

Synthesis of Polymer-Grafted Natural Rubbers by Radical Photopolymerization of Vinyl Monomers Initiated from the Rubber Chains

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Received 17 December 2008; accepted 18 February 2009

DOI 10.1002/app.30266

Published online 2 July 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The synthesis of polymer-grafted natural rubbers (NRs) was considered through photopolymerization of vinyl monomers initiated from *N,N*-diethyldithiocarbamate groups previously introduced onto *cis* 1,4-polyisoprene units of NR chains. The development of the procedure was made with methyl methacrylate (MMA) as monomer. First, initiation of MMA photopolymerization was tested using a model molecule of the *N,N*-diethyldithiocarbamate-functionalized 1,4-polyisoprene unit to verify the feasibility of the procedure considered. Then, MMA polymerization was successfully initiated from *N,N*-diethyldithiocarbamate-functionalized NR backbone used as macroinitiator, and the conditions of grafting were optimized. It was shown that MMA grafting could occur either in monomer me-

dium, in solution in toluene, and in latex medium, and that the quantities of homopolymer formed were still low. Thereafter, grafting studies were performed with other vinyl monomers (styrene, methacrylonitrile, acrylamide, acrylic acid) showing that grafting efficiency depends essentially on the nature of the monomer. The method developed here was shown particularly well adapted for the synthesis of polymer-grafted NR with monomers of low polarity. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2149–2160, 2009

Key words: graft copolymer; natural rubber; polyisoprene; chemical modification; photopolymerization; latex; *N,N*-diethyldithiocarbamate; grafting from; rubber; synthesis

INTRODUCTION

Compared with synthetic rubbers, natural rubber (NR) has enormous advantages of being renewable owing to its agricultural origin. Indeed, this material is extracted from the latex produced by *Hevea brasiliensis*, the rubber tree, so from this point of view it is of great interest. However, the commercial success of NR is also due to its excellent physical properties (i.e. strength, low heat build up, excellent flexibility, and resistance to impact and tear). On the other hand, NR has some drawbacks; for instance, low flame resistance, limited resistance to chemicals and solvents, as well as poor ozone and weathering performance, mainly owing to its unsaturated hydrocarbon chain structure. Moreover, its non-polar character causes limitation in a variety of applications. Consequently, chemical modification of NR has been widely considered as a manner to compensate these disadvantages. Among the well-known modified NR products one

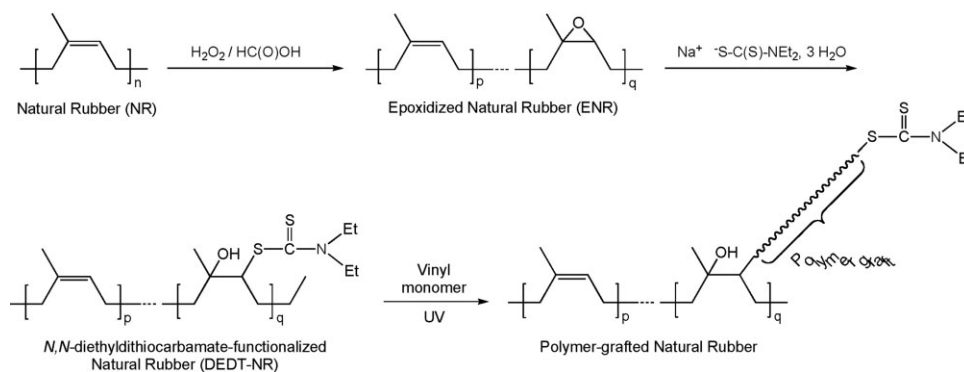
notes epoxidized NRs, maleated NRs, and graft copolymers.

The introduction of polymer grafts onto NR chains provides access to new elastomeric products with new and improved properties compared with those of NR.^{1–4} They can be used as compatible agent effective for the preparation of polymer blends.^{5,6}

In general, polymer-grafted NRs are synthesized according to the so-called “grafting from” method that proceeds by polymerization of a monomer initiated from initiator sites previously introduced on *cis* 1,4-polyisoprene chains of NR. The polymerization techniques generally used to achieve the “grafting from” are radical polymerization and ionic polymerization.^{7–9} The latter method has limits owing to the limited number of monomers capable of undergoing this type of polymerization and the stringent conditions required. For radical methods, thermal^{10–15} and redox^{16–23} initiators can be used. Most of the grafting reactions are carried out in latex medium.^{10,12,13,15–19} The photochemical initiation and ionizing radiation are also used but mainly in cases of surface treatment of materials and preparation of films.^{24–30}

The purpose of this article is to describe a procedure developed in our laboratory on the preparation of polymer-grafted NRs composed of flexible chains

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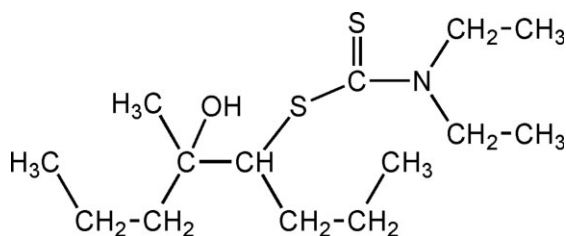
Scheme 1 Strategy used to synthesize polymer-grafted NR.

of *cis* 1,4-polyisoprene and rigid thermoplastic grafts in the side position of the rubber chains, and therefore capable to respond to the characteristics of thermoplastic elastomers. The principle of the synthesis is based on the “grafting from” method. In order to prepare graft copolymers with well-controlled structure and size, a controlled radical photopolymerization method was used to polymerize a range of vinyl monomers (alkyl acrylates and methacrylates, styrene, acrylonitrile, acrylamide, etc.) from *iniferter* groups whose particularity is to act both as polymerization initiator (*ini*), transfer agent (*fer*), and termination (*ter*), as described for the first time by Otsu et al. in 1982.³¹ The choice of initiating group was focused on iniferter structures of alkyl *N,N*-dialkyldithiocarbamate type. *N,N*-dialkyldithiocarbamate initiating species were previously incorporated into the side position of the NR chains via a two-step procedure to form the *N,N*-dialkyldithiocarbamate-functionalized NR (DEDT-NR) that was further used as macroinitiator (Scheme 1).

EXPERIMENTAL

Materials

NR latex (origin: Thailand) was a centrifuged field latex of *ca.* 42% dry rubber content (DRC), stabilized with ammonia to avoid rubber coagulation. Sinnopal NP 307 (polyoxyethylene nonylphenyl ether; nonionic surfactant from Cognis, Meaux, France) was used as received.



Scheme 2 HMPPDC.

The monomers: methyl methacrylate (MMA) (Aldrich, Stenheim, Germany), styrene (Acros, Geel, Belgium), methacrylonitrile (Merck, Darmstadt, Germany), acrylamide (Merck), and acrylic acid (Fluka, Stenheim, Germany), were purified by vacuum distillation prior to use.

