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New Strategy for the Synthesis of Halogen-Free Acrylate Macromonomers by Atom Transfer Radical Polymerization

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ABSTRACT: Atom transfer radical polymerization (ATRP) of *n*-butyl acrylate and *tert*-butyl acrylate using 2-hydroxyethyl 2-bromoisobutyrate as a functionalized initiator and an excess of *N,N,N′N′N″*-pentamethyldiethylenetriamine (PMDETA) relative to the initiator and CuBr catalyst yields halogen-free polymers with a terminal hydroxyl function in a one-pot reaction. The Br atoms of the other terminus would be detrimental for the synthesis of graft copolymers via ATRP. In our approach they are replaced by hydrogen atoms via transfer from PMDETA at the end of the polymerization. The subsequent esterification of the hydroxyl group with methacryloyl chloride leads to well-defined macromonomers with predictable molecular weights and low polydispersities ($M_w/M_n \leq 1.2$).

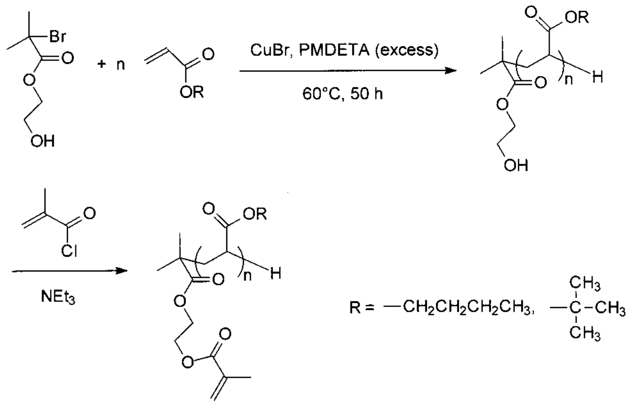
Introduction

Atom transfer radical polymerization (ATRP) is a powerful tool to prepare polymers with predictable molecular weights and low polydispersities.[1,2] With this controlled radical polymerization method a variety of polymer architectures and compositions is accessible,[3,4] e.g., block copolymers,[5] graft copolymers,[6] and hyperbranched polymers.[7,8] Functional groups can also be introduced easily, either through the monomers themselves or at the chain ends.[3] A smart method to incorporate terminal functional groups is the use of initiators containing hydroxyl or other functional groups.[9−12] Another way is the transformation of the halogen end groups by nucleophilic substitutions, addition of less reactive monomers, or radical reactions.[13−15]

An interesting group of functional polymers are macromonomers. Because of their polymerizable end group, it is possible to synthesize polymer brushes by homopolymerization[16,17] and comb-shaped or graft copolymers by copolymerization of the macromonomer with a comonomer.[18−21] Various methods have been used for the preparation of macromonomers with (meth-)acrylate polymerizable groups. Radical addition−fragmentation chain transfer agents, e.g., allyl sulfides,[22,23] and cobalt-mediated catalytic chain transfer (CCT) are suitable methods to synthesize macromonomers.[24] Recently, a macromonomer synthesis based on ATRP using vinyl-containing initiators was published.[25] Another possibility is the synthesis of an OH-functionalized polymer which is afterward esterified with (meth)-acryloyl chloride to yield the macromonomers. Group transfer polymerization (GTP) using a trimethylsiloxy-functionalized initiator[10] or free-radical polymerization with transfer to 2-mercaptoethanol[26,33] has been used to prepare OH-terminated polymers.

In this paper we report on the synthesis of macromonomers by ATRP using an OH-functionalized initiator. Generally, this method leads to polymers with a halogen terminus. To obtain macromonomers polymerizable by ATRP, it is necessary to reduce the Br termini to hydrogen atoms; otherwise, “macroinimers” are obtained which contain an initiator function as well as a polymerizable group leading to hyperbranched polymers.[8] A possible way to replace the Br termini by hydrogen atoms is the reduction with tributyltin hydride.[27] However, during our studies we found that the hydroxyl group of an OH-functionalized polymer reacts with the tin hydride forming an alcoholate, making the purification of the products difficult.

Scheme 1. Macromonomer Synthesis



In this paper we report a new synthetic strategy for acrylate macromonomers via ATRP (Scheme 1). By using 2-hydroxyethyl 2-bromoisobutyrate as initiator in the presence of CuBr and an excess of the ligand *N,N,N′,N′,N″*-pentamethyltriethylenediamine (PMDETA), it is possible to obtain polymers with >95% hydrogen end groups on one side and a hydroxyl function at the other chain end in a one-pot reaction. At the end of the polymerization, PMDETA acts as a transfer agent. This behavior has been examined recently by MALDI-TOF mass spectroscopy.[28]

The hydroxyl group is esterified quantitatively with methacryloyl chloride in a second reaction step and the resulting macromonomers have well-defined molecular weights and low polydispersities.

