Well-Defined Graft Copolymers Issued from Cyclobutenyl Macromonomers by Combination of ATRP and ROMP

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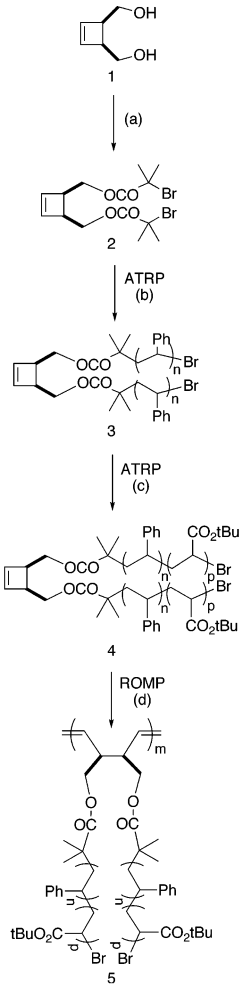
Development of living polymerization processes allows nowadays the synthesis of complex polymeric molecules with well-defined architectures such as miktoarm stars, α,*ω*-branched polymers, dendritic polymers, etc.[1] Graft copolymers offer the unique possibility of tailoring materials properties through their numerous structural variables that can be modified such as nature of the polymer backbone and composition and density of the grafts.[2] Through changes of these segments, properties such as morphology, order−disorder transitions, and phase behavior can be modified.[3] Because of their unique properties, grafts copolymers are used for a variety of applications, such as impact-resistant plastics, thermoplastic elastomers, compatibilizers, and polymeric emulsifiers.[2]

Some examples of graft copolymers obtained by combination of ATRP (atom transfer radical polymerization) and ROMP (ring-opening metathesis polymerization) have recently been reported in the literature. The synthesis of polynorbornene-*g*-poly(acrylic acid) has been performed in two steps: first ROMP of a norbornenyl-functionalized initiator and then ATRP of the side chains with *tert*-butyl acrylate. The acidolysis of *tert*-butyl acrylate groups into acrylic acid groups led to the final copolymer.[4] A similar strategy was used by Runge et al. to synthesize polynorbornene-*g*-polystyrene copolymers of high molecular weights.[5] Charvet et al. also reported an original one-pot synthesis of graft copolymers based on a metathesis backbone with poly(methyl methacrylate) grafts using a single ruthenium-based catalyst for both ATRP and ROMP.[6]

Herein we report the original synthesis of well-defined polybutadiene-*g*-(polystyrene-*b*-poly(acrylic acid)) copolymers by ROMP of α-cyclobutenyl macromonomers prepared by ATRP using a cyclobutenyl-functionalized initiator. The macromonomers polymerization method has proved to be one of the most useful ways to design and get well-defined graft copolymers since it allows a good control on grafts, on backbone lengths, and on grafts density.[7] The possibilities offered by the ROMP of macromonomers have been exploited in several studies in combination with anionic polymerization, cationic polymerization, or ROMP.[8] To our best knowledge, graft copolymers have never been synthesized by ROMP of macromonomers issued from ATRP, although the synthesis of α-norbornenyl macromonomers by ATRP has been very recently reported in the literature.[9] This original synthetic approach combines advantages of the macromonomers polymerization strategy, ATRP, and ROMP.[10]

A 3,4-difunctionalized cyclobutene **2** was used to initiate ATRP of vinylic monomers in order to obtain macromonomers for ROMP. Such a compound has been chosen due to its high reactivity in ROMP and its double functionality suitable for forming a high density of graft chains (Scheme 1).[11] Moreover, the cis stereochemistry is preferred to the trans stereochemistry as previous studies have revealed its higher reactivity in ROMP.[11] The original initiator **2** was synthesized by reaction of 2-bromoisobutyryl bromide with *cis*-3,4-bis(hydroxymethyl)-cyclobutene, **1** (Scheme 1).[12] The ^{1}H NMR spectrum of the final product showed characteristic signals of the cyclobutenyl unit at $\delta = 6.15$ ppm. The difunctional initiator **2** was first engaged in copper-mediated ATRP of styrene and *tert*-butyl acrylate (*t*BA) with a Cu(I)Br/PMDETA (*N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine) catalytic system at 100 and 60 °C, respectively (Scheme 1), to check its efficiency.[13] The $\ln([M]_0/[M])$ vs time plots (Figure 1) for polymerizations initiated by **2** are linear with both monomers showing first-order kinetics compatible with a constant concentration of active species. The number-average molecular weight vs conversion plots provided good agreement between experimental results and theoretical ones, and polydispersity indexes values were relatively low (1.10−1.30). All of the experimental criteria of a controlled polymerization shown in these experiments proved the efficiency of

