

# Initiation in free radical copolymerization studied by the nitroxide trapping method: styrene and acrylonitrile

W. Ken Busfield\*, Ian D. Jenkins and Michael J. Monteiro

School of Science, Griffith University, Nathan, Brisbane, Queensland 4111, Australia  
 (Received 21 February 1996; revised 19 April 1996)

The initiation steps in the copolymerization of styrene and acrylonitrile with *t*-butoxyl radicals have been investigated using the nitroxide trapping technique. *t*-Butoxyl radicals add to styrene five times more rapidly than to acrylonitrile whereas methyl radicals, formed by  $\beta$ -fragmentation of *t*-butoxyl radicals, add to acrylonitrile about four times faster than to styrene. Acrylonitrile also reacts fast with first generation styryl radical end groups. Trapped products containing both monomers can only be observed, however, by operating at very low nitroxide trap concentrations. This has been achieved by using a syringe pump to feed nitroxide trap to the reaction mixture at a controlled rate. Some information on rate constants for second monomer addition has been obtained. Solvent effects on the relative rates of addition of *t*-butoxyl radicals have been observed and discussed. Copyright © 1996 Elsevier Science Ltd.

(Keywords: initiation; free radical; styrene; acrylonitrile; nitroxide trapping; copolymerization)

## INTRODUCTION

The nitroxide radical trapping technique was developed at the Division of Chemicals and Polymers, CSIRO Melbourne. The success of the technique depends on the fact that certain stable nitroxide radicals react at close to diffusion controlled rates with carbon centred radicals to produce stable identifiable alkoxyamines, but do not react with oxygen centred radicals at 60–90°C, the normal conditions used for free radical polymerization. The technique has since been used extensively to investigate initiation mechanisms in many free radical polymerization systems<sup>1</sup> and other free radical reactions<sup>2</sup>. In this series of papers, we describe results obtained from the application of the technique to mixed monomer systems. Information has been obtained on the relative reactivity of monomers with initiator radicals, the effect of solvent and in some cases kinetic data for the early steps in copolymerization.

This paper covers the initial steps in the copolymerization of styrene (S) and acrylonitrile (A) initiated by thermal decomposition of di-*t*-butyl peroxyoxalate producing *t*-butoxyl radicals. These monomers exhibit strongly contrasting electron donating properties, and hence, there is a strong tendency to alternation in copolymerization. The copolymers of A and S are thermoplastics of increasing commercial importance due to their superior properties to those of polystyrene and the relative ease of fabrication.

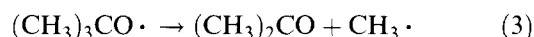
Initiation in the homopolymerization of both S and A has been previously investigated by the nitroxide trapping technique<sup>1,3</sup>, but there has been no previous work on initiation in copolymerization.

## RESULTS AND DISCUSSION

### Initiation mechanisms in the separate monomer systems

In a typical reaction, monomer is heated at 60°C with di-*t*-butyl peroxyoxalate (I, 1 equivalent,  $6.0 \times 10^{-3} \text{ mol l}^{-1}$ ) and 1,1,3,3-tetramethyl-1,3-dihydro-1H-isoin-dol-2-yloxyl (T, 2.2 equivalents,  $1.32 \times 10^{-2} \text{ mol l}^{-1}$ ) under vacuum for 10 half lives (68 min). The products are separated and quantified by h.p.l.c., and their structures elucidated by n.m.r. and other spectroscopic techniques. The products in order of elution with styrene and acrylonitrile as monomer are shown in *Schemes 1* and *2*, respectively. The yields in brackets are those achieved in previous studies<sup>1,3</sup>. There is reasonable agreement, except for the observation of a small yield of **4** which was not observed in the earlier study<sup>3</sup>.

In both monomer systems, the major product is tail addition by *t*-butoxyl radicals (i.e. products **3** and **5**). All the other products arise from reactions of methyl radicals produced by  $\beta$  scission of *t*-butoxyl radicals (reaction (3)).