UV light for photopolymerization reactions was provided by a 100 W low-pressure fluorescent lamp (Fisher Bioblock Scientific, Illkirch, France), emitting at 365 nm. The intensity measured at 30 cm of filter was equal to 7000 $\mu\text{W cm}^{-2}$.

Synthesis of the model molecule of *N,N*-diethyldithiocarbamate-functionalized 1,4-polyisoprene unit

The model molecule of *N,N*-diethyldithiocarbamate-functionalized 1,4-polyisoprene unit in DEDT-NR, i.e. *S*-(2-hydroxy-2-methyl-1-*n*-propylpentyl) *N,N*-diethyldithiocarbamate (HMPPDC) (Scheme 2), was synthesized according to the procedure described in a previous article.³² It was prepared from 4-methyloct-4-ene used as model molecule of 1,4-polyisoprene unit. Because of the 39 : 61 *cis/trans* molar composition of 4-methyloct-4-ene, two HMPPDC diastereomers were obtained in a 34 : 66 molar ratio (determination made by ¹H-NMR).

Synthesis of *N,N*-diethyldithiocarbamate-functionalized NRs

Three DEDT-NR macroinitiators (NR1, NR2, and NR3) with varying DEDT-NR contents (Table I)

TABLE I
Characteristics of the Synthesized DEDT-NR Latices

Macroinitiator	Epoxidation rate (%)	DEDT-NR unit content (%)	DRC (%)
NR1	11.2	4.3	5
NR2	19.7	8.1	5
NR3	37.5	13.6	5

were prepared according to the procedure previously described,³² i.e. by nucleophilic addition of sodium *N,N*-diethyldithiocarbamate trihydrate (DEDT-Na) on oxirane rings previously introduced along the *cis* 1,4-polyisoprene chains of NR. Partially epoxidized natural rubbers (ENRs) were initially prepared in latex medium: performic acid generated *in situ* by reaction of hydrogen peroxide upon formic acid was used as oxidation reagent. Addition of DEDT-Na onto ENR units was also carried out in latex medium. ¹H-NMR spectroscopy was used to determine the content in *N,N*-diethyldithiocarbamate-functionalized 1,4-polyisoprene units of the synthesized DEDT-NRs (Table I).

Radical photopolymerization of MMA initiated from HMPPDC

Initiator (HMPPDC), MMA, and toluene were charged in a Schlenk tube along with a magnetic stirring bar and the mixture deoxygenated via a series of freeze-pump-thaw cycles. The reaction mixture placed under nitrogen atmosphere was stirred at room temperature and the solution irradiated using a 100 W UV lamp emitting at 365 nm and at a distance of 10 cm from the Schlenk tube. A deoxygenated syringe was used to take samples during the reaction for ¹H-NMR and HPLC analyses to determine the proportions of remaining monomer and initiator, respectively. The polymer product in the withdrawn solution was precipitated in methanol and dried under vacuum until constant weight before being analyzed by SEC.

Samples for HPLC analyses were prepared by mixing part of the withdrawn solution in 90 : 10 (v/v) methanol/water in order to separate the PMMA formed from the solution to be analyzed.

Synthesis of polymer-grafted NRs by photopolymerization of vinyl monomers initiated from DEDT-NR

Polymerization in monomer medium

DEDT-NR was cut into small pieces and introduced in a Schlenk tube containing monomer (quantity dependent on the length of graft desired), and the mixture was shaken for 12 h in the dark. The reaction mixture was deoxygenated via several freeze-pump-thaw cycles and placed under nitrogen atmosphere at room temperature. The polymerization was initiated by irradiation with a 100-W UV lamp emitting at 365 nm and operating at a distance of 10 cm from the Schlenk tube. When the reaction was completed, the polymer products were precipitated in methanol, washed several times with distilled water, and dried under vacuum until constant weight. The mass of polymer formed was recorded, and the homopoly-

mer possibly formed during the grafting reaction was extracted via Soxhlet with acetone for 24 h (in the case of the synthesis of polyacrylamide-grafted NR, acetone was changed with water). After extraction, the polymer-grafted NR was recovered, dried under vacuum until constant weight before being weighed one more time, and the samples were analyzed by ¹H and ¹³C-NMR, and FT-IR.

Polymerization in solution in toluene

The procedure was identical to that used for the polymerization carried out in monomer medium. DEDT-NR was dissolved in toluene at a concentration of 0.05 g mL⁻¹. The system was mechanically stirred in toluene. After DEDT-NR dissolution in toluene, a quantity of selected monomer depending on the desired theoretical length of grafts was introduced into the solution of rubber. The mixture was then frozen in liquid nitrogen, and placed under nitrogen atmosphere by carrying out several cycles vacuum-nitrogen.

Polymerization in latex medium

A procedure same as that described above was used, but the monomer, used in a quantity depending on the desired theoretical length of grafts, was introduced directly into the DEDT-NR latex before placing it under nitrogen atmosphere.

Measurements

Liquid NMR spectra were recorded on a Bruker AC 400 Fourier-transform spectrometer, at 400.13 MHz for ¹H and at 100.62 MHz for ¹³C. Samples were analyzed in solution in chloroform-D (99.8% purity; Euriso-top, Gif sur Yvette, France). The chemical shifts were expressed in ppm in the δ scale, compared with the singlet of tetramethylsilane, as internal standard.

IR spectra were recorded on a Nicolet Avatar 370 FT-IR equipped with a DTGS detector, in the 4000–500 cm⁻¹ range. Liquid samples were analyzed between two KBr or NaCl cells, and solid ones as KBr pellets.

SEC measurements were performed on a Spectra System equipment from Thermo Finigan composed of a P 1000 pump, an AS1000 injector, a double detection system (UV 2000 spectrophotometer set at $\lambda = 254$ nm and RI 150 differential refractometer), in addition to a computer equipped with Chrom Quest 4.0 acquisition and PL Cirrus processing software. SEC analyses were carried out in THF at 35°C, with a 1.0 mL min⁻¹ flow-rate, through a column set built up with a pre-column PL Gel 5 μ m Guard (5 cm \times 7.5 mm) and two columns PL Gel 5 μ m Mixed D

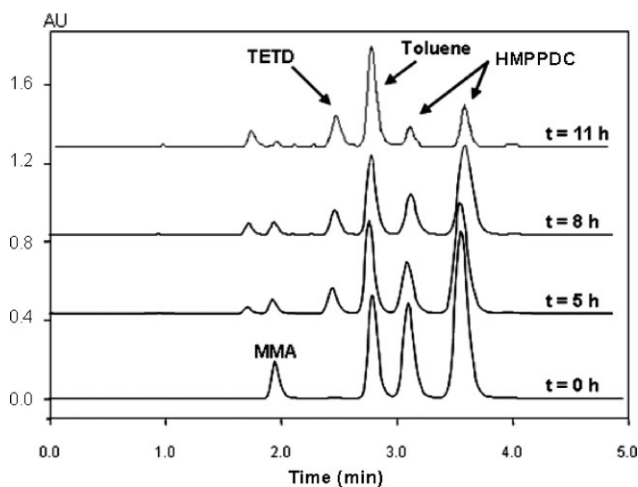


Figure 1 Example of kinetic of MMA photopolymerization initiated from HMPPDC in toluene: monitoring by HPLC ($[MMA] = 5 \text{ mol L}^{-1}$, $[HMPPDC] = 5.10^{-3} \text{ mol L}^{-1}$).

