A Profluorescent Azaphenalene Nitroxide for Nitroxide-Mediated Polymerisation

John M. Colwell,[A] *James P. Blinco,*[A] *Courtney Hulbert,*[A] *Kathryn E. Fairfull-Smith,*[A] *and Steven E. Bottle*[A,B]

[A]ARC Centre of Excellence for Free Radical Chemistry and Biotechnology, Queensland University of Technology, GPO Box 2434, Brisbane, Queensland, Australia

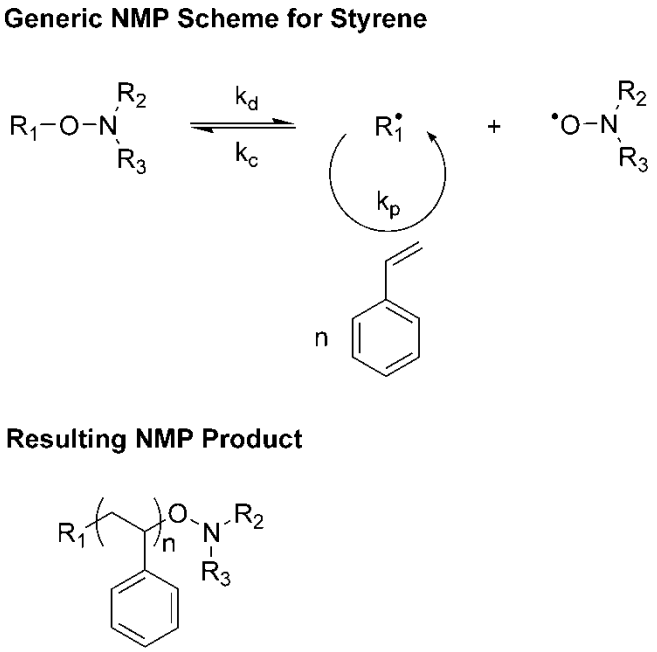
[B]Corresponding author. Email: s.bottle@qut.edu.au

Abstract

A novel nitroxide-mediated polymerisation (NMP) control agent; 1,1,3,3-tetramethyl-2,3-dihydro-2-azaphenalen-2-yloxyl (TMAO), was used in the free-radical polymerisation of styrene. The conversion of styrene during NMP was studied using FT-Raman spectroscopy and the effectiveness of TMAO as a NMP control agent was assessed by GPC analysis. Fidelity of the TMAO-alkoxyamine end-group on the synthesised polymers was confirmed by GPC, UV-Vis, and fluorescence spectroscopy analyses. Comparison to the well-known NMP control agent, TEMPO was made. TMAO showed control of molecular weight approaching that of TEMPO. Attempts to improve the properties of TMAO as a NMP control agent by synthesising an analogue with bulkier substituents around the nitroxide did not generate the target molecule but demonstrated some of the interesting chemistry of the azaphenalene ring system.

Introduction

Nitroxide-mediated polymerisation (NMP) is one of the most common living radical polymerisation techniques. NMP (Scheme 1) was developed at CSIRO in the mid-1980s,[1] and attracted wide-spread interest when Georges *et al.*[2] demonstrated that polystyrene with a relatively narrow molecular weight distribution could be prepared with TEMPO as control agent. Since then, a large number of nitroxides and derived alkoxyamines have been developed as control agents for NMP,[3, 4] and significant research continues in this important field.[3, 5]



Scheme 1. Top: generic scheme for nitroxide mediated polymerisation (NMP) of styrene. Bottom: resulting product from the NMP of styrene.

We have developed a novel nitroxide, TMAO, [1,1,3,3-tetramethyl-2,3-dihydro-2-azaphenalen-2-yloxyl][6] (Fig. 1) that possesses some of the structural rigidity of the isoindoline class of nitroxides, as well as some properties analogous to six-membered

TEMPO nitroxides. TMAO's similarity to TEMPO suggests that it may be a suitable NMP control agent and herein we report a study of the application of TMAO in the controlled free-radical polymerization of styrene.

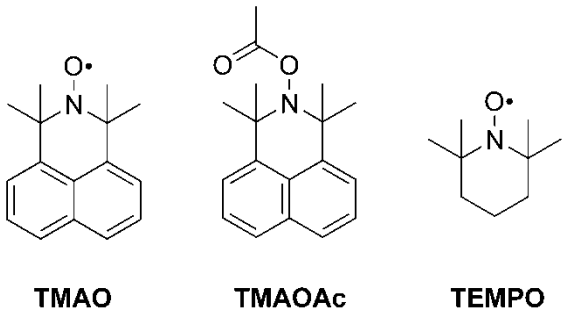


Fig. 1. Nitroxides and a fluorescent derivative used in this study.

In addition to its use as a NMP control agent, the integral fused aromatic ring of TMAO imparts fluorescence that becomes evident only subsequent to the radical scavenging reactions of the nitroxide. This suppressed, or as we have termed it, profluorescent nature can provide a useful analytical tool in the study of free radical polymerisation. For instance, Moad *et al.*[7] have employed this approach in a highly sensitive method for quantitatively determining radical yields in PLP experiments. Profluorescent nitroxides (PFNs) have also been used in methods for determining end-group fidelity and studying exchange rates in NMP through PFN/NMP control agent exchange reactions.[8-11] In addition, PFN have been directly applied for NMP,[12, 13] including for photo-induced NMP.[14, 15] These studies often involve PFN that rely on potentially labile linkages between the fluorophore and nitroxide (*i.e.*, ester, amide *etc.*), which could be cleaved thermally, oxidatively or *via* acid/base hydrolysis. In contrast, TMAO and derivatives thereof present a new class of profluorescent NMP control agents with robust carbon only frameworks linking the fluorophore and nitroxide. These robust carbon only frameworks not only improve the

stability of the PFN, the proximity of the spin to the conjugated aromatic fluorophore leads to enhanced fluorescence suppression. For TMAO, the fluorescence suppression of the naphthalene substructure caused by the presence of the nitroxide ($\Phi_{F\ alkoxy\ amine}$ / $\Phi_{F\ nitroxide}$ = 173)[6] is much greater than for ester-linked naphthalene-based PFNs. Naphthoate and naphthyl acetate derivatives of TEMPO show much lower fluorescence suppressions ($\Phi_{F\ alkoxy\ amine}$ / $\Phi_{F\ nitroxide} \leq 55$).[16] The greater fluorescence suppression shown for TMAO can lead to sensitivity enhancement during fluorescence sensing experiments.