Scheme 1. Graft Copolymer Synthesis



Reagents and conditions:
(a) : 2-bromoisobutyrylbromide, Et_3N, CH_2Cl_2, RT, 16h.
(b) : [Cu(I)Br]:[PMDETA]:[styrene]:[2] = 1:1:100:1, toluene (50% v/v), 100°C
(c) : [Cu(I)Br]:[PMDETA]:[*tert*-butyl acrylate]:[2] = 1:1:100:1, toluene (70% v/v), 60°C
(d) : Grubbs II, 1/10, toluene, 70°C

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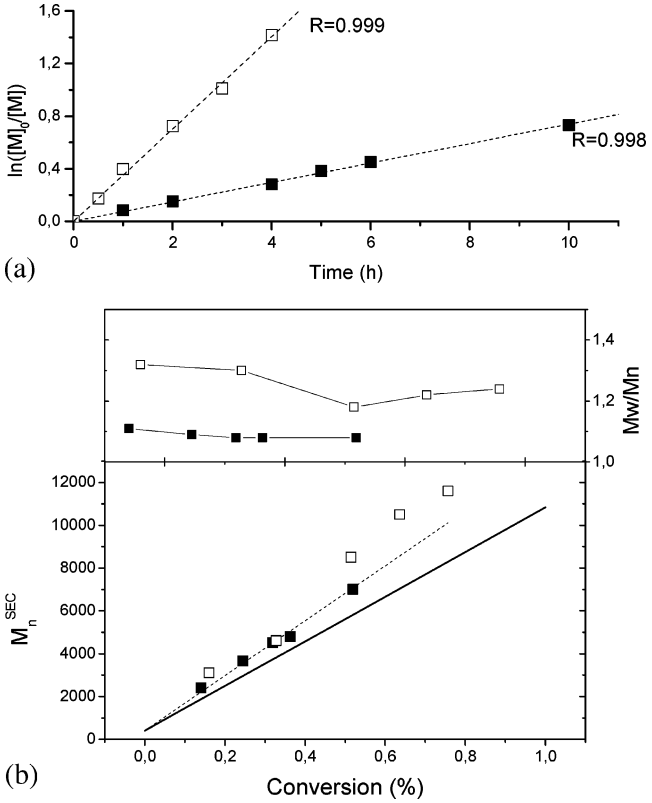

Figure 1. Kinetic studies of ATRP initiated by 3,4-difunctional cyclobutene **2**. Kinetic plots (a) and dependence of number-average molecular weights and PDI with monomer conversion (b) for the ATRP of styrene (■, $\overline{M}_{n,exp}$; —, $\overline{M}_{n,theo}$) and *tert*-butyl acrylate (□, $\overline{M}_{n,exp}$; - - -, $\overline{M}_{n,theo}$).

2 as an ATRP initiator. Moreover, the α-cyclobutenyl functionality survives intact the ATRP process as demonstrated by quantitative ^{1}H NMR analysis showing the characteristic resonance of the cyclobutenylalkene at 5.89 ppm.

The cleavage of the ester linkage between polystyrene and the cyclobutenyl alkene ($\overline{M}_n$ = 5000 g mol^{-1}, $\overline{M}_w/\overline{M}_n$ = 1.11) was performed according to a procedure already described in the literature[14] in order to check the efficiency of both initiator sites of **2**. As expected, the number-average molecular weight of the final product is about half the one of the macromonomer, with a narrow polydispersity index ($\overline{M}_n$ = 2800 g mol^{-1}, $\overline{M}_w/\overline{M}_n$ = 1.08), which proves the similar efficiency of both initiator sites of **2**.

