-vinylpyridine) (P4VP) brushes were prepared by SI-NMP on the surface of 3-methacryloxypropyltrimethoxysilane (3-MPS)-modified magnetite nanoparticles with an average diameter of 30 nm. The NMP-made P4VP polymer brushes were obtained at 130°C using 4-hydroxyl-TEMPO free radical as controlling agent and benzoyl peroxide (BPO) as initiator [42].

Recently, an efficient three-step grafting-from procedure was developed to obtain well-controlled PS grafted magnetic $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles [33]. In the first step, after modification of the surface charge of the nanoparticles and then replacement of H_2O by dimethylacetamide (DMAc), 3-aminopropyl triethoxysilane (APTES) was allowed to react with the surface. The corresponding amino-modified nanoparticles were then reacted with MAMA-NHS alkoxyamine (Scheme 13) to afford nanoparticles functionalized with SG1-based alkoxyamine. In the last step, polymerization of styrene was performed from the previously modified nanoparticles. The grafting-from strategy was also used to graft poly [styrene-*co*-(maleic anhydride)] (PSMA) chains from the Fe_3O_4 nanoparticle



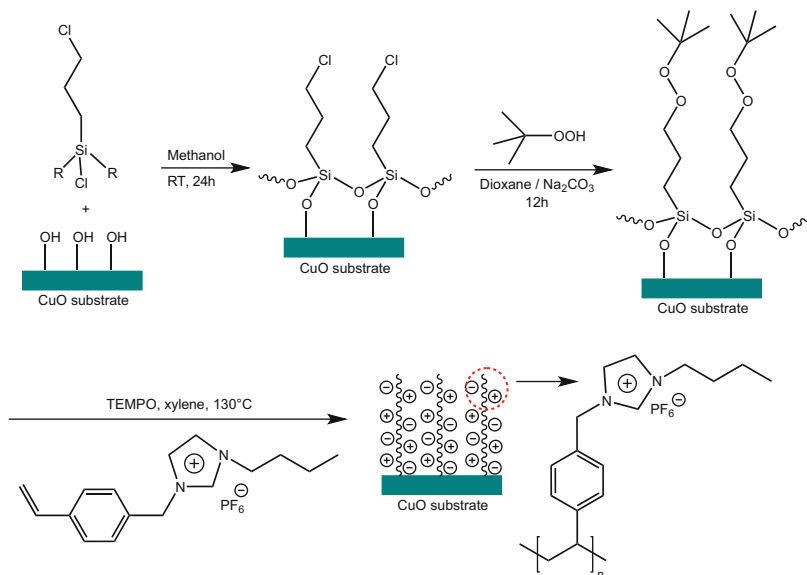
Scheme 12 Grafting-from of *N*-isopropyl acrylamide from the surface of γ - Fe_2O_3 nanoparticles attached to TIPNO-based alkoxyamine bearing a 1,2-diol



Scheme 13 Grafting-from strategy for preparation of well-defined PS-grafted magnetic γ - Fe_2O_3 nanoparticles

surface with TEMPO moieties [43]. For this, TEMPO was first immobilized onto Fe_3O_4 nanoparticles by the nucleophilic substitution reaction between 1-oxo-2,2,6,6-tetramethylpiperidinium bromide (TEMPO-Br) and hydroxyl groups on the Fe_3O_4 surfaces. In the second stage, PSMA- Fe_3O_4 was synthesized using TEMPO-immobilized Fe_3O_4 in the presence of styrene and maleic anhydride. Free TEMPO was also present in the system to enhance control of polymerization.

