DOI: 10.1002/masy.200950915

Progress in Controlled Grafting-From by Nitroxide Chemistry

Enrique Saldívar-Guerra,[*1] José Bonilla-Cruz,[1,2] Brenda Hernández-Mireles,[1]
Grisel Ramírez-Manzanares[3]

Summary: A number of substrates (polymers and silica) have been functionalized with nitroxide moieties in order to obtain alkoxyamine groups along the substrate. The functionalized substrates have been further heated in the presence of monomers in order to grow controlled grafts by the grafting – from technique. Tested substrates include polybutadiene (PB), polyisoprene (PI), styrene – isoprene (SIS) and styrene – butadiene (SBS) tri-block copolymers, EPDM, poly (dimethyl-siloxane) (PDMS), poly(ethylene glycol) and silica. Two chemical paths involving nitroxide chemistry have been used for the functionalization step and are discussed in this work. In the first path, the substrate is heated in the presence of a nitroxide radical (N) and a radical initiator (I) or using only nitroxide. In the second path, useful for substrates containing hydroxyl groups, the functionalization of the substrate is obtained using an N-oxoammonium TEMPO bromide salt in the presence of triethyl amine, which forms a peroxide group linked on one end to the substrate and on the other end to the TEMPO moiety. The mechanisms, structures and the resulting polymers (functionalized and grafted) have been studied by GPC, spectroscopic techniques and transmission electron microscopy.

Keywords: graft copolymers; nitroxide mediated polymerization

Introduction

In the last 2 decades a number of patents[1] describing polymer modification or controlled grafting of polymeric substrates via nitroxide mediated radical polymerization (NMRP) have been published. These techniques are very useful for the synthesis of polymers with functional groups or for the facile synthesis of polymeric structures that would be difficult to obtain by other routes. The applications include the synthesis of otherwise commodity polymers with improved properties, or specialty polymers such as compatibilizers, impact modifiers, dispersants, etc. The CSIRO patents[1a] describing the pioneer use of alkoxyamines for controlled polymerization contain a first example of these procedures; they showed the controlled growth of methyl acrylate grafts on a polybutadiene backbone. During the last fifteen years, patents using variations of these techniques were issued by several companies: e.g. Dow[1b] and Atofina issued patents for applications related to the technology for the production of high impact polystyrene (HIPS) and Ciba[1c,1d] issued two patents covering a broader range of grafted polymers. The standard procedure for the grafting of polymeric substrates via nitroxide chemistry involves two steps: 1) functionalization of the polymeric substrate with nitroxide moieties in order to form a multifunctional macroalkoxyamine and, 2) growth of grafts from the alkoxyamine sites in the polymer backbone by heating the macroalkoxyamine in the presence of monomer.

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[1] Centro de Investigación en Química Aplicada, Blvd. Enrique Reyna 140, Saltillo, Coahuila, México
E-mail: esaldivar@ciqa.mx

[2] Centro de Investigación en Materiales Avanzados, Monterrey, N.L. México

[3] CID, Centro de Investigación y Desarrollo Tecnológico, SA de CV. Av. de los Sauces 87 Mza 6, Lerma 52000, Edo. de México, México

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Naturally, the patents do not address fundamental scientific problems related to this technique, such as the mechanisms of functionalization and the resulting chemical structures, the efficiency of functionalization, the contribution and importance of side reactions (crosslinking and b-scission), the kinetics of graft growth and the morphology of the grafted copolymer. Our group has been working in this field for several years and in this paper we summarize some of our findings regarding these fundamental aspects with an emphasis on still unpublished results.

Functionalization and Grafting by NMRP

As mentioned above, the grafting-from of polymeric substrates via NMRP involves two steps: 1) functionalization of the polymeric substrates with nitroxide moieties and 2) growth of grafts from the alkoxyamine sites.

