

Polymer Communication

Evidence for the low thermal stability of poly(methyl methacrylate) polymer produced by atom transfer radical polymerisation

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Abstract

NMR spectroscopy confirmed the existence of a C–Br bond at the terminal chain end of low molecular weight poly(methyl methacrylate) (PMMA) produced by atom transfer radical polymerisation (ATRP). Polymer was prepared using the heterogeneous Cu(I)Br/2,2'-bipyridine (bpy) catalyst with ethyl-2-bromoisobutyrate used as the initiator. This structural feature was not evident in the matrix-assisted laser desorption/ionisation-time of flight (MALDI-TOF) mass spectrometry spectrum of the same polymer sample. The mass-to-charge ratios of the molecule ion peaks corresponded to a loss of methyl bromide (MeBr) from one chain end and concomitant cyclisation to give a lactone end group. Further information was obtained by means of matrix-assisted laser desorption/ionisation-collision induced dissociation (MALDI-CID) mass spectrometry. These spectra showed fragmentation patterns that were consistent with that shown previously for other alkyl methacrylate polymers. Evolved gas analysis detected the presence of MeBr in the volatiles collected when the polymer was heated from ambient temperature to 150°C. Furthermore, samples of PMMA, which had been previously heated to 150°C under an atmosphere of dinitrogen, were analysed by ¹³C NMR. Spectra were similar to the samples that had not been heated apart from a complete loss of the C–Br resonance at δ58 ppm and the appearance of other signals consistent with lactone formation. This was taken as evidence that PMMA terminated by a Br atom in this way, will undergo a thermal decomposition at ~150°C that is similar to that observed in the MALDI experiments. © 2000 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Atom transfer radical polymerisation; Poly(methyl methacrylate); Matrix-assisted laser desorption/ionisation-time of flight

1. Introduction

Atom transfer radical polymerisation (ATRP) is one of the most promising recent advances in the search for a commercially viable process that allows chemists to produce advanced designer polymers to order [1,2]. First reported by Sawamoto and co-workers in 1995 [3], a typical reaction makes use of an activated halide initiator (e.g. ethyl-2-bromoisobutyrate or trichlorobromomethane) with a copper(I)bromide catalyst complexed by 2,2'-bipyridine (bpy) or one of its derivatives [4]. Haddleton et al. have, more recently, employed catalysts based on 2-pyridinecarbaldehyde imines [5]. The now generally accepted representation of a classical ATRP reaction is depicted in Fig. 1. Originally developed using styrene [6,7], ATRP has now been successfully applied to a range of vinylic monomers

including alkyl methacrylates such as methyl methacrylate (MMA) [8] and *n*-butyl methacrylate (*n*-BMA) [9].

The Cu(bpy)₂ complex is central to the polymerisation mechanism and contains ligands in a cisoid conformation [10]. The π* orbitals on these ligands can accept electron density from the metal centre thus stabilising low oxidation states, in this case Cu(I). Abstraction of a bromine atom (Br[•]) from the alkyl halide initiator results in the formation of a proposed penta co-ordinated species, with the associated oxidation of Cu(I) to Cu(II) [10]. In this form, the two bpy ligands rotate to generate a distorted square based pyramidal geometry at the Cu(II) centre. The proposed mechanism of ATRP involves rapid shuttling of the Br[•] moiety between the copper complex and the growing polymer chain end. Propagation occurs when the Br[•] is resident on the Cu complex and the growing polymer chain end exists as a free radical. It has been observed that the polymerisation rate is faster when bromine is the leaving group rather than chlorine [8,11]. This has been attributed to the relative bond strength of the C–Br and C–Cl bonds. The greater lability of the C–Br bond results

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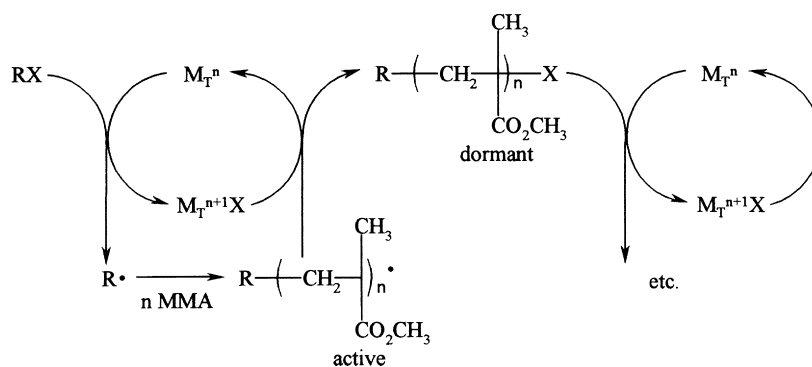


Fig. 1. A representation of the classical ATRP reaction scheme.

in the Br' spending a greater length of time with the Cu complex, which in turn results in a greater availability of the polymer chain end radical to attacking monomer. Both Cl and Br ended polymers give rise to a polymerisation process that exhibits many features of "living" polymerisation [12]. Recent characterisation of chain end structure by NMR has confirmed the presence of a C–Br bond [5], which has important consequences on the stability of PMMA produced by ATRP.

