ACS Macro Letters

Letter

pubs.acs.org/macroletters

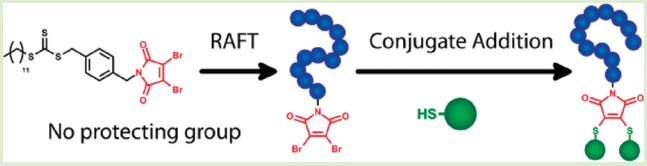
Dibromomaleimide End Functional Polymers by RAFT Polymerization Without the Need of Protecting Groups

Mathew P. Robin, Mathew W. Jones, David M. Haddleton,* and Rachel K. O'Reilly*

Department of Chemistry, Gibbet Hill Road, University of Warwick, Coventry, CV4 7AL United Kingdom

Supporting Information

ABSTRACT: Polymers bearing the dibromomaleimide (DBM) group as a functional chain end have been synthesized by RAFT polymerization. A DBM functional chain transfer agent (CTA) was utilized to afford well-defined P^{t}BA, PMA, and PTEGA, without the requirement of protecting group chemistry. It was found that RAFT polymerization of NIPAM and styrene with this CTA was severely retarded/inhibited which is ascribed to their relatively low propagation rate constants compared to acrylates. This observation is accounted for by a reversible trapping of propagating radicals by the DBM group in RAFT polymerizations using a monomer with low k_p. However, further attempts to synthesize DBM-terminated P^{t}BA and PMA by ATRP using an analogous initiator were unsuccessful, and broad PDI were observed. Furthermore, highly efficient postpolymerization functionalization of DBM-terminated PMA produced by RAFT, with the model compound thiophenol was also demonstrated.



The synthesis of polymers bearing maleimide functional groups is desirable due to the range of efficient post functionalization reactions possible.[1,2] For example, the reaction with thiols which proceeds via a Michael addition or the Diels–Alder cycloadditions with dieneophiles such as furan or anthracene, allow for postpolymerization functionalization of maleimide containing polymers. These "click" reactions have been utilized to form a variety of complex polymer architectures,[3−9] reversibly cross-linked networks,[10−12] and polymer–protein conjugates.[13−18]

Polymer end-group functionality is controlled in living polymerizations by incorporation of the desired functionality into the initiator or chain transfer agent. Indeed, maleimide terminated polyesters have been synthesized by ring-opening polymerization using a maleimide containing initiator,[9,19,20] or a furan-protected maleimide initiator has also been used.[21] This maleimide–furan system subsequently enabled the one-pot synthesis of telechelic α,ω-bismaleimide terminated polylactide allowing the formation of cyclic polymers on reaction with a bisthiol linker.[22] Recently, a maleimide containing initiator has also been used to synthesize polystyrene by cationic polymerization, with the resultant "macroinitiators" then polymerized to give polystyrene grafts.[23]

Due to the reactivity of the maleimide double bond toward radical polymerization, resulting in copolymerization,[24] it has usually been necessary to use protected maleimide initiators for the synthesis of polymers via reversible deactivation radical polymerization (RDRP) or controlled radical polymerization (CRP).[25] The Diels–Alder adduct with furan has been commonly utilized to protect the maleimide functionality in ATRP initiators[7,8,12,16,18] and RAFT agents,[26] while the use of alternative dieneophiles such as dimethylfulvene allows the thermal stability to be improved.[27] Although these polymerizations are successful, they often need to be stopped at relatively low conversions to prevent undesirable reactions. Alternatively, the maleimide end-group can also be introduced via postpolymerization functionalization, for example, by the reaction of RAFT polymers with a furan–maleimide containing diazo compound[13,17] or an excess of bismaleimide.[15,28] In all cases where a Diels–Alder adduct has been used, it is necessary to thermally deprotect the maleimide before reaction with thiols or other dieneophiles.

Recently, elegant work from Caddick and Baker has demonstrated that mono- and dibromomaleimides (DBM) undergo rapid and highly efficient conjugation with thiols via a substitution reaction as opposed to a nucleophilic addition.[29] The reaction is selective for thiols in the presence of other nucleophiles. It is also reversible, due to it being a substitution reaction, on addition of an excess of a competing thiol or by reduction with TCEP, unlike the conventional irreversible maleimide Michael addition conjugation. Furthermore, 2,3-DBM has been used to bridge the disulfide bond of the Grb2 adaptor protein,[30] and this concept has been extended to protein–polymer conjugates using a DBM-modified PEG to afford a polymer–protein conjugate.[31] Hence, in this study, we proposed exploring the introduction of a dibromomaleimide into a controlled radical initiator or chain transfer agent to allow for the facile preparation of end functionalized polymers without the need for protecting group chemistry to allow for reversible modification of the chain end using this new chemistry.