Functionalization step. This can be done in three different ways:

1. Bimolecular process using a nitroxide radical and a free radical source, usually a organic peroxide (Route A in Figure 1). A mixture of the polymeric substrate, a nitroxide radical and a free radical source are heated up to the temperature of free radical generation by the radical source. Radicals that are prone to hydrogen abstraction, such as *tert*-butylic radicals, are preferred. After hydrogen abstraction on the polymeric backbone a free radical is formed which is trapped by the nitroxide radical forming an alkoxyamine site.
2. Monomolecular process via an alkoxyamine. In this case, the polymer to be grafted is put in contact with an alkoxyamine R-ONx and the mixture is heated up to the temperature at which the alkoxyamine releases nitroxide radicals. The radical R creates radical sites at the polymer backbone, most likely by allylic hydrogen abstraction,[2] and these radicals are trapped by the nitroxide radical generating a multifunctional macroalkoxyamine.
3. Monomolecular process via a nitroxide radical (Route B in Figure 1). It is known that at certain conditions the nitroxide radicals are capable of undergoing hydrogen abstraction.[3,4] Recently we have shown that the monomolecular process can be performed by using a nitroxide radical instead of an alkoxyamine; however, the necessary conditions (high molar ratios of nitroxide to substrate and long reaction times) make this technique of little practical use and rather of scientific interest.

The techniques that use a nitroxide radical are shown schematically in Figure 1.

Experimental Part

Functionalization. Several polymeric substrates, most of them containing an unreacted double bond at each monomeric unit (polydienes), have been functionalized and further grafted with polystyrene or poly (styrene-co-maleic anhydride) grafts. In order to remove antioxidants before the functionalization step, commercial polymeric substrates were first purified by dissolution in a solvent, followed by precipitation with an excess of methanol and drying. The polymeric substrates used include low and high molecular weight polybutadiene (Aldrich, Mn = 5,000, PDI = 1.1 and Dynasol Elastomers, Mn = 170,000, respectively), EPDM (Keltan 4703 of DSM, $M_n = 105{,}500$, PDI = 1.98, 9%-wt. diene monomer) and butyl rubber (copolymer of poly(isobutylene-co-isoprene), Exxon Butyl 268, Mn = 192,000, PDI = 2.4, 1.5% mol of isoprene units). 2,5-Dimethyl-2,5-di(t-butylperoxy) hexane (DTBH) and *tert*-butyl peroxy benzoate (Akzo) were used as radical initiators. The nitroxides utilized include 4-oxo-2,2,6,6- tetramethyl-1-piperidinyloxy (4-oxo-TEMPO), 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (4-hydroxy-TEMPO), and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO). Styrene (St, 99+%), and maleic anhydride (MA) from Aldrich were used as received. Solvents toluene (Aldrich) and xylene (JT Baker) were also

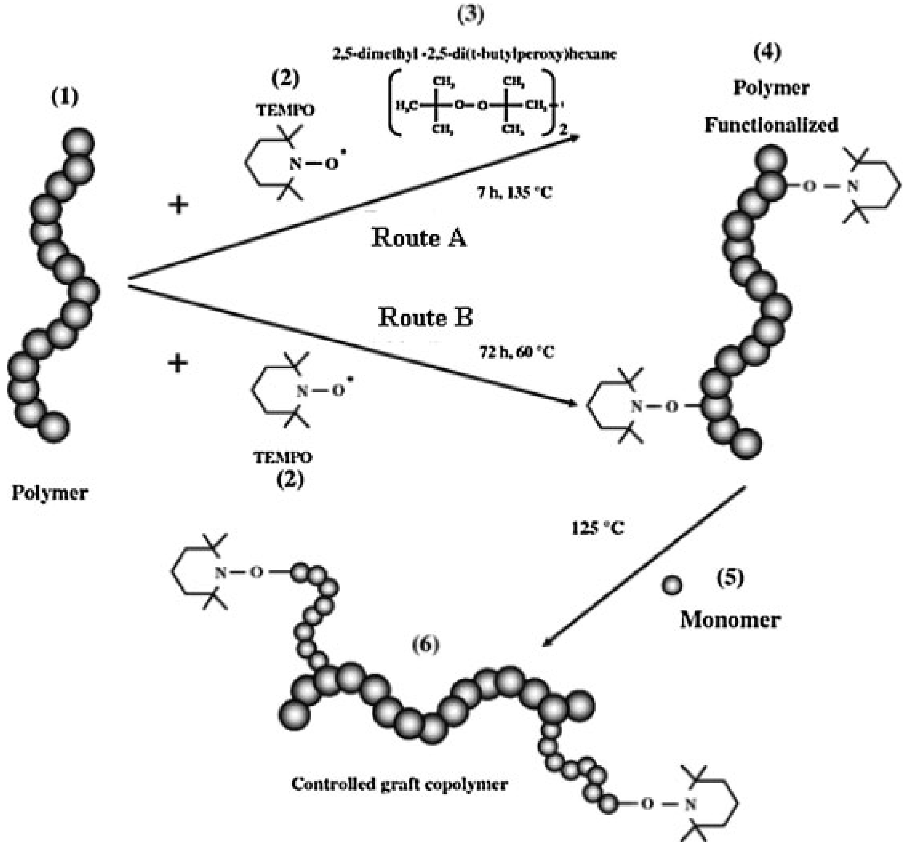

Figure 1.
Procedures for nitroxide functionalization of a polymeric substrate. Route A is a bimolecular process involving a nitroxide radical and a radical initiator. Route B is a monomolecular process involving only a nitroxide radical (an alkoxyamine can be used instead of the nitroxide radical).

