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Preparation of star block co-polymers by combination of cationic ring opening polymerization and atom transfer radical polymerization

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Abstract—The synthesis of star block co-polymers with polytetrahydrofuran (PTHF) core and poly(*tert*-butyl acrylate) (P*t*BA) shell was performed using a dual initiator, 4-hydroxy butyl bromoisobutyrate, by combination of cationic ring-opening polymerization (CROP) and atom transfer radical polymerization (ATRP). The *in situ* reaction of the hydroxyl groups originating from the dual initiator with trifluoromethane sulfonic anhydride provides a triflate ester initiating group for the CROP of THF. PTHF star polymers having three arms with tertiary bromide end groups $(PTHF)_3$ have been prepared by reaction of living PTHF chains with tris(2-aminoethyl)amine (TAEA) in the presence of 2,2,6,6-tetramethylpiperidine (TMP) as a proton trap. Subsequently, the star polymers were used as macroinitiators for the ATRP of *t*BA using the CuBr/N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA) catalyst system to obtain the tri-armed star block co-polymers (PTHF-*b*-P*t*BA)$_3$. The polymers were characterized with gel-permeation chromatography (GPC) and ^{1}H-NMR. Both techniques demonstrated the formation of tri-armed star block co-polymers.

Keywords: Atom transfer radical polymerization (ATRP); cationic ring-opening polymerization (CROP); star block co-polymer; polytetrahydrofuran; poly(*tert*-butyl acrylate).

1. INTRODUCTION

Polymer properties are influenced by their structure and topology. Therefore, the synthesis of complex macromolecular architectures to control polymer properties is a continuing theme in polymer chemistry. For example, non-linear polymers, such

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as star polymers, have attracted considerable attention in polymer science due to their unique properties in comparison to the corresponding linear polymers [1–4].

Generally, there are three methods for preparing star polymers: (1) living polymerization with a multifunctional initiator, (2) coupling of linear living polymers with a multifunctional coupling agent and (3) linking of linear living polymers with a divinyl compound. The synthesis of star polymers from vinyl monomers using living anionic polymerization [5, 6] and cationic polymerization [7, 8] has been studied extensively.

More recently, controlled/"living" radical polymerizations have been used for the synthesis of well-defined polymers. Among them, atom transfer radical polymerization (ATRP) [9–11] is one of the most versatile methods for the controlled radical polymerization of vinyl-type monomers. Such controlled radical polymerizations have been applied to the syntheses of well-defined block and graft co-polymers, star, miktoarm star and hyperbranched polymers, either by sequential monomer addition or by mechanism transformations [12–25]. Another fairly new strategy for the preparation of complex polymer architectures consists of the combination of controlled polymerization techniques by making use of heterofunctional initiators [26, 27]. This approach enables researchers to combine different types of monomers into one polymeric structure by a one-pot sequential two-step method. Moreover, it does not require any chemical transformation of polymeric end-groups to obtain the proper functionality for the subsequent polymerization steps.

In this work, the dual initiator 4-hydroxy-butyl-2-bromoisobutyrate (HBBIB), applied earlier to prepare block co-polymers [28], has been used for the combination of CROP and ATRP to prepare well-defined star block co-polymers based on poly(tetrahydrofuran) (PTHF) in the core and poly(*tert*-butyl acrylate) (P*t*BA) at the outer part of the star blocks. P*t*BA, on one hand, serves as model system for ATRP but, on the other hand, could also be used as precursor segment for pH-responsive poly(acrylic acid) segments. Recently, the research towards star block co-polymers has become popular, as these unimolecular core–shell architectures show higher stability in solution compared to micelles made from linear block co-polymers [29]. In general, the core serves as a microenvironment for the incorporation of a variety of compounds such as drugs [30].

