

# High fidelity vinyl terminated polymers by combining RAFT and cobalt catalytic chain transfer (CCT) polymerization methods†

Alexander H. Soeriyadi,<sup>a</sup> Cyrille Boyer,<sup>\*a</sup> James Burns,<sup>b</sup> C. Remzi Becer,<sup>b</sup> Michael R. Whittaker,<sup>a</sup> David M. Haddleton<sup>b</sup> and Thomas P. Davis<sup>\*a</sup>

Received 2nd June 2010, Accepted 8th July 2010

DOI: 10.1039/c0cc01694b

This document is shared for only research purposes and cannot be distributed without the permission of the authors and the publisher. Please visit [WWW.BECERGROUP.SEMS.QMUL.AC.UK/PUBLICATIONS.HTML](http://WWW.BECERGROUP.SEMS.QMUL.AC.UK/PUBLICATIONS.HTML) to get more info on our research interests!!!

In this work, we combine reversible addition fragmentation transfer polymerization (RAFT) with cobalt catalytic chain transfer (CCT) to obtain  $\omega$ -unsaturated polymers with relatively low polydispersity values.

Reversible addition fragmentation polymerization (RAFT) is a powerful approach to the synthesis of polymers with excellent control of architecture and end-groups.<sup>1</sup> RAFT has been applied to the syntheses of complex architectures, such as star,<sup>2</sup> hyper-branched polymers,<sup>3</sup> protein–polymer conjugates<sup>4</sup> and hybrid organic/inorganic nanoparticles.<sup>5</sup> The presence of RAFT end-groups can sometimes be problematic for specific applications as they can undergo degradation by aminolysis,<sup>6</sup> hydrolysis or thermolysis.<sup>7</sup> In addition, RAFT end-groups can exacerbate cytotoxicity in bio-applications.<sup>8</sup> In order to expand the utility of RAFT, researchers have described techniques to remove this end-group source of instability introducing a functional group, yielding monofunctional<sup>6b</sup> and telechelic polymers.<sup>8b,9</sup>

RAFT end-group removal strategies include a radical addition (from excess initiator) to remove the end-group, regenerating the RAFT agent, concurrently functionalizing the polymers (if a functional initiator is used).<sup>10</sup> Other strategies describe cleavage of the RAFT functionality by aminolysis or reduction to yield a thiol.<sup>6a</sup> The strong nucleophilic character of thiol can then be exploited for subsequent thiol–ene addition,<sup>11</sup> (Michael mechanism), thiol–bromo<sup>3a</sup> or thiol–isocyanate reactions<sup>12</sup> to introduce a new functional end. Alternatively, the radical addition of thiol onto an activated ene can be performed.<sup>11</sup> Finally, RAFT end-groups can be removed by a radical induced reduction in the presence of tributylstannane.<sup>13</sup>

In this communication, we present a straightforward method for the synthesis of vinylic terminated polymers obtained by RAFT polymerization by exploiting catalytic chain transfer polymerization (CCT). CCT, using the complex, (CH<sub>3</sub>OH)<sub>2</sub>Co–(dmgBF<sub>2</sub>)<sub>2</sub> (CoBF, presented in Scheme S1, ESI†), as a catalyst, is a powerful polymerization technique, nascent in the 1980s,<sup>14</sup> able to control the molecular weight and end-group functionality of polymers. CCTP has been reported for the polymerization of methacrylic and styrenic

monomer families resulting in the synthesis of macromonomers with excellent end-group control, suitable for further copolymerization reactions,<sup>15</sup> addition–fragmentation modification<sup>16</sup> or thiol–ene modification.<sup>11b</sup> In the present communication, the modification of polymer obtained by RAFT polymerization using CCT catalyst is reported *via* the removal of RAFT end-groups yielding vinylic endgroups.

The syntheses of both poly(methyl methacrylate), PMMA, and poly(*n*-butyl methacrylate), PBMA, were performed using 2,2′-azobisisobutyrate (AIBN) as initiator and 2-(2-cyano-propyl)dithiobenzoate (**1**) or 4-cyanopentanoic acid dithiobenzoate as chain transfer agents (**2**) at 80 °C in bulk. After 90 min (conversion approximately 70%), the final solution was divided into two fractions. The first fraction was precipitated in petroleum ether to yield a pink powder characteristic of polymer synthesized by RAFT polymerization using a dithioester agent. This fraction was analyzed using both NMR and GPC, revealing polymers with narrow polydispersities, and experimental molecular weights in accord with theoretical values (as shown in Table S1, ESI†). <sup>1</sup>H NMR data (Fig. 1A) confirmed the presence of RAFT agent end-groups by signals at 7.2–7.8 ppm and at 2.5 ppm from the Z and R groups, respectively.

