Synthesis of Amphiphilic Graft Copolymers of *n*-Butyl Acrylate and Acrylic Acid by Atom Transfer Radical Copolymerization of Macromonomers

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ABSTRACT: ω-Methacryloyl-functionalized poly(*tert*-butyl acrylate) (P*t*BA) and poly(*n*-butyl acrylate) (P*n*BA) macromonomers with different chain lengths were synthesized by atom transfer radical polymerization (ATRP). The terminal bromine atoms were removed by a chain transfer reaction and esterification. P*n*BA-*g*-P*t*BA graft copolymers and their "inverse" P*t*BA-*g*-P*n*BA counterparts with different chemical compositions were achieved by the "grafting through" approach via ATRP. The reactivity ratios of macromonomer and comonomer are close to unity, enabling the synthesis of graft copolymers with a statistical distribution of side chains. Amphiphilic PnBA-*g*-PAA graft copolymers and their "inverse" PAA-*g*-PnBA counterparts were achieved by quantitative hydrolysis of the poly(*tert*-butyl acrylate) segments to poly(acrylic acid) (PAA).

Introduction

Since its discovery,[1−3] atom transfer radical polymerization (ATRP) has proven to be a reliable and versatile method for synthesis of polymers with narrow molecular weight distributions and controlled structure. Copolymers with well-defined nonlinear architectures can be readily synthesized via ATRP. Various groups[4−6] have reported the synthesis of graft copolymers via ATRP using the "grafting from" approach. Recently, the groups of Gnanou[7] and Armes[8] separately reported the synthesis of heteroarm (AB_2-type or Y-shaped) stars via ATRP. Such a copolymer can be regarded as a graft copolymer with only one side chain in the middle of backbone.

An alternative strategy for the synthesis of graft copolymers is the so-called grafting through or macromonomer approach, which is achieved by copolymerization of a macromonomer and a low molecular weight comonomer via ATRP. We have previously investigated the copolymerization of methacryloyl-terminated PMMA macromonomers and MMA at 60 °C in toluene via conventional free radical polymerization using AIBN as an initiator[9,10] and found that with increasing macromonomer concentration the relative reactivity of the macromonomer decreased due to the enhanced viscosity. In the copolymerization of PMMA macromonomers with nBA the incompatibility of backbone and side chains is an additional complication.[10,11] Roos et al.[12] investigated the copolymerization of *n*-butyl acrylate and ω-methacryloyl-PMMA macromonomers via ATRP and found a much higher macromonomer reactivity ($1/r_1 = 2.2$) compared to that found in conventional radical polymerization ($1/r_1 = 1.37$) at the same concentration. They ascribed it to the increased time between two monomer additions in ATRP, facilitating the diffusion of the macromonomer to the active chain end. This conclusion was confirmed by Matyjaszewski's group[13] from investigation of the relative reactivity of (meth)acryloyl-capped poly(lactic acid) macromonomers in copolymerization with MMA via ATRP and Pan's group[14] from the copolymerization of methacryloyl-capped polytetrahydrofuran macromonomer and styrene via ATRP. Thus, the macromonomer (MM) method via ATRP allows to control (i) the chain length of side chains which is given by the MM, made by a living polymerization; (ii) the chain length of the backbone, controlled by a living polymerization process; and (iii) the average spacing of the side chains which is determined by the molar ratio of comonomer and MM as well as by the corresponding reactivity ratios.

If both the macromonomer and the graft copolymer are made by ATRP, it is essential to remove the terminal bromine atom; otherwise, hyperbranched polymers would result.[15] In a previous paper,[16] we described a novel synthesis of halogen-free acrylate macromonomers via ATRP. This synthetic strategy was based on the chain transfer nature of the ATRP catalyst ligand, *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA).[17] ATRP of acrylic monomers using a hydroxy-functionalized ATRP macroinitiator and an excess of PMDETA ligand (relative to CuBr) resulted in monohydroxyl-terminated halogen-free polymers. Subsequent esterification of the terminal hydroxyl groups using methacryloyl chloride afforded well-defined macromonomers.

In this paper, we describe the synthesis of well-defined graft copolymers with poly(*n*-butyl acrylate) (P*n*BA) backbone and poly(*tert*-butyl acrylate) (P*t*BA) side chains (P*n*BA-*g*-P*t*BA), which were achieved by the "grafting through" or macromonomer approach via ATRP (see Scheme 1). The same synthetic route was also employed to synthesize the "inverse" P*t*BA-*g*-P*n*BA graft copolymers. Subsequent hydrolysis resulted in the formation of amphiphilic P*n*BA-*g*-PAA graft copolymers and their "inverse" PAA-*g*-P*n*BA counterparts. These amphiphilic graft copolymers and their precursors were characterized using ^{1}H NMR spectroscopy, gel permeation chromatography (GPC), liquid adsorption chromatography at critical conditions (LACCC), and 2D chromatography.

