Synthesis of Macromonomers of Acrylic Acid by Telomerization: Application to the Synthesis of Polystyrene-*g*-Poly(acrylic acid) Copolymers

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ABSTRACT: The synthesis of macromonomers of acrylic acid was performed by telomerization in a three-step process. The first step was the telomerization of *tert*-butyl acrylate in the presence of thioglycolic acid. Different molecular weights were obtained with different ratios of the monomer to the transfer agent. Good control of the molecular weights and architectures of the oligomers (e.g., the presence of an acid function on the chain end) was observed. The transfer constant of *tert*-butyl acrylate with thioglycolic acid was assessed (chain-transfer constant = 0.6). In the second step, the terminal unsaturation of the oligomers was obtained by the reaction of the terminal acid groups with 2-isocyanatoethyl methacrylate to yield the macromonomers of *tert*-butyl acrylate. In the last step, the *tert*-butyl acrylate groups were hydrolyzed in the presence of trifluoroacetic acid at room temperature. The macromonomers were copolymerized with styrene to obtain graft copolymers, and the reactivity ratios were evaluated. Finally, the copolymers were characterized with surface electron microscopy and atom force microscopy. © 2006 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 45: 395–415, 2007

Keywords: copolymerization; graft copolymers; macromonomers; oligomers; telomerization

INTRODUCTION

Poly(acrylic acid) (PAA) and poly(methacrylic acid) are weak polyelectrolytes in which the degree of ionization is governed by the pH and ionic strength of the aqueous solution. For instance, PAA is virtually undissociated at a low pH (<4), whereas a fully charged chain results at a high pH (>8).[1–3] Moreover, these polymers are known to form interactions with various nonionic, proton-accepting polymers and with cationic polyelectrolytes in aqueous or organic media.[4] Thus, neutralization with organic or inorganic bases allow the preparation of polymers able to complex cations such as metal ions. These polymers are good candidates for the synthesis of ion-exchange membranes or can be used as mineral dispersants in the paper and

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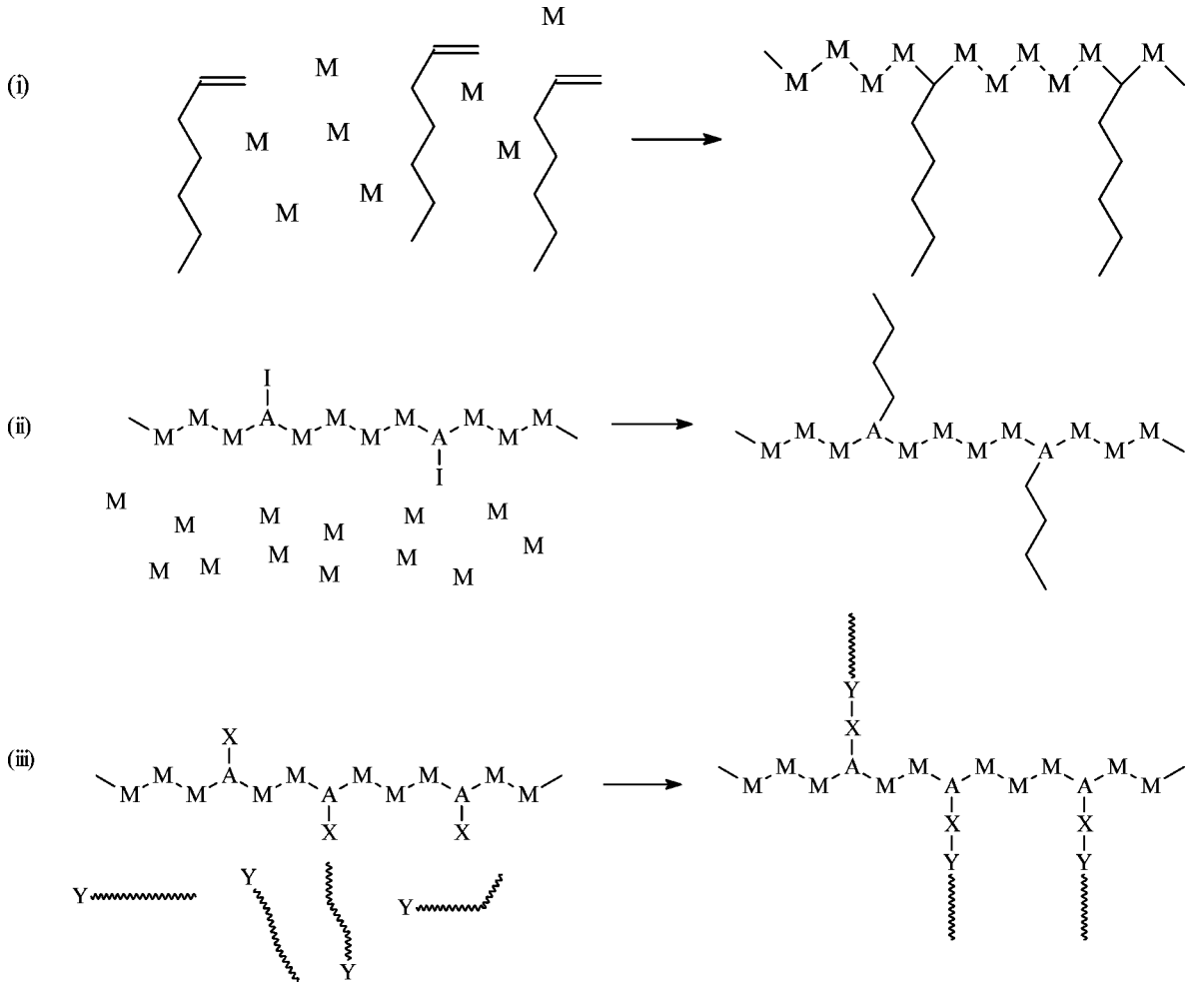


Scheme 1. General chemical methods for synthesizing graft copolymers (M is the monomer, and X, Y, and I are the functional groups).

paint industries.[5–9] Poly[(meth)acrylic acid] can be successfully used as a component of characteristic intelligent organic–inorganic hybrid materials, and recently, several authors have used these polymers to encapsulate active substances.[10–13] Thus, the simple modification of the pH allows the release of the active substances. These various applications have justified research of copolymers with good control over their architectures. In this article, the synthesis of poly[(meth)acrylic acid]-based grafted copolymers is studied. Generally, there are three methods of synthesize graft polymers (Scheme 1). The first one, which was widely used in the past decade, is the conventional radical polymerization of macromonomers. The second method is the grafting-from method, in which the side chains are initiated by pendant initiating groups fixed on the polymer backbone. The last method is the grafting-onto technique. The grafting of side chains onto a backbone is carried out via a coupling reaction. In this work, the chosen strategy is the copolymerization of macromonomers to lead to graft copolymers.

In the literature, few studies are devoted to the synthesis of macromonomers bearing carboxylic acid groups. Indeed, the presence of acid functions on the main chains disturbs the functionalization of the chain ends by an unsaturation. Rempp and coworkers,[14–18] Ito and a coworker,[19,20] and Boutevin et al.[21] summarized different methods used to obtain macromonomers. Ishizu and coworkers[22,23] obtained graft copolymers by the radical copolymerization of a macromonomer carrying a styrenic function. The macromonomer was synthesized by the rad-

ical polymerization of *tert*-butyl acrylate (*tert*-BuA) performed with 2,2′-azobis(*N,N*′-dimethyleneisobutyramidine) and with a transfer agent (allylmalonic acid diethyl ester). The functionalization was achieved in a second step by the reaction of the amidine function with chloromethyl styrene, and then the polymer was hydrolyzed in an acidic medium. The functionality in the double bond (f) was close to 1. Mueller and coworkers[24–27] proposed the synthesis of macromonomers by the atom transfer radical polymerization (ATRP) of *tert*-BuA with 2-hydroxyethyl 2-bromoisobutyrate as the functionalized initiator. These authors obtained monofunctional oligomers of *tert*-BuA with a terminal hydroxyl function in a one-pot reaction. The terminal halogen atoms of these oligomers are detrimental to the synthesis of graft copolymers via ATRP. Therefore, they were replaced by a hydrogen atom via transfer from *N,N,N*′*N*′*N*″-pentamethyldiethylenetriamine (PMDETA) with an excess of PMDETA at the end of the polymerization. The esterification of the hydroxyl group with methacryloyl chloride led to well-defined macromonomers with low polydispersity indices (PDIs; close to 1.2). McHale et al.[28] prepared macromonomers by the polymerization of acrylic acid in the presence of an addition–fragmentation chain-transfer agent.[29–35] The chain-transfer constant (C_T) for acrylic acid polymerization was measured for two addition–fragmentation chain-transfer agents: ethyl α-(bromomethyl)acrylate ($C_T = 1.25$) and *tert*-butyl α-(bromomethyl)acrylate ($C_T = 1.14$). The functionality in unsaturation was equal to 0.6 with ethyl α-(bromomethyl)acrylate and to 0.70 with *tert*-butyl α-(bromomethyl)acrylate at a low conversion rate (10%). Moreover, the functionality in unsaturation decreased versus the monomer conversion and did not allow the synthesis of a macromonomer with a high conversion rate. A second route was tested with *tert*-BuA, which was hydrolyzed in a second step to give the acrylic acid macromonomers. The latter were tested in copolymerization, and the authors showed that the acrylic acid macromonomers were more reactive than the *tert*-butyl macromonomer ones.

To the best of our knowledge, this is the first time that telomerization has been used to synthesize acrylic acid macromonomers. Telomerization presents various advantages; for instance, it can be used in industrial processes with low costs of production. We developed two strategies for the synthesis of acrylic acid macromonomers. The first strategy is the synthesis of acid acrylic oligomers by telomerization with 2-mercaptoethanol, and the unsaturation is inserted by a reaction with 2-isocyanatoethyl methacrylate (IEM). The second strategy is the synthesis of *tert*-butyl acrylic oligomers by telomerization in the presence of 2-mercaptoethanol or thioglycolic acid, and the insertion of unsaturation is performed by a reaction between the terminal functions (alcohol or acid) of the oligomers and acylating agent, that is, IEM. In the last step, the *tert*-BuA groups are hydrolyzed to give the acrylic acid macromonomers.

EXPERIMENTAL

Materials

tert-BuA (Aldrich; 99%) was vacuum-distilled (20 mmHg, 70 °C) before use; methacrylic acid (Aldrich; 99%) was used without purification. Thioglycolic acid (Aldrich; 99%), 2-mercaptoethanol (Fluka; 99%), acetonitrile (SDS; 99.9%), chloroform (SDS; 99.5%), dibutyl tin dilaurate (DBTDL; Aldrich; 95%), triethylamine (SDS; 98%), dioxane (SDS; 99%), trifluoroacetic acid (TFA; Aldrich; 99%), IEM (Aldrich; 99%), and an iodine solution (0.1 mol L^{-1}; Aldrich) were used without other purification. 2,2′-Azobisobutyronitrile (AIBN; Fluka; 98%) was purified by recrystallization in methanol and vacuum-dried (20 mmHg, 20 °C, 12 h).

Analytical Techniques

The molecular weights were measured by size exclusion chromatography (SEC) with polystyrene standards (Polymer Laboratories). The chromatograms were recorded on a Spectra-Physics apparatus equipped with an SP 8850 pump and a Spectra Physics SP 8430 RI differential refractometer and with Phenogel columns from Polymer Laboratories (Mixed D, 500 and 100 Å). Tetrahydrofuran (THF) was used as the solvent at a 0.8 mL min^{-1} flow rate at 30 °C.

The ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 200 and 400. Apparatus with tetramethylsilane as the reference and $CDCl_3$, dimethyl sulfoxide-d_6, or tetrahydrofuran-d_8 (THF-d_8) as the solvent.

The Fourier transform infrared (FTIR) analyses were performed on a Nicolet 510P spectrometer with an accuracy of ±2 cm^{-1}.

Gas chromatography (GC) was performed on a Delsi Instruments 330 apparatus equipped with a Shimadzu C-R6A integrator and a 2-M Carbowax 20M poly(ethylene glycol) column. Nitrogen was used as the gas vector at a pressure of 1.5 bar. The analysis was performed at an oven temperature of 150 °C. GC was used to determine the monomer conversion rate.

The glass-transition temperatures (T_g's) were determined by differential scanning calorimetry (DSC) with a PerkinElmer Pyris 1 apparatus calibrated with indium. The samples (ca. 10 mg) were heated from −100 to 100 °C at a rate of 20 °C/min.

Synthesis of the Methacrylic Acid Telomers with 2-Mercaptoethanol

A typical synthesis is given for a transfer agent/monomer molar ratio (R_0) of 0.125 [theoretical number-average polymerization degree ($DP_{n,theoretical}$) = 8]. Twenty grams (2.30×10^{-1} mol) of methacrylic acid, 2.24 g (2.80×10^{-2} mol) of 2-mercaptoethanol, and 50 mL of CCl_4 were introduced into a round-bottom flask fitted with a condenser. The solution was bubbled with argon for 20 min. After 14 h at 65 °C, the solution was cooled to room temperature. The telomer was filtered and washed with dichloromethane before vacuum drying (20 mmHg) for 48 h at room temperature. The telomer was characterized by ^{1}H NMR analysis.

Functionalization of the Methacrylic Acid Telomers with IEM

The methacrylic acid telomer (4 g, 3.6×10^{-3} mol; $DP_{n,theoretical} = 8$), 0.56 g (3.6×10^{-3} mol) of IEM, 0.2 mL of DBTDL, and 50.0 mL of THF were introduced into a 200-mL, two-necked flask equipped with a stirrer, a rubber septum, and a condenser. The reaction was carried out at 50 °C for 14 h.

Synthesis of the *tert*-BuA Monoadduct Bearing an Acid or Alcohol Function

tert-BuA (10 g, 8.0×10^{-2} mol), 6.24 g (8.0×10^{-2} mol) of mercaptoethanol or 7.36 g (8.0×10^{-2} mol) of thioglycolic acid, 15.6 g (1.6×10^{-1} mol) of triethylamine, and 100 mL of acetonitrile were introduced into a round-bottom flask fitted with a condenser. The mixture was heated at 60 °C for 6 hrs. The solvent was evaporated to give the functionalized monoadduct (yield = 95%).

Functionalization of the Monoadduct Bearing an Alcohol Function with IEM

An alcohol-functionalized monoadduct (2.06 g, 1.0×10^{-2} mol), 1.20 g (1.0×10^{-2} mol) of acryloyl chloride, and 10 mL of dried chloroform were introduced into a flask. The reaction was carried out at room temperature for 24 h. The solvent was evaporated to recover the functionalized monoadduct.

A monoadduct (2.06 g, 1.0×10^{-2} mol) bearing an alcohol function and 50 mL of chloroform were dried by azeotropic distillation with a Dean–Stark vessel. After drying, 1.56 g (1.0×10^{-2} mol) of IEM, 0.01 mL of DBTDL, and 10 mL of chloroform were introduced into the flask. The reaction was carried out at 60 °C for 6 h.

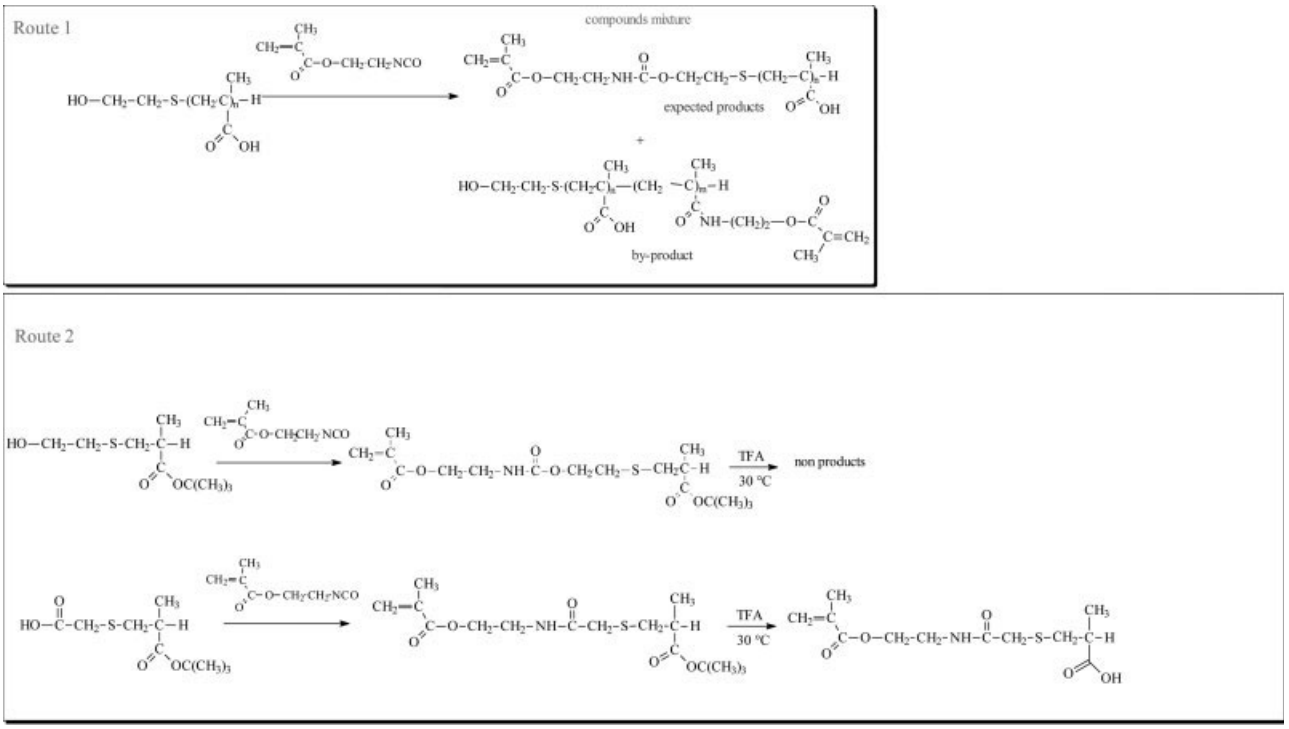
Synthesis of the *tert*-Butyl Acrylic Telomer with 2-Thioglycolic Acid

Different telomerizations were performed in acetonitrile with different R_0 values ranging from 0.330 to 0.020 and with 2-thioglycolic acid.

For example, with $R_0 = 0.330$, 20 g (0.156 mol) of *tert*-BuA, 4.80 g (0.053 mol) of thioglycolic acid, 0.26 g (1.6×10^{-3} mol, $C_0 = [\text{initiator}]_0/[\text{monomer}]_0 = 0.01$) of AIBN, and 50 mL of acetonitrile were introduced into a round-bottom flask. The solution was degassed for 15 min with argon. The reaction was carried out at 70 °C for 14 h. The solvent and the excess of the telogen were removed by distillation under reduced pressure (10^{-2} mmHg, 90 °C). The products were characterized with SEC, ^{1}H NMR, and ^{13}C NMR analyses. This telomer appeared as a viscous liquid (yield = 90%).

Functionalization of the *tert*-Butyl Acrylic Telomer [Number-Average Polymerization Degree (DP_n) = 3.4] with IEM

The functionalization of *tert*-BuA telomers was performed with IEM. For instance, 5.26 g (0.01 mol) of a *tert*-BuA telomer bearing an acid function was dissolved in 200 mL of toluene and dried for 4 h at 130 °C by azeotropic distillation with a Dean–Stark vessel. After drying, 1.56 g (0.01 mol) of IEM and 0.02 mL of DBTDL were



Scheme 2. Different pathways for the synthesis of (meth)acrylic acid macromonomers.

added with a syringe. The reaction was carried for 6 h at 60 °C, and at last the toluene was evaporated under reduced pressure. The macromonomer appeared as a viscous liquid. This product was analyzed with ^{1}H NMR and Fourier Transfer Infrared (FTIR).

Hydrolysis of the *tert*-BuA Functions

Five grams of the macromonomer (DP_n = 6.3; 0.032 mol of the *tert*-BuA function), 5.6 g (0.050 mol) of TFA, and 25 mL of $CHCl_3$ were introduced into a flask. The reaction was left at room temperature for 36 h. The solvent was removed, and the product was dissolved in THF before being precipitated in pentane. The solid was filtered and dried in a vented oven.

Determination of C_T of Thioglycolic Acid according to O'Brien's Method

Samples were taken out of the solution every 15 min and quenched by immersion in an ice bath. The mercaptan consumption was evaluated by the titration of mercaptan groups with a 5×10^{-3} mol L^{-1} solution of iodine in acetonitrile. Titrations were repeated three times for each sample. The monomer consumption was evaluated by GC with acetonitrile as the internal reference.

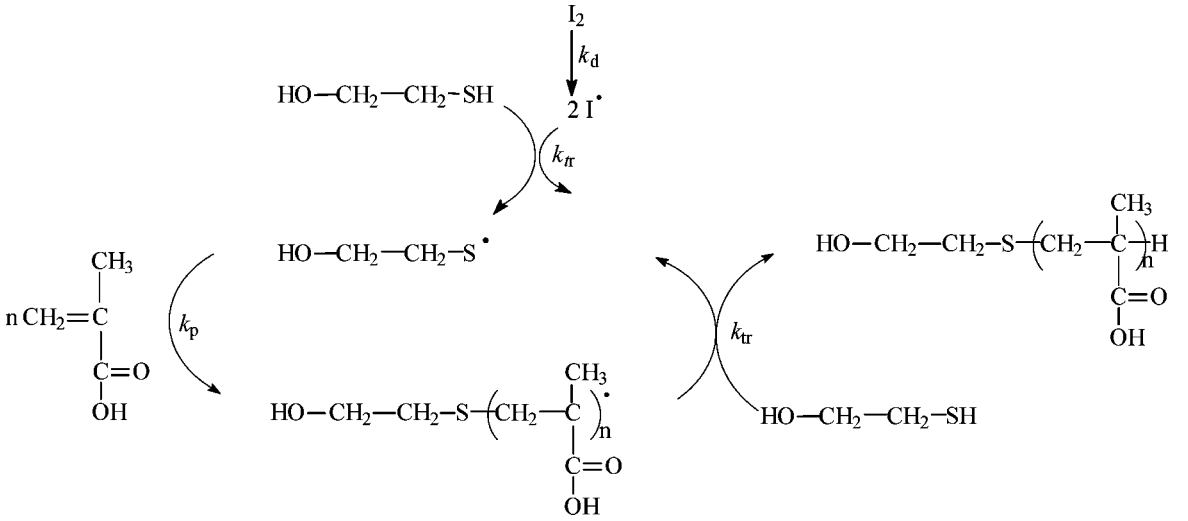
RESULTS AND DISCUSSION

In this work, we develop different strategies for the synthesis of acrylic acid macromonomers, and they are summarized in Scheme 2. The first way (route 1) is the direct use of alcohol-functionalized methacrylic acid adducts. The transformation of the alcohol groups is performed in a second step by a reaction with IEM. This strategy is limited by the competitive reaction of alcohols and acids with isocyanate. In this way, we tested the use of the catalyst (DBTDL) to favor the first reaction. In the first part, the telomerization of *tert*-BuA was performed with 2-mercaptoethanol.