There has been only one report describing SI-NMP from a metal oxide other than those of titanium and iron, namely from a copper oxide surface [44]. In this study, poly(ionic liquid) was grafted onto micro/nanoscale CuO/Cu surfaces by bimolecular-initiated polymerization with TEMPO nitroxide. For this purpose, the peroxide groups were first introduced onto micro/nanoscale CuO surfaces by reaction of 3-chloropropyltrimethoxysilane (immobilized on the CuO surface) with

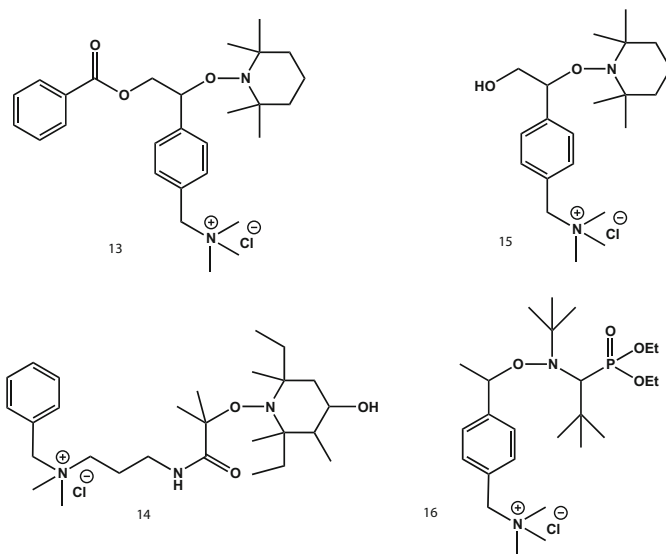


Scheme 14 Process of poly(ionic liquid) growth at CuO surface

tert-butyl hydroperoxide. Polymerization of 1-(4-vinylbenzyl)-3-butylimidazoliumhexafluorophosphate, an ionic liquid monomer, from the peroxide-activated CuO surface in the presence of TEMPO led to the formation of polymer brushes (Scheme 14).

2.3 NMP from Clay Mineral Surfaces

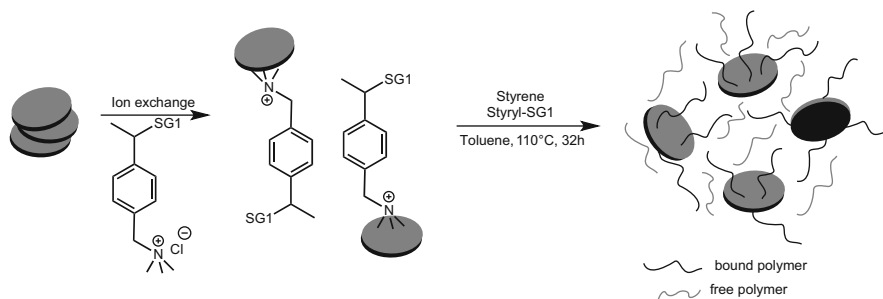
The main approach for immobilization of functional groups that can initiate or mediate SI-NMP on clay mineral surfaces is based on noncovalent electrostatic interactions. Indeed, clay minerals present the ability to exchange cations in the interlayer spacing with other ionic species present in solution. Sogah and coworkers were the first to report an efficient approach for the direct synthesis of dispersed SI-NMP-made silicate nanocomposites. Typically, they performed an intergallery polymerization via a montmorillonite (MMT)-anchored TEMPO-based alkoxyamine initiator bearing a benzyltrimethylammonium **13** (Scheme 15) moiety [45]. Other alkoxyamines bearing cationic groups were also attached on MMT surfaces. A cationic alkoxyamine **14** based on 2,6-diethyl-2,3,6-trimethyl-piperidine-4-hydroxy-*N*-oxyl nitroxide was directly intercalated into MMT layers. PBA chains were then grown, exhibiting tunable M_n in the 1,000–14,000 g mol⁻¹ range and a dispersity of 1.5, allowing facile re-dispersion of the resulting composite in apolar solvents [46]. In another example, a three-step procedure was proposed by Shen et al. for grafting PS chains on the surface of MMT [47]. The first step