These factors all demonstrate the potential of TMAO and related systems as NMP control agents. Here we describe the first NMP studies in this field using this nitroxide class, report some of the properties of the synthesised polymers, and outline our initial attempts to further improve TMAO as a NMP control agent through chemical modification.

Results and Discussion

The controlled synthesis of polystyrene was undertaken, employing 1,1,3,3-tetramethyl-2,3-dihydro-2-azaphenalenyl-2-oxy (TMAO) as a NMP control agent. Dibenzoyl peroxide (BPO) was used as a free-radical initiator, with the polymerisation conducted at 125 °C. Gel permeation chromatography (GPC) analysis of the purified polymers showed the presence of two main components. One component was a minor, very high molecular weight fraction that eluted mostly at the molecular weight cut-off for the GPC columns (500 000 g mol^{-1}). The major generated component increased in molecular weight as the polymerisation proceeded (Fig. 2). The minor, high molecular weight component was assumed to be from uncontrolled, or ‘dead’, polymer that was not end-labelled with TMAO. A ‘dead’

fraction was also observed where TEMPO was used as control agent. In further developments of this approach to polymer synthesis, this uncontrolled fraction may be minimised by initiating the polymerisation using a unimolecular TMAO-alkoxyamine rather than the bimolecular TMAO-BPO system used here, or by increasing the concentration of TMAO. Both of these approaches have previously been found to improve outcomes for TEMPO/BPO/Styrene polymerisation systems.[2, 17]

The presence of TMAO in the major, controlled molecular weight, fraction of the synthesised polymers was confirmed by dual-wavelength absorbance detection during GPC analysis (Fig. 2). Absorbance at 290 nm (characteristic for TMAO) in TMAO-polystyrene showed strong intensity relative to the absorbance at 254 nm (combined absorbance of styrene and TMAO). The relative intensity at 290 nm decreased as the molecular weight of the polystyrene increased due to the increasing number of absorbing styrene units in the polymer chain compared to the TMAO end-group. Where TEMPO was used as a control agent, the relative intensity of the absorbance at 290 nm compared to absorbance at 254 nm was very low (0.006 compared to 0.11 for an equivalent TMAO-NMP product). These combined results are consistent with the idea that TMAO was attached to the polystyrene chains in the major polymer fraction.

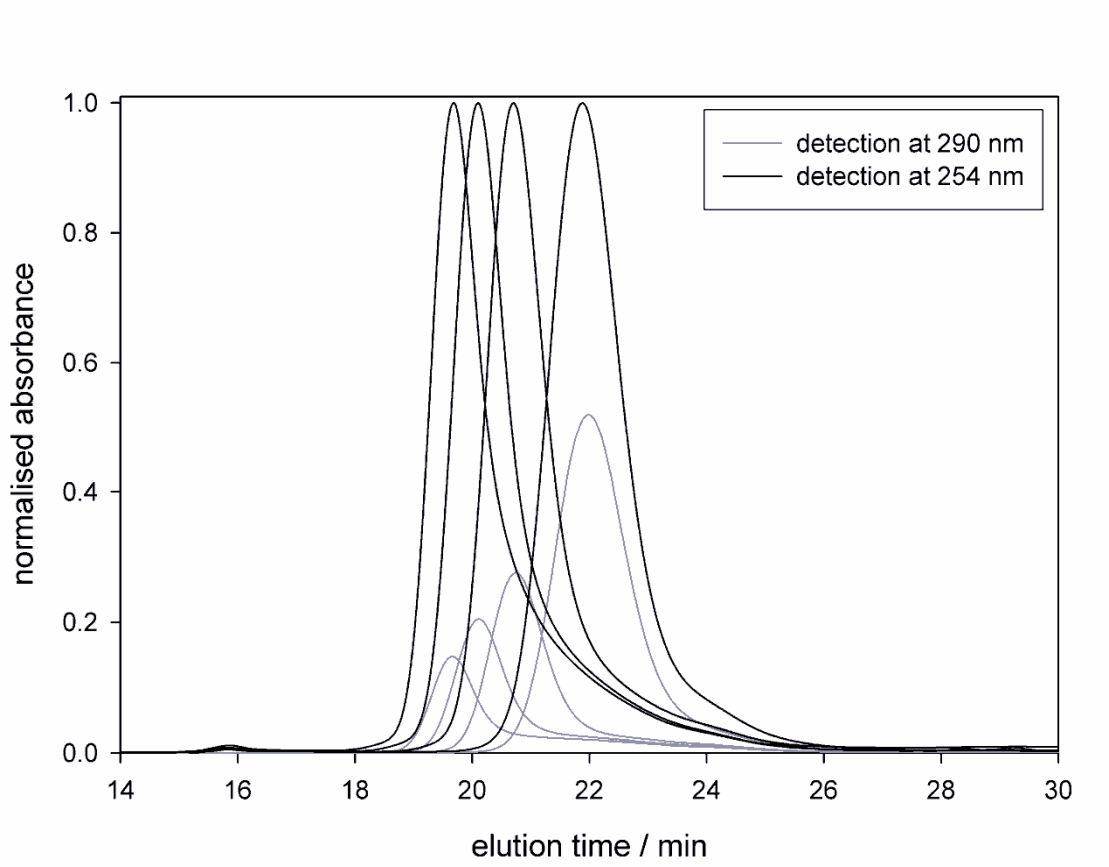


Fig. 2. Normalised GPC traces for TMAO-polystyrene over increasing polymerisation times (right to left; 3.4 to 16.8 h corresponding to α = 0.07 to 0.40). (—) detection at 254 nm, (—) detection at 290 nm.