Synthesis of the Macromonomers by the Functionalization of Methacrylic Acid Telomers

Transfer Reaction (Telomerization)

The raducal transfer reaction (Telomerization)[36–51] is based on the transfer reaction of growing



Scheme 3. Mechanism of the radical-transfer reaction (telomerization).

radicals onto thiols[52–54] or halogenated compounds[46,55] and is well adapted to the synthesis of functionalized oligomers with a good control of the molecular weights (from 1000 to 10,000 g/mol; Scheme 3).

The first step is related to the telomerization of methacrylic acid with 2-mercaptoethanol as a transfer agent. This reaction allows us to obtain oligomers carrying a hydroxyl chain-end function. This reaction was performed at 65 °C for 14 h in CCl_4 as the solvent in the presence of AIBN as the initiator. Under these conditions, the synthesized oligomers precipitated in the medium. They were recovered by filtration and washed with pentane before being dried under vacuum.

The presence of the transfer agent in the oligomer structure is confirmed by ^{1}H NMR. The O*H* signal appears at 4.8 ppm [in deuterated dimethyl sulfoxide (DMSO)], and the signal at 3.5 ppm is attributed to the methylene in the α position of the OH group. The CH_2 signal of the transfer agent in the α position of the S atom is masked by the peak of DMSO (at ca. 2.5 ppm). DMSO was selected as the solvent for ^{1}H NMR to characterize the OH and COOH signals. Moreover, the CH_3 signal of the monomer was observed around 1 ppm, the CH_2 signal was observed around 2 ppm, and finally, the acid proton signal was observed around 12.4 ppm. The experimental number-average polymerization degree ($DP_{n,experimental}$) can be assessed with ^{1}H NMR (taking into account the COOH and OH integrals):

$$DP_{n,experimental} = \int COOH \Big/ \int OH \qquad (1)$$

$DP_{n,theoretical}$ was calculated with the molar ratio of the monomer to the transfer agent (R_0; eq 2). This equation is valid for conversion rates close to 1 and whatever C_T value. Different oligomers were synthesized with various values of R_0. The number-average molecular weights (M_n's) and PDIs of the oligomers were measured by SEC analysis in dimethylformamide (DMF) as the eluent. The SEC analysis was calibrated with polystyrene standards. Thus, the $DP_{n,experimental}$ value is close to the $DP_{n,theoretical}$ value when CCl_4 is used as the solvent, whereas in acetonitrile, we observe low control of $DP_{n,experimental}$ (Table 1):

$$DP_{n,theoretical} = 1/R_0 = [M]_0/[T]_0 \qquad (2)$$

where $[T]_0$ and $[M]_0$ are the transfer-agent and monomer concentrations, respectively, at the initial time.

Thus, the telomerization reaction is a convenient reaction adapted to obtain functionalized methacrylic acid oligomers.

Functionalization of the Methacrylic Acid Oligomers

The functionalization of the methacrylic acid oligomers was performed with IEM. The reaction of isocyanate functions onto alcohol ones was per-

Table 1. Variation of $DP_{n,experimental}$ and $DP_{n,theoretical}$ according to the Nature of the Solvent and R_0 for the Telomerization Reaction of Methacrylic Acid with 2-Mercaptoethanol

		Acetonitrile		CCl_4	
R_0	$DP_{n,theoretical}$	$DP_{n,experimental}$[a]	M_n[b] (PDI)	$DP_{n,experimental}$[a]	M_n[b] (PDI)
0.250	4	6.5	800 g mol^{-1} (1.7)	3.5	400 g mol^{-1} (1.4)
0.125	8	12	1500 g mol^{-1} (1.8)	7.6	850 g mol^{-1} (1.6)

[a] Measured with ^1H NMR.
[b] Measured with SEC (with DMF as the eluent).

formed with or without a catalyst (DBTDL). To obtain information about this reaction, it was tested on model molecules such as methoxyethanol and propionic acid. The reactions of these model molecules with IEM allowed us to obtain two different functions: amide and urethane groups (Scheme 4). The ^1H NMR spectra of the products coming from the reaction of IEM with the alcohol group and from the reaction of IEM with the acid group show a peak around 7.4 ppm ascribed to a urethane function and a peak around 7.9 ppm ascribed to an amide function, respectively. These two signals are characteristic of these two reactions and permit us to evaluate if a competition reaction occurs when the alcohol and acid functions are in the presence of IEM.

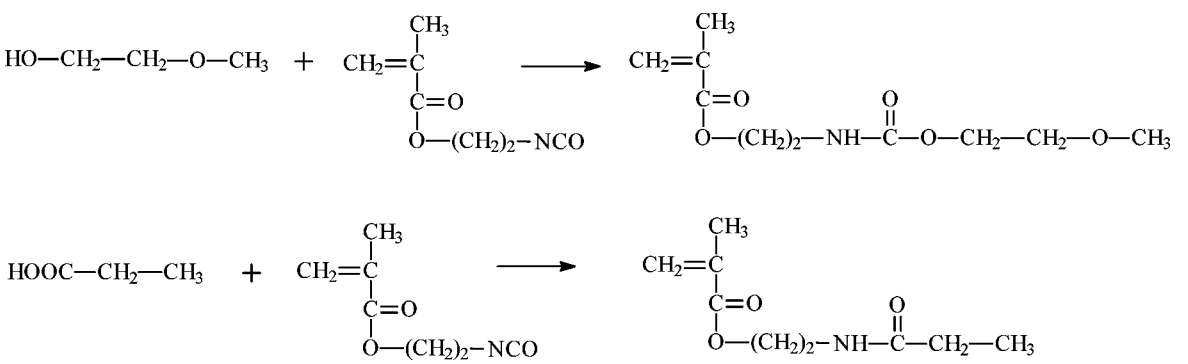
A mixture of the two compounds (methoxy ethanol and propionic acid) was reacted with IEM. The reaction was carried out at 60 °C for 6 h in the presence of different amounts of DBTDL. At the end of the reaction, the product was characterized by ^1H NMR. A comparison of the integrals of the amide peak around 7.9 ppm ($NH_{7.9ppm}$) and of the urethane peak ($NH_{7.4ppm}$) makes it possible for us to evaluate the yield (β) of the isocyanate/alcohol reaction:

$$\beta = \frac{\int NH_{7.4ppm}}{\int NH_{7.4ppm} + \int NH_{7.9ppm}} \times 100 \qquad (3)$$

The yield of the reaction is 66 and 75% without and with 0.1% DBTDL as the catalyst, respectively. Therefore, the use of the catalyst does not favor the isocyanate/alcohol reaction.

However, this reaction was tested with a methacrylic acid oligomer (DP_n = 7.6). In this case, a new signal appeared around 6.2 ppm and was attributed to urea N*H* coming from the reaction of isocyanate with moisture (see Scheme 1 in the supplementary material).

This result shows that oligomers have to be carefully dried before use. The only method that allowed us to eliminate the presence of water without any side reactions was the azeotropic distillation of water with DMF with a Dean–Stark vessel. With this experimental technique, the formation of urea was avoided. However, we did not succeed in favoring the isocyanate/alcohol reaction and did obtain oligomers with a perfectly well-defined structure. Thus, this method



Scheme 4. Study of the reactivity of isocyanate groups with alcohol and acid functions.

is not adequate for the synthesis of methacrylic acid macromonomers.

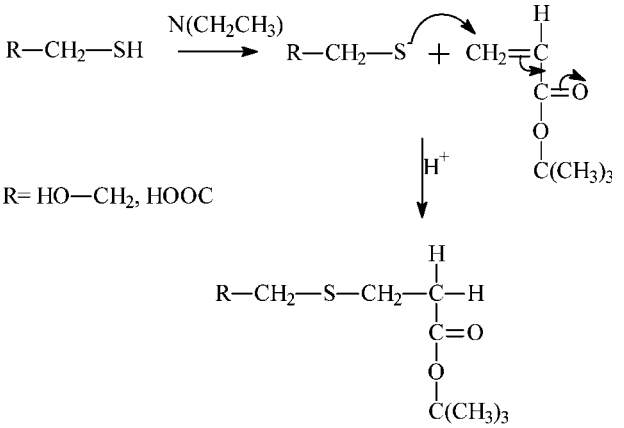
Synthesis of the Methacrylic Acid Macromonomers with *tert*-BuA Oligomers

In this second part, the synthesis of *tert*-BuA oligomers was performed, and they were functionalized with IEM. The *tert*-butyl function is commonly used as protection for acid functions in organic chemistry. Indeed, these esters are easily hydrolyzed to lead to acid functions. This procedure adds a new step to the macromonomer synthesis, but the functionalization of the oligomers is made easier by the presence of only one chain-end function that can react. However, two conditions have to be respected for this method: the deprotection must be easy and quantitative, and it must not affect the double bond of the macromonomer. To check this method, practical conditions were experimentally tested on a model molecule.

Synthesis of the tert-BuA *Monoadduct with Thioglycolic Acid or 2-Mercaptoethanol*

In this part, the synthesis of model molecules was performed to make ^{1}H NMR interpretations easier. The synthesis of the monoadduct was carried out in acetonitrile with *tert*-BuA and two transfer agents: 2-mercaptoethanol and thioglycolic acid. The reactions were carried out without a radical initiator but with triethylamine according to a nucleophilic mechanism (Michael addition; Scheme 5). The triethylamine allows the formation of the corresponding thiolate by displacing the acid–base equilibrium. The thiolate can be thus added to the double bond (acrylate or methacrylate double bond; Scheme 5). The advantage of this synthesis is the acquisition of the monoadduct in a very high yield and with a high purity.

The nucleophilic addition reaction was carried out at room temperature for 4 h in the presence of 2-mercaptoethanol, *tert*-BuA, acetonitrile, and triethylamine. In the case of *tert*-BuA, this reaction was exothermic and quickly occurred, whereas the reaction was slower in the case of *tert*-butyl methacrylate, taking 6 h at 60 °C. At the end of the reactions, the solvents were evaporated, and the products were isolated by extraction (water/chloroform). In the ^{1}H NMR spectrum, the disappearance of the S*H* group signal at 1.5 ppm and of the acrylate double bond



Scheme 5. Synthesis of alcohol- or acid-functionalized monoadducts by nucleophilic addition.

around 5.5–6.5 ppm confirms that the addition occurred. Other displacements confirm the structure of the monoadduct: peaks at 2.65 and 2.55 ppm are attributed to the C*H*$_2$ in the α and β positions of the S atom, respectively. The signal characteristic of the *tert*-butyl group appears around 1.4 ppm. The presence of the telogen agent is confirmed by various signals: the alcohol signal appears around 4.8 ppm, and the signals of C*H*$_2$ in positions α and β of the alcohol function are located at 3.6 and 2.8 ppm, respectively (see Fig. 1 in the supplementary material).