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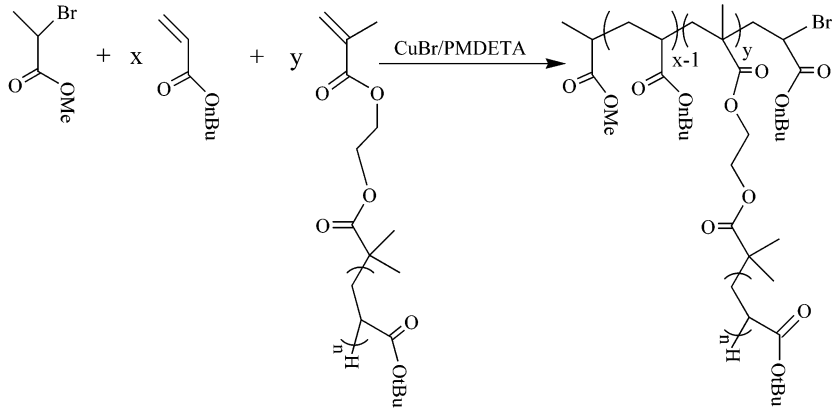
Scheme 1. Synthesis of PnBA-*g*-PtBA Graft Copolymers via the Macromonomer Method



Experimental Part

Materials. *tert*-Butyl acrylate (tBA) and *n*-butyl acrylate (nBA, both donations of BASF AG) were fractionated from CaH_2 at 45 mbar, stirred over CaH_2, and a small amount of the nonvolatile stabilizer Irganox 1010 (Ciba-Geigy), degassed by three freeze−pump−thaw cycles, and condensed under high vacuum before polymerization. CuBr (95%, Aldrich) was purified as follows: first, stirring in acetic acid overnight; after filtration it was washed with ethanol and diethyl ether and dried in the vacuum oven. All solvents were dehydrated with CaH_2 and condensed under vacuum. Methyl 2-bromopropionate (MBP, 98%), ethylene glycol (anhydrous, 99.8%), 1,3-dinitrobenzene (97%), methacryloyl chloride (98%), 2-bromoisobutyryl bromide (98%), and *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA, 99%) were purchased from Aldrich and used as received without further purification. 2-Hydroxyethyl 2-bromoisobutyrate (HEBIB) was prepared as described in the literature.[18]

Synthesis of Macromonomers. A one-pot synthesis of the bromine-devoid, OH-functional precursors was presented in our previous paper.[16] For the synthesis of macromonomer precursors (e.g., bromine-free PtBA-OH) with relatively low molecular weight (target $DP_n \leq 20$), the procedure was modified as follows: first, ATRP of tBA monomer using the HEBIB initiator to obtain bromine-terminated PtBA, followed by removal of the bromine atoms via radical transfer reaction to obtain the halogen-free hydroxy-terminated PtBA (PtBA-OH). Further esterification of the hydroxyl groups of PtBA-OH using methacryloyl chloride afforded the *ω*-methacryloyl-PtBA macromonomer (PtBA-MM). A typical synthesis of low-molecular-weight PtBA-MM is as follows: first, in an oxygen-free glovebox, CuBr (0.223 g, 1.56 mmol), PMDETA (0.270 g, 1.56 mmol), tBA (10.000 g, 78.0 mmol), and acetone (1 g) were charged in a 100 mL flask, and 0.5 g decane was added as internal standard for GC measurements to determine the conversion of tBA monomer. After the mixture was stirred to a homogeneous solution, the HEBIB initiator (1.098 g, 5.2 mmol, target $DP_n = 15$) was added dropwise under vigorous stirring; the color changed to green immediately, indicating the start of polymerization. The flask was sealed and stirred at 40 °C until conversion reached 98% after 8 h. The solution was exposed to air, diluted by acetone, and passed through an alumina/silica column to remove the ATRP catalyst. The solvent was removed under vacuum to yield white bromine-capped PtBA-OH (yield: 10.1 g, 91%); GPC (vs PtBA standards): $M_n = 2090$, $M_w/M_n = 1.25$.

In an oxygen-free glovebox, the purified bromine-terminated PtBA-OH (10 g, 4.78 mmol) was dissolved in a mixture of ethyl acetate (3.0 g) and PMDETA (16.5 g, 95.7 mmol) in a 100 mL flask. After stirring to a homogeneous solution, CuBr (0.342 g, 2.39 mmol) and 1,3-dinitrobenzene (DNB, 40 mg, 0.24 mmol) were charged into the flask. The flask was sealed and stirred in an oil bath at 50 °C for 48 h. After cooling to room temperature, the solution was exposed to air and passed through an alumina/silica column, followed by precipitation of PtBA from cold water to remove the spent Cu(II) and PMDETA. The polymer was dissolved in benzene and freeze-dried overnight to yield the white bromine-free PtBA-OH (yield: 8.1 g, 84%). THF GPC (vs PtBA standards): $M_n = 2280$, $M_w/M_n = 1.20$.

The molar fraction of residual Br end groups of PtBA after chain transfer reaction, x_{Br}, was determined by the following checking ATRP experiment, where PtBA-OH was used as a potential macroinitiator. PtBA-OH (0.50 g, 0.22 mmol) was dissolved in PMDETA (38 mg, 0.22 mmol), tBA (5.64 g, 44.0 mmol), decane (0.28 g), and acetone (0.56 g) in a 50 mL flask. After stirring to a homogeneous solution, CuBr (31 mg, 0.22 mmol) was charged into the flask. The flask was sealed and stirred in an oil bath at 60 °C for 12 h. After cooling to room temperature, the solution was exposed in air to stop the reaction, and the polymer was characterized by GPC. x_{Br} was calculated using eq 1:

$$x_{Br} = \frac{M_M[M]_0 x_p}{(M_{n,ad} - M_{n,PtBA})[PtBA]_0} \quad (1)$$

where M_M, $[M]_0$, and x_p are molecular weight, initial molar concentration, and conversion of tBA, respectively; $M_{n,ad}$ is the number-average molecular weight of new polymer which is polymerized by initiation of the potential PtBA macroinitiator, and $M_{n,PtBA}$ is the number-average molecular weight of the PtBA used as macroinitiator. This equation is derived assuming that x_{Br} is equal to the "initiator efficiency, *f*, of the PtBA precursor. Using $f = x_{Br} = DP_{n,th}/\Delta DP_n$ with $DP_{n,th} = [M]_0 x_p/[PtBA]_0$, $\Delta DP_n = (P_{n,ad} - P_{n,PtBA})$, and $M_n = DP_n/M_M$ results eq 1.

