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Ultrafast and Reversible Multiblock Formation by the SET-Nitroxide Radical Coupling Reaction

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The single electron transfer-nitroxide radical coupling (SET-NRC) reaction has been used to produce multiblock polymers with high molecular weights in under 3 min at 50°C by coupling a difunctional telechelic polystyrene (Br-PSTY-Br) with a dinitroxide. The well known combination of dimethyl sulfoxide as solvent and Me_6TREN as ligand facilitated the in situ disproportionation of Cu^IBr to the highly active nascent Cu^0 species. This SET reaction allowed polymeric radicals to be rapidly formed from their corresponding halide end-groups. Trapping of these carbon-centred radicals at close to diffusion controlled rates by dinitroxides resulted in high-molecular-weight multiblock polymers. Our results showed that the disproportionation of Cu^I was critical in obtaining these ultrafast reactions, and confirmed that activation was primarily through Cu^0. We took advantage of the reversibility of the NRC reaction at elevated temperatures to decouple the multiblock back to the original PSTY building block through capping the chain-ends with mono-functional nitroxides. These alkoxyamine end-groups were further exchanged with an alkyne mono-functional nitroxide (TEMPO–≡) and 'clicked' by a Cu^I-catalyzed azide/alkyne cycloaddition (CuAAC) reaction with N_3–PSTY–N_3 to reform the multiblocks. This final 'click' reaction, even after the consecutive decoupling and nitroxide-exchange reactions, still produced high-molecular-weight multiblocks efficiently. These SET-NRC reactions would have ideal applications in re-usable plastics and possibly as self-healing materials.

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Introduction

Nitroxide (aminoxyl) radicals can react with carbon-centred radicals at close to diffusion controlled rates to form alkoxyamines.[1] This nitroxide radical coupling (NRC) technique of trapping transient radicals allowed the study of the complex initiation pathways in free-radical polymerizations,[2,3] and recently emerged as a powerful technique for the synthesis of complex polymer architectures (termed ATNRC). ATNRC through trapping of mono- and multifunctional nitroxides can vary the polymer chain-end functionality or create a variety of polymer architectures.[4] The reaction conditions in these studies, however, required high temperatures (e.g., >70°C), very high levels of copper (sometimes in a 10-fold excess to halide groups), and long reaction times (4–12 h). Kinetic simulations showed that the overall rate of alkoxyamine formation in polymeric systems was only limited by the rate of carbon-centred radical formation.[5] Our group attained ultrafast radical formation through single electron transfer (SET) to achieve a reaction with 'click'-type attributes at room temperature, which included near quantitative yields, selectivity in the presence of functional groups, rapid rates of alkoxyamine formation, and non-toxic byproducts.[6] Moreover, this reaction was reversible at high temperatures, and we demonstrated the further functionalization of end-groups through competitive exchange with other functional nitroxides.[6]

Click reactions have become an important tool for the modification and coupling of small molecule[7] and macromolecular systems to create new advanced materials.[8,9] In the polymer field, the Cu^I-catalyzed azide/alkyne cycloaddition (CuAAC) coupling reaction has been the dominant click reaction used to prepare complex architectures such as dendrimers, stars, miktoarm stars, and polymer grafts.[9,10] Recently, there has been a significant push to develop new click-type/coupling chemistries. Important examples include the thiol-based thiol-ene,[11] thiol-yne,[12] and thio-bromo[13] reactions, as well as hetero-Diels–Alder cycloadditions.[14]

SET from Cu^0 significantly increased the rate of carbon-centred radical production from polymeric chains with halide end-groups. To achieve this, nascent Cu^0 should be formed in situ. By starting with Cu^I, Cu^0 can be produced in situ through the disproportionation of Cu^I species (e.g., Cu^IBr; see Eqn 1) in selective solvents (e.g., dimethyl sulfoxide (DMSO), alcohols) and ligands (e.g., tris[2-(dimethylamino)ethyl]amine (Me_6TREN)). Single electron transfer-'living' radical polymerization (SET-LRP) was the first technique to utilize this approach, allowing the ultrafast production of well-controlled acrylate polymerizations at room temperature.[15] Similarly, we reported[6] the rapid (<7 min) formation of three-arm star polymers at room temperature using a tri-nitroxide core, linear polystyrene chains with halide chain-ends (PSTY-Br), and NRC methodology. We subsequently established that the SET-NRC reaction was much faster than previously thought, and highly effective as an ultrafast click-type reaction as demonstrated by the formation of two-arm PSTY in less than 1 min

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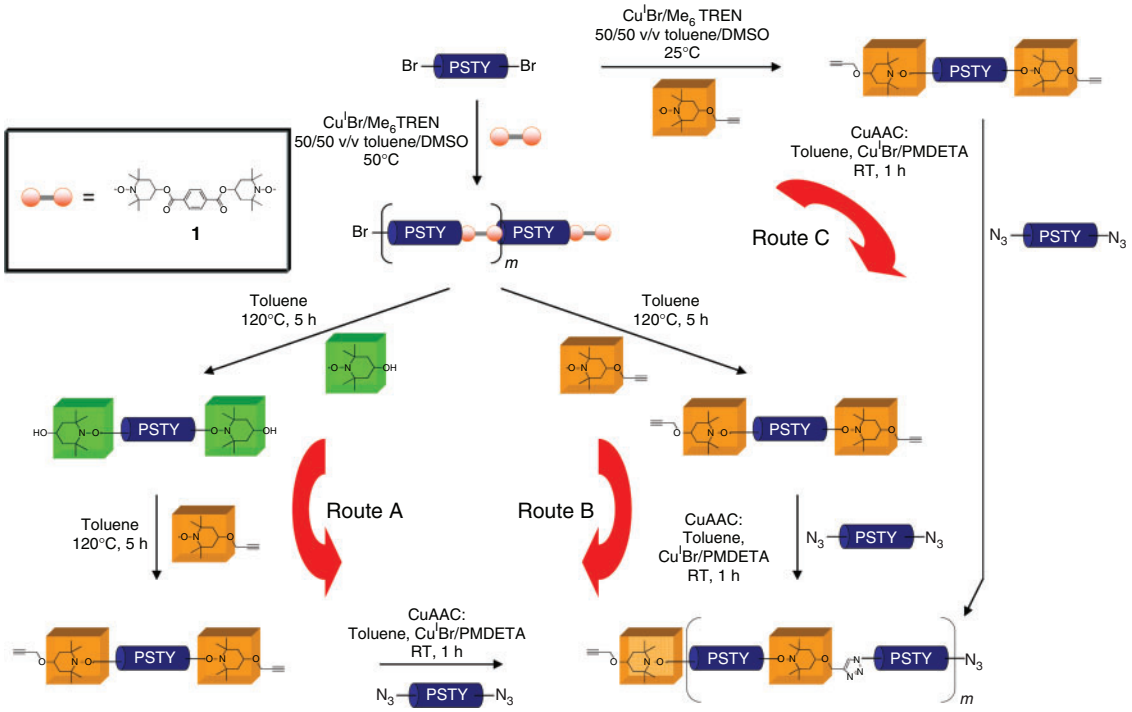


Scheme 1. Synthetic strategies for the formation of multiblocks using the SET-NRC reaction, decoupling and exchange with functional nitroxides, and the reformation of multiblocks by a CuAAC reaction.

at room temperature.[5] In fact, this reaction appeared essentially complete upon the addition of Cu^{I}Br. Kinetic simulations also showed: negligible radical–radical bimolecular termination ($<10^{-4}$%), Cu^{0} dominated activation, and confirmed that the persistent radical effect (through deactivation by Cu^{II}Br$_2$) had no effect until conversions of greater than 99%.

$$2Cu^{I}Br \underset{}{\overset{K_{disp}}{\rightleftharpoons}} Cu^{0} + Cu^{II}Br_2 \qquad (1)$$

In this work, we demonstrate the utility of the SET-NRC reaction through the ultrafast formation of multiblock polymers from the reaction between Br–PSTY–Br and a dinitroxide (Scheme 1). There are many reports in the literature of multiblock (co)polymers produced from difunctional polymers but none with the speed and versatility of the NRC technique. Some examples include the coupling of dihydroxy telechelic polymers with a 2,4-toluene diisocyanate coupling agent at 60°C for 12 h[16] and the use of *N*,*N*-dicyclohexylcarbodiimide (DCC) as a coupling agent for dihydroxy and dicarboxylated polymers with a reaction time of 12 h.[17] PSTY with telechelic thiol end-groups has also been homo-coupled to form disulfide linkages between the PSTY building blocks.[18]

