Dehalogenation of polymers prepared by atom transfer radical polymerization

*Veerle Coessens, Krzysztof Matyjaszewski**

Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, PA 15213, USA; km3b+@andrew.cmu.edu.

(Received: August 24, 1998; revised: October 28, 1998)

SUMMARY: Polymers prepared by atom transfer radical polymerization (ATRP) have well-defined end groups, predetermined by the initiator used. A typical initiator is an alkyl halide from which the halogen is transferred to one chain end. To remove the halogen end group, dehalogenation with trialkyltin hydride has been used. Procedures for the removal of the polymer halogen end groups are described, one of them being a one-pot reaction where the dehalogenation of the polymer chain ends occurs immediately after polymerization.

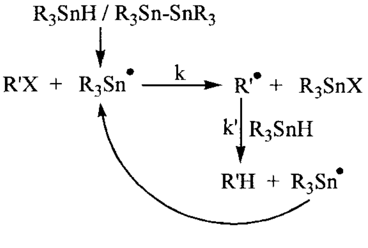
Introduction

Atom transfer radical polymerization (ATRP) is a controlled free radical polymerization process which enables the preparation of polymers with predictable molecular weights, low polydispersities ($\overline{M}_w/\overline{M}_n < 1.3$) and with well-defined functional end groups[1–4]. The use of initiators containing functional groups and the conversion of the halide end groups into other functional end groups has already been demonstrated in previous reports[2,5,6]. In this paper, the replacement of the halogen end group by a hydrogen is described.

The presence of halogen (end) groups in polymer chains may not be desirable, for example during the processing of the polymer. Therefore, an easy procedure to replace the halogen by hydrogen end groups is needed.

A wide range of procedures is available for conducting an organic halide hydrogenolysis, some of them proceeding via a free radical pathway[7–9]. Trialkyltin hydrides are common dehalogenation reagents which react with organic halides via a free radical chain mechanism (Scheme 1)[10]. The trialkyltin radical, generated by means of a radical initiator such as AIBN (2,2′-azobisisobutyronitrile) or by photolysis of distannanes, abstracts the halogen atom from the organic halide providing an organic radical. This radical reacts subsequently with a trialkyltin hydride with the formation of the reduced product and a new trialkyltin radical.

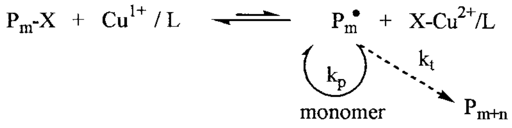
Scheme 1: Dehalogenation of an alkyl halide RX with tributyltin hydride



At 25 °C, the rate constant k for the reaction of an alkyl halide with the trialkyltin radical, is in the order of $k = 10^7\ \text{M}^{-1}\cdot\text{s}^{-1}$ for X = Br and about $k = 10^2\ \text{M}^{-1}\cdot\text{s}^{-1}$ for X = Cl. The hydrogen atom transfer from the tin hydride to the carbon radical is also very fast, $k' \approx 10^4–10^6\ \text{M}^{-1}\cdot\text{s}^{-1}$ at 25 °C[9,11,12]. At least one equivalent of tin hydride is required for complete hydrogenolysis.

Since ATRP is a 'living' radical polymerization process which uses an organometallic complex to establish an equilibrium between active and dormant chain ends, all chains are terminated by halogens (dormant species) but re-activation with the formation of a radical is possible (Scheme 2)[3,13]. Therefore, by adding at least one equivalent of trialkyltin hydride at the end of the polymerization reaction, it should be possible to convert all halogen chain ends into hydrogen end groups.

