

## **Control of the Radical Polymerization by 2,2,15,15-tetramethyl-1-aza-4,7,10,13-tetraoxacyclopentadecan-1-oxyl and its Sodium Salt**

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## Summary

The control of the radical polymerization of styrene by 2,2,15,15-tetramethyl-1-aza-4,7,10,13-tetraoxacyclopentadecan-1-oxyl is reported here in bulk at 90 °C, 120 °C and in miniemulsion. Similarly the control by its sodium complex is reported in bulk at 90 °C.

## Keywords

crowner, ESR/EPR, nitroxide, polystyrene, radical polymerization.

## Introduction

Thanks to its interesting properties, the conventional free radical polymerization is applied in order to produce many commercial polymers. Among its advantages are the possibility to polymerize a wide range of monomers<sup>[1]</sup> (e. g. acrylates, acrylamides, styrenes and vinyls), the compatibility with many solvents and functional groups<sup>[1]</sup> (e. g. NR<sub>2</sub>, COOH, OH and NCO) and convenient conditions under which this reaction can be performed.<sup>[1]</sup> The temperature range extends from 0 to 150 °C in bulk, in solution, in suspension or in emulsion. Although a radical polymerization requires oxygen free conditions, it can be carried out in water.<sup>[2, 3]</sup> However, its structure control is less efficient when compared to ionic polymerization in terms of molecular weight distribution<sup>[1]</sup>, end-group functionalities and chain branching<sup>[2, 4]</sup>.

This caveat is related to the reaction mechanism in itself. In consequence to these difficulties, a polydispersity ( $I = M_w/M_n$ ) lower than 1.5 can hardly be reached.<sup>[5]</sup> Since the 1980s, several techniques were developed in order to alleviate this drawback. All these enhancements rely on obtaining dormant species in equilibrium with an active form from propagating chain radicals (Scheme 1).

Insert Scheme 1

Nowadays, five methods using a reversible termination or a reversible chain transfer as depicted in Scheme 1 have been designed.<sup>[6]</sup> They have been named

“living” or “controlled” free radical polymerization processes. They involve nitroxide<sup>[5, 7]</sup>, cobalt/porphyrin complexes<sup>[8]</sup>, or copper(I)/bipyridine complexes<sup>[9, 10]</sup> (reversible termination, equation (1) in Scheme 1). As an alternative, an “iodine transfer”<sup>[11-13]</sup>, a reversible addition-fragmentation chain transfer (RAFT)<sup>[14-16]</sup>, or a macromolecular design via interchange of xanthate (MADIX)<sup>[17]</sup> can be applied (reversible chain transfer, equation (2) in Scheme 1). Others techniques do exist but they are seldom used or have only been recently devised.<sup>[18-24]</sup>

#### Insert Scheme 2

2,2,6,6-tetramethyl piperidinyl-1-oxy **1** (TEMPO) is one of the most commonly used compound in a living free radical polymerization process based upon nitroxides (Scheme 2). Similarly, *di*tert*io*butylnitroxide **2** has recently been applied (Scheme 2) and its use in radical processes is growing.<sup>[25, 26]</sup> Two severe drawbacks of TEMPO namely are a long induction time (around 10 h with styrene at 120 °C)<sup>[5]</sup> and a working temperature above 120 °C, preventing a polymerization to be carried out in aqueous dispersed systems.<sup>[3]</sup> However, a polymerization with TEMPO can be obtained under high pressure in an aqueous medium. Unfortunately some autopolymerization of styrene cannot be neglected at such a high temperature, leading to an increase of the polydispersity.<sup>[3, 27]</sup> In

order to avoid the limitations associated with **1**, several groups have synthesized and tested nitroxides allowing lower temperature conditions.<sup>[2, 4, 25, 26, 28-34]</sup>

Hereunder we will report the styrene polymerization in bulk at 90 and at 120 °C and in miniemulsion at 90 °C in the presence of 2,2,15,15-tetramethyl-1-aza-4,7,10,13-tetraoxacyclopentadecan-1-oxyl **3** (Scheme 3) and in the presence of its sodium complex. We will focus on the linear evolution of  $M_n$  as a function of the conversion. Styrene was used as the reference monomer and all data were compared with TEMPO as the counter-radical.