The second fraction was subjected to a further CCT reaction; CoBF solution was added directly to the polymerization mixture under nitrogen and the mixture was allowed to react for three hours (Scheme 1). Two different [RAFT]<sub>0</sub>/[CoBF]<sub>0</sub> ratios were tested 2000 and 80 000 (Table S1, ESI†). After 14 h, the polymer was isolated by several precipitations to yield a colorless powder. The absence of pink color was indicative of RAFT end-group removal as confirmed by UV-visible spectrophotometry. The C=S group presents a very strong absorption at around 305 nm. Fig. S1 (ESI†) shows the UV-vis spectra before and after reaction with CoBF for PMMA and PBMA. A similar result was observed for both concentrations of CoBF implying that the concentration of CoBF required for the end-group modification is at the ppm level (or catalytic amount). The loss of RAFT end-groups can be attributed to either a radical addition of the initiator or by a transfer reaction caused by CoBF. The transfer constant of methacrylates to CCT agent is extremely large (leading to some suggestions of a diffusion controlled reaction), C<sub>s</sub> ≈ 20 000.<sup>14d</sup> In contrast, the transfer reaction to RAFT agent is governed by a transfer constant of around 50.<sup>17</sup> This difference between the transfer constants permits the use of catalytic quantities of CoBF.

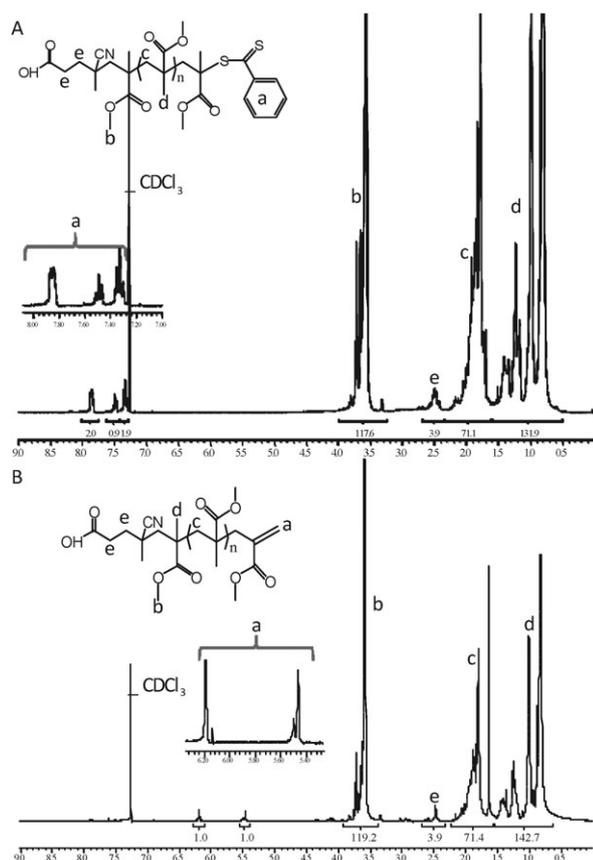
After successful transfer to CoBF, vinylic bonds should be observed using NMR. <sup>1</sup>H NMR analysis of PMMA oligomer

<sup>a</sup> Centre for Advanced Macromolecular Design (CAMD), School of Chemical Engineering, The University of New South Wales, Sydney, NSW 2052, Australia.