After quantitative removal of the bromine end groups, the OH-functionalized PtBA (PtBA-OH) was esterified using methacryloyl chloride to obtain the PtBA-based macromonomer. PtBA-OH (5.0 g, 2.19 mmol) was dissolved in 30 mL of dried CH_2Cl_2 and triethylamine (0.443 g, 4.39 mmol) in a 50 mL dried flask. The solution was immersed into ice water, and methacryloyl chloride (1.38 g, 13.16 mmol) was added dropwise. After stirring for 3 h, the ice water bath was removed, and the solution was stirred at room temperature for another 24 h. The resulting insoluble amine hydrochloride salt was removed by filtration. PtBA was precipitated from a 4.0 wt % sodium carbonate aqueous solution and deionized water separately at 5 °C to remove the small molecular impurities. The polymer was dissolved in benzene and freeze-dried overnight to yield the slightly yellow PtBA-based macroinitiator (yield: 4.2 g, 81%). ^{1}H NMR studies [($CDCl_3$, δ in ppm: 1 H (6.03, *H*−C=), 1 H (5.50, *H*−C=), 4 H (4.25, −COOCH_2CH_2-OOC−)] indicate the essentially full functionalization of the macromonomer (>95%). The quantitative conversion of OH-functionalized polymer to macromonomer was also verified by liquid adsorption chromatography under critical conditions (LACCC).

Synthesis of Graft Copolymers. In a typical polymerization, a flask was charged with tBA_{37}-MM (3.2 g, 0.7 mmol), CuBr (0.03 g, 0.2 mmol), nBA (3.2 g, 25 mmol), PMDETA (0.036 g, 0.2 mmol), ethyl acetate (14 g, 160 mmol), and decane

(internal standard, 0.9 g, 6.8 mmol). The solution was stirred vigorously until the macromonomer and CuBr were completely dissolved. Finally, the initiator (MBP, 0.032 g, 0.2 mmol) was added; the flask was sealed and placed in an oil bath at 90 °C for 12 h. After heating was stopped, the reaction mixture was cooled to room temperature and diluted with THF. The catalyst was removed by an adsorption filtration through an alumina/silica column. The solvent was removed by evaporation, and the resulting polymer was freeze-dried from benzene. Residual macromonomer was separated by ultrafiltration of the copolymer in methanol. A cellulose acetate membrane (Schleicher & Schüll, Dassel) with a nominal exclusion size of 4 kDa was suitable to separate the residual MM completely (nBA_{128}-*g*-$(tBA_{37})_{3.7}$: yield: 72%; GPC: $M_{n,visco} = 33\,200$, $M_w/M_n = 1.46$). For the raw product obtained with a tBA_{85}-MM the purification was as follows: The polymer was dissolved in methanol at 50 °C and cooled to 5 °C, and the precipitate centrifugated at 5 °C for five times to remove the residual macromonomers, $CuBr_2$, and PMDETA.

For all graft copolymers the conversion of macromonomer was calculated using the GPC results. The requirements for this method are the knowledge of the initial weight of macromonomer and comonomer as well as the comonomer conversion measured by GC. As PtBA and PnBA have very similar refractive indices, the peak areas in GPC eluograms can be directly compared. The macromonomer conversion, x_{MM}, can be calculated from the peak ratio of incorporated macromonomer relative to the initial amount (incorporated MM + residual MM):

$$x_{MM} = \frac{F_{RI,graft} - F_{RI,PnBA}}{F_{RI,total} - F_{RI,PnBA}} \quad (2)$$

The peak fraction of incorporated MM arises from the area of pure graft copolymer ($F_{RI,graft}$) reduced by the area generated from the comonomer ($F_{RI,PnBA}$). The peak fraction from the total MM is obtained by integrating the area of the complete eluogram ($F_{RI,total}$) and subtracting the peak area $F_{RI,PnBA}$. The theoretical, apparent molecular weights of the macromonomer-free graft copolymers can be evaluated by importing the eluogram of the pure graft copolymer ($F_{RI,graft}$) into the GPC software.

Hydrolysis of PtBA Segments. The *tert*-butyl ester groups of the purified graft copolymers were hydrolyzed using HCl in refluxing dioxane for 24 h. After hydrolysis only the NMR signal corresponding to the methylene protons of the *n*-butyl ester remains in the region of the *tert*-butyl groups (1.68−1.52 ppm). The method to determine the degree of hydrolysis can be simplified by comparison of the integral of this peak with that of the methyl group of PnBA at 1.10 ppm. Evaluation of all graft copolymers resulted in a degree of hydrolysis >95%.

Analysis. *Gas Chromatography (GC).* Monomer conversion was determined by GC (Fisons GC 8000, Thermo Quest) from the concentration of residual monomer, with decane as an internal standard, using a polymethylsiloxane capillary column and an injection temperature of 200 °C. The conversion of nBA was determined at a constant temperature of 60 °C for 8 min. For tBA the following temperature program was used: 2 min at 60 °C, increasing to 120 °C with a rate of 20 K/min, and holding the temperature another 2 min.

