Controlled Free Radical Polymerization of Styrene Initiated from Alkoxyamine Attached to Polyacrylate Chemisorbed onto Conducting Surfaces

Samuël Voccia,† Christine Jérôme,† Christophe Detrembleur,† Philippe Leclère,‖
Rachel Gouttebaron,§ Michel Hecq,§ Bernard Gilbert,‡ Roberto Lazzaroni,‖ and
Robert Jérôme*,†

*Center for Education and Research on Macromolecules (CERM), University of Liege,
Centre de Recherche en Science des Matériaux Polymères (CRESMAP) B6 Sart-Tilman,
B-4000 Liege, Belgium, Laboratory of Analytical Chemistry and Electrochemistry,
University of Liege, B6 Sart-Tilman, B-4000 Liege, Belgium, Service de Chimie
Inorganique et Analytique LASSIE, University of Mons-Hainaut, Av. Nicolas Copernic,
B-7000 Mons, Belgium, and Service de Chimie des Matériaux Nouveaux Centre de
Recherche en Science des Matériaux Polymères (CRESMAP) Université de
Mons-Hainaut Place du Parc 20, B-7000 Mons, Belgium*

Received July 18, 2002. Revised Manuscript Received December 10, 2002

A new inimer that associates an alkoxyamine, which is an initiator/mediator in nitroxide mediated radical polymerization (NMP), and a polymerizable acrylate has been synthesized and used in a two-step "grafting-from" method. The acrylate has been first electropolymerized under a cathodic potential, such that the polymer is chemisorbed on the cathode. NMP of styrene has then been initiated from the electrografted polyacrylate chains with formation of polystyrene with controlled molecular weight and narrow polydispersity.

Introduction

The success of a large range of applications in microelectronics and biotechnology requires the coating of solid substrates by adhering thin polymer films with specific properties. As a rule, preformed polymer chains are grafted onto solid surfaces ("grafting to" technique).[1−3] However, the grafting density rapidly levels off because the access to the surface decreases as the number of grafted chains increases.

Recently, attention has been paid to a "grafting from" method, which consists of initiating polymerization from compounds attached to the surface.[3] Examples of controlled polymerization initiated from the surface have been reported, including atom transfer radical polymerization (ATRP),[4,5] reversible addition−fragmentation transfer (RAFT)[6,7,8], nitroxide-mediated polymerization (NMP,)[9,10] and ring-opening polymerization (ROP).[11] This technique, which is usually applied to insulating surfaces (i.e., silicon wafers, silica particles, and glass substrates), leads to adhering thin films with a higher grafting density and that are useful, e.g., as photoresists in microlithographic applications.[12]

When conducted under appropriate conditions of solvent and cathodic potential, the electropolymerization of (meth)acrylic monomers results in the chemisorption of the polymer on the conducting surface (Ni, steel, carbon).[13−15] This type of modified surface can find application, for example, in electrochemical sensoring. The main limitations of this electrochemical grafting-from technique have to be found in the monomers that can be used, i.e., (meth)acrylates with electrochemically stable ester group, and in the low thickness of the films (<100 nm). Recently, our laboratory reported on the electrografting of an acrylate with a ring-opening metathesis polymerization (ROMP) initiator in the ester (thus an inimer), followed by the initiation of the

---

[*] To whom correspondence should be addressed via e-mail: rjerome@ulg.ac.be.

[†] CERM, University of Liege.

[‡] Laboratory of Analytical Chemistry and Electrochemistry, University of Liege.

[§] LASSIE, University of Mons-Hainaut.

[‖] CRESMAP, Université de Mons-Hainaut.

(1) Koutsos, V.; Van der Vegte, E. M.; Hadziioannou, G. *Macromolecules* **1999**, *32*, 1233.

(2) Prucker, O.; Naumann, C. A.; Rühe, J.; Knoll, W.; Franck, C. W. *J. Am. Chem. Soc.* **1999**, *121*, 8766.

(3) Zhao, B.; Brittain, W. J. *Prog. Polym. Sci.* **2000**, *25*, 677.