used as received. In a typical functionalization experiment 10 g of the polymeric substrate were dissolved in 90 mL of toluene and heated at 90–120 °C depending on the initiator used. The nitroxide radical was added in the initial mixture in a molar ratio calculated in order to generate a given number of nitroxide groups attached per rubber molecule. Typical ratios used were 5 to 10 moles of nitroxide per mol of polymer. The initiator amount was calculated in order to obtain a molar ratio of 1.3 to 2.7 moles of nitroxide per mole of initiator.

The initiator was added dropwise throughout the reaction in order to minimize crosslinking reactions. Typical reaction times were 4–6 h. After functionalization, the polymer was recovered by precipitation with methanol and purified by two or three cycles of dissolution and re-precipitation and characterized by proton nuclear magnetic resonance (^{1}H-NMR), Fourier transform infrared spectroscopy (FTIR) and gel permeation chromatography (GPC).

Grafting. Functionalized rubber was dissolved in a monomer mixture (with or without solvent) and then heated up to the reaction temperature (125 to 135 °C). The reaction mixture was kept at this temperature with agitation for at least 8 hours. Typical reaction conditions consisted of 10 to 33 wt. % of functionalized polymer in the monomer mixture (free of solvent). In some cases solvent was added to the reaction mixture in order to form a solution of 15 wt. % of solids (monomers at total conversion plus rubber) with respect to the solvent.

Results and Discussion

Functionalization. ^{1}H-NMR and FTIR have been used to demonstrate the presence of nitroxide groups attached to the polymer backbone after the functionalization procedure. To this end, nitroxides containing hydroxyl groups, carbonyl groups or other groups giving characteristic spectroscopic signals are preferred for the functionalization step (such as 4-OH-TEMPO or 4-OXO-TEMPO).[2,5] ^{1}H-NMR spectroscopy can also provide a quantitative measure of the level or efficiency of functionalization achieved. For example, polybutadiene grafted with TEMPO or 4-OXO-TEMPO shows, among others, characteristic resonances at 1.10–1.17 and 2.5, corresponding to methyl and methylene groups in the piperidinic ring, respectively. The integration of the area corresponding to those signals leads to the quantification of efficiency of functionalization, which can be defined as:

$$\%Efficiency = \frac{moles\ Nitroxide\ in\ substrate}{initial\ charge\ moles\ Nitroxide} * 100$$

Typical grafting efficiencies obtained are in the range 50–80%. The functionalized polymers have also been characterized by GPC. Most of the functionalized polymers show a slight shift of the whole molecular weight distribution (MWD) towards higher molecular weights (MW), which can be attributed to an increase in the hydrodynamic volume of the polymer with respect to the virgin polymer. New tails present in the MWD after functionalization are presumably due to branching and incipient crosslinking reactions (high MW end) or to β-scission (low MW end). In order to avoid or minimize crosslinking reactions, the level of solids in the functionalization step must be restricted to relatively low values (at most 10–33% wt.-%) depending on the MW of the substrate. The higher the MW of the substrate the lower the solids concentration allowed in the functionalization solution in order to avoid crosslinking. For a given MW there is a critical polymer concentration of the functionalization solution above which catastrophic crosslinking (gelation) will occur.

Figure 2 shows GPC traces for virgin and functionalized EPDM with two different nitroxides (4-OXO-TEMPO and TEMPO). Both functionalized EPDM's show a slight shift of the MWD towards higher MW's and illustrate the typical behavior of most polymeric substrates after functionalization.

In a variation of this procedure it is possible to generate a chemically-functionalized polymer by growing short grafts of functional monomers, or by replacing the nitroxide moieties in the backbone by a functional monomer that does not homopolymerize (such as maleic anhydride) or homopolymerizes slowly. In this respect, controlled functionalization via NMP has some advantages over reactive extrusion procedures: i) better control of the level of functionalization (number of functional groups per chain) and ii) (in most cases) no degradation of the original chains. However, in the case of butyl rubber, under some reactions conditions, it has been observed that the process of nitroxide functionalization results in a shift of the MWD towards lower MW due to scission reactions. This is usually undesirable if the mechanical or rheological properties of the polymer are to be maintained at some level after functionalization (with functional groups different from nitroxide) or grafting.

