

Computational Design of pH-Switchable Control Agents for Nitroxide Mediated Polymerization†

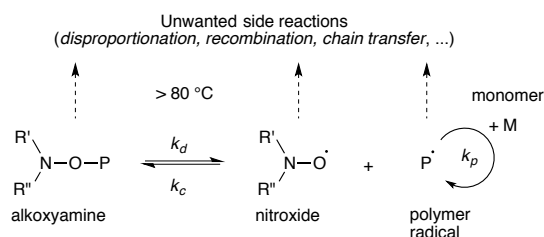
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In the present work we use accurate quantum chemistry to evaluate several known and novel nitroxides bearing acid-base groups as pH-switchable control agents for room temperature NMP. Based on G3(MP2,CC)(+)//M06-2X/6-31+G(d) calculations with UAKS-CPCM/M06-2X/6-31+G(d) solvation corrections, a number of novel nitroxides are predicted to be suitable for controlled polymerization of bulk styrene at room temperature when deprotonated (*i.e.* negatively charged), while remaining inert when neutral. These include an α -ethyl analogue of 3-carboxy-PROXYL and novel derivatives of 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide (TIPNO) that have been modified to include acidic groups. Among the other species evaluated, 3,4-dicarboxy-PROXYL, α -carboxylated PROXYL and the phosphoric acid derivative of *N*-(2-methylpropyl)-*N*-(1-diethylphosphono-2,2-dimethylpropyl)-*N*-oxyl (SG1) are predicted to undergo suitable pH-switching at around 60°C, and may also be fitting for some applications.

Introduction

Controlled (living) radical polymerization (CRP) is an invaluable technique for synthesising functional materials with predetermined molecular weights and architectures.¹ Control is achieved by maintaining the concentration of the propagating polymeric radicals at a sufficiently low level, relative to the total number of polymer chains, by reversibly trapping them as a dormant form that is protected from deactivation *via* various side-reactions. There are several successful CRP types, differing principally in the chemistry of this dynamic equilibrium, including: atom transfer radical polymerization (ATRP),² reversible addition-fragmentation chain transfer (RAFT)³ and nitroxide mediated polymerization (NMP).⁴

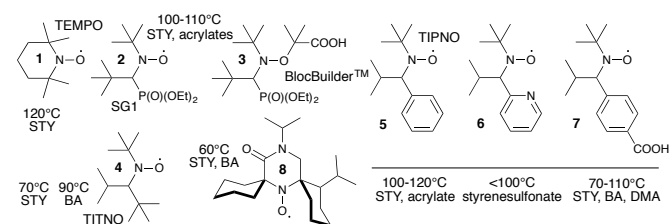
controlling the activation and deactivation of the nitroxide. For high temperature nitroxides such as TEMPO, this is easily managed in that the alkoxyamines are stable at normal service / storage temperatures and are easily activated for polymerization by heating. However, for a room temperature active NMP agent, some means of (reversibly) deactivating the alkoxyamine is essential. One possible strategy for switching the reactivity of nitroxides and their alkoxyamines is *via* pH. As shown in **Figure 1**, both the nitroxide and alkoxyamine feature polar bonds, stability of which should in principle be susceptible to the external electric fields. In practical terms, manipulating the leaving group on the initial alkoxyamine is only likely to be effective for the first initiation step, as the leaving group will become an increasingly remote end group on the growing polymer radical.



Scheme 1. General scheme of the main equilibrium, propagation and competing side-reactions in the NMP.

Of these techniques, NMP (**Scheme 1**) offers a number of attractive advantages including the low toxicity of the colourless and odourless nitroxide control agent, and the ease of post-functionalization of the polymer chain. However, the requirement for relatively high polymerization temperatures contributes to the high-energy costs associated with the process, and increases the interference from unwanted side-reactions within the polymerization.⁵ Thus, an on-going challenge is the design of new nitroxides that are capable of operating at lower temperatures. Several successful strategies of increasing the alkoxyamine decomposition rate k_d , employing polarity and steric hindrance of the nitroxide, have been reported (see **Scheme 2**, as well as refs 6 and 7). Despite these important advances, a universal approach to a room temperature NMP remains elusive.