Matrix-assisted laser desorption/ionisation (MALDI) mass spectrometry has been shown to be a powerful technique for the determination of end groups for PMMA polymers [13]. It has been known for some time that the combined mass of both end groups of a linear polymer can be calculated from matrix-assisted laser desorption/ionisation-time of flight (MALDI-TOF) data. It has more recently been shown, however, that the masses of the individual end groups may be measured from matrix-assisted laser desorption/ionisation-collision induced dissociation (MALDI-CID) data from alkyl methacrylate polymers [14,15].

In this paper, we describe a chain end dissociation reaction in PMMA oligomers produced by ATRP that has not been reported previously. Samples of low molecular weight PMMA characterised by MALDI-TOF and MALDI-CID gave spectra consistent with loss of methyl bromide (MeBr) followed by a cyclisation reaction to give a lactone end group. Evolved gas analysis detected the loss of MeBr when the same samples were heated from ambient temperature to 150°C, confirming the low thermal stability of the terminal C–Br bond. ¹³C NMR spectra of samples of PMMA, which had been previously heated to 150°C, showed a complete loss of the terminal C–Br resonance as well as the appearance of other signals consistent with lactone formation.

2. Experimental

2.1. Polymer synthesis

MMA (ICI Acrylics) was further purified using a 4 Å

molecular sieve column under dry dinitrogen. Anhydrous ethyl acetate, copper(I)bromide, ethyl-2-bromoisobutyrate and 2,2'-bipyridine (all Aldrich) were used without further purification. All polymerisations were performed using a Schlenk line and glassware that had been dried overnight in a glass drying cabinet (Gallenkamp) at ~180°C. In a typical reaction Cu(I)Br and bpy were introduced to a 100 ml round-bottomed flask fitted with a sidearm condenser and oxygen removed by three successive vacuum–dinitrogen purges. Ethyl acetate and MMA were then added using dry glass Gastight syringes. The resultant mixture was then heated with stirring to 90°C before addition of initiator via a glass Hamilton syringe. Typical reactant concentrations were as follows; [MMA]₀ = 4.67 M, [EtOAc]₀ = 5.12 M, [Cu(I)Br]₀ = 23.9 mM, [bpy]₀ = 71.6 mM and [ethyl-2-bromoisobutyrate]₀ = 95.4 mM (i.e. [Cu(I)Br]₀: [bpy]₀: [initiator]₀ = 1:3:4).

Purification of PMMA produced in this way was achieved by resuspension of the reaction mixture in THF (Fisher) followed by filtration through a small column of alumina (activated, Brockmann I, 58 Å, Aldrich) and finally precipitation into a 10-fold excess of hexane (Fisher). The alumina filtration step was necessary to remove Cu down to "acceptable limits".² Conversion was determined gravimetrically after the polymer had been dried in a vacuum oven (Gallenkamp) at 80°C for 3 h.

2.2. Analytical methods

Molecular weight distributions were generated in chloroform (Aldrich) at 30°C using a Knauer gel permeation chromatograph fitted with mixed gel columns (2 × 10 μm, Polymer Laboratories) and a Miran 1FF infra-red detector. Calibration was made with PMMA standards (Polymer Laboratories). ¹³C- and ¹H-NMR spectra were run in CDCl₃ (Cambridge Isotope Laboratories, Inc.) at 25°C on a JEOL GSX400 instrument. The time-lag focusing MALDI data were obtained using a TofSpec 2E (Micromass,

² XRF data showed the Cu content of PMMA after filtration through a short column of alumina to be <20 ppm.

