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
paint industries. 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. Thus, the simple modification of the pH allows the release of the active substances. Thus, the simple modification of the pH allows the release of the active substances. 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, Ito and a co-worker, and Boutevin et al. summarized different methods used to obtain macromonomers. Ishizu and coworkers obtained graft copolymers by the radical copolymerization of a macromonomer carrying a styrenic function. The macromonomer was synthesized by the rad-

Scheme 1. General chemical methods for synthesizing graft copolymers (M is the monomer, and X, Y, and I are the functional groups).
The first strategy is the synthesis of acid acrylic oligomers by telomerization with 2-mercaptetoehanol, 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-butyl 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%), dioxyanide (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 ¹³C NMR spectra were recorded on a Bruker AC 200 and 400. Apparatus with tetramethylsilane as the reference and CDCl₃, dimethyl sulfoxide-d₆, or tetrahydrofuran-d₈ (THF-d₈) 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 ($DP_{n,\text{theoretical}}$) = 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 CCl₄ 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; $DP_{n,\text{theoretical}}$ = 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-Butyl Acrylic Telomers 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) of AIBN, and 10 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%).
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 macro-monomer appeared as a viscous liquid. This product was analyzed with 1H NMR and Fourier Transfer Infrared (FTIR).

Hydrolysis of the tert-BuA Functions

Five grams of the macromonomer (DPn = 6.3; 0.032 mol of the tert-BuA function), 5.6 g (0.050 mol) of TFA, and 25 mL of CHCl3 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 radical transfer reaction (Telomerization)36–51 is based on the transfer reaction of growing
radicals onto thiols\textsuperscript{52–54} or halogenated compounds\textsuperscript{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\textsubscript{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 \textsuperscript{1}H NMR. The OH 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 \textit{z} position of the OH group. The \textit{CH}\textsubscript{2} signal of the transfer agent in the \textit{y} position of the S atom is masked by the peak of DMSO (at ca. 2.5 ppm). DMSO was selected as the solvent for \textsuperscript{1}H NMR to characterize the OH and COOH signals. Moreover, the \textit{CH}\textsubscript{3} signal of the monomer was observed around 1 ppm, the \textit{CH}\textsubscript{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\textsubscript{n, experimental}) can be assessed with \textsuperscript{1}H NMR (taking into account the COOH and OH integrals):

\[
\text{DP}_{n,\text{experimental}} = \int \text{COOH} / \int \text{OH} \quad (1)
\]

DP\textsubscript{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\textsubscript{n,experimental} value is close to the DP\textsubscript{n, theoretical} value when CCl\textsubscript{4} is used as the solvent, whereas in acetonitrile, we observe low control of DP\textsubscript{n,experimental} (Table 1):

\[
\text{DP}_{n,\text{theoretical}} = 1/R_0 = [M]_0/[T]_0 \quad (2)
\]

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-
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 $^1$H 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 $^1$H NMR. A comparison of the integrals of the amide peak around 7.9 ppm ($\text{NH}_{7.9\text{ppm}}$) and of the urethane peak ($\text{NH}_{7.4\text{ppm}}$) makes it possible for us to evaluate the yield ($\beta$) of the isocyanate/alcohol reaction:

$$\beta = \frac{\int \text{NH}_{7.4\text{ppm}}}{\int \text{NH}_{7.9\text{ppm}}} \times 100 \quad (3)$$

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 ($\text{DP}_n = 7.6$). In this case, a new signal appeared around 6.2 ppm and was attributed to urea $\text{NH}$ 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](image)

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

<table>
<thead>
<tr>
<th>$R_0$</th>
<th>$\text{DP}_{n,\text{theoretical}}$</th>
<th>$\text{DP}_{n,\text{experimental}}$</th>
<th>$M_n$ (PDI)</th>
<th>$\text{DP}_{n,\text{experimental}}$</th>
<th>$M_n$ (PDI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.250</td>
<td>4</td>
<td>6.5</td>
<td>800 g mol$^{-1}$ (1.7)</td>
<td>3.5</td>
<td>400 g mol$^{-1}$ (1.4)</td>
</tr>
<tr>
<td>0.125</td>
<td>8</td>
<td>12</td>
<td>1500 g mol$^{-1}$ (1.8)</td>
<td>7.6</td>
<td>850 g mol$^{-1}$ (1.6)</td>
</tr>
</tbody>
</table>

*a* Measured with $^1$H NMR.  
*b* Measured with SEC (with DMF as the eluent).
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 1H 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 1H NMR spectrum, the disappearance of the SH group signal at 1.5 ppm and of the acrylate double bond 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 CH₂ 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 CH₂ 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. 1H NMR shows the total disappearance of the HS 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 CH₂ adjacent to the position of the acid function (i) appears at 3.3 ppm, and the CH₂ 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

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**Scheme 5.** Synthesis of alcohol- or acid-functionalized monoadducts by nucleophilic addition.
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 azotropic 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 ¹H NMR.

