Solution homopolymerizations of *n*-butyl acrylate and styrene mediated using 2,2,5-trimethyl-4-tert-butyl-3-azahexane-3-oxyl (TITNO)

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A B S T R A C T

Use of Styryl-TITNO (the styrene alkoxyamine of 2,2,5-trimethyl-4-tert-butyl-3-azahexane-3-oxyl) as mediator for nitroxide-mediated polymerization (NMP) of *n*-butyl acrylate (BA) and styrene has been investigated at temperatures ≤ 110 °C. Very good control of molecular weight and molecular weight dispersity with no measurable loss of active chains, and no evidence of tails in the molecular weight distribution as conversion increases, was observed at 90 °C for BA and at 70 °C for styrene. The alkoxyamine dissociation equilibrium constant values determined for polyBA-TITNO (8.5×10^{-11} mol L^{-1} at 90 °C) and polystyrene-TITNO (3.1×10^{-9} mol L^{-1} at 70 °C) are consistent with those required for control when using more established nitroxides that require higher temperatures to achieve these values. The lower optimum polymerization temperatures with Styryl-TITNO as mediator provide new opportunities for NMP and are especially significant for styrene since this appears to eliminate completely the complications from thermal initiation.

1. Introduction

Rizzardo and Solomon [1] were first to report use of nitroxides for control of radical polymerization and employed 2,2,6,6-tetramethyl-piperidine-N-oxyl (TEMPO) (Fig. 1). Subsequently, successful control of molecular weight and molecular weight distribution in TEMPO-mediated polymerization of styrene was reported by Georges et al. [2], and since then nitroxide-mediated polymerization (NMP) has become a major research topic in polymer science [3]. Use of traditional nitroxides (e.g. TEMPO and its derivatives) is largely limited to controlled NMP of styrenic monomers at high temperatures (typically 125–135 °C). The discovery that acyclic nitroxides with a C–H bond α to the nitroxide nitrogen are capable of controlling NMP of a much wider range of monomers (including styrenic monomers and acrylates) at lower temperatures (typically 110–125 °C) is one of the more important developments in NMP. The most significant of these 'second generation' nitroxides (Fig. 1) are *N*-(tert-butyl)-*N*-(1-diethylphosphono-2,2-dimethyl-propyl)nitroxide (SG1) [4] and 2,2,5-trimethyl-4-phenyl-3-azahexane-3-oxyl (TIPNO) [5,6]. More recently [7], we reported the design, synthesis and initial evaluation of a new acyclic nitroxide, 2,2,5-trimethyl-4-tert-butyl-3-azahexane-3-oxyl (TITNO, Fig. 1), that effects controlled NMP at much lower temperatures, namely at 70 °C for styrene and at 90 °C for *n*-butyl acrylate (BA).

Successful control of molecular weight and molecular weight dispersity in NMP depends upon the equilibrium constant $K = k_d/k_c$, where k_d and k_c are the rate coefficients for dissociation of the alkoxyamine and for combination of the chain radical with the nitroxide, respectively (Scheme 1). Our previous work showed that the styryl alkoxyamine of TITNO (Styryl-TITNO, see Fig. 1) affords excellent control in NMP of styrene at 70 °C and BA at 90 °C, i.e., at temperatures much lower than the optimum polymerization temperature ranges (typically 110–125 °C [8–14]) for the well-established acylic nitroxide alkoxyamines; the reasons for this have already been discussed [7]. In this paper, we present exhaustive data from evaluation of Styryl-TITNO for effecting solution homopolymerisation of BA and styrene at different temperatures and with different levels of excess TITNO. Thorough analysis of the data is presented and provides further insight into the effect of polymerization conditions on "livingness", and its variation with conversion, and on the values of *K*.
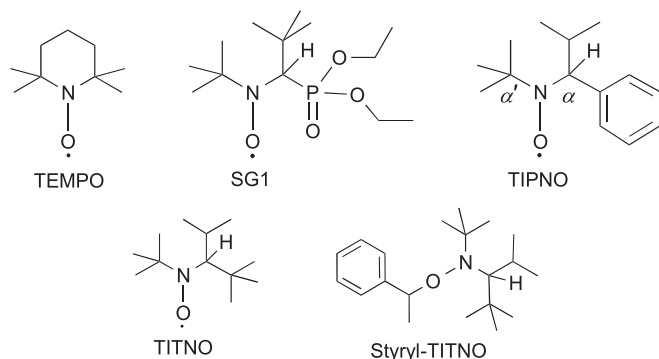
Fig. 1. Structures of well-established nitroxides (TEMPO, SG1 and TIPNO) and of the new nitroxide (TITNO) and its styryl alkoxyamine (Styryl-TITNO).

2. Experimental

2.1. Materials

All reagents and solvents were used as received (supplied by Sigma–Aldrich except for methanol, which was supplied by Fisher Scientific). Styrene, BA and anisole were purified by distillation under vacuum on a vacuum line just prior to use in solution polymerizations. TITNO and Styryl-TITNO were synthesised and characterised as described in a previous paper [7].

2.2. Analytical methods

A Perkin–Elmer Clarus 500 gas–liquid chromatograph (GLC) was used to determine the amount of unreacted monomer in solution polymerizations with dimethylacetamide (DMAc) as the internal standard. A sample ($\sim$50 mg) of polymerization solution of accurately known weight was precipitated by addition to an accurately known weight ($\sim$10 g) of a $\sim$2%(w/w) solution of accurately known concentration of DMAc in methanol; the mixture was stirred with a magnetic bar for 1 h before being filtered through a 0.2 μm pore size Millipore filter. The resulting solution ($\sim$1 μL) was auto-injected into the vaporization port (at 90 °C) and separation achieved on a Hewlett–Packard HP-FFAP column (10 m $\times$ 0.532 mm $\times$ 1.00 μm) with helium as the carrier gas

flowing at 30 ml min^{-1} with an inlet pressure of 80 psi, components being detected using a flame ionization detector (at 250 °C) with hydrogen as the combustion gas. Molecular weight distribution and molecular weight averages were determined by gel permeation chromatography (GPC) in tetrahydrofuran (THF) at room temperature using 5 μm Phenogel columns of 500, 5×10^4 and 5×10^6 Å porosity in series and a Shodex RI-101 differential refractometer. Solutions of polymer in THF (ca. 0.2%(w/v), 500 μL) were injected into the THF carrier solvent flowing at 1 ml min^{-1}. Calibration was performed with polystyrene standards in the molecular weight range 600–7,700,000 and data were analysed using PSS WinGPC Unity software.

2.3. Solution polymerizations

The following description is typical of the procedures used. Differences between reactions were only with respect to the reaction temperature and/or the amounts of excess TITNO and/or the scale of the reaction.