## Experimental part

### *Materials*

Styrene (STY) was purchased from Aldrich and stored at -4 °C. The included 4-*tert*-butylcatechol inhibitor was removed either by using an inhibitor-remover packaging (from Aldrich) or by styrene distillation under reduced pressure. Benzoyl peroxide (BPO), TEMPO, hexadecane were used as purchased from Aldrich, as well as all the other compounds involved in the synthesis of **3**, **3Li** and **3Na**. All solvents were purchased from Biosolve. Dowfax 8390, an anionic surfactant, was purchased from Dow Chemical Company. Chromatographic separations were performed on Aldrich Silicagel 60 (230-400 mesh) for column chromatography.

### *Measurements*

Gel permeation chromatography (GPC) experiments were achieved in THF solution (from Biosolve, stabilized with BHT) at 22 °C with a flow rate of 1.0 cm<sup>3</sup>.min<sup>-1</sup> by using a WATERS Model 510 pump, a Model 410 refractive index detector (at 40 °C) and a Model 486 UV detector (at 254 nm). 50 µl injections were performed by means of a WATERS Model WISP 712 autoinjector in a low molecular weight set of columns i.e. a PLgel guard (5 µm particles) 50\*7.5 mm precolumn followed by two successive PLgel columns of 50 nm (5 µm particles) and 10 nm (5 µm particles). Polystyrene samples from Polymer Laboratories (M = 580 to M = 7.1\*10<sup>6</sup>) were the calibration standards. Data acquisition and processing were performed by means of the WATERS Millennium32 (v3.05) software. The conversion was measured by gravimetry. The ESR spectra were recorded at room temperature on a Bruker ESP 300E spectrometer fitted with a X-band resonator (9.41 GHz), a Bruker ER035M NMR gaussmeter and an HP 8535B microwave frequency counter. The signal was detected at a 100 kHz magnetic field modulation. The UV spectra were acquired on an HP 8453 UV-Visible spectrophotometer with an HP 89090A heating unit.

### *Polymerization*

#### **BULK**

In 50 ml flasks, styrene, nitroxide and BPO were mixed as described hereunder. The mixture was thoroughly degassed for 30 minutes by argon bubbling and then dipped into an oil bath heated at the appropriate temperature. Aliquots were picked at various time intervals and stored over hydroquinone. They were

characterised by gel permeation chromatography. The conversion was measured by gravimetry.

*Bulk 90*:  $m_{\text{BPO}} = 0.256$  g,  $m_3 = 0.280$  g,  $m_{\text{STY}} = 20.005$  g.

*Bulk 120*:  $m_{\text{BPO}} = 0.260$  g,  $m_3 = 0.281$  g,  $m_{\text{STY}} = 20.015$  g.

*Bulk Na*:  $m_{\text{BPO}} = 0.041$  g,  $m_{3\text{Na}} = 0.100$  g,  $m_{\text{STY}} = 3.334$  g.

*TEMPO 90*:  $m_{\text{BPO}} = 0.658$  g,  $m_{\text{TEMPO}} = 0.378$  g,  $m_{\text{STY}} = 50.016$  g.

## **MINIEMULSION**

The miniemulsion was prepared as follows: the monomer, the nitroxide, the BPO and the hexadecane were poured into water and a surfactant. They were mixed by using a high shear mixer (Ystral X1020) for 5 minutes at room temperature. An homogenous emulsion was obtained at room temperature by means of a sonifier (Dr. Hielscher UP 400S) operated for 5 minutes at 50 % duty, on power 5 and on pulsed mode.

*Miniemulsion*:  $m_{\text{BPO}} = 0.123$  g,  $m_3 = 0.136$  g,  $m_{\text{STY}} = 10.040$  g,  $m_{\text{hexadecane}} = 0.505$  g,  $m_{\text{Dowfax 8390}} = 0.315$  g,  $m_{\text{H}_2\text{O}} = 40.058$  g.

## **Results and discussion**

### *Synthesis and ESR*

The synthesis of **3** has already been described elsewhere.<sup>[35, 36]</sup> It is summarized in Scheme 3.