In the case of the acid-functionalized monoadduct, 2-mercaptoethanol was replaced by the thioglycolic acid under similar experimental conditions. ^{1}H NMR shows the total disappearance of the *H*S signal of the thioglycolic acid around 2.0 ppm and of the acrylic double bond centered at 5.5–6.5 ppm. The signal of C*H*$_2$ adjacent to the position of the acid function (*i*) appears at 3.3 ppm, and the C*H*$_2$ signals (*d* and *e*) of the acrylate monomers appear at 2.8 and 2.5 ppm, respectively (Fig. 1). However, in the case of thioglycolic acid, a byproduct can be observed that can be ascribed to the reaction of thiol with acid functions to give a thioester group. This product can also react with the double bond of *tert*-BuA to give an acid-functional product. FTIR analysis confirms the presence of the acid functions (3200–3400 cm^{-1}) and of the ester function (ca. 1730 cm^{-1}).

Synthesis of the tert-BuA *Based Macromonomers by the Reaction of IEM with Model Molecules*

The second step consists of the connection of the unsaturation to the oligomers to lead to the

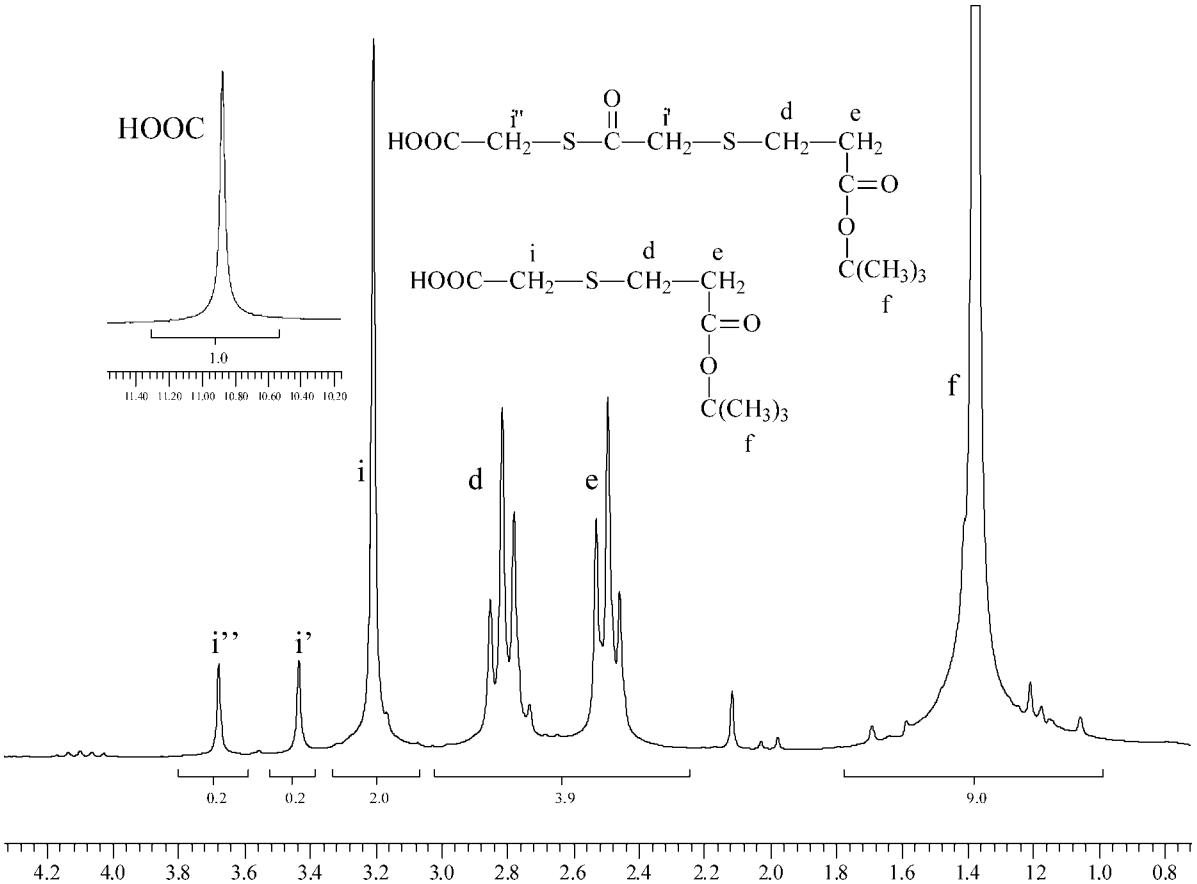


Figure 1. ^{1}H NMR spectrum of the product obtained by the nucleophilic addition of thioglycolic acid to *tert*-BuA ($CDCl_3$).

macromonomer. The link connecting the unsaturation to the telomer must be resistant to the hydrolysis of *tert*-butyl acrylic groups. To study the resistance of different functions (amide or urethane) during the hydrolysis treatment, the syntheses of different model molecules were investigated.

The monoadduct bearing alcohol or acid end groups was dried by azeotropic distillation in toluene (Dean–Stark vessel) at 130 °C for 6 h. The solution was cooled at 60 °C, and IEM was added to the reaction mixture in the presence of DBTDL. The reaction was carried out until the total disappearance of the isocyanate band (2240 cm^{-1}) measured by FTIR. Drying was necessary to avoid the appearance of urea functions (the reaction of isocyanate with residual water) characterized by a signal toward 6.4 ppm in ^{1}H NMR.

Synthesis of the Macromonomer by the Reaction of IEM with the Alcohol-Functionalized Monoadduct. This product was characterized by ^{1}H NMR analysis (see Fig. 2 in the supplementary material). The disappearance of the alcohol function (at 4.8 ppm) and the appearance of the proton of a urethane function at 7.4 ppm confirmed that the reaction had occurred. The shift of CH_2—NCO of IEM from 3.6 to 3.3 ppm showed the formation of urethane —CH_2—N(H)—CO—. Moreover, the displacement of the signal of CH_2 at 3.5 (the α position of an alcohol function) to 4.1 ppm was proof of the total conversion of this CH_2 to urethane. The FTIR analysis confirmed the total disappearance of the isocyanate function (2240 cm^{-1}).

Synthesis of the Macromonomer by the Reaction of IEM with the Acid-Functionalized Monoadduct. According to ^{1}H NMR (Fig. 2), the disappearance of the peak of the acid group (ca. 10 ppm), the appearance of a signal around 7.4 ppm in $CDCl_3$ (7.6 ppm in DMSO), attributed to the N*H* of the amide function, and the total displacement of the signals of methylene of IEM, which shifted from 5.60 and 6.10 ppm to 5.55 and

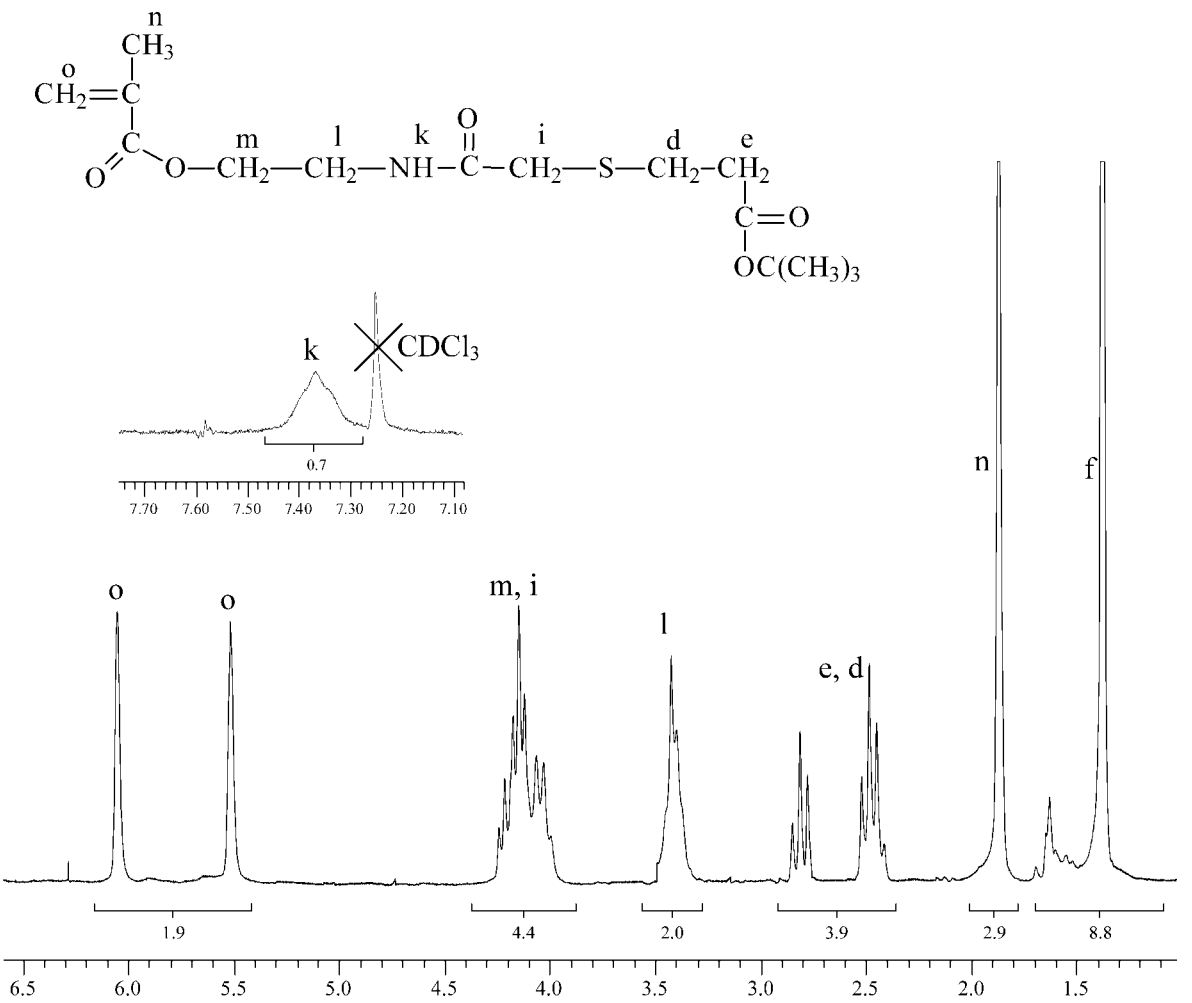


Figure 2. ^{1}H NMR spectrum of the macromonomer obtained by the reaction of the acid-functionalized monoadduct with IEM.

6.05 ppm, showed that the reaction was quantitative. Moreover, the displacement of the signal of the CH_2 (*l*) in the α position of the isocyanate function from 3.5 to 4.0 ppm confirmed the appearance of the urethane function. At last, SEC chromatograms clearly showed the addition of IEM to the acid-functionalized monoadduct (see Fig. 3 in the supplementary material).

Hydrolysis of the tert*-Butyl Acrylic Functions*

In the literature, many methods allowing the hydrolysis of *tert*-butyl acrylic groups[56–59] have been described. However, in our case, this hydrolysis must be carried out in the softest way to avoid the degradation of the macromonomer and to preserve the function connecting the telomer to the double bond.