(30 cm \times 7.5 mm) in series. Toluene was used as marker ($t_R = 20.38 \text{ min}$) and calibration was accomplished with polystyrene standards. All samples (5 mg mL^{-1} in 1 : 1000 (v/v) toluene/THF mixture) were filtered through $0.45 \mu\text{m}$ microfilter prior to analysis.

Analytical HPLC analyses were performed on a Waters modular equipment including a Model 510 pump module, a Model U6K injector, an AIT CHROMATO Kromasil C18 column (4.6 mm I.D. \times 150 mm length; particle size: $5 \mu\text{m}$, pore size = 100 \AA), a double detection system (a Model 996 UV/vis. photodiode array detector set at $\lambda = 254 \text{ nm}$ and a Model 410 differential refractometer), and a computer using Empower software for system command, data acquisition and processing. Analyses were carried out in isocratic mode using 90 : 10 (v/v) MeOH/H₂O mixture as mobile phase, at a flow-rate adjusted to 1 mL min^{-1} .

Preparative HPLC analyses were carried out using a Waters Delta prep 4000 apparatus equipped with a μ Bondapak C18 column (Waters, 40 mm I.D. \times 100 mm length; particle size: 15–20 μm , pore size = 125 \AA), a Model 490E variable wavelength UV/vis. detector set at $\lambda = 254 \text{ nm}$, a Model 401 differential refractometer, and a fraction collector. Analyses were carried out in isocratic mode using 90 : 10 (v/v) MeOH/H₂O mixture as mobile phase, at a flow-rate of 25 mL min^{-1} .

MALDI-TOF experiments were performed using a Bruker BIFLEX III TOF mass spectrometer. The instrument was equipped with a N₂ laser emitting at 337 nm, a 2-GHz sampling rate digitizer, a pulsed ion extraction source, and a reflectron. Spectra were acquired in the positive-ion mode. The acceleration voltage was 19 kV. Typically, 100 single-shot acquisitions were summed to give a composite mass spectrum. All data were reprocessed using the Bruker

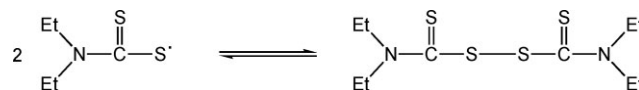
XMASS software. The mass scale was calibrated externally using PEG 1500. MALDI-TOF analysis of the polymers used dithranol (DIT) (Aldrich) as matrix. Inhibitor-free tetrahydrofuran (THF) and anhydrous methanol were also purchased from Aldrich. LiCl, NaCl, KCl, RbCl, CsCl, AgTFA (silver trifluoroacetate), and trifluoroacetic acid were purchased from Acros. The analytes, matrix, and AgTFA were dissolved in THF at concentrations of 10 g/L. Alkali salts were dissolved in acetone. The sample solution was mixed at a volume ratio of 1 : 10 : 1 Vanalyte/Vmatrix/Vcation). The dried droplet method was used to prepare sample target; $1 \mu\text{L}$ of sample mixture was applied to the sample target and air-dried.

RESULTS AND DISCUSSION

Radical photopolymerization of MMA initiated from HMPPDC

One example of kinetic study of MMA polymerization followed by HPLC is given in Figure 1. The kinetic plot shows that the conversion of HMPPDC is very low, indicating that photodissociation is not instantaneous or that the reactive radical formed prefers to recombine again with the *N,N*-diethyldithiocarbamyl radical rather than to initiate radical polymerization of MMA. The formation of tetraethylthiurame disulfide (TETD) suggests that *N,N*-diethyldithiocarbamyl radicals may react with each other to form TETD according to the equation given in Scheme 3 and therefore that the polymerization is not entirely "living", which was also confirmed by MALDI-TOF mass spectrometry. TETD can be formed either during the initial dissociation of HMPPDC, as has been shown previously, or by deactivation of the chain ends during propagation of monomer. The second explanation is more plausible because of the further increase of the molecular weight of PMMA formed during the polymerization (Fig. 2). In addition, the absence of a peak characteristic of carbon disulfide in the chromatogram of the reaction mixture after 11 h implies that deactivation of chain ends according to the mechanism proposed by R.S. Turner³³ has not occurred.

PMMA samples were analyzed by MALDI-TOF spectrometry (Fig. 3). A main series of peaks was noted on the mass spectra, showing the presence of two families of PMMA (the mass difference between two successive peaks in each family corresponds to the mass of PMMA unit). However, contrary to



Scheme 3 Recombination of *N,N*-diethyldithiocarbamyl radicals to form TETD.

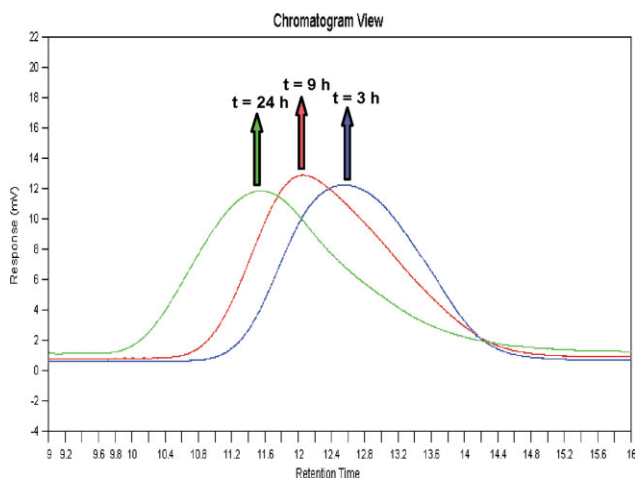


Figure 2 Photopolymerization of MMA initiated from HMPPDC in toluene: progress of SEC chromatogram of PMMA formed during grafting time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

what was expected, the PMMA macromolecules characterized here by MALDI-TOF spectrometry did not contain *N,N*-diethyldithiocarbamate chain-ends. In fact, each of the two PMMA families characterized was composed of PMMA chains containing each one the 2-hydroxy-2-methyl-1-*n*-propylpentyl group at one chain-end and a PMMA unit at the other one, but the difference between the two fami-

lies comes from the PMMA chain-end which is either saturated or unsaturated (difference of two mass units between two peaks characteristic of each family). This MALDI-TOF analysis not only shows that the initiation is efficient from the 2-hydroxy-2-methyl-1-*n*-propylpentyl radicals but also demonstrated the existence of termination reactions by disproportionation. In addition to the main series of peaks, a second one was also noted on the MALDI-TOF mass spectra of PMMA samples (labeled with an asterisk on the mass spectrum given in Fig. 3). It was similar to the first one, but with a difference of plus 18 mass units. These peaks correspond to PMMA families similar to those described above, but the mass difference is not yet explained.