Inspired by Caddick and Baker,[29] we designed and prepared a new dibromomaleimide functional RAFT agent (**3**) in three

Received: November 11, 2011
Accepted: December 14, 2011
Published: December 23, 2011

   dx.doi.org/10.1021/mz200164x | *ACS Macro Lett.* 2012, 1, 222–226

Scheme 1. Synthesis of DBM Functional RAFT Agent (3)

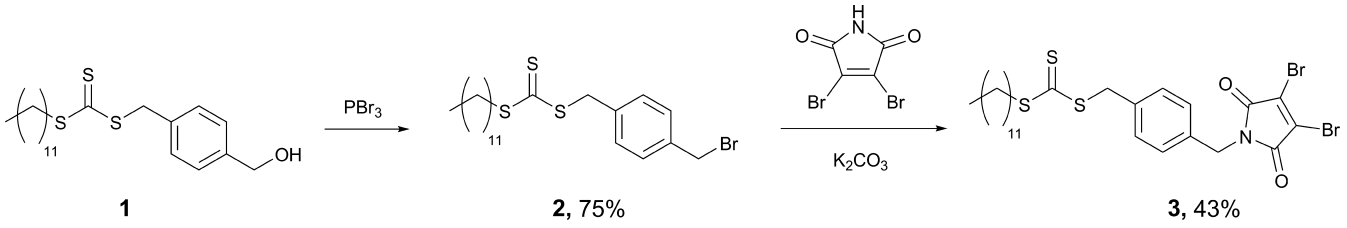


Table 1. RAFT Polymerizations Conducted with CTA (3), Performed at 65 °C in Dioxane

polymer	monomer	[3/M/AIBN]	time (h)	M_n[a] (kg·mol^{-1})	$M_{n,th}$[b] (kg·mol^{-1})	M_w/M_n[a]	conv.[b] (%)
4a	^{t}BA	1:50:0.1	3	2.5	3.0	1.31	37
4b	^{t}BA	1:50:0.1	6	5.7	6.0	1.15	84
5	^{t}BA	1:100:0.1	3	10.5	11.4	1.15	84
6	MA	1:50:0.1	3	4.3	4.2	1.20	54
7	MA	1:100:0.1	3	6.9	6.9	1.14	73
8	TEGA[c]	1:50:0.1	16	5.5	5.9	1.27	48
9	TEGA[c]	1:100:0.1	16	12.9	17.9	1.32	79
10	NIPAM	1:50:0.1	16	0.8	0.7	1.12	1
11	Sty[d]	1:90:0[d]	16	1.0	1.0	1.41	4
12	Sty[d]	1:900:0[d]	16	27.1	33.4	1.35	35

[a]Molecular weight data were obtained by SEC. Samples were taken without fractionation or precipitation. [b]Monomer conversion monitored by ^{1}H NMR spectroscopy. $M_{n,th}$ calculated from monomer conversion. [c]Triethyleneglycol monomethyl ether acrylate. [d]Styrene polymerizations were conducted in bulk, with thermal initiation at 110 °C.

steps, according to Scheme 1. The reactivity of the dibromomaleimide group toward sulfur-based nucleophiles necessitated initial formation of the trithiocarbonate. The alcohol containing trithiocarbonate (**1**), a chain transfer agent (CTA), was prepared from 1-dodecanethiol, carbon disulfide, and 4-(chloromethyl)benzyl alcohol, as previously reported,[32] with subsequent bromination to give **2** following column chromatography. Alkylation of the commercially available 2,3-dibromomaleimide with **2** following the procedure of Weinreb et al.[33] gave the desired CTA (**3**) in about 30% overall yield. Characterization by ^{1}H and ^{13}C NMR spectroscopy confirmed the desired structure (Figure S1 and S2), with the characteristic signals of the dibromomaleimide group identified by ^{13}C NMR at 163.6 and 129.5 ppm along with the diagnostic resonance attributable to the trithiocarbonate group at 223.5 ppm.

