Macromol. Symp. **2004**, *210*, 147-155

Synthesis of Halogen-Free Amino-Functionalized Polymethyl Methacrylate by Atom Transfer Radical Polymerization (ATRP)

Veera Bhadraiah Sadhu, Jürgen Pionteck, Dieter Voigt, Hartmut Komber, Brigitte Voit*

Institut für Polymerforschung Dresden e.V., Hohe Strasse 6, 01069 Dresden, Germany
E-mail: pionteck@ipfdd.de

Summary: In order to obtain amino-terminated polymethyl methacrylate (PMMA-NH_2) free of halogen we used the atom transfer radical polymerization (ATRP) to polymerize methyl methacrylate (MMA) in presence of an initiator containing an alkyl bromide unit and a protected amine functional group. The use of CuBr / N,N,N',N",N"-pentamethyldiethylenetriamine (PMDETA) as co-catalyst system results in a polymer free of halogen due to hydrogen transfer from PMDETA to the growing polymer chain. However, side reactions occur affecting the typically "living" character of the ATRP. The measured molecular weights are consistently higher than the theoretical ones and the molecular weight distributions are relatively broad.

Keywords: amino-containing initiator; atom transfer radical polymerization (ATRP); functionalization of polymers; polymethyl methacrylate (PMMA)

Introduction

Atom transfer radical polymerization (ATRP) offers the possibility to obtain polymers with well-defined functionality, controlled molecular weight, and low polydispersity.[1,2] Typically, alkyl halides, which may carry a functional group, are used as initiators leading to polymers with an (functionalized) alkyl group at the one (starting) end and a "living" halide functionality at the other end. The halogen end groups may be used for further functionalization, but this is often connected with undesired side reaction.[3] Halogen caused side reactions (elimination, radical processes) may also occur under processing conditions and therefore it is advantageous to remove the halogen before further processing. For this, a wide range of methods are available. E.g. it was possible to convert all terminal halogens into hydrogen end groups by treating with trialkyltin hydride.[4] Recently, the synthesis of halogen-free acrylate macromonomers by ATRP in a one-pot reaction using a catalytic system containing CuBr and an excess of N,N,N',N",N"-pentamethyldiethylenetriamine (PMDETA) has been reported.[5] Due to the replacement of the halogen by hydrogen atoms via hydrogen transfer from PMDETA at the end of the polymerization halogen free products have been

DOI: 10.1002/masy.200450617

obtained. However, in ref. [6] it was shown that the halogen-hydrogen exchange starts already in early stages of the polymerization, even under mild conditions, but to a degree which does not hinder the complete conversion of the studied acrylic monomers and retaining the controlled character of the ATRP.

We studied the applicability of this method for the bulk synthesis of amino-terminated PMMA, which is an interesting material for reactive processing, e.g. in blends. To hinder amino-caused side reactions and interfering of the amino-group with the catalyst system, the amino functionality of the initiator had to be protected before use. In order to obtain low molecular weight polymers, which can be analysed with sufficient accuracy, a relatively high initiator/monomer ratio has been used. The transformation of the terminal bromide into hydrogen and side reactions have been analysed by MALDI TOF MS and ^{1}H NMR spectroscopy.

Experimental Section

Materials. Methyl methacrylate (MMA, 99 %, Aldrich) was vacuum distilled and stored over molecular sieve under argon. Copper (I) bromide (99.999 %, Aldrich) was purified as follows: CuBr was stirred with glacial acetic acid for 24 h and washed consecutively with acetic acid, ethanol and diethyl ether for several times and dried under vacuum at 40°C for 3 days and stored under argon atmosphere. N,N,N',N",N"-pentamethyldiethylenetriamine (PMDETA) (99 %, Aldrich), anisole (99.7 % anhydrous, Aldrich), bromoisobutyryl bromide (Merck), diaminoethane (Merck), dichloromethane (Acros) dried over molecular sieve, tetrahydrofuran (THF) (Acros), triethylamine (Fluka), alumina (Merck), trifluoroacetic acid (99 %, Aldrich), and di-tert-butyl dicarbonate (Fluka) were used as received.