Styryl-TITNO ($\sim$0.30 g, 1.00 mmol) and TITNO (0–16 mol% relative to Styryl-TITNO) were dissolved in BA or styrene ($\sim$100 mmol). The resulting solution was then mixed with anisole (10 g) in a 50 ml Schlenk tube before being degassed by three freeze–pump–thaw cycles on a vacuum line. Polymerizations were carried out at controlled temperature in a preheated oil bath, which was placed on a magnetic hot-plate stirrer (IKA RCT classic) equipped with an electronic contact thermometer (VT-5), and stirred with a magnetic stirrer at 400 rpm. Solution polymerizations of BA were performed at 90 °C, whereas styrene polymerizations were conducted at three temperatures (70, 90 and 110 °C). Samples ($\sim$0.5 g) were taken at selected time intervals through a rubber septum using a glass syringe fitted with a 15 cm stainless steel needle.

3. Results and discussion

In designing the polymerization experiments, the decision to use $\sim$50 wt% solution polymerizations was made so that a single reaction could easily be sampled across a wide range of conversion, from low to very high, without problems due to viscosity build-up. Anisole was selected as the solvent because it does not possess weak C–H bonds and so has low activity in chain transfer, thus ensuring that contributions from chain transfer to solvent would be insignificant.
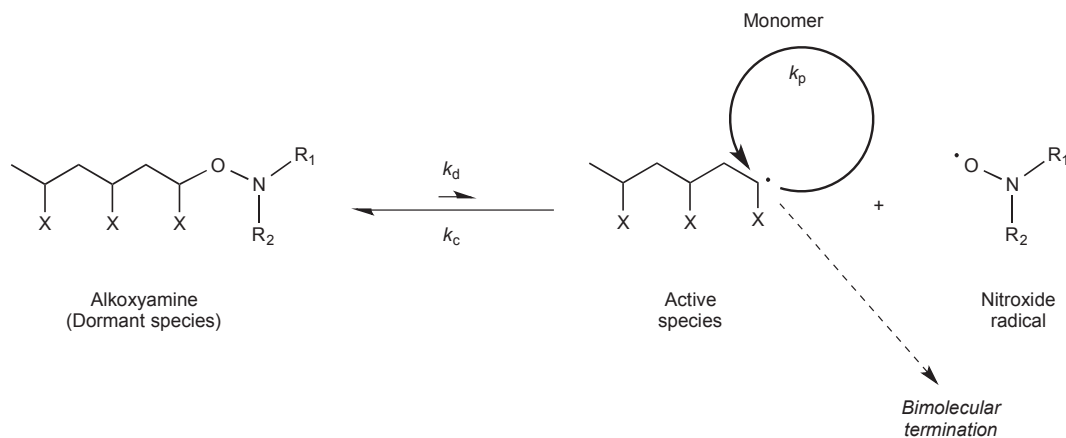
Scheme 1. The mechanism for NMP of a vinyl monomer, showing the critical role of the activation–deactivation equilibrium in ensuring (i) that the dormant chain concentration is very high compared to the active chain radical concentration so that bimolecular termination becomes an event of low probability and (ii) that there is rapid exchange between the activated and deactivated states of a chain so that all chains grow with the same probability.

3.1. Tests of "livingness" in NMP mediated by Styryl-TITNO

A linear increase of number-average molecular weight, M_n, with conversion often is used as a test of "livingness" in polymerisations. Since the value of M_n includes the contribution from end-groups (i.e. the molecular weight of Styryl-TITNO in the present work), it is more accurate to establish how the number-average degree of polymerization, x_n, varies with conversion. However, use of either M_n or x_n for such tests has limitations and, in some scenarios, could disguise non-livingness in polymerizations where each chain should be initiated by an activating species (as in use of an alkoxyamine as initiator). For example, termination by disproportionation will not change the number of chains (or, therefore, the value of x_n at a given conversion), just the molecular weight distribution. Use of such plots for radical polymerizations of styrene and BA is more valid because termination is predominantly by combination, in which case the number of chains will reduce, and x_n will increase, as a consequence of termination reactions, thus providing evidence of reduced livingness. Contributions from thermal initiation in styrene polymerizations, however, would have the effect of increasing the number of chains and reducing x_n at a given conversion; whilst this effect could counteract exactly the effects of termination by combination and lead to an overall linear variation of x_n with conversion, this would be highly fortuitous and it is more likely that an overall reduction or increase in the number of chains would be observed. In all the scenarios described above, the molecular weight dispersity, $Đ_M$, will increase and so the variation of $Đ_M$ with conversion must also be considered in order to assess the degree of livingness.

As is evident from this discussion, although calculation of x_n eliminates the complicating effects of end-groups on M_n (particularly important at low conversions), the underlying quantity of importance is the number of chains present. Hence, an alternative to using x_n is to calculate the total number of moles, N_{total}, of polymer chains according to the equation

$$N_{total} = \frac{f_c m_M + m_{S-T}}{M_n^{exp}} \tag{1}$$

where f_c is the measured fractional monomer conversion, m_M is the mass of monomer used, m_{S-T} is the mass of Styryl-TITNO used, and M_n^{exp} is the measured number-average molecular weight of the polymer at the corresponding monomer conversion. Although use of N_{total} is effectively equivalent to using x_n, it provides a much clearer and more obvious test of livingness because its value should not change under truly living conditions and should have a constant value equal to the initial number of moles of alkoxyamine used in the polymerization, making it easier to see more subtle deviations from livingness than in plots of x_n versus conversion. As already stated, if bimolecular termination of propagating chains occurs in the radical polymerizations of styrene and BA reported herein, this will be principally by combination, so the value of N_{total} would be expected to reduce if bimolecular termination is significant and there would also be a corresponding increase in $Đ_M$. Additionally, N_{total} and $Đ_M$ should increase if there is a significant contribution from thermal generation of radicals in styrene polymerizations. Hence we have used plots of the variation of N_{total} and $Đ_M$ with conversion to evaluate livingness in the present work.

3.2. Theory for kinetics analysis of NMP mediated by Styryl-TITNO

Most kinetics studies of NMP have been carried out on polymerizations of styrene mediated by TEMPO and its derivatives at temperatures in the range 125–130 °C, at which thermal self-initiation by styrene makes a significant contribution. Fukuda et al. [15–17] were the first to propose a stationary-state model for NMP in which the rate of initiation, R_i, is significant, even in the absence of added initiator, due to thermal generation of radicals from styrene. When the stationary state condition is reached shortly after the start of polymerization, the rates of radical formation and loss are equal and the rate of polymerization can be described by the standard first order kinetics relationship

$$\ln\left(\frac{[M]_0}{[M]_t}\right) = k_p[\dot{P}]t \tag{2}$$

where $[M]_0$ and $[M]_t$ are the concentrations of monomer at the start of the reaction and at time t, respectively, k_p is the rate coefficient for propagation and $[\dot{P}]$ is the stationary state concentration of propagating chain radicals. Thus, for a specific monomer, the rate of NMP is controlled by $[\dot{P}]$ and hence by the position of the activation–deactivation equilibrium shown in Scheme 1. The equilibrium constant, K, is defined by Refs. [12,14,18,19].