As one drives the polymerization temperature closer to room temperature, this raises a second challenge – that of



Scheme 2. Nitroxide radicals, monomers (STY - styrene, BA - butylacrylate, DMA – dimethylacrylamide, VC – vinyl chloride) and temperatures in exemplary NMPs: 2,2',6,6'-tetramethylpiperidine-*N*-oxyl (TEMPO, **1**),^{8,9} *N*-(2-methylpropyl)-*N*-(1-diethylphosphono-2,2-dimethylpropyl)-*N*-oxyl (SG1, **2**)¹⁰ and its alkoxyamine initiator BlocBuilder™ (**3**),¹¹ 2,2,5-trimethyl-4-tert-butyl-3-azahexane-3-oxyl (TITNO, **4**)¹², 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide (TIPNO, **5**) and its derivatives **6** and **7**,^{13,14,15,16} malonyl radical derived nitroxide **8**.¹⁷

In recent years, a number of nitroxide control agents containing acid/base functional groups have been developed. These were initially designed with a view to increasing the water solubility of the nitroxides and/or alkoxyamine initiators, rather than switching the reactivity itself. Thus, in a number of cases, the kinetic behaviour of these reagents in their charged and non-charged forms has not yet been directly compared.¹⁸ Nonetheless, the prospect of exploiting polar effects to pH switch reactivity has received increasing attention, and a number of literature examples are shown in **Scheme 3**. Summarising these results, protonation of basic groups on either the nitroxide or leaving group can lead to decreases in k_d of around an order of magnitude in both non-polar and

polar solvents, consistent with the behaviour expected from **Figure 1**. Interestingly, in the literature examples thus far tested negative charges have been shown to have a negligible effect. For example, Bertin *et al.*¹⁹ have shown experimentally that the ionisation of COOH in the leaving alkyl fragment of BlocBuilder™ (**3**) has little effect on its decomposition rate constant k_d , though it dramatically increases its solubility in polar solvents, while Edeleva *et al.*²⁰ found that deprotonation of carboxy groups on **10** also had negligible effect on k_d . Significantly, both of these experiments were carried out in polar solvents.

Recently, we have shown that negative charges can exert much larger pH-switches on the stability of nitroxides in low polarity environments.²¹ Using high-level *ab initio* molecular orbital theory calculations, validated by mass spectrometry experiments,²² we have shown that, for example, the gas-phase bond dissociation energies (BDEs) of a range of alkoxyamines of 4-carboxy-TEMPO (**12**) are reduced by around 20 kJ mol⁻¹ upon deprotonation of the carboxylic acid group. It is worth noting that this increase in radical stability (by more than 2300 fold) is significantly greater than any of the effects so far reported for positive charges, and acts over a much longer range (5.7 Å from negative charge to radical centre, compared with 3.5 Å in **10**). We have shown that the effects are electrostatic and can be replicated when the charged group is replaced with an electric field of the same polarisation. Moreover, this long-range radical stabilisation can occur whenever delocalised radicals interact with localised negative charges, and arises in the increased polarisability of

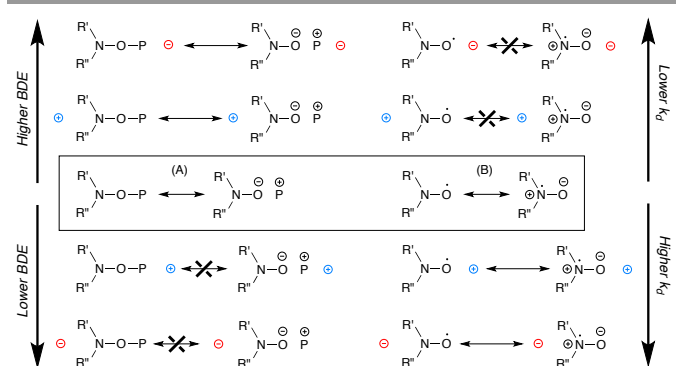


Figure 1. Effects of charged groups on the stabilities of the alkoxyamine and product nitroxide radical. On the nitroxide side a positive charge should stabilise the alkoxyamine and destabilise the nitroxide radical, leading to high BDEs and lower values of k_d , while a negative charge should do the opposite. On the leaving group side a positive charge should destabilise the alkoxyamine and stabilise the radical (provided it remained associated with it), leading to low BDEs and higher values of k_d , while a negative charge should do the opposite.