tert-Butyl-N-(2-amino-ethyl) carbonate. A method similar to that reported in ref. [7] was used. A solution of 17.5 g (0.08 mol) di-tert-butyl dicarbonate in 180 ml of 1,4-dioxane was slowly added into a stirred solution of 36 g (0.6 mol) diaminoethane in 180 ml of 1,4-dioxane over a period of 3 h at room temperature. After two days, the precipitate formed was filtered off and the 1,4-dioxane and excess diaminoethane were removed in vacuum from the filtrate. 300 ml water were added to the residue and the water-insoluble bis(N,N'-tert-butyloxycarbonyl)-1,2-diaminoethane was removed by filtration. From the aqueous solution saturated with sodium chloride the product was extracted with dichloromethane. The collected organic phase was dried over sodium sulfate and eventually evaporated under reduced pressure to give 90-95 % of tert-butyl-N-(2-amino-ethyl) carbonate as colourless oil.

^{1}H NMR (DMSO-*d*$_6$): δ 1.37 ((**CH**$_3$)$_3$C-), 2.52 (-N**H**$_2$), 2.73 (-**CH**$_2$NH$_2$), 2.9 (-**CH**$_2$NH-), 5.74 ppm (-**NH**-).

Synthesis of the Initiator (I). tert-Butyl-N-(2-amino-ethyl) carbonate (17.7 g), triethylamine (11.33 g), and dry dichloromethane (180 ml) were placed in a three-neck round-bottomed flask. 2-Bromoisobutyryl bromide (25.4 g) was added slowly with stirring at 0°C. The reaction was left for 48 h with continuous stirring at room temperature. Triethylammonium bromide was formed as white precipitate and filtered off. After removal the solvent in vacuum from the filtrate a yellow solid is left. The product was dissolved in methanol and precipitated into water saturated with Na_2CO_3. Yield: 90-95 %. mp 94-96°C.

^{1}H NMR (DMSO-*d*$_6$): δ 1.38 ((**CH**$_3$)$_3$C-), 1.86 ((**CH**$_3$)$_2$C-), 3.02 (-**CH**$_2$-NH-COO-), 3.12 ((-**CH**$_2$-NH-CO-), 6.8 (-CH$_2$-N**H**-COO-), 8.0 ppm (-CH$_2$-N**H**-CO-).

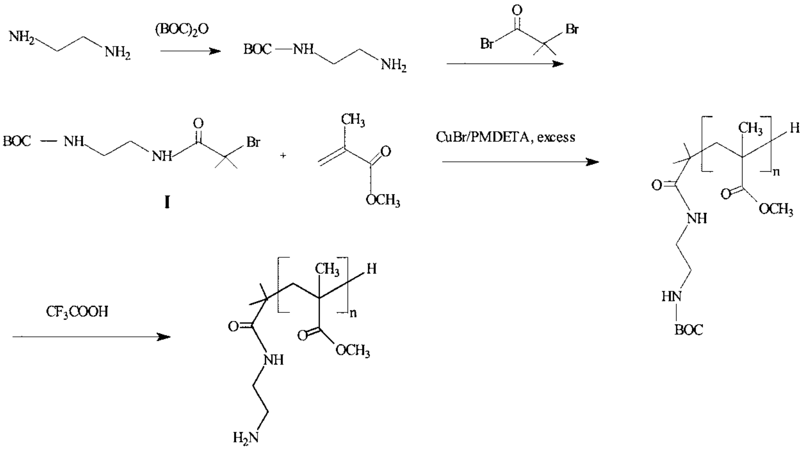
Polymerization. Most samples were prepared by bulk polymerization. CuBr was placed in a dried Schlenk tube. The tube was evacuated and flushed with argon three times. Then the degassed methyl methacrylate, PMDETA, and the initiator were added to the tube and stirred until the system became homogeneously green. The resulting solution was freed from oxygen by performing three freeze-pump-thaw cycles and kept under argon.. The tube was tempered in a bath at the desired temperature and the ATRP was started by adding the initiator. After the polymerization was completed the polymerization mixture was dissolved in THF. The catalyst was removed by passing the solutions through a column of alumina/silica. The polymer was precipitated in n-hexane and dried at 50 °C in vacuum. The BOC protecting group was removed by treating with trifluoroacetic acid (25 % by volume) in dichloromethane for 2 days at room temperature. The solution was neutralized with triethylamine, subsequently precipitated into n-hexane, and vacuum dried.