The extent of reaction (3) can be used as a radical clock. By comparing the product yields of methyl with *t*-butoxyl radical addition for each system, *t*-butoxyl radicals react six times faster with styrene than with acrylonitrile (whilst previous results from Rizzardo *et al.*<sup>1,3</sup> suggest a factor of 18). However, there is convincing evidence that reaction (3) is strongly solvent dependent<sup>4</sup>, thus comparison of reactions in different solvents are unreliable.

### Initiation mechanisms in the mixed monomer system

When both monomers are mixed in the reaction vessel

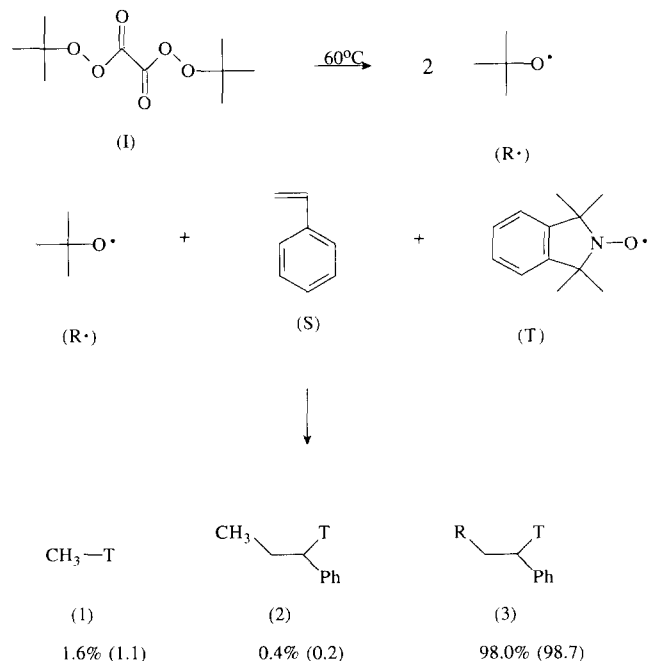
\* To whom correspondence should be addressed

under identical conditions and with similar concentrations of I and T to the separate monomer systems, the reaction products for the mixed monomers are simply a combination of those observed with the separate monomers. For example, the relative product yields with a 1 : 1 molar mixture are shown in *Table 1*.

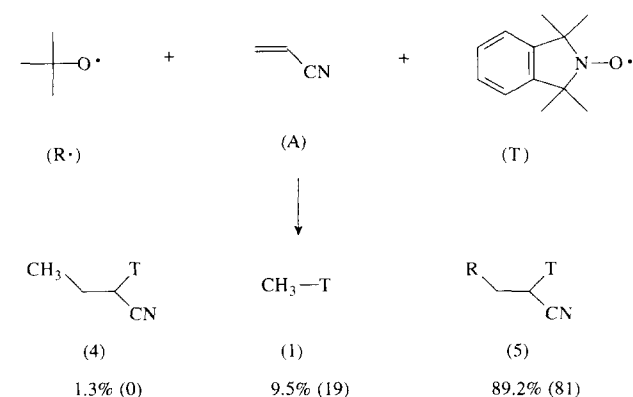
The ratio of the rates of reaction of *t*-butoxyl radicals with S and A can be obtained directly from these results.

$$k_S/k_A = 4.97 \quad (\text{Solvent S : A} = 1 : 1)$$

From the results of Moad *et al.*<sup>5</sup>, *t*-butoxyl radicals are considered to be electrophilic. Therefore, it is expected



**Scheme 1** Products formed from the reaction of *t*-butoxyl radicals with styrene in the presence of T (values in parentheses are percentage yields obtained by Rizzardo *et al.*<sup>1</sup>)



**Scheme 2** Products from the reaction of *t*-butoxyl radicals with acrylonitrile in the presence of T (values in parentheses are percentage yields obtained by Rizzardo *et al.*<sup>3</sup>)