Following the successful preparation of this new dibromomaleimide chain transfer agent (**3**), its ability to control the polymerization of a range of vinyl monomers was explored. Initially we investigated the control reaction of **3** in the presence of 0.1 equiv of AIBN in dioxane at 65 °C, and this showed no reaction after 6 h (by both ^{1}H NMR spectroscopy and HPLC analysis), confirming that the dibromomaleimide group was stable under these model radical polymerization conditions. This is in contrast to other unprotected maleimides that are known to react in the presence of a radical initiator. Following this promising result, a series of polymerizations were performed (Table 1).

Initial polymerization of ^{t}BA (**4**) was found to proceed reasonably rapidly, with 37% conversion reached after 3 h (**4a**) and 84% conversion achieved after 6 h (**4b**), to give a well-defined polymer with M_w/M_n = 1.15, as measured by SEC. Interestingly, doubling the equivalents of monomer from 50 to 100 (**5**) while keeping monomer concentration constant led to a more rapid reaction, with 84% conversion achieved after just 3 h (vide infra). Again, the polymer, as characterized by SEC, was well-defined (Figure S3), while the UV−vis spectrum of the polymer, provided by a PDA detector fitted to the SEC, showed the characteristic trithiocarbonate absorbance (λ_{max} = 307 nm), confirming the presence of the RAFT end-group (Figure S4). The ^{13}C NMR spectrum of **5** showed resonances at 163.6 and 129.5 ppm, indicating the polymer also contained the dibromomaleimide end-group (Figure S6). Kinetic analysis of this ^{t}BA polymerization confirmed a linear increase of molecular weight with conversion, with measured and theoretical values (based on conversion) in good agreement, and gave a linear first-order rate plot, although an induction period of approximately 40 min was observed (Figures S7−S9).

Subsequently, polymerizations with a range of monomers (acrylate, acrylamide, and styrene) were attempted (**6**−**11**) under the conditions highlighted in Table 1. It was anticipated that **3** would be a good CTA for these monomers as benchmarking polymerizations with the alcohol analogue (**1**) had proceeded to high conversions, with good control over molecular weight under identical conditions (Table S1), demonstrating that the choice of R and Z group was suitable for this range of monomers. However, it was found that only the MA (**6** and **7**) and TEGA (**8** and **9**) polymerizations proceeded to high conversion. The MALDI-ToF mass spectra of PMA (**6**) and PTEGA (**8**) using an alkali salt as cationization agent,[34,35] further confirmed the presence of the dibromomaleimide group at the polymer chain end with excellent agreement between observed and theoretical masses and isotope pattern (Figures S10−S13). The presence of a single discrete molecular species in both cases suggests a high degree of end-group fidelity, which is desirable for later end-group modification.

In contrast to the acrylic monomers, NIPAM (**10**) and Sty (**11**) showed significantly slower polymerization rates compared to the polymerization under identical conditions with a related CTA (**1**) which does not contain dibromomaleimide functionality. Given that polymerizations (**10**) and (**11**) proceeded to low conversion after 16 h, we postulated that

dx.doi.org/10.1021/mz200164x | ACS Macro Lett. 2012, 1, 222−226

this is due to the dibromomaleimide group reacting reversibly with radicals present in the system thereby retarding polymerization for these monomers which have a low propagating rate constant relative to acrylic monomers.

Three approaches were taken to test the hypothesis of reversible addition of propagating radicals to the dibromomaleimide group. First, polymerizations with (**1**) as RAFT agent and 1 equiv of 2,3-dibromomaleimide as an additive were explored (Table S2). Retardation of the polymerization of all these monomers was observed when compared to the polymerizations of (**1**) with no additive. In addition, styrene polymerizations with the commercially available RAFT agents 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid and 4-cyano-4-(phenylcarbonothioylthio) pentanoic acid (a trithiocarbonate and dithioester, respectively) were also performed in the presence of 1 equiv of 2,3-dibromomaleimide as an additive. In both cases a 10-fold reduction in conversion was observed when compared to styrene polymerization in the absence of additive. This is clear evidence that the retardation effect is attributable to the dibromomaleimide group. The observation that the linear growth of the molecular weight with conversion and first-order kinetics was maintained in these polymerizations (Figures S14–S16) also demonstrates that dibromomaleimide does not irreversibly terminate polymerization nor act as a chain transfer agent.