The quantification of the hydrolysis rate was carried out via the monitoring of the ratio of the COOH signal integral (12 ppm) to the *tert*-butyl signal integral (1.40–1.145 ppm):

$$\text{Hydrolysis (\%)} = \frac{\int \text{COOH}}{\int \text{COOH} + \frac{\int (\text{CH}_3)_3}{9}} \qquad (4)$$

Various hydrolysis techniques were evaluated with different reagents, including hydrochloric acid, acetic acid, and TFA, and they are summarized in Table 1 in the supplementary material.

Techniques requiring high reaction temperatures have been rejected because polymerization of the double bond could occur. The technique using TFA led to the total hydrolysis of the *tert*-butyl ester groups.

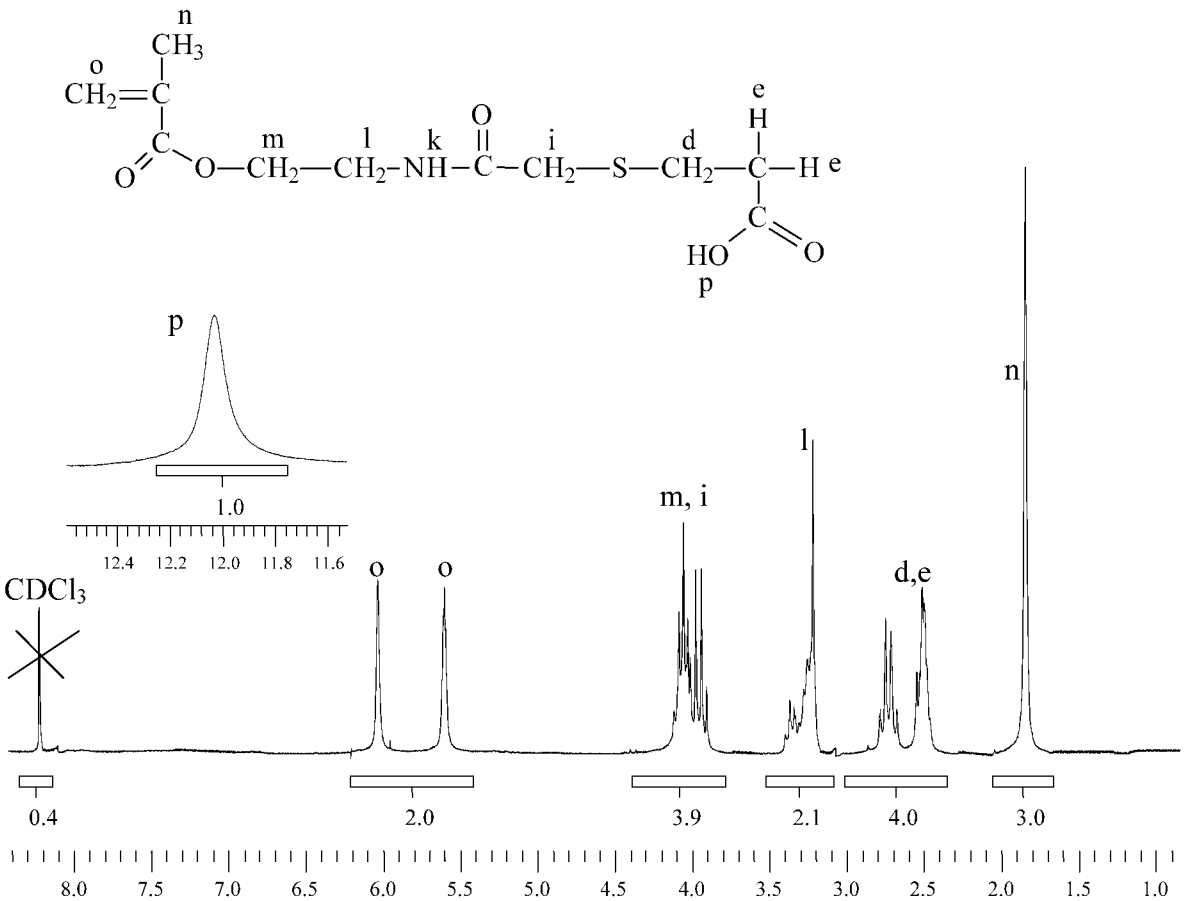


Figure 3. ^{1}H NMR spectrum of the macromonomer obtained after hydrolysis (200 MHz, $CDCl_3$).

The model molecules were tested in a TFA/chloroform mixture (1.5 equiv of TFA to 1 equiv of *tert*-butyl) at 30 °C for 36 h. At the end of the reaction, the solvent was evaporated. The product was isolated by extraction with a 50/50 (v/v) water–ether mixture. The product obtained was characterized by ^{1}H NMR and SEC analysis.

In the case of the model molecule carrying a urethane function, we observed the degradation of the latter (the disappearance of the signals of the double bond at 5.55 and 6.05 ppm and the absence of the N*H* signal assigned to the urethane group at 7.4 ppm).

In the case of the model molecules carrying the amide bond, ^{1}H NMR revealed the good resistance of these functions to acid hydrolysis. Figure 3 exhibits the spectrum of the acid-functionalized macromonomer obtained by the reaction of the acid-functionalized compound with IEM after the hydrolysis step. The *tert*-butyl group (*f*; 1.40–1.45 ppm) totally disappeared, whereas a new signal (*p*) centered at 10 ppm appeared (corresponding to the COOH group). The other signals (*o*, *n*, *d*, and *e*) remained unchanged. Moreover, the FTIR spectrum showed an increase in the intensity of the band around 3200–3600 cm^{-1} (which became broad and intense). The characteristic band of amide functions (at 1690 cm^{-1}) was still observed.

Starting from these results, we chose to synthesize macromonomers from the telomerization of *tert*-BuAs that were hydrolyzed in a second step.

Telomerization of *tert*-BuA

The telomerization of *tert*-BuA was carried out in acetonitrile at 70 °C for 14 h in the presence of a transfer agent (thioglycolic acid) and initiated by AIBN. At the end of the reaction, the solvent and the monomer that did not react were removed by distillation under reduced pressure.

Table 2. DP_n Values of the Oligomers Obtained by the Telomerization of *tert*-BuA in the Presence of Thioglycolic Acid Initiated with AIBN

		DP_n						
Run	R_0	Theoretical	SEC	NMR	M_n (SEC)	PDI (SEC)	Functionality[a]	Yield (%)
T0	1	1	1.8	1.9	340	1.35	1	70
T1	0.330	3	3.4	3.7	550	1.70	0.98	94
T2	0.200	5	5.2	6.3	890	1.75	0.96	95
T3	0.125	8	7.8	9.2	1078	1.80	0.93	97
T4	0.100	10	10.3	11.1	1398	1.82	0.92	96
T5	0.050	20	23.5	25.2	3344	1.87	0.83	95
T6	0.020	50	60	—	7760	1.86	0.68	95

[a] Measured by titration.

Table 2 summarizes the characteristics of the different telomers from various R_0 values; the transfer-agent concentration was allowed to control the molecular weights. The functionality of the acid functions of these oligomers was assessed by titration with a methanolic sodium hydroxide solution (0.01 N). The oligomers with a low molecular weight ($M_n < 2000$ g mol^{-1}) present a functionality close to 0.80–0.90, whereas the oligomers with a high molecular weight ($M_n > 5000$ g mol^{-1}) present a low functionality (close to 0.3–0.5). This decrease in the functionality can be explained by the direct initiation of polymerization from moieties coming from the decomposition of the initiator. Thus, the telomerization appears to be an easy process for obtaining functionalized oligomers.

SEC chromatograms showed a typical molecular weight distribution of the telomers (see Fig. 4 in the supplementary material), and the PDI was in agreement with that generally obtained with this type of polymerization. Moreover, it is

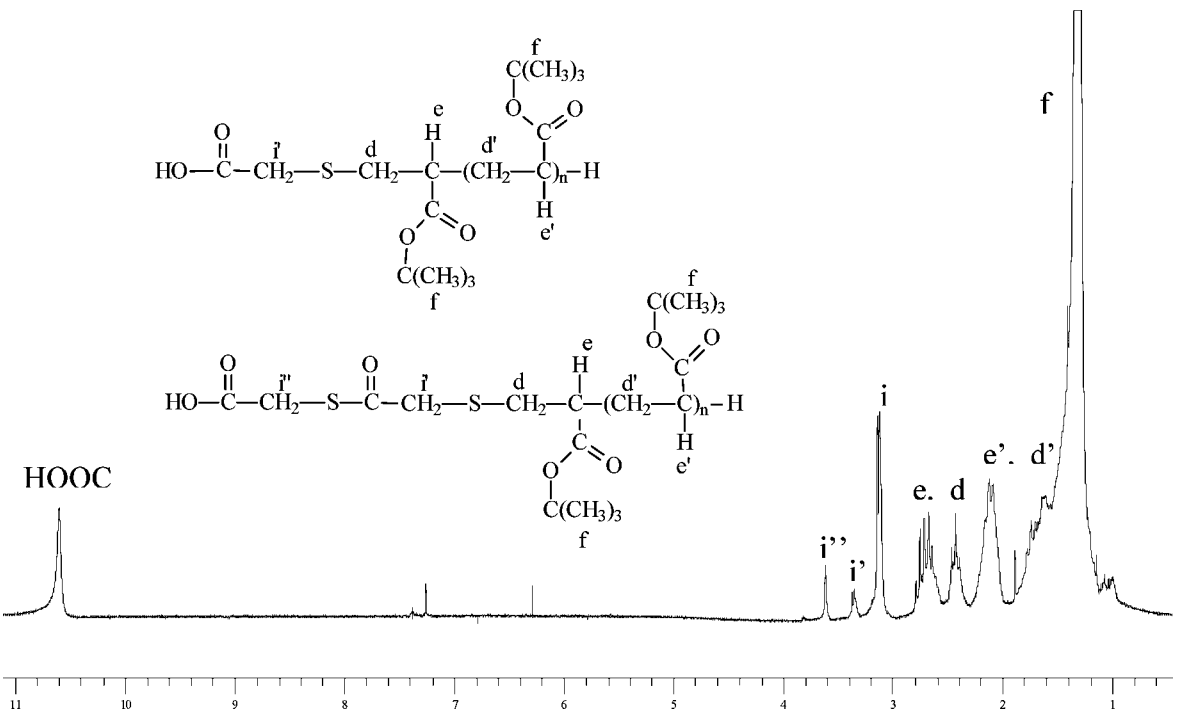


Figure 4. ^{1}H NMR spectrum of telomers of *tert*-BuA with thioglycolic acid ($CDCl_3$, 400 MHz).

possible to distinguish different adducts, that is, the monoadduct, diadduct, and so forth.