(4) Matyjaszewski, K.; Miller, P. J.; Shukla, N.; Immaraporn, B.; Gelman, A.; Luokala, B. B.; Siclovan, T. M.; Kickelbick, G.; Vallan, T.; Hoffman, M.; Pakula, T. *Macromolecules* **1999**, *32*, 8716.

(5) Husseman, M.; Malmstrom, E. E.; McNamara, M.; Mate, M.; Mecerreyes, D.; Benoit, D. G.; Hedrick, J. L.; Mansky, P.; Huang, E.; Russel, T. P.; Hawker, C. J. *Macromolecules* **1999**, *32*, 1424.

(6) Baum, M.; Brittain, W. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2000**, *41*, 1315.

(7) Nuβ, S.; Böttcher, H.; Wurm, H.; Hallensleben, M. L. *Angew. Chem., Int. Ed.* **2001**, *40*, 4016.

(8) Tsujii, Y., Ejaz, M.; Sato, K.; Goto, A.; Fukuda, T. *Macromolecules* **2001**, *34*, 8872.

(9) Baum, M.; Brittain, W. J. *Macromolecules* **2002**, *35*, 610.

(10) Möller, M.; Nederberg, F.; Lim, L. S.; Kange, R.; Hawker, C. J.; Hedrick, J. L.; Gu, Y.; Shah, R.; Abbott, N. L. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 3529.

(11) Benoit, D.; Chaplinsky, V.; Braslau, R.; Hawker, C. J. *J. Am. Chem. Soc.* **1999**, *121*, 3904.

(12) Huseman, M.; Morrison, M.; Benoit, D.; Frommer, B.; Mate, C. M.; Hinsberg, W. D.; Hedrick, J. L.; Hawker, C. J. *J. Am. Chem. Soc.* **2000**, *122*, 1844.

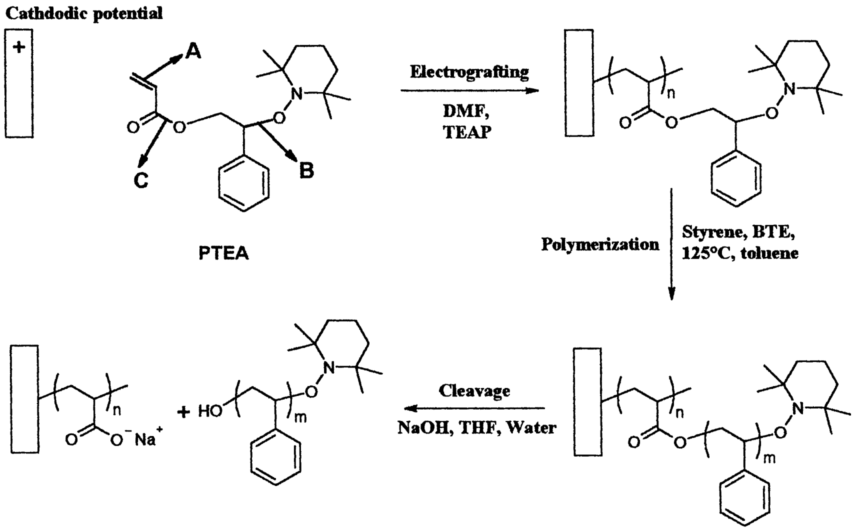
(13) Tanguy, J.; Deniau, G.; Augé, C.; Zalczer, G.; Lecayon, G. *J. Electroanal. Chem.* **1994**, *377*, 115.

(14) Baute, N.; Calberg, C.; Dubois, P.; Jérôme, C.; Jérôme, R.; Martinot, L.; Mertens, M.; Teyssié, Ph. *Macromol. Symp.* **1998**, *134*, 157.

(15) Baute, N.; Teyssié P.; Martinot, L.; Mertens, M.; Dubois, P.; Jérôme, R. *Eur. J. Inorg. Chem.* **1998**, 1711.

10.1021/cm0207705 CCC: $25.00

Scheme 1. Two-step "Grafting-from" Strategy



norbornene polymerization from the surface.[16] So, the usual limitations of the electrochemical techniques can be overcome by this strategy.