Scheme 15 Structure of cationic alkoxyamines used for SI-NMP from clay surfaces

consisted in attaching 2-methacryloyloxy ethyl trimethylammonium chloride to the surface of MMT by an ion-exchange reaction. Then, the alkoxyamine-functionalized MMT was reacted with the previously introduced methacrylate function in the presence of BPO and TEMPO at 90°C. PS chains with controlled M_n and low dispersity were then successfully grown from the MMT surface by SI-NMP. Polystyrene-*block*-polycaprolactone (PS-*b*-PCL) diblock copolymers were also grafted to MMT surfaces in one-step in situ living polymerization from a silicate-anchored bifunctional initiator based on TEMPO **15** (Scheme 15) via divergent chain growth [48]. Recently, Paulis et al. performed SI-NMP of methyl methacrylate (MMA)/butyl acrylate using modified MMT macroinitiator [49]. The macroinitiator was synthesized by NMP of vinylbenzyl trimethylammonium chloride, MMA, and styrene at 90°C using Blocbuilder MA as alkoxyamine. The obtained macroinitiator of 1,000 g mol⁻¹ was exchanged with the sodium cations of MMT to yield surface-modified reactive MMT. SI-NMP of MMA/butyl acrylate from reactive MMT surfaces allowed exfoliation of the clay. The composite was then used as master batch in the mini-emulsion polymerization of MMA/butyl acrylate.

A similar strategy has been used to allow SI-NMP from other clay minerals such as laponite [50] and saponite [51]. In the case of laponite, a SG1-based alkoxyamine bearing an ammonium group **16** (Scheme 15) was first immobilized by cation exchange (Scheme 16) [50]. Then, PS chains were obtained from its surface in the presence of a sacrificial alkoxyamine initiator to afford composites exhibiting improved colloidal stability in inorganic solvent. Transmission electron



Scheme 16 SI-NMP of styrene from laponite clay platelets

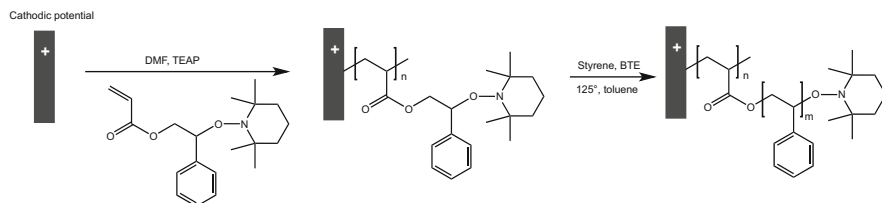
microscopy (TEM) performed on these samples demonstrated a completely exfoliated structure of the clay tactoids within the polymer matrix.

Alternatively, different reports describe the immobilization of free-radical initiators carrying cationic groups on mineral clay surfaces for subsequent SI-NMP of vinylic monomers performed in the presence of an efficient nitroxide mediator [52–55]. For example, Mittal reported the immobilization of 4,4-azobis(4-cyanovaleric acid)-based initiator bearing long alkyl chains and two cationic groups for subsequent SI-NMP of lauryl methacrylate in the presence of SG1 [52]. The same approach was employed by Billon and coworkers for the preparation of (co) polymer/mica composites [53–55]. Mica SI-NMP proceeds in two steps: (1) mica surface modification via ion exchange of 2,2-azobis(isobutyramidine hydrochloride) as a free-radical initiator bearing a cationic moiety, and (2) SI-NMP of butyl acrylate performed from the initiator-bound mica in the presence of free SG1 nitroxide. In the case of copolymer/mica composites, polymerization of butyl acrylate followed by polymerization of a mixture of styrene and a modified alizarin dye monomer were performed. Although control was lost during the polymerization of the second block, colored diblock copolymer/mica composites were indeed obtained [54]. Interestingly, the colors of poly(styrene-*co*-alizarin)/mica composites were strongly related to both the adsorption density of macromolecular chains on the mica surface and the dye content [55].

Besides noncovalent interactions, covalent immobilization has also been used to link TEMPO-based alkoxyamine bearing a trichlorosilane group onto a magadiite interlayer surface [56]. SI-NMP of styrene from the radical initiator immobilized on magadiite occurred in a controlled manner. Moreover, the fine dispersion state of magadiite in the PS matrix contributed to an increase in the thermal stability of PS.