Results and Discussion

The basic building block, Br–PSTY–Br, was synthesized by ATRP to produce a polymer with a number-average molecular weight, M_n, of 4700 and a polydispersity index (PDI) of 1.09. A large amount of Cu^{II}Br$_2$ (20% relative to Cu^{I}Br) in the reaction mixture ensured a narrow molecular weight distribution and high chain-end functionality. This Br–PSTY–Br building block formed high-molecular-weight multiblocks being linked by the dinitroxide **1** through the SET-NRC reaction. This one pot batch reaction at 50°C contained Cu^{I}Br and Me$_6$TREN in a 50/50 v/v toluene/DMSO solvent mixture. We used a higher than normal reaction temperature (50°C) for this type of NRC,[6] in order to solubilize and maintain a homogeneous reaction solution mixture of the resulting high-molecular-weight polymer product throughout the reaction. Fig. 1 shows the molecular weight distributions (MWDs) through the course of the SET-NRC reaction. After only 3 min, high-molecular-weight polymer formed, and the MWD remained relatively constant even after prolonged reaction times. This indicated that most of the coupling reactions took place within the first 3 min. We observed a distribution at a lower peak molecular weight ($M_{p1} = 4240$) relative to that of the starting Br–PSTY–Br ($M_{p2} = 4920$) (see Fig. 1B), and identified this as monocyclic PSTY with a lower hydrodynamic volume.[19,20] Scheme 2 shows the mechanism by which the monocyclic species can be formed. The peak at M_{p3} (9490) did not change with time and was most likely attributable to a cyclic structure consisting of two PSTY chains coupled together by two dinitroxide linkers. It was very unlikely that the cyclic structures formed by the bimolecular termination of two chain end radicals[5] because of the very low probability of the simultaneous activation of both ends of a PSTY chain to radicals. The decoupling experiments described below support this assertion.

The very rapid multiblock formation by SET-NRC in the batch reaction led us to attempt to control the MWD by feeding the Br–PSTY–Br into a solution of dinitroxide **1**, Me$_6$TREN, and Cu^{I}Br in 50/50 v/v toluene/DMSO. Under these conditions, the molecular weight should increase linearly with the amount of Br–PSTY–Br fed into the reaction mixture. Fig. 2A shows the evolution of the MWD as a function of Br–PSTY–Br fed into a reaction mixture that contained an equimolar ratio of Cu^{I}Br to polymer Br end-groups. It can be seen that after the addition of only 0.1 equivalents of Br–PSTY–Br to **1**, a new peak at 6309 ($\log M_P = 3.8$) formed, assigned to a PSTY chain with a dinitroxide attached to both ends, along with higher-molecular-weight species. With an increase in the amount of Br–PSTY–Br fed into

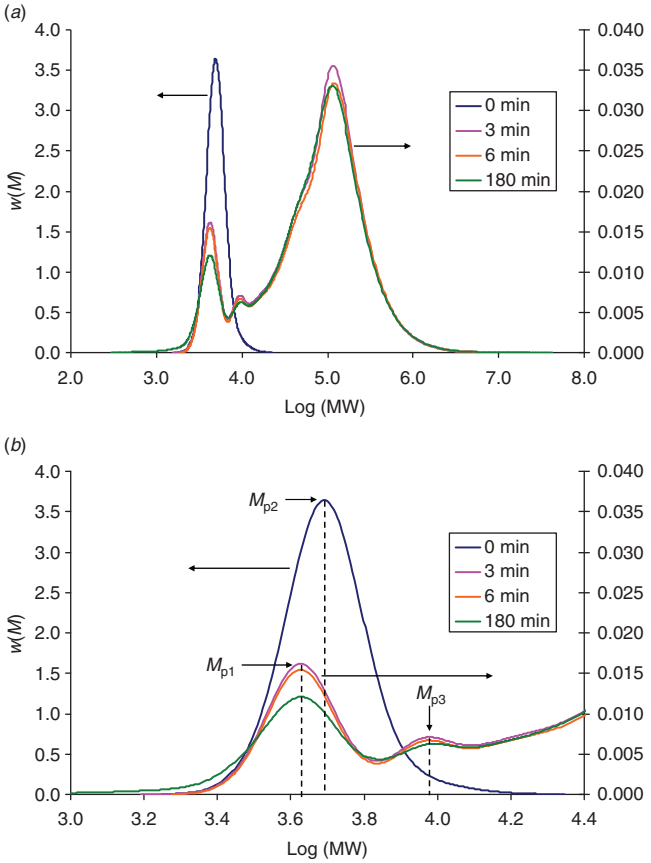


Fig. 1. Weight-normalized size exclusion chromatography (SEC) for the batch SET-NRC coupling reaction between Br–PSTY–Br ($M_n = 4700$, PDI = 1.09) and dinitroxide using Cu^IBr (three-fold excess to bromine end-groups) at 50°C in 50/50 v/v toluene/DMSO and Me_6TREN. (A) Weight-normalized SEC for overall MWD. (B) Weight-normalized SEC of low MWD ($M_{p1} = 4240$, $M_{p2} = 4920$, $M_{p3} = 9490$). All SEC chromatograms were weight normalized and then replotted as $w(M)$ versus log (MW).

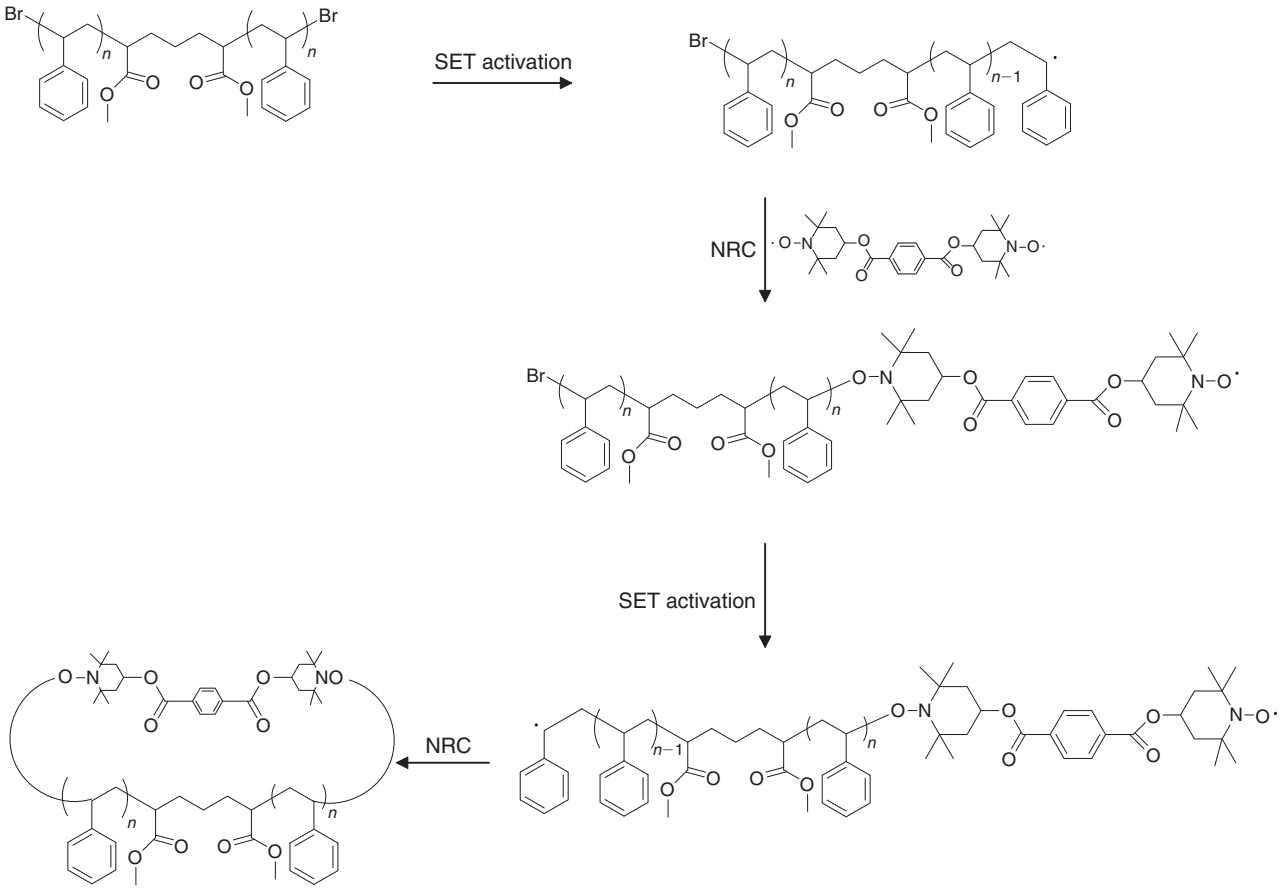
the reaction, the M_n increased from 4700 to 32000 (Fig. 2C) and the PDI increased from 1.09 to 3.5 (Fig. 2D). Increasing the Cu^IBr stoichiometry to three equivalents relative to the Br end-groups resulted in higher M_n and PDI values (Fig. 2C and D).