This work aims at extending the electrografting of an inimer to an acrylate bearing an alkoxyamine in the ester group. The purpose is to combine the electropolymerization of the acrylate with the initiation of the controlled radical polymerization of styrene by NMP from the chemisorbed polyacrylate. Evidence for the control of the radical grafting-from step will be provided. Scheme 1 illustrates the main steps of the process and points out three characteristic features of the inimer, i.e., the electropolymerizable and graftable acrylic double bond (A), the thermally unstable bond of the alkoxyamine (B), and the hydrolyzable ester (C). Cleavage of the C−O (Scheme 1; arrow C) bonds after the two grafting-from steps has the advantage of releasing the PS chains primarily for analytical purposes, and ultimately for applications, such as lithography.

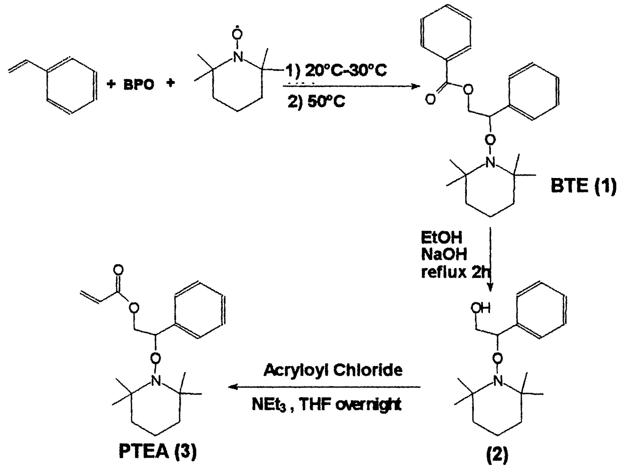
Experimental Section

Materials. Ethyl acrylate (EA, Aldrich) and styrene (Aldrich) were dried over calcium hydride and distilled under reduced pressure. Dimethylformamide (DMF, Aldrich) was dried over P_2O_5 and distilled under reduced pressure. Tetraethylammonium perchlorate (TEAP, Fluka) was heated in a vacuum at 80 °C for 12 h prior to use.

2-Phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethylbenzoate (BTE, (1) in Scheme 2) was synthesized according to a known recipe.[17] 2-Phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethylacrylate (PTEA) was synthesized according to the three-step procedure reported for preparation of the methacrylic ester analogue ((3) in Scheme 2).[15] The molecular structure of the monomer was ascertained. IR: KBr cm^{-1} 3030 (aromatic C−H), 2970 (aliphatic C−H), 1720 (C=O, ester), 1636 (C=C, acrylic), 1623 (C=C, aromatic), 1200. ^1H NMR: $CDCl_3$: d (ppm) 0.67−1.54 (several peaks, 18H, 3 × CH_2, 4 × CH_3), 4.35 (m, 1H, CH), 4.65 (m, 1H, CH), 4.94 (m, 1H, CH), 5.76 (d, 1H, CH), 6.02 (q, 1H, CH), 6.26 (d, 1H, CH), 7.22−7.32 (5H, Ar−H).

Chemisorption of the NMP Initiator onto the Surface of Steel and Carbon (Plates and Fibers). PTEA was electropolymerized in a one-compartment cell equipped with a Pt counter-electrode and a Pt pseudo-reference;[18] the working electrode was nickel and steel plates (10 × 20 mm). PTEA was dissolved in dry dimethylformamide (0.2−1.5 M) containing tetraethylammonium perchlorate (TEAP) (5 × 10^{-2} M) as a conducting salt. The water content of this solution was measured by the Karl Fischer method (Tacussel aquaprocessor) and ascertained to be lower than 10 ppm. All the electrochemical experiments (cyclic voltammetry, CV) were carried out in a glovebox under an inert and dry atmosphere at room temperature using an EG&G potentiostat/galvanostat (M273). The steel electrodes were previously cleaned in an ultrasonic bath with heptane (PA) and acetone (PA), then dried overnight at 150 °C under vacuum. Just before use, the top oxide layer of steel was removed by four cathodic scans performed in acetonitrile added with TEAP. It was rinsed with pure DMF and acetonitrile before characterization.