2.4 NMP from Metal and Semiconductor Surfaces

As a result of their conduction properties, metallic surfaces are particularly attractive materials. Jérôme and coworkers reported a two-step procedure to



Scheme 17 Two-step grafting-from strategy using electrochemistry

functionalize steel with polymer brushes [57]. The electrografting of an inimer to an acrylate bearing a TEMPO-based alkoxyamine moiety on the ester group was used for the preparation of polyacrylate brushes. After the electrografting process, SI-NMP of styrene was performed in the presence of a free-radical initiator (Scheme 17). Grafted PS chains were removed from the surface under acidic hydrolysis. The restored metal substrate was then used for further electrochemical reactions. A similar procedure was also applied to stainless steel surfaces [58]. To this end, the electrografting of poly[2-phenyl-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)-ethyl acrylate] (PPTEA) onto stainless steel was first carried out and then followed by the NMP of 2-(dimethylamino ethyl)acrylate and styrene or *n*-butyl acrylate, initiated from the electrografted polyacrylate chains in the presence of a TIPNO-based alkoxyamine. In order to impart antibacterial properties to the obtained materials, quaternization of the grafted copolymers was then performed. Jérôme and coworkers also reported an electrochemical approach based on the simultaneous electrodeposition of silver and the electrografting of polymer chains grafted onto stainless steel and used as a cathode [59]. This strategy allowed the synthesis of poly(ethyl acrylate), PPTEA, and poly(8-quinolinyl acrylate). Hence, silver-immobilized polymer films having antibacterial properties were efficiently prepared in a single step.

A colored polymer/aluminum hybrid pigment was synthesized by NMP initiated from the surface of aluminum flakes [60]. The latter were coated with a thin silica layer. In this case, the chemical grafting of the initiator was performed through silylation reactions. The initiator used was an SG1-based alkoxyamine functionalized with an alkoxy silane moiety. This compound was previously prepared from the intermolecular radical 1,2-addition of Blocbuilder MA in the presence of 3-(trimethoxysilyl)propyl acrylate. Styrene or *n*-butyl acrylate were then copolymerized with vinyl dye monomer in a controlled manner.

Many reports related to SI-CRP on metal describe the use of gold nanoparticles and mainly from SI-ATRP. We note only one report describing the modification of gold nanoparticles with SI-NMP. In this report, the NMP initiator was a TEMPO-derivative functionalized with disulfide as ligand for the synthesis of gold nanoparticles [61]. Two populations of gold nanoparticles, of 1.5 and 5.5 nm diameter, covered with PS of $10,000 \text{ g mol}^{-1}$ were prepared.

Similarly, CdSe nanoparticles have been functionalized using ligand exchange reactions [62]. The nanoparticles were stabilized by the tri-*n*-octylphosphine oxide

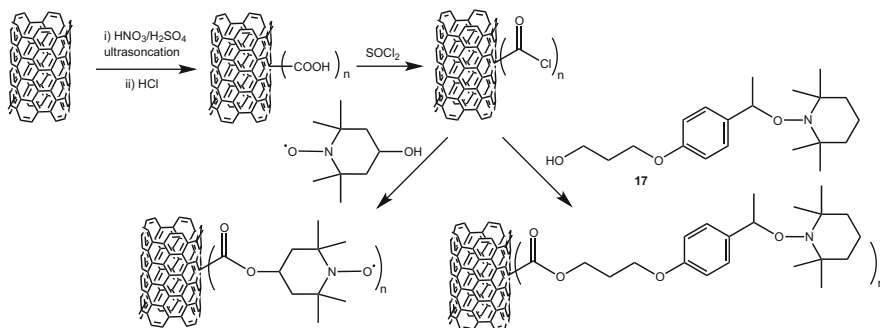
ligand. TEMPO-based alkoxyamines containing phosphine groups were introduced to CdSe nanoparticles following a ligand-exchange strategy. First, the tri-*n*-octylphosphine oxide ligand was replaced with pyridine, followed by exchange with the appropriate alkoxyamine. From the surface of functionalized CdSe nanoparticles, PS and poly(styrene-*co*-MMA) copolymers were efficiently obtained.