#### Insert Scheme 3

The synthesis of **4** has been carried out according to ref. <sup>[37]</sup> followed by a reduction by  $\text{AlLiH}_4$ . The oxidation of **5** was difficult to achieve and several experiments had to be performed. A 30 % aqueous hydrogen peroxide solution with some sodium tungstate as a catalyst only gives a yield of 11 % after 40 h. It reached 26 % after 70 hours. The reaction conditions have been kept constant at room temperature. Over-oxidation occurred when the reaction involved *meta* chloroperbenzoic acid (*m*-CPBA). Ultimately, a 70 % yield was obtained by means of a proportion modified Brik procedure<sup>[38]</sup> and a flash chromatography with dichloromethane/ethanol 950/50 V/V as eluent. The Brik procedure is a biphasic *in situ* generation of dimethyldioxirane by oxone ( $\text{KHSO}_5$ ) over acetone. The alkoxyamine of styrene has not been successfully obtained using the Miura's procedure.<sup>[39]</sup>

The metal complex synthesis has been carried out according to ref. <sup>[35]</sup> by using  $\text{MBPh}_4$  ( $\text{M} = \text{Li}^+, \text{Na}^+, \text{K}^+$ ). In every case, a good yield has been reached with the exception of the potassium complex. The ESR experiments are summarized in Table 1. It gives the respective hyperfine coupling constants and the g-factors for **3**, **3Li** and **3Na** in several solvents.

Insert Table 1

All the spectra have been simulated with an EPR software from Duling *et al.*<sup>[40, 41]</sup> It was impossible for **3** to find a correlation between the  $E(T)N$  of the solvent and the  $a_N$  or the g-factor. The spectra of **3Li** and **3Na** (Figure 1) show triplets of quadruplets with a  $a_N \approx 15.8$  G and  $a_{\text{Metal}} \approx 2.5$  G. Our goal is to obtain the highest value for  $a_N$  ; it implies that the B mesomeric form (Scheme 4) is favoured. Considering that the lithium and sodium salts are innocuous, their ecological impact is low. The oversized potassium does not enter into the crown ; therefore only the spectrum of **3** could be observed (Figure 1).

Insert Figure 1

Insert Scheme 4

The UV spectra of **3** in styrene have been recorded for several concentrations. **3** shows two absorption peaks, viz. at 313 nm ( $\epsilon = 46 \text{ mol}^{-1}.\text{dm}^3.\text{cm}^{-1}$ ) and at 417 nm ( $\epsilon = 4 \text{ mol}^{-1}.\text{dm}^3.\text{cm}^{-1}$ ).

*Polymerization*

Three polymerization processes for **3** have been studied : in bulk at 90 °C (Bulk 90 in Figure 2-4 and Table 2), in bulk at 120 °C (Bulk 120) and in miniemulsion at 90 °C (Miniemulsion). The polymerization of **3Na** was only performed in bulk at 90 °C (Bulk Na). After removing the inhibitor from the monomer by a distillation, the BPO initiator was added with an initial concentration around 45 mM. In all the experiments, a Nitroxide to Initiator ratio of 1.1 was used. Table 2 summarizes our results. They are compared to data obtained by Georges *et al.*<sup>[5]</sup> for TEMPO at 120 °C (TEMPO 120) and to our experiments for TEMPO at 90 °C (TEMPO 90).

Insert Table 2

Insert Figure 2

Figure 2 shows the evolution of the conversion *versus* time. Disregarding the reaction conditions, the rate of **3** is faster than TEMPO at 120 °C. The reaction rate follows the order Bulk 120 > Miniemulsion > Bulk 90. In the case of TEMPO at 120 °C, an inhibition time of 10 hours was observed before normal polymerization occurred. The conversion at 90 °C with the same nitroxide was only 4 % after 51 hours

### **Bulk 90**

The variation of  $M_n$  versus Conversion (Figure 3) is not entirely linear ; the presence of thermal radicals certainly accounts for this curvature. The experimental  $M_n$  reproduced in Table 2 are significantly higher than the theoretical values showing that the number of chains is lower than what is expected.

Insert Figure 3

The polymerization rate depends on the instantaneous concentration of BPO and should slowly decrease over time. When analyzing the  $\ln([M]_0/[M])$  versus Time plot (Figure 4), the linear variation for neat styrene in bulk cannot be reproduced here ; thermally generated radicals control the polymerization rate. A  $\ln([M]_0/[M])$  variation yields a straight line when the radical concentration stays equal throughout the reaction. It seems not to be the case here by considering that the half-time of the BPO initiator (approximately 1.5 hour) is short as compared to the reaction time.