Scheme 2. Three-Step Synthesis of PTEA (3) with the Intermediate Formation of BTE (1) and 2-Phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethanol (PTE) (2)



Carbon fibers were previously cleaned with heptane (PA) and acetone (PA) under ultrasonic irradiation. They were dried overnight in vacuo at 150 °C before being glued onto steel plate electrodes with a conducting silver laquer in order to optimize the electrical contact. After use, carbon fibers were rinsed with pure DMF and acetonitrile, and then characterized.

---

(16) Detrembleur, C.; Jérôme, C.; Claes, M.; Louette, P.; Jérôme, R. *Angew. Chem. Int. Ed.* **2001**, *40*, 1269.

(17) Gravert, D. J.; Dalta, A.; Wentworth, P., Jr.; Janda, K. D. *J. Am. Chem. Soc.* **1998**, *120*, 9481.

(18) Mertens, M.; Calberg, C.; Martinot, L.; Jérôme, R. *Macromolecules* **1996**, *29*, 4910.

Nitroxide-Mediated Polymerization (NMP) of Styrene from Poly(PTEA) Films Chemisorbed on Steel or Carbon Fibers. Samples coated by a thin poly(PTEA) film were immersed in freshly distilled styrene (5 mL in 2 mL of toluene) added with various amounts of 2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethylbenzoate (BTE) in a closed tube under nitrogen at 125 °C for 18 h. After extraction by dry THF (a good solvent for polystyrene) in a Soxhlet extractor for 1 week, the coated steel plates were dried in vacuo, and the surface was analyzed by Raman, IR, contact angle, and environmental scanning electron microscopy (ESEM).

Degrafting of the PS Chains from Steel. To recover the PS and analyze it by SEC, the ester functions of the pregrafted polyacrylate chains were hydrolyzed. Both alkaline and acid hydrolysis were tested in the following conditions: in THF (10 mL) by NaOH (1 mL, 10 N) or HCl (1 mL, 1 N), under vigorous stirring at 25 °C for 20 or 1 h, respectively, and the polystyrene chains were released (Scheme 1; 3rd step).

Characterization Methods. The samples were characterized by measurement of the contact angle of water droplets, infrared spectroscopy (FTIR, reflection−absorption technique, Brucker spectrophotometer), Raman spectroscopy (Dilor spectrometer, SuperLabram type equipped with an 800−2000 CCD detector cooled by liquid nitrogen and a microscope. Because of the dispersion of the grating and the use of a 1-in. CCD detector, the full spectrum had to be recorded in two parts (first area 150−1800 cm^{-1}, second area 2400−3600 cm^{-1})), X-ray photoelectron spectroscopy (XPS, VG-ESCALAB 220iXL spectrometer with the monochromatized Al Kα radiation at 1486.6 eV), and environmental scanning electron microscopy (ESEM, FEG XL-30, FEI Company). Size-exclusion chromatography (SEC, Hewlett-Packard 1090 liquid chromatograph equipped with a 1037A refractive index detector) was performed in THF at 40 °C (polystyrene standards were used for calibration). Thermogravimetric analysis (TGA) was carried out with a TA instrument Q500 thermogravimetric analyzer. The μTA 2290 micro-thermal analyzer (TA Instruments) equipped with the TopoMetrix Explorer TMX2100 scanning probe microscope was used for microthermal analysis. At selected locations, the temperature was raised, typically at a 5 °C/s rate, and the power at the tip was compared with a similar tip left in air. Temperature was scanned up to 200 °C and modulated by a 2 kHz signal with amplitude of 5 °C. Measurements were repeated at different locations to check the homogeneity of the samples.