$$K = \frac{[\dot{P}][RNO^\bullet]}{[P-ONR]} \tag{3}$$

where $[RN\dot{O}]$ and $[P-ONR]$ are the stationary state concentrations of nitroxide and polymeric alkoxyamine, respectively. Assuming that all molecules of alkoxyamine initiate a chain and that bimolecular termination is negligible, then $[P-ONR]$ is equal to the initial concentration of alkoxyamine. For Styryl-TITNO polymerizations, therefore,

$$K = \frac{[\dot{P}][TITNO]}{[Styryl-TITNO]_0} \tag{4}$$

where $[Styryl-TITNO]_0$ is the initial concentration of Styryl-TITNO. If an excess of nitroxide is added to a polymerization at levels of >1 mol% of the initial alkoxyamine concentration in order to shift the activation–deactivation equilibrium towards the dormant species and provide greater control (as has been used for styrene polymerizations in this work), then the nitroxide concentration can be assumed to be approximately constant and equal to the initial concentration of excess nitroxide ($[TITNO]_0$ in the present work) because only a tiny proportion of the alkoxyamine is dissociated at any instant in time. Letting the ratio $[TITNO]_0/[Styryl-TITNO]_0 = r$, Equation (4) can then be rewritten as

$$K = [\dot{P}]r \tag{5}$$

Fig. 2. Plots of $\ln([M]_0/[M]_t)$ vs t and $t^{2/3}$ for solution polymerization of BA at 90 °C mediated by Styryl-TITNO with $[BA]_0/[Styryl-TITNO]_0 = 101.0$.
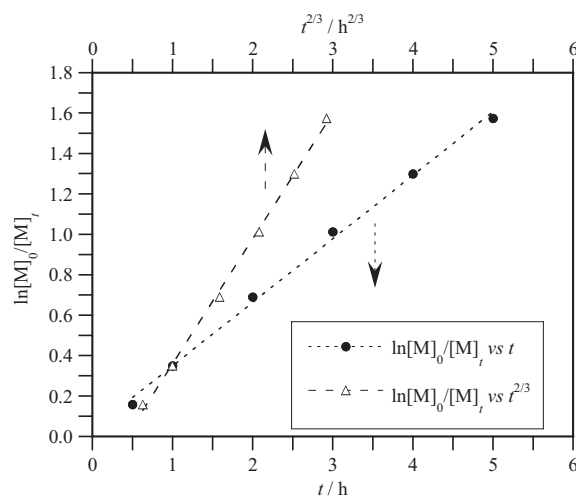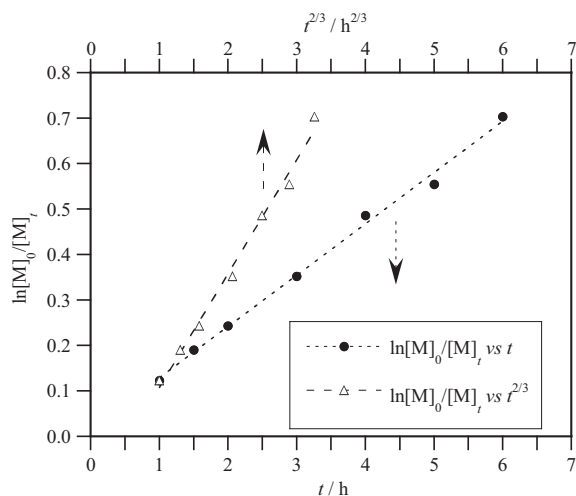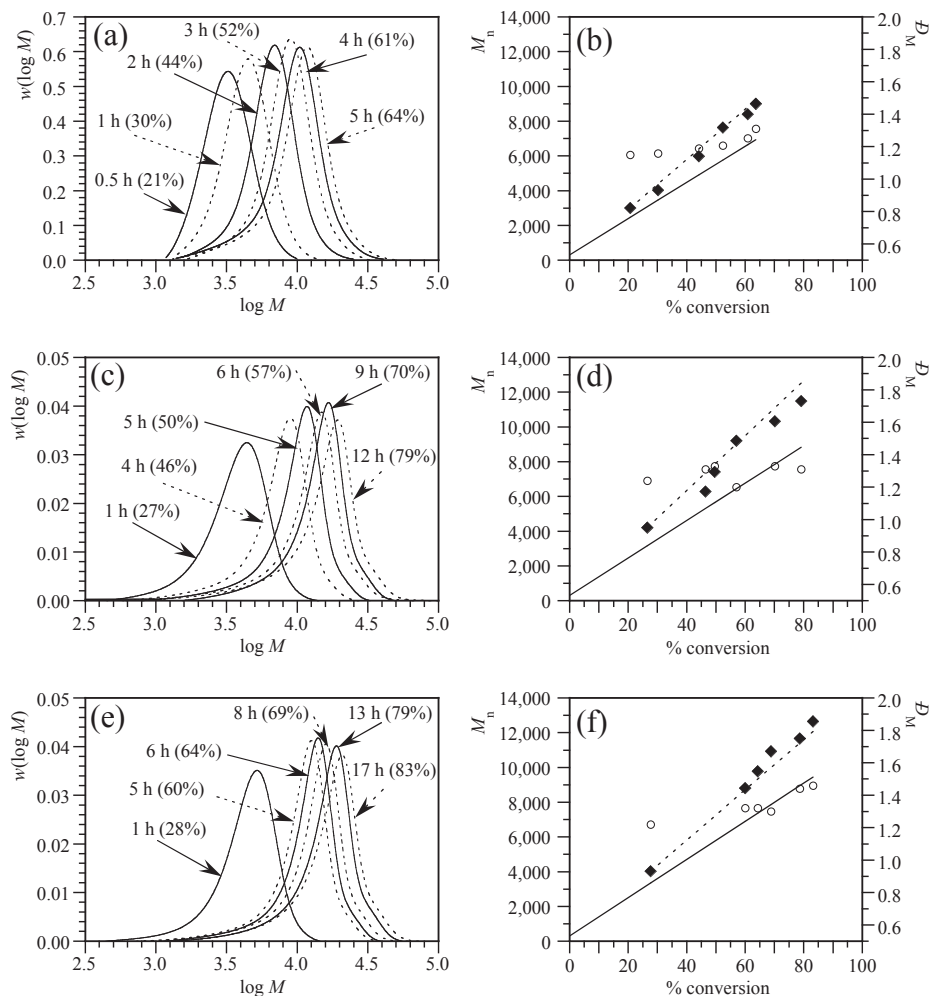
Fig. 3. Plots of $\ln([M]_0/[M]_t)$ vs t and $t^{2/3}$ for solution polymerization of BA at 90 °C mediated by Styryl-TITNO with $[BA]_0/[Styryl\text{-}TITNO]_0 = 106.5$ and 15.9 mol% added excess TITNO.

In accord with Equation (2), $[\dot{P}]$ can be obtained from the slope of a plot of $\ln([M]_0/[M]_t)$ vs t using a literature value for k_p. Since the value of r is known for each reaction, it therefore is possible to determine K experimentally for those polymerizations in which excess TITNO is used.