The dual initiator contains a bromoisobutyrate group for the ATRP of *t*BA and a hydroxyl function that can be transformed into a triflate ester for the initiation of the CROP of THF. The triflate ester initiation system was first used for the CROP of THF, which, after reaction with a multifunctional amine [31], led to a star polymer, $(\mathrm{PTHF})_3$, with three tertiary bromide end-groups. This star polymer was then used as a macroinitiator for the ATRP of *t*BA to prepare tri-armed star block co-polymers, $(\mathrm{PTHF}\text{-}b\text{-}\mathrm{P}t\mathrm{BA})_3$, with predetermined molecular weight and controlled structure.

2. MATERIALS AND METHODS

2.1. Materials

The inhibitor in *tert*-butyl acrylate (Acros, 99%) was removed by passing the monomer over a basic aluminum oxide column (Aldrich) and was stored in a freezer under nitrogen atmosphere. CuBr (Aldrich, 98%) was purified first by stirring with acetic acid, then by washing with methanol (MeOH), and finally by drying *in vacuo* at 70°C. N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA; Acros, >99%) and tris(2-aminoethyl)amine (TAEA; Aldrich, 96%) were purified by distillation over CaH_2. Trifluoromethane sulfonic anhydride (Tf_2O; Acros, >98%) was purified by distillation under atmospheric pressure (bp 81–83°C). Dichloromethane was extracted three times with pure sulfuric acid and was washed three times with a concentrated solution of sodium hydroxide (10%, w/v). Then, it was washed several times with distilled water until the pH became neutral. The purified dichloromethane was dried for several hours on magnesium sulfate, filtered off, and then refluxed for 2 h over calcium hydride. Dichloromethane was distilled, stored over calcium hydride and refluxed over calcium hydride before use. THF (Acros, 99.8%) was used after distillation over sodium in the presence of benzophenone. 2,6-Di-*tert*-butylpyridine (DTBP; Maybridge Chemicals, >97%) was used as received. 2,2,6,6-Tetramethylpiperidine (TMP; Acros, 98%) was purified by fractional distillation over CaH_2 and stored over 4 Å molecular sieves (bp 152°C).

The dual initiator (4-hydroxy butyl bromoisobutyrate) was synthesized from 1,4-butane diol and 2-bromoisobutyric acid as described elsewhere [28].

2.2. Preparation of PTHF star polymers by CROP of THF with HBBIB/Tf_2O/DTBP

A typical procedure for the two-stage polymerization of THF was as follows. In a flame-dried, two-necked flask, a certain amount of dichloromethane, DTBP and Tf_2O was placed at 0°C under a nitrogen atmosphere. To this solution, 4-hydroxy butyl bromoisobutyrate (HBBIB) was added under vigorous stirring, and the mixture was stirred for 1 h at 0°C. The initiator solution was brought to 20°C, after which an initial amount of THF (10 vol%) was introduced. After 2 h, the main amount of THF (90 vol%) was added. After the prescribed reaction time stirring at room temperature, TAEA was added to the polymerization mixture, immediately followed by the addition of TMP. The polymer was precipitated in cold pentane, filtered off on a cold glass filter, and finally dried *in vacuo*.

Just before the addition of TAEA, samples for GPC and NMR analysis were removed from the reaction mixture with a syringe and transferred into 0.1 ml methanol to terminate the polymerization.

2.3. Preparation of PTHF-PtBA star block polymers by ATRP of tBA with the CuBr/PMDETA catalyst system

The synthesis of the PTHF-P*t*BA star block polymers was accomplished by the ATRP of *t*BA in bulk with CuBr/PMDETA as a catalyst. To a Schlenk tube equipped with a magnetic stirring bar, the degassed monomer, ligand, CuBr and macroinitiator were added, in the order mentioned, with a $[I]_0/[PMDETA]_0/[CuBr]_0$ ratio of $1:3:3$. The tube was degassed by three freeze-pump-thaw cycles, left *in vacuo* and placed in a thermostated oil bath. The polymerization was carried out at 60°C for prescribed reaction time. After the polymerization, the reaction mixture was diluted with THF and passed through a column of neutral alumina to remove the catalyst. The excess of THF and the unreacted monomer were evaporated under reduced pressure. The resulting polymer was dissolved in THF and precipitated into ice-cold water. After decantation, the polymer was dissolved in a minimum amount of dichloromethane and dried over Na_2SO_4, and the organic phase was removed by evaporation.