Results and Discussion

For a double bond to be electropolymerized under a cathodic potential, substitution by an electron-withdrawing group is required, which makes (meth)acrylates quite appropriate monomers. Moreover, under suitable conditions of potential and solvent, the poly(meth)acrylate chains which are initiated from the electrode surface are chemisorbed on it (grafting-from process). A major condition to be met, however, is that the monomer is adsorbed on the electrode, which is possible when the donor number of the solvent is high enough, such as that of DMF.[15]

To overcome the limitation of the electrografting process which is restricted to (meth)acrylates, we have been interested in an inimer, the 2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethylacrylate (PTEA), which consists of an acrylate double bond and an initiator for the controlled radical polymerization in the ester group. A general strategy can then be proposed, which is illustrated in Scheme 1. Polyacrylate chains are first electrografted-from the solid surface, followed by the grafting-from of, e.g. polystyrene, initiated and controlled by the alkoxyamine according to a nitroxide-mediated process (NMP). Quite interestingly, the ester groups of the polyacrylate chains are easily hydrolyzed with release of the polystyrene chains, which is a substantial advantage for measuring the molecular weight of these chains and to assess their controlled growth.

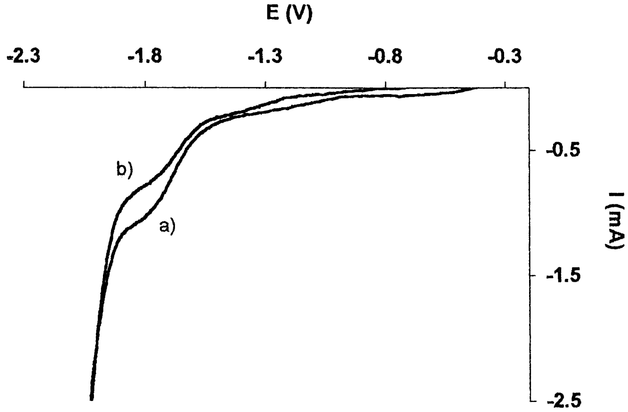


Figure 1. Voltammogram for the grafting of PTEA (0.4 M) in DMF + TEAP (0.05 M): (a) 1st scan, (b) 2nd scan.

1. Electrografting of the PTEA Inimer. The electropolymerization of the PTEA inimer in DMF (0.2−1.5 M) added with a conducting salt (TEAP) has been studied by cyclic voltammetry by using a steel plate as a cathode. As is usually the case for the cathodic polymerization of acrylates, two reduction waves are observed.[18,19] At the less-cathodic potential (peak I), a species is formed which is responsible for the initiation of the monomer polyaddition and for the chemisorption of the growing chains. At the more-cathodic potential of peak II, a species that initiates the monomer polymerization is also formed, but the growing chains are no longer chemisorbed onto the cathode surface. At this potential, pregrafted chains can be detached from the surface.[17] When the potential is held at the maximum of peak I, the cathode is rapidly passivated which is confirmed by the intensity of peak I which dramatically decreases when the potential scanning is repeated until the potential of peak I (Figure 1). This passivation is the signature of an insulating polyacrylate film deposited on the cathode surface. The electrochemical stability of the C−O bond of the alkoxyamine has been ascertained by the cyclic voltammetry of a nonpolymerizable model for PTEA, i.e., 2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethylbenzoate (BTE), dissolved in DMF (0.1 M) together with TEAP (0.05 M). No reaction is observed in the potential range from 0 to −2.5 V. Moreover, the electrografting of polyethylacrylate which is easily carried out in DMF,[20] is not at all perturbed when the monomer solution is added with BTE. The PTEA inimer thus behaves as traditional alkyl acrylates which are ideal precursors of thin films chemisorbed onto conducting substrates.

The poly(PTEA) films accordingly deposited are too thin to be observed visually. Nevertheless, the hydrophobicity of the steel surface has changed as confirmed by the contact angle of water which is 95° ± 2°, compared to 85° ± 3° for neat steel. Moreover, carbon, oxygen, and nitrogen atoms have been detected on the surface by XPS analysis. The atomic ratios extracted

---

(19) Mertens, M.; Calberg, C.; Baute, N.; Jérôme, R.; Martinot, L. *J. Electroanal. Chem.* **1998**, *441*, 237.