**Synthesis of the Macromonomer by the Reaction of IEM with the Alcohol-Functionalized Monoadduct.** This product was characterized by ¹H 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 CH₂—NCO of IEM from 3.6 to 3.3 ppm showed the formation of urethane—CH₂—N(H)—CO—. Moreover, the displacement of the signal of CH₂ at 3.5 (the z position of an alcohol function) to 4.1 ppm was proof of the total conversion of this CH₂ 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 ¹H 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 CDCl₃ (7.6 ppm in DMSO), attributed to the NH 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
6.05 ppm, showed that the reaction was quantitative. Moreover, the displacement of the signal of the \( \text{CH}_2 \) \((l)\) in the \( \alpha \) 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):

\[
\text{Hydrolysis (\%)} = \frac{\int \text{COOH}}{\int \text{COOH} + \int \text{CH}_3}\]

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.

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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 1H 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 NH signal assigned to the urethane group at 7.4 ppm).

In the case of the model molecules carrying the amide bond, 1H 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 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.

Table 2. $D_{P_n}$ Values of the Oligomers Obtained by the Telomerization of tert-BuA in the Presence of Thioglycolic Acid Initiated with AIBN

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

$^a$ Measured by titration.

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 DPₙ and Mₙ were calculated according to eq 2 that were valid only for conversion rates close to 1 and whatever Cᵢ value. ¹H 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 CH₂ 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 CH₂ (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 (i₀) 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 DPₙ,experimen-

\[
\text{DP}_n = \frac{f e + f i}{10} \frac{i + i’}{2} 
\]

where \(f\), \(e\), \(i\), and \(i’\) correspond to the integral of the (CH₃)₃ signal at 1.4 ppm, CH at 1.6 ppm, and CH₂ of the transfer agent, respectively (Fig. 4).

Assessment of Transfer Constant Value of Thioglycolic Acid

In this study, Cᵢ values were determined in acetonitrile according to two methods: Mayo’s method⁶⁰ and O’Brien and Gornick’s method.⁶¹ The Cᵢ value has a great influence on the molecular weights obtained but more especially on the PDI. Indeed, a Cᵢ value higher than 1 involves a significant consumption of the telogen at the begin-

\[
\ln\left(\frac{\text{T}}{\text{M}}\right)_0 = \frac{\ln C_T}{C_1}R_0 
\]

Thus, plotting \(\ln\left(\text{T}/\text{M}\right)_0\) versus \(\ln([\text{M}]_0/[\text{M}]_i)\) allows us to calculate the Cᵢ value from the slope of the obtained straight line.

The telomerization of tert-BuA was also studied with O’Brien and Gornick’s⁶¹ 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 \(\ln(\text{T}/\text{T})_0\) versus \(\ln([\text{M}]_0/[\text{M}]_i)\) for a telomerization with \(R_0 = 0.20\). The slope of the straight line gives a Cᵢ 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 ¹H NMR, and the displacements of the signal are gathered in Figure 6. These signals are in agree-
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 (DPn(f)) of the macromonomer as follows:

\[
DP_n(f) = \frac{\int f}{\int o} \tag{8}
\]

where \(f\) and \(o\) correspond to the integrals of the (CH\(_3\))\(_3\) signal at 1.4 ppm and of CH\(_2\) at 5.55 and 6.05 ppm, respectively (Fig. 6).

\(f\) was reached by the calculation of the ratio of DPn (before the reaction with IEM) to DPn(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:

\[
f = \frac{DP_n}{DP_n(f)} \tag{9}
\]

DPn and DPn(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 DPn(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 DPn(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\(^{-1}\) (\(v_{\text{C=O acid}} = 1715\) cm\(^{-1}\) and \(v_{\text{C=O ester}} = 1730\) 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:

\[
\text{Hydrolysis (\%)} = \frac{\int \text{COOH}}{\int \text{COOH} + \frac{\int \text{(CH}_3)}{g}} \tag{10}
\]

Moreover, the macromonomers were analyzed with \(^{13}\)C NMR. The CH\(_3\)— carbon signal of the

| 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   | Methyl methacrylate           | 0.63             |
| acid           | Styrene                        | 21               |
| 2-Mercaptotanol| Methyl methacrylate           | 0.41             |
|                | 2-Dimethylaminomethyl methacrylate | 0.60        |
| 3-Thiopropionic acid | Methyl methacrylate | 0.38             |
| 2-Aminoethane thiol | Methyl methacrylate | 0.003            |
|                | Styrene                        | 7                |

* The data were taken from ref. 63.
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$^6$,65 and 100$^6$,64 respectively].