Synthesis of PMMA-grafted NRs (NR-*g*-PMMA)

The first works on the synthesis of polymer-grafted NRs was considered with MMA as a monomer model. This monomer was selected to undertake the development of methodology for the synthesis of graft copolymers derived from NR.

Three DEDT-NRs were used as macroinitiator: **NR1**, **NR2**, and **NR3**, having various rates in DEDT-NR units: 4.3%, 8.1%, and 13.6%, respectively (Table I).

Studies on MMA photopolymerization initiated from DEDT-NRs were carried out in monomer medium, in solution in toluene, and in latex medium. In all cases, the polymers obtained after

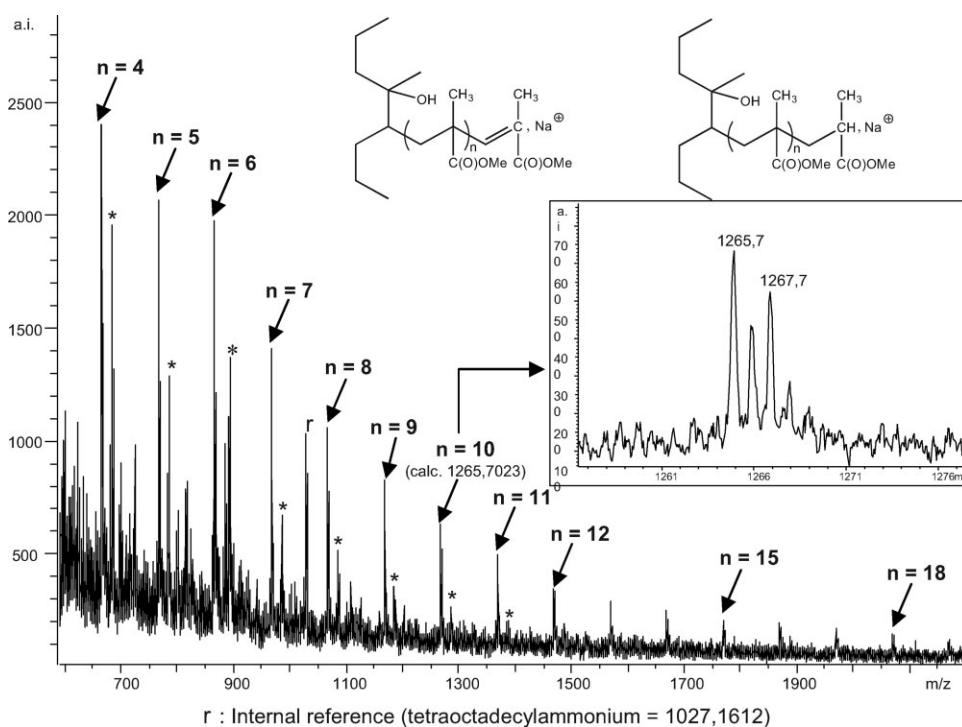


Figure 3 MALDI-TOF mass spectrum of PMMA formed during MMA photopolymerization initiated from HMPPDC.

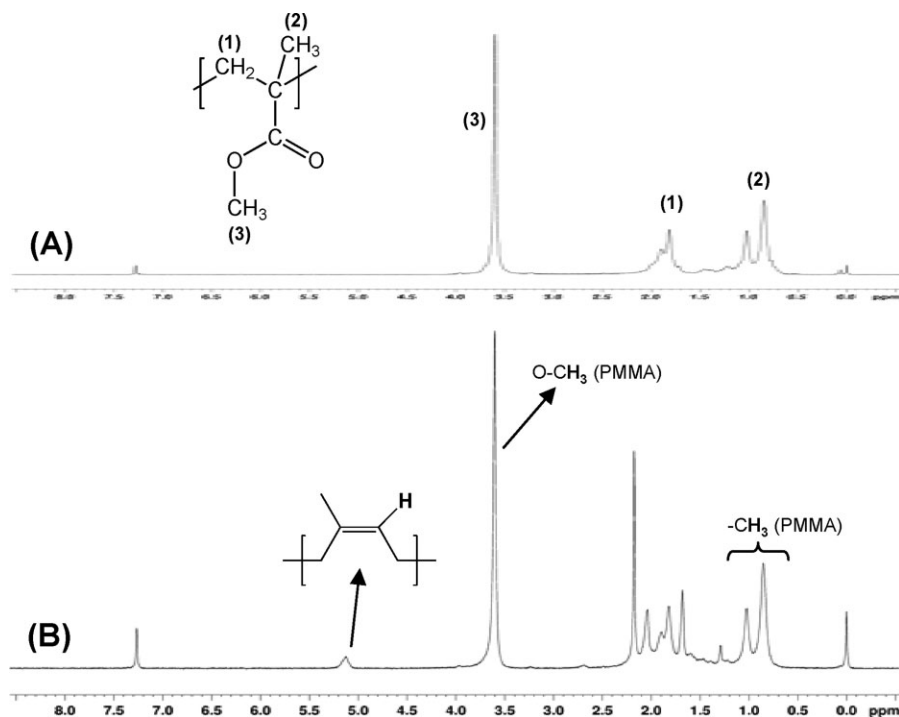


Figure 4 MMA photopolymerization initiated from DEDT-NR: ¹H-NMR spectra of (A) soluble fraction and (B) insoluble fraction.

photopolymerization were isolated by precipitation in methanol, and dried under vacuum until constant weight. After drying, the crude polymer mixture was weighed, and then extracted with acetone for 24 h to eliminate the PMMA homopolymer possibly formed during the photopolymerization. The products contained in each of the two fractions were separately recovered, dried under vacuum until constant weight, and then analyzed by ¹H- and ¹³C-NMR, and FT-IR spectroscopy.

The ¹H-NMR analyses of the polymer fractions soluble in acetone [Fig. 4(A)] showed only the presence of PMMA homopolymer. The absence of the signal at about $\delta = 5.2$ ppm, characteristic of the proton on carbon-carbon double bond of 1,4-polyisoprene units, showed that these fractions did not contain graft copolymer or DEDT-NR. On the other hand, the signals characteristic of PMMA are noted on the spectra: a singlet at $\delta = 3.6$ ppm corresponding to $-\text{O}-\text{CH}_3$ protons of PMMA and two singlets at $\delta = 0.9$ ppm and $\delta = 1.0$ ppm characteristic of protons of methyls on PMMA chains.