Gel Permeation Chromatography (GPC). The measurements for the PtBA macroinitiators, macromonomers, and resulting copolymers were performed using THF as eluent at a flow rate of 1.0 mL/min at room temperature using RI and UV ($\lambda = 254$ nm) detection. Column set: 5μ PSS SDVgel, 10^5, 10^4, 10^3, 10^2 Å, 30 cm each. PtBA and PnBA standards (PSS, Mainz) were used for the calibration of the column set. To obtain true molecular weights for the graft copolymers, the GPC columns (5μ PSS SDVgel, 10^6, 10^5, 10^3 Å, 30 cm each) were connected to a viscometer (Viscotek H 502 B), and universal calibration was used. This method was not available for all copolymers. Correction factors, $\gamma = M/M_{app}$, were calculated by Radke according to a recently published method for star polymers[19] using numerical simulations of branched polymers in pores of GPC columns.

^1H NMR. Spectra were recorded with a Bruker AC-250 spectrometer at room temperature in dioxane-d_8 and $CDCl_3$.

LACCC and 2D Chromatography. Liquid adsorption chromatography at critical conditions (LACCC) measurements for nonhydrolyzed macromonomers and graft copolymers were conducted on a Thermo Separation Products (TSP) HPLC system at a flow rate of 0.5 mL/min. An PL-EMD 960 evaporative light scattering detector operating at 50 °C with a gas flow of 3.5 L/min was used for mass detection. 10 μL of ca. 0.5 wt % polymer solutions was injected. All measurements were carried out at a constant column temperature of 35 °C. The critical eluent composition for PnBA on a normal-phase system is THF/*n*-hexane = 31.6/68.4 wt %; for PtBA the ratio is THF/*n*-hexane = 36.4/63.6 wt %. On the reversed-phase HPLC column the critical composition for PnBA is THF/acetonitrile = 52.0/48.0 wt %. 2D chromatography was carried out on the reversed-phase system under the critical conditions of PnBA. The concentration of nonhydrolyzed graft copolymer was 9 mg/mL, where 100 μL was injected; the flow rate in the first dimension (HPLC pump P4000, TSP) varied between 0.5 and 0.04 mL/min. The eluate was collected in 100 μL loops and periodically injected (2 min) into the SEC columns (three PSS high-speed 5μ SDV gel columns, 7 cm, linear, 10^5 and 10^3 Å, flow rate = 6 mL/min) through an injection valve. Detection was performed with a photodiode array detector ($\lambda = 254$ nm) and the PL EMD-960.

Results and Discussion

Synthesis of PtBA and PnBA Macromonomers. The precursor synthesis was carried out using an OH-functionalized initiator in the presence of CuBr and an excess of PMDETA as described in our previous paper.[16] Principally, an excess of PMDETA relative to the amount of CuBr acts as a chain transfer agent in the course of polymerization. At longer reaction times potentially active macromolecules are gradually converted into inactive macromolecules devoid of terminal bromine.[17] The quantitative removal is important to prevent formation of hyperbranched polymers in the subsequent ATRP copolymerization.[15] This synthetic strategy has been well established for macromonomers with molecular weights larger than 3000 g/mol.

However, for the synthesis of PtBA macromonomers with molecular weights below 3000 g/mol, the procedure had to be modified. A relatively high radical concentration at the early stage of polymerization unavoidably leads to recombination of the growing chains, leading to a poor control of the polymerization. To avoid recombination, the ratio of catalyst to ligand was kept equimolar, and the relative amount of CuBr to initiator was decreased in order to decrease the radical concentration. After purification of PtBA-OH polymers, a large excess of PMDETA and a small amount of CuBr were added to the polymer solution in ethyl acetate (typical ratios are given in Table 1) in order to remove the bromine end groups. As shown in the GPC traces (Figure 1a), still a slight amount of recombination reaction occurred, leading to a small shoulder at relatively low elution volume. Addition of 1,3-dinitrobenzene (DNB, 0.5 mol % relative to PtBA) as a chain transfer agent leads to a monomodal size distribution (Figure 1b). As the molecular weight is very low, some oligomers were lost during precipitation in cold water, leading to higher molecular weight and narrower distribution of the bromine-devoid PtBA-OH.

To determine the residual Br content, we tried to use the OH-functional polymers as macroinitiators for ATRP. On the basis of the GPC traces before and after

Table 1. Experimental Conditions and Results for the Synthesis of OH-Functionalized PtBA (PtBA-OH) and PnBA (PnBA-OH) Polymers

	$[M]_0$:$[I]_0$:$[CuBr]_0$:$[Lig]_0$	T/°C	x_p[b]	x_{Br}[c]/%	f[d]	$M_{n,GPC}$[e]/g/mol	M_w/M_n
tBA_{20}-OH	(1) 15:1:0.3:0.3	40	0.98	>0.99	0.98	2090	1.25
	(2) 1:0.5:25 (DNB)[a]	40		<0.01		2280	1.20
tBA_{37}-OH	22:1:0.8:1.6	40	0.97	0	0.95	3100	1.19
tBA_{85}-OH	80:1:1.5:3	40	1.00	0	0.98	10500	1.16
nBA_{22}-OH	20:1:1:2	60	0.99	0	0.91	3000	1.17

[a] To remove Br end groups, a molar feed ratio of $[PtBA]_0$:$[CuBr]_0$:$[PMDETA]_0$. [b] Monomer conversion. [c] Molar fraction of bromine-capped polymers. [d] $f = M_{n,theo}/M_{n,GPC}$. [e] Determined from PtBA, PnBA calibration curve after purification.