These results were puzzling. We did not expect high-molecular-weight polymer after the addition of 0.1 equivalents of Br–PSTY–Br because of the large excess of dinitroxide relative to Br groups. Based on previous reactions,[6] we expected that the Br chain-ends would simply be exchanged for nitroxides. To unravel this conundrum, we first conducted a batch reaction with only 0.1 equivalents of Br–PSTY–Br relative to dinitroxide (Fig. 3, curve a). The Cu^IBr, as in all previous experiments, was added as the final reagent just before the start of the reaction. As expected, there was a slight shift to a higher molecular weight corresponding to •ON–T–PSTY–T–NO•, a second peak corresponding to the coupling of two PSTY chains, and a low population of high-molecular-weight species. The next experiment was carried out under identical conditions, but this time the Cu^IBr was added first to the reaction mixture containing **1**, Me_6TREN, DMSO, and toluene; and left to equilibrate for 30 min. We observed a very different MWD (Fig. 3, curve b), one with high molecular weight, when Br–PSTY–Br was added as the last reagent and just before the start of the reaction. This MWD was near identical to the feed reaction after the addition of 0.1 equivalents of Br–PSTY–Br (Fig. 3, curve c).

These results suggest that the rate of disproportionation plays an important role in controlling the MWD, especially during the feed process. In batch reactions, the SET-NRC process was very fast relative to disproportionation so that low levels of deactivator ($Cu^{II}Br_2$) were present in the reaction mixture (as Cu^IBr was added as the last reagent just before the start of the reaction). Kinetic simulations showed that the concentration of $Cu^{II}Br_2$ from this type of reaction increased linearly with conversion.[5] In a feed process, Cu^IBr has time to disproportionate, allowing the copper species to reach their equilibrium concentrations. This resulted in a high $Cu^{II}Br_2$ concentration at the initial stage of the reaction, in which deactivation of the chain-end radicals by $Cu^{II}Br_2$ now successfully competed with nitroxide trapping. Therefore, α,ω-telechelic PSTY (i.e., •ON–T–PSTY–Br) initially formed, and over time could form higher molecular weight polymer.

An important feature of the NRC methodology was the reversibility of this reaction at elevated temperatures. In our previous work,[6] we used the reversibility of this reaction to change the chemical functionality of the polymer chain-ends through exchange with functional nitroxides. Here, the multiblock polymer was decoupled at 120°C in the presence of either a high excess of TEMPO-OH (route A) or TEMPO–≡ (route B) relative to the original PSTY building block, and the chain ends capped with the respective functional nitroxide. Fig. 4A shows the near quantitative cleavage of the multiblock (curve a) to give lower molecular weight difunctional PSTY capped with TEMPO-OH (curve b). The MWD of the multiblock ($M_n = 36970$, PDI = 5.29) decreased to a value close to that of the original starting PSTY building block with an M_n of 5010 and PDI of 1.10. Assignments of the TEMPO-OH groups by ^1H NMR spectroscopy confirmed the capping of the polymer chain-ends by these nitroxides (Fig. 5B). The characteristic peaks for the methyl groups on the nitroxide (denoted as h), and the characteristic splitting of the broad peak f were consistent with previously reported ^1H NMR spectra[2,6] of small molecule diastereomers capped with nitroxides. Exploiting the versatility of the decoupling and exchange reaction, we then exchanged the TEMPO-OH on the PSTY chain ends with an alkyne TEMPO (TEMPO–≡). Curve c in Fig. 4A shows only a slight change in the MWD ($M_n = 5350$, PDI = 1.10). The distinct l and k resonances arising from the alkyne moiety in the ^1H NMR spectrum (Fig. 5C) confirmed exchange of the TEMPO-OH to TEMPO–≡ end-groups. These exchange reactions, through a two-step process to obtain the alkyne-functionalized polymer, demonstrated the versatility of the nitroxide exchange process. It was also possible to obtain the alkyne-functionalized polymer directly by performing the multiblock decoupling reaction in the presence of TEMPO–≡. Fig. 4B shows the near quantitative cleavage of the multiblock (curve a) to give lower molecular weight difunctional PSTY capped with TEMPO–≡ (curve b) ($M_n = 5470$ and PDI = 1.10). The capping with TEMPO–≡ during the decoupling process was again confirmed by ^1H NMR spectroscopy (Fig. 5D).

Importantly, the decoupling reaction shed light on the nature of the cyclic polymer products obtained from the multiblock synthesis (Fig. 1). As shown in Fig. 4C, the MWD of the low M_n cyclic polymer ($M_{p1} = 4263$; curve a) shifts to higher M_n ($M_{p2} = 5702$; curve b) upon decoupling because of an increase in hydrodynamic volume associated with the change from a cyclic structure to a linear structure. The decoupling process also gave



Scheme 2. Proposed mechanism for the formation of monocyclic PSTY chains.

rise to a mono-modal distribution, indicative of near quantitative decoupling of the multiblock and cyclic products. We can consequently conclude that the low M_n cyclic structure arises from the coupling of the chain ends of a single PSTY chain through a single dinitroxide (Scheme 2) rather than from the radical–radical termination of two simultaneously activated chain ends. The C–C bond that results from the latter process (i.e., through radical termination between radicals on each end of the polymer chain) would not decouple under these conditions. The presence of cyclic PSTY species observed in our multiblock systems was not unexpected. Lonsdale et al.[20] showed that cyclization of α,ω-telechelic PSTY (i.e., ≡–PSTY–N_3) by the CuAAC reaction in toluene resulted in a high yield (∼83%) of monocyclic polymer. Their results were in agreement with predicted values determined from the Jacobson–Stockmyer equation.[21] In our SET-NRC system, monocyclic polymers can only form from the precursor •ON–T–PSTY–Br. However, the many competitive reaction with free dinitroxide and other functional PSTY chains results in a low amount of •ON–T–PSTY–Br and thus a small amount of cyclic polymer in our system.

We demonstrated the reversibility and orthogonal nature of the NRC decoupling reactions by a CuAAC click reaction between the ≡–TEMPO–PSTY–TEMPO–≡ and N_3–PSTY–N_3. The three different routes (see Scheme 1) gave high-molecular-weight polymer after 60 min (Fig. 7). The highest molecular weight polymer produced was by route C (curve a) because of the minimal number of reaction steps to produce the starting material (≡–TEMPO–PSTY–TEMPO–≡). A slightly lower molecular weight distribution (curve b) was produced by route B, and the lowest distribution (curve c) produced by route A. The latter two multiblock formations showed lower molecular weight distributions. This was presumably because of the increased number of synthetic steps and consequent loss of chain-end functionality. In comparison to the multiblock formed from Br–PSTY–Br and dinitroxide (**1**) there was no evidence of monocyclic or dicyclic species in the size exclusion chromatograms (Fig. 7, curves b and c). The peak (M_{p2} in curve a) did not move to higher molecular weight over time and we postulated this to be a small amount of dicyclic PSTY (i.e., two PSTY chains to form one cyclic structure).

Conclusion

SET-NRC reactions produce high-molecular-weight multiblock polymers from Br–PSTY–Br in the presence of a dinitroxide in under 3 min at 50°C. The highly active Cu^0, formed in situ from the disproportionation reaction of Cu^IBr in the presence of DMSO and Me_6TREN, significantly accelerates the activation of the polymer halides to the carbon-centred macroradicals that are subsequently trapped by the nitroxides. Our results showed that the disproportionation reaction of Cu^I to give Cu^0 and Cu^{II} was critical in obtaining ultrafast reactions. The results also confirmed that activation was primarily through Cu^0, thus providing additional support for the SET mechanism. A feature of this NRC reaction is its reversibility at elevated temperatures. Taking advantage of this, we decoupled the multiblock polymer to obtain