The polymerization in solution was done with a solvent/MMA ratio of 1/1 by weight.

Analysis. The ^{1}H NMR spectra were recorded on a Bruker DRX 500 spectrometer operating at 500.13 MHz. Gel permeation chromatography (GPC) measurements were performed with a modular chromatographic equipment (KNAUER) containing a refractive index detector at ambient temperature. A single PL Mixed-B column Hibar PS 40 (Merck) was used. The sample concentration was c = 2 g/l and the injection volume was 20 µl. Chloroform was used as eluent at room temperature with a flow rate of 1 ml/min. Linear PMMA standards (Polymer Laboratories) were used for calibration. MALDI TOF mass spectra were acquired on a HP G2030A MALDI TOF MS system (Hewlet Packard). The desorption/ionization was induced by a pulsed N_2 laser. Dihydroxy benzoic acid and sodium trifluoroacetate / KCl were used as matrix and cationizing agent, respectively. All spectra were obtained at an accelerating potential of 24 kV in linear mode and positive polarity using a TLF-unit.

Results and Discussion

The CuBr / PMDETA catalyst system was selected for the atom transfer radical polymerization of MMA with a two-fold excess of ligand relative to the initiator in order to obtain halogen free polymers in a one-pot reaction.[5] The initiator containing a protected amine group was synthesized according to Scheme 1 that also describes the expected polymerization mechanism.



Scheme 1. Synthesis of amino-terminated PMMA by ATRP

The desired reaction product is a polymer with the protected amine group at the one end and devoid of terminal bromine at the other end. The used concentration of the initiator was relatively high in order to obtain low molecular weight polymers. This allows to analyse the structure of the terminal sites with sufficient accuracy. Representative compositions, polymerization conditions and characteristics of the resulting products are summarized in Table 1.

Table 1. Conditions and analytical data for the ATRP of MMA in bulk and solution with I (Scheme 1) as initiator and CuBr/PMDETA as catalyst ($[CuBr]_0/[PMDETA]_0 = 1/2$).

No.	$[CuBr]_0$ / $[I]_0$	solvent	T	$t_{pol.}$	$[MMA]_0$ / $[I]_0$	convn.	$M_{n,calc}$ [a)]	$M_{n,GPC}$	f =	M_w/M_n
	mol/mol		°C	min	mol/mol	%	g/mol	g/mol	$M_{n,cal}/M_{n,GPC}$	
1	1		60	10	20/1	82	1870	5200	0.36	2.86
2	1		25	30	100/1	53	5540	22400	0.24	2.18
3	0.5		25	60	100/1	80	8240	7750	1.06	1.79
4	0.5		0	240	100/1	n.d.	n.d.	24950	n.d.	2.55
5	0.3		25	90	100/1	43	4530	25700	0.18	2.45
6	0.2		25	180	100/1	22	2430	6050	0.40	2.06
7	0.1		60	180	100/1	42	4430	26050	0.17	1.53
8	0.1		25	360	100/1	n.d.	n.d.	23350	n.d.	1.62
9	1	toluene	25	300	100/1	42	4430	8150	0.54	2.20
10	0.5	toluene	60	180	20/1	98	2190	5350	0.40	2.40
11	1	anisole	90	360	200/1	58	11800	66000	0.18	2.61
12	1	anisole	60	360	200/1	45	9240	49150	0.18	2.23
13	1	anisole	25	1440	200/1	75	15200	28400	0.53	2.21
14	1	anisole	25	1440	100/1	92	9440	18600	0.50	2.50
15	1	anisole	25	30	20/1	66	1550	2200	0.70	2.16.

