2,2,6,6-Tetramethylpiperidin-1-ylthiyl, the sulfur analogue of TEMPO, as an initiator for the controlled radical polymerisation of styrene

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2,2,6,6-Tetramethylpiperidin-1-ylthiyl (TEMPS), the sulfur analogue of the well known TEMPO free radical, has been investigated as an initiator/moderator for the controlled/living radical polymerisation (CRP) of styrene. Polymerisations were carried out at 125 °C using benzoyl peroxide and AIBN as conventional thermal initiators. The results show that TEMPS has a significant effect on the polymerisations but unlike CRP carried out using TEMPO they do not follow a 'living' pathway.

Introduction

Recent years have witnessed an immense level of interest in the development of new reagents and initiator systems that allow us to exert a large degree of control over conventional free radical polymerisations, so-called controlled/living radical polymerisation (CRP).[1] CRP combines the simplicity of radical polymerisation with the advantages of living polymerisation leading to macromolecular materials with very closely defined structures and physical characteristics.

Amongst the first attempts at creating a living free radical polymerisation process was the pioneering work of Otsu who utilized organic disulfides, **1**–**3**, as initiators/moderators for the polymerisation of styrene[2,3] and methyl methacrylate.[4] While the polymerisations which included these disulfides displayed some of the characteristics of living polymerisations, they did not generally produce materials with accurately controlled molecular weights and narrow polydispersities, and Otsu used the term iniferter (*ini*tiator-trans*fer* agent-*ter*minator) to describe these disulfide initiators.[5]

Subsequently a variety of compounds, particularly stable free radicals and transition metal complexes, have been investigated as CRP initiators. These can be divided into three broad classes; (i) nitroxide radical mediated polymerisation (NMP), which utilizes stable nitroxide radicals such as TEMPO **4** (Fig. 1) or their alkoxyamine precursors **5**, in conjunction with conventional thermal initiators;[6–9] (ii) atom transfer radical polymerisation (ATRP), which uses transition metal complexes and organic halides as catalytic initiators;[10] (iii) addition–fragmentation processes, such as the RAFT process, which involves addition of thiocarbonyl compounds **6** to conventional radical polymerisations.[11–13] Each of these classes of CRP offers its own advantages and challenges. Nonetheless, there remains a need for the development of alternative initiator systems and several different types of compound, including verdazyl and triazolinyl radicals[14,15] and borinate derivatives[6] have been investigated for this purpose.

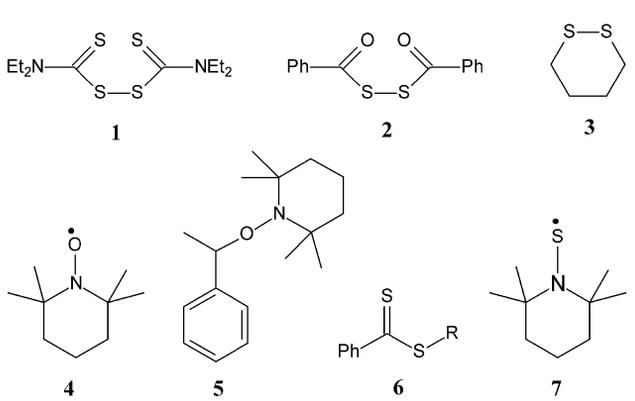
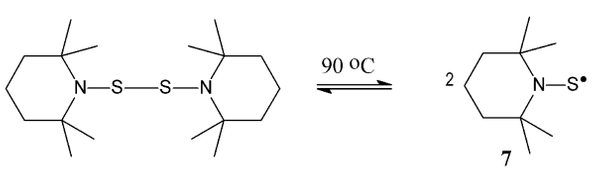


Fig. 1 Compounds that have been investigated as CRP initiators.

Our own interest lies in the synthesis and applications of sulfur–nitrogen based free radicals.[16] We were keen to explore whether these species could be used to control the polymerisation of vinyl monomers in an analogous manner to NMP. Herein we describe our studies into the polymerisation of styrene using 2,2,6,6-tetramethylpiperidin-1-ylthiyl, TEMPS **7** (Fig. 1), the sulfur analogue of TEMPO. Although TEMPS has been known for many years its chemistry remains relatively unexplored.[17,18] At room temperature, unlike TEMPO, TEMPS exists as the corresponding disulfide. However, upon heating to 90 °C homolytic fission of the sulfur–sulfur bond occurs, generating the corresponding radical (Scheme 1).[17]



Scheme 1 Dissociation of 2,2,6,6-tetramethylpiperidin-1-yl disulfide into TEMPS.