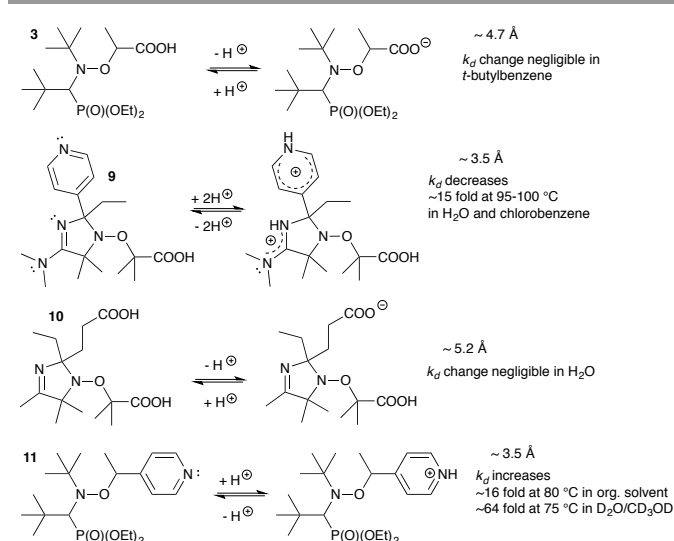
resonance-stabilised radicals, which allows them to minimise electron-electron repulsion.²³

While electrostatic effects are largely quenched in water and highly polar solvents such as acetonitrile and DMSO,²⁴ our theoretical and experimental results prove that they stay largely intact in non-polar organic solvents such as toluene and dichloromethane.²⁵ Thus, provided solubility issues can be overcome, one should in principle be able to increase the k_d in a nitroxide polymerization by 3 orders of magnitude (or more)

through deprotonation of an acid-base group. This raises the exciting prospect of substantially lowering the polymerization temperature of NMP while simultaneously introducing a convenient “on-off switch”. This could potentially enable faster polymerization of a broader range of monomers, under milder conditions and correspondingly diminish the occurrence of the undesired side-reactions that occur at high temperatures. Moreover, the polymer chains so formed will be capped with a pH-sensitive nitroxide, potentially useful for post-functionalization²⁶ *via* nitroxide radical coupling (NRC)²⁷ or binding to various bioactive substrates.²⁸

To date our experimental studies have focussed on the performance of the commercially available reagent 4-carboxy-TEMPO. Whilst this species has a demonstrable pH switch, even in the moderately low polar solvent dichloromethane,²⁵ the solution-phase pH switch on this nitroxide is not sufficient for low temperature NMP. Instead, our preliminary experimental results suggest that, even when switched “on”, it can only lower the temperature for NMP from 120°C to around 100°C, still too high to be practically useful (see Figure S1 of the ESI). To achieve pH-switchable low temperature NMP, we need to design novel nitroxides that are both more stable to begin with and/ or have larger pH switches.

To address this problem, in the present work, we use rigorously benchmarked^{21,29,30} quantum-chemical calculations to assess the suitability of several known and novel nitroxides with acidic substituents for the bulk NMP of styrene (STY). We aim to identify the structures that (i) form NO–STY bonds that



Scheme 3. Literature examples of pH effects on alkoxyamine k_d . For further details see ref 19 for **3**, ref 20 for **9** and **10**, and refs 31,32 for **11**.

are initially weaker than those in TEMPO–STY and (ii) can be weakened even further by deprotonating the acid-base group.

Theoretical Methodology

Standard *ab initio* molecular orbital theory and density functional theory (DFT) calculations were carried out using

Gaussian 09,³³ Molpro 2009.1,³⁴ ADF 2010.01³⁵ and Q-Chem 3.2 and 4.0.³⁶ Calculations were performed at a high-level of theory, previously shown to successfully reproduce a broad general test set of gas-phase bond dissociation energies,²⁹ as well as the solution-phase equilibrium constants of combination reactions in NMP,³⁰ and (gas-phase) pH-switches on alkoxyamine bond dissociation energies.²¹

For all species either full systematic conformational searches (at a resolution of 120°) or, for more complex systems, energy-directed tree searches³⁷ were carried out to ensure global, and not merely local minima were located. These conformational searches were performed in toluene solution using UAKS³⁸-CPCM³⁹/M06-2X⁴⁰/6-31+G(d) method. Geometries of all species were then refined *via* full optimisation at the M06-2X/6-31+G(d) level and frequencies were also calculated at the same level and scaled by the recommended scaling factors.⁴¹

Accurate energies for all species were then calculated using double-layer ONIOM-type method. The core layer was calculated using composite high-level *ab initio* G3(MP2,CC)(+) method,⁴² whereas M06-2X/6-31+G(d) method was applied to the full system. Entropies and thermal corrections at temperatures ranging from 25 to 120 °C were calculated using standard textbook formulae⁴³ for the statistical thermodynamics of an ideal gas under the harmonic oscillator approximation in conjunction with the optimised geometries and scaled frequencies. Reaction Gibbs free energies were computed using Gibbs fundamental equation.