Scheme 2: Mechanism of ATRP



In order to investigate the feasibility of the dehalogenation reaction using a CuBr/ligand system as radical generator, model studies were performed. 1-Phenylethyl bromide, methyl 2-halopropionate and ethyl 2-bromoisobutyrate were used as model compounds for the end groups of respectively polystyrenes, polyacrylates and polymethacrylates. Afterwards, low molecular weight polymers with bromine and chlorine end groups were prepared and subsequently dehalogenated. The transformation of the end groups was observed using different analytical methods such as ^{1}H NMR, MALDI-TOF MS (matrix assisted laser desorption ionization, time of flight mass spectrometry) and ESIMS (electrospray ionization mass spectrometry).

1022-1336/99/0202–0066$17.50+.50/0

Experimental part

Materials

Methyl acrylate and methyl methacrylate were purified by distillation, styrene was filtered through alumina. Benzene was distilled from CaH_2, then degassed by bubbling nitrogen through. THF was distilled from Na/benzophenone. CuBr was purified by stirring in acetic acid, washing with methanol then drying. All other reagents, purchased from Aldrich or Acros, were used as received.

Analysis

GPC measurements were carried out using a Waters 510 liquid chromatography pump equipped with four Phenogel columns (100 Å, 1000 Å, linear and guard) in series with a Waters 410 differential refractometer. GPC was calibrated using linear polystyrene or poly(methyl methacrylate) standards. A 300 MHz Bruker NMR spectrometer was used for ^1H NMR analysis. MALDI-TOF MS spectra (in linear mode) were obtained using a PerSeptive Biosystems Voyager Elite instrument, equipped with a N_2 laser at 337 nm. Dithranol, 0.1 M in THF, doped with Na^+, was used as the matrix solution. ESIMS was conducted using a Finnegan LCQ, equipped with an octupole and an ion trap mass analyzer. Polymer solutions (10^{-4} M in methanol, doped with Na^+) were injected. The spray voltage was 0.02 kV, the capillary voltage 0.07 V.

Model studies

The model compounds 1-phenylethyl bromide, methyl 2-bromopropionate, methyl 2-chloropropionate or ethyl 2-bromoisobutyrate were dissolved in benzene (0.5 M) and CuBr/*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (1%) were added. Then, 1.1 equivalent of tributyltin hydride was added and samples were taken at regular time intervals. The dehalogenation reaction was followed by GC analysis.

Preparation of pMA-Br and subsequent hydrogenolysis

Method 1: Methyl acrylate (5 ml, 55.5 mmol), 2,2′-dipyridyl (bipy, 514 mg, 3.3 mmol), CuBr (15.7 mg, 1.1 mmol), methyl 2-bromopropionate (0.3 ml, 2.6 mmol) and ethylene carbonate (5 g) were stirred for 2 h at 90 °C. Then, tributyltin hydride (2.1 ml, 7.8 mmol) was added and the reaction was further stirred for 3 h at 90 °C. The polymer was purified by passing the reaction mixture through alumina and by repeated precipitation in hexane.

^1H NMR ($CDCl_3$): $\delta = 4.3$ (—C**H**(COOMe)—Br) has disappeared after dehydrogenation.

ESIMS: $m = 87 + n(86) + 1 + 23$ (Na).

Method 2: Methyl acrylate (5 ml, 55.5 mmol), CuBr (204 mg, 1.3 mmol), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (225 mg, 1.3 mmol) and methyl 2-bromopropionate (0.3 ml, 2.6 mmol) were stirred at 60 °C for 1 h. Afterwards, the polymer was purified by passing through alumina and precipitation in hexane.

Further hydrogenolysis:

a) pMA-Br, CuBr, *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine and tributyltin hydride were mixed in degassed benzene at a 1/0.5/0.5/3 ratio and the reaction mixture was stirred overnight at 60 °C. The polymer was purified as mentioned before.

b) pMA-Br, AIBN (2,2′-azobisisobutyronitrile) and tributyltin hydride were mixed in benzene at a 1/0.5/3 ratio and treated as mentioned above.