Our work described herein, utilising the TEMPS radical as a CRP initiator/mediator for the polymerisation of styrene, provides a link between the previously reported disulfide iniferters and TEMPO-assisted NMP.

Results and discussion

Nitroxide mediated radical polymerisation is technically one of the most simple CRP processes requiring only the addition of the desired radical, *e.g.* TEMPO, to a conventional thermally-initiated radical polymerisation. Mechanistically,

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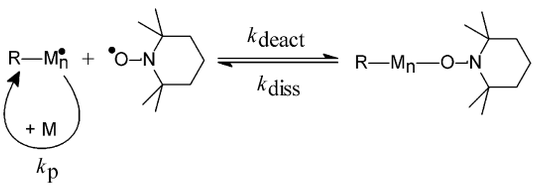
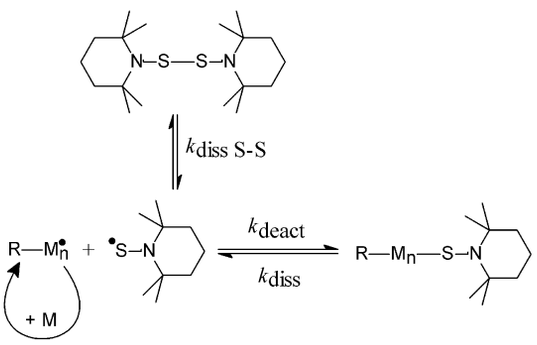
TEMPO forms a weak bond with the growing macroradical and an equilibrium is rapidly established (Scheme 2), in which



Scheme 2

the nitroxide-capped macroradicals undergo a succession of dissociation–monomer addition–deactivation cycles whereby they are alternatively transformed from dormant alkoxyamines into active radicals by thermal homolysis. The process is very similar to that proposed by Otsu for his disulfide iniferters.[6] Therefore TEMPS, in principle, should also follow a similar pathway (Scheme 3).



Scheme 3

Polymerisation of styrene was achieved by heating the monomer at 125 °C in the presence of 2,2,6,6-tetramethylpiperidin-1-yl disulfide and either benzoyl peroxide (BPO) or azoisobutyronitrile (AIBN) as conventional thermal initiators. At this temperature the 2,2,6,6-tetramethylpiperidin-1-yl disulfide undergoes homolytic fission generating the TEMPS free radical (Scheme 1). The initial concentrations of 2,2,6,6-tetramethylpiperidin-1-yl disulfide and thermal initiators were based on those reported previously in NMP,[7,8] assuming that at this temperature all of the disulfide dissociates into TEMPS. Solutions were degassed prior to use and the reactions run under nitrogen.

In each case it was found that the percentage monomer conversion increased linearly with time and, as illustrated in Fig. 2,

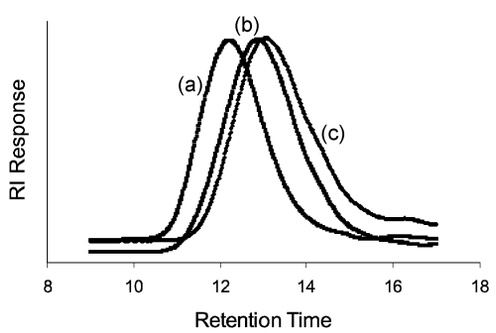


Fig. 2 GPC elution curves for polymers obtained from the polymerisation of styrene using TEMPS and AIBN for (a) 1.5, (b) 3 and (c) 6 hours. $[TEMPS]_0 : [AIBN]_0 = 2.5 : 1$.

GPC elution curves of the polymers shifted to the higher molecular weight side with reaction time. The GPC chromatographs of several of the polymers showed evidence of a second low molecular weight species. The second peak is always considerably smaller than the main peak. In each case the physical characteristics of the low molecular weight peak remained constant, with a M_n of *ca.* 1500 and a M_w of *ca.* 2300 and M_n/M_w of *ca.* 1.53. The exact origin of this trace of low molecular weight polymer is unclear at present although we note that similar unexplained features have been observed in other CRP processes.[1]

The GPC analysis of the polymers showed that although the number average molecular weight, M_n, of the polymers increased with time, the increase was not linear. Furthermore, the M_n/M_w of the resulting polymers does not remain constant but increases as a function of time (Fig. 3). This indicates that the polymerisations do not proceed *via* a living process.