Theoretical values of DP_n and M_n were calculated according to eq 2 that were valid only for conversion rates close to 1 and whatever C_T value. ^{1}H NMR spectra confirmed the structure of the telomers (Fig. 4) by the *tert*-butyl group signals at 1.40–1.45 ppm (*f*) and by the CH and CH_2 groups of poly(*tert*-butyl acrylate) at 1.70 (*d*′) and 2.05 ppm (*e*′), respectively. The presence of the transfer agent (thioglycolic acid) was also confirmed by the signal at 3.20 ppm attributed to the CH_2 (*i*) between the carboxylic acid function and the S atom. In the case of thioglycolic acid, a side by product was observed that could be ascribed to the dimer of thioglycolic acid with a thioester group. The presence of this product was confirmed by the two signals at 3.42 (*i*′) and 3.63 ppm (*i*″). Then, a comparison of the integrals of signals *i*, *i*′, or *i*″ of the transfer agent with the integrals of signals *f* and *e* of *tert*-BuA allowed us to calculate $DP_{n,experimental}$:

$$DP_n = \frac{\int e + f/10}{\int i + i'/2} \quad (5)$$

where $\int f$, $\int e$, *i*, and *i*′ correspond to the integral of the $(CH_3)_3$ signal at 1.4 ppm, CH at 1.6 ppm, and CH_2 of the transfer agent, respectively (Fig. 4).

Assessment of Transfer Constant Value of Thioglycolic Acid

In this study, C_T values were determined in acetonitrile according to two methods: Mayo's method[60] and O'Brien and Gornick's method.[61] The C_T value has a great influence on the molecular weights obtained but more especially on the PDI. Indeed, a C_T value higher than 1 involves a significant consumption of the telogen at the beginning of the reaction and leads to the formation of a mixture of oligomers (low molecular weights, i.e., mono-, di-, and triadducts) and nonfunctional polymer with high molecular weights.

Several methods allow the determination of the transfer constants. The first and most widely used one was described by Mayo.[60] This method requires a plot of the reverse of the initial number-average polymerization degree $[(DP_n)_i]$ versus R_0 (eq 6). The main drawback of this method is that it is only applicable for low conversion rates. In our case, the measured value was 0.60 in acetonitrile at 70 °C in the presence of AIBN as the initiator:

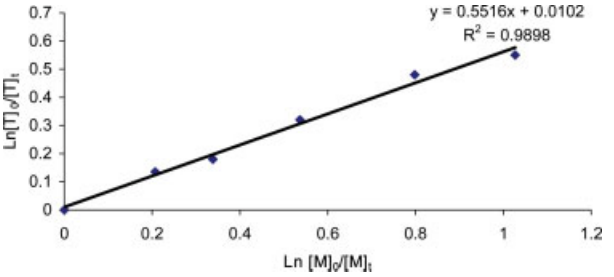


Figure 5. Evaluation of C_T according to O'Brien and Gornick's method for the free-radical telomerization of *tert*-BuA with thioglycolic acid. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

$$1/(DP_n)_i = C_T([T]_0/[M]_0) = C_T \cdot R_0 \quad (6)$$

The method of O'Brien and Gornick[61] allows us to measure C_T by taking into account the conversion rates:

$$Ln([T]_t/[T]_0) = C_T Ln([M]_t/[M]_0) \quad (7)$$

Thus, plotting $Ln([T]_t/[T]_0)$ versus $Ln([M]_t/[M]_0)$ allows us to calculate the C_T value from the slope of the obtained straight line.

The telomerization of *tert*-BuA was also studied with O'Brien and Gornick's[61] method under the same conditions used for Mayo's method.[60] The reaction was monitored by sampling, and each aliquot was quenched in ice to stop the reaction. The monomer and telogen conversions were determined by GC and iodine titration, respectively.

Figure 5 shows the evolution of $Ln([T]_o/[T]_t)$ versus $Ln([M]_o/[M]_t)$ for a telomerization with $R_0 = 0.20$. The slope of the straight line gives a C_T value of 0.55. This value is in good agreement with other values measured with other styrenic, methacrylic, or acrylic monomers and other thiols (Table 3).

Synthesis of the tert-BuA *Macromonomers through the Addition of the* tert-BuA *Oligomer to 2-Isocyanatoethylmethacrylate*

The second step of the synthesis resulted in the connection of the unsaturation to the oligomers to lead to the macromonomers. The technique has already been described in this article. The obtained products were characterized with ^{1}H NMR, and the displacements of the signal are gathered in Figure 6. These signals are in agree-

Table 3. C_T Values Observed for Different Telogens and for Different Monomers

Thiol	Monomer	C_T[a]
1-Butane thiol	Methyl methacrylate	0.66
	Styrene	25
Thioglycolic acid	Methyl methacrylate	0.63
	Styrene	21
2-Mercaptoethanol	Methyl methacrylate	0.41
	2-Dimethylaminoethyl methacrylate	0.60
3-Thiopropionic acid	Methyl methacrylate	0.38
2-Aminoethane thiol	Methyl methacrylate	0.003
	Styrene	7

[a] The data were taken from ref. 63.

ment with the signals obtained in the case of the model molecule.

Using these various signals makes it possible to calculate the final number-average polymerization degree ($DP_n^{(f)}$) of the macromonomer as follows:

$$DP_n^{(f)} = \frac{\int f \Big/ 9}{\int o \Big/ 2} \quad (8)$$

where $\int f$ and $\int o$ correspond to the integrals of the $(CH_3)_3$ signal at 1.4 ppm and of $CH_2{=}C$ at 5.55 and 6.05 ppm, respectively (Fig. 6).

f was reached by the calculation of the ratio of DP_n (before the reaction with IEM) to $DP_n^{(f)}$ (after the reaction with IEM; eq 9). The functionality was close to 1 for low-molecular-weight oligomers, showing that the reaction was total. High-molecular-weight oligomers presented a weaker functionality:

$$f = DP_n/DP_n^{(f)} \quad (9)$$

DP_n and $DP_n^{(f)}$ correspond to the number-average polymerization degrees determined before the reaction with IEM by eq 4 and determined after the reaction with IEM by eq 8, respectively.

In conclusion, telomerization seems to be an efficient method for synthesizing *tert*-BuA macromonomers with low molecular weights (<3000 g mol^{-1}).

Hydrolysis of the tert*-BuA Functions by TFA and Acquisition of the Acrylic Acid Macromonomers*

The reaction was carried out in chloroform at room temperature in the presence of TFA (1.5 equiv of TFA to 1 equiv of *tert*-butyl groups) for 36 h (see the Hydrolysis of the *tert*-BuA Functions section). At the end of the reaction, the macromonomer with $DP_n^{(f)}$ values of 6.4 and 9.5 precipitated in the solvent. This was eliminated by evaporation, and the macromonomer was dissolved in THF and finally precipitated in pentane to eliminate the residual TFA. In the case of $DP_n^{(f)} = 3$, the macromonomer could not be precipitated in pentane. The solvent and TFA (bp = 72 °C) were removed only by distillation.

The physicochemical properties of the macromonomers were modified. They became soluble in polar solvents, such as dioxane, THF, DMF, DMSO, and water, and insoluble in pentane, chloroform, dichloromethane, acetone. Moreover, their aspect changed, and they appeared as white powders after hydrolysis. This change was in agreement with their T_g variations (Table 4).

FTIR showed the appearance of a strong acid band around 3200–3600 cm^{-1} and a slight displacement of the ester band from 1730 to 1715 cm^{-1} ($\upsilon_{C=O\ acid} = 1715$ cm^{-1} and $\upsilon_{C=O\ ester} = 1730$ cm^{-1}). The characteristic band of amide functions (at 1690 cm^{-1}) could still be observed. The other adsorption bands remained unchanged. Lastly, ^{1}H NMR confirmed the absence of the *tert*-butyl groups and a new signal assigned to the carboxylic acid group (see Fig. 5 in the supplementary material). The quantification of the hydrolysis rate was carried out via the monitoring of the ratio of the COOH integral signal (12 ppm) to the *tert*-butyl integral signal (1.40–1.145 ppm). The yield of the hydrolysis was better than 90% under these conditions:

$$\text{Hydrolysis (\%)} = \frac{\int \text{COOH}}{\int \text{COOH} + \frac{\int (CH_3)_3}{9}} \quad (10)$$

Moreover, the macromonomers were analyzed with ^{13}C NMR. The CH_3— carbon signal of the

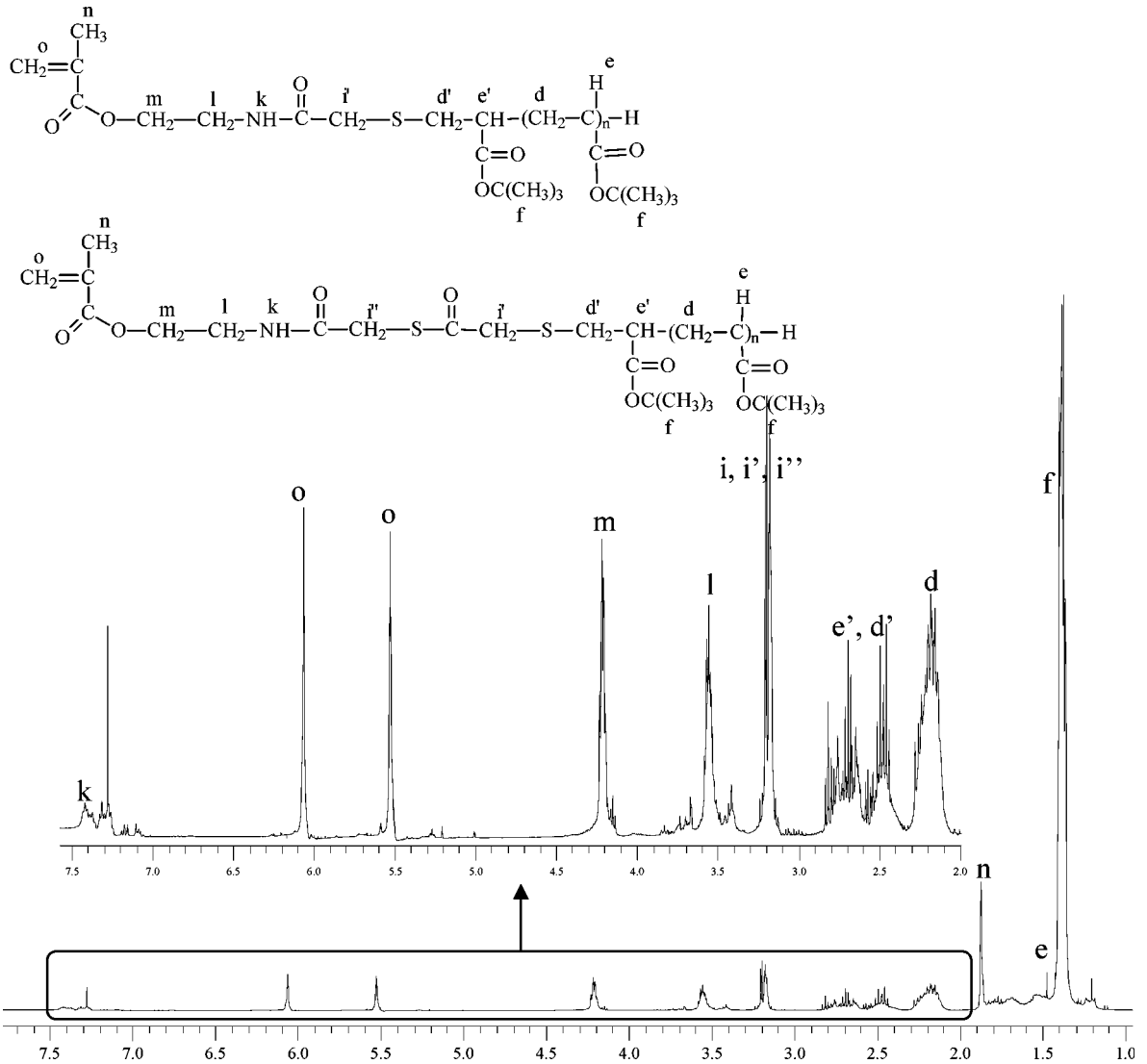


Figure 6. ^{1}H NMR spectrum of the acrylate macromonomer obtained by the reaction of HOOC-P(*tert*-BuA) with IEM (400 MHz, $CDCl_3$).

tert-butyl groups appearing at 28 ppm totally disappeared at the end of the hydrolysis step. The macromonomers after hydrolysis exhibited T_g's higher than those before hydrolysis. This increase in T_g confirmed the hydrolysis of the *tert*-BuA group [Table 5; the T_g values of poly(*tert*-butyl acrylate) with M_n = 30,000 g mol^{-1} and of PAA are 30[64,65] and 100 °C,[64] respectively].