The synthesis of block copolymers was then achieved using polystyrene macromonomers **3** as macroinitiators in a second ATRP with *tert*-butyl acrylate (Table 1). Polystyrene macroinitiators were obtained at low conversions to prevent the loss of the chain-end functionality which can occur at high conversion with PMDETA ligand.[15] Experimental molecular weights of the final polymers were in good agreement with the calculated ones (Table 1). Furthermore, the unimodal SEC traces (Figure 2) with low polydispersity indexes (values between 1.16 and 1.20) indicated that the second block was initiated quantitatively. These results suggest that the polymerization proceeded in a controlled manner and exclude the hypothesis that the cyclobutenyl unsaturation is involved in the *tert*-butyl acrylate ATRP. Our results are in contrast to those of Cheng et al., who observed competitive reactivity of the norbornenyl functionality in the polymerization of *tert*-butyl acrylate and methyl acrylate under the same conditions.[9] Using our methodology, a range of well-defined α-cyclobutenylpolystyrene-*b*-poly(*tert*-butyl acrylate)s macromonomers **4** have been successfully synthesized with various blocks lengths (Table 1).

Prior to attempting ROMP on macromonomers, the reactivity of **2** toward Grubb's generation I catalyst ($(Cy_3P)_2RuCl_2(CHPh)$) was studied (monomer-to-initiator ratio = 10:1, toluene, 30 °C). The monomer consumption (followed by ^{1}H NMR) was complete after 6 h. Isolation and purification of the final polymer led to a well-defined polybutadiene ($\overline{M}_n$ = 3600 g mol^{-1}, $\overline{M}_w/\overline{M}_n$ = 1.14) bearing ATRP initiator sites which could be used in a "grafting from" strategy to prepare graft copolymers.[4,5]

The first attempt using Grubb's I and a polystyrene macromonomer **3** (Table 1, entry 1) was then realized at 50 °C (monomer-to-initiator ratio = 10:1, toluene). After 48 h, SEC traces revealed a bimodal distribution with two peaks located at M_p = 3900 g mol^{-1} and M_p = 11 000 g mol^{-1}. This result shows that the macromonomer had only partially reacted. Modification of the experimental conditions (solvent, concentration, temperature, reaction time) did not improve the low conversion of the macromonomer, and similar results were observed for α-cyclobutenylpolystyrene-*b*-poly(*tert*-butyl acrylate) macromonomers **4**. The reactivity of Grubb's I catalyst seems to be too low toward our macromonomers, probably as a consequence of the steric hindrance effect of the two polymeric chains, as already observed with a norbornene bearing two polymeric chains.[16]

The second-generation Grubb's catalyst (Grubb's II) ($(IMesH_2)(Cy_3P)RuCl_2(CHPh)$), one of the most active ROMP catalysts commercially available, is less used despite its higher activity, as the polymerizations are, in general, not controlled.[17] However, it has already been used for polymerization of hindered macromonomers, leading to well-defined graft copolymers with narrow polydispersity indexes.[16] The first attempt with Grubb's II and macromonomer **3** (Table 1, entry 1) led to higher conversion than with Grubb's I under similar conditions, but the macromonomer conversion was still incomplete. By increasing the temperature from 50 up to 70 °C, macromonomer concentration from 0.01 up to 0.06 mol L^{-1}, and reaction time from 48 to 76 h, a polymer with a narrow and unimodal molecular weight distribution was obtained ($\overline{M}_n$ = 10 400 g mol^{-1}, $\overline{M}_w/\overline{M}_n$ = 1.25). The same conditions were successfully applied to macromonomer **4** (Table 1, entry 3): a well-defined polybutadiene-*g*-(polystyrene-*b*-poly(*tert*-butyl acrylate)) co-