The analyses by ¹H-NMR, ¹³C-NMR, and FT-IR spectroscopies of the polymer portions insoluble in acetone confirmed the formation of NR-g-PMMA copolymers. *Cis* 1,4-polyisoprene backbone is apparent in ¹H-NMR by the signal at $\delta = 5.2$ ppm corresponding to the proton on carbon-carbon double bond of 1,4-polyisoprene units, and PMMA grafts by the singlet at $\delta = 3.6$ ppm characteristic of $-\text{O}-\text{CH}_3$ protons of PMMA units, and two other ones at $\delta =$

0.9 ppm and $\delta = 1.0$ ppm corresponding to protons of methyls on PMMA chains. The graft copolymer structure of the product was also proved in ¹³C-NMR by the presence on the spectra of a peak at $\delta = 177$ ppm characteristic of carbonyl carbons of PMMA units, and two peaks at $\delta = 125$ ppm and $\delta = 135$ ppm corresponding to unsaturated carbons of *cis* 1,4-polyisoprene units. FT-IR analysis (Fig. 5) confirmed the formation of graft copolymers as the presence the $\nu_{\text{C}=\text{O}}$ valence absorption band at 1728 cm^{-1} and the $\nu_{\text{C}=\text{C}}$ one at 1664 cm^{-1} .

The main parameters (monomer concentration, DEDT-NR unit content in DEDT-NR macroinitiator) that may influence the reaction of PMMA grafting onto NR chains were studied.

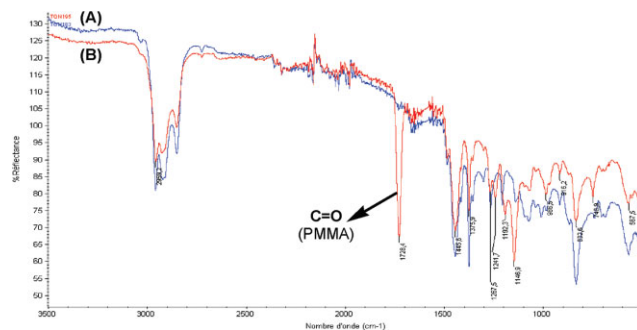


Figure 5 Superposition of IR spectra of (A) DEDT-NR and (B) NR-g-PMMA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

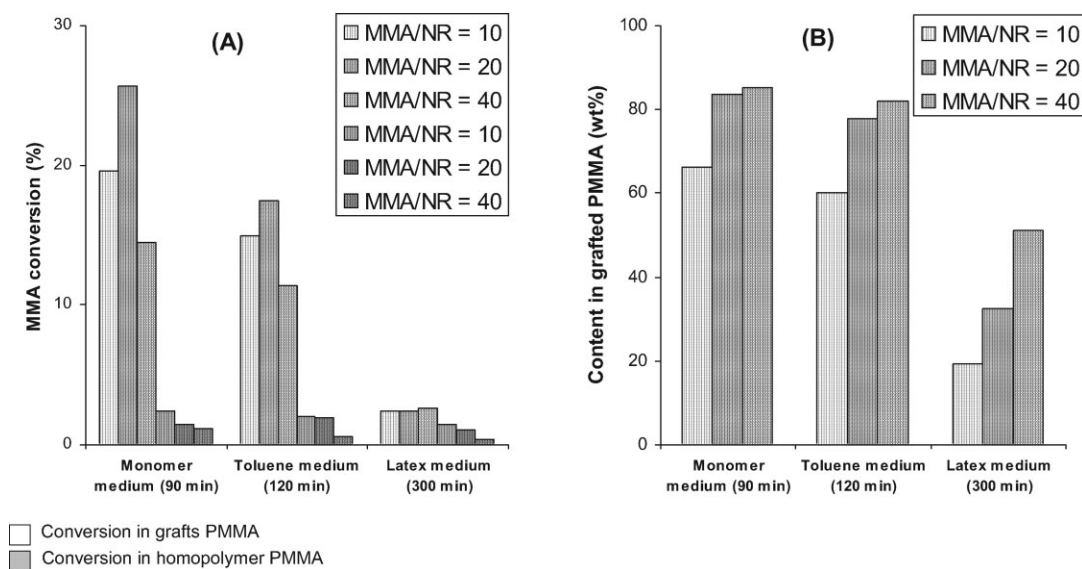


Figure 6 Photopolymerization of MMA initiated from DEDT-NR in monomer medium, toluene solution, and latex medium, respectively: Influence of MMA concentration on (A) the conversion of MMA in grafts and in homopolymer, respectively, and (B) the content of grafted PMMA. Reaction conditions: NR2 as macroinitiator, room temperature.

After each experiment, the proportions of MMA transformed in grafts and in homopolymer, respectively, were calculated by applying the following relationships [eqs. (1) and (2)]:

$$\text{Conversion of MMA in grafts (\%)} = \frac{m_{\text{co}} - m_{\text{NR}}}{m_{\text{MMA}}} \times 100 \quad (1)$$

$$\text{Conversion of MMA in homopolymer (\%)} = \frac{m_h}{m_{\text{MMA}}} \times 100 \quad (2)$$

where m_{co} is the weight of PMMA-grafted NR obtained (fraction insoluble in acetone), m_{NR} is the weight of DEDT-NR used for the reaction, m_{MMA} is the weight of MMA used for the reaction, and m_h is the weight of homopolymer formed (fraction soluble in acetone).

The content of grafted PMMA in the graft copolymer was obtained from the following relationship [eq. (3)]:

$$\text{Content in grafted PMMA (wt\%)} = \frac{m_{\text{co}} - m_{\text{NR}}}{m_{\text{co}}} \times 100 \quad (3)$$

Influence of the concentration in monomer

To study the effects of MMA concentration on the PMMA grafting rate onto NR, three MMA/DEDT-NR weight ratios (g/g) were considered: 10, 20, and 40. The grafting was performed successively in monomer medium, in solution in toluene, and in latex medium, with NR2 as macroinitiator.

The efficiency of the grafting is influenced by the nature of the reaction medium regardless of the concentration in MMA (Fig. 6). The significant decrease in performance following the order: monomer medium > toluene medium > latex medium was expected due to the opacity of latex medium limiting the penetration of UV rays. However, the fact that the PMMA grafting can occur in latex medium, even if the grafting rate remains low compared with those obtained in other conditions, is an interesting result in terms of future development.