As further proof for end-functionalisation of the polystyrene by TMAO, analysis by UV-Vis and fluorescence spectroscopy was conducted. By UV-Vis, a combination of typical TMAO absorbance spectra and aggregate-like absorbance was observed for dilute solutions of the TMAO-polystyrene NMP product in DCM. For fluorescence spectroscopy, excimer-like emission was seen to be the dominant phenomenon. The excimer-like emission and aggregate-like absorbance were evident as broad, featureless peaks. These peaks occurred at longer wavelengths than the typical fluorescence emission or UV-Vis absorbance for TMAO and its diamagnetic derivatives. A similar phenomenon has been reported for naphthalene-labelled polystyrene that was prepared by ATRP.[18] Excimer-like fluorescence, as seen here, may arise from particular polymer conformations that increase physical interactions

between TMAO end-groups. It is also possible that the polystyrene chains interfere with the fluorescence emission in some manner. It is expected that the observed phenomena are due to interaction of TMAO end-groups and not due to a physical interaction of free TMAO, or a small fluorescent analogue, with polystyrene. To assess this, a mixture of a small fluorescent analogue of TMAO (2-acetoxy-1,1,3,3-tetramethyl-2,3-dihydro-2-azaphenalene, TMAOAc - Fig. 1) and polystyrene was prepared and analysed by fluorescence spectroscopy. The mixture of TMAOAc and polystyrene produced a typical TMAOAc spectrum and not the excimer-like emission observed from the TMAO-polystyrene NMP product (Fig. 3). This supports that the TMAO is bound to the polystyrene as shown by the GPC analysis.

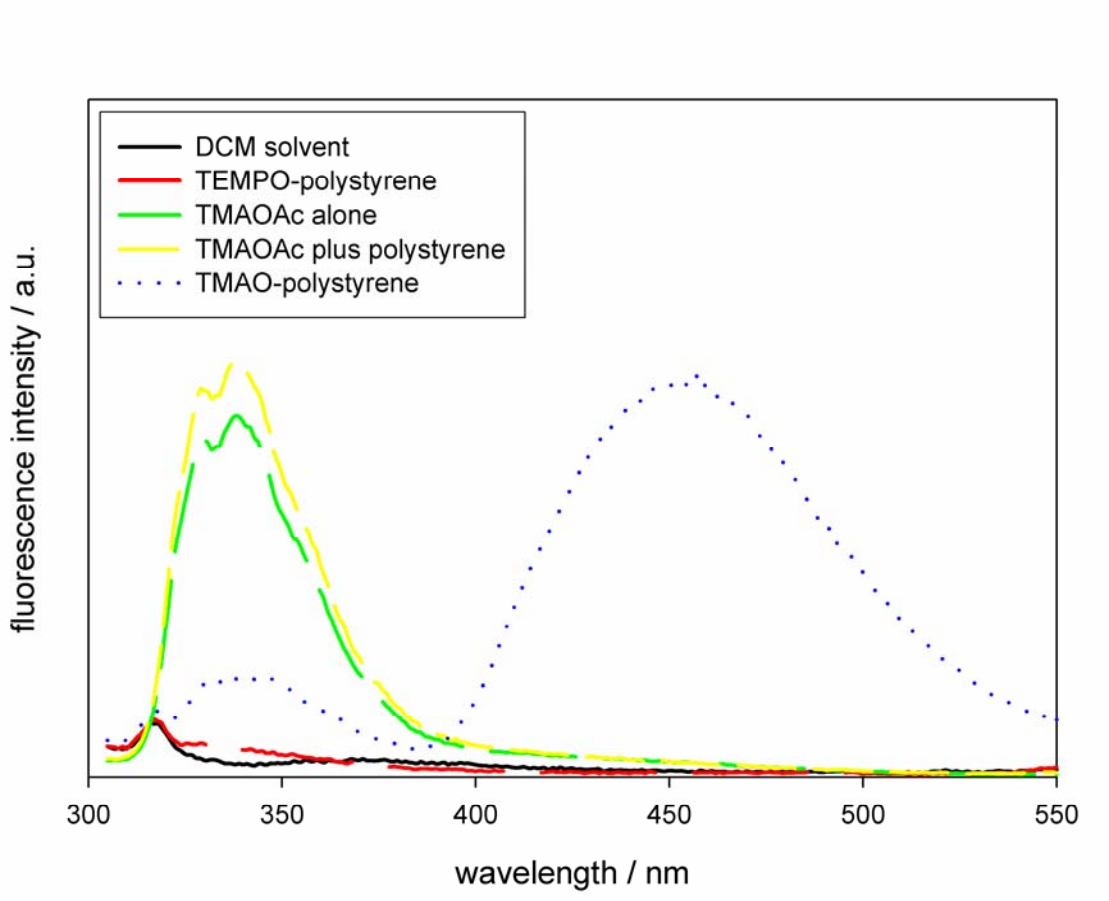


Fig. 3. Fluorescence emission spectra (λ_{ex} = 290 nm) from: (—) DCM solvent, (— —) TEMPO-polystyrene NMP product, (— —) TMAOAc alone, (— —) physical mixture of polystyrene and TMAOAc, and (····) TMAO-polystyrene NMP product. All measurements were made using DCM as solvent. Concentrations (± 3%): TEMPO-polystyrene NMP product, 1.7×10^{-5} M; TMAOAc alone, 3.2×10^{-6} M; physical mixture of polystyrene and TMAOAc, 1.6×10^{-2} w/v% and 3.2×10^{-6} M; TMAO-polystytrene NMP product ($\overline{M_n}_{GPC}$ = 17 900), 8.8×10^{-6} M. For the polymer products, the $\overline{M_n}_{GPC}$ was

used in the calculation of molar concentrations. Both TMAOAc samples have been scaled; actual intensities were a factor of ~ 3.5 higher than shown. Spectra only changed in intensity for higher concentrations of TMAOAc (1.7×10^{-5} M).