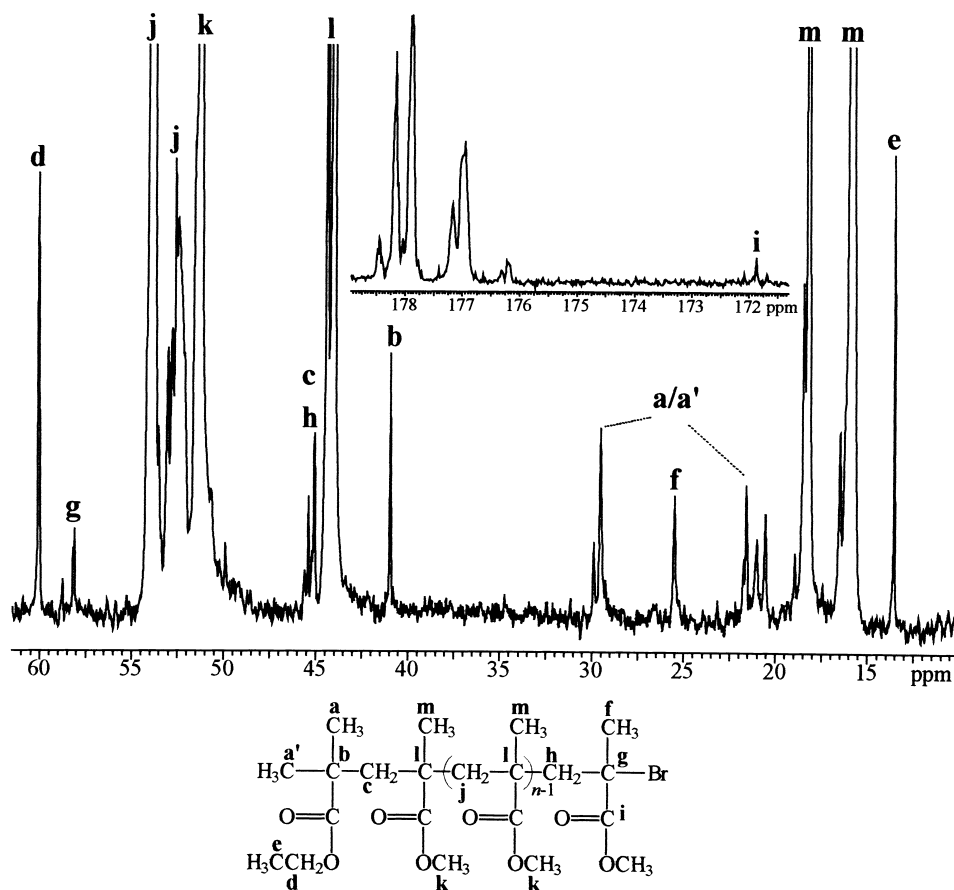


Fig. 2. ^{13}C NMR spectrum of low molecular weight PMMA ($M_n = 3200$) produced by ATRP. Important resonances are indicated, showing their assignment assuming an oligomeric structure as in **1**, Fig. 3.

Manchester, UK) MALDI-TOF mass spectrometer, operated at an accelerating voltage 20 kV in the reflectron mode of operation. MALDI-CID experiments were performed in an AutoSpec 5000 orthogonal acceleration (oa)-TOF (Micromass) tandem mass spectrometer equipped with a MALDI source. This hybrid sector-oa-TOF instrument and the sample preparation conditions have been described in more detail elsewhere [14,15]. Evolved gas analysis was performed in a 7070EHF (Micromass) GC-MS instrument fitted with an Envirochem 810A purge and trap.

3. Results and discussion

3.1. Molecular characterisation

Low molecular weight PMMA was produced by ATRP using the system detailed in Section 2. Samples at three different molecular weights were prepared aiming for theoretical values ($M_{n,\text{th}}$) of 2000, 3000 and 7000. GPC analysis of these samples showed their actual values M_n to be 2300 (1.3), 3200 (1.2) and 7100 (1.3), respectively; polydispersities (M_w/M_n) are shown in brackets.

3.2. NMR analysis

The ^{13}C NMR spectra obtained for all three samples confirmed the existence of a C–Br bond at the terminal chain end. A typical spectrum is given in Fig. 2, where the important resonances have been assigned. The full structure of the oligomer is shown graphically as **1** in Fig. 3. These assignments are shown to be in agreement with that reported previously [5]. Additionally, small resonances in the region $\delta 35\text{--}50$ ppm, indicated that a very low number of chain ends were terminated with a C–H bond instead of the normal C–Br. ^1H NMR experiments on the same polymers detected low levels of a vinylidene end group, indicating that oligomers of the form depicted in **2** in Fig. 3 are also present. Spectra showed that there were 0.06 vinylidene end groups per 100 polymerised MMA units. Assuming an oligomeric structure, as in **1**, Fig. 3, the molecular weight (M_n) of the polymer samples could be estimated from the relative intensity of the two different alkyl ester resonances. The two signals in question are those arising from alkyl protons in the CH_3OCO moiety in the repeat unit and the $\text{CH}_3\text{CH}_2\text{OCO}$ group in the initial unit of the chain. The number average molecular weight (M_n) was then calculated