Second, to explore this effect further, Sty was polymerized with **3** in an increased monomer to chain transfer agent ratio, 900:1 (**12**), while keeping monomer concentration constant. The effect was that conversion increased to 35% over 16 h as compared to 4% for the 90:1 ratio concentration. It is proposed that the decrease in the concentration of dibromomaleimide decreases the proportion of dibromomaleimide "capped" radicals, thereby shifting the equilibrium between propagating radicals and dibromomaleimide "capped" radicals toward the propagating species, which results in an increase in rate and, hence, conversion in a given time.

Third, the Sty polymerization was repeated with 90 equiv of monomer with CTA (**1**) in the presence of 0, 0.01, 0,05, 0.1, 0.5, and 1 equiv of 2,3-dibromomaleimide; Table S3. After 16 h of reaction, a clear increase in conversion and M_n with decreasing dibromomaleimide concentration was observed (Figure 1 and Table S3). SEC chromatograms for each of these samples also demonstrate this trend and show well-defined polymer peaks for the lower dibromomaleimide concentrations (Figure S17). With the retardation effect of dibromomaleimide on the kinetics of polymerization for monomers with relatively low propagation constants in RAFT reactions established, we were interested in exploring if a similar effect would be observed in ATRP.

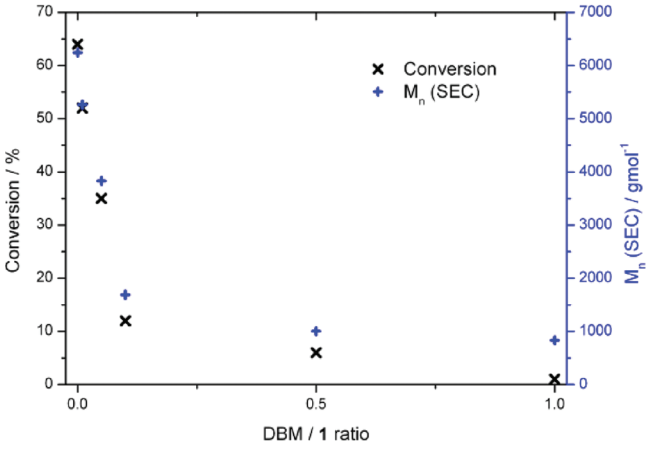
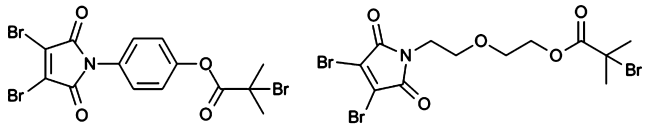


Figure 1. Conversion and M_n (obtained by SEC) vs the molar ratio of 2,3-dibromomaleimide [(DBM)]/[**1**] for RAFT polymerizations of Sty with **1** in the presence of 2,3-dibromomaleimide.

We recently reported the synthesis of dibromomaleimide functional polymers synthesized by ATRP using two independent post-polymerization modification approaches.[36] It was demonstrated that the polymerization of oligo(ethylene glycol) methacrylates was severely retarded in the presence of the dibromomaleimide moiety and as a consequence, alternative strategies were investigated. As a complement to the present RAFT study, we explored the viability of the synthesis of α-dibromomaleimide functional polymers by ATRP using functionalized initiators (**13** and **14**, Figure 2).



13 **14**

Figure 2. Synthesized dibromomaleimide ATRP initiators **13** and **14**.

As an initial study, initiator **13** was employed under relatively standard ATRP conditions for the polymerization of MA and ^{t}BA, with experimental details and results summarized in Table 2. In both cases, the polymerizations proceeded at an appreciable rate, with linear first-order kinetics observed throughout (Figure S18–S21). Analysis of the polymerization samples by SEC, however, indicated a loss of control, with bimodal traces observed for each sample (Figure S22 and S23). Because bimodality was observed at relatively low conversions, this was attributed to the copolymerization of the dibromomaleimide end-group with the propagating chain end.