Preparation of pSty-Br and subsequent hydrogenolysis

Styrene (3 ml, 26 mmol), CuBr (0.111 g, 0.8 mmol), ethylbromobenzene (0.13 ml, 1 mmol) and *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (0.13 g, 0.8 mmol) were stirred for 3.5 h at 85 °C. Tributyltin hydride (0.8 ml, 3 mmol) and benzene (3 ml) were added and the reaction mixture was further stirred for 3 h. The polymer was purified by precipitation (3 ×) in methanol.

^1H NMR ($CDCl_3$): $\delta = 4.5$ (—C**H**(Ph)—Br) has disappeared after dehydrogenation. MALDI-TOF MS: $m = 105 + n(104) + 1 + 23$ (Na).

Preparation of pMMA-Br and subsequent hydrogenolysis

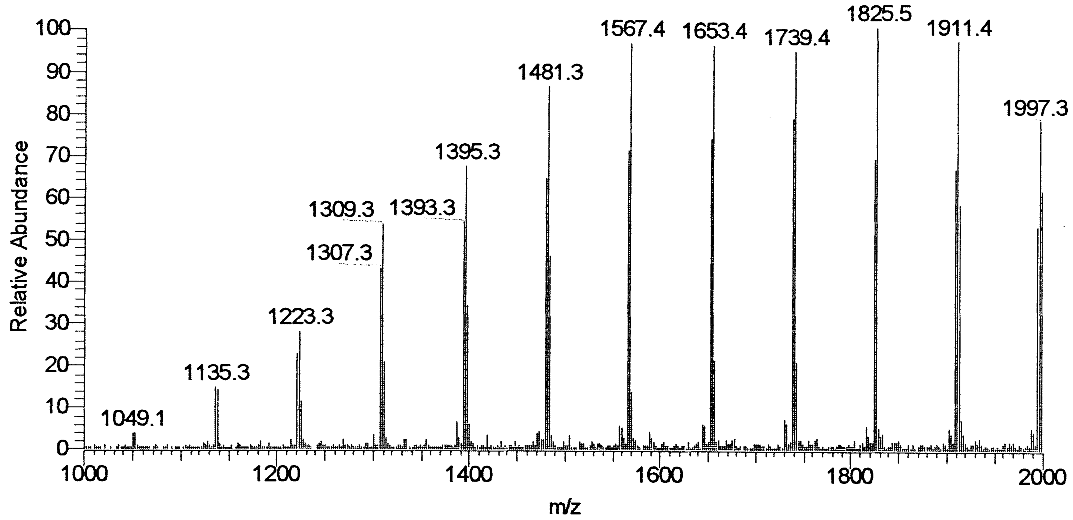
Methyl methacrylate (3 ml, 28 mmol), CuBr (0.1 g, 0.7 mmol), 2,2′-dipyridyl (0.33 g, 2.1 mmol), ethyl 2-bromoisobutyrate (0.2 ml, 1.4 mmol) and *p*-methoxybenzene (3 g) were stirred at 85 °C for 1.5 h. Then, tributyltin hydride (1.1 ml, 4.2 mmol) was added, the mixture was further stirred for 3 h and the polymer was purified by precipitation in hexane.

MALDI-TOF MS: $m = 101 + n(100) + 1 + 23$ (Na).

Results and discussion

The compounds 1-phenylethyl bromide, methyl 2-halopropionate and ethyl 2-bromoisobutyrate were used as end group models for respectively polystyrene, poly(methyl acrylate) and poly(methyl methacrylate). They were dissolved in degassed benzene (0.5 M solution) and reacted with 1.1 equivalent of tributyltin hydride at room temperature. As radical generator, a catalyst complex used in ATRP, CuBr/*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine, was used. Under these reaction conditions, GC analysis showed that the dehalogenation reaction was very fast. For 1-phenylethyl bromide, methyl 2-bromopropionate and ethyl 2-bromoisobutyrate, 80% of the bromine was replaced by hydrogen within less than 2 min. The reaction of methyl 2-chloropropionate proceeded significantly slower, 80% of the reaction being completed after 10 min. The apparent reaction rate constant was $1.56\ 10^{-2}\ \mathrm{M}^{-1}\cdot \mathrm{s}^{-1}$ at room temperature. The results of these model studies indicate that the dehydrogenation reaction proceeds fast and that only a slight excess of tributyltin hydride is needed.