2.4. Characterization

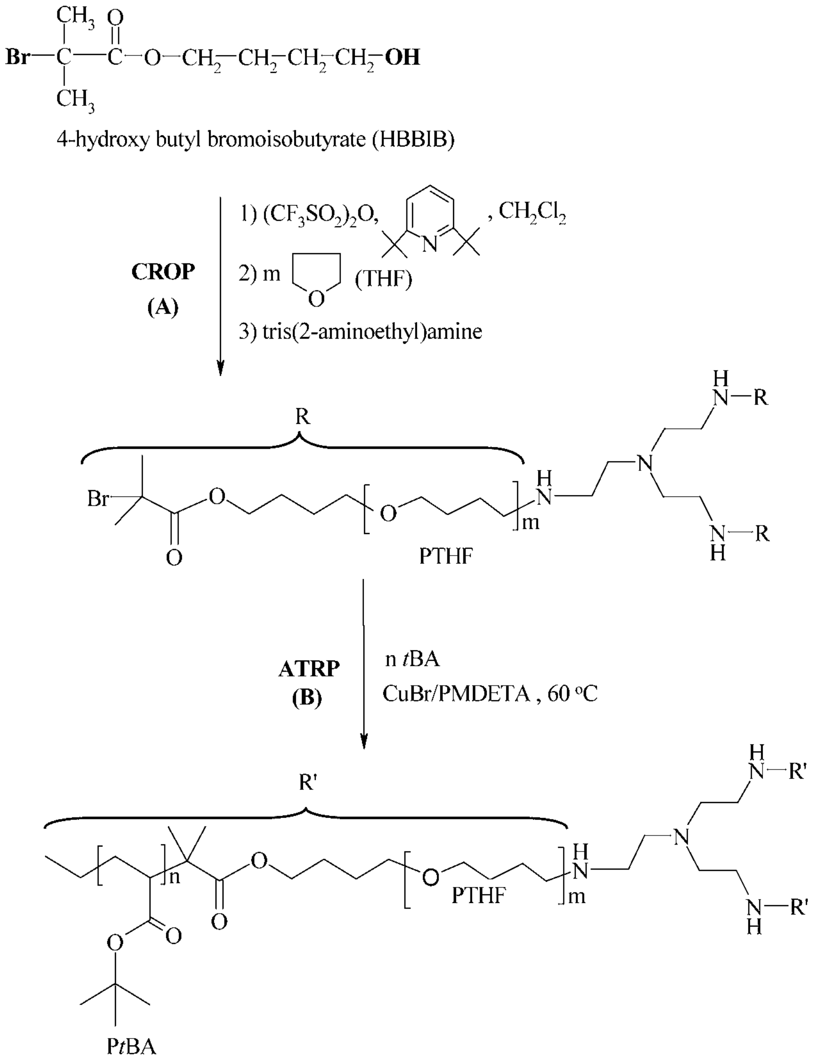
^{1}H-NMR spectra were recorded on a Bruker AM500 spectrometer and were measured in $CDCl_3$ at room temperature. GPC was performed on a Waters instrument, with a refractive-index (RI) detector (2410 Waters), equipped with 10^3, 10^4 and 10^5 Å serial columns. Polystyrene standards were used for calibration and $CHCl_3$ was used as an eluent at a flow rate of 1.5 ml/min. Molecular weight and molecular weight distributions were determined using the Breeze Millennium software.

3. RESULTS AND DISCUSSION

The synthetic strategy followed for the preparation of PTHF-P*t*BA star block copolymers *via* the sequential CROP-ATRP route with HBBIB as a dual initiator is depicted in Scheme 1.