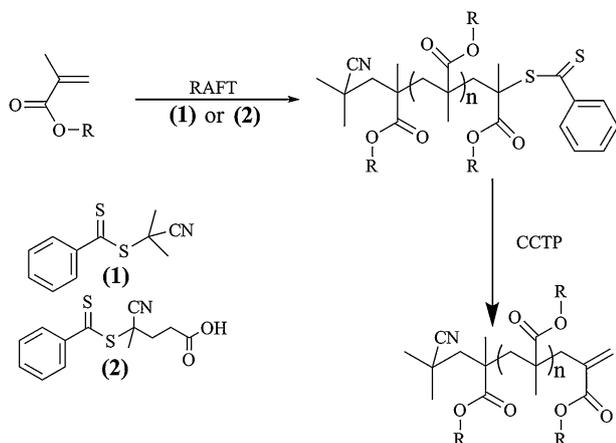
E-mail: cboyer@unsw.edu.au, t.davis@unsw.edu.au

<sup>b</sup> Department of Chemistry, University of Warwick, Coventry, CV4 7AL, UK

† Electronic supplementary information (ESI) available: UV-vis, NMR, MALDI-TOF and ESI spectra, GPC traces, experimental part. See DOI: 10.1039/c0cc01694b



**Fig. 1**  $^1\text{H}$  NMR spectra of PMMA: (A) terminated by RAFT agent (before addition of CoBF) ( $M_{n,\text{NMR}} = 4200 \text{ g mol}^{-1}$ ), and (B) after reaction with CoBF ( $M_{n,\text{NMR}} = 4050 \text{ g mol}^{-1}$ ), recorded in  $\text{CDCl}_3$ , purified by several precipitations (at least 5 times) in petroleum ether.



**Scheme 1** Chemical modification of RAFT end-group using CCTP polymerization (CoBF as catalyst), with  $\text{R} = -\text{OCH}_3$  or  $-\text{O}(\text{CH}_2)_3\text{CH}_3$ .

(with a molecular weight lower than  $4300 \text{ g mol}^{-1}$ ) was carried out before and after addition of CoBF (see Fig. 1 and Fig. S2, ESI $^\dagger$ ). After addition of CoBF and careful purification by multiple precipitations, RAFT end-group signals (Z group) were absent, and new signals at 5.46 and 6.19 ppm attributed to methacrylic double bond were observed. It is noteworthy that the signals from the vinyl-terminated polymer are slightly different from the signals corresponding to monomer

(5.50 and 6.05 ppm), proving that the signals do not emanate from residual trace of monomer. In addition, the molecular weights calculated by  $^1\text{H}$  NMR before (using RAFT end-group as a reference signal) and after modification (using the vinylic group as a reference) were in agreement (Table S1, ESI $^\dagger$ ). Thus, after the addition of CoBF in solution minimal polymerization occurred (less than 5%) in accord with the monomer conversion determined by  $^1\text{H}$  NMR. Low monomer conversion was ensured by using relatively high CoBF concentrations (the concentration used was consistent with dimer/trimer synthesis in a conventional CCT polymerization—as we confirmed in a separate control experiment, data not shown). The GPC traces (Fig. S3, ESI $^\dagger$ ) were consistent with minimal chain growth in the CCT phase of the experiment and verified the absence of any new low molecular weight material. No significant change in the polydispersity index ( $< 1.2$ ) was observed.

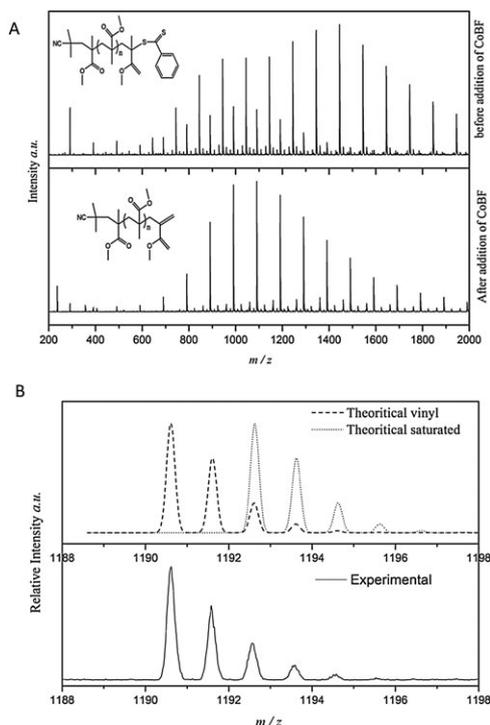
Moreover, in order to further investigate the removal of the thio-carbonyl thio end group from RAFT, further GPC analysis was done using a UV detector. The GPC traces (Fig. S4, ESI $^\dagger$ ) were used to compare the responses of PMMA and PBMA containing RAFT end groups with the polymers after RAFT end group modification with addition of CoBF. It can be seen clearly that the GPC traces of RAFT-polymers show significant responses on the UV detector ( $\lambda = 305 \text{ nm}$  due to the absorbance peak for thio-carbonyl thio). In contrast, after the addition of CoBF, it is interesting to note the absence of signal on the UV detector confirming the effective removal of the RAFT end group.