With respect to the mechanism of functionalization, spectroscopic evidences (^{1}H-NMR) are consistent with allylic hydrogen abstraction as the most likely mechanism for nitroxide functionalization in the case of polybutadiene,[2] although other mechanisms, such as addition to the double bond followed by hydrogen abstraction, are also feasible.[6] Several side reactions, such as scission, branching and crosslinking, are usually present in some extent, depending on the reaction conditions and the structure of the substrate.

Grafting

Figure 3 shows GPC traces for the grafting of styrene on a 4-OXO-TEMPO functiona-

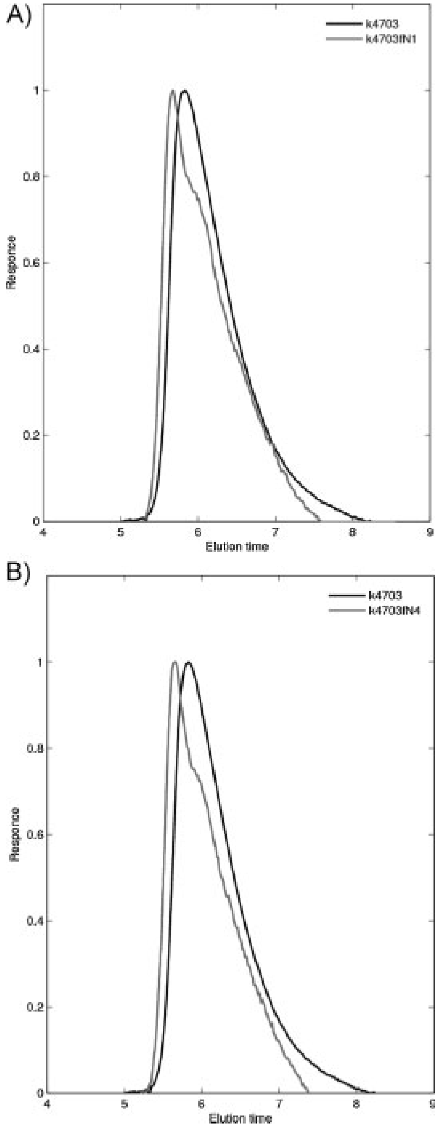

Figure 2.
GPC traces of a EPDM substrate (K4703, DSM) before and after functionalization with 4-OXO-TEMPO (K4703fN1, Fig. A) and TEMPO (K4703fN4, Fig. B).

lized polybutadiene and for the grafting of styrene and maleic anhydride on virgin EPDM (control experiment) and on EPDM substrates functionalized with two nitroxides (4-OXO-TEMPO and TEMPO).

The gradual shift of the MWD towards higher MW observed in Figure 3D, corresponding to the 4-OXO-TEMPO functionalized polybutadiene substrate, is typical of the controlled grafting of polymeric substrates and it is essentially different from the shifting pattern shown by systems growing grafts without the mediation of controlling species, such as high impact polystyrene.[2,5,7] Due to the thermal autoinitiation exhibited by styrene and by the system styrene-maleic anhydride,[8] free polymer (or copolymer) will be formed simultaneously to the grafted chains and this polymer will also grow in a controlled fashion given the presence of the alkoxyamine sites along the polymer backbone. The situation is analogous to that occurring when styrene is polymerized in the presence of an alkoxyamine. In the latter, as the polymerization proceeds and more chains are formed by thermal autoinitiation, there will be more dead chains and the control of the polymerization will gradually deteriorate; therefore, if controlled growth of the grafts is desired, care should be taken of achieving a good balance between the total amount of alkoxyamine sites and the expected number of chains started by thermal autoinitiation (which increases with time and temperature of reaction).