a) $M_{n,cal}$ (g/mol) = $[M]_0/[I]_0$ x conversion (%/100) x 100.12 + molecular weight of the initiator;
n.d.: not determined

The data in Table 1 indicate that the polymerization of MMA in bulk as well as in solution has an uncontrolled character resulting in rather broad molecular weight distribution and higher experimental M_n-values than the calculated ones. The initiator efficiency f (in ideal case: $f = 1$) is low (Note: The conversion was calculated from the yield, which was determined gravimetrically, not considering possible fractionation).

The polymerization is highly exothermic. To improve the control over the polymerization conditions the catalyst/initiator molar ratio was decreased up to 0.1, the polymerization temperature reduced to 0°C, and the polymerization mixture diluted. However, even under mild conditions no controlled character of the ATRP was observed. This is likely caused by the fact that the coordination complexes between copper and aliphatic amines have a lower redox potential than the typically used copper/bipyridine complexes[8] resulting in a higher concentration of active radicals which favours undesired side reactions. In ref. [8] also deviations from the ideal living character of the ATRP of MMA have been observed. Additionally, in our system interactions of the initiator with the catalyst system can not be excluded, even if the amino-containing initiator is used in its protected form. Furthermore, the propagation rate constants of MMA are very high.[9] When using an initiator with a slow initiation rate, especially in presence of the highly active catalyst system CuBr/PMDETA for the propagation reaction, a broad molecular weight distribution can be expected. With forming the first active initiator radicals the fast propagation will consume a large quantity of the monomer molecules, while active initiator species formed at later times can not participate in the polymerization process. This explains also the low initiator efficiency.

To study the reasons for the uncontrolled character of the ATRP we analysed the structure of the terminal PMMA groups. Under the polymerization conditions used the expected termination reaction is the bromine exchange by hydrogen from the PMDETA forming polymers devoid of halogen, proven for different acrylates for similar polymerization conditions.[5,6] Figure 1 clearly shows the dominance of the halogen-free amino-terminated polymethyl methacrylate (NH_2-PMMA-H) in the MALDI TOF mass spectra. The main peaks in the NH_2-PMMA-H spectrum correspond to NH_2-PMMA-H ($m = 129 + n\,(100.12) + 1 + M^+$), whereas the peaks of NH_2-PMMA-Br should appear at $m = 129 + n\,(100.12) + 79/81 + M^+$.

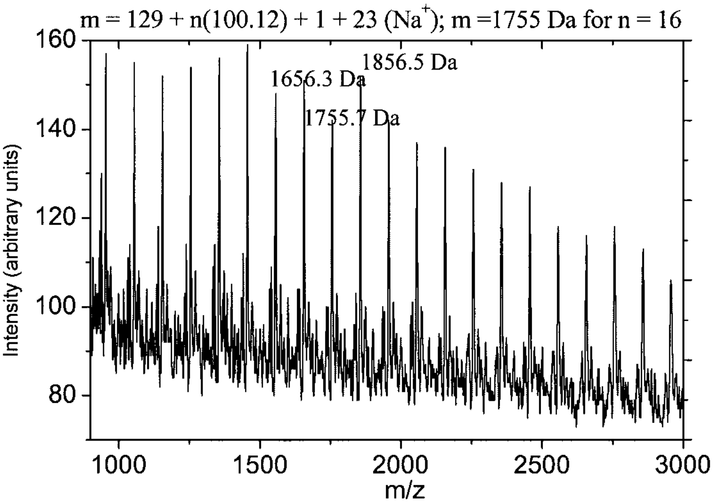


Fig. 1. MALDI TOF MS of PMMA-NH_2 (sample 1, Table 1). The dominant series of peaks correspond to the amino-functionalized hydrogen-terminated polymer chains.