(20) Jérôme, C.; Jérôme, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 2488.

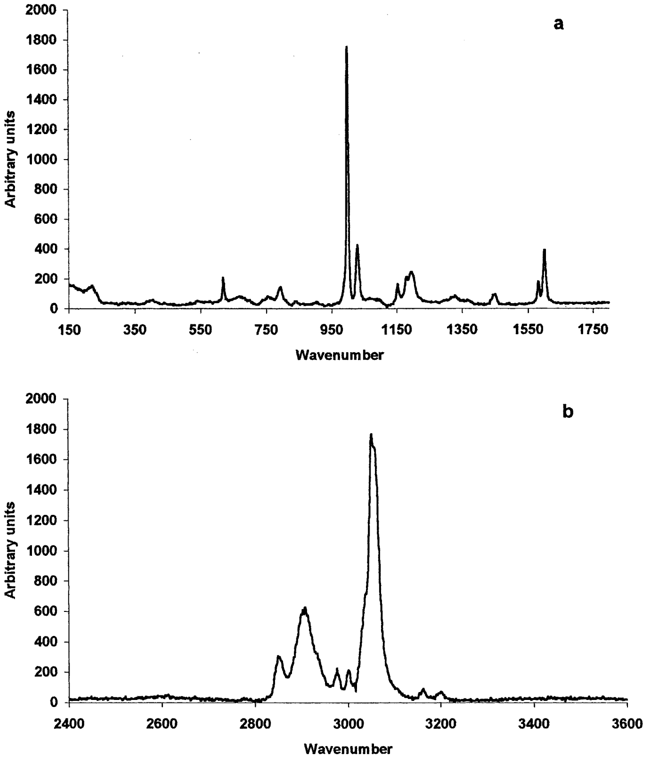


Figure 2. Raman spectrum for PS grafted steel: (a) first area, 150−1800 cm^{-1}; (b) second area, 2400−3600 cm^{-1}.

from the XPS spectrum are C/O = 7.6 and O/N = 3.75, which is in accordance with the theoretical values C/O = 6.7 and O/N = 3. Iron oxide (Fe_2O_3; oxygen at 530.4 eV) is also detected, which indicates that the organic film is thinner than 10 nm, which is the depth of analysis for this compound.

2. NMP of Styrene from an Electrografted Poly(PTEA) Film. Steel, onto which a poly(PTEA) film has been chemisorbed, has been immersed in styrene (5 mL in 2 mL of toluene) containing various amounts of "free" initiator (BTE), thus a derivative of the same alkoxyamine as that attached to PTEA. After 18 h of polymerization at 125 °C, the polymerization medium is viscous because of the styrene polymerization self-initiated and initiated by the "free" initiator at 125 °C. The steel plates have been extensively washed with THF (a good solvent for polystyrene) in a Soxhlet extractor for 120 h. A transparent film can then be observed visually on the surface of steel, which is a macroscopic evidence for the surface modification by the NMP process.

This preliminary observation was confirmed by the surface analysis by FTIR−RAS and Raman spectroscopy. IR absorption peaks and Raman bands characteristic of polystyrene are unambiguously observed (Figure 2), despite the extensive extraction by a good solvent (THF). Furthermore, the contact angle has decreased from 95° for poly(PTEA) to 89° ± 2°, which is the value measured for a solvent-cast polystyrene film (88° ± 2°). Observed by environmental scanning electron microscopy (ESEM), the organic film appears to be homogeneous and the surface is smoother than the original steel surface, particularly when styrene is polymerized in the presence of "free" initiator.

To confirm that the styrene polymerization has been initiated from the alkoxyamines of the electrografted poly(PTEA) film, NMP of styrene has been repeated with a bare steel plate and all the other conditions being the same. After 18 h at 125 °C, although styrene was at least partly polymerized, no significant amount of polystyrene was left on the steel surface. The same conclusion was drawn whenever the steel plate was pregrafted by a poly(alkyl acrylate) film.[20] Clearly, the grafting of polystyrene from the steel surface is possible only when polyacrylate chains bearing an alkoxyamine have previously been grafted-from the steel surface.