Experimental Section

Materials. *n*-Butyl acrylate (nBA, BASF AG) and *tert*-butyl acrylate (tBA, BASF AG) were fractionated from CaH_2 over a 1 m column at 45 mbar, stirred over CaH_2, degassed, and distilled in high vacuum. CuBr was purified by stirring in acetic acid overnight. After filtration it was washed with ethanol and ether and then dried. *N,N,N′,N″,N″*-Pentameth-

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Table 1. Reaction Conditions and Results for OH-Functionalized PtBA and PnBA

run	$[M]_0$:$[I]_0$:$[CuBr]_0$:$[Lig]_0$	T/°C	t/h	x_p[a]/%	$M_{n,theo}$/ g/mol	$M_{n,GPC}$[b]/g/mol	M_w/M_n
			PtBA−OH				
MM22tBA	22:1:0.8:1.6	40	70	97	2940	3100	1.19
MM100tBA	100:1:1.5:3	40	70	100	13010	13600	1.16
			PnBA−OH				
MM20nBA	20:1:1:2	60	60	99	2740	3000	1.17
MM80nBA	80:1:1.4:2.8	60	60	100	10450	11200	1.19

[a] Monomer conversion. [b] Expected $M_n = M_{monomer}[M]_0x_p/[I]_0$.

yldiethylenetriamine (PMDETA, Aldrich) was degassed and distilled on the vacuum line. 2-Hydroxyethyl 2-bromoisobutyrate (HEBIB) was prepared according to the literature.[29] ^{1}H NMR ($CDCl_3$): δ = 4.31 ($-CH_2-OCO$), 3.85 ($-CH_2-OH$), 1.97−1.92 ($-CH_3$, $-OH$) ppm. All other reagents were used as received.

Preparation of HO−PnBA−H by Bulk ATRP of nBA. All operations were carried out under a nitrogen atmosphere. The flask was charged with CuBr, PMDETA, and nBA (molar ratio = 1:2:20) and stirred until the system became homogeneously green. Then the initiator HEBIB ($[HEBIB]_0/[nBA]_0$ = 1:20) was added dropwise. As soon as the initiator was added, the system became deep green, indicating the start of the polymerization. The flask was immersed in an oil bath heated at 60 °C and stirred for 60 h. Conversion was determined by GC measurements, using 10% decane as an internal standard. After heating was stopped, the reaction mixture was cooled to room temperature and diluted with THF. The solution was then passed over alumina/silica to remove Cu complexes prior to removal of the solvent (yield: 99%; GPC: M_n = 3000, M_w/M_n = 1.17).

Preparation of HO−PtBA−H by ATRP of tBA. All operations were carried out under a nitrogen atmosphere. The flask was charged with CuBr, PMDETA, and tBA (molar ratio = 0.8:1.6:22) and acetone (10 wt %) as internal standard and in order to enhance the solubility of $CuBr_2$ and stirred until the system became homogeneous yellow. By adding the initiator ($[HEBIB]_0/[tBA]_0$ = 1:22) dropwise, the color changed to slightly green indicating the start of the polymerization. The flask was immersed in an oil bath, heated at 40 °C, and stirred for 70 h (yield: 97%; GPC: M_n = 3100, M_w/M_n = 1.19).

Macromonomer Synthesis. After freeze-drying, 20 g of OH-functionalized polymer was dissolved in 400 mL of THF and a 1.1 molar excess of triethylamine with regard to the OH end group was added. The solution was cooled with ice water, and a 10 molar excess of methacryloyl chloride relative to the OH end groups was added dropwise. After 3 h the ice water was removed, and the solution was stirred another 24 h at room temperature.

Analysis. GPC measurements were carried out using a Waters 510 LC pump equipped with four PSS SDV-gel columns (5 μ, 30 cm; 10^5 Å, 10^4 Å, 10^3 Å, 10^2 Å) in series with a 410 differential refractometer and a Waters 996 UV detector. Calibration was based on PnBA and PtBA standards (PSS, Mainz) using PSS WinGPC V.6 software. ^{1}H NMR spectra were recorded with a Bruker AC-250 MHz spectrometer at 25 °C in $CDCl_3$. Liquid adsorption chromatography under critical conditions (LACCC) measurements were conducted on a Thermo Separation Products (TSP) HPLC system at a flow rate of 0.5 mL/min. An evaporative light scattering detector (ELSD, PL-EMD 960) operating at 50 °C with gas flow of 3.5 L/min was used for mass detection. A 10 μL aliquot of ca. 0.5 wt % polymer solutions was injected. All measurements were carried out at a constant column temperature of 35 °C. The normal phase system consists of two Nucleosil silica gel columns (250 × 4 mm) with 5 μm average particle size and 100 and 300 Å pore diameter. For PnBA the critical conditions are THF: *n*-hexane (31.6:68.4), and for PtBA they are (36.4:63.6).