Beside the main product, peaks corresponding to Br-terminated polymers and a third series of minor peaks properly caused by combination of two radicals and corresponding to m = 129 +

n (100.12) + 129 + M^+ could be observed, especially at short polymerization times. Figure. 2 give a detailed peak assignment to the different reaction products.

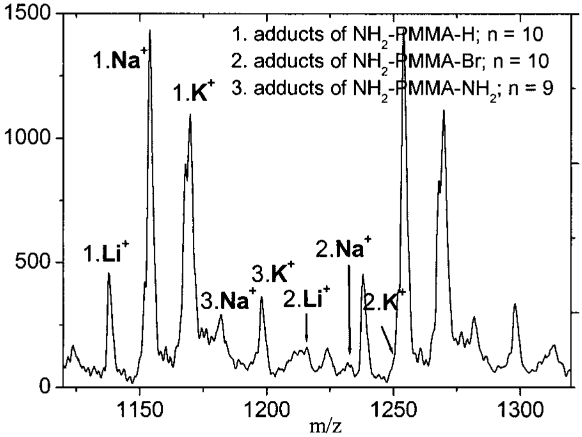


Fig. 2. Detailed peak assignment of main and side products in the sample 15 (Table 1), taken after 30 min. (MMA conversion 66 %).

Another side reaction is detected by ^1H NMR spectroscopy. Figure 3 shows the NMR spectra of protected and deprotected amino end group functionalized PMMA devoid of Br (sample 1 in Table 1). The peaks at 5.45 and 6.21 ppm could be assigned to the olefin double bonds formed due to dehydrobromination. According to the signal intensities about 30 % of the polymer chains underwent this elimination reaction. The product is not easy to prove by MALDI TOF MS since the molar mass difference between hydrogen terminated polymers and dehydrobrominated ones is 2 Da only, and appears as small left-hand shoulder of the main product peaks.

To evaluate the stability of the amino-terminated PMMA we analyzed the structure before and after processing in a DACA Micro Compounder (DACA Instruments). The shear rate is comparable to conventional extrusion processes. After processing at 180°C no changes in the NH_2-PMMA-H structure could be observed. At higher temperatures side reactions occur forming a main product of unknown structure (with 50 Da molar mass difference compared to NH_2-PMMA-H, Fig. 4) and increased molecular weight.