The effect of the *N*-substituent of the maleimide has been widely studied in radical polymerizations.[37] A second (*N*-alkyl) dibromomaleimide initiator (**14**) was synthesized and studied for the polymerizations of MA and ^{t}BA in an attempt to reduce the propensity of the dibromomaleimide to undergo copolymerization with propagating chains. Polymerizations of MA and ^{t}BA initiated by (**14**) proceeded rapidly, with comparable rates to those initiated with **13**. Again, linear first order kinetics were observed (Figures S24–S27), consistent with a well-controlled polymerization; however, bimodal SEC traces were obtained for each of the reaction samples (Figures S28 and S29). We propose that the difference in polymerization results between the ATRP and the RAFT systems may be due to the difference in active radical species in the two systems; in the former, the radical can be considered "caged"; however, in the latter it has been demonstrated to be a "free" propagating radical. This is consistent with the previous observations that the monomer reactivity ratios measured for ATRP are significantly different to free radical polymerization.[38−40] Whereas for RAFT polymerization, reactivity ratios are the same as a RAFT chain transfer event.[41] Following the unsuccessful synthesis of well-defined dibromomaleimide functional polymers via ATRP, further studies were conducted using the polymers synthesized by RAFT.

dx.doi.org/10.1021/mz200164x | *ACS Macro Lett.* 2012, 1, 222–226

Table 2. ATRP Polymerizations Conducted with Initiators 13 and 14, Performed in Toluene[a] at 65 °C

polymer	monomer	[I/M]	time (h)	M_n[b] (kg·mol^{-1})	$M_{n,th}$[c] (kg·mol^{-1})	M_w/M_n[b]	conv.[c] (%)
15[d]	MA	1:50	3	7.4	3.5	1.34	73
16[d]	^{t}BA	1:50	3	5.1	6.2	1.94	90
17[e]	MA	1:50	3	5.9	3.5	1.54	72
18[e]	^{t}BA	1:50	3	5.4	6.6	1.44	96

[a]1:1 v/w with monomer. [b]Molecular weight data were obtained by SEC. Samples were taken without fractionation or precipitation. [c]Monomer conversion monitored by ^{1}H NMR spectroscopy. $M_{n,th}$ calculated from monomer conversion. [d]Initiator (**13**) employed. [e]Initiator (**14**) employed.

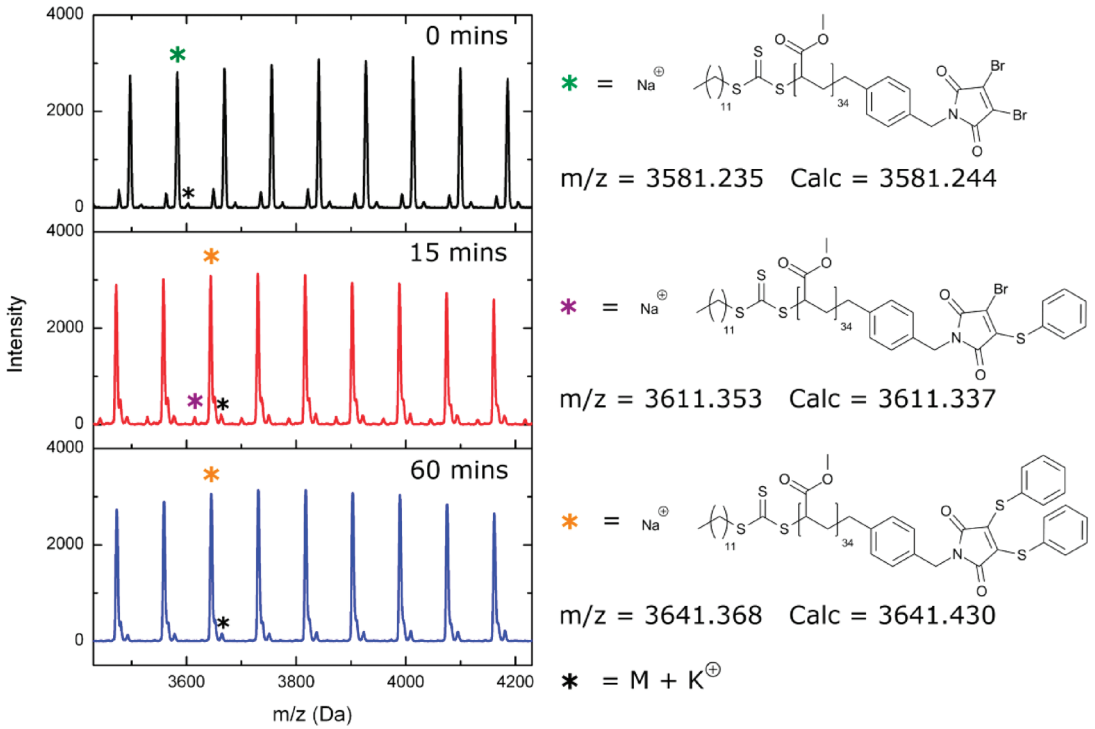


Figure 3. MALDI-ToF MS analysis of postpolymerization functionalization of **6** with thiophenol. Spectrum collected in linear mode, with high resolution masses obtained in reflectron mode.