The concept of a persistent radical effect (PRE), originally proposed by Fischer [20,21], arises from recognition that the concentrations of nitroxide radicals and propagating chain radicals may be neither stationary nor equal (even in the absence of excess nitroxide), but instead that they depend on time. Fischer considered that active species are generated only from dissociation of alkoxyamine and that there are no other radical sources (e.g. conventional initiator or thermal initiation of monomer, i.e. $R_i = 0$). Since nitroxide radicals are persistent and do not undergo termination, an excess of free nitroxide builds up when bimolecular termination of chain radicals occurs and causes $[\dot{P}]$ to reduce. Under conditions where the PRE is significant, $[\dot{P}] \propto t^{-1/3}$ and the polymerization proceeds according to

$$\ln\left(\frac{[M]_0}{[M]_t}\right) = \left(\frac{3k_p}{2}\right)\left(\frac{K[Styryl-TITNO]_0}{6k_t}\right)^{1/3} t^{2/3} \qquad (6)$$

where k_t is the rate coefficient for bimolecular termination (as defined by $-d[\dot{P}]/dt = 2k_t[\dot{P}]^2$). Under these conditions, plots of the

Fig. 4. Plots of the evolution of MWD with time (corresponding % conversions are shown in parentheses) and of measured M_n (solid diamonds), theoretical M_n (solid lines), theoretical M_n based on the moles of active chains calculated from the first sample (dashed lines) and measured $Đ_M$ (open circles) vs % conversion for solution polymerizations of styrene at 90 °C mediated by Styryl-TITNO with $[styrene]_0/[Styryl\text{-}TITNO]_0 \approx 100$ and different levels of added excess TITNO: (a)–(b) 0 mol%; (c)–(d) 5.7 mol%; and (e)–(f) 15.9 mol%.

data according to Equation (2) are curved, whereas plots of $\ln([M]_0/[M]_t)$ vs $t^{2/3}$ are linear. Unfortunately, due to uncertainties in the value of k_t (and its variation with conversion), it is not possible to determine K with any confidence through analysis of data using Equation (6). Hence, evaluation of K has been restricted to analysis of polymerization kinetics using Equations (2) and (5) (i.e. for those reactions in which excess TITNO was employed).

3.3. Kinetics of BA solution homopolymerization mediated by Styryl-TITNO

The use of Styryl-TITNO for control of NMP at temperatures below 100 °C was first evaluated by performing solution polymerizations of BA at 90 °C. The results were included in a limited way when describing the discovery of TITNO [7]. In the Supplementary Information we present a full set of results and discuss them in greater detail. The focus in this section is on further kinetics analysis of the data presented in the Supplementary Information and additional data that enable the value of K to be evaluated.

The kinetics of BA polymerization at 90 °C in the absence of added TITNO has been analysed using Equation (2) (stationary-state, first order polymerization) and Equation (6) (accounting for the PRE), giving the plots shown in Fig. 2. Note that the data fits in this, and subsequent, kinetics plots have not been forced through the origin due to uncertainties over the initial data arising from the heat up period when the reaction tube was added to the oil bath; this has been done because, although this effect would not be expected to introduce a large deviation of data from passing through the origin, it will affect a precise fit of the data. On this basis, the experimental data give good linear fits to both equations (each with a correlation coefficient of 0.999). Recognising that the deviations of the data from passing through the origin will be real, but should not be large because the polymerizations are relatively slow, then it is not unreasonable or inconsistent to compare the linear fits in terms of their quality (correlation coefficient) and the closeness to which they extrapolate to the origin. On this basis, the plot according to Equation (2) is considered better because it passes much closer to the origin. Hence, the results indicate that the radical concentration remains approximately constant throughout the polymerization and that there was an insignificant contribution from termination reactions. This inference is entirely in accord with the data presented in Figs. S1 and S2.

A further Styryl-TITNO mediated polymerization of BA was conducted at 90 °C in the presence of an added 15.9 mol% excess of TITNO to Styryl-TITNO in order facilitate determination of K through application of Equations (2) and (5). Fig. 3 shows again that plots of Equations (2) and (6) are linear, with the former giving the better fit in terms of being far closer to passing through the origin.

The value of $[\dot{P}]$ (5.32×10^{-10} mol L^{-1}) was determined from the slope of the plot of $\ln([M]_0/[M]_t)$ vs t (using [22] $k_p = 58,840$ L mol^{-1} s^{-1} at 90 °C). When combined with the value of r (0.159) and Equation (5), this gives $K = 8.5 \times 10^{-11}$ mol L^{-1} for BA polymerization mediated by Styryl-TITNO at 90 °C. This value is comparable with literature values of K reported for NMP of BA mediated at much higher temperatures by Styryl-SG1 ($K = 1.1 \times 10^{-10}$ mol L^{-1} at 125 °C) [14] and by Polystyryl-SG1 ($K = 1.7 \times 10^{-10}$ mol L^{-1} at 120 °C) [8]. Thus TITNO is providing levels of control similar to SG1 in BA polymerization, but at the much lower temperature of 90 °C.

It should be noted that the value of K ($= k_d/k_c$) obtained from the BA polymerization cannot be directly correlated with the value of k_d for Styryl-TITNO reported previously [7]. This is because all the evidence indicates that initiation is largely complete early in the polymerization (see Figs. S1 and S2) and, on initiation, the Styryl-TITNO converts into poly(*n*-butyl acrylate)-terminated TITNO

alkoxyamine (PBA-TITNO), which will have a different value of k_d from that of Styryl-TITNO. Hence, the value of K determined for BA polymerization represents the equilibrium of the reaction after the rapid initiation period and relates to k_d for PBA-TITNO.