Table 1. Macromonomers Characteristics

	polystyrene macromonomers **3**[a]				polystyrene-*b*-poly(*tert*-butyl acrylate) macromonomers **4**[b]			
entry	conv (%)	$\overline{M}_{n,theo}$[c]	$\overline{M}_{n,SEC}$[d]	$\overline{M}_w/\overline{M}_n$[d]	conv (%)	$\overline{M}_{n,theo}$[e]	$\overline{M}_{n,SEC}$[d]	$\overline{M}_w/\overline{M}_n$[d]
1	20	2495	3500	1.11	31	5487	6700	1.20
2	10	1453	1500	1.14	40	4063	5100	1.17
3	7	1141	1800	1.15	25	3400	4300	1.17
4	16	2078	2600	1.10	47	5612	7200	1.16

[a] [Cu(I)Br]:[PMDETA]:[styrene]:[**2**] = 1:1:100:1, toluene (50% v/v), 100 °C. [b] [Cu(I)Br]:[PMDETA]:[*t*BA]:[**2**] = 1:1:50:1, toluene (70% v/v), 60 °C. [c] $M_{n,theo}$ = 104([St]$_0$/[I]$_0$ × conversion) + $M_{initiator}$. [d] Determined by SEC in THF at 35 °C vs polystyrene standard. [e] $M_{n,theo}$ = 128([*t*BA]$_0$/[I]$_0$ × conversion) + $M_{initiator}$.

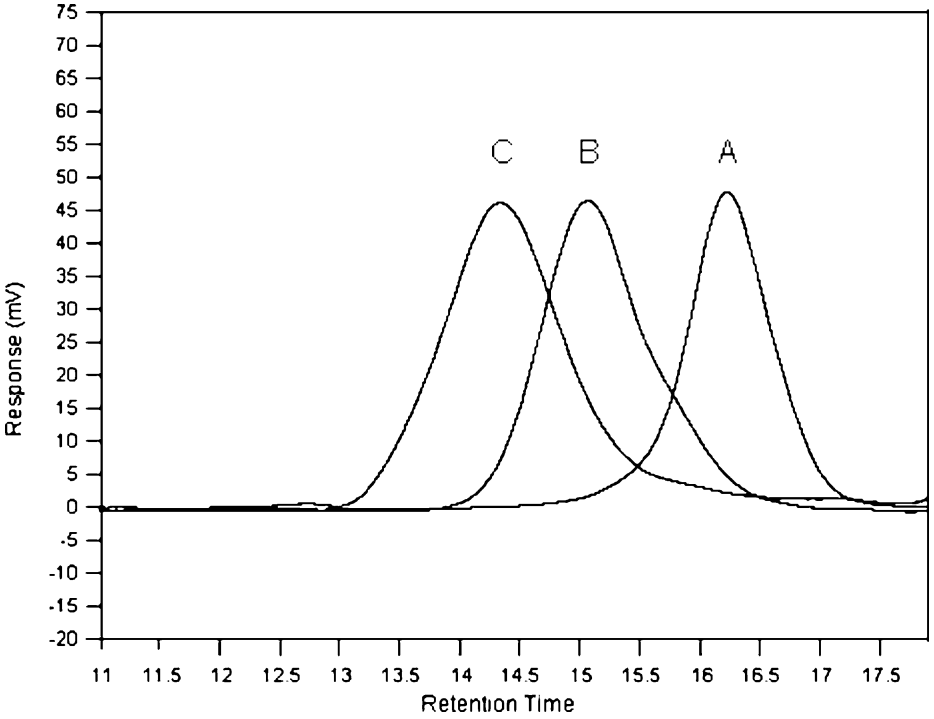

Figure 2. SEC traces of polystyrene macromonomer (A), polystyrene-*b*-poly(*tert*-butyl acrylate) macromonomer (B) (Table 1, entry 3), and polybutadiene-*g*-(polystyrene-*b*-poly(*tert*-butyl acrylate)) graft copolymer (C).