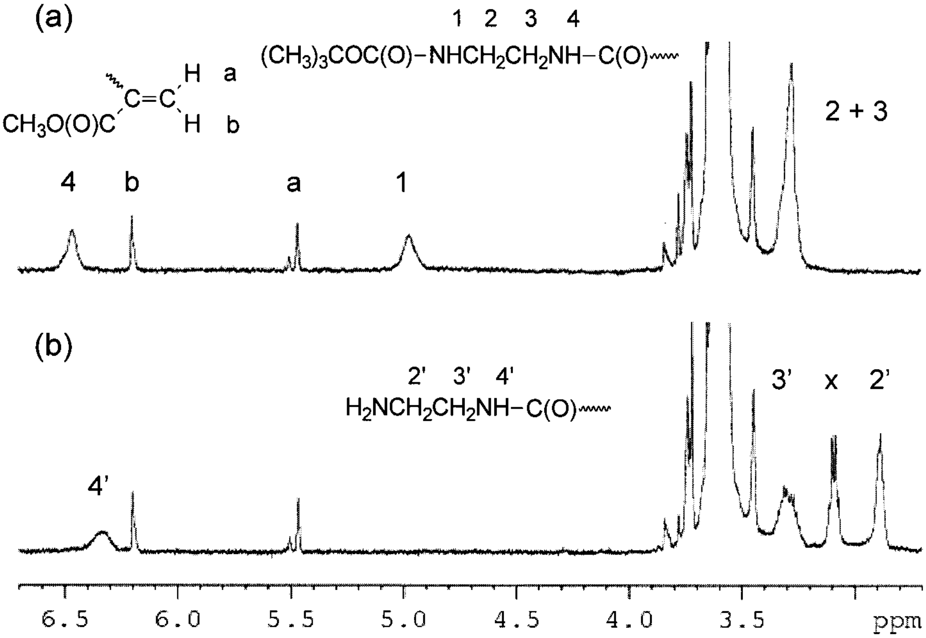


Fig. 3. ^{1}H NMR spectra of the protected (a) and deprotected (b) amino end-group functionalized PMMA; Region showing the signals of the R-NH-CH_2CH_2-NH-R' moiety and of the olefinic group formed by HBr elimination (x: CH_2 signal of Et_3N traces; truncated signal at ~ 3.6 ppm: OCH_3 group of PMMA).

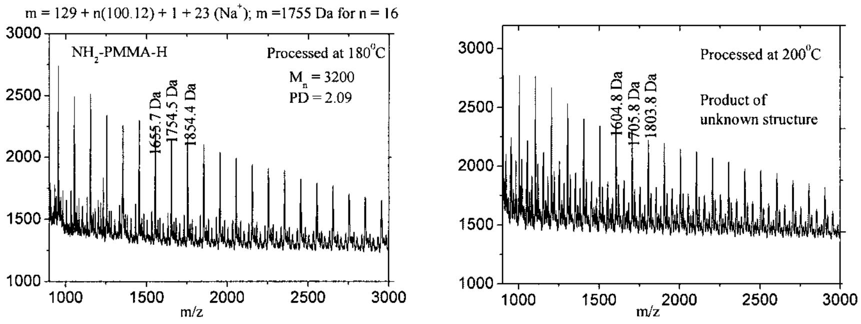


Fig. 4. MALDI TOF mass spectra of PMMA-NH_2 processed in a DACA Micro Compounder for 10 min. with 100 rpm at 180 °C (left) or 200 °C (right)

Conclusions

Atom transfer radical polymerization using the CuBr/PMDETA catalyst system and an initiator containing a protected amino functionality is a suitable technique to synthesize amino-functionalized PMMA devoid of halogen. However, the ATRP of MMA under these conditions proceeds in uncontrolled fashion. The initiator efficiency is smaller than 1, the number average molecular weight of the product higher than the theoretical one, and an untypical high polydispersity is observed, even under mild polymerization conditions. The reasons for this are different terminating reactions. While the bromine exchange with hydrogen results in the desired halogen free product, further side reactions occur as dehybromination and bimolecular radical termination.

However, the main product contains one amino end group and is free of halogen. During melt processing of the product at 180°C no structural changes could be observed, so that it can be used for reactive melt processing , e.g. in blends.

Acknowledgements

The authors are grateful to the Deutsche Forschungsgemeinschaft (Collaborative Research Centre 287) for the financial support, Mrs. P. Treppe for GPC measurements, and Mr. H. Kunath for technical assistance.

[1] K. Matyjaszewski, J.S. Wang, *Macromolecules* **1995**, 28, 7901.
[2] M. Kato, M. Kamigaito, M. Sawamato, T. Higashimura, *Macromolecules* **1995**, 28, 1721.
[3] H. Malz, H. Komber, D. Voigt, I. Hopfe, J. Pionteck, , *Macromol. Chem. Phys.* **1999**, 200, 642.
[4] V. Coessens, K. Matyjaszewski, *Macromol. Rapid Commun.* **1999**, 20, 66.
[5] F. Schön, M. Hartenstein, A.H.E. Müller, *Macromolecules* **2001**, 34, 5934.
[6] M. Bednarek, T. Biedron, P. Kubisa, Macromol. *Chem. Phys.* **2000,** 201, 58.
[7] C. Duan Vo, D. Kuckling, H.-J. P. Adler, M. Schönhoff, *Colloid Polym. Sci.* **2002**, 280, 400.
[8] J. Xia and K. Matyjaszewski, *Macromolecules* **1997**, 30, 7697.
[9] K. Matyjaszewski, J. L. Wang, T. Grimaud, D. A. Shipp, *Macromolecules* **1998**, 31, 1527.