Insert Figure 4

However, the increasing molecular weights and the relatively low polydispersities suggest that this process is a living polymerization.

**Bulk 120**

At this temperature, the BPO decomposition is swift. As expected, a faster polymerization rate is observed at the beginning of the reaction (Figure 2). Later on, it is probably controlled by thermal initiation or will depend on the equilibrium constant<sup>[42]</sup> ; this explains why the straight line does not pass through zero in the  $\ln([M]_0/[M])$  versus Time graphic (Figure 4).

In this case, experimentally measured  $M_n$  ( $M_n$  Exp.) is lower than simulated  $M_n$  ( $M_n$  calc.) at the end of the reaction (Table 2). At lower conversions, the nitroxide deactivation causes a higher molecular weight than what is theoretically expected. However, at the end, this effect is compensated by a thermal initiation and a chain transfer to the monomer ; therefore lower molecular weights are obtained. This behaviour also accounts for the very high polydispersity.

### **Miniemulsion**

When the miniemulsion results are compared to Bulk 90, a higher polymerization rate, higher molecular weights and higher polydispersities are observed. This increased rate may be the result of a compartmentalisation in the emulsion polymerization, leading to a less bimolecular termination. The higher molecular weights and polydispersities suggest more nitroxides side reactions or a nitroxides partitioning to the aqueous phase. Furthermore the latter may also explain the higher polymerization rate due to a higher fraction of propagating chains inside the particles.

### **Bulk Na**

The general behaviour of **3Na** is close to TEMPO. When using **3Na** as the counter radical, the reaction has an inhibition period of 7.5 hours and a slower rate than **3**. A 75% conversion is the maximum yield reached by **3Na**.

### **Conclusion**

By analyzing Figure 3, it can be concluded that there is some control with **3** and **3Na** because  $M_n$  linearly increases with conversion and because the polydispersities are not very high. Ultimately, the results should be better if more ideal experimental conditions were met, as for instance with another initiator or a different initiator/nitroxide ratio. These enhancements are still under evaluation in our laboratory.

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## Captions

Figure 1. ESR spectra of **3** (a, experimental) and **3Na** (b, experimental ; c, simulated) in dichloromethane at Room Temperature. The ESR recording conditions are described in Table 1

Figure 2. Conversion vs. Time for **3**, **3Na** and TEMPO

Figure 3.  $M_n$  vs. Conversion for **3**, **3Na** and TEMPO

Figure 4.  $\ln[M]_0/[M]$  vs. Time for **3**, **3Na** and TEMPO

Scheme 1

Scheme 2

Scheme 3

Scheme 4

Table 1. Features of nitroxides **3**, **3Li**, **3Na** and **3K** At Room Temperature. ESR conditions: 0.5 G for modulation amplitude, time constant of 163.84 ms, scan time of 84 s and 2 W for power. The receptor gain was adjusted to obtain a good signal to noise ratio.  $[\text{Nitroxide}]_0 \approx 300 \text{ mM}$ .

Table 2. Different Free radical Polymerization Process of Styrene carried out in Presence of **3**, **3Na** and TEMPO using BPO as initiator and a Nitroxide to BPO ratio of 1.1.

Table 1: Features of nitroxides **3**, **3Li**, **3Na** and **3K** At Room Temperature.

ESR conditions: 0.5 G for modulation amplitude, time constant of 163.84 ms, scan time of 84 s and 2 W for power. The receptor gain was adjusted to obtain a good signal to noise ratio.  $[\text{Nitroxide}]_0 \approx 300 \text{ mM}$ .

Compound	Solvent ( $E(T)N$ )	$a_N$ /G	$a_{\text{Metal}}$ /G	g-factor
<b>3</b>	Toluene (0.099)	14.97		2.0056 <sub>3</sub>
	Dichloromethane (0.31)	15.30		2.0056 <sub>1</sub>
	Ethanol (0.65)	15.61		2.0055 <sub>3</sub>
	MMA	15.00		2.0056 <sub>3</sub>
	STY	15.04		2.0056 <sub>3</sub>
<b>3Li</b>	Dichloromethane	15.81	2.41	2.0055 <sub>1</sub>
<b>3Na</b>	Dichloromethane	15.86	2.58	2.0055 <sub>0</sub>
<b>3K</b>	Dichloromethane	15.33		Not measured

Table 2: Different Free radical Polymerization Process of Styrene carried out in Presence of **3**, **3Na** and TEMPO using BPO as initiator and a Nitroxide to BPO ratio of 1.1.