Free energies of solvation in bulk styrene solution (modelled as toluene) were computed using the CPCM-UAKS/B3LYP/6-31G+(d) method in conjunction with relaxed solution-phase geometries. Free energies of each species in bulk monomer solutions at the desired temperature were calculated as the sum of the corresponding gas-phase free energies and the obtained free energies of solvation, and included a phase change correction term $RT \ln(RT/P)$, where R is the universal gas constant, T is the absolute temperature and P is the pressure.

Equilibrium constants were defined and calculated as follows:

$$K_{eq}(T) = \frac{k_c}{k_d} = (c^\circ)^{\Delta n} \exp\left(\frac{\Delta G}{RT}\right) \quad (\text{Eq. 1})$$

In this formula, k_c and k_d are rate constants of combination between the nitroxide and propagating polymer, and corresponding alkoxyamine decomposition, respectively (not calculated in this study); ΔG is the Gibbs free energy of unimolecular decomposition, c° is the standard unit of concentration (equal to P/RT for the gas-phase ΔG and to 1M for already corrected solution-phase ΔG), and Δn is the change of moles in the reaction.

Results and Discussion

Our design strategy is to start with a known nitroxide that is already highly stabilised and incorporate a remote negative charge (e.g., in the form of carboxylate or phosphate group) so

as to induce further stabilisation upon its deprotonation. We already know²¹ that the largest pH-switches⁸ are observed for more stabilised radicals and relatively destabilised anions, and that multiple charges lead to higher switches. On these grounds we have formed the test set shown in **Figure 2**, which includes a number of known compounds (**7**, **12**, **13**, **14**, **15**, **16**)^{15,44} and several synthetically achievable derivatives of known compounds (**17**, **18**, **19-23**).⁴⁵ To the best of our knowledge, none of these compounds have been assessed for their pH switching ability before. **Figure 2** shows their calculated $\log K$ values for trapping of a styrene dimer radical in toluene solution at both 25 °C and 120 °C. It is well known that TEMPO is successful in mediating styrene polymerization at 120 °C,⁸ hence we use the homolysis equilibrium constant K for the corresponding alkoxyamine TEMPO–STY as a reference (green line in **Figure 2**): systems with a lower K are expected to succeed, whereas species with $\log K > 12$ would be too stable to release the propagating radicals at a sufficient rate.⁴⁶

From **Figure 2** we note that protonated 4-carboxy-TEMPO **12** performs almost identically to the non-substituted TEMPO itself – its $\log K$ is *ca.* 12 at 120 °C, but is too high at room temperature to afford polymerization. Deprotonation lowers these values by several orders of magnitude, however insufficiently to reach the threshold at 25 °C. Neutral 5-carboxy-TMIO **15** forms bonds that are slightly weaker than those of TEMPO, however $\log K$ of its deprotonated state is almost identical to that of 4-COO⁻-TEMPO. The pH-switch in

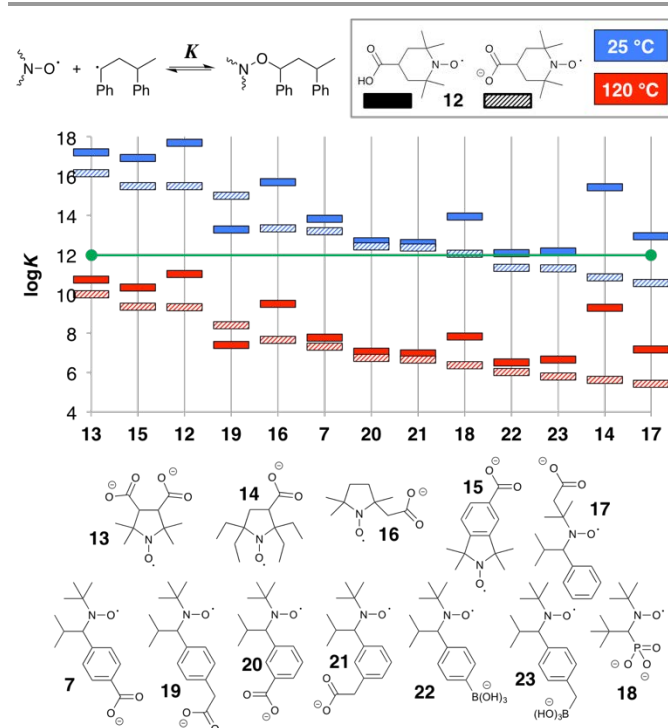


Figure 2. Logarithms of the NO-C bond homolysis equilibrium constants (combination is defined as the forward reaction, decomposition – the reverse one), obtained from the BDFEs for the tested nitroxides with a styryl dimer propagating radical,⁴⁷ calculated in the bulk styrene solution at 25 °C and 120 °C. Green line corresponds to $\log K = 12$. Structures of only the anionic forms are shown.