Finally, the efficiency of the reaction was evaluated using ESI-MS analysis on a short oligomer of PMMA (Fig. 2A and Fig. S5, ESI $^\dagger$ ). Before modification, ESI-MS revealed the presence of different populations. The major population corresponds to RAFT terminated PMMA, while the minor populations can be attributed to the fragmentation (degradation) of RAFT end-groups during the analysis or some species that is the product of the polymerization (as has been reported earlier).<sup>18</sup> After reaction with CoBF, a new population of chains attributable to the vinyl terminated PMMA was observed by ESI-MS (Fig. 2B).

Moreover, in order to increase our confidence that the resulting polymers were only terminated by a vinyl end group and not constituted by a mixture of saturated and unsaturated species due to the proximity of the peaks, a simulation is provided in Fig. 2B. By comparing the theoretical and experimental mass spectra, we can prove the absence of saturated compound. Furthermore, we also carried out MALDI-TOF analysis (Fig. S7, ESI $^\dagger$ ) of macromers obtained *via* polymerization run #4 to test for the presence of higher molecular weight species. MALDI-TOF analysis also gave data consistent with NMR, UV-visible and ESI-MS spectra. Similar results were obtained for PBMA.

We subsequently carried out copolymerizations of both PMMA and PBMA macromonomers with ethyl acrylate (EA) using toluene as a solvent under standard free radical polymerization conditions to yield a graft poly(EA-g-MMA).

A successful copolymerization was evidenced using GPC data, Fig. S6 (ESI $^\dagger$ ). The initial peak originating from the macromonomer shifted from low molecular weight to high



**Fig. 2** (A) ESI-MS spectra PMMA ( $M_n = 1000 \text{ g mol}^{-1}$ , run #1 of Table S2, ESI<sup>†</sup>) before (above) and after (below) addition of  $\text{CoBF}_4$ ; (B) comparison between vinyl/saturated theoretical and experimental spectra for  $\text{DP}_n = 11$ .

molecular weight after copolymerization. We estimated (using GPC data) that all the PBMA macromonomer was consumed, while 5% of un-reacted PMMA macromonomer was observed at the end of the copolymerizations.

In this communication, we have presented a straightforward method to transform RAFT end-groups into vinyl groups for PMMA and PBMA. The macromonomers, thus obtained, were successfully copolymerized with ethyl acrylate to yield graft copolymers. Further work using this approach, *i.e.* the combination of RAFT and CCT polymerization, is under investigation to prepare well-defined telechelic polymers, block and graft copolymers.

## Notes and references

- (a) G. Moad, E. Rizzardo and S. H. Thang, *Aust. J. Chem.*, 2006, **59**, 669–692; (b) H. Willcock and R. K. O'Reilly, *Polym. Chem.*, 2010, **1**, 149–157.
- E. Setijadi, L. Tao, J. Liu, Z. Jia, C. Boyer and T. P. Davis, *Biomacromolecules*, 2009, **10**, 2699–2707.