Detailed analysis of MMA conversions [Fig. 6(A)] showed that the MMA conversions were very low, even for the reactions carried out in monomer medium and in toluene solution. The increase in viscosity of the reaction medium observed during the grafting progress was probably the cause to the limitation of MMA conversion rate. The grafting efficiency, which can be estimated by comparing the proportions of MMA converted in grafts with the one in homopolymer, was shown to be optimal when the grafting was carried out in monomer medium with a MMA / DEDT-NR weight ratio of ~ 20 . Under these

TABLE II
Influence of MMA Concentration on the Average Length of PMMA Grafts Formed in Side Position of NR Chains

MMA/DEDT-NR (g/g)	\overline{DP}_n		
	Monomer medium	Toluene medium	Latex medium
10	20	15	3
20	53	36	5
40	60	47	11

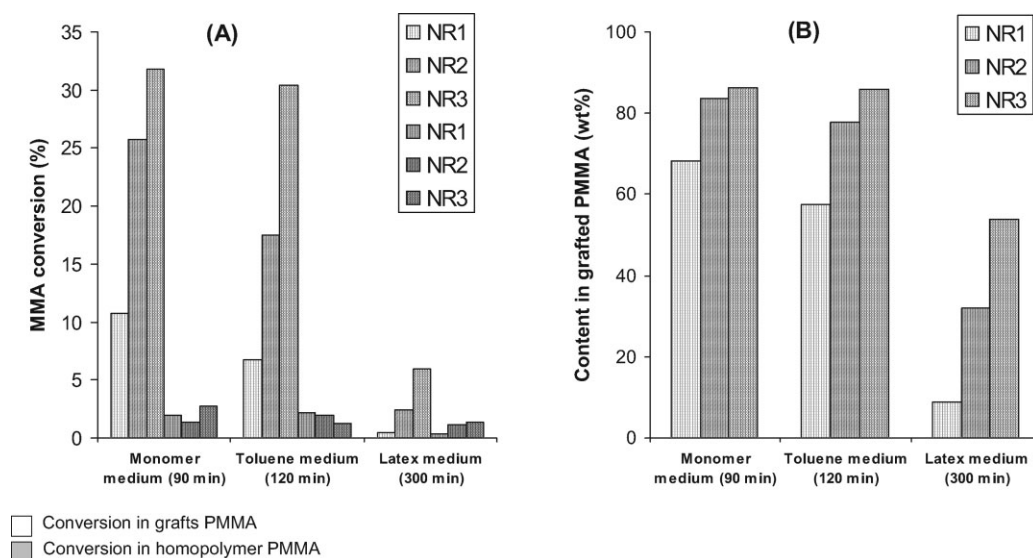


Figure 7 Photopolymerization of MMA initiated from DEDT-NR in monomer medium, toluene solution, and latex medium, respectively: Influence of the content in DEDT-NR units in the macroinitiator (NR1, NR2, and NR3, respectively used) on (A) the conversion of MMA in grafts and in homopolymer, respectively, and (B) the content in grafted PMMA. Reaction conditions: MMA/DEDT-NR = 20 (w/w), room temperature.

conditions, very high grafting efficiencies were obtained, showing that the probabilities for secondary initiations, such as from DEDT³⁴ formed *in situ* during the grafting reaction, are very low. However, contrary to what was noted in monomer medium and in toluene solution, the efficiency of the grafting carried out in latex medium improved by increasing the MMA/DEDT-NR weight ratio.

Contrary to the MMA conversions, the contents in grafted PMMA in graft copolymers were relatively high (between 20 and 90 wt %), even when the reactions were carried out in latex medium [Fig. 6(B)]. In all cases, they increased with increasing MMA concentration. However, contrary to what was observed for the conversion of MMA in PMMA grafts [Fig. 6(A)], the amount of grafted PMMA in the copolymers prepared in monomer medium and in toluene solution reached a plateau when MMA / DEDT-NR weight ratio higher ~ 20 are used. In the case of copolymers obtained in latex medium, no plateau was observed and the content in grafted PMMA continued to increase with increasing monomer concentration.

The average lengths of grafts (\overline{DP}_n) increase with an increasing MMA/DEDT-NR weight ratio as summarized in Table II. The calculations assume that all *N,N*-diethyldithiocarbamate sites present on the DEDT-NR chains initiate MMA polymerization to form PMMA grafts.

Influence of the rate in DEDT-NR units in the DEDT-NR macroinitiator

To study the influence of this parameter, NR1, NR2, and NR3 were successively used as macroinitiators,

with a MMA/DEDT-NR weight ratio = 20. As before, the grafting was carried out at room temperature.

As noted in the previous study dealing with the influence of MMA concentration, the order of reactivity decreases as follows: monomer medium > toluene medium \gg latex medium whatever the macroinitiator used (Fig. 7). The results given in Figure 7(A) show that in same medium, the conversion of MMA in grafts increases with increasing the concentration in DEDT-NR units within NR chains. It was the same concerning the efficiency of grafting.

Regarding the contents in grafted PMMA in the graft copolymers, their evolution was comparable with that of the conversions of MMA in grafts [Fig. 7(B)].

In terms of average length of PMMA grafts (Table III), it is quite surprising to note that the higher the content in DEDT-NR units in DEDT-NR is, the higher the \overline{DP}_n values of PMMA grafts are.

Synthesis of polystyrene-grafted NRs

The studies with styrene were performed by considering a styrene/DEDT-NR weight ratio = 20. The

TABLE III
Influence of DEDT-NR Unit Content in DEDT-NR on the Average Length of PMMA grafts Formed in Side Position of NR chains of NR-g-PMMA

DEDT-NR sample	\overline{DP}_n		
	Monomer medium	Toluene medium	Latex medium
NR1	38	24	2
NR2	53	36	5
NR3	44	42	8