2.5 NMP from Carbon Surfaces

Carbon-based materials have attracted wide interest in the materials science community for decades. These materials are extremely light and versatile. Indeed, depending on the local bonding of the constituting carbon atoms, their properties can be easily tuned. Diamond, carbon black, and graphite are well-known examples of carbon-based materials; more recently discovered allotropes are fullerenes, carbon nanotubes (CNTs), and graphene. Of these carbon-based materials, CNTs are particularly studied because of their unique electronic, mechanical, thermal, and chemical properties. To target specific applications, a number of experiments have focused on the chemical modification of CNTs [63], including the use of CRP techniques [64]. SI-NMP involves first attaching either an alkoxyamine moiety or a nitroxide to the CNT surfaces, or the in situ synthesis of an alkoxyamine.

In order to facilitate anchoring of an initiator at the surface of CNTs (and carbon in general), these substrates first need to be treated. For instance, carboxylic acid groups can be introduced to single-walled nanotubes (SWNTs) and multiwalled carbon nanotubes (MWNTs) by oxidation of the pristine nanotubes in the presence of HNO₃ or H₂SO₄/HNO₃. The corresponding acid chloride derivatives are then obtained by action of thionyl chloride in the presence of carboxylic acid-functionalized CNTs. Introduction of the initiator/controller agent is finally performed by esterification of 4-hydroxy TEMPO [65] or TEMPO-based alkoxyamine bearing a hydroxyl group with acid chloride-functionalized CNTs [66–68] (Scheme 18). Conventional radical polymerization of styrene, initiated by AIBN or simple heating, in the presence of nitroxide-carrying CNTs provided CNT–PS conjugates [65]. CNTs functionalized with TEMPO-based alkoxyamine **17** were used to perform SI-NMP of different monomers such as styrene, 4-vinylpyridine, and styrene sulfonate (SS). The resulting MWCNT–PS and MWCNT–PS-*b*-P4VP exhibited relatively good dispersibility in various organic solvents [66], whereas MWCNT–P4VP presented good dispersibility in acidic aqueous solutions. MWCNT–PSS composites afforded stable dispersions in aqueous solutions over a large pH range [67]. In addition, SI-NMP of butyl acrylate and *N,N*-dimethylacetacetamide (DMAAm) were also successfully performed from CNTs [69].

In addition to the modification of oxidized CNTs, another strategy consists in performing radical addition reactions onto the carbon–carbon double bond of CNTs, allowing introduction of specific groups able to initiate or mediate



Scheme 18 Synthesis of carbon-nanotube-supported TEMPO nitroxide or TEMPO-based alkoxyamine initiator

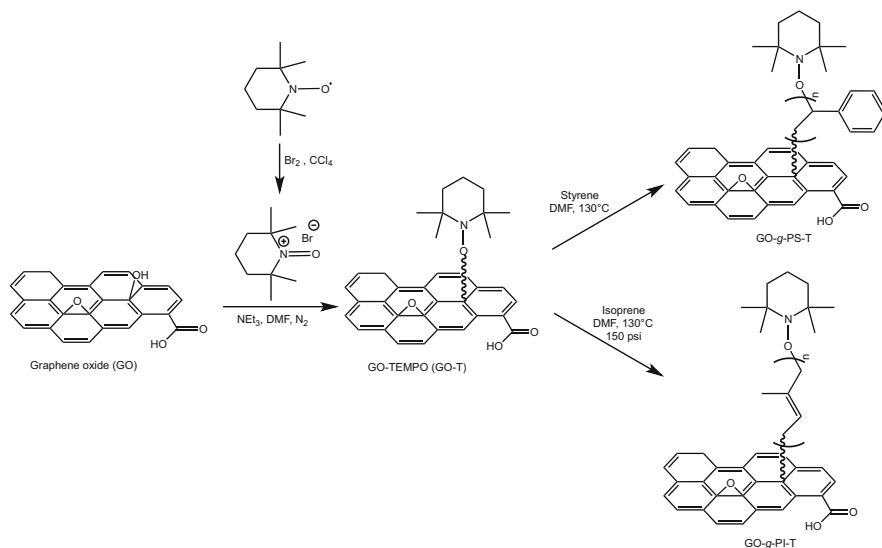
SI-NMP [70, 71]. For instance, heating of nitrogen-doped CNTs in the presence of both dibenzoyl peroxide and TEMPO afforded the corresponding alkoxyamine-modified CNTs. The SI-NMP of styrene then provided PS brushes [70].