3.1. Synthesis of (PTHF)$_3$ by CROP with the dual initiator HBBIB

The proposed CROP reaction sequence is outlined in route A of Scheme 1: the alcohol function of the dual initiator reacts with one molecule of Tf_2O, in the presence of DTBP as proton trap, to produce the corresponding triflate ester *in situ*. As described by Dubreuil and Goethals [32], bulky trifate esters give relatively slow initiation and therefore the polymerization has to be performed in two stages. In the first stage, a small amount of THF is added to the triflate ester prepared *in situ* to allow the initiation to occur. In the second stage, the main amount of the monomer is introduced to start the polymerization. Finally, after the prescribed reaction time, the star polymer is formed by introducing tris(2-aminoethyl)amine



Scheme 1. Synthesis of (PTHF-*b*-P*t*BA)3 star block co-polymers.

(TAEA) as a multifunctional terminating agent. In this way, tri-armed star PTHF with moderately low polydispersities (<1.5) and controlled molecular weight could be prepared.

The NMR spectra and GPC analyses demonstrate the formation of tri-armed star polymer. Figure 1 depicts the ^{1}H-NMR spectrum of the Br-functionalized star PTHF. From the integral values of the PTHF signal at 3.41 ppm ($I_{3.41}$) and the end-group peak at 4.19 ppm ($I_{4.19}$), $M_{\mathrm{n,NMR}}$ can be calculated as follows:

$$M_{\mathrm{n,NMR}} = ((I_{3.41}/4)/(I_{4.18}/2)) \times M_{\mathrm{w}}(\mathrm{THF}) + (M_{\mathrm{w}}(\mathrm{HBBIB}) \times \text{number of arms})$$

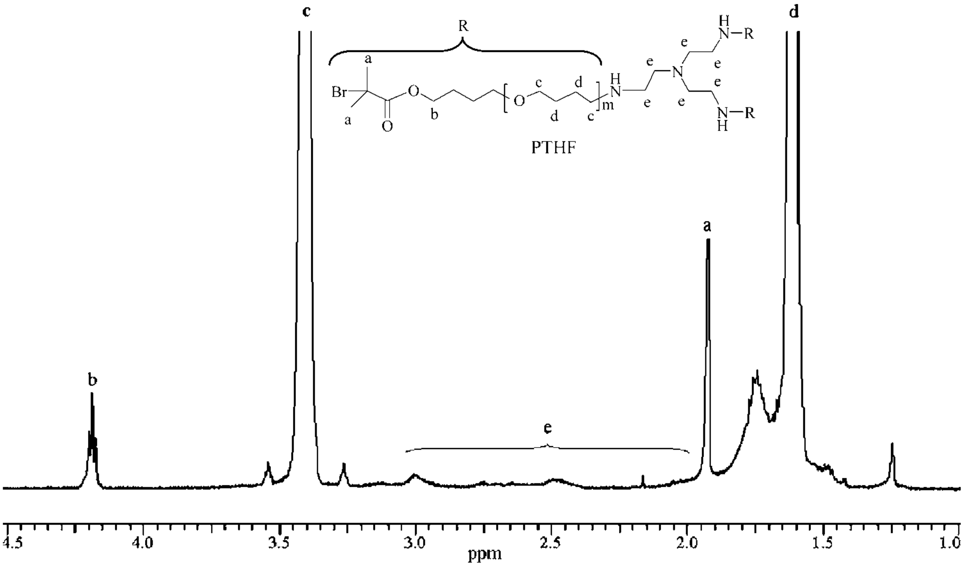


Figure 1. ^{1}H-NMR spectrum of $(PTHF)_3$ macroinitiator (PII) in $CDCl_3$.

The number of arms of the different PTHF macroinitiators was determined by the integration of the signal at 4.19 ppm ($-OCH_2$) of PTHF and the signal at 2–3 ppm ($-NCH_2CH_2$) of the amine core. The number of arms determined in this way was always in good agreement with the theoretical values.

The results for the synthesis of tri-armed star PTHF that can act as a macroinitiator for the ATRP of *t*BA, are listed in Table 1 (Run PI and PII). There is a good agreement between the theoretical molecular weights calculated from

$$M_{\mathrm{n,theo}} = [\mathrm{M}]_0/[\mathrm{I}]_0 \times \text{conversion\%} \times M_{\mathrm{w}}(\mathrm{THF}) \times \text{number of the arms}$$

and the calculated ones from ^{1}H-NMR and GPC.

