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Simultaneous atom transfer and nitroxide mediated controlled free radical polymerization of styrene†

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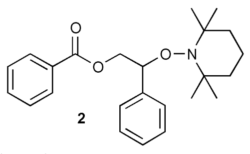
Equimolar mixtures of NMRP and ATRP initiators lead to polystyrene that is unimodal by GPC; the mechanism of action most consistent with the data suggests that under the reaction conditions, TEMPO and Cl end groups scramble rapidly relative to the propagation rate, and result in a single type of polymer chain.

Recent developments in controlled free radical polymerizations of vinyl monomers mediated by either Cu complexes (atom transfer radical polymerization, ATRP) or by TEMPO-derivatives (nitroxide mediated radical polymerizations, NMRP) have stimulated much research as they yield homopolymers and block copolymers with predictable MWs along with narrow polydispersities.[1]

While ATRP and NMRP are almost always used separately, we wondered whether the ATRP and NMRP initiators could each be used as the end groups on a single polymer chain. Critical to the success of this idea is whether the ATRP and NMRP end groups show crossover reactivity. If no crossover occurs, then the end groups of a one-pot mixed ATRP–NMRP initiator system should operate independently and grow polymers of different molecular weights if the rates of polymerization are different. If ATRP and NMRP end groups do exchange, however, then the structure of the resulting polymers will be sensitive to the relative rates of exchange and propagation.

To first address the issue of end group reactivity, four initiators (**1**–**4**) were used to synthesize polystyrene (PS): the monofunctional ATRP initiators benzyl chloride **1** and 4-(pyren-1-yl)butyl 3-chloromethylbenzoate **3**,[2] the monofunctional NMRP initiator 2-phenyl-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)ethyl benzoate **2** and the symmetrical difunctional NMRP initiator bisphenol A bis[2-phenyl-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)ethyl carbonate] **4**.



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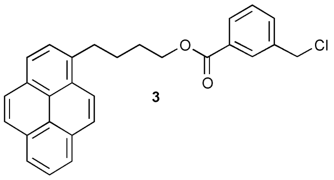

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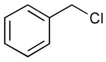

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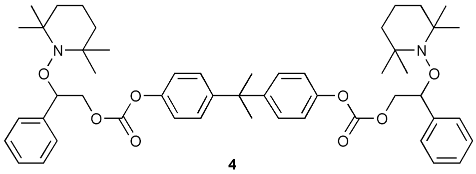

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Polymerization conditions were chosen where both ATRP and NMRP mechanisms should be able to function, and were not varied during the study. Reaction solutions were first degassed with three freeze–pump–thaw cycles, and the polymerizations run at 135 °C under nitrogen (4 h), with equimolar amounts of initiator, CuCl, hexamethyltriethylenetetramine (N_4)[3] and acetic anhydride.[4] The results are listed in Table 1.

Prototypical ATRP and NMRP initiators were first tested separately as control reactions. Under exclusive ATRP conditions monofunctional initiator **1** (benzyl chloride) gave **PS-1a** (M_n = 36 000 g mol^{-1}, 70% conversion) and PDI of 1.89 (Table 1, entry **1a**). Polymerization of styrene using **1** under the modified ATRP–NMRP conditions (addition of acetic anhydride) also yielded PS with a broad MWM_n (distributions (MWD) PDI = 2) and polydispersity index, of 62 000 g mol^{-1} (42% conversion) (Table 1, entry **PS-1b**). Unlike typical ATRP conditions where the catalyst is a greenish colour, the modified reaction solution is deep blue.[5] Both experiments show that for **1**, the ATRP mechanism does not effectively control the polymerization under these conditions, and autopolymerization likely dominates. Polymerization of **3** under ATRP conditions is fast (100% conversion) and yields **PS-3** with a M_n of 28 000 g mol^{-1}, significantly closer to the theoretical M_n of 21 000 g mol^{-1}. The GPC chromatograms at 254 and 350 nm are both unimodal; the 350 nm trace is slightly shifted towards lower MW as expected for a chromophoric endgroup.[6] Polymerization of styrene with NMRP initiator **2** under exclusive NMRP conditions (no CuCl–N_4) was slow (14% conversion) and resulted in low molecular weight **PS-2** (M_n = 4600 g mol^{-1},

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† The IUPAC name for a nitroxide is aminoxyl.