The postpolymerization modification of dibromomaleimide-terminated PMA prepared by RAFT using a model thiol was subsequently explored. Thiophenol was chosen as this gives a clearly assignable mass shift allowing analysis by MALDI-ToF mass spectrometry, as well as being UV−vis active, allowing characterization with SEC coupled to a PDA detector. In the reaction of **6** with 10 equiv thiophenol in THF at ambient temperature, only a minor population of monosubstituted PMA was observed by MALDI-ToF MS after 24 h. However, in the reaction of **6** with 2.5 equiv of thiophenol in the presence of 2.5 equiv of the base catalyst imidazole, a very rapid reaction was observed.

MALDI-ToF MS showed that, after 15 min, the major product was the dithiophenol-maleimide terminated PMA (**19**), and after 60 min, no starting material or monosubstituted PMA remained (Figure 3). SEC analysis showed no appreciable change in the molecular weight distribution of the thiol functionalized product (Figure S30). In contrast, the UV−vis spectrum of the product (**19**) obtained using the SEC's PDA detector showed an absorbance maxima at 415 nm attributed to the dithiophenol-maleimide group, in addition to the λ_{max} at 307 nm due to the trithiocarbonate group (Figure S31). Current work is exploring these chemistries in a range of polymer coupling and functionalization applications. We are particularly excited by the opportunity to allow for reversible cleavage of the linkage under mild conditions.

■ ASSOCIATED CONTENT

Supporting Information

Materials and apparatus, synthetic protocols, and NMR, SEC, and MALDI-ToF MS data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: r.k.o-reilly@warwick.ac.uk; d.m.haddleton@warwick.ac.uk.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors would like to thank the EPSRC and the University of Warwick for funding. The SECs used in this research were obtained through Birmingham Science City: Innovative Uses for Advanced Materials in the Modern World (West Midlands Centre for Advanced Materials Project 2), with support from Advantage West Midlands (AWM) and part funded by the

European Regional Development Fund (ERDF). D.M.H. is a Royal Society Wolfson fellow.