3. Degrafting and SEC Analysis of the Polystyrene (PS) Chains. The PS chains are attached to the poly(PTEA) backbone through an ester, which is easily hydrolyzed at high or low pH. It is thus possible to release PS and to have it characterized by SEC. PS degrafting is complete within the limits of detection of Raman spectroscopy. The surface was also analyzed by XPS after the PS chains were degrafted at high pH or at low pH. The surface recovered after treatment at high pH shows the carbon (1s) peaks characteristic of poly(acrylic acid), i.e., one peak at ca. 285 eV for the combined contribution of C*−C−C=O (42%) and C*−C=O (29%) and a second peak at 289.2 eV for C=O (29%). The alkaline degrafting of PS has thus maintained the underlying polyacrylic chains immobilized on the surface. In contrast, the PS acidic degrafting restores the steel surface, and an acrylate, e.g. ethyl acrylate, can be electrografted from it again. The steel surface was actually corroded by the acid, which explains why the polyacrylic chains were detached in addition to PS.

M_n of the chains degrafted under alkaline conditions has been compared with M_n of PS formed in solution (Table 1). When the amount of "free" initiator is high enough (expt. 1 to 3), the M_ns for grafted and ungrafted PS chains are in good agreement. Discrepancies in M_n or polydispersity are observed between the two populations of PS chain when their length is increased, i.e., when less or no "free" initiator is used (expt. 4 and 5). More experiments would be needed to assess the reproducibility and to account for this observation. Nevertheless, it must be noted that NMP from a solid surface is controlled only when an initiator/mediator is added to the monomer solution. According to Brittain et al.,[6] in the absence (or with a too low amount) of an initiator/mediator, self-initiation of the styrene polymerization dominates and the chain growth is out of control. These experiments suggest that the analysis of the chains formed in solution provide valuable information on the molecular weight and polydispersity of the tethered polymer.

The thickness of the PS film was estimated by a local thermal analysis, the microthermal analysis (μTA). Indeed, AFM can be equipped with a probe which provides information on both the morphology and the thermal properties of the surface. μTA consists of a tiny resistive thermal probe that collects images in relation to the sample topography and thermal conductivity.[21] The AFM tip is an ultra-miniaturized resistive heater and a temperature sensor. Moreover, when an image has been recorded it is possible to select locations on the surface for further examination by local thermal

---

(21) Song, M.; Hourston, D. J.; Reading, M.; Hammiche, A.; Pollock, H. M. *Polymer* **1996**, *37*, 243.

Table 1. Radical Grafting of Polystyrene from a Precoated Steel Surface[a]

exp.	grafted PS M_n + (PDI)	ungrafted PS M_n + (PDI)	theoretical M_n	styrene/BTE (mol/mol)	styrene conversion (%)
1	23000 (1.10)	24000 (1.23)	26000	420	60
2	30000 (1.20)	32000 (1.20)	38000	640	57
3	32000 (1.10)	35000 (1.20)	53000	1110	47
4	45000 (1.35)	78000 (1.40)	104000	3330	30
5	246000 (1.75)	230000 (2.20)		no BTE added	

[a] 5 mL of styrene was dissolved in 2 mL of toluene, and this solution was added with various amounts of “free” initiator (BTE) and heated at 125 °C for 18 h.

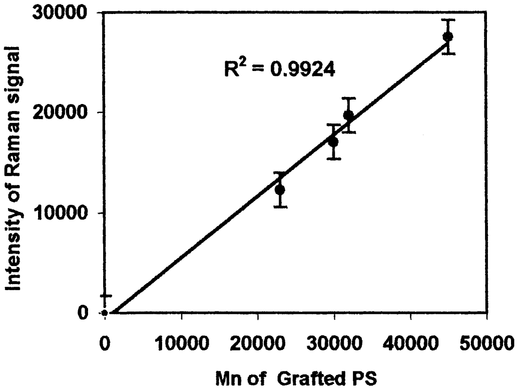


Figure 3. Plot of the Raman signal at 1000 cm^{-1} vs M_n of grafted PS.