Evidence of end-labelling of polystyrene by TMAO through UV-Vis, fluorescence spectroscopy and GPC analyses indicates that TMAO is bound to the polystyrene chains and this predominates in the controlled molecular weight fraction. Therefore, TMAO is likely to be acting as a control agent during polymerisation. Analysis of the main, TMAO-containing, GPC component in each TMAO-polystyrene sample showed polydispersity indices (PDIs) increasing to around 1.35 – 1.40 throughout the polymerisation. Comparatively, when TEMPO was used as control agent a PDI of 1.3 was achieved (comparable to the results of Georges *et al.*[2]). A summary of the synthesis conditions used and the resultant products is shown in Table 1.

Table 1. Summary of polymer synthesis conditions and resultant products

Molar Ratios				Rxn time	Conv, α[A]	$\overline{M_{n\ theor}}$[B]	$\overline{M_{n\ GPC}}$	PDI[C]
Styrene	BPO	TMAO	TEMPO	/ h				
1	-	-	-	23.7	0.86 ± 0.01	-	147 400[D]	1.8[D]
500	1	-	-	7.5	0.82 ± 0.01	22 390	49 100[D]	2.6[D]
500	1	-	2	23.7	0.65 ± 0.01	17 190	19 300	1.30
500	1	2	-	3.4	0.07 ± 0.03	2 340	6 400	1.20
500	1	2	-	7.0	0.20 ± 0.02	5 470	10 100	1.28
500	1	2	-	11.0	0.28 ± 0.02	8 070	13 100	1.31
500	1	2	-	16.8	0.40 ± 0.02	11 200	14 900	1.39
500	1	2	-	30.0	0.60 ± 0.01	16 670	17 900	1.34

[A]Calculated from FT-Raman spectra using Equation 1.

[B]$\overline{M_{n\ theor}}$ = $[\text{styrene}]_0/[\text{BPO}]_0 \times 104.15 \times \text{conversion} + M_r$ end-cap. Calculation of $\overline{M_{n\ theor}}$ using this equation is based on the assumption that the polymerisation is a living system. That is, quantitative initiation by BPO is rapidly achieved and auto-initiation by styrene does not occur.

[C]From the major fraction in GPC.

[D]Part of the sample eluted at the molecular weight cut-off for the GPC columns (500 000 g mol^{-1}).

The relatively low PDIs of the TMAO-polystyrene NMP products suggests that some reasonable degree of control has been achieved during polymerisation. To test the degree of control achieved by employing TMAO as a NMP control agent, a plot of $\overline{M_n}$ *versus* conversion was constructed (Fig. 4). The non-linearity of the plot and the discrepancy between the predicted and experimental data suggests that TMAO/BPO/styrene is not achieving complete control of the polymerisation. The non-linearity of these data may arise from non-quantitative initiation from the BPO and the formation of additional radicals through thermal auto-initiation of styrene. These phenomena would both change the number of growing polymer chains and cause deviation from linearity. To further assess this polymerisation system, analysis of styrene consumption as a function of polymerisation time was performed.

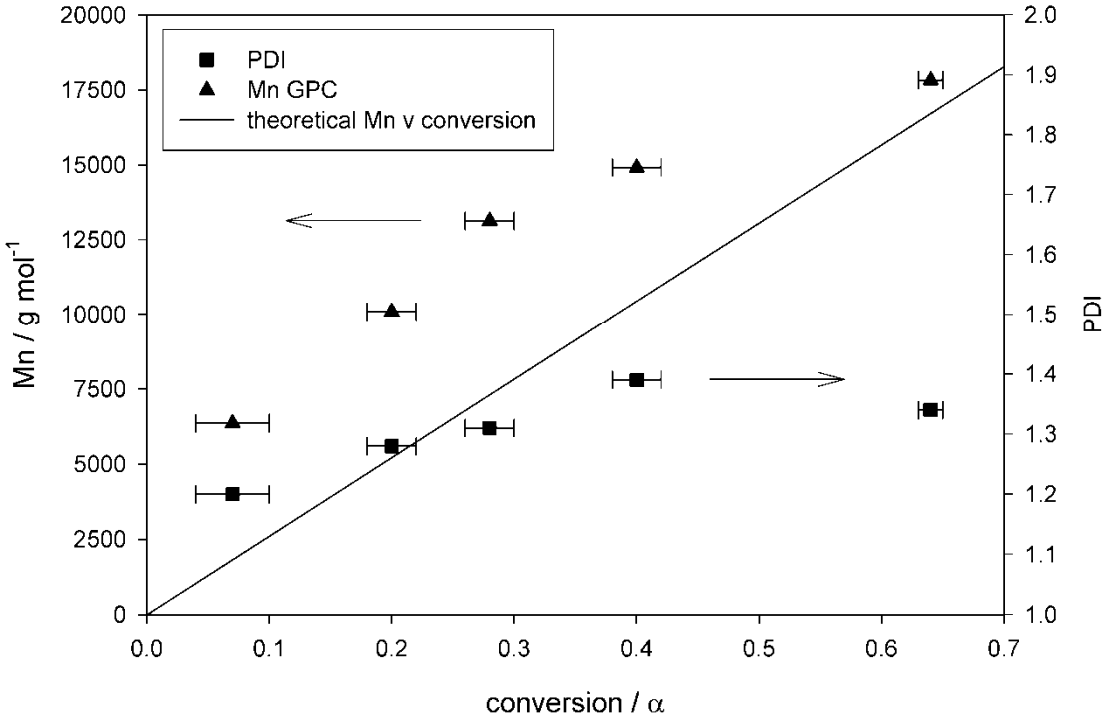


Fig. 4. $\overline{M_n}$ *versus* conversion and PDI *versus* conversion for polystyrene synthesised using TMAO as control agent. (▲) $\overline{M_{n\ GPC}}$; (■) PDI; (—) predicted $\overline{M_n}$ *versus* conversion based on a living system with a constant number of active chains.