Table 4. DP_n Values of the Macromonomers Obtained by the Reaction of IEM with Telomers of *tert*-BuA

Macromonomer	R_0	DP_n (SEC)	$DP_n^{(f)}$ (NMR)	PDI	f
M1	0.330	3.4	3.5	1.70	0.97
M2	0.200	5.2	5.5	1.75	0.94
M3	0.125	9.2	9.9	1.80	0.93
M4	0.050	23.5	27	1.84	0.87
M5	0.020	60	88	1.90	0.68

Table 5. Variation of T_g for Various Macromonomers before and after Hydrolysis

		T_g (°C)	
Run	$DP_n^{(f)}$	Before Hydrolysis	After Hydrolysis
M1	3.9	−40	20
M2	6.3	−10	30
M3	9.2	0	100

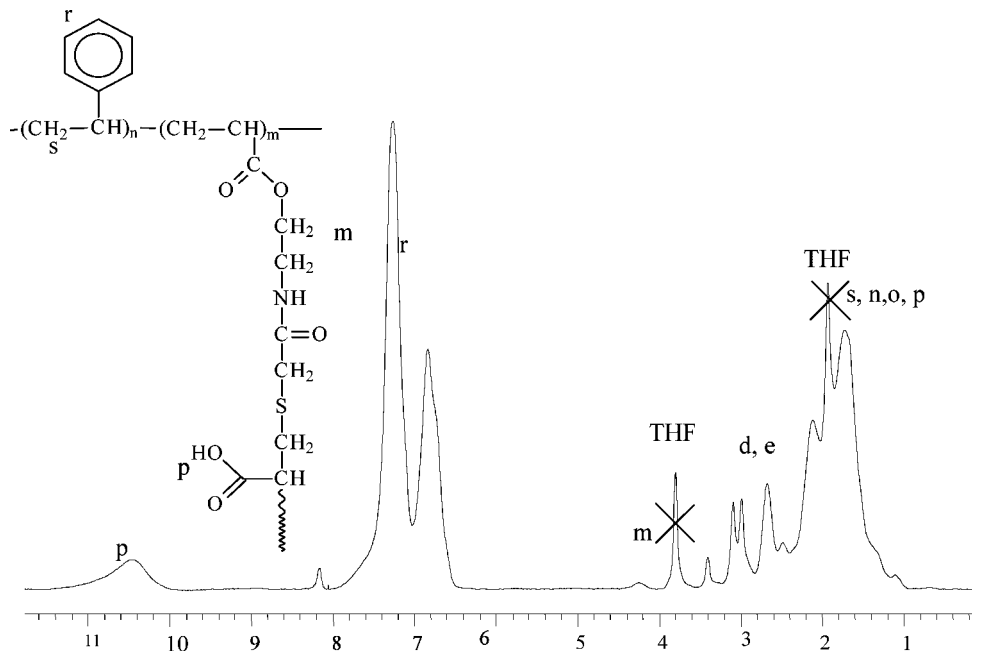


Figure 7. ^{1}H NMR spectrum of the poly(styrene-*g*-acrylic acid) graft copolymers (THF-d_8).

Copolymerization with Styrene

The macromonomers were copolymerized with styrene as the comonomer in the presence of AIBN. These copolymers should present various chemical properties because of the different chemical properties of the two monomers. Indeed, the polystyrene segments are hydrophobic, whereas the PAA segments are hydrophilic. The introduction of grafts bearing acid functions into polystyrene should allow us to improve their adhesion properties or to reach new applications (e.g., cation-exchange membrane). Only a few works[57] describe the synthesis of polystyrene-*g*-poly(acrylic acid) (PS-*g*-PAA) copolymers. Obtained PS-*g*-PAA graft copolymers with the UV irradiation of polystyrene swollen with benzophenone and acrylic acid. Thus, they obtained various copolymers with different contents in acrylic acid. However, the reaction was carried out on films, and during the irradiation, some degradation of the chains occurred. Jiang et al.[34,35] proposed a similar grafting of acrylic acid onto poly(styrene-*b*-butadiene) in the presence of AIBN in solution. In this work, a new process for obtaining graft copolymers was reported with the copolymerization of our macromonomers with styrene.

The copolymerization of these macromonomers with styrene was performed in DMF at 70 °C in the presence of AIBN as the initiator. The choice of DMF as the solvent was justified by the low solubility of the macromonomer in other organic solvents.

The consumption of the monoadduct during copolymerization with styrene was followed with SEC analysis (see Fig. 6 in the supplementary material). This figure shows that the intensity of the macromonomer peak (monoadduct) decreases and a new distribution appears at a low elution time corresponding to the appearance of the graft copolymers.

At the end of the reaction, the copolymers containing 10–30 wt % macromonomer were precipitated in methanol to eliminate the acrylic acid macromonomers that did not react. The copolymers containing 50 wt % macromonomer did not precipitate in methanol and was precipitate in pentane; they were only washed with methanol. ^{1}H NMR showed that all the macromonomer that did not react totally disappeared after the treatment (an absence of a peak toward 5.5 and 6.0 ppm; Fig. 7). Moreover, ^{1}H NMR of the graft copolymers showed the presence of the acid functions toward 10.5 ppm (COOH) and the presence of the —OCH_2— of the macromonomer, which appeared at 4.0 ppm (THF-d_8). The protons of the aromatic rings of styrene appeared around 6.7–7.2 ppm (Fig. 7). Table 6 summarizes the results for the copolymers obtained with the macromonomers.

Table 6. Results of the Copolymerization of the Acrylic Acid Macromonomer with Styrene

	Macromonomer		Experimental Conditions		Copolymers	
Run	DP_n[a]	Functionality[a]	m of Styrene (n)	m of the Macromonomer (n)	M_n (g mol^{-1})[a]	PDI[a]
Blank	—	—	10.4 g (0.1 mol)	—	35,000	2.2
Copo1	6.3	0.98	10.4 g (0.1 mol)	10.0 g (1.4×10^{-2} mol)	23,500	2.4
Copo2	9.2	0.97	10.4 g (0.1 mol)	1.1 g (1.2×10^{-3} mol)	24,100	2.2
Copo3	9.2	0.97	10.4 g (0.1 mol)	5.0 g (5.6×10^{-3} mol)	29,000	1.9
Copo4	9.2	0.97	10.4 g (0.1 mol)	10.0 g (11.2×10^{-3} mol)	28,200	2.4

[a] Determined with SEC.
[b] n and m correspond to number of mol and to molecular weight respectively.

The presence of the macromonomer in the copolymer was confirmed by FTIR. The adsorption band of the acid functions at 3200–3500 and 1715 cm^{-1} and the presence of polystyrene at 3100 cm^{-1} were observed. The amide band was observable around 1650 cm^{-1} (Fig. 8).

Moreover, the ^{13}C NMR analysis confirmed the presence of polystyrene by the carbon of the aromatic rings around 128 ppm and of the acid functions toward 170 ppm characteristic of the macromonomer (Fig. 9).

Characterization of the Copolymers

The synthesized copolymers were analyzed by DSC and showed two T_g's, that is, 80 and 100 °C, which were attributed to polystyrene and PAA segments, respectively (see Fig. 7 in the supplementary material). Moreover, the observation of two T_g's meant, as expected, the presence of two phases in the copolymer, which was confirmed by surface electron microscopy (SEM) and atomic force microscopy (AFM) analyses. Figure 10 shows SEM photographs of PS-*g*-PAA (50/50 w/w) copolymers with nodules 30 nm in diameter. The regularity of the nodules and their small size confirmed that the two phases were perfectly dispersed. Indeed, a mixture of the two homopolymers gave another morphology, that is, large nodules (1–10 μm).

AFM photographs were taken in the tapping mode, (i.e., in the intermittent mode). This mode avoids the deformation of the surface of a sample. In this mode, the point oscillates at a given frequency and hits the surface. When the oscillating cantilever contacts the surface (with bumps and depression), its oscillation is neces-

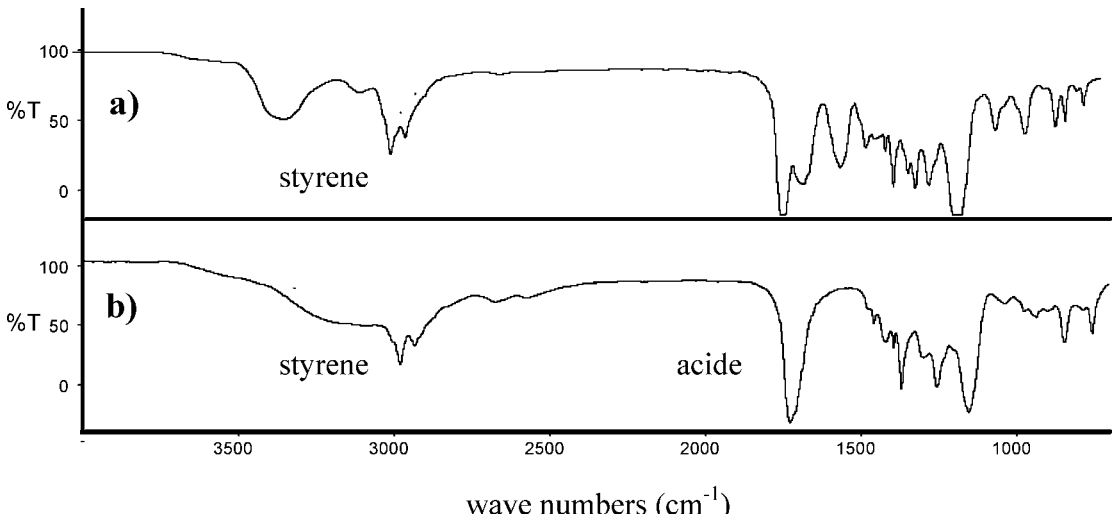


Figure 8. FTIR spectra of the copolymers obtained by the copolymerization of the macromonomer with styrene: (a) PS-*g*-PAA obtained by the copolymerization of the macromonomer with $DP_n = 1$ and styrene (composition = 90/10 w/w) and (b) PS-*g*-PAA obtained by the copolymerization of the macromonomer with $DP_n = 10$ and styrene (composition = 70/30 w/w).