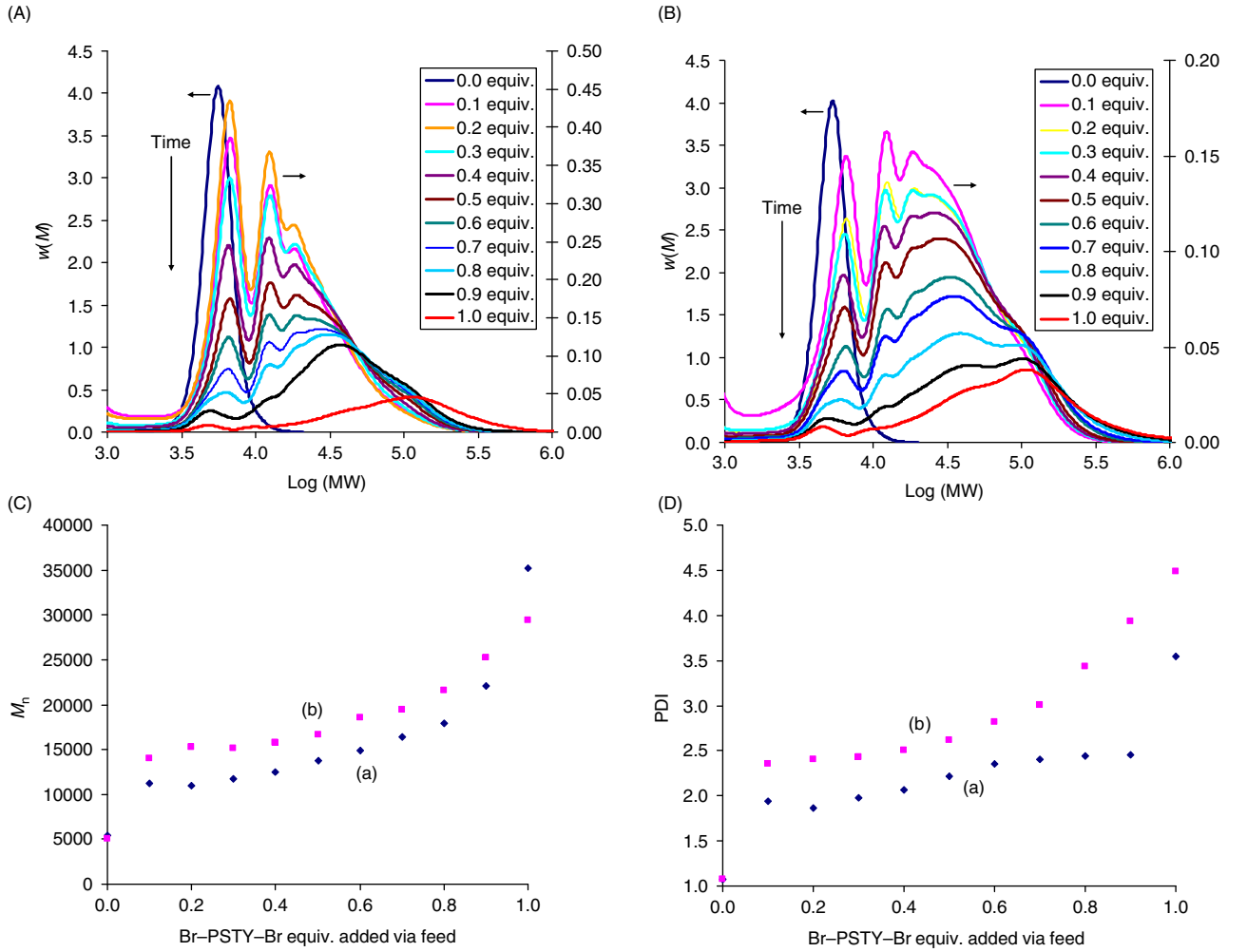


Fig. 2. SET-NRC coupling reaction performed by feeding Br–PSTY–Br ($M_n = 4700$, PDI = 1.09) into a solution of dinitroxide **1**, $Cu^{I}Br$ and Me_6TREN in 50/50 v/v toluene/DMSO at 50°C. (A) Weight-normalized size exclusion chromatography (SEC) for $Cu^{I}Br$ (1 equivalent relative to bromine end-groups) over 4 h. (B) Weight-normalized SEC for $Cu^{I}Br$ (3 equivalents relative to bromine end-groups) over 4 h. (C) M_n versus equivalents of Br–PSTY–Br added by the feed. (D) PDI versus equivalents of Br–PSTY–Br added by the feed. Curve a: 1 equivalent $Cu^{I}Br$ relative to bromine end-groups. Curve b: 3 equivalents of $Cu^{I}Br$ relative to bromine end-groups. All SEC chromatograms were weight normalized and then replotted as $w(M)$ versus log (MW).

the original PSTY building block capped with TEMPO-OH or TEMPO–≡. An exchange reaction between HO–TEMPO–PSTY–TEMPO–OH and TEMPO–≡ gave ≡–TEMPO–PSTY–TEMPO–≡, which was then further 'clicked' with N_3–PSTY–N_3 to reform multiblocks. Size exclusion chromatography confirmed the efficiency of these consecutive decoupling, nitroxide exchange, and CuAAC reactions.

Experimental

Materials

Silica gel 60 (230–400 mesh ATM (SDS), TLC plates (silica gel 60 F254), sodium chloride (Univar, 99.9%), methanol (Univar, AR grade), sodium hydrogen carbonate (Merck, AR grade), *n*-hexane for gas chromatography (GC) analysis (Scharlau, 96%), terephthaloyl chloride (Aldrich, >99%), sulfuric acid (Laboratory-Scan, AR grade), acetonitrile (Laboratory-Scan, HPLC grade), hydrogen peroxide 30% w/w (Univar, AR grade), 2,2,6,6-tetramethyl-4-piperidinol (Aldrich, 98%), chloroform ($CHCl_3$, Pronalys, 99%), dichloromethane (DCM, Labscan, AR grade), diethyl ether (Et_2O, Pronalys, AR grade), tetrahydrofuran (THF, HPLC grade, Lichrosolv, 99.8%), toluene (HPLC, LABSCAN, 99.8%), dimethyl sulfoxide (DMSO, LABSCAN, 99.8%), triethylamine (TEA, Fluka, purum), dimethyl 2,6-dibromoheptanedioate (DMDBHD, Aldrich, 97%), cuprous bromide ($Cu^{I}Br$, Aldrich, 99.999%), cupric bromide ($Cu^{II}Br_2$, Aldrich, 99%), and *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%) were all used as received. Styrene (STY, Aldrich, 99%, 10–15 ppm 4-*tert*-butyl catechol inhibitor) was purified by passage through a column of activated basic alumina (Aldrich, Brockmann I, standard grade, ~150 mesh, 58 Å). Me_6TREN was synthesized following the previously described method by Ciampolini et al.[22] TEMPO–≡ was synthesized following the previously described method by Reiser et al.[23]

Synthesis

4-Hydroxy-2,2,6,6-tetramethylpiperidin-1-yloxyl (TEMPO-OH) (Fig. 6)[6]

To a solution of 2,2,6,6-tetramethyl-4-piperidinol (5.00 g, 31.8 mmol) in MeOH (59.2 mL) was added $NaHCO_3$ (2.13 g, 25.4 mmol), $Na_2WO_4{\cdot}2H_2O$ (0.305 g, 0.923 mmol), and MeCN (4.23 mL, 82.5 mmol). H_2O_2 30% w/w (11.8 mL, 0.110 mol)

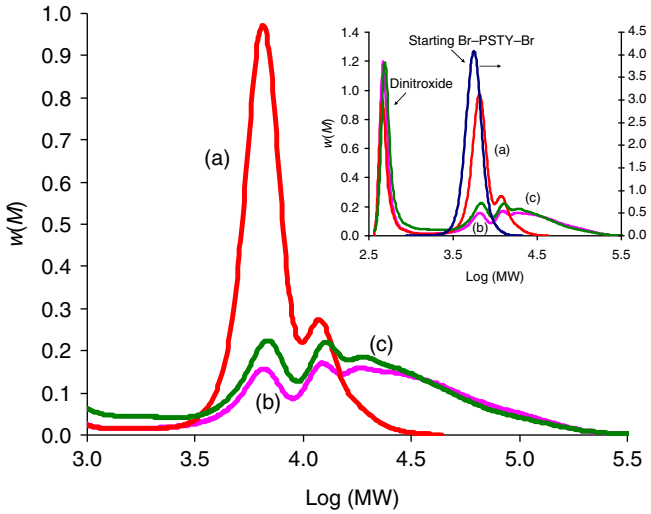


Fig. 3. Weight-normalized size exclusion chromatography (SEC) for (a) a batch SET-NRC reaction with 0.1 equivalents of Br–PSTY–Br ($M_n = 4700$, PDI = 1.09) relative to dinitroxide with $Cu^{I}Br$ added last, (b) a batch reaction with 0.1 equivalents of Br–PSTY–Br ($M_n = 4700$, PDI = 1.09) relative to dinitroxide **1** and letting the $Cu^{I}Br$ equilibrate for 30 min, and then adding the polymer last, (c) a feed reaction when 0.1 equivalents of Br–PSTY–Br were fed into the reaction mixture using $Cu^{I}Br$ (3 equivalents relative to bromine end-groups). Reactions were carried out at 50°C using Me_6TREN in 50/50 v/v toluene/DMSO. All SEC chromatograms were weight normalized and then replotted as $w(M)$ versus log (MW).

was then added dropwise. After stirring in air at room temperature for 38 h the orange/red solution was diluted with brine (100 mL) and extracted with dichloromethane (3 × 60 mL). The organic layer was washed with brine (60 mL) and dried over Na_2SO_4. Removal of the solvent under vacuum gave a bright orange residue that was triturated with hexane to yield 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-yloxyl (TEMPOL) as an orange solid (4.84 g, 88%). R_f (50% EtOAc/hexane) 0.22; ν_{max}/cm^{-1} 3402br, 2974, 2948, 2928, 2858br. *m/z* (GC-MS, EI^+) 172 (M^+, 11%), 158 (6), 142 (8), 85 (33), 71 (100), 57 (51), 41 (97). Only one peak was observed in the GC-MS chromatogram.