The conversion *versus* time plots in Fig. 5 show that TMAO has a much shorter induction time than TEMPO and retardation of polymerisation occurred when compared to styrene/BPO/TEMPO, styrene/BPO, and styrene alone. The rapid trapping of initially formed styryl radicals by TMAO, or TEMPO, causes the observed induction periods, after which the polymerisation rate becomes more dependent on the thermal (spontaneous) polymerisation of styrene.[19] The short induction period and the observed retardation of polymerisation indicates that the TMAO-polymer adducts show a high coupling rate constant, k_c, and a low dissociation rate constant, k_d. Even so, for retardation of polymerisation to occur, the TMAO adducts must have been labile to some degree under the polymerisation conditions employed.

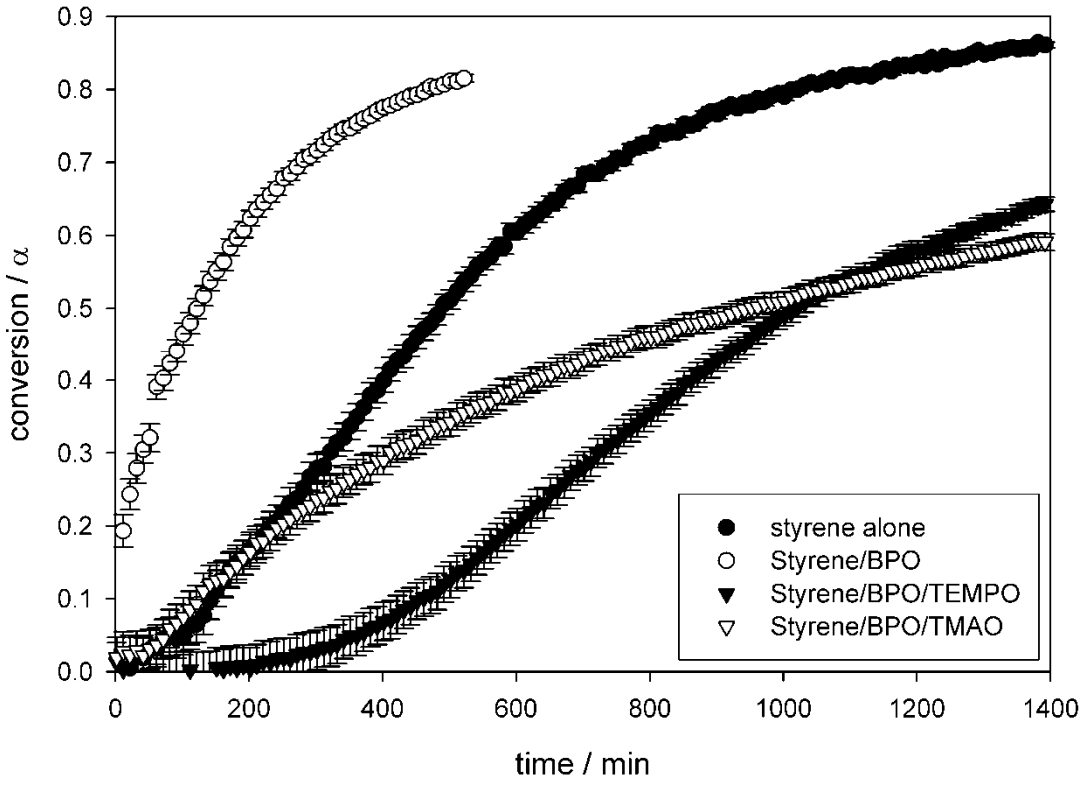


Fig. 5. Conversion *versus* time found by FT-Raman monitoring at 125 °C for: (●) styrene alone; (○) styrene/BPO; (▼) styrene/BPO/TEMPO; and, (▽) styrene/BPO/TMAO.

The observed lability of TMAO is in agreement with what has been found when TMAO was applied as a degradation sensor during the thermo-oxidative degradation of polypropylene (PP).[20] During degradation of PP, carbon-centred radicals are formed. Under oxidative conditions, these radicals can propagate and ultimately lead to failure of the polymer. By trapping the carbon-centred radicals produced during degradation of PP, PFN such as TMAO may act both as stabilisers and sensors. TMAO was found to be a stabiliser for PP during thermo-oxidation, but its fluorescence emission did not increase beyond a certain level during ageing. This is in contrast to what was observed for 1,1,3,3-tetramethylisoindolin-2-yloxyl (TMIO) based PFN where a more stable non-radical adduct is generated. The absence of an increase in TMAO fluorescence emission, yet clear stabilisation of PP indicated that the TMAO did not form stable radical adducts under these thermo-oxidative conditions (150 °C / O_2), but remained in equilibrium as a persistent radical capable of stabilising PP. Even though TMAO-polymer adducts have been shown to be thermally labile, the results from this study suggest that the strength of the TMAO-polymer bond in the context of NMP is still too high to achieve good control under the conditions employed here. To increase the control of polymerisation for TMAO, the stability of the alkoxyamine formed during polymerisation must be modified so that the trapping reaction becomes more reversible. One method that has been used previously to reduce the stability of nitroxide radical traps, and improve their ability to control free-radical polymerisations, is to introduce larger groups around the nitroxide moiety. One relevant example where this approach has proven successful is using the ethyl analogue, 1,1,3,3-tetraethylisoindolin-2-yloxyl (TEISO - Fig. 6, right). TEISO gave good control during NMP of styrene[21] and showed faster C-O bond

homolysis of an alkoxy amine adduct[22] when compared to the less hindered methyl analogue, TMIO (Fig. 6, left).