Results and Discussion

Polymerization of nBA and tBA by ATRP Using Excess PMDETA. The polymerizations were carried out using a 2-fold excess of PMDETA relative to the initiator (e.g., $[M]_0$:$[I]_0$:$[CuBr]_0$:$[PMDETA]_0$ = 20:1:1:2) in order to obtain halogen-free polymers in one reaction step. Table 1 gives an overview about the resulting macromonomers having molecular weights between 3000 and 13 600 g/mol and polydispersities below 1.2. To distinguish between bromine and hydrogen end groups, one polymer (sample MM20nBA) was tested as a macroinitiator (MI) for the polymerization of nBA ($[nBA]_0$:$[MI]_0$:$[CuBr]_0$:$[PMDETA]_0$ = 200:1:1:1). The polymerization was carried out at 50 °C for 20 h (corresponding to 80 half-lives, see below). The GPC trace in Figure 1 does not show any increase of the molecular weight; no conversion of the monomer occurred. This means that all Br end groups of the polymer are replaced by H atoms.

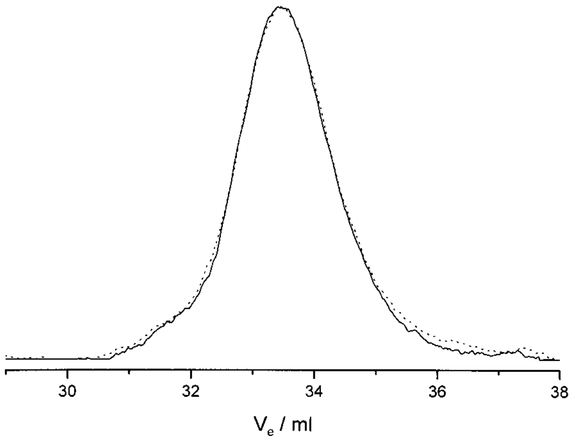

Figure 1. PnBA (M_n = 3000 g/mol, M_w/M_n = 1.17) after 99% monomer conversion (20 h; · · ·) cannot reinitiate polymerization and the molecular weight does not increase (—).

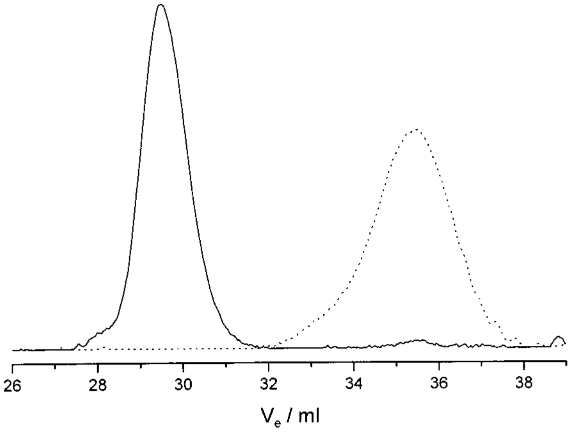

Figure 2. Polymer after 52% monomer conversion (15 min; · · ·) reinitiates the polymerization; the product (—) contains no residual macroinitiator.

As an evidence that the hydrogen transfer from PMDETA takes place at the end of the reaction only, another polymerization was carried out under equal