3.4. Solution homopolymerization of styrene mediated by Styryl-TITNO

Mediation of styrene solution polymerizations using Styryl-TITNO required more detailed studies in order to identify conditions that give control similar to that realised with BA, in particular, the effects of excess TITNO and polymerization temperature. The results from these studies are described here for the first time.
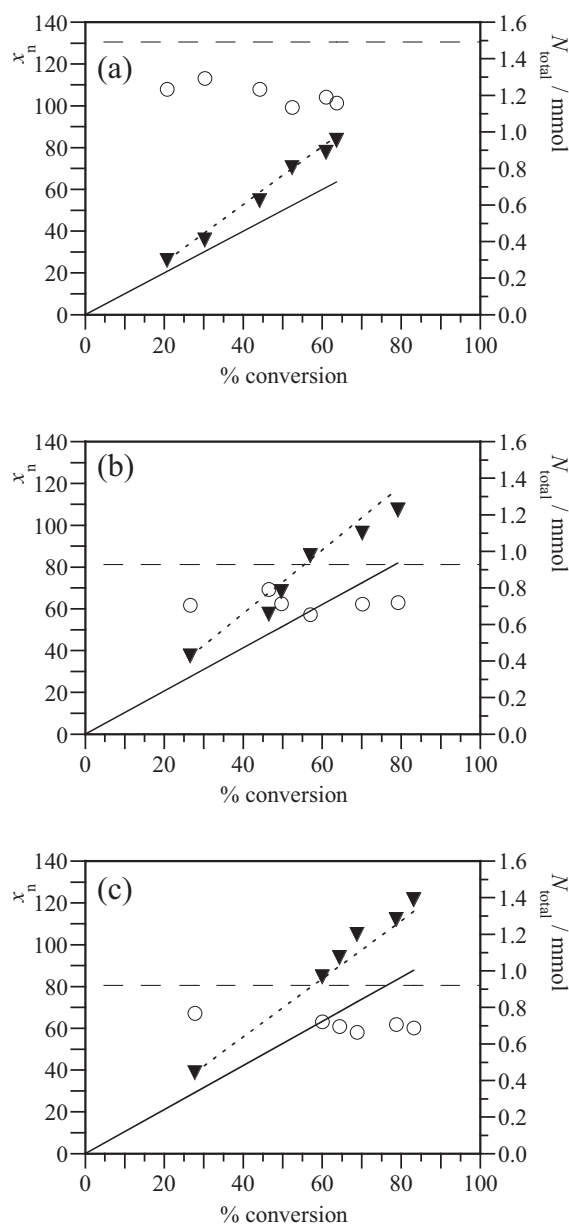
Fig. 5. Plots of measured x_n (solid triangles), theoretical x_n (solid lines), theoretical x_n based on the moles of active chains calculated from the first sample (short-dashed lines), measured N_{total} (open circles) and theoretical N_{total} (long-dashed lines) with conversion for solution polymerization of styrene at 90 °C mediated by Styryl-TITNO with [styrene]$_0$/[Styryl-TITNO]$_0 \approx 100$ and different levels of added excess TITNO: (a) 0 mol%; (b) 5.7 mol%; and (c) 15.9 mol%. The lower theoretical values of N_{total} for (b) and (c) arise because those polymerizations were performed at a smaller scale.
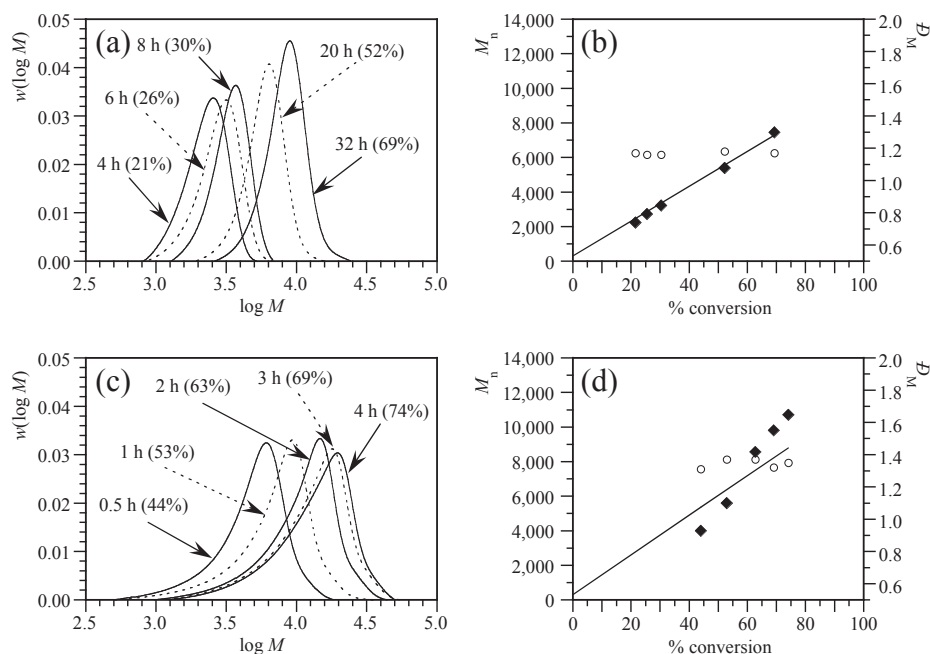
Fig. 6. Plots of the evolution of MWD with time (corresponding % conversions are shown in parentheses) and of measured M_n (solid diamonds), theoretical M_n (solid lines) and measured $Đ_M$ (open circles) vs % conversion for solution polymerizations of styrene mediated by Styryl-TITNO with [styrene]$_0$/[Styryl-TITNO]$_0$ ≈ 100 performed at (a)—(b) 70 °C and (c)—(d) 110 °C in the presence of 16.4 and 16.0 mol% TITNO, respectively. The axis scales are the same as used in Fig. 4 to facilitate comparisons. {Note that Fig. 6(a) is a slightly modified version of a figure presented previously [7] and is included here to facilitate easy direct comparison with MWD data presented in Figs. 4(a, c and e), 6(c) and S1(a)}.

3.4.1. Effect of excess TITNO

Styryl-TITNO-mediated polymerization of styrene was first conducted at 90 °C in the absence of added excess TITNO, i.e. under the conditions that gave good control in BA polymerization. Fig. 4(a)—(b) show evolution of the molecular weight distribution (MWD) with time, and variation of number-average molecular weight, M_n, and molecular weight dispersity, $Đ_M$, with conversion, from which it can be seen that (i) a small tail of lower molecular weight polymer is present in the MWD and becomes more evident as conversion increases, (ii) M_n increases approximately linearly with conversion, but begins to deviate from the theoretical line early in the polymerization, and (iii) $Đ_M$ increases slightly with conversion to a value of 1.31 at 63.6% conversion. These observations are indicative of loss of active chains, but only early in the polymerization, as is further evident from the close fit of the M_n data to the theoretical line based on the value of N_{total} at 20.7% conversion (i.e., for the first sample removed).

Use of excess TITNO at the start of polymerization should help to eliminate the loss of active chains by pushing the activation—deactivation equilibrium (see Scheme 1) towards the dormant alkoxyamine and reducing the value of [Ṗ], thereby improving control of polymerization. Hence, in an attempt to achieve better control, two further polymerizations were carried out at 90 °C using added excess TITNO at levels of 5.7 and 15.9 mol% to the Styryl-TITNO. Fig. 4(c)—(f) show that, even for these polymerizations, there are tails in the MWDs that do not move to higher molecular weight as conversion increases, i.e., that some chains still undergo irreversible termination early in the polymerization, an inference that is confirmed by the lack of any significant improvement in the control of M_n and the relatively high values of $Đ_M$ (1.33—1.46) at higher conversions.