polymer, having a low polydispersity index ($\overline{M_n}$ = 8200 g mol^{-1}, $\overline{M_w}/\overline{M_n}$ = 1.21) was obtained (Figure 2C). As they may assume shapes from random coils to rigid rods, graft polymers cannot be accurately characterized using standard SEC connected to a refractive index detector. It is known in the literature that the measured values for the molecular weights underestimate the true molecular weights of comb polymers by up to a factor of 10.[5] In addition, anomalous elution times and separations of these polymers in SEC have been reported.[18] As a consequence, the difference between theoretical and experimental $\overline{M_n}$ values for the graft copolymer is presumed to be a result of the difference in hydrodynamic volumes of this polymer compared to linear polystyrene standards. The absence of residual macromonomer on the SEC traces and the complete disappearance of the signal of the cyclobutenic unsaturation in the ^{1}H NMR spectrum show that the reaction went to completion. This result confirms the preservation of the cyclobutenyl unit during macromonomer synthesis using ATRP.

The easy removal of the *tert*-butyl groups after polymerization yields poly(acrylic acid) side chains that have a number of important applications.[19] The removal of *tert*-butyl groups was first achieved with macromonomers **4** by treatment with a mixture of dichloromethane and trifluoroacetic acid until the de-*tert*-butylated polymers precipitated. The disappearance of *tert*-butyl signal (δ = 1.44 ppm) and the persistence of the signal of cyclobutene unit (δ = 5.89 ppm) on the ^{1}H NMR spectrum of the final copolymer proves that acidolysis occurs without alteration of the ester linkages between the cyclobutene unit and polymeric chains.

Preliminary results concerning the solubility of polystyrene-*b*-poly(acrylic acid) macromonomers in water showed that macromonomers are easily soluble in water for a 80:20 molar ratio of hydrophilic poly(acrylic acid):hydrophobic polystyrene. For higher proportion of the hydrophobic block (70:30), the addition of K_2CO_3 was necessary to ensure complete solubilization. As the efficiency of polystyrene-*b*-poly(acrylic acid) copolymers as stabilizers in emulsion polymerizations as already been demonstrated,[20] these macromonomers could be engaged in ROMP in emulsion where they could simultaneously act as surfactant and monomer.[21] The same treatment on polybutadiene-*g*-(polystyrene-*b*-poly(*tert*-butyl acrylate)) led to an amphiphilic polybutadiene-*g*-(polystyrene-*b*-poly(acrylic acid)) copolymer as shown by the disappearance of *tert*-butyl signal (δ = 1.44 ppm) in the ^{1}H NMR spectrum.

In conclusion, the synthesis of well-defined polybutadiene-*g*-(polystyrene-*b*-poly(*tert*-butyl acrylate)) and polybutadiene-*g*-(polystyrene-*b*-poly(acrylic acid)) graft copolymers has been successfully carried out through the "polymacromonomer" strategy by combination of ATRP and ROMP. α-Cyclobutenylpolystyrene-*b*-poly(*tert*-butyl acrylate) macromonomers with various block lengths have been obtained by ATRP using an original cyclobutenyl-functionalized initiator. This method enables the synthesis of well-defined macromonomers with controlled molecular weight and composition as well as narrow molecular weight distribution and could be applicable to a wide range of monomers. ROMP of the resulting macromonomers allows for a good control over length and nature of the backbone and offers the possibility to adjust the graft density via copolymerization with others monomers. Acidolysis of the *tert*-butyl groups of both macromonomers and final copolymers leads, on one hand, to polystyrene-*b*-poly(acrylic acid) macromonomers and, on the other hand, to amphiphilic graft copolymers with potential attractive properties. This original combination of ATRP and ROMP with the macromonomer strategy can be considered as a new and versatile synthetic method for the preparation of a broad variety of graft copolymers based on a polybutadiene backbone. Last, the possibility of synthesizing nonsymmetric cyclobutenic compounds[22] bearing initiator sites of different nature could lead to macromonomers substituted with two polymeric chains of different nature, giving access to environmentally responsive graft copolymers.[23] Further studies concerning macromonomers, graft copolymers, and their properties are now in progress and will be reported in due time.

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Supporting Information Available: Detailed synthetic procedures for the initiator and polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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