Graphene is considered one of the most important materials of the next 20 years. Indeed, this material combines several outstanding properties never observed before in a single material, such as remarkably high electron mobility at room temperature [72], tunable band gap [73], high strength [74], and transparency [75]. Because of these features, even unmodified graphene is a good candidate for several applications. The incorporation of graphene into polymers has attracted attention not only as a route to original materials exhibiting structural and functional properties superior to those of the pure components, but also to previous nanocomposite systems obtained with other nanofillers. Modification of graphene with grafted polymer chains was recently reviewed by Salavagione et al. [76] and Layek and Nandi [77]. Only one report describes SI-NMP from a graphene surface [78]. In this study, graphene oxide-*g*-polystyrene and graphene oxide-*g*-polyisoprene were synthesized using a two-step procedure involving (1) application of an oxoammonium salt (TEMPO-Br) to modify the surface of graphene oxide with TEMPO, and (2) styrene or isoprene graft polymerization from the TEMPO-functionalized graphene oxide surface (Scheme 19).

2.6 NMP from Polymer Surfaces

Synthetic and natural polymers are also used as substrates for SI-NMP. The two principal strategies used to modify polymer substrates are (1) direct attachment of initiators to a polymer surface bearing suitable functional groups, and (2) in the case of inert polymers, appropriate treatment or activation to introduce functional groups prior to anchoring of the initiator.

Merrifield polymer resins are often used as substrates for polymer brush synthesis using NMP. To achieve this, TEMPO is reduced with sodium ascorbate,



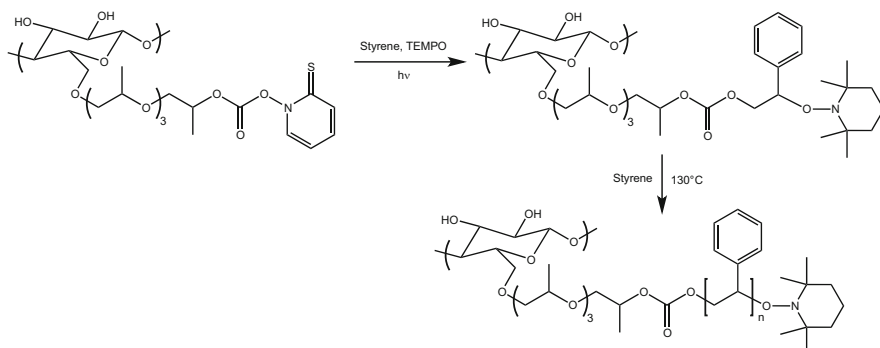
Scheme 19 Preparation of TEMPO-Br and subsequent functionalization of graphene oxide (GO) to graphene oxide-TEMPO (GO-T) and graft polymerization of styrene and isoprene from GO-T

deprotonated, and then allowed to react with the benzyl chlorides of the resin to covalently bind TEMPO via an ether linkage [79]. The immobilized alkoxyamine can then be used for preparation of PS-based polymer brushes [80–82].

SG1 nitroxide was attached to latex particles made of poly(styrene-*co*-chloromethylstyrene) of 60 nm diameter previously prepared via atom transfer radical addition [83]. Microspheres grafted with the homopolymer poly(2-dimethylamino ethyl acrylate) (PDMAEA), as well as block copolymers poly(styrene-*b*-DMAEA) and poly(butyl acrylate-*b*-DMAEA) were prepared by SI-NMP in DMF at 112°C , with the initial addition of free SG1 to ensure polymerization control.