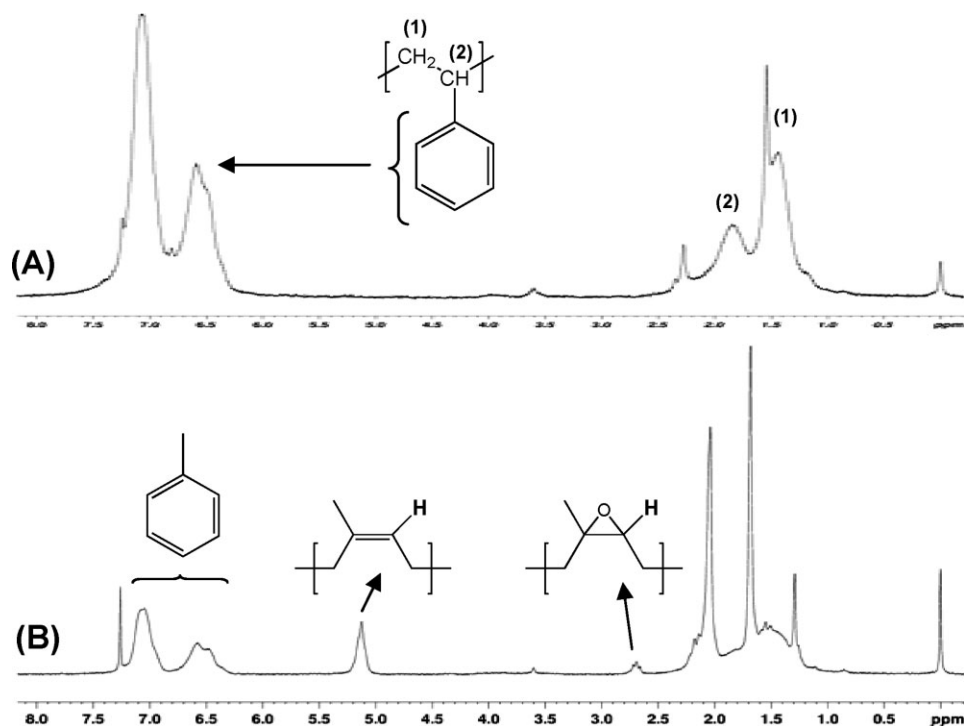


Figure 8 Photopolymerization of styrene initiated from DEDT-NR: $^1\text{H-NMR}$ spectra of (A) soluble fraction and (B) insoluble fraction.

procedures of synthesis and reaction conditions were identical to those used for grafting of PMMA onto NR. The crude mixtures obtained after grafting were extracted with acetone, and the respective soluble and insoluble fractions isolated were analyzed by $^1\text{H-NMR}$.

Analyses by $^1\text{H-NMR}$ of the fractions soluble in acetone [Fig. 8(A)] showed the single presence of homopolystyrene. Only signals corresponding to aromatic protons of polystyrene structures were noted on the spectra: two signals at $\delta = 6.6$ ppm and at $\delta = 7.1$ ppm corresponding to the aromatic protons, and two other ones at $\delta = 1.4$ ppm and at $\delta = 1.9$ ppm cor-

responding to the alkyl protons of polystyrene backbone. By contrast, the fractions insoluble in acetone [Fig. 8(B)] contained polystyrene-grafted NR as confirmed by $^1\text{H-NMR}$. The polystyrene grafts were characterized by the signals at $\delta = 6.6$ ppm and $\delta = 7.1$ ppm characteristic of polystyrene aromatic protons, and rubber backbones by the signal at $\delta = 5.2$ ppm corresponding to the proton on carbon-carbon double bond of 1,4-polyisoprene units of NR chains. A triplet at $\delta = 2.7$ ppm corresponding to protons of oxirane rings of residual epoxidized 1,4-polyisoprene units was also observed.

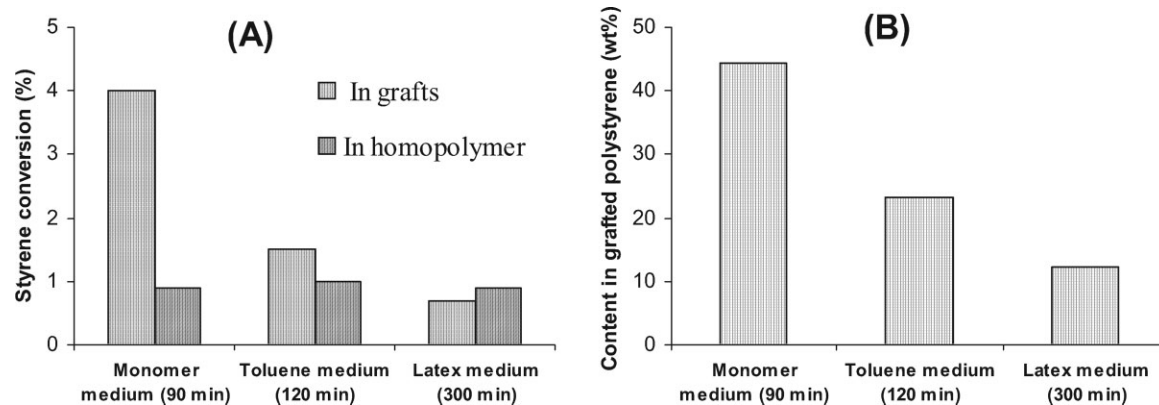


Figure 9 Photopolymerization of styrene initiated from DEDT-NR: Influence of the nature of the reaction medium on (A) the conversion of styrene in grafts and homopolymer, respectively, and (B) the content in grafted polystyrene. Reaction conditions: NR2 as macroinitiator, styrene/DEDT-NR = 20 (w/w), room temperature.

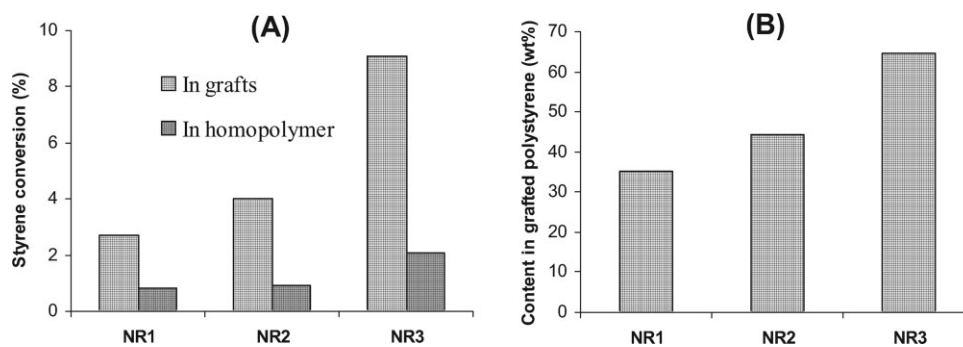


Figure 10 Photopolymerization of styrene initiated from DEDT-NR: Influence of the content in DEDT-NR units in the macroinitiator (NR1, NR2, and NR3, respectively used) on (A) the conversion of styrene in grafts and in homopolymer, respectively, and (B) the content in grafted polystyrene. Reaction conditions: in monomer medium, styrene/DEDT-NR = 20 (w/w), room temperature, 90 min.

For the first study, the synthesis of polystyrene-grafted NR was performed with NR2 as macroinitiator and experiments were performed in monomer medium, in solution in toluene, and in latex medium. The results show that the grafting of polystyrene onto NR was more difficult than that of PMMA as the grafting rates obtained are much lower [Fig. 9(A)]. For example, considering experiments carried out in same conditions in monomer medium [Figs. 6(A) and 9(A)], the conversion of styrene in polystyrene grafts after 90 min of irradiation was only 4%, compared with 25% obtained with MMA. The order of reactivity depending on the nature of the medium used was the same as that observed with MMA, i.e. monomer medium > toluene medium \gg latex medium. However, the contents in grafted polystyrene obtained were nevertheless quite acceptable, even in latex medium in which a grafting rate of 13% was obtained [Fig. 9(B)].