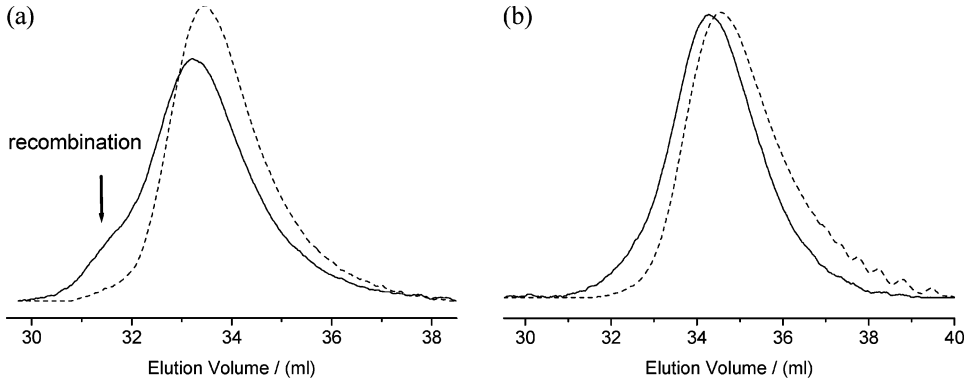


Figure 1. GPC traces (RI signal) of macromonomer precursors: (a) polymerization of tBA with the feed ratio of [M]/[I]/[CuBr]/[PMDETA] = 25/1/0.3/0.3 (– – –) and followed by removal of Br end groups with [PtBA]/[CuBr]/[PMDETA] = 1/0.5/25 (—); (b) polymerization of tBA with the feed ratio of [M]/[I]/[CuBr]/[PMDETA] = 15/1/0.3/0.3 and followed by removal of Br end groups with [PtBA]/[CuBr]/[PMDETA] = 1/0.5/25, and a small amount of *m*-dinitrobenzene (0.5 mol % relative to PtBA) was added.

polymerization, no polymer with Br end groups remained. Finally, the OH-functionalized polymers were converted to the corresponding macromonomers with methacryloyl chloride. ^{1}H NMR was used to investigate the structure, the degree of purity, and functionality. From the integration of the vinyl protons and the methylene protons of the initiator a degree of functionalization >95% was calculated. Also, no detectable amounts of residual methacryloyl chloride could be detected. Liquid adsorption chromatography under critical conditions (LACCC)[20] was used to determine the degree of functionalization. In LACCC, OH-functionalized polymers and macromonomers are completely separated due to different adsorptive interactions with the column material.[21] No additional peak of the OH-functionalized PtBA were detected from the LACCC traces of macromonomers, indicating that the degree of functionalization was essentially complete.

Synthesis of Graft Copolymers PnBA-*g*-PtBA. The graft copolymers were obtained by ATRP copolymerization of nBA with three different PtBA-MM. Kinetic experiments were carried out in order to investigate the consumption of MM and comonomer in the course of polymerization. Figure 2 shows the first-order time–conversion plot for the copolymerization of PtBA macromonomer tBA_{37}-MM with nBA. A slight induction period for the consumption of MM and comonomer is detected; this is ascribed to the time needed to dissolve CuBr completely. After this induction period conversions of MM and comonomer are equal up to ca. 70%, indicating homogeneous distribution of side chains. In the late stage of polymerization only the comonomer is incorporated into the graft copolymer. This is attributed to the increasing viscosity of the reaction system limiting the mobility of the MM relative to nBA. In the other copolymerizations the relative reactivity ratio of macromonomer was always in the range of 1.0–1.3 as determined from the fraction of residual MM. Figure 3 shows the corresponding apparent molecular weights of graft

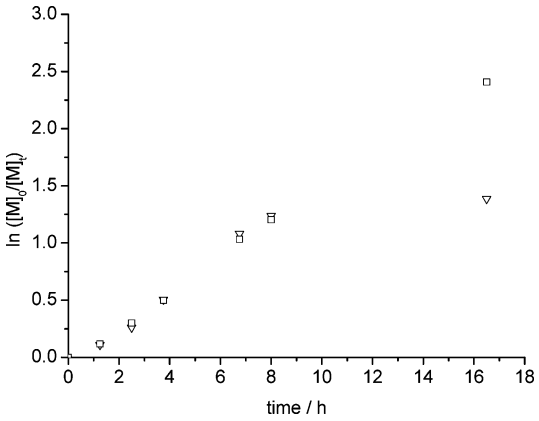


Figure 2. First-order time–conversion plot for the ATRP of nBA comonomer (□) and tBA_{37}-based macromonomer (▽) using methyl 2-bromopropionate as an initiator at 90 °C. Conditions: $[M]_0/[I]_0/[CuBr]_0/[PMDETA]_0$ = 130/1/1.1/1.1, weight concentration of comonomer and MM in feed $m_{0,nBA}/m_{0,PtBA}$ = 1 in 30 wt % ethyl acetate (Table 2, entry 2).

copolymer after removal of the residual macromonomer. Up to 50% total conversion, the molecular weight follows the theoretical line. The deviation at higher conversion can be explained by the elution behavior of branched structures, having a smaller hydrodynamic volume than linear polymers. The polydispersity index passes through a minimum at ca. 70% overall conversion, increasing at the end of the polymerization due to recombination reactions. To minimize the polydispersity and the chemical heterogeneity, in most cases, copolymerizations were terminated at an overall conversion of approximately 70%.