REFERENCES

(1) Hall, D. J.; Van Den Berghe, H. M.; Dove, A. P. *Polym. Int.* **2011**, *60*, 1149.
(2) Mansfeld, U.; Pietsch, C.; Hoogenboom, R.; Becer, C. R.; Schubert, U. S. *Polym. Chem.* **2010**, *1*, 1560.
(3) Dag, A.; Durmaz, H.; Hizal, G.; Tunca, U. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 302.
(4) Dag, A.; Durmaz, H.; Tunca, U.; Hizal, G. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 178.
(5) Durmaz, H.; Dag, A.; Hizal, G.; Tunca, U. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 5083.
(6) Durmaz, H.; Dag, A.; Onen, C.; Gok, O.; Sanyal, A.; Hizal, G.; Tunca, U. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 4842.
(7) Gacal, B.; Durmaz, H.; Tasdelen, M. A.; Hizal, G.; Tunca, U.; Yagci, Y.; Demirel, A. L. *Macromolecules* **2006**, *39*, 5330.
(8) Gok, O.; Durmaz, H.; Ozdes, E. S.; Hizal, G.; Tunca, U.; Sanyal, A. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 2546.
(9) Xiong, X.; Xu, Y. *Polym. Bull.* **2010**, *65*, 455.
(10) Canadell, J.; Fischer, H.; De With, G.; van Benthem, R. A. T. M. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 3456.
(11) Gousse, C.; Gandini, A.; Hodge, P. *Macromolecules* **1998**, *31*, 314.
(12) Syrett, J. A.; Mantovani, G.; Barton, W. R. S.; Price, D.; Haddleton, D. M. *Polym. Chem.* **2010**, *1*, 102.
(13) Heredia, K. L.; Grover, G. N.; Tao, L.; Maynard, H. D. *Macromolecules* **2009**, *42*, 2360.
(14) Kosif, I.; Park, E.-J.; Sanyal, R.; Sanyal, A. *Macromolecules* **2010**, *43*, 4140.
(15) Li, M.; De, P.; Li, H.; Sumerlin, B. S. *Polym. Chem.* **2010**, *1*, 854.
(16) Mantovani, G.; Lecolley, F.; Tao, L.; Haddleton, D. M.; Clerx, J.; Cornelissen, J. J. L. M.; Velonia, K. *J. Am. Chem. Soc.* **2005**, *127*, 2966.
(17) Tao, L.; Kaddis, C. S.; Ogorzalek Loo, R. R.; Grover, G. N.; Loo, J. A.; Maynard, H. D. *Chem. Commun.* **2009**, 2148.
(18) Geng, J.; Mantovani, G.; Tao, L.; Nicolas, J.; Chen, G.; Wallis, R.; Mitchell, D. A.; Johnson, B. R. G.; Evans, S. D.; Haddleton, D. M. *J. Am. Chem. Soc.* **2007**, *129*, 15156.
(19) Gramlich, W. M.; Robertson, M. L.; Hillmyer, M. A. *Macromolecules* **2010**, *43*, 2313.
(20) Xu, N.; Du, F.-S.; Li, Z.-C. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 1889.
(21) Pounder, R. J.; Stanford, M. J.; Brooks, P.; Richards, S. P.; Dove, A. P. *Chem. Commun.* **2008**, 5158.
(22) Stanford, M. J.; Pflughaupt, R. L.; Dove, A. P. *Macromolecules* **2010**, *43*, 6538.
(23) Kuroda, S.; Hagiwara, T. *Polymer* **2011**, *52*, 1869.
(24) Chen, G. Q.; Wu, Z. Q.; Wu, J. R.; Li, Z. C.; Li, F. M. *Macromolecules* **2000**, *33*, 232.
(25) Moad, G.; Rizzardo, E.; Thang, S. H. *Acc. Chem. Res.* **2008**, *41*, 1133.
(26) Bays, E.; Tao, L.; Chang, C. W.; Maynard, H. D. *Biomacromolecules* **2009**, *10*, 1777.
(27) Tolstyka, Z. P.; Kopping, J. T.; Maynard, H. D. *Macromolecules* **2007**, *41*, 599.
(28) Li, M.; De, P.; Gondi, S. R.; Sumerlin, B. S. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 5093.
(29) Tedaldi, L. M.; Smith, M. E. B.; Nathani, R. I.; Baker, J. R. *Chem. Commun.* **2009**, 6583.
(30) Smith, M. E. B.; Schumacher, F. F.; Ryan, C. P.; Tedaldi, L. M.; Papaioannou, D.; Waksman, G.; Caddick, S.; Baker, J. R. *J. Am. Chem. Soc.* **2010**, *132*, 1960.
(31) Schumacher, F. F.; Nobles, M.; Ryan, C. P.; Smith, M. E. B.; Tinker, A.; Caddick, S.; Baker, J. R. *Bioconjugate Chem.* **2011**, *22*, 132.
(32) Petzetakis, N.; Dove, A. P.; O'Reilly, R. K. *Chem. Sci.* **2011**, *2*, 955.
(33) Joyce, R. P.; Gainor, J. A.; Weinreb, S. M. *J. Org. Chem.* **1987**, *52*, 1177.
(34) Ladavière, C.; Lacroix-Desmazes, P.; Delolme, F. *Macromolecules* **2009**, *42*, 70.
(35) Strube, O. I.; Nothdurft, L.; Drache, M.; Schmidt-Naake, G. *Macromol. Chem. Phys.* **2011**, *212*, 574.
(36) Jones, M. W.; Strickland, R. A.; Schumacher, F. F.; Caddick, S.; Baker, J. R.; Gibson, M. I.; Haddleton, D. M. *J. Am. Chem. Soc.* **2012**, DOI: 10.1021/ja210335f.
(37) Clark, S. C.; Hill, D. J. T.; Hoyle, C. E.; Jonsson, S.; Miller, C. W.; Shao, L. Y. *Polym. Int.* **2003**, *52*, 1701.
(38) Shinoda, H.; Matyjaszewski, K. *Macromolecules* **2001**, *34*, 6243.
(39) Roos, S. G.; Müller, A. H. E.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 8331.
(40) Lad, J.; Harrisson, S.; Haddleton, D. M. *Advances in Controlled/Living Radical Polymerization*; American Chemical Society: Washington, DC, 2003; Vol. *854*, p 148.
(41) Moad, G.; Rizzardo, E.; Thang, S. H. *Polymer* **2008**, *49*, 1079.