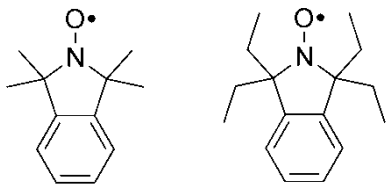


Fig. 6. Left: 1,1,3,3-tetramethylisoindolin-2-yloxyl (TMIO). Right: 1,1,3,3-tetraethylisoindolin-2-yloxyl (TEISO).

In accordance with the observed effects caused by the enhanced steric bulk of the ethyl groups over methyl groups, we attempted the synthesis of the ethyl analogue of TMAO, 1,1,3,3-tetraethyl-2,3-dihydro-2-azaphenalen-2-yloxyl (TEAO – Scheme 2) as a means to create an improved NMP control agent based on the azaphenalene substructure.

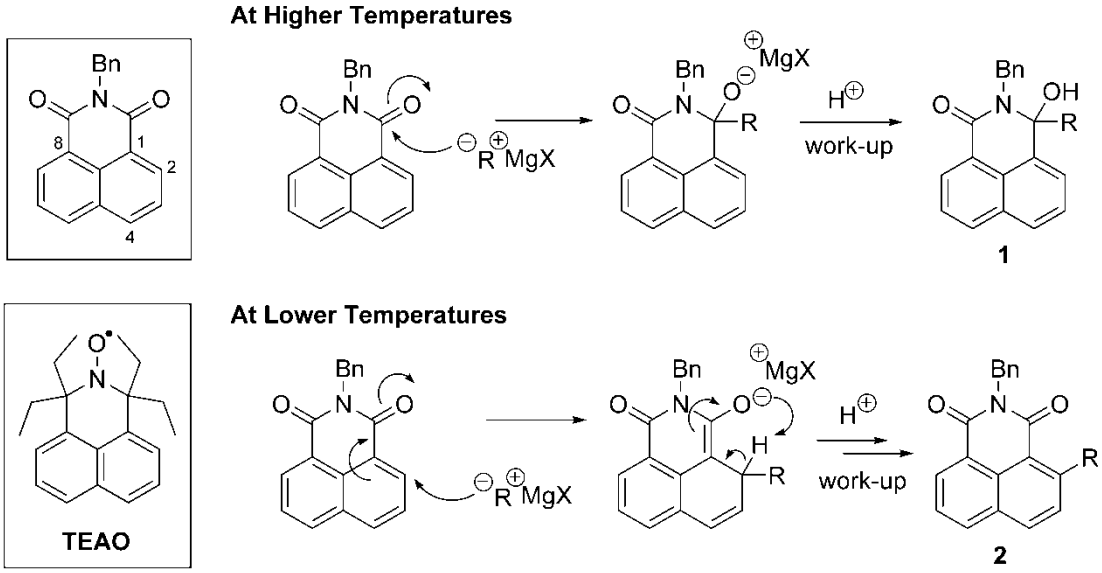
The key synthetic step in the process used to produce azaphenalene and isoindoline nitroxide derivatives involves the exhaustive alkylation of a benzyl protected phthalimide (or naphthalimide) with an excess of alkyl Grignard reagent. In all cases only modest yields of the desired product are achieved (ca. 15-45%),[6, 9, 23] but it has been previously shown for benzyl protected phthalimide that alkylation with an ethyl as opposed to a methyl Grignard reagent leads to an increase in yield (37% for ethyl compared to 28% for methyl)[24]. Initial attempts to produce the tetra-ethyl azaphenalene product were undertaken using identical conditions to those that were used to produce the tetra-methyl adduct. On work-up of the reaction and inspection by TLC, however, there were no discernable spots that could be assigned as the desired product. Potentially, increased steric crowding near the carbonyls in the

naphthalimide, compared to the phthalimide analogues, may make the addition of all four ethyl groups problematic. For this reason, attempts were made to make an ethyl-tri-methyl adduct in one pot by first adding one equivalent of ethyl magnesium bromide in refluxing ether, allowing for single alkylation under milder conditions, followed by an excess of methyl magnesium iodide in a higher boiling solvent. Again, after work-up of the reaction, none of the expected product could be observed by TLC. Attempts were then made to add the ethyl/methyl groups sequentially and isolate the intermediates to try to ascertain where the reaction was differing from the standard exhaustive methylation. The mono-ethylation of *N*-benzyl-1,8-naphthalimide was carried out by reaction with 1.5 equivalents of ethyl magnesium bromide in toluene at 100 °C for 3 hours followed by standard work-up (please see experimental section for more information). This reaction yielded one major product that was able to be recrystallised in methanol.

When characterised by ^{1}H NMR spectroscopy, it was clear that a mono-ethyl adduct had been produced. However, there was no splitting of the benzylic methylene protons, which might be expected for a non-symmetrical mono-addition product (**1**, Scheme 2) due to the formation of the new chiral centre. Inspection of the aromatic region of the spectra suggested that the ethyl group had added to the "ortho", or 2-position, of the aromatic ring rather than reacting with the carbonyl (**2**, Scheme 2). There is literature precedent[25] for similar systems acting as Michael acceptors to give a conjugate addition at the 2-position and the ring then being re-aromatised during work-up. Based on this precedent we have tentatively assigned this product as the 2-substituted regioisomer, although NMR does not exclude 4-substitution as a possible structural candidate (see supplementary material).