For the copolymers synthesized with tBA_{85}-MM, residual macromonomer and impurities were completely removed by precipitation from cold methanol for five times. The other copolymers with relatively smaller molecular weight macromonomers were purified by

Table 2. Experimental Conditions and Results for the Synthesis of PnBA-*g*-PtBA Graft Copolymers

designation	$P_{n,MM}$[a]	[M]:[I]:[CuBr]:[PMDETA]	w_{nBA}/w_{MM}	$x_{p,nBA}$[b]	10^{-3} $M_{n,app}$[c]	PDI	w_{tBA}[d]	γ[e]	10^{-3} M_n	$P_{n,th,nBA}$[g]	$P_{n,nBA}$[h]	f_{init}[i]	N_{sc}[k]	s[m]
nBA_{138}-*g*-$(tBA_{85})_{2.0}$	85	140:1:0.8:0.8	1.25	0.70	34.8	1.68	0.56	1.11	39.6[p]	98	138	0.71	2.0	46
nBA_{128}-*g*-$(tBA_{37})_{3.7}$	37	130:1:1.1:1.1	1	0.72	24.5	1.46	0.52	1.26 (1.36)	33.2[f]	93	128	0.73	3.7	27
nBA_{111}-*g*-$(tBA_{37})_{10}$	37	210:1:8:8	0.33	0.46	45.8	1.95	0.79	1.55 (1.35)	61.8[f]	97	111	0.87	10	10
nBA_{118}-*g*-$(tBA_{20})_{4.3}$	20	150:1:1:1	2	0.54	22.0	1.34	0.43	1.17	25.7[p]	81	118	0.69	4.3	23
nBA_{224}-*g*-$(tBA_{20})_{4.1}$	20	150:1:1:1	3	0.80	34.5	1.46	0.27	1.12	38.6[p]	120	224	0.54	4.1	44
nBA_{167}-*g*-$(tBA_{20})_{1.7}$	20	150:1:1:1	6	0.78	23.9	1.31	0.17	1.06	25.5[p]	117	167	0.70	1.7	62
nBA_{129}-*g*-$(tBA_{20})_{1.5}$	20	150:1:1:1	6	0.71	18.8	1.18	0.19	1.07	20.1[p]	107	129	0.83	1.5	52

[a] Number-average degree of polymerization of macromonomer. [b] Conversion of nBA, as measured by GC. [c] Determined by GPC using linear PnBA standards. [d] Fraction of tBA units in copolymer measured by ^{1}H NMR. [e] Correction factor for comb-shaped polymers, $\gamma = M_n/M_{n,app}$, from simulation,[19] values in parentheses: from experiment. [f] Determined by GPC with viscosity detector using universal calibration. [g] Expected degree of polymerization of PnBA: $P_{n,th,nBA} = [nBA]_0 x_{p,nBA}/[I]_0$. [h] Degree of polymerization of backbone, $P_{n,nBA} = (1 - w_{tBA})M_n/128 + N_{sc}$. [i] Initiator efficiency, $f_{init} = P_{n,th}/P_{n,nBA}$. [k] Average number of side chains per backbone, $N_{sc} = w_{tBA}M_n/(128P_{n,MM})$. [m] Spacing, $s = P_{n,nBA}/(N_{sc} + 1)$. [p] Calculated as $M_n = \gamma M_{n,app}$ (see note e).

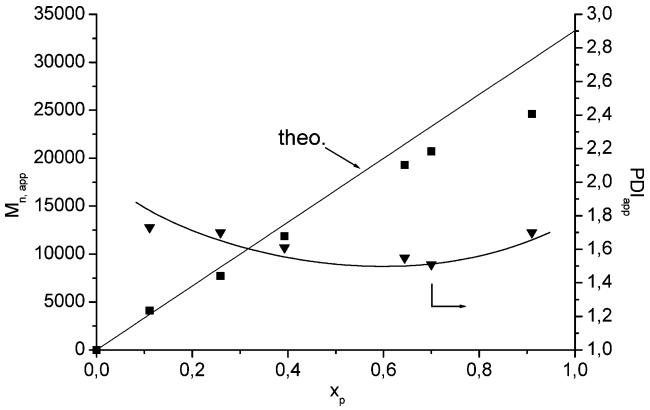


Figure 3. Apparent number-average molecular weight and polydispersity as a function of the overall conversion of tBA_{37}-based macromonomer (MM) and nBA comonomer from the experiment in Figure 2.

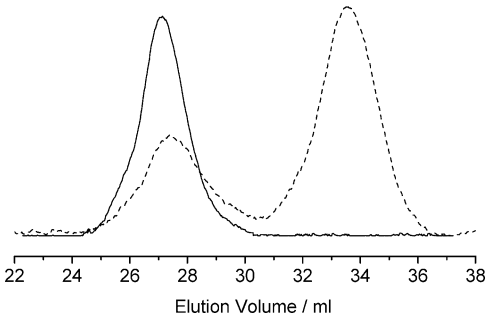


Figure 4. GPC traces (RI signal) for graft copolymer tBA_{472}-*g*-$(nBA_{22})_{14.5}$ before (– – –) and after ultrafiltration (—). Conditions: $[M]_0/[I]_0/[CuBr]_0/[PMDETA]_0 = 1000/1/8/8$, weight concentration of nBA_{22}-based macromonomer (MM) and tBA comonomer in weight feed ratio of $W_{0,PnBA}/W_{0,tBA} = 1$ in 30 wt % ethyl acetate/acetone (Table 3, entry 2).

ultrafiltration in methanol. Molecular weights were determined by GPC using a PtBA calibration curve.