In order to investigate the dehalogenation of polymer chains, halogen-terminated, low molecular weight poly-pMA-Br :



pMA-H :

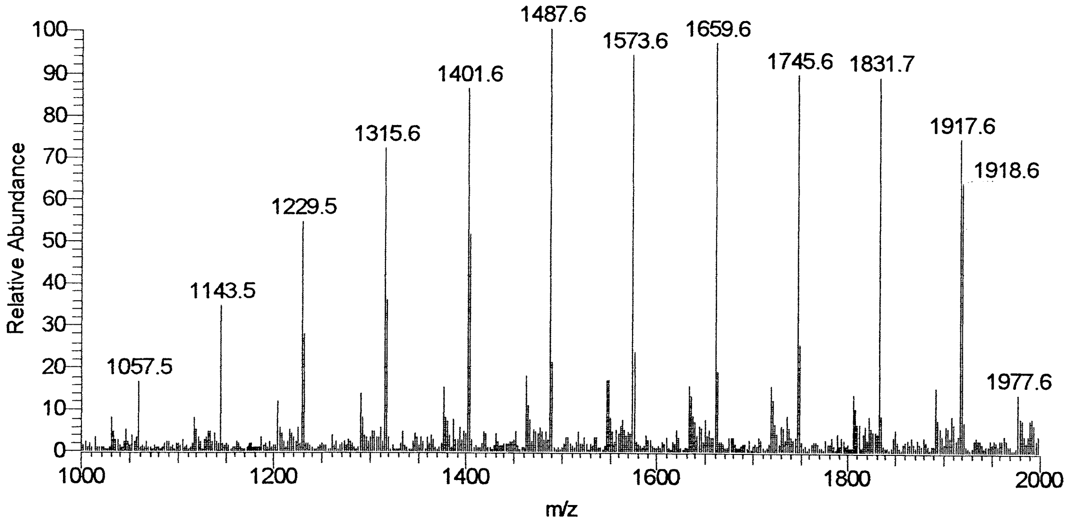
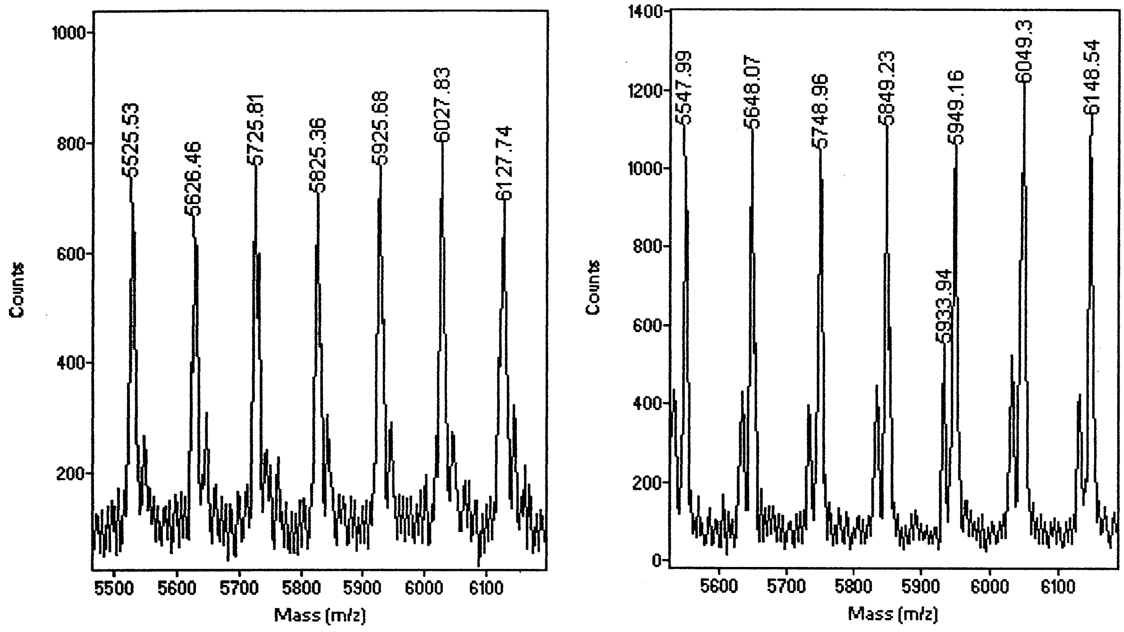