analysis (LTA). The probe is positioned at one selected point, and the temperature is ramped between two predetermined limits at a rate (5−25 °C/s) which is very high compared to traditional thermal analysis. When the polymer sample is softening the thermal probe tends to penetrate the film, and the vertical displacement of the probe detected by the position-sensitive detector of the AFM apparatus can give a very rough estimation of the film thickness. Typically, a thickness of 80−90 nm has been estimated for polystyrene with M_n of 73 000 for the ungrafted PS. This value is higher than the value reported by Husseman et al.[5] meaning that the PS chains are highly stretched.

The two-step grafting-from technique has been extended to carbon fibers to increase the surface area of the conducting substrate (18.85 cm^2/cm fiber mesh) and the amount of polymer deposited. The density of the initiator units on the surface was determined by thermogravimetric analysis of the fibers coated by poly(PTEA). From the weight loss and the molecular weight of PTEA, a value of 36 initiator units per nm^2 has been found, which is greater than the value reported by Rühe et al. for an initiator layer deposited on silica particles (0.8−1.6 molecules per nm^2).[22] Similarly, the grafting density of the PS chains ($M_{n\ SEC} = 29\ 000$) has been estimated at 1.7 molecules per nm^2. This value is one hundred times greater than the value reported by Hadtziiannou et al.[1] by the grafting to method for PS of the same M_n (0.022 molecule per nm^2).

Because the probing depth of the Raman spectroscopy exceeds the thickness of the organic film, the intensity of the Raman signal is proportional to the film thickness. This expectation is confirmed by Figure 3, which shows that the intensity of the Raman signal for the aromatic units of PS at 1000 cm^{-1} linearly changes with M_n of the grafted PS chains, all the experimental conditions being kept constant (power of the laser, aperture, number of scans, etc.). According to Figure 3, M_n of the PS chains grafted in expt 4 (Table 1) is consistent with a controlled growth in contrast to what happened in solution. When no “free” initiator is added to styrene, the control of the chain growth is lost for the two populations of PS chains (expt 5, Table 1).

Conclusions

Steel has been successfully coated by a two-component polymer layer by a two-step grafting-from technique. The key compound is an inimer, whose polymerizable moiety is an acrylate easily adsorbed onto steel and electropolymerized at a cathodic potential, such that the chains are chemisorbed on the surface with a high (grafting) density (first step). The initiator fragment of the inimer is an alkoxyamine, thus a typical dormant species in the nitroxide-mediated radical polymerization of styrene. Actually, polystyrene has been grafted from the alkoxyamines of the pregrafted polyacrylate film. Growth of the densely grafted PS brushes is controlled only when a “free” initiator is added to styrene solution in which precoated steel has been immersed. Whenever this condition is fulfilled, there is a good agreement between M_ns of the grafted and the ungrafted chains. It must be noted that the grafted PS chains can be released from the surface by hydrolysis (alkaline or acidic) of the ester groups of the underlying polyacrylate layer. This opportunity allows the grafted PS chains to be characterized in solution (SEC). More importantly, polymer degrafting by an acidic treatment restores the metal substrate which can be used for further electrochemical reactions as demonstrated by the subsequent electrografting of poly(ethylacrylate). This opportunity opens the way to the patterning of surfaces by combining traditional microlithographic techniques and electrochemistry.

We are grateful to the Services Fédéraux des Affaires Scientifiques, Techniques et Culturelles in the frame of the Pôles d’Attraction Interuniversitaires: Chimie Supramoléculaire et Catalyse Supramoléculaire (PAI V). S.V. is grateful to the Fonds pour la Formation à la Recherche dans l’Industrie et dans l’Agriculture (FRIA) for a fellowship. C.J. is a Research Associate by the Fonds National de la Recherche Scientifique (FNRS). M.H. and R.G. thank the European Community and the Ministère de la Région Wallonne for financial support.

CM0207705

---

[22] Prucker, O.; Rühe, J. *Macromolecules* **1998**, *31*, 592.