As shown in Table 2, the backbone chain length was kept in the range of 140 ± 30 monomer units in most cases; only the graft copolymer nBA_{224}-*g*-$(tBA_{20})_{4.1}$ is leading to a higher backbone chain length as a consequence of the higher comonomer conversion ($x_{p,nBA} = 0.8$). The average spacing between two macromonomers and thus the number of side chains were varied by using different comonomer ratios. The degree of branching reaches from weakly branched structures (nBA_{129}-*g*-$(tBA_{20})_{1.5}$) with 1.5 incorporated MM in average to highly branched products (nBA_{111}-*g*-$(tBA_{37})_{10}$) with 10 incorporated MM per backbone.

Synthesis of Graft Copolymers PtBA-*g*-PnBA. The "inverse" graft copolymers were obtained by a similar approach copolymerizing PnBA-MM with tBA. Also in this case the incorporation of macromonomer depends on the viscosity of the system. Therefore, a 30 wt % solution of macromonomer and comonomer in ethyl acetate/acetone was used for the polymerization. Addition of acetone is necessary to increase the deactivator concentration; the polydispersities of the final products are below 1.3. Figure 4 shows the GPC eluogram from tBA_{472}-*g*-$(nBA_{22})_{14.5}$ before and after ultrafiltration. The MM can be separated quantitatively by ultrafiltration dissolving the raw product in methanol. Compared to the PnBA-*g*-PtBA graft copolymers the relative reactivity ratio of PnBA-MM is in the range of 0.7; the value is significantly smaller than the one obtained for the PtBA-MM. This is attributed to the degree of purity for the macromonomer. Variation of all reaction parameters always lead to macromonomer conversion <40%; also, the appendant comonomer conversion was ≤50% for the PtBA-*g*-PnBA system (Table 3).

Characterization of Graft Copolymers by 2D Chromatography. To evaluate the average number of side chains, a combination of LACCC and GPC was used. It has been shown earlier that two-dimensional (2D) chromatography allows for the independent determination of the side chains in graft copolymers, in addition to residual macromonomer and nongrafted backbone. To investigate these parameters, the critical conditions of PnBA were set up on a reversed-phase column set. Under these conditions there is no separation according to the molecular weight of PnBA, whereas PtBA standards elute in SEC mode, i.e., earlier than PnBA. For graft copolymers this results in a separation, which depends on the overall number of tBA units. For the determination of the exact number of incorporated MM per backbone a PtBA calibration curve was set up.

Figure 5 shows the 2D chromatogram of the graft copolymer nBA_{128}-*g*-$(tBA_{37})_{3.7}$ after ultrafiltration. The elution volume of PnBA in LACCC is 4.81 mL. At this volume no peak is detected, which indicates the absence of PnBA homopolymer. The graft copolymer peak can be subdivided into two parts of different chemical compositions. At 4.41 mL (HPLC) the graft copolymer elutes, which represents the main part of the product with 61%. From the PtBA calibration curve a PtBA molecular weight of ca. 15 000 g/mol is evaluated. As the molecular weight of the macromonomer is 4970

Table 3. Experimental Conditions and Results for the Synthesis of PtBA-*g*-PnBA Graft Copolymers

entry	$[M]_0$:$[I]_0$:$[CuBr]_0$	w_{tBA}/w_{MM}	$x_{p,tBA}$	$x_{p,MM}$	w_{tBA}[a]	w_{tBA}[b,c]	$M_{n,visko}$[c]/g/mol	PDI
tBA_{495}-*g*-$(nBA_{22})_{5.6}$	1000:1:8	3	0.50	0.37	0.80	0.83	74 500	1.27
tBA_{472}-*g*-$(nBA_{22})_{14.4}$	1000:1:8	1	0.47	0.32	0.59	0.61	91 800	1.20

[a] Fraction of tBA segments as calculated from initial weight and conversion. [b] Fraction of tBA segments determined by NMR. [c] Visco-GPC results measured after ultrafiltration.