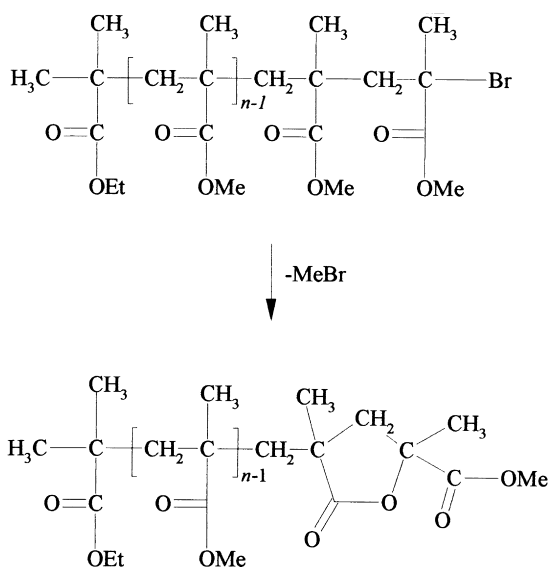


Fig. 5. Proposed reaction scheme for the dissociation observed during MALDI experiments and when polymer was heated to 150°C.

from $[1 + \text{Na}]^+$, would be seen in the MALDI-TOF spectra (sodium ions are typically the cationisation agent in the MALDI-TOF experiment). No peaks, corresponding to **1**, were observed. It has recently been shown, however, that molecule ions are not always observed in the MALDI-TOF spectra from PMMA polymers, which have chlorinated end groups [16]. In contrast to this observation, it was noted that the expected ion peaks were in fact observed in the MALDI-TOF spectrum if the same polymer was derivatised so that no chlorine atoms were present. This suggests that the presence of a terminal Cl atom may affect fragmentation of these polymers in the MALDI instrument.

In the case of the Br-terminated polymer, an intense series of ion peaks were seen in the MALDI-TOF spectra, that did not correspond to those expected from the NMR data. PMMA with a terminal C–Cl was also looked at and the findings will be reported in a subsequent paper [17]. These peaks had mass-to-charge ratios that were equivalent to the oligomeric species **1** having lost methyl bromide, to possibly form oligomers with structure **3**, Fig. 3. To gain more information on the fragmentation mechanism of the oligomers, MALDI-CID spectra were recorded. This technique has previously been shown to provide information on the masses of individual end groups of PMMA oligomers [14]. Fig. 4(a) shows a typical MALDI-CID fragmentation spectrum from the $[3 + \text{Na}]^+$ ion, where n is 19. The intense series of ion peaks seen in the spectra at low mass-to-charge ratios (m/z 100–600), labelled **A** and **B**, were used to infer end group information. Fig. 4(b) shows the proposed fragmentation pathways to generate the **A** and **B** series of ions. The mass-to-charge ratios of these fragment ion peaks were consistent with a loss of MeBr followed by cyclisation of the final two monomer repeat units to give a lactone end group. Matyjaszewski et al. [18–21] have already reported

on HBr loss in MALDI-MS of poly(acrylates) produced by ATRP. Fragmentation patterns from the polymer backbone and chain ends were similar to that reported previously for other alkyl methacrylate polymers [15]. The full structure of the oligomeric species, proposed from the MALDI-TOF and MALDI-CID data, is **3**. Further investigation into the exact mechanism of lactone ring formation is needed and is part of an ongoing investigation in our laboratory.

3.4. Evolved gas analysis

Evolved gas analysis identified MeBr as one of the components present in the volatiles collected when the polymer was heated from ambient temperature to 150°C. Other species present in significant quantities were unreacted monomer and solvent (hexane) used in purification. Thus it would seem that the dissociation observed in the MALDI source can also occur by a thermal pathway. Further evidence to support this belief was obtained from ^{13}C NMR analysis of PMMA samples that were heated to 150°C under an atmosphere of dinitrogen. Polymer, in the solid phase, was heated to this temperature and held there for 15 min before being cooled back to room temperature. The ^{13}C NMR spectra of these samples showed a complete disappearance of the C–Br peak at $\delta 58$ ppm (peak g in Fig. 2). Furthermore two new sets of signals appeared in the region $\delta 172$ –173 and $\delta 179$ –180 which were assigned to the two carbonyls present in the lactone end group in **3**. It seems most likely, from the evidence presented here, that the reaction proceeds via loss of MeBr and cyclisation of the chain end, giving rise to the observed lactone ring (see Fig. 5).

4. Conclusion

In this paper, we report the unexpected dissociation reaction involving the chain end of PMMA oligomers produced by ATRP, during MALDI analysis. Data are consistent with dissociation, to form MeBr, preceding a cyclisation of the terminal two repeat units of the polymer chain, giving rise to a lactone end group. Support for this hypothesis comes from evolved gas analysis and ^{13}C NMR, which confirm the loss of methyl bromide and ring formation when polymer samples are heated from ambient temperature to 150°C. This would seem to be inconsistent with the observations of Moineau et al. [22], where PMMA produced by a Ni based ATRP system with a high thermal stability is reported. It is, however, worth pointing out that the authors do comment on a small weight loss at 250°C during isothermal experiments.

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