In a second study, the purpose was to examine the influence of the rate of DEDT-NR units contained in the DEDT-NR macroinitiator. The experiments were carried out in monomer medium. The results obtained with the different macroinitiators, i.e. NR1, NR2, and NR3 (Fig. 10), showed that the conversion of styrene in polystyrene grafts [Fig. 10(A)] and the rate of grafted polystyrene in the copolymer [Fig. 10(B)] increased with increasing concentration of initiating units in the macroinitiator, as expected. However, the increase of the proportion of styrene converted in homopolymer was more sur-

prising, as well as that of the average length of grafts (Table IV). Because same styrene/DEDT-NR weight ratios were used for each experiment, the average length of the grafts should normally decrease.

Synthesis of polymethacrylonitrile-grafted NRs

The grafting of polymethacrylonitrile onto NR was performed in monomer medium, in solution in toluene, and in latex medium, respectively.

In methacrylonitrile medium, no graft copolymer formed by using NR2 as macroinitiator, most likely due to the insolubility of NR2 in methacrylonitrile. The result was same in latex medium: no polymethacrylonitrile grafting was observed whatever the conditions used, even after 24 h of irradiation.

On the other hand, the grafting of polymethacrylonitrile was achieved with success in toluene medium onto NR1, NR2, and NR3, using a methacrylonitrile/DEDT-NR weight ratio = 20. It was confirmed by the analyses of the fractions insoluble in acetone, performed in FT-IR (Fig. 11: presence of a $\nu_{\text{C}\equiv\text{N}}$ absorption band at 2234 cm^{-1} and a $\nu_{\text{C}=\text{C}}$ one at

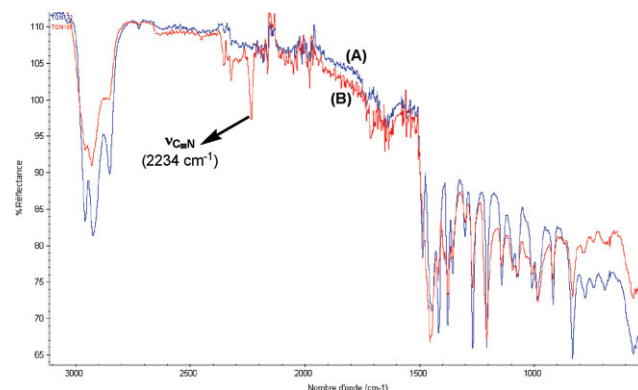


Figure 11 Superposition of IR spectra of (A) DEDT-NR and (B) polymethacrylonitrile-grafted NR. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE IV
Influence of DEDT-NR Unit Content in DEDT-NR on the Average Length of Polystyrene Grafts Formed in Side Position of NR chains of NR-g-PS

	DEDT-NR		
	NR1	NR2	NR3
\overline{DP}_n	9.2	7.9	12.0

TABLE V
Photopolymerization of Methacrylonitrile Initiated from DEDT-NR
in Toluene Medium

Macroinitiator	Irradiation time (h)	Methacrylonitrile conversion		Content in grafted polymethacrylonitrile in the graft copolymer (%)
		In grafts (%)	In homopolymer (%)	
NR1	2	0.2	0.4	3.8
NR2	2	0.3	0.5	5.7
NR3	2	0.4	2.4	7.4
NR3	24	2.9	0.8	36.7

1664 cm^{-1}) and ^{13}C -NMR (presence of a peak at $\delta = 122$ ppm corresponding to $-\text{C}\equiv\text{N}$ carbons), respectively. However, it was noted that the grafting rate was very slow and long irradiation times were necessary to obtain significant rates in grafted polymethacrylonitrile (Table V).

Synthesis of polyacrylamide[and poly(acrylic acid)]-grafted NRs

Because acrylamide and acrylic acid are strongly hydrophilic monomers, attempts of photopolymerizations initiated from DEDT-NR were performed only in a latex medium.

The crude polymer mixtures obtained with acrylamide were extracted with distilled water. Analyses of both soluble and insoluble fractions by ^1H -NMR, showed that the grafting did not occur. Soluble portion contained polyacrylamide homopolymer. The lack of grafting can be explained by considering the opposed polarities of the acrylamide monomer and the radical centers on the 1,4-polyisoprene chains of NR.

When acrylic acid was used, DEDT-NR coagulation was systematically observed immediately after introduction of the monomer in the reaction medium, even when this last was stabilized with high proportions of Sinnopal NP 307 surfactant (up to 10 phr compared with the amount of dry rubber). Consequently, the grafting of poly(acrylic acid) onto NR could not be considered.

CONCLUSION

A new procedure of synthesis of polymer-grafted NRs has been developed with the aim of preparing graft copolymers containing low proportions of homopolymer. The methodology adopted was to initiate the photopolymerization of a vinyl monomer from *N,N*-diethyldithiocarbamate groups previously introduced onto *cis* 1,4-polyisoprene units of NR chains. The feasibility of the grafting method considered was successfully tested using a model molecule of the initiating *N,N*-diethyldithiocarbamate-functionalized 1,4-polyisoprene unit, i.e. *S*-(2-hydroxy-2-methyl-1-*n*-propylpentyl) *N,N*-diethyldithiocarbamate.

After having proved the feasibility of the "grafting from" method considered, a systematic study of the synthesis of polymer-grafted NR was performed. Various graft copolymers derived from NR were successfully prepared by photopolymerization of vinyl monomers (MMA, styrene, methacrylonitrile) initiated from *N,N*-diethyldithiocarbamate-functionalized NRs (DEDT-NRs) acting as macroinitiators. Analysis methods, i.e. SEC, ^1H -NMR, ^{13}C -NMR, and FT-IR, were used to characterize the formation of the various polymer-grafted NRs. The studies showed that the grafting success was crucially dependent on the nature of the monomer. The ability of the monomer to polymerize from DEDT-NR macroinitiator was limited to its hydrophobic nature.

The synthesis of PMMA-grafted NR and polystyrene-grafted NR was successfully carried out in monomer medium, in solution in toluene, and also in latex medium. The reaction medium affects the grafting yield, with the highest yields being obtained in a monomer medium and the lowest in latex one. In all cases, increasing the concentration of monomer and the density of initiating units in the DEDT-NR macroinitiator resulted in a high proportion of grafted polymer within the graft copolymer and an increase in the average chain length of the grafts (\overline{DP}_n). Moreover, the proportions of homopolymer formed during the grafting process were still low whatever the medium considered.

The grafting reaction was less successful with hydrophilic monomers (methacrylonitrile, acrylamide, acrylic acid) compared with hydrophobic ones. Polymethacrylonitrile-grafted NRs could be prepared in toluene but with low yields. No grafting was observed with acrylamide and acrylic acid.

The authors acknowledge fellowship from Agence Universitaire de la Francophonie (AUF).

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