3.2. *Syntheses of (PTHF-b-PtBA)$_3$ with (PTHF)$_3$ as a macroinitiator for the ATRP of tBA*

$(PTHF)_3$, prepared by the CROP of THF, has been used to initiate the polymerization of *t*BA by ATRP with the CuBr/PMDETA initiating system at 60°C (route B in Scheme 1). The reaction conditions and results are given in Table 1. The GPC traces of linear PTHF, $(PTHF)_3$ and the corresponding star block co-polymer (PTHF-*b*-P*t*BA)$_3$ are shown in Fig. 2. After the polymerization of *t*BA, the GPC trace shifts to higher molecular weight, which demonstrates the formation of the P*t*BA blocks. Moreover, the complete disappearance of the signal of the macroinitiator indicates that the macroinitiator was fully converted to the star block co-polymer (Fig. 2).

^{1}H-NMR measurements confirmed the incorporation of the P*t*BA blocks into the star block co-polymer (Fig. 3). From the ^{1}H-NMR-spectrum, the molecular weight ($M_{\mathrm{n,NMR}}$) of the star block co-polymer could be determined using the integration of

Table 1.
Synthesis of (PTHF-*b*-P*t*BA)$_3$ derived from (PTHF)$_3$ macroinitiator

Run	Monomer	$M_{n,arm}$[c] (kg/mol)	$[M]_0/[I]_0$	Initiator	Time (h)	Conversion (%)	$M_{n,GPC}$ (kg/mol)	$M_{n,NMR}$ (kg/mol)	$M_{n,theo}$ (kg/mol)	Mw/M_n
PI	THF	2.65	166	HBBIB	0.16	9.6[a]	4.66[c]	5.50	4.20	1.48
PII	THF	2.88	145	HBBIB	0.16	10.6[a]	4.49[c]	5.60	4.05	1.42
PIII	*t*BA	—	400	PI	7	30[b]	26.50[d]	28.80	21.00	1.36
PIV	*t*BA	—	600	PII	21.5	53[b]	38.80[d]	44.10	46.30	1.39
PV	*t*BA	—	1000	PII	42	25[b]	55.80[d]	47.25	37.60	1.35

[a] Determined by ^{1}H-NMR.

[b] Determined gravimetrically.

[c] $M_{n,GPC} = M_{n,GPC}(exp) \times 0.44$ (0.44 is the correction factor for PTHF on a GPC instrument with $CHCl_3$ as an eluent and calibrated with linear PS standards).

[d] The molecular weights were calculated based on linear polystyrene standards.

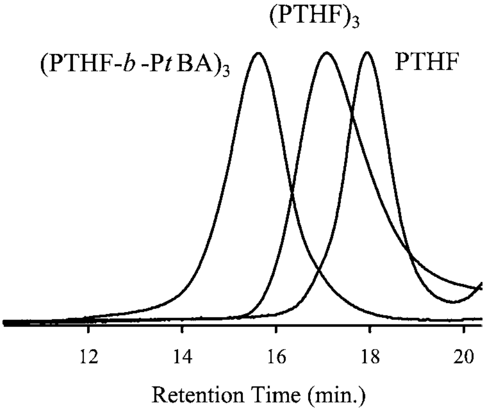


Figure 2. GPC traces of linear PTHF, (PTHF)$_3$ (PII in Table 1) and corresponding star block co-polymer (PTHF-*b*-P*t*BA)$_3$ (PV in Table 1).