Table 4. DP$_n$ Values of the Macromonomers Obtained by the Reaction of IEM with Telomers of tert-BuA

<table>
<thead>
<tr>
<th>Macromonomer</th>
<th>$R_0$ (SEC)</th>
<th>DP$_n$ (NMR)</th>
<th>PDI</th>
<th>$f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>0.330</td>
<td>3.4</td>
<td>3.5</td>
<td>1.70</td>
</tr>
<tr>
<td>M2</td>
<td>0.200</td>
<td>5.2</td>
<td>5.5</td>
<td>1.75</td>
</tr>
<tr>
<td>M3</td>
<td>0.125</td>
<td>9.2</td>
<td>9.9</td>
<td>1.80</td>
</tr>
<tr>
<td>M4</td>
<td>0.050</td>
<td>23.5</td>
<td>27</td>
<td>1.84</td>
</tr>
<tr>
<td>M5</td>
<td>0.020</td>
<td>60</td>
<td>88</td>
<td>1.90</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Run</th>
<th>DP$_n^{(f)}$</th>
<th>$T_g$ (°C) Before Hydrolysis</th>
<th>$T_g$ (°C) After Hydrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>3.9</td>
<td>−40</td>
<td>20</td>
</tr>
<tr>
<td>M2</td>
<td>6.3</td>
<td>−10</td>
<td>30</td>
</tr>
<tr>
<td>M3</td>
<td>9.2</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>
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 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. 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. 1H NMR showed that all the macromonomer that did not react totally disappeared (an absence of a peak toward 5.5 and 6.0 ppm; Fig. 7). Moreover, 1H NMR of the graft copolymers showed the presence of the acid functions toward 10.5 ppm (COOH) and the presence of the —OCH3— of the macromonomer, which appeared at 4.0 ppm (THF-d8). 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.

Figure 7. 1H NMR spectrum of the poly(styrene-g-acrylic acid) graft copolymers (THF-d8).
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 3\(_g\)'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 3\(_g\)'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 \(\mu m\)).

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-

<table>
<thead>
<tr>
<th>Run</th>
<th>DP(_n)^{a}</th>
<th>Functionality(^{a})</th>
<th>(m) of Styrene ((n))</th>
<th>(m) of the Macromonomer ((n))</th>
<th>(M_n) (g mol(^{-1}))(^{a})</th>
<th>PDI(^{a})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>—</td>
<td>—</td>
<td>10.4 g (0.1 mol)</td>
<td>—</td>
<td>35,000</td>
<td>2.2</td>
</tr>
<tr>
<td>Copo1</td>
<td>6.3</td>
<td>0.98</td>
<td>10.4 g (0.1 mol)</td>
<td>10.0 g (1.4 (\times) (10^{-2}) mol)</td>
<td>23,500</td>
<td>2.4</td>
</tr>
<tr>
<td>Copo2</td>
<td>9.2</td>
<td>0.97</td>
<td>10.4 g (0.1 mol)</td>
<td>1.1 g (1.2 (\times) (10^{-3}) mol)</td>
<td>24,100</td>
<td>2.2</td>
</tr>
<tr>
<td>Copo3</td>
<td>9.2</td>
<td>0.97</td>
<td>10.4 g (0.1 mol)</td>
<td>5.0 g (5.6 (\times) (10^{-3}) mol)</td>
<td>29,000</td>
<td>1.9</td>
</tr>
<tr>
<td>Copo4</td>
<td>9.2</td>
<td>0.97</td>
<td>10.4 g (0.1 mol)</td>
<td>10.0 g (11.2 (\times) (10^{-3}) mol)</td>
<td>28,200</td>
<td>2.4</td>
</tr>
</tbody>
</table>

\(^{a}\) Determined with SEC.  
\(^{b}\) \(n\) and \(m\) correspond to number of mol and to molecular weight respectively.

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

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**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).
necessarily 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...
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.

REFERENCES AND NOTES