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

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Received 2nd June 2010, Accepted 8th July 2010
DOI: 10.1039/c0cc01694b

In this work, we combine reversible addition fragmentation
transfer polymerization (RAFT) with catalytic chain transfer (CCT) to obtain
α-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.1 RAFT has been applied to
the syntheses of complex architectures, such as star,2 hyper-
branched polymers,3 protein–polymer conjugates4 and hybrid
organic/inorganic nanoparticles.5 The presence of RAFT end-
groups can sometimes be problematic for specific applications
as they can undergo degradation by aminolysis,6 hydrolysis or
thermolysis.7 In addition, RAFT end-groups can exacerbate
cytotoxicity in bio-applications.8 In order to expand the utility of
RAFT, researchers have described techniques to remove
this end-group source of instability introducing a functional
agent. This fraction was analyzed using both NMR and GPC,
revealing polymers with narrow polydispersities, and experi-
mental molecular weights in accord with theoretical values
(as shown in Table S1, ESI†).1 H NMR data (Fig. 1A) con-
ﬁrmed 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 synthesis of both poly(methyl methacrylate), PMMA, and
dpoly(n-butyl methacrylate), PBMA, were performed using
2,2′-azobisisobutyrate (AIBN) as initiator and 2-(2-cyano-
propyl)dithiobenzoate (1) or 4-cyanopentanoic acid dithio-
benzoate 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
copolymer synthesized by RAFT polymerization using a dithioester
agent. This fraction was analyzed using both NMR and GPC,
revealing polymers with narrow polydispersities, and experi-
mental molecular weights in accord with theoretical values
(as shown in Table S1, ESI†).1 H NMR data (Fig. 1A) con-
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respectively.

The second fraction was subjected to a further CCT
reaction; CoBF solution was added directly to the polymeri-
mixture under nitrogen and the mixture was allowed to
react for three hours (Scheme 1). Two different [RAFT]0/
[CoBF]0 ratios were tested 2000 and 80000 (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 con-
stant of methacrylates to CCT agent is extremely large
(leading to some suggestions of a diffusion controlled reaction),
Cs ≈ 20 000.14d In contrast, the transfer reaction to RAFT
agent is governed by a transfer constant of around 50.17 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.18 H NMR analysis of PMMA oligomer

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

6338 | Chem. Commun., 2010, 46, 6338–6340
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(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 $^1$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†). Thus, after the addition of CoBF in solution minimal polymerization occurred (less than 5%) in accord with the monomer conversion determined by $^1$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†) 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†) 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 ($\lambda = 305$ 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†). 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). 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†) 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†). The initial peak originating from the macromonomer shifted from low molecular weight to high

**Scheme 1** Chemical modification of RAFT end-group using CCT polymerization (CoBF as catalyst), with $R = -OCH_3$ or $-O(CH_2)_3CH_3$, (with a molecular weight lower than 4300 g mol$^{-1}$) was carried out before and after addition of CoBF (see Fig. 1 and Fig. S2, ESI†). 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

![Fig. 1](image-url)
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