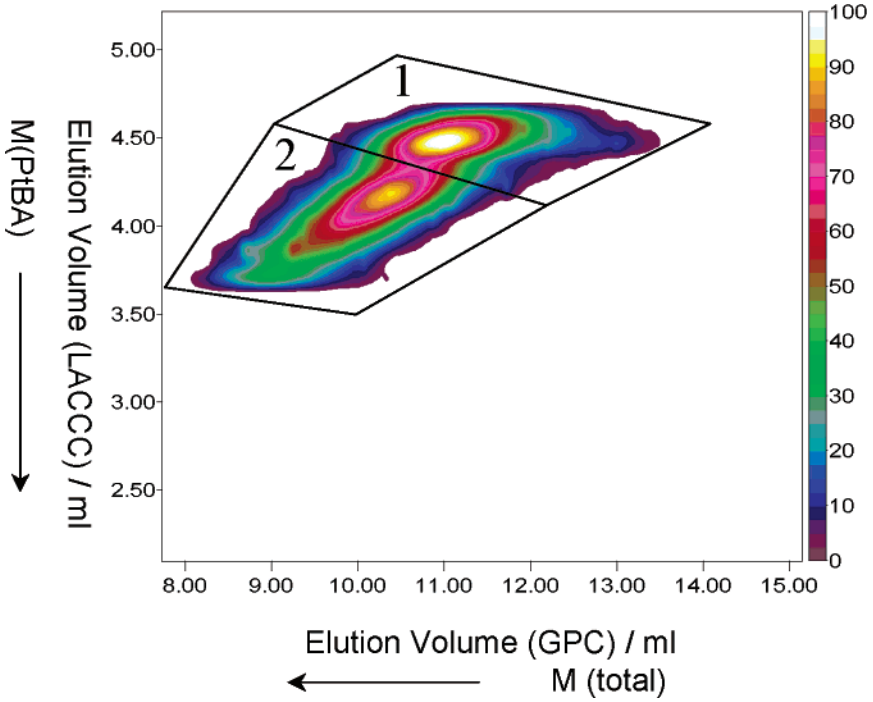


Figure 5. Two-dimensional chromatogram of the nBA_{128}-*g*-$(tBA_{37})_{3.7}$ graft copolymer after ultrafiltration (LACCC: liquid adsorption chromatography under critical conditions).

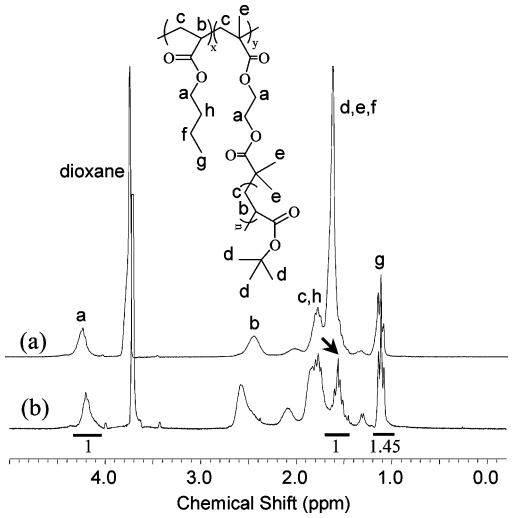


Figure 6. ^{1}H NMR spectra of (a) the nBA_{128}-*g*-$(tBA_{37})_{3.7}$ graft copolymer and (b) the corresponding nBA_{128}-*g*-$(AA_{37})_{3.7}$ graft copolymer in dioxane-d_8.

g/mol, on average three MM are incorporated per backbone. The second peak at 4.13 mL (HPLC) and 10.2 mL (GPC) represents a side product with 39%. From the correlation of the HPLC volume a molecular weight of 25 000 g/mol is estimated, corresponding to ca. 5 incorporated macromonomers per backbone; we assign this peak to the product of recombination. These values agree well with those obtained from GPC and ^{1}H NMR.

Figure 6 shows the ^{1}H NMR spectra of the nBA_{128}-*g*-$(tBA_{37})_{3.7}$ graft copolymer and the corresponding hydrolyzed graft copolymer [nBA_{128}-*g*-$(AA_{37})_{3.7}$]. Since dioxane-d_8 is a good solvent for these two copolymers, all signals of the copolymers can be observed from ^{1}H NMR spectra. This provides an efficient way to evaluate the chemical composition of the copolymers. Integral analysis indicates that the fraction of the tBA units in the nBA_{128}-*g*-$(tBA_{37})_{3.7}$ graft copolymer is 52%. The evaluated fractions of tBA units in the PnBA-*g*-PtBA graft copolymers are summarized in Table 2.

The degree of hydrolysis was also evaluated by the ^{1}H NMR studies. Assuming that only tBA units of the graft copolymers have been hydrolyzed, since nBA units, as a primary ester shows an extremely low tendency to hydrolyze under these reaction conditions; if the tBA units of the nBA_{128}-*g*-$(tBA_{37})_{3.7}$ graft copolymers have been quantitatively hydrolyzed, an integral ratio of the signals at $\delta = 4.2$, $\delta = 1.6$, and $\delta = 1.1$ should be 1:1.07:1.42 according to the chemical composition of this graft copolymer.

As shown in Figure 6, the strongest signal at $\delta = 1.6$ (see Figure 6a) suppressed remarkably after hydrolysis (marked by an arrow, see Figure 6b, predominately contributed by $COOCH_2CH_2CH_2CH_3$), which becomes comparable to the signal at $\delta = 4.2$. However, integral ratio of the signals at $\delta = 1.6$ and $\delta = 1.1$ is 1/1.45, which is smaller than the theoretical integral ratio of 1/1.33. Clearly, the integral of the signal at $\delta = 1.6$ was not correctly estimated due to partially overlap of the signals in this range, which leads to the integral ratio of the signals at $\delta = 4.2$ and $\delta = 1.6$ is 1/1, rather than the theoretical integral ratio of 1/1.07. Considering the integral analysis error due to the partially overlap of

the signals at $\delta = 1.6$, roughly equal integrals of the signals at $\delta = 4.2$ and $\delta = 1.6$ indicate that the hydrolysis of tBA units has been essentially completed (>95%). The essentially quantitative hydrolysis of these graft copolymers was also confirmed by the potentiometric titration studies of these graft copolymer aqueous solutions, which will be discussed in a subsequent paper about the aqueous solution behavior of these amphiphilic graft copolymers in comparison to the corresponding diblock copolymers.

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