Interestingly, in the original synthesis of the tetramethyl analogue TMAO, using excess methyl Grignard reagent,[6] no aromatic ring substitution was detected. To explore this further a similar experiment using only one equivalent of methyl Grignard reagent was undertaken. Upon work-up, a product with substitution at the 2-position on the aromatic ring was again observed, however in a much lower yield and which co-crystallized with the naphthalimide starting material. Notably, when the ethyl Grignard reagent is added to the naphthalimide a homogenous reaction mixture is formed indicating the initial adducts of the Grignard reaction remain in solution. However, when methyl Grignard reagent is added to the naphthalimide, a large insoluble mass is initially generated and this is only solubilised once reflux at 160 °C is achieved. It is possible that at lower temperatures the formation of the 2-addition (see Scheme 2 bottom pathway) is the prominent reaction, but at the elevated temperatures the addition to the carbonyl becomes more competitive (see Scheme 2 top). In the case of the methyl reaction, the formation of the insoluble mass indicates the carbonyl addition product has limited solubility and this drives the formation of this product as it drops out of solution. As the ethyl reaction mixture is homogenous at the lower temperature, the only isolated product is the (favoured) addition at the 2-position. Whatever the basis for the difference in the reaction mechanism and the position of the ring substitution, these results demonstrate that alternative synthetic strategies are necessary to achieve the goal of increased steric bulk azaphenalene-based NMP control agents. Investigations continue, involving changing the reaction conditions as well as introducing the naphthalimide to the Grignard reagent at higher temperatures in order to potentially lead to the desired tetraalkyl azaphenalene analogues. Based on the results for the tetramethyl analogue, the generation of

enhanced steric bulk azaphenalene nitroxides holds the prospect of providing new capping agents useful in controlled polymerisation studies.



Scheme 2. Left, top: numbering system used for *N*-benzyl-1,8-naphthalimide and derivatives. Left, bottom: the desired product from the tetraethylation of *N*-benzyl-1,8-naphthalimide, 1,1,3,3-tetraethyl-2,3-dihydro-2-azaphenalen-2-yloxyl (TEAO). Right: proposed mechanisms for alkyl Grignard addition to *N*-benzyl-1,8-naphthalimide. Top: mechanism at higher temperatures. Bottom: mechanism at lower temperatures.

Conclusions

The nitroxide-mediated polymerisation of styrene was undertaken using the profluorescent nitroxide, TMAO. End-labelling was confirmed by UV-Vis, fluorescence spectroscopy, and GPC analyses. The properties of TMAO as a polymerisation control agent were found to approach TEMPO with respect to its ability to control the molecular weight distribution. Further improvement of TMAO as an NMP control agent requires the synthesis of bulkier tetraethyl analogues. Attempts to modify the structure of TMAO using established synthetic approaches proved unsuccessful. Attempted alkylation using ethyl magnesium iodide gave conjugate

addition to the naphthalene ring, rather than the expected addition at the imide carbonyls, which indicates that alternate synthetic routes need to be discovered.

Experimental

Materials

Styrene (L.R., Ajax Finechem) was purified by passing through aluminium oxide 90 active basic (particle size: 0.063 – 0.200 mm). Dibenzoyl peroxide (BPO), 75%, was purchased from Merck and purified by recrystallisation from chloroform/methanol. TMAO and *N*-benzyl-1,8-naphthalimide were prepared as described in a previous publication.[6] Liquid chromatography grade dichloromethane was used as solvent for all UV-Vis and fluorescence spectroscopy measurements. All other reagents were of analytical reagent grade purity, or higher.

Characterisation Methods

GPC analysis was performed using a Waters GPC system equipped with a Waters 2487 dual wavelength absorbance detector (operating at 254 and 290 nm) and a Waters 2414 refractive index detector connected in series. Three consecutive Phenomenex Phenogel 5μ columns (10^4 Å, 10^3 Å, 50 Å), preceded by a guard column, were used. The system was operated at 30 °C using tetrahydrofuran as eluent at a flow rate of 1 mL min^{-1}. A 7-point calibration using polystyrene standards (1.35×10^3 – 3.821×10^5 g mol^{-1}) was used to obtain molecular weights and polydispersities.

UV-Vis spectroscopy was undertaken using a Varian Cary 50 spectrophotometer.

Fluorescence emission spectra were collected using a Varian Cary Eclipse fluorescence spectrophotometer with excitation at 290 nm.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer and referenced to the relevant solvent peak.

Mass spectra were recorded on an Agilent QTOF LC/MS 6520 using electrospray ionisation (recorded in the positive mode) with a methanol mobile phase and are reported as (*m/z* (%)).

Nitroxide-Mediated Polymerisation

In a typical procedure, BPO (4.09 mg, 1.69×10^{-2} mmol) and TMAO (8.12 mg, 3.38×10^{-2} mmol), or TEMPO (5.38 mg, 3.38×10^{-2} mmol) were dissolved in styrene (0.888 g, 8.45 mmol), then added to a glass reaction vessel equipped with a stir bar and attached to a vacuum line. The solution was degassed by three freeze-pump-thaw cycles. The degassed vessel was flame-sealed and then placed in a thermostated aluminium heating block, which was connected to a Fourier transform-Raman (FT-Raman) spectrometer and maintained at 125 °C over the duration of the reaction (3.5 - 30 hours). The reaction vessel was then broken open and the reaction mixture dissolved in toluene. The toluene solution was filtered through a cotton wool plug to remove glass from the broken vessel, then precipitated in cold methanol (1:10). The precipitated product was collected and washed with methanol followed by drying to constant mass under vacuum. Molecular weight distributions were measured using GPC and conversion was determined by FT-Raman spectroscopy as described below. For some samples, UV-Vis and fluorescence spectroscopy analyses were also undertaken.

Kinetic Measurements by FT-Raman Spectroscopy

FT-Raman spectroscopic measurements were carried out on a Perkin-Elmer System 2000 NIR FT-Raman spectrometer, equipped with a diode-pumped Nd-YAG laser (λ = 1064 nm) as an excitation source and a room temperature InGaAs photoelectric detector. The backscattered radiation was collected at 180° to the excitation. Spectra were recorded every 10 min in the range 200 - 3800 cm^{-1} at a laser power of 320 mW. 32 co-added scans were taken for each spectrum with a spectral resolution of 8 cm^{-1}. Samples were prepared in 50 × 12 mm, flame-sealed glass tubes as per the nitroxide-mediated polymerisation procedure, above. Flame-sealed tubes were placed in a preheated (125 °C), thermo-stated aluminium heating block mounted on a moveable stage inside the spectrometer. Spectra were recorded from the moment the sample was placed in the heating block.