As for the BA polymerizations, plots of x_n and N_{total} vs conversion shown in Fig. 5 provide greater clarity and confirm that in each case there is a reduction in N_{total} early in the polymerization, after which the value of N_{total} remains constant within experimental error. As a consequence, the x_n data deviate from the theoretical lines calculated from [Styryl-TITNO]$_0$, but fit well to theoretical lines calculated using the values of N_{total} corresponding to the first
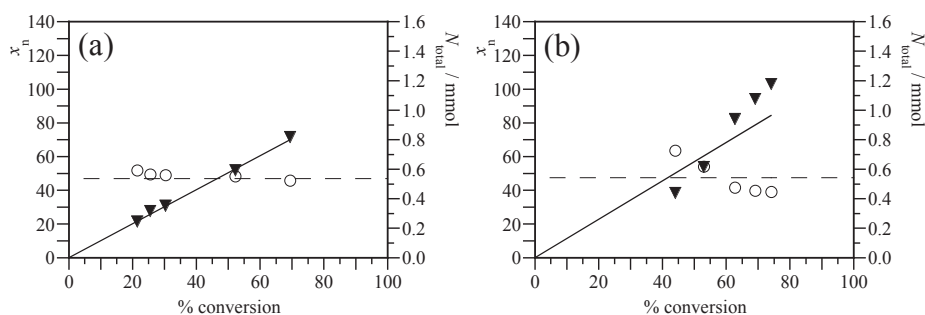
Fig. 7. Plots of measured x_n (solid triangles), theoretical x_n (solid lines), measured N_{total} (open circles) and theoretical N_{total} (long-dashed lines) with conversion for solution polymerization of styrene mediated by Styryl-TITNO with [styrene]$_0$/[Styryl-TITNO]$_0$ ≈ 100 performed (a) at 70 °C and (b) at 110 °C in the presence of 16.4 and 16.0 mol% added excess TITNO, respectively. The axis scales are the same as used in Fig. 5 to facilitate comparisons. The different theoretical values of N_{total} arise because the polymerizations were performed at slightly different scales.
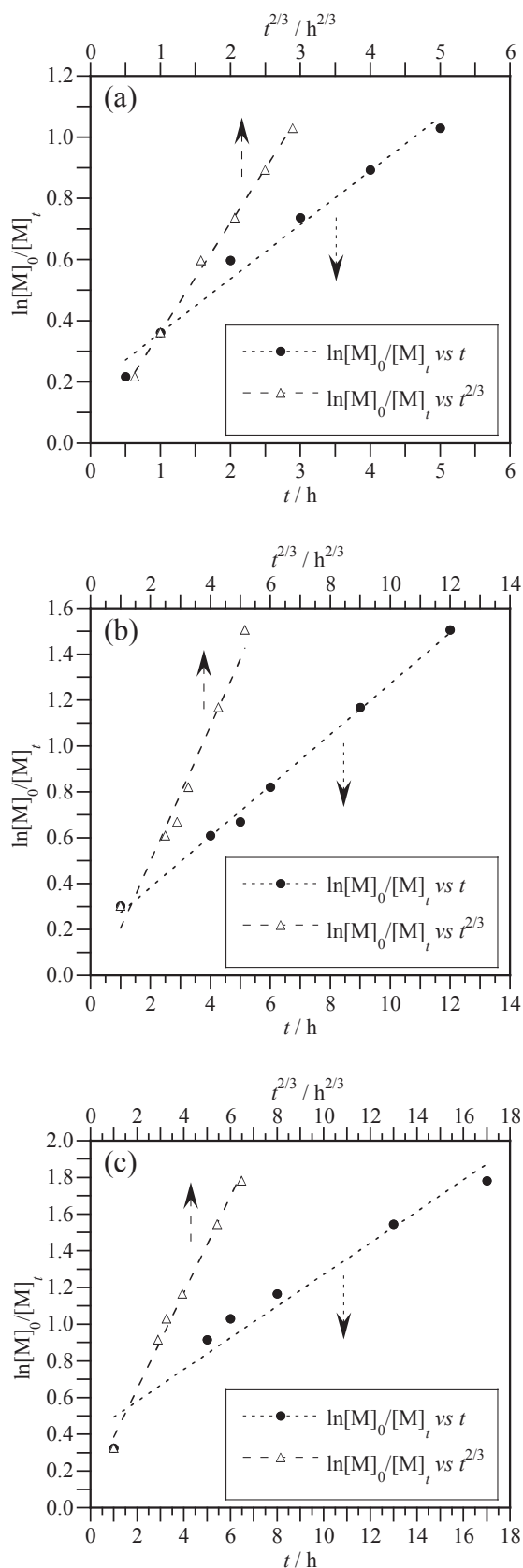
Fig. 8. Plots of $\ln([M]_0/[M]_t)$ vs t and $t^{2/3}$ for solution polymerization of styrene at 90 °C mediated by Styryl-TITNO with $[\text{styrene}]_0/[\text{Styryl-TITNO}]_0 \approx 100$ and different levels of added excess TITNO: (a) 0 mol%; (b) 5.7 mol%; and (c) 15.9 mol%.

sample removed from each polymerization. A similar observation has been reported when using an excess of SG1 in styrene polymerizations mediated by the SG1-based alkoxyamine, MAMA (N,N-tert-butyl-N-[1-diethylphosphono-2,2-dimethyl-propyl] nitroxide) [23]. Thus it is clear from these results that, unlike for BA, a very high degree of livingness in Styryl-TITNO mediated polymerization of styrene cannot be realised fully at 90 °C and that other temperatures needed to be explored.

3.4.2. Effect of polymerization temperature

Control in NMP relies on suppression of bimolecular termination by keeping [Ṗ] low and on rapid shuffling of propagating chains between the dormant and active states. The effect of temperature on NMP of styrene has been investigated by many groups using different initiation systems, e.g., TEMPO/BPO [24], polystyryl-TEMPO macroinitiator (PS-TEMPO) [25], and the SG-1-based alkoxyamine initiator, MAMA [23]. For each particular system, there is an optimum polymerization temperature for achieving best control of M_n and $Đ_M$, but in all styrene NMP systems, control diminishes when the polymerization temperature is above about 115 °C [23] due to the increase in rate of termination and, in particular, significant contributions from styrene thermal initiation. The effect of temperature on Styryl-TITNO mediated polymerization of styrene was studied by performing further experiments at 70 and 110 °C, with the expectation that overall control would improve as the polymerization temperature reduced. The polymerizations were performed in the presence of ∼16 mol% added excess TITNO to Styryl-TITNO so that they could be correlated with the polymerization in which approximately the same level of excess TITNO was used at 90 °C (note that the use of excess TITNO in these experiments was precautionary). The results are shown in Figs. 6 and 7 for comparison with those for the latter reaction shown in Figs. 4(e–f), 5(c).

At both 70 and 110 °C there is continuous growth of the polystyrene chains, as is evident in Fig. 6 from movement of the MWDs to higher molecular weight with conversion. However, as expected, close comparison of the MWDs in Figs. 4(e), 6(a and c) reveals that a lower molecular weight tail arising from loss of active chains is most prominent and extends to relatively high molecular weights for polymerization at 110 °C. More importantly, at 70 °C the lower molecular weight tail is absent, indicating that there is a high degree of control at this temperature. The same inferences can be made from comparison of the M_n and $Đ_M$ data presented in Figs. 4(f), 6(b and d). As the polymerization temperature increases, M_n deviates from the theoretical line to a greater extent and $Đ_M$ increases. At 70 °C, however, the M_n data are close to theoretical prediction and the values of $Đ_M$ are relatively low (1.15–1.20) and do not change significantly with conversion.