*Dinitroxide **1** (Fig. 8), Bis(2,2,6,6-tetramethylpiperidin-4-yloxyl) Terephthalate*

Terephthaloyl chloride (0.725 g, 3.57 mmol) was dissolved in dry toluene (17.9 mL) under argon. A solution of TEMPOL (1.84 g, 10.7 mmol) and dry TEA (4.998 mL, 35.3 mmol) in dry toluene (28.6 mL) was added dropwise to the stirring acid chloride solution. After stirring at room temperature for 48 h under argon, the solvent was removed under vacuum yielding an orange/red solid which was purified by flash chromatography (50/50 EtOAc/hexane) (0.604 g, 36%). R_f (50% EtOAc/hexane) 0.55. The presence of the paramagnetic nitroxide moieties precluded direct analysis by NMR spectroscopy. Consequently, dinitroxide (**1**) was reduced to the corresponding hydroxylamine with phenylhydrazine. δ_H ($CDCl_3$): 1.28 (s, 12H, CH_3CNO), 1.29 (s, 12H, CH_3CNO), 1.80 (m, 4H, $CHCH_2C$), 2.06 (m, 4H, $CHCH_2C$), 5.33 (m, 2H, $COOCHCH_2$), 6.83 (m, phenylhydrazine), 7.26 (m, phenylhydrazine), 7.35 (s, benzene), 8.05 (s, 4H, ArH). The ^1H NMR spectrum also contained resonances attributable to excess phenylhydrazine and its oxidation product, benzene.

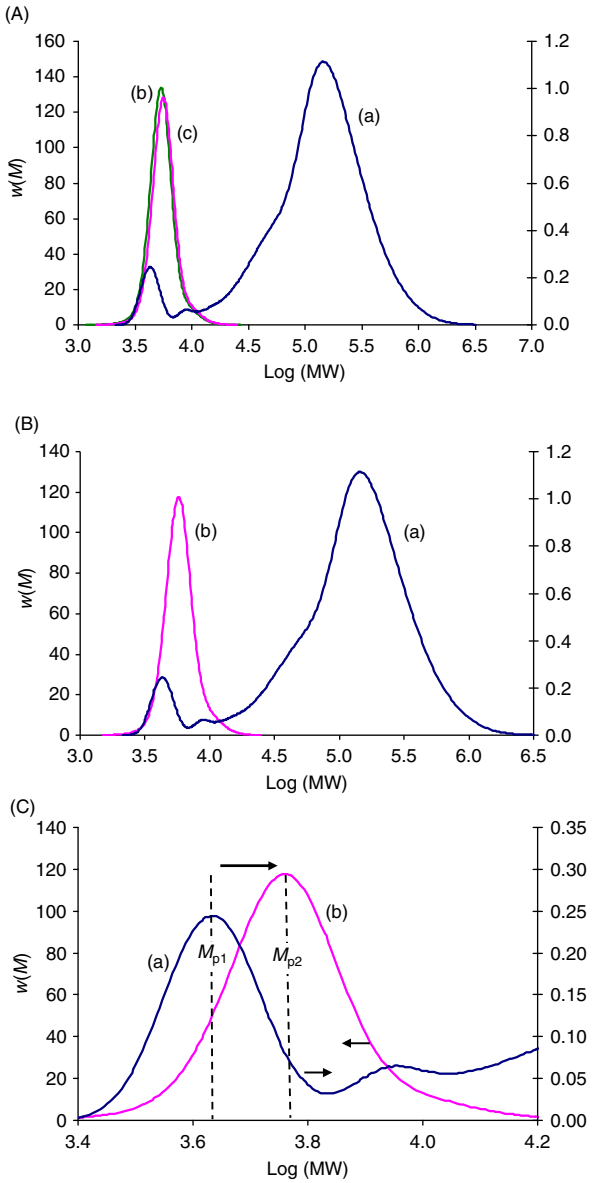


Fig. 4. Weight-normalized distributions by size exclusion chromatography (SEC). (A) Curve a: Multiblock formed through the batch SET-NRC reaction between Br–PSTY–Br ($M_n = 4700$, PDI = 1.09) and dinitroxide using $Cu^{I}Br$ (3 equivalents relative to bromine end-groups) at 50°C in 50/50 v/v toluene/DMSO and Me_6TREN. Curve b: Decoupled multiblock in the presence of TEMPO-OH for 5 h in toluene at 120°C. Curve c: Nitroxide exchange reaction of HO-TEMPO–PSTY–TEMPO-OH with TEMPO–≡ for 5 h in toluene at 120°C. (B) Curve a: identical to curve a in (A). Curve b: Decoupled multiblock in the presence of TEMPO–≡ for 5 h in toluene at 120°C. (C) Magnified view of the low molecular weight region of (B). All SEC chromatograms were weight normalized and then replotted as $w(M)$ versus log (MW).

Synthesis of Polymers

Br–PSTY–Br (Fig. 9)

Styrene (15.39 g, 0.1480 mol), PMDETA (0.351 mL, 1.68×10^{-3} mol), DMDBHD (0.73 mL, 3.36×10^{-3} mol), and $Cu^{II}Br_2$/PMDETA (0.133 g, 3.36×10^{-4} mol) were added to a Schlenk flask and deoxygenated by bubbling with argon for 20 min with vigorous stirring. The contents were stirred for an hour under argon. $Cu^{I}Br$ (0.241 g, 1.68×10^{-3} mol) was then added under a positive argon flow and the contents deoxygenated

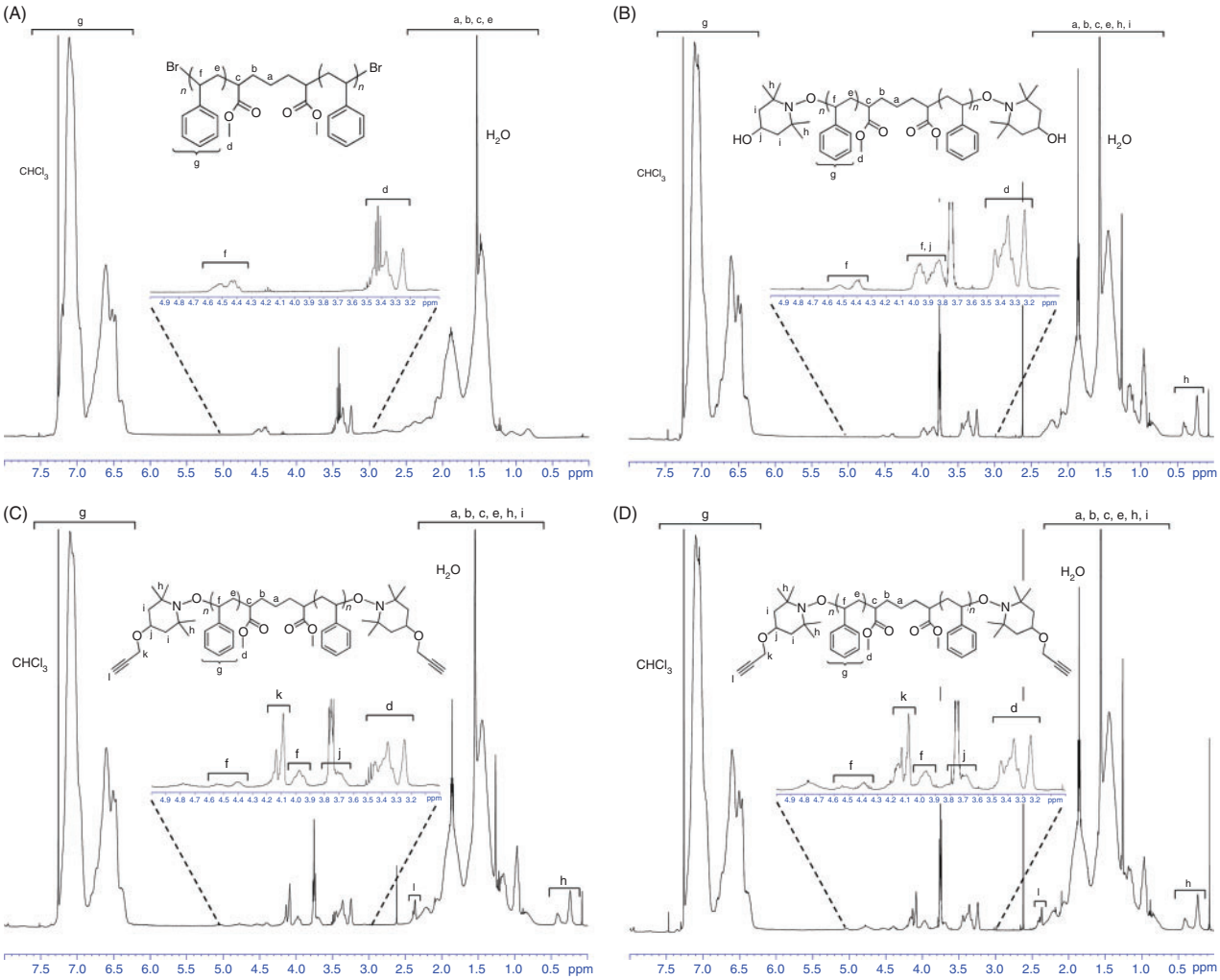


Fig. 5. ^{1}H NMR spectra of: (A) starting Br–PSTY–Br ($M_n = 4700$, PDI = 1.09). (B) HO-TEMPO–PSTY–TEMPO-OH ($M_n = 5010$, PDI = 1.10) after exchange reactions with multiblocks. (C) ≡–TEMPO–PSTY–TEMPO–≡ ($M_n = 5350$, PDI = 1.10) after nitroxide exchange with HO-TEMPO–PSTY–TEMPO-OH ($M_n = 5010$, PDI = 1.10). (D) ≡–TEMPO–PSTY–TEMPO–≡ ($M_n = 5470$, PDI = 1.10) after exchange reactions with multiblocks. Inset: expanded region between 3 and 5 ppm.