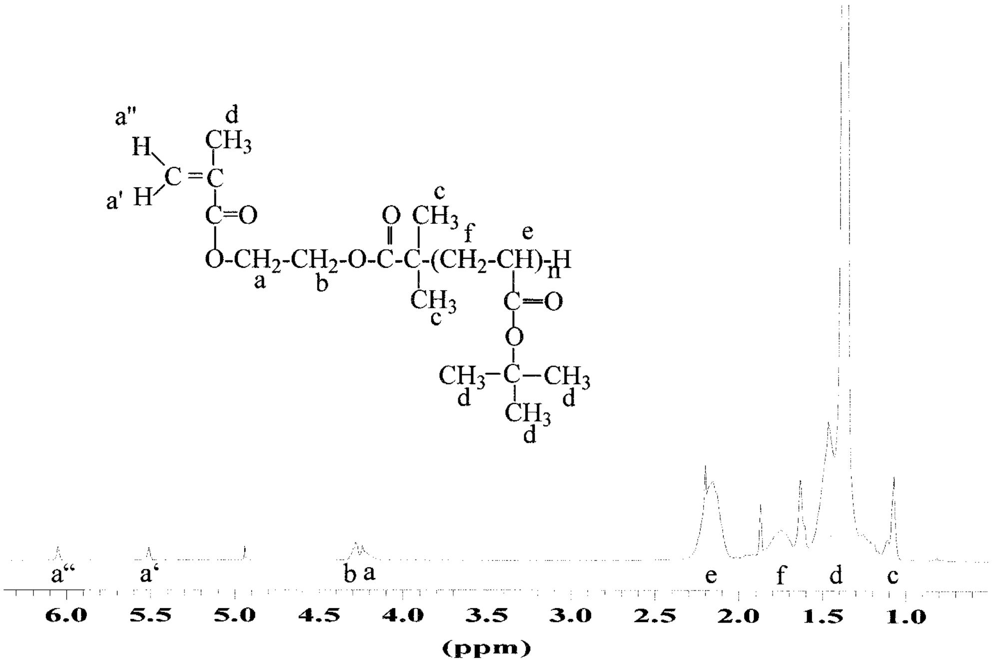

Figure 3. ^{1}H NMR of PtBA macromonomer (M_n = 3650 g/mol, M_w/M_n = 1.19).

conditions, but the polymerization was terminated after 15 min (52% monomer conversion). The resulting polymer (M_n = 1330 g/mol, M_w/M_n = 1.17) was purified and subsequently tested as a macroinitiator as well. Under the same conditions used before (T = 50 °C, t = 20 h) the polymerization was carried out. The GPC curve in Figure 2 shows an molecular weight of 17 000 g/mol and M_w/M_n = 1.08, while the peak from the macroinitiator practically completely disappeared. Hence, it follows that nearly all polymer chains carried a Br end group after 50% monomer conversion.

Esterification of the OH-Functionalized Polymer. In a second reaction step the OH-function of the H-terminated polymers was esterified with methacryloyl chloride. The macromonomers were characterized by ^{1}H NMR spectroscopy. Figure 3 shows the spectrum of a PtBA macromonomer with M_n = 3650 g/mol and M_w/M_n = 1.19. Peak (d) is assigned to the *tert*-butyl groups; peaks (e) and (f) are assigned to the methylene and methine protons, respectively, of the repeat units. The small peaks (a) and (b) between 4.17 and 4.32 ppm are attributed to the methylene protons from the initiator moiety. The small peaks (a′) and (a″) which appear at 5.52 and 6.05 ppm can be attributed to the vinyl protons, indicating a successful esterification. A degree of functionalization of 95% was calculated by integration of the vinyl protons and the methylene protons in the initiator moiety.

A more suitable method to determine the degree of functionalization very precisely is liquid adsorption chromatography under critical conditions (LACCC), which was established by Belinkii et al.[30] and Entelis et al.[31] At a certain critical solvent composition the elution volume of the polymers is independent of their molecular weight; it only depends on their polarity.[32] The OH-functionalized polymer is more polar than the macromonomer. Therefore, it has a higher elution volume due to stronger interactions with the column material.[33] As seen in Figure 4, the peaks for the OH-functionalized polymer and the macromonomer are separated completely. Since the macromonomer has no additional peak at the elution volume of the OH-functionalized polymer, it is obvious that the degree of functionalization is 100%.

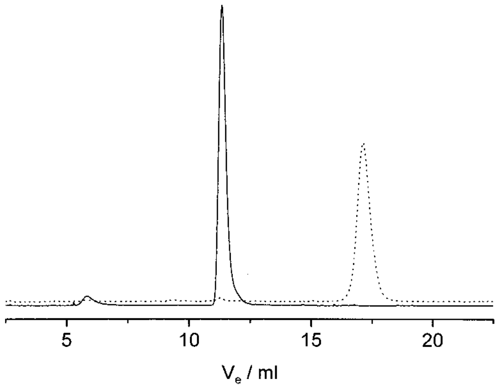

Figure 4. LACCC of OH-functionalized PnBA (· · ·) and PnBA macromonomer (—).

Conclusions

When PMDETA is used in ATRP in excess to the initiator, it acts as a ligand during polymerization and as a transfer agent at the end of the polymerization. This provides an elegant way to prepare H-terminated polymers by ATRP in a one-pot reaction. If 2-hydroxyethyl 2-bromoisobutyrate is used as an initiator for the polymerization, the resulting products carry a hydroxyl group at one chain end and a hydrogen atom at the other end. An additional reaction step for the reduction of the Br end groups, e.g., with Bu_3SnH,[27] can be omitted.

The consecutive esterification of the hydroxyl group is quantitative, and well-defined macromonomers are obtained. This new strategy is a simple and effective way to prepare macromonomers by ATRP. Results of the copolymerization of these macromonomers with nBA and tBA will be published elsewhere.

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