Table 1 MWD of PS obtained using modified NMRP–ATRP conditions

Entry	Initiator(s)	Reaction	$M_{n,\ calc.}$[a]/ g mol^{-1}	$M_{n,\ exp.}$ GPC[b]/ g mol^{-1}	PDI	Conversion[c] (%)
PS-1a	**1**	ATRP[d]	21 000	36 000	1.89	69
PS-1b	**1**	ATRP/Ac_2O[e]	21 000	62 000	1.97	42
PS-2	**2**	NMRP[d]	21 000	4 600	1.32	14
PS-3	**3**	ATRP[d]	21 000	28 000	1.52	100
PS-4	**1,2**	NMRP–ATRP[f]	10 500	9 000	1.29	50
PS-5	**2,3**	NMRP–ATRP[f]	10 500	9 000	1.46	60
PS-6	**3,4**	NMRP–ATRP[f]	10 500	18 500	1.42	73
PS-7	**PS-6**	Hydrolysis[g]	n/a	15 000	1.25	n/a

[a] Based on ratio of moles of initiation sites and styrene for 100% initiation and 100% conversion. [b] Based on PS standards, THF, UV (254 nm) detector. [c] Based on isolated yield. [d] 200 equiv. of styrene. [e] Ac_2O equimolar to **1**. [f] 100 equiv. of styrene. [g] In KOH–dioxane, 80 °C overnight, followed by acidification (HCl) and precipitation into MeOH–water.

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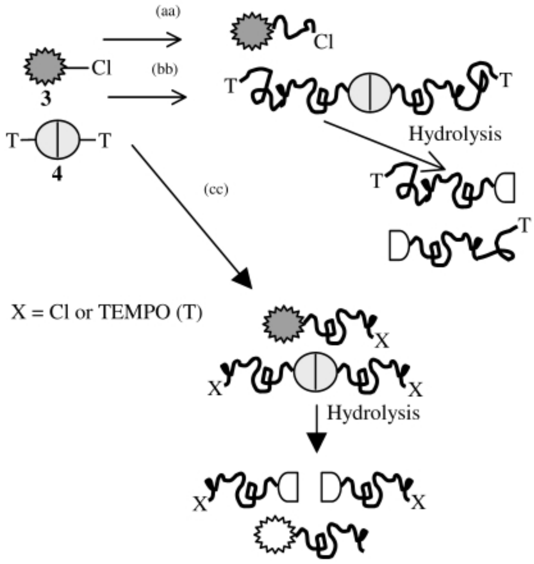

Scheme 1 Scenarios (aa)–(cc) for the polymerisation of styrene in a one-pot mixture of ATRP and NMRP initiators **3** and **4**.

PDI = 1.32), which if extrapolated to 100% conversion results in M_n of 29 000 g mol^{-1}. Combining monofunctional ATRP and NMRP initiators **1** and **2**, respectively, together (one pot), obtains **PS-4** that was *monomodal* by GPC (M_n = 9000 g mol^{-1}, PDI = 1.29, 50% conversion). The monomodal distribution has several mechanistic interpretations: either (a) **1** or **2** initiates and propagates; or (b) **1** and **2** each initiate, but they propagate independently and at the same rate; or (c) the chlorine atom and nitroxide radicals exchange rapidly between end groups relative to propagation, *i.e.* the end groups don't remain unique.

To test for scenario (a) and to determine if the ATRP initiator led to polymer, UV-tagged **3** was employed together with **2**. The resulting polymer **PS-5** again was unimodal by GPC (M_n = 9000 g mol^{-1}, PDI = 1.46, 60% conversion), similar to **PS-4**. Most significantly, GPC traces recorded at 254 and 320 nm were superimposable and confirmed that initiation of at least the benzyl chloride functionality occurs in the mixture.