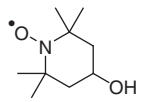


Fig. 6. TEMPO-OH.

by bubbling with argon for a further 5 min. The reaction vessel was then sealed and placed in an oil bath at 80°C. The reaction was stopped by quenching in liquid nitrogen followed by exposure to air. The contents were diluted with DCM and passed through an activated basic alumina column. The solvent was removed under vacuum and the residue dissolved in a minimal amount of DCM. The polymer was precipitated into 10× volume of MeOH, collected by filtration, and dried under vacuum. The resulting polymer was analyzed by size exclusion chromatography (SEC) ($M_n = 4700$, PDI = 1.09).

N_3–PSTY–N_3 (Fig. 10)

NaN_3 (139.12 mg, 2.14×10^{-3} mol) was added to a solution of Br–PSTY–Br ($M_n = 4700$, PDI = 1.09, 503 mg, 1.07×10^{-4} mol) in DMF (3 mL). The reaction mixture was stirred for 16 h at 25°C. The polymer was precipitated in a 10× volume MeOH, recovered by vacuum filtration, and washed exhaustively with water and MeOH. The azide-functionalized polymer was dried under vacuum ($M_n = 4640$, PDI = 1.09).

SET-NRC

Batch Process

Br–PSTY–Br ($M_n = 4700$, PDI = 1.09, 120 mg, 2.56×10^{-5} mol), dinitroxide **1** (10.6 mg, 2.22×10^{-5} mol), and Me_6TREN (35.2 mg, 1.53×10^{-4} mol) (Fig. 11) were placed in a 10 mL Schlenk flask and dissolved in 50/50 v/v toluene/DMSO (1 mL). Oxygen was removed from the solution by three successive freeze–pump–thaw cycles. Cu^IBr (22.0 mg, 1.54×10^{-4} mol) was then added to the frozen solution and the flask re-evacuated. The Schlenk flask was back-filled with argon, sealed, and placed in an oil bath at 50°C with stirring. The reaction was sampled at regular time intervals and analyzed by SEC.

General Method for Feed Formation of Multiblocks

Dinitroxide **1** (21.2 mg, 4.44×10^{-5} mol) and Me_6TREN (70.4 mg, 3.06×10^{-4} mol or 23.5 mg, 1.02×10^{-4} mol) were placed in a 10 mL Schlenk flask and dissolved in 50/50 v/v

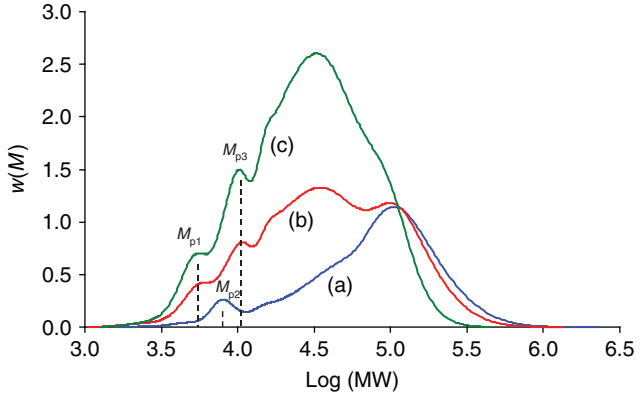
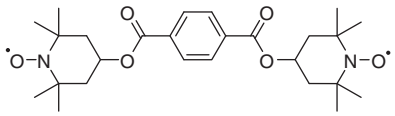


Fig. 7. Weight-normalized size exclusion chromatography (SEC) for multiblock formed by the CuAAC coupling reaction through: (a) route C – between ≡–TEMPO–PSTY–TEMPO–≡ ($M_n = 5350$, PDI = 1.06) and N_3–PSTY–N_3 ($M_n = 4640$, PDI = 1.09), (b) route B – between ≡–TEMPO–PSTY–TEMPO–≡ ($M_n = 5470$, PDI = 1.10) and N_3–PSTY–N_3 ($M_n = 4640$, PDI = 1.09), and (c) route A – between ≡–TEMPO–PSTY–TEMPO–≡ ($M_n = 5350$, PDI = 1.10) and N_3–PSTY–N_3 ($M_n = 4640$, PDI = 1.09). All reactions used Cu^IBr/PMDETA in toluene at 25°C. All SEC chromatograms were weight normalized and then replotted as $w(M)$ versus log (MW).



1

Fig. 8. Dinitroxide **1**.

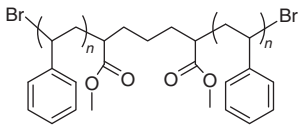


Fig. 9. Br–PSTY–Br.

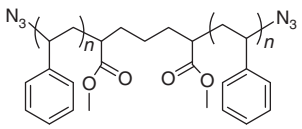


Fig. 10. N_3–PSTY–N_3.

toluene/DMSO (1.0 mL). Oxygen was removed from the solution by three successive freeze–pump–thaw cycles. The Schlenk flask was back-filled with argon, and then Cu^IBr (44.1 mg, 3.07×10^{-4} mol or 14.7 mg, 1.02×10^{-4} mol) was added to the solution under a positive argon flow. The Schlenk flask was sealed and placed in an oil bath at 50°C with stirring. Br–PSTY–Br ($M_n = 4700$, PDI = 1.09, 240 mg, 5.11×10^{-5} mol) was dissolved in 50/50 v/v toluene/DMSO (1.0 mL). Oxygen was removed from the solution by three successive freeze–pump–thaw cycles. The Br–PSTY–Br solution was then placed under an argon atmosphere and added to the previously degassed solution using a syringe pump (1.0 mL at 0.0042 mL min^{-1}). The reaction was then sampled at regular time intervals and analyzed by SEC.

Batch Process – 0.1 Equivalents of Br–PSTY–Br

Br–PSTY–Br ($M_n = 4700$, PDI = 1.09, 12 mg, 2.55×10^{-6} mol), dinitroxide **1** (10.6 mg, 2.22×10^{-5} mol), and Me_6TREN (35.2 mg, 1.53×10^{-4} mol) were placed in a 10 mL Schlenk flask and dissolved in 50/50 v/v toluene/DMSO (0.55 mL). Oxygen was removed from the solution by three successive freeze–pump–thaw cycles. The Schlenk flask was back-filled with argon, and then Cu^IBr (22.0 mg, 1.54×10^{-4} mol) was added to the solution. The Schlenk flask was sealed and placed in an oil bath at 50°C, with stirring. The reaction was sampled at regular time intervals and analyzed by SEC.

Batch Process – 0.1 Equivalents of Br–PSTY–Br, Letting Cu Species Reach Equilibrium First

Dinitroxide **1** (10.6 mg, 2.22×10^{-5} mol) and Me_6TREN (35.2 mg, 1.53×10^{-4} mol) were placed in a 10 mL Schlenk flask and dissolved in 50/50 v/v toluene/DMSO (0.45 mL). Oxygen was removed from the solution by three successive freeze–pump–thaw cycles. The Schlenk flask was back-filled with argon, and then Cu^IBr (22.0 mg, 1.54×10^{-4} mol) was added to the solution under a positive argon flow. The Schlenk flask was sealed and placed in an oil bath at 50°C, with stirring for 30 min to let the copper species reach equilibrium. Br–PSTY–Br ($M_n = 4700$, PDI = 1.09, 12.0 mg, 2.55×10^{-6} mol) was dissolved in 50/50 v/v toluene/DMSO (0.1 mL). Oxygen was removed from the solution by three successive freeze–pump–thaw cycles. The Br–PSTY–Br solution was then placed under an argon atmosphere and added to the previous solution in one batch. The reaction was sampled at regular time intervals and analyzed by SEC.

Decoupling and Exchange Reactions

Nitroxide Exchange of Multiblock with TEMPO–≡

Multiblock ($M_n = 36970$, PDI = 5.29, 106.6 mg) and TEMPO–≡ (272.6 mg, 1.30×10^{-3} mol) were placed in a Schlenk flask equipped with a Teflon screw cap and dissolved in toluene (1.2 mL). Oxygen was removed from the solution by purging with argon (15 min). The flask was sealed under argon and placed in an oil bath at 120°C with stirring for 5 h. The reaction mixture was quenched by cooling in an ice bath and the solvent removed under a flow of air. The residue was dissolved in a minimal amount of DCM and the polymer precipitated in a 10× volume of MeOH. The resulting white precipitate was collected by vacuum filtration and dried under vacuum, to give ≡–TEMPO–PSTY–TEMPO–≡ ($M_n = 5470$, PDI = 1.10).