The N-terminus of peptide sequences obtained from solid phase synthesis was transformed into a carboxylic acid group by the action of glutaric anhydride. NMP initiator tethered to the N-terminus of the peptide was then introduced via reaction of the benzylic amine of a fluorine-labeled alkoxyamine with the previously modified peptide. The peptide-supported initiator was then used to create block copolymers, under conditions that promote sequential NMP of *tert*-butyl acrylate and methyl acrylate [84].

Natural polymers such as cellulose and natural rubber were also subjected to SI-NMP. NMP was the first living radical polymerization method to be used in cellulose grafting. Daly et al. [85] reported the first use of nitroxide-mediated, controlled radical grafting from cellulose and cellulose derivatives. Controlled radical grafting from hydroxypropyl cellulose (HPC) was performed using TEMPO monoadducts, formed from the HPC–Barton carbonate derivative



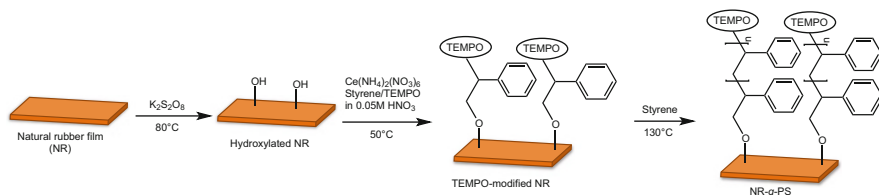
Scheme 20 NMP-mediated controlled radical grafting from hydroxypropyl cellulose

(carbonates of *N*-hydroxypyridine-2-thione) (Scheme 20). Photolysis of this derivative in the presence of styrene and TEMPO provided an adduct. Heating the macroinitiator at 130°C provided styrene–HPC graft copolymers. An increase in grafted polymeric chain length with increasing polymerization time was observed. The dispersity of the PS grafts ranged from 1.3 to 1.5.

Natural rubber (NR) in the form of a solid film was modified by grafting with PS using TEMPO as nitroxide mediator in an SI-NMP process [86]. The attachment of TEMPO on the NR substrate was carried out in a two-step process (Scheme 21). The first step was to introduce active functional groups for transformation into radical species. For this, hydroxylation of the NR substrate by thermal decomposition of potassium persulfate was chosen. In the second step, the hydroxyl group of the hydroxylated NR was dissociated with the aid of ceric ions and transformed into an active alkoxy radical, which reacted with styrene and then TEMPO. The resulting rubber was a TEMPO-modified NR, which was then used for PS grafting from the NR surface (Scheme 21). The authors showed that by using either the “optical slicing” or “z-scanning” approach, a “homogeneous grafting” of about 30 mol% PS occurred inside the bulk NR substrate.

3 Conclusion

Many results in the literature demonstrate that SI-NMP is a powerful way to control chain length, distribution, and composition of a large range of polymers grafted onto various organic and inorganic surfaces. Thanks to this approach, a wide variety of materials finding application in fields of major importance such as coatings, compatibilizing agents, electronics, and biomaterials have been successfully prepared. The main advantage of SI-NMP is that this technique does not require any addition of metal or metal salt. However, despite the development of efficient strategies to obtain NMP-grafted polymer on surfaces, there is still room to improve the SI-NMP process. Indeed, the synthetic procedures used to anchor alkoxyamine



Scheme 21 Synthesis of polystyrene grafted onto the surface of natural rubber using SI-NMP

on the surface often require multistep pathways. Moreover, in order to reach a good level of control, polymerization reactions have to be performed in the presence of free alkoxyamine as sacrificial initiator. These points will have to be addressed in order to push further the development of SI-NMP. In the future, SI-NMP initiated photochemically could also be an attractive way of grafting polymer chains onto surfaces.

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