Process	Time /H	Conversion /%	$M_n$ Exp.	$M_n$ Calc.	$I^a$	$f^b$
Bulk 90	0.50	2	1009	313	1.18	0.31
	1.50	22	7564	4293	1.86	0.57
	2.58	40	12950	7916	1.63	0.61
	3.50	49	13972	9761	1.77	0.70
	6.50	62	18605	12339	1.65	0.66
	25.25	95	25392	18950	1.63	0.75
Bulk 120	0.50	36	12493	7194	1.61	0.58
	1.50	49	15017	9844	1.76	0.66
	2.58	63	16616	12691	2.06	0.76
	3.50	72	17884	14343	2.36	0.80
	6.50	98	17642	19665	3.51	1.11
Mini-emulsion	0.50	16	9130	3236	2.18	0.35
	1.58	38	17389	7517	2.26	0.43
	3.67	62	25883	12311	2.38	0.48
	6.08	74	29632	14809	2.86	0.50
Bulk Na	17.25	36	9367	7273	1.18	0.78
	24.25	56	12248	11124	1.21	0.91
	41.50	64	15916	12789	1.26	0.80
	48.75	68	16551	13622	1.29	0.82
	65.75	72	15954	14499	1.42	0.91
TEMPO 90	0.50	0.2	443	36	1.00	0.08
	25.25	1.3	670	237	1.18	0.35
	30.47	1.9	762	346	1.23	0.45
	51.60	4.3	1176	785	1.31	0.67

<sup>a</sup>  $I = M_w/M_n$  <sup>b</sup>  $f (= M_n \text{ calc.}/M_n \text{ exp.})$  is the efficiency of the initiating step