The variation of x_n and N_{total} with conversion presented in Figs. 5(c), 7(a and b) show these trends more clearly. There is good agreement between theoretical and experimental x_n for polymerization at 70 °C, but an increasing positive deviation from the theoretical line as temperature increases to 90 °C and then 110 °C. Whilst at 90 °C there is an initial reduction in N_{total} after which it becomes approximately constant, at 110 °C there is a continuous reduction in N_{total}, showing that active chains are lost at a significant rate throughout the reaction at this temperature. In addition, early in the polymerization at 110 °C, the initial value of N_{total} is significantly higher than the theoretical value (i.e., higher than [Styryl-TITNO]₀), most probably due to a significant contribution from thermal generation of radicals by styrene, which will proceed more rapidly as temperature increases and at lower conversions (because it depends on [styrene]³ [26]). In accord with the inferences from Fig. 6(a and b), Fig. 7(a) shows that for polymerization at 70 °C N_{total} remains approximately constant and equal to
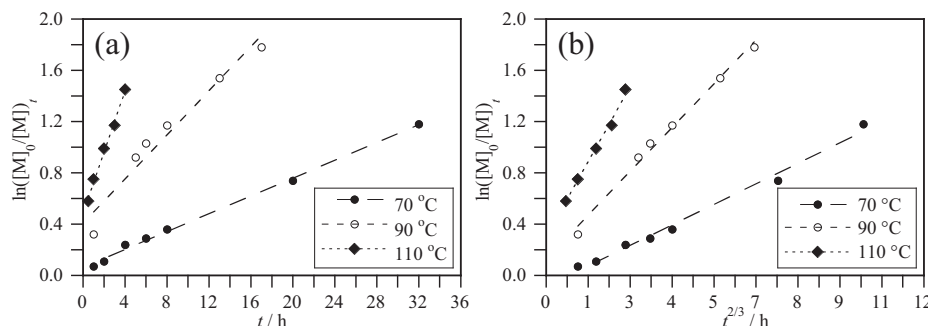
Fig. 9. Plots of (a) $\ln([M]_0/[M]_t)$ vs t and (b) $\ln([M]_0/[M])$ vs $t^{2/3}$ for polymerizations of styrene at 70, 90 and 110 °C mediated by Styryl-TITNO with $[\text{styrene}]_0/[\text{Styryl-TITNO}]_0 \approx 100$ and ~16 mol% of free TITNO.

[Styryl-TITNO]$_0$ as conversion increases, whilst $Đ_M$ remains low throughout, thus showing that there is no significant loss of active chains. Hence, Styryl-TITNO mediated polymerization of styrene has a high degree of livingness when performed at 70 °C with ~16 mol% added excess TITNO. The results also imply that in all NMPs of styrene at temperatures ≥90 °C (as is the case for most reports in the literature), irrespective of the alkoxyamine used, thermal generation of radicals from styrene and loss of active chains will invariably occur with consequent significant reductions in the degree of livingness. The discovery of TITNO as a mediator that facilitates control of styrene NMP at 70 °C, therefore, is both significant and important.

3.5. Kinetics of styrene homopolymerization mediated by Styryl-TITNO

Plots of $\ln([M]_0/[M]_t)$ vs t and $t^{2/3}$ for the solution polymerizations of styrene at 90 °C with different levels of excess TITNO are presented in Fig. 8. It can be seen that, although the data fit well to a linear variation of $\ln([M]_0/[M]_t)$ with t (with correlation coefficients of 0.991, 0.998 and 0.997), there is evidence of curvature (particularly for 0 and 15.9 mol% excess TITNO) and, unlike for BA, the lines deviate substantially from passing through the origin. In contrast, the plots of $\ln([M]_0/[M]_t)$ vs $t^{2/3}$ give good linear fits to Equation (6) (with correlation coefficients of 0.999, 0.985 and 0.996) that pass close to the origin.

Fig. 9 shows the plots of both $\ln([M]_0/[M]_t)$ vs t and $t^{2/3}$ for styrene polymerizations in the presence of ~16 mol% added excess TITNO at different temperatures. The plot of $\ln([M]_0/[M]_t)$ vs t at 70 °C is linear and on extrapolation is very close to passing through the origin, observations that are consistent with an absence of significant termination. At 90 and 110 °C, however, the data fit better to Equation (6), indicating that termination is contributing at these temperatures, though it must be recognised that the equation comes from the PRE theory for polymerizations in the *absence* of an initial excess of nitroxide, so strictly is not valid for the styrene polymerizations in which excess TITNO is added from the start. Also, as discussed when presenting the kinetics theory, calculation of K from the plot of Equation (6) for the data from the polymerization with no added TITNO requires knowledge of k_t, the value of which is not known with any certainty. Hence, despite evidence of a PRE, Equation (6) does not afford a reliable method for determination of K. Since the simpler theory gives good linear fits of the data from the time of the first sample onwards, it is not unreasonable to employ the theory for analysis in this region. Furthermore, the simpler theory facilitates easy calculation of K using accurately-known Arrhenius parameters for k_p of styrene [27]. Thus the fits to Equation (2) in the region of linear variation of $\ln([M]_0/[M]_t)$ with t for the styrene polymerizations with added

excess TITNO have been used to determine values of K from Equations (2) and (5) in the same way as for BA. The resulting data are presented in Table 1, which also includes data from analysis of the BA polymerizations performed at 90 °C for comparison.

The values of $k_p[\dot{P}]$ given in Table 1 are the slopes in the linear region of $\ln([M]_0/[M]_t)$ vs t plots and are proportional to the rate of polymerization ($= k_p[\dot{P}][M]_t$). As expected, therefore, rates of polymerization reduce as the level of added excess TITNO increases, and increase as temperature increases. The values of $[\dot{P}]$ were determined from $k_p[\dot{P}]$ data using well-established, reliable values for k_p. For the two BA polymerizations $[\dot{P}]$ is in the range $5-15 \times 10^{-10}$ mol L^{-1}, whereas for styrene the range is $2-5 \times 10^{-8}$ mol L^{-1}. Thus the BA polymerizations proceeded at much lower values of $[\dot{P}]$, but with rates of polymerization similar to those for styrene due to the much higher k_p for BA compared to styrene.

Values of K determined from $[\dot{P}]$ and r for polymerizations performed with added excess TITNO also are included in Table 1. It can be seen that K is a factor of ~22× smaller for BA than styrene at 90 °C with $r \approx 0.16$, which results in the much lower value of $[\dot{P}]$. Thus, in the polymerization of BA, the equilibrium between dormant and active species is shifted further towards the dormant species than for styrene, and this contributes to the better control of M_n and $Đ_M$ at 90 °C for BA compared to styrene. Benoit et al. [8] reported that the activation energy, E_d, for the dissociation of polystyrene-SG1 (121 kJ mol^{-1}) was lower than for PBA-SG1 (130 kJ mol^{-1}), corresponding to a lower value of k_d for polystyrene-SG1 at a given temperature. Our results are consistent with their observations and imply that k_d for PBA-TITNO is lower

Table 1
Kinetic parameters for solution polymerizations of BA and styrene mediated by Styryl-TITNO.