Nitroxide Exchange of Multiblock with TEMPO-OH

Multiblock ($M_n = 36970$, PDI = 5.29, 119.5 mg) and TEMPO-OH (305.6 mg, 1.77×10^{-3} mol) were placed in a Schlenk flask equipped with a Teflon screw cap and dissolved in toluene (1.4 mL). Oxygen was removed from the solution by purging with argon (15 min). The flask was sealed under argon and placed in an oil bath at 120°C with stirring for 5 h. The reaction mixture was quenched by cooling in an ice bath and the solvent removed under a flow of air. The residue was dissolved in a minimal amount of dichloromethane and the polymer precipitated in a 10× volume of MeOH. The resulting white precipitate was collected by vacuum filtration and dried under vacuum, to give HO-TEMPO–PSTY–TEMPO-OH ($M_n = 5010$, PDI = 1.10).

Nitroxide Exchange of HO-TEMPO–PSTY–TEMPO-OH with TEMPO–≡

HO-TEMPO–PSTY–TEMPO-OH ($M_n = 5010$, PDI = 1.10, 60.0 mg, 1.20×10^{-5} mol) and TEMPO–≡ (100.92 mg, 4.80 ×

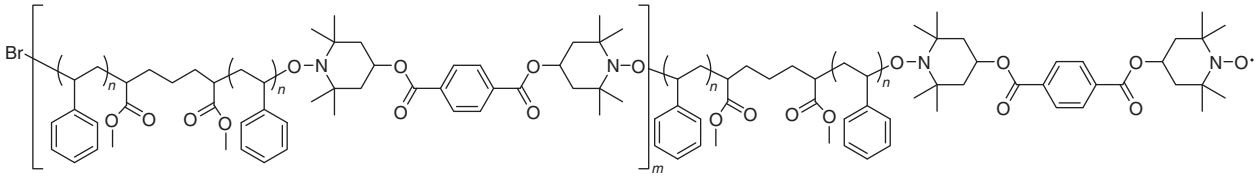


Fig. 11. Multiblocks.

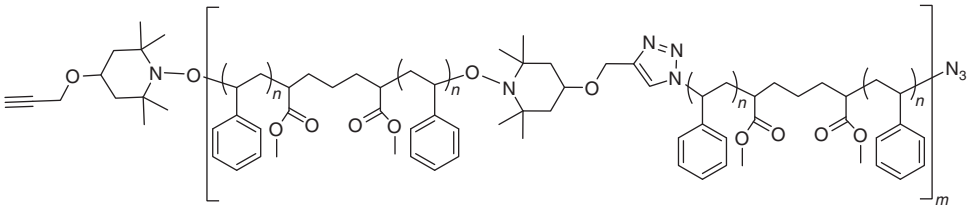


Fig. 12. Reformed multiblocks.

10^{-4} mol) were placed in a Schlenk flask equipped with a Teflon screw cap and dissolved in toluene (0.9 mL). Oxygen was removed from the solution by purging with argon (15 min). The flask was sealed under argon and placed in an oil bath at 120°C with stirring for 5 h. The reaction mixture was quenched by cooling in an ice bath and the solvent removed under a flow of air. The residue was dissolved in a minimal amount of DCM and the polymer precipitated in a 10× volume of MeOH. The resulting white precipitate was collected by vacuum filtration and dried under vacuum, to give ≡–TEMPO–PSTY–TEMPO–≡ ($M_n = 5350$, PDI = 1.10).

NRC Functionalization of Br–PSTY–Br with TEMPO–≡

Br–PSTY–Br ($M_n = 4700$, PDI = 1.09, 100 mg, 2.13×10^{-5} mol), TEMPO–≡ (10.75 mg, 5.11×10^{-5} mol), and Me_6TREN (10.78 mg, 4.68×10^{-5} mol) were placed in a 10 mL Schlenk flask and dissolved in 50/50 v/v toluene/DMSO (1.1 mL). Oxygen was removed from the solution by purging with argon (15 min). $Cu^{I}Br$ (6.72 mg, 4.68×10^{-5} mol) was then added under a positive argon flow. The reaction vessel was sealed and placed in an oil bath at 25°C with stirring for 30 min. The contents were then diluted with DCM and passed through an activated basic alumina column. The solvent was removed under reduced pressure, and the residue was dissolved in a minimal amount of DCM. The polymer was precipitated in a 10× volume of MeOH. The resulting white precipitate was collected by vacuum filtration and dried under vacuum, to give ≡–TEMPO–PSTY–TEMPO–≡ ($M_n = 5350$, PDI = 1.06).

Cu-Catalyzed Huisgen 1,3-Cycloaddition (CuAAC) Reaction of ≡–TEMPO–PSTY–TEMPO–≡ with N_3–PSTY–N_3 to Reform Multiblock (Fig. 12)

A typical procedure is as follows:

≡–TEMPO–PSTY–TEMPO–≡ ($M_n = 5350$, PDI = 1.06, 30 mg, 5.61×10^{-6} mol), N_3–PSTY–N_3 ($M_n = 4640$, PDI = 1.09, 26.04 mg, 5.61×10^{-6} mol), and PMDETA (1.94 mg, 1.12×10^{-5} mol) were placed in a 10 mL Schlenk flask and dissolved in toluene (0.7 mL). Oxygen was removed from the solution by purging with argon (15 min). $Cu^{I}Br$ (1.61 mg, 1.12×10^{-5} mol) was then added under a positive argon flow. The reaction vessel was sealed and placed in an oil bath at 25°C with stirring for 60 min. The reaction was sampled and analyzed by SEC.

Techniques

SEC

All polymer samples were dried under vacuum for 2 days at 25°C before analysis. The dried polymer was dissolved in THF (Labscan, 1 mg mL^{-1}) and the resulting solution filtered using a 0.45 μm PTFE syringe filter. Analysis of the MWDs of the polymers was accomplished using a Waters 2695 Separations Module, fitted with a Waters 410 refractive index detector maintained at 35°C, a Waters 996 Photodiode Array detector and two Ultrastyragel linear columns (7.8 × 300 mm) arranged in series. These columns were maintained at 40°C for all analyses, and were capable of separating polymers in the molecular weight range of 500 to 4 million g mol^{-1} with high resolution. All samples were eluted at a flow rate of 1.0 mL min^{-1}. Calibration was performed using narrow molecular weight PSTY standards (PDI ≤ 1.1) that ranged from 500 to 2 million g mol^{-1}. Data acquisition was performed using Empower software and molecular weights were calculated relative to PSTY standards. All SEC chromatograms were weight normalized and then replotted as $w(M)$ versus log (MW).

^{1}H and ^{13}C NMR Spectroscopy

All NMR spectra were recorded on a Bruker DRX 400 MHz or Bruker DRX 500 MHz spectrometer in deuterated chloroform utilizing an internal lock from residual solvent.

Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR)

ATR-FTIR spectra were obtained using a horizontal, single bounce, diamond ATR accessory on a Nicolet Nexus 870 FT-IR. Spectra were recorded between 4000 and 500 cm^{-1} for 32 scans at 4 cm^{-1} resolution with an OPD velocity of 0.6289 cm s^{-1}. Solids were pressed directly onto the diamond internal reflection element of the ATR without further sample preparation.

Accessory Publication

ATR-FTIR and ^{1}H NMR spectra are provided on the Journal's website.

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References

[1] (a) A. L. J. Beckwith, V. W. Bowry, G. Moad, *J. Org. Chem.* **1988**, *53*, 1632. doi:10.1021/JO00243A008
(b) A. L. J. Beckwith, V. W. Bowry, K. U. Ingold, *J. Am. Chem. Soc.* **1992**, *114*, 4983. doi:10.1021/JA00039A005

[2] (a) E. Rizzardo, A. K. Serelis, D. H. Solomon, *Aust. J. Chem.* **1982**, *35*, 2013.
(b) W. K. Busfield, I. D. Jenkins, M. J. Monteiro, *Polymer* **1997**, *38*, 165. doi:10.1016/S0032-3861(96)00493-4

[3] W. K. Busfield, I. D. Grice, I. D. Jenkins, M. J. Monteiro, *J. Chem. Soc., Perkin Trans. 2* **1994**, 1071. doi:10.1039/P29940001071

[4] (a) K. Matyjaszewski, B. E. Woodworth, X. Zhang, S. G. Gaynor, Z. Metzner, *Macromolecules* **1998**, *31*, 5955. doi:10.1021/MA9807264
(b) Q. Fu, C. Liu, W. Lin, J. Huang, *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 6770. doi:10.1002/POLA.22985
(c) C. Liu, M. Pan, Y. Zhang, J. Huang, *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 6754. doi:10.1002/POLA.22983
(d) W. Lin, Q. Fu, Y. Zhang, J. Huang, *Macromolecules* **2008**, *41*, 4127. doi:10.1021/MA702404T
(e) Q. Fu, W. Lin, J. Huang, *Macromolecules* **2008**, *41*, 2381. doi:10.1021/MA7028117
(f) R. Nicolay, L. Marx, P. Hemery, K. Matyjaszewski, *Macromolecules* **2007**, *40*, 9217. doi:10.1021/MA701923Q