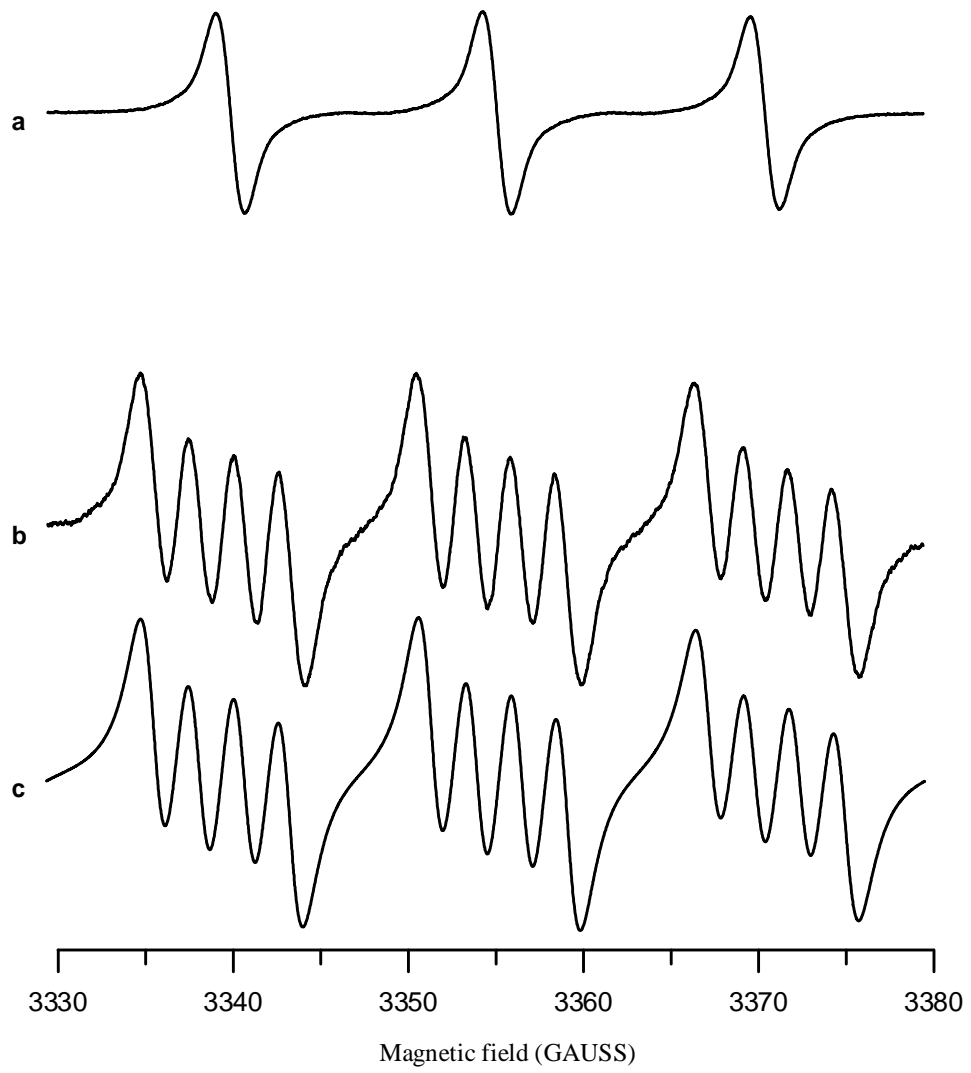


Figure 1

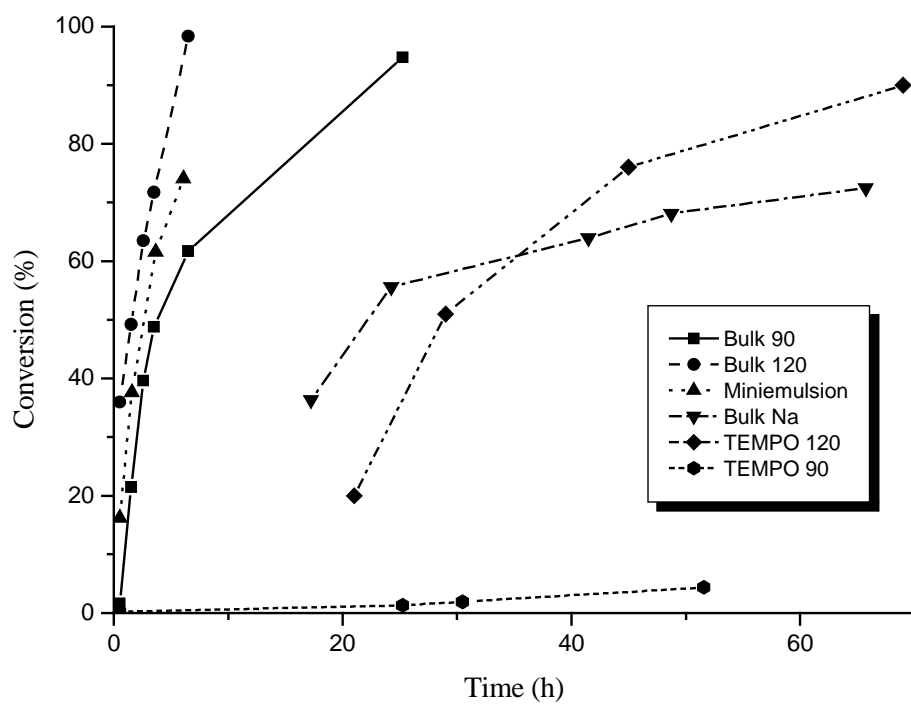


Figure 2

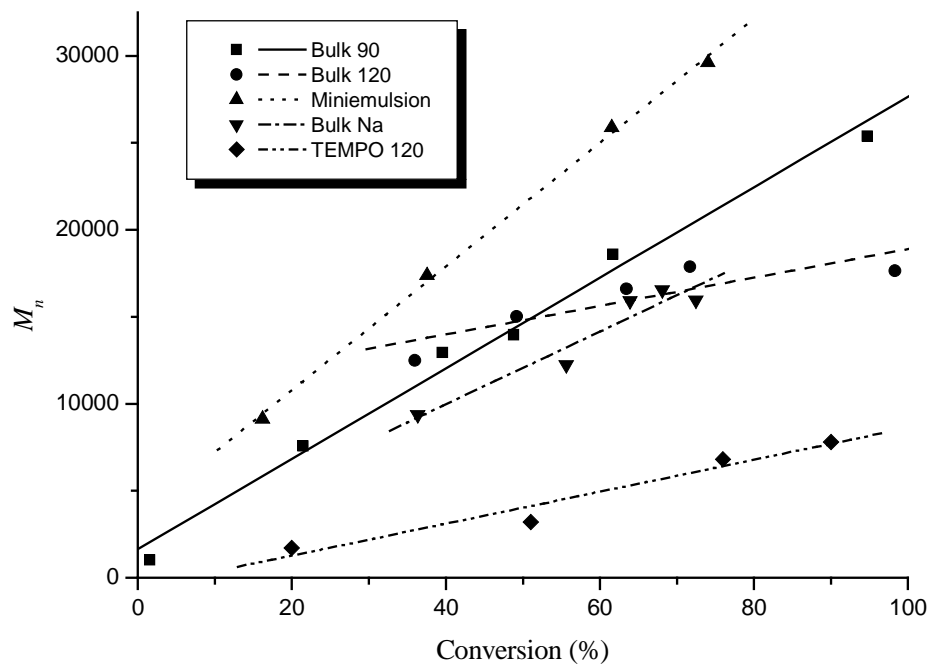


Figure 3