Fig. 1. ESIMS spectrum of respectively pMA-Br and pMA-H

mers were prepared by ATRP. Poly(methyl acrylate), polystyrene and poly(methyl methacrylate) were prepared under different experimental conditions, listed in Tab. 1.

The CuBr/ligand system as well as AIBN were used as radical generators in the dehalogenation reaction of purified pMA-Br (No. 2, Tab. 1). Under the experimental conditions, listed in Tab. 2, dehalogenation occurred completely, without the occurrence of any side reactions. The CuBr/ligand system and the chemical initiator AIBN are thus both suitable as radical source. Dehalogenation of the polymer chains should therefore be possible in a one-pot reaction, immediately after the polymerization.

In the first entry (No. 1, Tab. 1), pMA-Br was polymerized in ethylene carbonate at 90 °C and at about 95% conversion – after a sample was withdrawn from the reaction mixture – tributyltin hydride (3 eq. towards the end groups) was added. After stirring for 3 h under the same reaction conditions, the polymer was purified by precipitation (see Experimental part). When the ^{1}H NMR spectra of both polymer samples, before and after treatment with tributyltin hydride, were compared, it was observed that after the treatment, the peak at 4.3 ppm corresponding to —C**H**(COOMe)—Br had disappeared. As shown in Fig. 1, the ESIMS spectra show respectively pMA-Br (*m*



pMMA-Br **pMMA-H**

Fig. 2. MALDI-TOF MS spectrum of respectively pMMA-Br and pMMA-H

Tab. 1. Reaction conditions for the preparation of low molecular weight polymers by ATRP

No.	Polymer	Ratio CuX/ligand	Solvent	Temp. in °C	$\overline{M}_n$ [a]	$\overline{M}_w/\overline{M}_n$ [a]
1	pMA-Br	CuBr/bipy 1/3	ethylene carbonate	90	2100	1.2
2	pMA-Br	CuBr/L[b] 1/1	–	60	1680	1.1
3	pMA-Cl	CuCl/L 1/1	–	60	1460	1.2
4	pSty-Br	CuBr/L 1/1	–	85	2960	1.1
5	pMMA-Br	CuBr/bipy 1/3	*p*-methoxybenzene	85	9200	1.2

[a] Molecular weight and polydispersities determined by GPC.

[b] L = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine.

Tab. 2. Reaction conditions for the dehalogenation of purified pMA-Br (No. 2, Tab. 1)

Polymer	Radical source	Reducing agent	Solvent	Temp. in °C
pMA-Br	CuBr/l	Bu_3SnH	benzene	60
pMA-Br	AIBN	Bu_3SnH	benzene	60

= 87 + *n*(86) + 79/81 + 23) and pMA-H (with Na^+, major series or with H^+, minor series). Additional experiments showed that a smaller excess of tributyltin hydride (1.5 eq.) was sufficient to obtain complete dehalogenation within 1 h.

The presence of a solvent is important in order to mix the polymer with the tributyltin hydride. As demonstrated, the dehalogenation reaction can be conducted in solvents such as ethylene carbonate, benzene or *p*-methoxybenzene. In case the polymerization reaction was performed in bulk, benzene was added simultaneously with the tin hydride and the mixture was vigorously mixed.