[5] J. Kulis, C. A. Bell, A. S. Micallef, M. J. Monteiro, *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 2214. doi:10.1002/POLA.23991

[6] J. Kulis, C. A. Bell, A. S. Micallef, Z. Jia, M. J. Monteiro, *Macromolecules* **2009**, *42*, 8218. doi:10.1021/MA9014565

[7] (a) M. J. Joralemon, R. K. O'Reilly, J. B. Matson, A. K. Nugent, C. J. Hawker, K. L. Wooley, *Macromolecules* **2005**, *38*, 5436. doi:10.1021/MA050302R
(b) R. J. Thibault, K. Takizawa, P. Lowenheilm, B. Helms, J. L. Mynar, J. M. J. Frechet, C. J. Hawker, *J. Am. Chem. Soc.* **2006**, *128*, 12084. doi:10.1021/JA0648209
(c) M. Malkoch, R. J. Thibault, E. Drockenmuller, M. Messerschmidt, B. Voit, T. P. Russell, C. J. Hawker, *J. Am. Chem. Soc.* **2005**, *127*, 14942. doi:10.1021/JA0549751

[8] (a) X. Luo, G. Wang, X. Pang, J. Huang, *Macromolecules* **2008**, *41*, 2315. doi:10.1021/MA800117D
(b) X. Jiang, E. B. Vogel, M. R. Smith, III, G. L. Baker, *Macromolecules* **2008**, *41*, 1937. doi:10.1021/MA7027962
(c) R. K. O'Reilly, M. J. Joralemon, C. J. Hawker, K. L. Wooley, *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 5203. doi:10.1002/POLA.21602
(d) R. Vestberg, M. Malkoch, M. Kade, P. Wu, V. V. Fokin, K. B. Sharpless, E. Drockenmuller, C. J. Hawker, *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 2835. doi:10.1002/POLA.22178
(e) H. C. Kolb, M. G. Finn, K. B. Sharpless, *Angew. Chem. Int. Ed.* **2001**, *40*, 2004. doi:10.1002/1521-3773(20010601)40:11<2004::AID-ANIE2004>3.0.CO;2-5

[9] W. H. Binder, R. Sachsenhofer, *Macromol. Rapid Commun.* **2007**, *28*, 15. doi:10.1002/MARC.200600625

[10] (a) J.-F. Lutz, *Angew. Chem. Int. Ed.* **2007**, *46*, 1018. doi:10.1002/ANIE.200604050
(b) C. Kluger, W. H. Binder, *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 485. doi:10.1002/POLA.21867
(c) C. N. Urbani, C. A. Bell, D. Lonsdale, M. R. Whittaker, M. J. Monteiro, *Macromolecules* **2008**, *41*, 76. doi:10.1021/MA701993W
(d) C. N. Urbani, C. A. Bell, D. E. Lonsdale, M. R. Whittaker, M. J. Monteiro, *Macromolecules* **2007**, *40*, 7056. doi:10.1021/MA071121N
(e) C. N. Urbani, C. A. Bell, M. R. Whittaker, M. J. Monteiro, *Macromolecules* **2008**, *41*, 1057. doi:10.1021/MA702707E
(f) C. N. Urbani, D. E. Lonsdale, C. A. Bell, M. R. Whittaker, M. J. Monteiro, *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 1533. doi:10.1002/POLA.22528
(g) M. R. Whittaker, C. N. Urbani, M. J. Monteiro, *J. Am. Chem. Soc.* **2006**, *128*, 11360. doi:10.1021/JA0645990
(h) H. Gao, K. Matyjaszewski, *Macromolecules* **2006**, *39*, 4960. doi:10.1021/MA060926C
(i) Y.-Y. Yuan, Y.-C. Wang, J.-Z. Du, J. Wang, *Macromolecules* **2008**, *41*, 8620. doi:10.1021/MA801452N
(j) C. Hua, S.-M. Peng, C.-M. Dong, *Macromolecules* **2008**, *41*, 6686. doi:10.1021/MA800857D

[11] (a) L. M. Campos, K. L. Killops, R. Sakai, J. M. J. Paulusse, D. Damiron, E. Drockenmuller, B. W. Messmore, C. J. Hawker, *Macromolecules* **2008**, *41*, 7063. doi:10.1021/MA801630N
(b) K. L. Killops, L. M. Campos, C. J. Hawker, *J. Am. Chem. Soc.* **2008**, *130*, 5062. doi:10.1021/JA8006325

[12] (a) G. Chen, J. Kumar, A. Gregory, M. H. Stenzel, *Chem. Commun.* **2009**, 6291. doi:10.1039/B910340F
(b) D. Konkolewicz, A. Gray-Weale, S. Perrier, *J. Am. Chem. Soc.* **2009**, *131*, 18075. doi:10.1021/JA908206A

[13] B. M. Rosen, G. Lligadas, C. Hahn, V. Percec, *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 3931. doi:10.1002/POLA.23519

[14] (a) S. Sinnwell, C. V. Synatschke, T. Junkers, M. H. Stenzel, C. Barner-Kowollik, *Macromolecules* **2008**, *41*, 7904. doi:10.1021/MA8013959
(b) L. Nebhani, S. Sinnwell, A. J. Inglis, M. H. Stenzel, C. Barner-Kowollik, L. Barner, *Macromol. Rapid Commun.* **2008**, *29*, 1431. doi:10.1002/MARC.200800244
(c) A. J. Inglis, S. Sinnwell, T. P. Davis, C. Barner-Kowollik, M. H. Stenzel, *Macromolecules* **2008**, *41*, 4120. doi:10.1021/MA8002328
(d) A. J. Inglis, S. Sinnwell, M. H. Stenzel, C. Barner-Kowollik, *Angew. Chem. Int. Ed.* **2009**, *48*, 2411.

[15] (a) V. Percec, T. Guliashvili, J. S. Ladislaw, A. Wistrand, A. Stjerndahl, M. J. Sienkowska, M. J. Monteiro, S. Sahoo, *J. Am. Chem. Soc.* **2006**, *128*, 14156. doi:10.1021/JA065484Z
(b) V. Percec, A. V. Popov, E. Ramirez-Castillo, M. Monteiro, B. Barboiu, O. Weichold, A. D. Asandei, C. M. Mitchell, *J. Am. Chem. Soc.* **2002**, *124*, 4940. doi:10.1021/JA0256055
(c) B. M. Rosen, X. Jiang, C. J. Wilson, N. H. Nguyen, M. J. Monteiro, V. Percec, *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 5606. doi:10.1002/POLA.23690
(d) B. M. Rosen, V. Percec, *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 4950. doi:10.1002/POLA.22328
(e) B. M. Rosen, V. Percec, *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 5663. doi:10.1002/POLA.22888

[16] H.-Q. Xie, X.-Q. Tao, J.-S. Guo, *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *61*, 407.

[17] K. M. Huh, Y. H. Bae, *Polymer* **1999**, *40*, 6147. doi:10.1016/S0032-3861(98)00822-2

[18] (a) M. R. Whittaker, Y.-K. Goh, H. Gemici, T. M. Legge, S. Perrier, M. J. Monteiro, *Macromolecules* **2006**, *39*, 9028. doi:10.1021/MA061070E
(b) N. V. Tsarevsky, K. Matyjaszewski, *Macromolecules* **2002**, *35*, 9009. doi:10.1021/MA021061F
(c) V. Lima, X. Jiang, J. Brokken-Zijp, P. J. Schoenmakers, B. Klumperman, R. Van Der Linde, *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 959. doi:10.1002/POLA.20558

[19] (a) B. A. Laurent, S. M. Grayson, *Chem. Soc. Rev.* **2009**, *38*, 2202. doi:10.1039/B809916M
(b) D. Geiser, H. Hocker, *Macromolecules* **1980**, *13*, 653. doi:10.1021/MA60075A032
(c) J. Roovers, P. M. Toporowski, *Macromolecules* **1983**, *16*, 843. doi:10.1021/MA00240A002

[20] D. E. Lonsdale, C. A. Bell, M. J. Monteiro, *Macromolecules* **2010**, *43*, 3331. doi:10.1021/MA902597P

[21] H. Jacobson, W. H. Stockmayer, *J. Chem. Phys.* **1950**, *18*, 1600. doi:10.1063/1.1747547

[22] M. Ciampolini, N. Nardi, *Inorg. Chem.* **1966**, *5*, 41. doi:10.1021/IC50035A010

[23] A. Gheorghe, A. Matsuno, O. Reiser, *Adv. Synth. Catal.* **2006**, *348*, 1016. doi:10.1002/ADSC.200606043