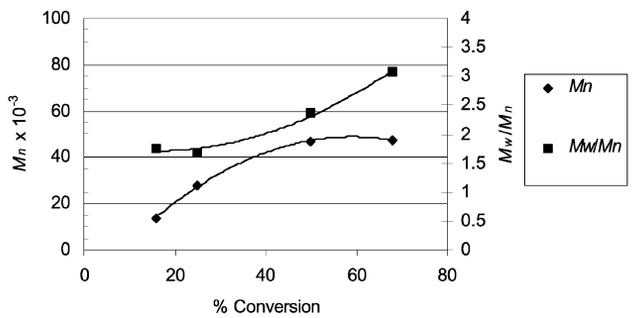


Fig. 3 Evolution of M_n and M_w/M_n as a function of % monomer conversion. $[TEMPS]_0 : [BPO]_0 = 2.5 : 1$.

The rate of conversion of polymerisations carried with TEMPS was higher than for analogous reactions carried out with TEMPO. For example, Georges *et al.* reported only 20% conversion of styrene after 21 hours reaction time and 76% conversion after 45 hours ($[BPO]_0 = 0.036$ M and TEMPO/BPO = 1.2),[7] whereas polymerisations of styrene carried out under analogous conditions using TEMPS and BPO gave greater than 60% conversion in only three hours. This could be due to the fact that the sulfur–carbon bonds formed by TEMPS and the growing polymer chain are weaker than the oxygen–carbon bonds formed by TEMPO, *i.e.* for TEMPS K_{diss} (Scheme 3) is less than K_{deact}. The rate of conversion of styrene using TEMPS was also more rapid than polymerisation carried out in the presence of disulfide iniferters **1**–**3**.

From these results it is apparent that the polymerisations including TEMPS do not follow a similar pathway to those involving TEMPO. One possibility is that the interaction of TEMPS with the growing macroradicals is not as facile as that of TEMPO, leading to a faster rate of conversion and broader molecular weight distribution. Alternatively, it is possible that even at the reaction temperature of 125 °C the equilibrium between 2,2,6,6-tetramethylpiperidin-1-yl disulfide and TEMPS (Scheme 3) lies slightly towards the left-hand-side, resulting in a lower availability of TEMPS radicals to form a bond with the growing polymer chains. In order to probe this further we have carried out a series of experiments utilising larger initial quantities of 2,2,6,6-tetramethylpiperidin-1-yl disulfide, which should increase the number of available TEMPS radicals in solution. The results are compiled in Table 1. When the ratio of 2,2,6,6-tetramethylpiperidin-1-yl disulfide to thermal initiator is 0.6 : 1 then, after three hours at 125 °C, the polydispersity, M_w/M_n of the resulting polymer is 4.01. As this ratio is increased to 0.75 : 1 and 1.25 : 1 then the M_w/M_n of the polymers decreases to 3.83 and 1.89 respectively, with a concomitant reduction in the percentage monomer conversion. When a large excess of 2,2,6,6-tetramethylpiperidin-1-yl disulfide is present (ratio of 2.5 : 1) then the polymerisation is severely retarded and only 1% conversion is achieved after three hours.

Otsu and coworkers reported that related thiyl radicals do not readily initiate the polymerisation of styrene.[2] Consistent with this, polymerisations carried out with tetramethylpiperidin-1-yl disulfide only (*i.e.* no AIBN or BPO) resulted in only

Table 1 The results of the polymerisation of styrene in the presence of the TEMPS after 3 hours at 125 °C

Entry	Thermal initiator	Ratio[a]	% Conversion	$M_n \times 10^{-3}$	M_w M $\times 10^{-3}$	M_n/M_w
1	BPO	0.6 : 1	64	15.4	61.7	4.01
2	BPO	0.75 : 1	68	23.0	88.1	3.83
3	AIBN	0.75 : 1	48	58.2	110.9	1.91
4	BPO	1.25 : 1	23	32.8	62.0	1.89
5	AIBN	1.25 : 1	29	54.0	119.7	2.22
6	BPO	2.5 : 1	1	71.0	162.4	2.29

[a] Ratio of [tetramethylpiperidin-1-yl disulfide]$_0$/[thermal initiator]$_0$. Initial concentration of BPO or AIBN = 0.036 M.