To similarly test if the NMRP initiator led to polymer, 0.5 equiv. of the difunctional initiator **4** was employed with one equiv. of **3**. This experiment allows three scenarios to be distinguished (see Scheme 1): (aa) if only **3** initiates and propagates, then a monomodal GPC trace with overlapping 254/350 nm GPC absorbances would result; (bb) if only compound **4** initiates and propagates, then no GPC trace would be observed at 350 nm and hydrolysis of the carbonate linkage would cut the resulting PS in half; (cc) if both types initiate and the end groups exchange more rapidly than propagation occurs, then a bimodal GPC trace would result with the low MW peak being UV-active at 350 nm. Hydrolysis of the carbonate linkage should halve the MW of the peak that doesn't absorb at 350 nm and return to an overlapping 254/350 nm GPC chromatogram.

This combination of **4** and **3** yielded **PS-6** (M_n = 18 500 g mol^{-1}, maximum peak at 30 000 g mol^{-1}, and PDI = 1.42, 73% conversion) that was *bimodal* at 254 nm and *unimodal* at 350 nm (Fig. 1). The 350 nm UV-active peak at M_n ~ 15 000 g mol^{-1} confirms that **3** has initiated and propagated in the presence of **4**, consistent with the experiment in entry **3**. A separate peak at ~ 30 000 g mol^{-1} in the 254 nm trace confirms that **4** also initiates and propagates in the presence of **3**. Since both initiators lead to polymer, these data eliminate scenarios (aa) and (bb) where only a single initiator leads to polymer.

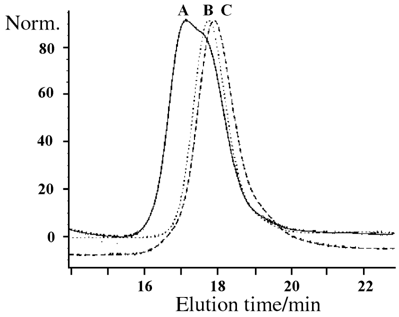

Fig. 1 GPC chromatogram of **PS-6** at 254 nm (A), 350 nm (B), and of **PS-7** at 254 nm (C).

Hydrolysis of **PS-6** yields **PS-7** that is *unimodal* at 254 nm (M_n = 15 000 g mol^{-1}, PDI = 1.25), and is now superimposable with the 350 nm GPC trace of **PS-5** (Fig. 1). Since all three PS blocks have the same MW, these data indicate that either the two propagation mechanisms form polymer at the same rate [*cf.* scenario (b)], or some process permutes the end groups rapidly enough to have a single propagation rate constant describe chain growth [scenario (c)].

From the productivity and MWD of the resulting PS as compared to the controls, it is clear that the modified reaction conditions affect both the ATRP and NMRP processes and most reasonably point to a common propagation mechanism for each of the two initiators in the reaction. For this to occur, Cl and nitroxide end groups must exchange rapidly relative to propagation. Crossover experiments in NMRP processes show that nitroxide end groups freely permute between growing polymer chains *via* indiscriminate nitroxide–radical recombinations,[7] and presumably do so in the present experiments as well. By homolysing the benzyl chloride end group, the ATRP mechanism similarly generates benzyl radicals and the opportunity to redeposit the $\mathrm{Cl}^{\bullet}$ onto a nitroxide derived free radical. Thus, Cu^{I} amine complexes might reasonably catalyse the exchange between Cl and nitroxide end groups, and provide a mechanism for the global exchange of end groups.

In summary, the data presented herein indicate that under our reaction conditions, the NMRP and ATRP mechanisms do not operate independently and end group crossover occurs. Consequently, both initiators lead to polymers that grow at a common rate. However, the data don't distinguish if ATRP, NMRP, or both mechanisms are responsible for chain growth.

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Notes and references

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