The grafting reaction in the case of EPDM substrates shows a more complex behavior than in the polybutadiene case, suggesting the presence of side reactions (scission) at the beginning of the grafting procedure. This phenomenon, evidenced by the appearance of a new peak in the MWD in the region of low MW leading to a bimodal MWD, occurs for both, the virgin (Figure 3A) and the functionalized EPDM's (Figure 3B, C), suggesting that it is not due to the presence of the nitroxide moieties, and it is rather a consequence of the reaction conditions. The GPC traces corresponding to longer reaction times (> 200 min) in Figure 3B and C seem to indicate that the chains belonging to the two peaks in the MWD grow grafts and shift towards higher MW's. This explanation is speculative as the grafted polymer is mixed with free polymer which was not separated from the final material, making it difficult to

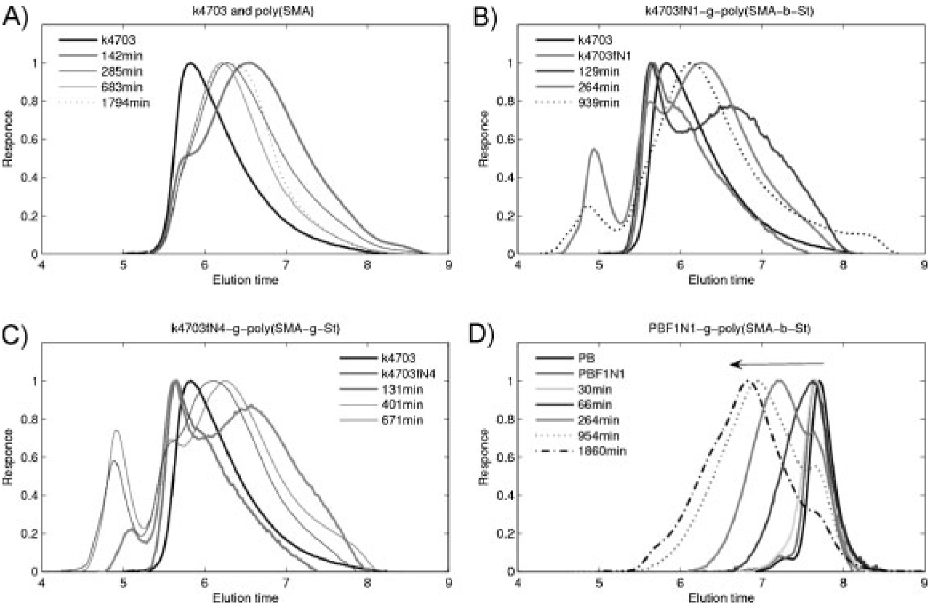

Figure 3.
GPC traces corresponding in each graph to virgin, nitroxide-functionalized and S-MA grafted polymeric substrates at different times of the grafting reaction. Figure 3A corresponds to EPDM Keltan 4703 (DSM) without functionalization (control experiment). Fig 3B and 3C correspond to EPDM Keltan 4703 with 4-OXO-TEMPO and TEMPO respectively. Figure 4D belongs to low MW polybutadiene with 4-OXO-TEMPO.

interpret the results.[1] It should be possible to grow grafts of monomers that do no exhibit thermal autoinitiation, such as butyl acrylate, if a proper nitroxide is utilized (SG1 or second generation Ciba nitroxides). Work in this direction is underway in our laboratory.

In order to estimate the grafting efficiency, defined as the fraction of alkoxyamine sites in the polymer substrate that end up growing a grafted chain, it is necessary to characterize the number of branches in the polymer. This is considerably more difficult to estimate than the functionalization efficiency. It can be attempted by ^{13}C NMR, but the associated signals will be difficult to detect except for cases in which the number of branches per number of carbons in the backbone of the chain is relatively high. We have also used GPC measurements with viscometric and light scattering detectors (in addition to the refractive index detector) but the experimental conditions required by the theory for the application of this technique (Zimm-Stockmayer)[9] are difficult to meet in the case in which the chemical nature of the grafts is not the same as that of the polymer backbone. In this case it is necessary to find a solvent for which the dn/dc (derivative or refractive index with respect to concentration) is the same (or very similar) for both homopolymers. By using this technique with a rough approximation to the required conditions, we have been able to estimate an efficiency of grafting of around 40% for the grafting of polybutadiene with styrene, a value which is relatively low; however, this figure corresponds to a low molecular weight polybutadiene (Mn = 5000) with an average of 6.5 alkoxyamine groups along the polymer backbone, conditions that may result in steric hindrance that avoids the complete

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[1] It is possible to separate the grafted from the free polymer; however, this requires special techniques such as liquid adsorption chromatography.

utilization of all the potential grafting sites. Studies with higher MW substrates and with model polymers in which the Zimm-Stockmayer theory is strictly applicable (for example grafts of polyisoprene on a polyisoprene substrate) should help to get a better assessment of the potential of these techniques for the precise synthesis of grafted polymers.