- (a) J. Xu, L. Tao, C. Boyer, A. B. Lowe and T. P. Davis, *Macromolecules*, 2010, **43**, 20–24; (b) A. P. Vogt, S. R. Gondi and B. S. Sumerlin, *Aust. J. Chem.*, 2007, **60**, 396–399.
- (a) C. Boyer, V. Bulmus, T. P. Davis, V. Ladmiraal, J. Liu and S. Perrier, *Chem. Rev.*, 2009, **109**, 5402–5436; (b) K. L. Heredia, G. N. Grover, L. Tao and H. D. Maynard, *Macromolecules*, 2009, **42**, 2360–2367; (c) P. De, M. Li, S. R. Gondi and B. S. Sumerlin, *J. Am. Chem. Soc.*, 2008, **130**, 11288–11289.
- (a) A. B. Lowe, B. S. Sumerlin, M. S. Donovan and C. L. McCormick, *J. Am. Chem. Soc.*, 2002, **124**, 11562–11563; (b) C. Boyer, V. Bulmus, P. Priyanto, W. Y. Teoh, R. Amal and T. P. Davis, *J. Mater. Chem.*, 2009, **19**, 111–123.
- (a) D. L. Patton, M. Mullings, T. Fulghum and R. C. Advincula, *Macromolecules*, 2005, **38**, 8597–8602; (b) X.-P. Qiu and F. M. Winnik, *Macromol. Rapid Commun.*, 2006, **27**, 1648–1653; (c) J. Xu, J. He, D. Fan, X. Wang and Y. Yang, *Macromolecules*, 2006, **39**, 8616–8624.
- A. Postma, G. Moad, M. S. O'Shea and T. P. Davis, *Macromolecules*, 2005, **38**, 5371–5374.
- (a) D. Pissuwan, C. Boyer, K. Gunasekaran, T. P. Davis and V. Bulmus, *Biomacromolecules*, 2010, **11**, 412–420; (b) C.-W. Chang, E. Bays, L. Tao, S. N. S. Alconcel and H. D. Maynard, *Chem. Commun.*, 2009, 3580–3582.
- (a) P. J. Roth, F. D. Jochum, R. Zentel and P. Theato, *Biomacromolecules*, 2010, **11**, 238–244; (b) C. Boyer, J. Liu, V. Bulmus, T. P. Davis, C. Barner-Kowollik and M. H. Stenzel, *Macromolecules*, 2008, **41**, 5641–5650; (c) B. Boutevin, G. David and C. Boyer, *Adv. Polym. Sci.*, 2007, **206**, 31–135.
- (a) S. Perrier, P. Takolpuckdee and C. A. Mars, *Macromolecules*, 2005, **38**, 2033–2036; (b) M. Chen, G. Moad and E. Rizzardo, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 6704–6714.
- (a) A. B. Lowe, *Polym. Chem.*, 2010, **1**, 17–36; (b) G.-Z. Li, R. K. Randev, A. H. Soeriyadi, G. Rees, C. Boyer, Z. Tong, T. P. Davis, C. R. Becer and D. M. Haddleton, *Polym. Chem.*, 2010, DOI: 10.1039/c0py00100g; (c) C. Boyer, V. Bulmus and T. P. Davis, *Macromol. Rapid Commun.*, 2009, **30**, 493–497; (d) C. Boyer and T. P. Davis, *Chem. Commun.*, 2009, 6029–6031.
- H. Li, B. Yu, H. Matsushima, C. E. Hoyle and A. B. Lowe, *Macromolecules*, 2009, **42**, 6537–6542.
- Y. K. Chong, G. Moad, E. Rizzardo and S. Thang, *Macromolecules*, 2007, **40**, 4446–4455.
- (a) A. Gridnev, *J. Polym. Sci., Part A: Polym. Chem.*, 2000, **38**, 1753–1766; (b) J. P. A. Heuts, G. E. Roberts and J. D. Biasutti, *Aust. J. Chem.*, 2002, **55**, 381–398; (c) T. P. Davis, D. M. Haddleton and S. N. Richards, *Macromol. Chem. Phys.*, 1994, **34**, 243–324; (d) T. P. Davis, D. Kukulj, D. M. Haddleton and D. R. Maloney, *Trends Polym. Sci.*, 1995, **3**, 365–373.
- (a) J. Chiefari, J. Jeffery, J. Krstina, C. L. Moad, G. Moad, A. Postma, E. Rizzardo and S. H. Thang, *Macromolecules*, 2005, **38**, 9037–9054; (b) L. M. Muratore, T. P. Davis and K. Steinhoff, *J. Mater. Chem.*, 1999, **9**, 1687–1691.
- (a) D. M. Haddleton, M. C. Crossman, K. H. Hunt, C. Topping, C. Waterson and K. G. Suddaby, *Macromolecules*, 1997, **30**, 3992–3998; (b) D. M. Haddleton, E. Depaquis, E. J. Kelly, D. Kukulj, S. R. Morsley, S. A. F. Bon, M. D. Eason and A. G. Steward, *J. Polym. Sci., Part A: Polym. Chem.*, 2001, **39**, 2378–2384.
- Y. K. Chong, J. Krstina, T. P. T. Le, G. Moad, A. Postma, E. Rizzardo and S. H. Thang, *Macromolecules*, 2003, **36**, 2256–2272.
- A. Feldermann, A. Ah Toy, T. P. Davis, M. H. Stenzel and C. Barner-Kowollik, *Polymer*, 2005, **46**, 8448–8457.