M[a]	T/°C	$[I]_0$[b]/mmol	$[M]_0/[I]_0$	r[c]	$k_p[\dot{P}]$[d]/s^{-1}	$[\dot{P}]$[e]/mol L^{-1}	K[f]/mol L^{-1}
BA	90	1.19	101.0	0	8.73×10^{-5}	14.8×10^{-10}	–
BA	90	0.86	106.5	0.159	3.13×10^{-5}	5.32×10^{-10}	8.5×10^{-11}
Styrene	90	1.49	100.9	0	4.91×10^{-5}	5.39×10^{-8}	–
Styrene	90	0.92	104.3	0.057	3.08×10^{-5}	3.38×10^{-8}	2.0×10^{-9}
Styrene	90	0.92	105.6	0.160	2.39×10^{-5}	2.62×10^{-8}	4.1×10^{-9}
Styrene	70	0.99	96.6	0.164	0.97×10^{-5}	2.01×10^{-8}	3.1×10^{-9}
Styrene	110	0.94	110.2	0.163	6.63×10^{-5}	4.18×10^{-8}	6.9×10^{-9}

[a] M = monomer.
[b] $[I]_0 = [\text{Styryl-TITNO}]_0$.
[c] $r = [\text{TITNO}]_0/[\text{Styryl-TITNO}]_0$.
[d] $k_p[\dot{P}]$ obtained as the slopes of $\ln[M]_0/[M]_t$ vs t plots.
[e] Calculated from $k_p[\dot{P}]$ using k_p values derived from the k_p Arrhenius parameters for BA [22] and styrene [27] (giving for BA at 90 °C $k_p = 58,840$ L mol^{-1} s^{-1} and for styrene $k_p = 482, 911$ and 1585 L mol^{-1} s^{-1} at 70, 90 and 110 °C, respectively).
[f] Calculated from Equation (5) using the values of $[\dot{P}]$ and r given in the table.

Table 2
Equilibrium constants (K) for NMP of BA and styrene using various alkoxyamines.

Alkoxyamine	Monomer	$T/^{\circ}C$	K/mol L^{-1}	r[a]	Method	Reference
Styryl-TEMPO	Styrene	125	2.1×10^{-11}	–	EPR[b]	[16]
Styryl-SG1[c]	Styrene	123	6.1×10^{-9}	–	PRE analysis[c]	[10]
	BA	125	1.1×10^{-10}	0.76	Excess nitroxide[d]	[14]
		115	4.3×10^{-11}	0.90	Excess nitroxide	[14]
PS-SG1	Styrene	120	6.0×10^{-9}	–	EPR	[8]
	BA	120	1.7×10^{-10}	–	EPR	[8]
	Styrene	125	1.9×10^{-8}	2.62	Excess nitroxide	[9]
	Styrene	115	7.7×10^{-9}	2.50	Excess nitroxide	[9]
BlocBuilder	Styrene	115	2.2×10^{-9}	0.05	Excess nitroxide	[12]
Styryl-BIPNO	Styrene	123	1.1×10^{-8}	–	SEC[e]	[13]
Styryl-TIPNO	Styrene	123	7.5×10^{-9}	–	SEC	[13]
Styryl-(N-β-Sulfinyl)	Styrene	110	3.3×10^{-9}	–	EPR	[11]
	Styrene	90	5.2×10^{-10}	–	EPR	[11]
Styryl-TITNO	Styrene	70	3.1×10^{-9}	0.16	Excess nitroxide	This work
	Styrene	90	2.0×10^{-9}	0.06	Excess nitroxide	This work
	Styrene	90	4.1×10^{-9}	0.16	Excess nitroxide	This work
	Styrene	110	6.9×10^{-9}	0.16	Excess nitroxide	This work
	BA	90	8.5×10^{-11}	0.16	Excess nitroxide	This work

[a] $r = $ [Added excess nitroxide]$_0$/[Alkoxyamine]$_0$.
[b] The concentration of free nitroxide formed during polymerization was determined by EPR spectroscopy.
[c] The value of K was calculated using the Fischer persistent radical effect (PRE) theory via Equation (6).
[d] The value of K was calculated using the excess nitroxide method via Equations (2) and (5).
[e] The concentration of free nitroxide formed during polymerization was determined indirectly from size exclusion chromatography data.

than that for polystyrene-terminated TITNO (PS-TITNO), for which k_d is considered to be similar to that of Styryl-TITNO and too high at 90 °C for control of styrene polymerization. The lower value of k_d at 70 °C for styrene leads to a lower value of K (=3.1 $\times$ 10^{-9} mol L^{-1}) which, when combined with significantly reduced rates of styrene thermal initiation and bimolecular termination at 70 °C, gives rise to the observed high degree of control.

The values of K for Styryl-TITNO mediated polymerizations determined in this work (3.1–6.9 $\times$ 10^{-9} mol L^{-1} with an r value of ∼0.16) are collected in Table 2 together with those reported for other alkoxyamines. The BA polymerization data were discussed earlier in this paper, so the focus here is on the styrene polymerizations. With the notable exception of Styryl-TEMPO (which has a very low value of K), the value of K for Styryl-TITNO mediated polymerization of styrene at 70 °C (3.1 $\times$ 10^{-9} mol L^{-1}) is at the lower end of the range of K (3–19 $\times$ 10^{-9} mol L^{-1}) for controlled mediation with the other alkoxyamines *at higher temperatures* (110–125 °C), consistent with the observed high degree of control of M_n and $Đ_M$ when using Styryl-TITNO at 70 °C. Styryl-(N-β-Sulfinyl) alkoxyamine has structural similarity to Styryl-TITNO in terms of the α- and α′-substituents to the N atom and has been used to mediate styrene polymerization at 90 °C with $K = 5.2 \times 10^{-10}$ mol L^{-1}, which is approximately an order of magnitude *lower* than K for Styryl-TITNO at 90 °C. Thus Styryl-TITNO is unique in its ability to control NMP of styrene and BA at temperatures below 100 °C, which arises principally from its low value of E_d (104 kJ mol^{-1}) in comparison to other more well-established styryl alkoxyamines (116–133 kJ mol^{-1}), as discussed previously [7].

4. Conclusions

Use of Styryl-TITNO as mediator for NMP of BA and styrene has been investigated at temperatures ≤110 °C. Very good control of M_n and $Đ_M$ with no measurable loss of active chains, and no evidence of low molecular weight tails in the MWD as conversion increases, was observed for BA at 90 °C, whereas for styrene the lower temperature of 70 °C was necessary in order to achieve this level of control. There is clear evidence that in styrene NMP good control of M_n and $Đ_M$ is lost at the higher temperatures of 90 and 110 °C due to contributions from styrene thermal initiation and bimolecular

termination, which are particularly significant at lower conversions (i.e. higher [styrene]), as might be expected given that the rate of thermal initiation [26] is proportional to [styrene]^3.

The differences in optimum polymerization temperature can be related to the already-established values of K required for control in NMP of BA (typically $K \sim 10^{-10}$ mol L^{-1}; see Table 2) and styrene (typically $K \sim 2$–8×10^{-9} mol L^{-1}; see Table 2), recognising that for PBA-TITNO $K = 8.5 \times 10^{-11}$ mol L^{-1} at 90 °C and for PS-TITNO $K = 3.1 \times 10^{-9}$ mol L^{-1} at 70 °C. As shown previously [7], the much lower value of E_d for TITNO alkoxyamines is responsible for its ability to achieve the necessary values of K at temperatures much lower than possible for the more established nitroxides, such as TEMPO, TIPNO and SG1. This is especially significant for NMP of styrene since it appears to eliminate completely the complications that arise from styrene thermal initiation at higher temperatures. In subsequent papers, we will demonstrate successful use of Styryl-TITNO for synthesis of block copolymers in solution and for effecting homopolymer and block copolymer synthesis in mini-emulsion polymerizations.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2013.12.060.

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