Bromine end groups are more easily transformed than chlorine end groups, therefore, pMA-Cl was synthesized and treated with tin hydride. The ESIMS spectrum showed that dehalogenation was complete (≥95% dehalogenation) after 3 h reaction at 60 °C, as no peaks corresponding to pMA-Cl were observed.

The dehalogenation reaction is also useful for other polymers as demonstrated respectively with polystyrene (No. 4) and poly(methyl methacrylate) (No. 5, Tab. 1). In both cases, MALDI-TOF MS spectra showed the conversion of the bromine into hydrogen end groups. As an example, details of the MALDI-TOF MS spectra of pMMA-Br and pMMA-H are shown in Fig. 2. The peaks in the pMMA-Br spectrum correspond to $m = 115 + n(100) + 79/81 + 23$. The minor peaks are due to the loss of the bromine end group. The peaks in the pMMA-H spectrum correspond to $m = 115 + n(100) + 1 + 23$. The minor peaks, with mass 15 a.m.u. lower, apparently correspond to the loss of a methyl group, which could have been occurred during the MALDI process or during the functionalization process. For polystyrene, the dehalogenation observed in the MALDI-TOF MS spectra was supported by the ^1H NMR spectrum: the peak at 4.5 ppm corresponding to —**CH**(Ph)—Br disappeared completely.

Conclusion

From this work we can conclude that the dehalogenation of polymers, prepared by ATRP, occurred readily with tributyltin hydride in a one-pot reaction. It was demonstrated that for polystyrene, poly(methyl acrylate) and poly(methyl methacrylate) with bromine or chlorine end groups, the halogen end groups were replaced by hydrogen upon addition of a slight excess of tributyltin hydride at the end of the polymerization. Purified polymer was dehalogenated with tributyltin hydride in combination with the radical source, AIBN.

Acknowledgement: The authors wish to acknowledge the *Industrial Members of the ATRP Consortium at Carnegie Mellon University* and *the National Science Foundation* for the financial support of this research.

1) J. S. Wang, K. Matyjaszewski, *J. Am. Chem. Soc.* **117**, 5614 (1995)

2) K. Matyjaszewski, *Controlled Radical Polymerization, Vol. 685*, American Chemical Society, Washington, DC, San Francisco, CA 1997

3) K. Matyjaszewski, J. S. Wang, *Macromolecules* **28**, 7901 (1995)

4) M. Sawamoto, M. Kamigaito, *Trends Polym. Sci.* **4**, 371 (1996)

5) K. Matyjaszewski, V. Coessens, Y. Nakagawa, J. Xia, J. Qiu, S. Gaynor, S. Coca, C. Jasieczek, *ACS Symposium Series* 704, 16 (1998)

6) V. Coessens, Y. Nakagawa, K. Matyjaszewski, *Polym. Bull. (Berlin)* **40**, 135 (1998)

7) E. J. Corey, J. W. Suggs, *J. Org. Chem.* **40**, 1975 (1975)

8) A. R. Pinder, *Synthesis* 425 (1980)

9) J. T. Groves, S. Kittisopikul, *Tetrahedron Lett.* **49**, 4291 (1977)

10) D. P. Curran, *Synthesis* 417 (1988)

11) D. P. Curran, “Radical Addition Reactions”, in: *Comprehensive Organic Synthesis*, B. M. Trost, I. Fleming, Eds., Pergamon, New York 1992, p. 715

12) L. J. Johnston, J. Lusztyk, D. D. M. Wayner, A. N. Abeywickreyma, A. L. J. Beckwith, J. C. Scaiano, K. U. Ingold, *J. Am. Chem. Soc.* **107**, 4594 (1985)

13) T. E. Patten, J. Xia, T. Abernathy, K. Matyjaszewski, *Science* **272**, 866 (1996)