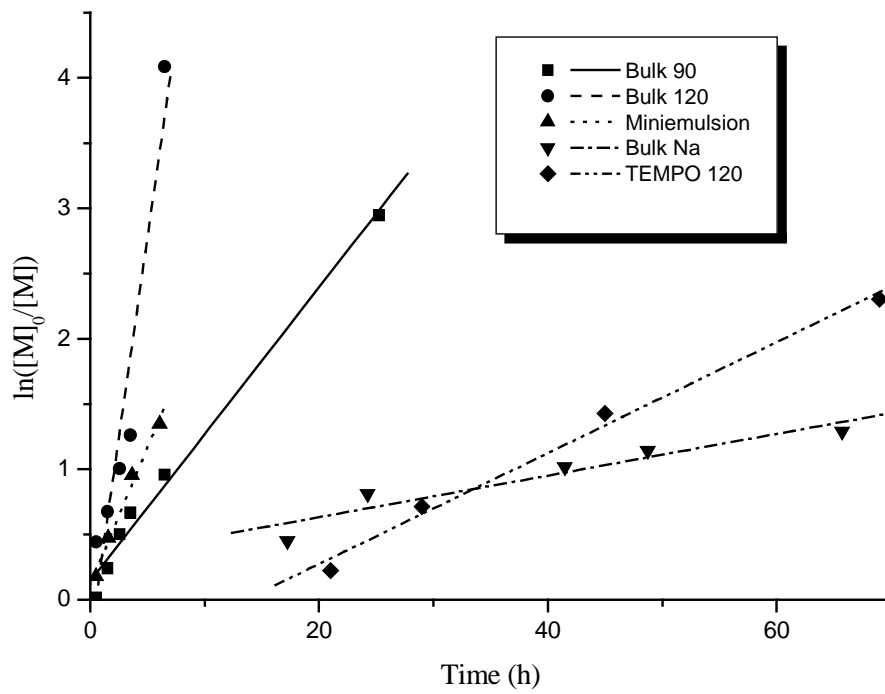
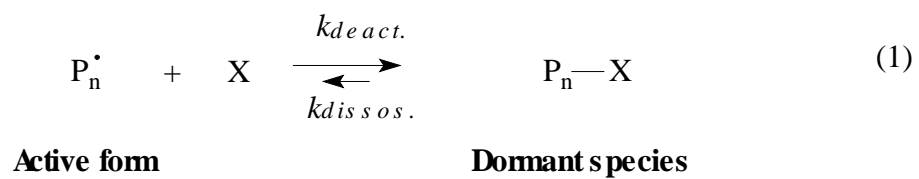
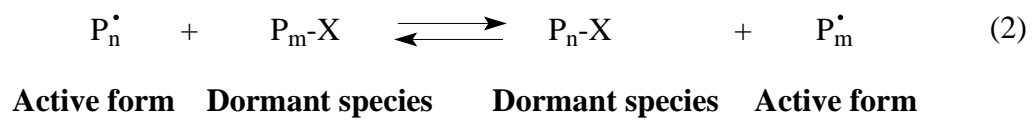
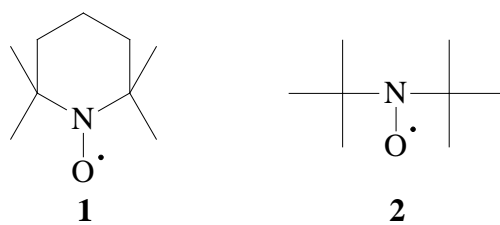