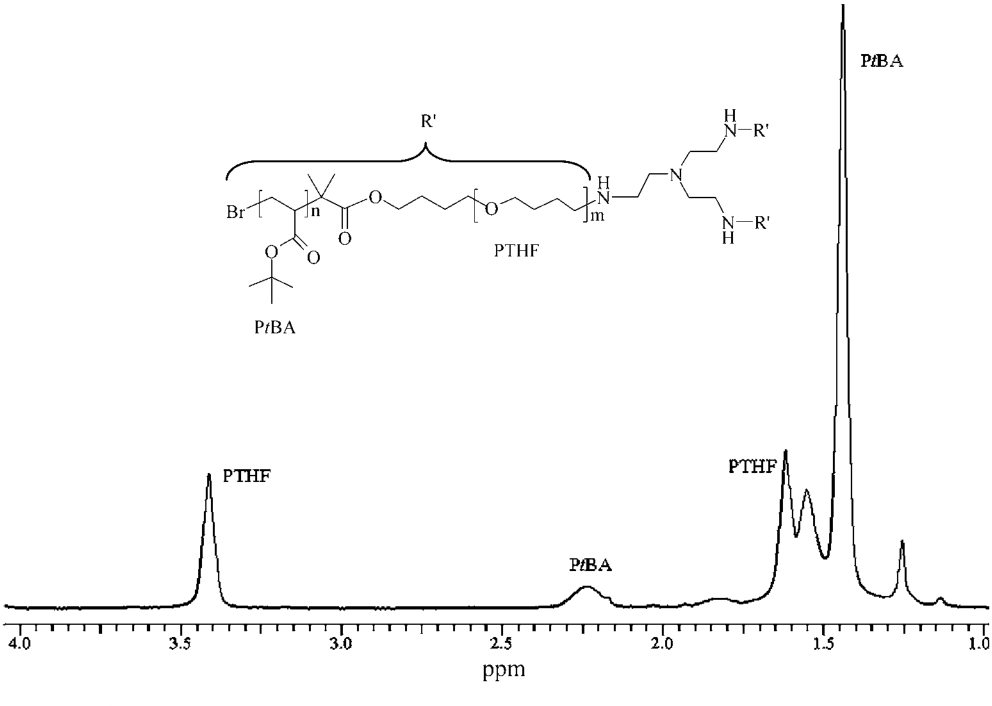


Figure 3. ^{1}H-NMR spectrum of (PTHF-*b*-P*t*BA)$_3$ (PIII) in CDCl$_3$.

the signals appearing at 1.43 ppm ($-C(CH_3)_3$) of P*t*BA and the signal at 3.41 ppm ($-OCH_2$) of PTHF.

As can be seen in Table 1, star block co-polymers with different molecular weights were prepared using different initial monomer/initiator ratios (entries PIII–PV). Although the hydrodynamic volumes of P*t*BA are not exactly the same as those of the linear PS standards used for GPC calibration, the resulting experimental molecular weights are close to the theoretical molecular weights of (PTHF-*b*-P*t*BA)$_3$ calculated from:

$$M_{\mathrm{n,theo}} = (([\mathrm{M}]_0/[\mathrm{I}]_0) \times \text{conversion\%} \times M_{\mathrm{w}}(t\mathrm{BA})) + M_{\mathrm{n,NMR}} \text{ of the macroinitiator}$$

Moreover, the molecular weight distributions of the obtained star block co-polymers are rather narrow. These results imply that the polymerization of *t*BA using (PTHF)$_3$ as a macroinitiator and CuBr/PMDETA as a heterogeneous catalyst system proceeds in a controlled manner with a high initiation efficiency.

4. CONCLUSIONS

The dual initiator HBBIB, bearing initiator groups for both CROP and ATRP techniques, has first been used for the synthesis of well-defined tri-armed star-shaped PTHF macroinitiators. It was shown that these macroinitiators contained the functional end-groups that can serve as initiators for ATRP. Tri-armed PTHF-Br quantitatively initiated the ATRP of *t*BA, leading to well-defined PTHF-*b*-P*t*BA star block co-polymers with different chain lengths. This approach has the advantage that it does not require any chemical transformation of polymeric end-groups to obtain a proper functionality for subsequent polymerization steps. In principle, the same strategy can be applied for the design of a variety of star block co-polymers by making use of other multifunctional amines (different number of arms) and other monomers for the ATRP reaction.

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