The consumption of styrene was calculated from the FT-Raman spectra. Fourier self-deconvolution (FSD) of the FT-Raman spectra was required before calculation of styrene consumption due to significant overlap of bands. FSD was undertaken using Grams 32/AI software. A gamma factor of 7.6085 and a smoothing (Bessel function) factor of 67.3613 were used for FSD of all spectra. Conversion of styrene was calculated from deconvoluted spectra as follows:

$$\alpha_t = 1 - \frac{(A_{1630}/A_{1000})_t}{(A_{1630}/A_{1000})_{t=10\ min\ for\ styrene\ alone}} \qquad \text{Equation 1}$$

Where α_t is the conversion of styrene at time, t; A_{1630} is the area of the deconvoluted vinyl band at 1630 cm^{-1}; and, A_{1000} is the area of the deconvoluted aromatic ring-breathing mode at 1000 cm^{-1}. The reference sample used to determine the ratio, A_{1630}/A_{1000}, for $\alpha_t = 0$ was styrene alone after 10 min of heating. Since the polymerisation rate was initially low for this sample, it was expected to give the most

accurate ratio (A_{1630}/A_{1000}) for $\alpha_t = 0$ after thermal stabilisation. The upper limit of error in these measurements was estimated from the difference in conversion found by substituting $(A_{1630}/A_{1000})_{t=10 \text{ min for styrene alone}}$ with $(A_{1630}/A_{1000})_{t=30 \text{ min for styrene alone}}$ in Equation 1.

2-Acetoxy-1,1,3,3-tetramethyl-2,3-dihydro-2-azaphenalene (TMAOAc)

A solution of TMAO (0.2 g, 8.3×10^{-1} mmol) in dry THF (10 mL) was treated with palladium (22 mg, 2.1×10^{-2} mmol, 2.5 mol%, 10% on charcoal) and stirred under a balloon of hydrogen gas for 30 minutes. The reaction mixture was cooled to 0 °C and triethylamine (0.23 mL, 2.08 mmol) and acetyl chloride (0.15 mL, 2.08 mmol) were added. The resulting mixture was stirred at 0 °C for 30 minutes after which time the cooling bath was removed and stirring was continued for an additional 1 hour. The mixture was filtered through celite and concentrated *in vacuo*. Water (30 mL) was added and the mixture was extracted with ethyl acetate (3 × 30 mL). The combined organic extracts were dried (anhydrous Na_2SO_4) and evaporated at reduced pressure. The resulting residue was purified by silica gel chromatography (eluent 100% chloroform) to give the *title compound* (0.17 g, 72%) as a cream-coloured solid, mp 111-113°C. ν_{max} (ATR)/cm^{-1} 1759 (C=O). δ_H (400 MHz, $CDCl_3$) 7.74 (dd, J = 7.8, 1.6 Hz, 2 H, Ar-H), 7.43-7.50 (m, 4 H, Ar-H), 2.14 (br s, 3 H, CH_3), 1.69 (s, 6 H, 2 × CH_3), 1.65 (s, 6 H, 2 × CH_3). δ_C (100 MHz, $CDCl_3$) 170.7, 140.4, 133.4, 126.7, 125.7, 121.7, 63.3, 30.9, 27.8, 19.2 (one signal obscured by overlapping). *m*/*z* (ESI) 284 (20%, MH^+), 306 (20, MNa^+), 589 (100, $2MNa^+$). HRMS *m*/*z* (ESI) calcd. 284.1645 for $C_{18}H_{22}NO_2$ (MH^+), found 284.1641.

N-benzyl-2-ethyl-1,8-naphthalimide

N-benzyl-1,8-naphthalimide (1.0 g, 3.48 mmol) was suspended in toluene (50 mL) and commercially available ethyl magnesium bromide (1.8 mL, 3 M solution in diethyl ether, 5.4 mmol, 1.5 equiv.) was added *via* syringe. The solution was refluxed for 3 hours at 100 °C producing a yellow-brown solution, which was cooled and quenched with ammonium chloride (ca. 50 mL). The aqueous layer was extracted with hexane (3 × 50 mL), and the combined hexane extractions washed with water (ca. 25 mL) and sodium bicarbonate (ca. 15 mL). The yellow-coloured, washed hexane extract was then dried (anhydrous Na_2SO_4) before evaporation of the solvent to yield a crude, yellow-brown material (1.1 g). The crude material was recrystallised from methanol to give the *title compound* (0.67 g, 61%) as an off-white crystalline solid, mp 142–144°C. δ_H (400 MHz, $CDCl_3$) 8.61 (dd, J = 7.3, 1.2 Hz, 1H, Ar-H), 8.10 (dd, J = 8.1, 1.2 Hz, 1H, Ar-H), 8.04 (d, J = 8.5 Hz, 1H, Ar-H), 7.66 (dd, J = 8.0, 7.4 Hz, 1H, Ar-H), 7.51-7.56 (m, 3H, Ar-H), 7.26-7.31 (m, 2H, Ar-H), 7.19-7.24 (m, 1H, Ar-H), 5.38 (s, 2H, CH_2), 3.44 (q, J = 7.4 Hz, 2H, CH_2), 1.34 (t, J = 7.5 Hz, 3H, CH_3). δ_C (100 MHz, $CDCl_3$) 164.1, 153.2, 137.6, 134.1, 128.7, 125.9, 122.2, 118.7, 43.4, 29.5, 14.9. *m*/*z* (ESI) 316 (5%, MH^+), 338 (60, MNa^+), 653 (100, $2MNa^+$). HRMS *m*/*z* (ESI) calcd. 316.1332 for $C_{21}H_{17}NO_2$ (MH^+), found 316.1335.

Acknowledgements

We would like to acknowledge the support of the Australian Research Council under the ARC Centres of Excellence program, CE0561607. The authors also acknowledge William Johnston for assistance with some of the GPC and fluorescence measurements.

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