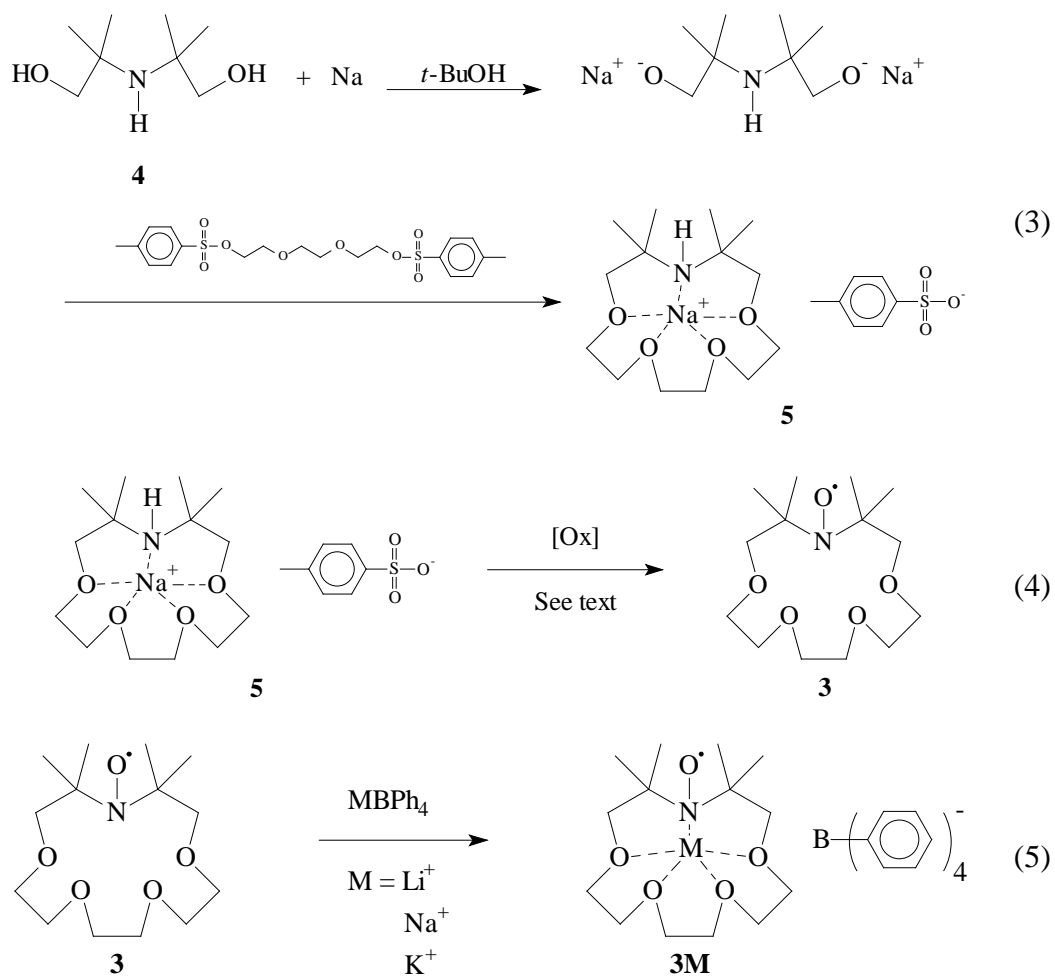
Figure 4

**Reversible termination****Reversible chain transfer**

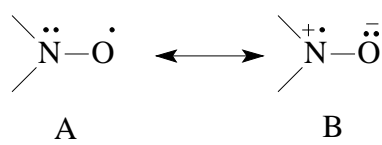
Scheme 1



Scheme 2



Scheme 3



(6)

Scheme 4