Kinetics of grafting. As mentioned above, the grafting reaction of styrene on a polymeric backbone functionalized with alkoxyamine moieties is kinetically analogous to the thermal autopolymerization of styrene in the presence of a low molecular weight alkoxyamine. This is demonstrated in Figure 4, in which the evolution of the logarithmic conversion of styrene with time of reaction is plotted for three different cases: i) grafting of virgin polybutadiene (PB-ST), ii) grafting of functionalized polybutadiene (PBF-ST) and iii) autoinitiated thermal polymerization of styrene (ST).

The data corresponding to controlled and uncontrolled grafting are overlapped and show slightly slower kinetics than the styrene autopolymerization. Equation (1), first derived by Fukuda[10] and Matyjaszewski[11] describes the logarithmic conversion of a nitroxide controlled polymerization under the assumption of quasi-equilibrium for the living and dormant species and for nitroxides with relatively low equilibrium constant, such as TEMPO and TEMPO derivatives. For these nitroxides the rate of polymerization is independent of the concentration of alkoxyamine, and is described by equation (1)

$$Ln\left(\frac{1}{(1-x)}\right) = k_p\left(\frac{R_i}{k_t}\right)^{1/2} t \qquad (1)$$

Where x is the fractional conversion of monomer, R_i is the rate of initiation (mol $L^{-1}s^{-1}$), k_p and k_t are the propagation and termination rate coefficients ($Lmol^{-1}s^{-1}$) respectively and t is time in s.

The data show that the grafting reactions follow a nearly linear behavior, consistent with a constant concentration of living polymer, which is a necessary but not sufficient condition for a living/controlled polymerization. On the other hand, the thermal autopolymerization of styrene deviates from linearity at moderate conversions, behavior which is attributed to the gel effect (diffusion control of the termination step) given the high molecular weight species present in this case.

In general, in order to assess the level of control in the graft growth, the detailed characterization of the branches is required, which, as mentioned above, is a challenging task. A further complication arises in those cases in which free polymer (due to autoinitiation) is generated during the grafting reaction. In the latter, the separation of free from grafted polymer must be done first, either by two-dimensional chromatographic techniques (chromatographic cross-fractionation)[12] or by dissolution/precipitation techniques with selective mixtures of solvents. Once the grafted polymer is isolated, and in some cases where the branches can be cleaved off the main chain and analyzed separately, a detailed assessment of the level of control is possible. This can be done, for example, by chemically digesting the backbone of the chain in the case of polybutadiene. By using this technique we have measured polydispersities of 1.4–1.5 for polystyrene grafts in polybutadiene previously functionalized with 4-OXO-TEMPO.[2]

Morphology. The level of grafting (number and length of grafts), together with the molecular weight of the substrate, has a marked influence on the morphology of the resulting graft copolymer, ultimately affecting mechanical, optical, transport and other properties of the polymer, and determining its suitability for specific applications. In principle, the morphology of graft copolymers could be predicted by Field-Theoretic Computer Simulation (FTCS) methods,[13] related to Dynamic Density Functional Theory (DDFT), but these calculations are not trivial and may be very computationally demanding. Figure 5 shows transmission electron microscopy micrographs of polybutadiene substrates of low and high molecular weight, functio-

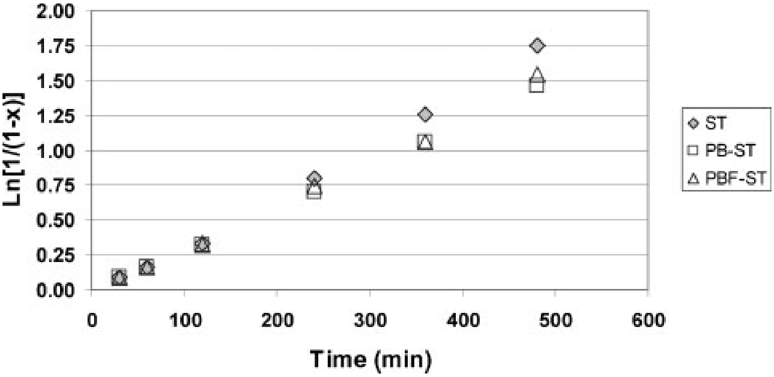

Figure 4.
Kinetics of styrene polymerization/grafting: i) autopolymerization (ST); ii) in the presence of non-functionalized low MW polybutadiene (PB-ST), and iii) in the presence of nitroxide-functionalized low MW polybutadiene (PBF-ST, controlled grafting). Reactions were run in bulk at 125 °C with a wt. ratio of 10/90 polybutadiene/styrene (cases ii and iii).