this system is non-surprisingly smaller, because the carboxylate group in **15** is stabilised *via* conjugation with the aromatic ring. 3,4-Dicarboxy-PROXYL **13** behaves similarly to **12**, however, when doubly deprotonated, its log*K* drops by several orders of magnitude. While it is still above 12 at 25 °C, it is expected to afford significant lowering of the polymerization temperature to 60 °C and possibly less (see Table S1 of the ESI[†]). Likewise, at lower temperatures log*K* of α -carboxylated PROXYL **16** is switched from >12 to <12. The SG1 derivative **18** forms weaker bonds compared to TEMPO even when unswitched, which are weakened even further in its (2-) form to also allow for polymerization temperatures potentially <60 °C (see Table S1 of the ESI[†]).

Furthermore, the carboxy-analogue of TIPNO **7** can also be potentially useful at lower temperatures, although its pH-switch is less pronounced due to aromatic resonance stabilisation of the anion. However, disrupting the conjugation between COOH and aromatic ring by introducing a -CH₂-spacer (**19**) does not improve its behaviour. Instead, the NO-C bond of this nitroxide is strengthened upon deprotonation of a remote carboxylate. This arises from its enhanced conformational flexibility leading to an intramolecular H-bond between the carboxylate of the nitroxide and hydrogen atom(s) of the propagating radical moiety, as shown in Figure S2 of the ESI[†]. Similar intramolecular bonding increases the BDEs of the deprotonated *meta*-carboxy derivatives of TIPNO, **20** and **21**.

Interestingly, this complication is eliminated when COOH group in TIPNO derivatives is substituted by the boronic acid, and correspondingly log*K* values of nitroxides **22** and **23** at 25 °C in neutral form are still above the threshold and hence stable, while switched to anionic form by hydroxylation their log*K* lowers to *ca.* 11.3. An alternative carboxylate derivative of TIPNO, **17**, performs even better in that it affords a larger switch and is predicted to be able to control the NMP of styrene at room temperature. Finally, the PROXYL analogue **14** reveals similar behaviour and also has log*K* < 12 when deprotonated. This nitroxide is characterised with the largest switch, presumably due to the proximity of the charge to the formal radical centre.

Conclusions

In summary, we suggest, based on high-level theoretical calculations, that an α -ethyl analogue of 3-carboxy-PROXYL **14** and several novel derivatives of TIPNO (**17**, **22** and **23**) are expected to control styrene NMP at room temperature, provided their respective acid-base groups are in an anionic form (*i.e.*, carboxylic groups are deprotonated and boronic acid groups are dehydroxylated) and the polarity of the environment is kept low. We also show that certain doubly-charged nitroxides – a derivative of the commercially available SG1 with the (2-)-charged phosphate **18** and 3,4-dicarboxy-PROXYL **13** – also lower the required polymerization temperature to approximately 60 °C, as does α -carboxylated PROXYL **16**. The principal synthetic challenge in implementing these findings experimentally is that of maintaining the

solubility of the deprotonated nitroxide in bulk monomer solution (see Figure S3 of the ESI[†]), however, we envisage that this could be achieved through inclusion of additional unreactive lipophilic side chains on the nitroxide or the choice of solvent.⁴⁸ Lower polymerization temperatures are beneficial not only economically, but also in that they are likely to help diminish the occurrence of unwanted side-reactions. Our results thus offer new strategies for improving the NMP conditions, broadening the scope of controlled monomers and forming polymer chains, capped with a pH-sensitive nitroxide end-group, suitable for further functionalization.

Conflict of interest

There are no conflicts to declare.

Acknowledgements

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Notes and References

§ We define pH-switch on HA-X-R BDFE as BDFE(HA-X-R) – BDFE(-A-X-R). In this was, positive switch means that upon deprotonation the bond is weakened (the BDFE is lowered).

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