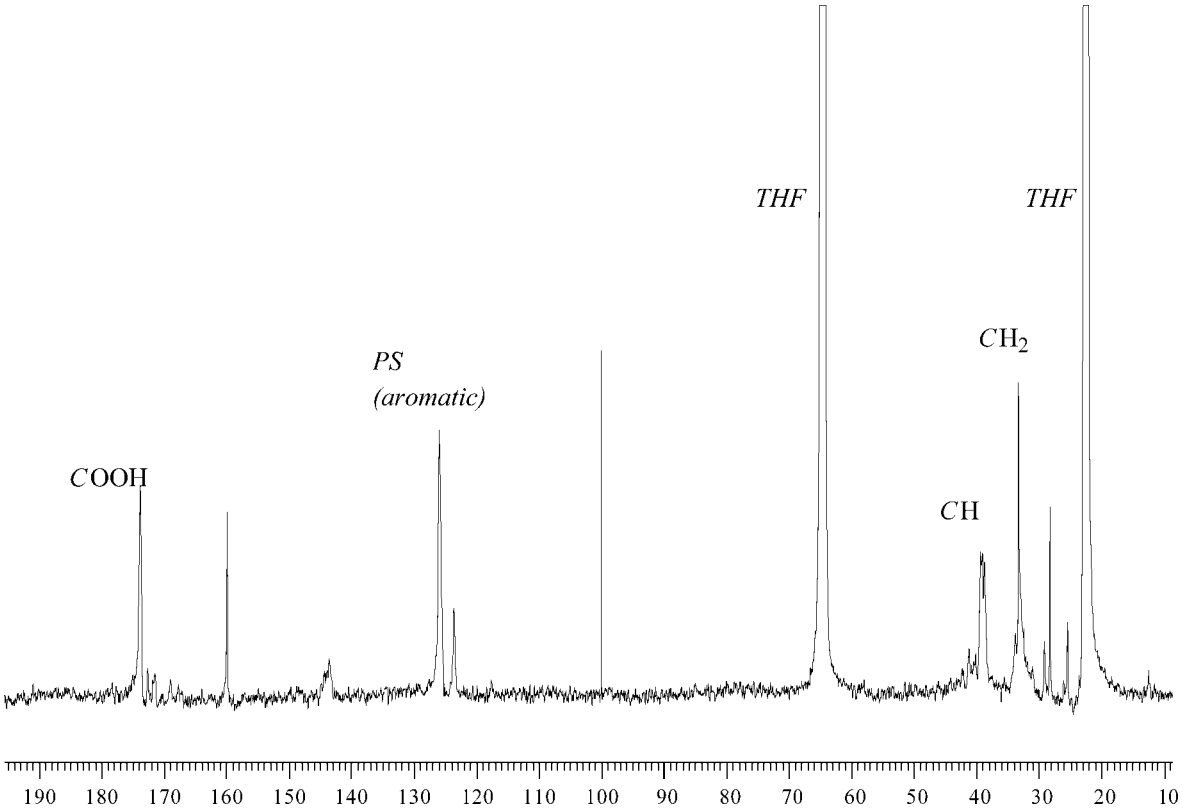


Figure 9. ^{13}C NMR spectrum of the polystyrene-*g*-acrylic acid graft copolymers.

sarily reduced because of energy loss caused by the tip contacting the surface. The reduction in the oscillation amplitude permits the measurement of the surface features. Thus, it is possible to carry out viscoelastic cartographies of surfaces (hard zones and softer zones). In our case, the white zones correspond to the hard zones.

Figure 11 shows the topography of the surface and its roughness. Thus, the surface consists of a multitude of peaks that are on a nanometer

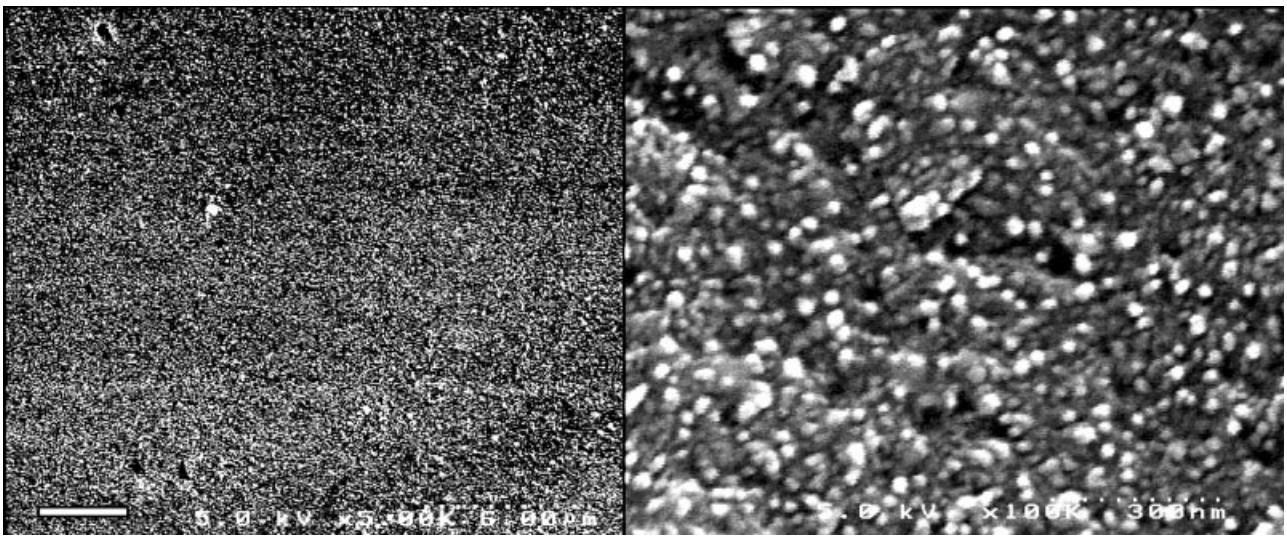


Figure 10. SEM photographs of the PS-*g*-PAA copolymer (50/50 w/w). On the left, 1 cm corresponds to 3 μm; on the right, 1 cm corresponds to 150 nm.

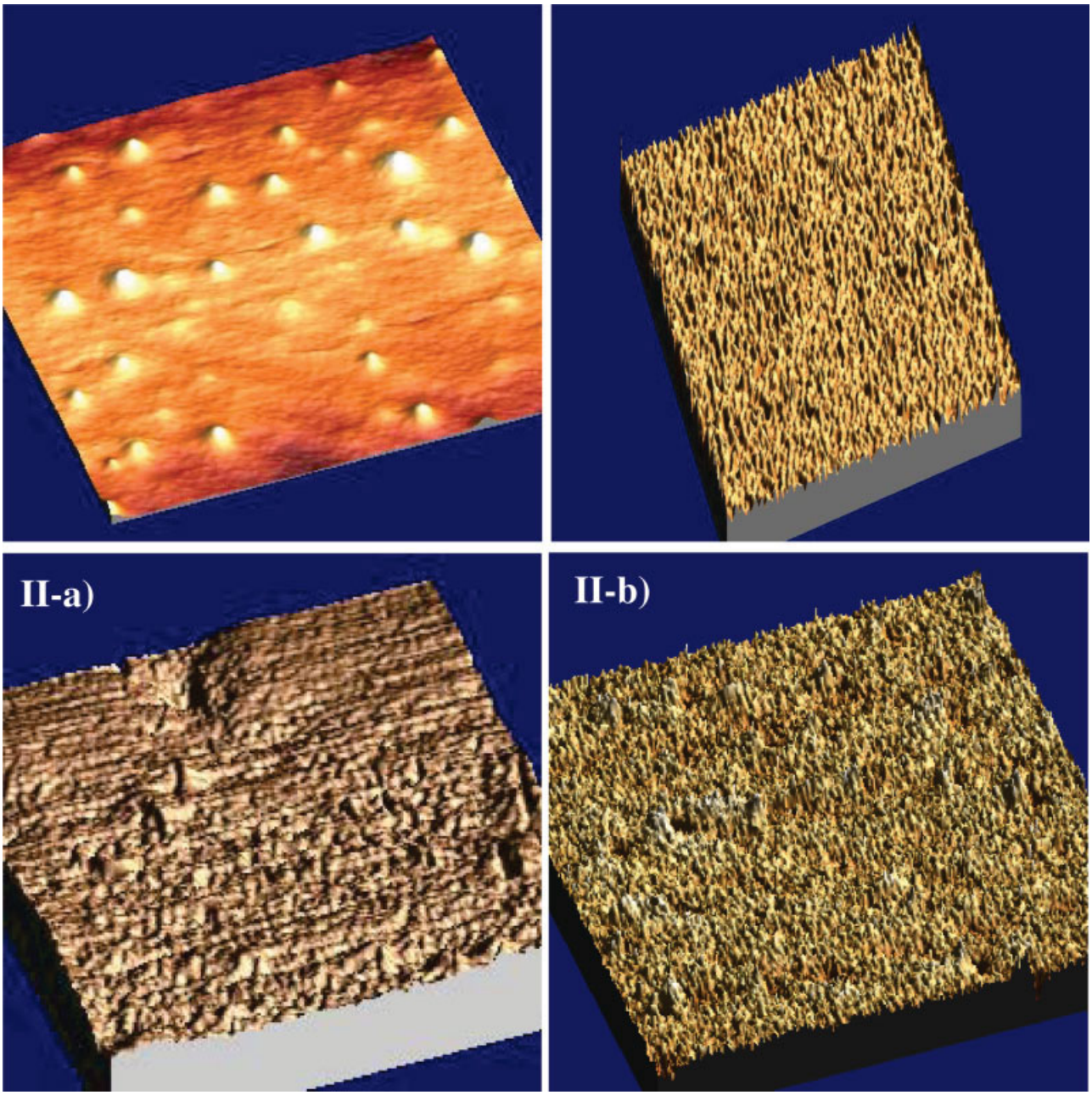


Figure 11. AFM images of surfaces of PS-*g*-PAA copolymers. I- and II- correspond to PS-*g*-PAA graft copolymers with 50/50 (w/w) and 90/10, respectively. Note: Topological or height 3D image (a), amplitude or phase 3D image (b) (1 cm corresponds to 200 nm). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

scale and are regularly spaced. AFM confirms the multiphase structure observed by SEM.

CONCLUSIONS

In this study, two different strategies for the synthesis of (meth)acrylic acid macromonomers have been investigated. The first method deals with the direct functionalization of oligomers of (meth)acrylic acid with 2-mercaptoethanol obtained by the telomerization of (meth)acrylic acid with IEM. Unfortunately, this method does not give good results, and many byproducts have been observed.

The second method consists of the synthesis of macromonomers of *tert*-BuA. Before the syn-

thesis of the oligomers, we synthesized model molecules as monoadducts that we functionalized with various acylating agents. Lastly, the *tert*-BuA functions were hydrolyzed in the presence of TFA, and only the amide functions were resistant to this treatment. Thus, this method was chosen to obtain acrylic acid macromonomers. The synthesis of *tert*-BuA oligomers was obtained by telomerization with thioglycolic acid. The concentration of thioglycolic acid allowed us to control the molecular weights as well as PDIs of these oligomers. The functionality in the acid groups of the oligomers was close to 0.90. The transfer constant of thioglycolic acid was determined to be equal to 0.55. In a second step, the unsaturation was introduced at the chain end by the reaction of IEM with acid functions of oligomers to lead to the macromonomers of *tert*-BuA. In the last step, the quantitative hydrolysis of *tert*-BuA groups in the presence of TFA led to acrylic acid macromonomers. These macromonomers were copolymerized with styrene, and the obtained graft copolymers presented two T_g's and a phase-segregated structure.

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