nalized with different levels of nitroxide. Figure 5A, corresponding to a low molecular weight PB (5,000) and low level of functionalization, exhibits a lamellar morphology. Figure 5B and C correspond to a high molecular weight polybutadiene with high and low levels of functionalization, respectively. For a low level of functionalization the salami morphology typical of a HIPS is obtained, indicating that the additional grafting induced by the alkoxyamine sites does not have a significant influence in the morphology. On the opposite, for a high level of functionalization the morphology obtained is of core-shell type, as more interfacial area can be stabilized by the additional grafting.

Applications. Grafted copolymers with controlled architecture can be used in a number of applications, such as advanced thermoplastics, impact modifiers, compatibilizers, etc. Graft copolymers of butyl rubber with grafts of styrene – maleic anhydride copolymer (SMGBR) or functionalized butyl rubber with single maleic anhydride groups replacing the alkoxyamine moieties along the chain (maleated butyl rubber, MBR), have been prepared and they are being tested in different applications. In one case, SMGBR and MBR have been used as impact modifiers in blends of these materials with nylon 6, showing good results. In another case, these materials have been used as coupling agents in the dispersion/exfoliation of nanoclays (Cloisite 20 A) in a matrix of butyl rubber in order to increase the gas impermeability of butyl rubber. This last application is an alternative to the use of bromo butyl rubber for the exfoliation of nanoclays in a butyl rubber matrix, that has been recently reported.[14] The grafting or functionalization of butyl rubber via nitroxide chemistry is a challenging application of these techniques since butyl rubber contains a low number of remaining double bonds (coming from the copolymerization of isobutylene with small amounts of isoprene). Current work of our group in this application will be published soon.

Grafting from surfaces. In a variation of the nitroxide chemistry discussed so far for the controlled grafting or functionalization of substrates, we have also synthesized polymer grafts of styrene – maleic anhydride from a silica surface using a two-step procedure. In the first step (schematically shown in Figure 6) the silica surface (or any other substrate containing –OH groups) reacts in mild conditions (25–50 °C) with a solution of a TEMPO N-oxoammonium bromide salt (TEMPO bromide salt for short) (1) in

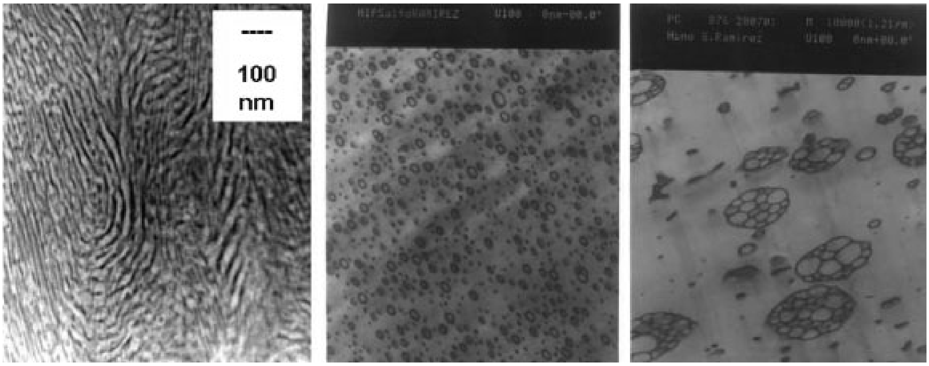

Figure 5.
Transmission electron microscopy micrographs of: i) low MW PB with high level of functionalization (left); ii) high MW PB with high level of functionalization (center) and iii) high MW PB with low level of functionalization (right).

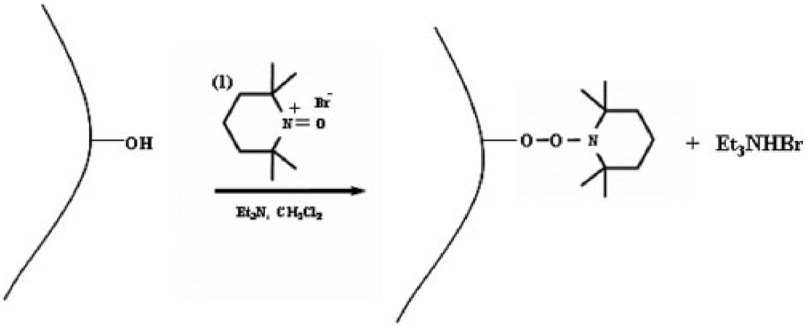

Figure 6.
First step of nitroxide functionalization of a surface or substrate containing –OH groups. The substrate is put in contact with a solution of TEMPO bromide salt and reacts in mild conditions (25–50 °C) forming a peroxide group linked to the surface on one side and to a TEMPO moiety on the other.