10% monomer conversion after six hours, significantly less than the thermal self-initiated polymerisation of styrene which results in 50% monomer conversion after four hours at 127 °C.[19]

After precipitation from methanol and drying, the polystyrene produced in these experiments were free-flowing white powders, the TGA thermograms of which were very similar to that of a polystyrene standard. Only the polymers produced using a large excess of the parent disulfide were discoloured, having a pale yellow appearance, indicating that the material was contaminated with sulfur-containing impurities.

Experimental

Initiators

Benzoyl peroxide and AIBN were purchased commercially and used as received. 2,2,6,6-Tetramethylpiperidin-1-yl disulfide was prepared from 2,2,6,6-tetramethylpiperidine (Aldrich) and sulfur dichloride (Aldrich) following the method outlined in reference 10. 2,2,6,6-Tetramethylpiperidine (6.6 g, 0.046 mol) was dissolved in DMF (20 cm^3) and cooled to −50 °C. Sulfur dichloride (1.2 g, 0.012 mol) in DMF (10 ml) was added dropwise over a period of 30 minutes. The solution was slowly warmed to room temperature before being poured into water (20 cm^3). The resulting cream coloured precipitate was filtered off and recrystallised from ethanol. Yield 1.2 g (30%); Found C, 63.13; H, 10.57; N, 8.10; S, 18.68% $C_{18}H_{36}N_2S_2$ requires C, 62.78; H, 10.46; N, 8.14; S, 18.62%; *m*/*z* 344.3 (M^+), 204.1, 172.1, 126.2, 69.1, 41.0.

Polymerisation experiments

All reactions and manipulations were carried out under an atmosphere of dry nitrogen using standard double-manifold techniques. Monomers were distilled under reduced pressure prior to use. The polymerisations were carried out in dry Schlenk tubes. Monomer and initiators were introduced into the reaction tube under inert atmosphere. The mixture was thoroughly degassed before being placed in an oil bath held at the desired temperature by an IKAMAG digital thermometer/stirrer hotplate. Percentage conversions were determined by gravimetry or thermal gravimetric analysis. Upon completion of the reactions the polymer mixtures were dissolved in THF and then re-precipitated by adding the THF solutions to methanol.

Characterisation

Mass spectra were recorded using a VG Micromass 7070F spectrometer using EI ionisation. Infra red spectra were recorded on an ATI Mattson Genesis Series spectrometer. Thermal Gravimetric Analysis (TGA) was carried out on a Mettler-Toledo TA8000 instrument using a heating rate of 20 °C min^{-1} from 30 to 550 °C.

Elemental analysis was carried out by the Microanalysis Service at the Department of Chemistry, University of Manchester.

GPC analysis employed THF as eluent at a flow rate of 1.0 ml min^{-1} through a column set consisting of one PLgel precolumn (5 cm 5 μm) and two PLgel 30 cm mixed bed 5 μm columns, all held at 35 °C, a Pl labs LALS detector and a Viscotec model 250 combined viscometry/RI detector also held at 35 °C. Data analysis was accomplished using viscotec trisec data acquisition and manipulation Software with universal and conventional calibration using polystyrene standards.

Conclusions

Our studies show that the TEMPS free radical has a significant effect on the polymerisation of styrene. However, unlike its analogue TEMPO, it does not lead to a controlled/living free radical polymerisation and its behaviour is more reminiscent of dialkyl disulfide iniferters **1**–**3**. The rate of monomer conversion in polymerisations using TEMPS as a moderator is significantly faster than those that utilise TEMPO.

A criterion that is frequently used to characterise a controlled/living polymerisation is a linear evolution of conversion with time but with a near constant and narrow polydispersity. The reactions reported here show deviations from linearity and a broadening of the polydispersity with time, indicating that bimolecular, irreversible termination reactions are taking place. A further possibility is that during the polymerisation slight decomposition of the TEMPS or the tetramethylpiperidin-1-yl disulfide takes place, producing impurities that are capable of initiating or terminating polymer chains.

The role of TEMPS in the polymerisation of styrene is complex and we are currently carrying out further studies in order to elucidate its mode of action. Furthermore, we are exploring the use of other sulfur–nitrogen radicals as CRP initiators/moderators.

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