CH_2Cl_2 in the presence of tri-ethyl amine (Et_3N). This forms a peroxide group linked to the surface on one side and to the nitroxide group on the other side. In a second step the functionalized surface is heated in the presence of monomer, the peroxide bond splits into an initiating radical attached to the surface and a nitroxide radical, so the radical attached to the surface propagates generating a graft whose growth is controlled by the nitroxide radical released. This novel reaction is at present being studied in our lab in order to understand the underlying mechanism and to improve the yield. More work using this synthetic strategy is under way on other surfaces and on polymeric substrates containing –OH groups.

Conclusions

Grafting-from techniques using nitroxide chemistry is a powerful tool for the design of advanced polymeric materials with a specific architecture. It is possible to achieve some level of control on the number and length of the grafts, although more detailed characterization is needed before a better assessment of the level of synthesis precision and control that can be achieved with these tools can be done. The commercial availability of nitroxide radicals and new synthetic routes using nitroxide chemistry offer a good potential for the commercial application of these techniques.

[1] [1a] US 4 581 429 (**1986**), CSIRO: D. H. Solomon, E. Rizzardo, P. Cacioli; [1b] US 5 721 320 (**1997**), The Dow Chemical Company: D. B. Priddy, I. Q. Li; [1c] US 6 521 710 (**2003**), Ciba Specialty Chemicals Corporation: M. Roth, R. Pfaendner, P. Nesvadba; [1d] US 6 525 151 (**2003**), Ciba Specialty Chemicals Corporation: M. Roth, R. Pfaendner; [1e] WO2009/065774A1 (**2009**), Ciba Holding Inc.: E. Saldívar-Guerra, G. Luna-Bárcenas, J. Ramírez-Contreras, J. Bonilla-Cruz, R. Pfaendner.

[2] J. Bonilla-Cruz, E. Saldívar-Guerra, J. R. Torres-Lubián, R. Guerrero-Santos, B. López-Carpy, G. Luna-Bárcenas, *Macromol. Chem. Phys.* **2008**, *209*, 2268.

[3] T. J. Connolly, J. C. Scaiano, *Tetrahedron Lett.* **1997**, *38*, 1133.

[4] E. Saldívar-Guerra, J. Bonilla, G. Zacahua, M. Albores-Velasco, *J. Polym. Sci. A: Polym. Chem. 2006*, *44*, 6962.

[5] J. Bonilla-Cruz, C. Guerrero-Sánchez, U. Schubert, E. Saldívar-Guerra, submitted *European Polym. J* **2009**.

[6] J. E. Babiarz, G. T. Cunkle, A. D. DeBellis, D. Eveland, S. D. Pastor, S. P. Shum, *J. Org. Chem.* **2002**, *67*, 6831.

[7] B. López-Carpy, M.S. Thesis (in Spanish), National Autonomous University of Mexico **2006**.

[8] J. Bonilla-Cruz, L. Caballero, M. Albores-Velasco, E. Saldívar-Guerra, J. Percino, V. Chapela, *Macromol. Symp.* **2007**, *248*, 132.

[9] B. H. Zimm, W. H. Stockmayer, *J. Chem. Phys.* **1949**, *17*, 1301.

[10] T. Fukuda, T. Terauchi, *Chem. Lett.* **1996**, *4*, 293.

[11] D. Greszta, K. Matyjaszewski, *Macromolecules*, **1996**, *29*(24), 7661.

[12] H. Pasch, *Phys. Chem. Chem. Phys.* **1999**, *1*, 3879.

[13] G. H. Fredricskon, V. Ganesan, F. Drolet, *Macromolecules* **2002**, *35*, 16.

[14] W. Weng, B. Rodgers, R. N. Webb, B. S. Hsiao, Isobutylene Polymer Nanocomposite as Advanced Tire Innerliner Materials, paper presented at MACROMEX 2008: Inaugural Mexican-American Conference on Advances in Polymer Science, Los Cabos, Mexico, December 7–10, **2008**.