**Table 1** Products formed from 1 : 1 mixed monomer reaction of styrene and acrylonitrile with *t*-butoxyl radicals in the presence of high nitroxide trap concentrations

Product	MeAT	MeT	RAT	MeST	RST
%	3.0	1.5	15.9	0.5	79.1

that the reaction will be faster with an electron rich styrene monomer than acrylonitrile where the cyano group reduces the electron density of the  $\pi$  system. Conversely, methyl radicals have been shown to behave in a nucleophilic manner<sup>6,7</sup>. True to character, they react six times faster with acrylonitrile than with styrene (products 4 and 2).

In a corresponding study<sup>8</sup> of the mixed monomer system vinyl acetate (V) and acrylonitrile (A), a second monomer addition product, RVAT, was observed. It is formed by the reaction of  $RV\cdot$  with A to form  $RVA\cdot$  followed by trapping with T, thus A competed successfully with T.

In order to improve the chance of observing second monomer addition products in the S/A system, a syringe injection technique was used to keep the nitroxide trap concentration at a low and constant level during the reaction. In the traditional (static) method, an excess of trap was required to ensure efficient trapping of all free radicals in the system and to ensure a reasonably constant concentration for kinetic purposes. A typical reaction using the syringe injection technique is as follows. A solution of I ( $0.012 \text{ mol l}^{-1}$ ) and T ( $5.26 \times 10^{-3} \text{ mol l}^{-1}$ ) in a mixture of the two monomers was placed in a reaction vessel under argon gas at  $60^\circ\text{C}$ . The vessel was then injected with a solution of T ( $0.474 \text{ mol l}^{-1}$ ) in  $100 \mu\text{l}$  of the same mixed monomer by a motor driven  $200 \mu\text{l}$  syringe. The rate of injection was designed to compensate for the loss of T in radical termination reactions over 68 min (10 half lives of I at  $60^\circ\text{C}$ ). Therefore, throughout the reaction, [T] is close to the starting mixture concentration of  $5.26 \times 10^{-3} \text{ mol l}^{-1}$ . The required rate of addition of T was determined by following the rate of disappearance of T in a u.v./visible spectrophotometer at 417 nm for the reaction of I ( $0.0085 \text{ mol l}^{-1}$ ) in excess styrene in the presence of T ( $0.0175 \text{ mol l}^{-1}$ ) in an otherwise evacuated vessel at  $60^\circ\text{C}$ . The reaction alkoxyamine products and S showed negligible absorbance at this wavelength. The extinction coefficient for T was pre-measured,  $\epsilon = 7.6 \pm 0.51 \text{ mol}^{-1} \text{ cm}^{-1}$  (cf. literature value<sup>9,10</sup> of  $7.911 \text{ mol}^{-1} \text{ cm}^{-1}$ ). A typical result is shown in *Figure 1*, curve A. In order to keep the concentration of T constant, it must be added at a rate indicated by curve B. This was approximated by manually adjusting the linear flow rates of the syringe pump at each half life to follow curve C.

With this technique, new peaks were observed on the h.p.l.c. chromatogram. Two of the products, identified as (6) and (7), are isomers of the second monomer addition product, RSAT, see *Figure 2*. The two isomers of RSAT always appeared in an approximately 1 : 1 ratio, suggesting that the unpaired electron in  $RSA\cdot$  occupies a *p* orbital so that nitroxide trapping can occur at equal rates above or below the plane (see *Scheme 3*).

Two other small peaks, resolved by h.p.l.c. with relative elution times typical of dimeric species, could not be conclusively identified because there was insufficient material for satisfactory characterization by  $^{13}\text{C}$  n.m.r., and mass spectrometry was inconclusive. However, the products contain both the *t*-butoxy and the trap moieties, and are suspected to be isomers of the second monomer addition product, RSST. An alternative possibility is compound RAST. However, reactivity ratios for styrene/acrylonitrile copolymerization show

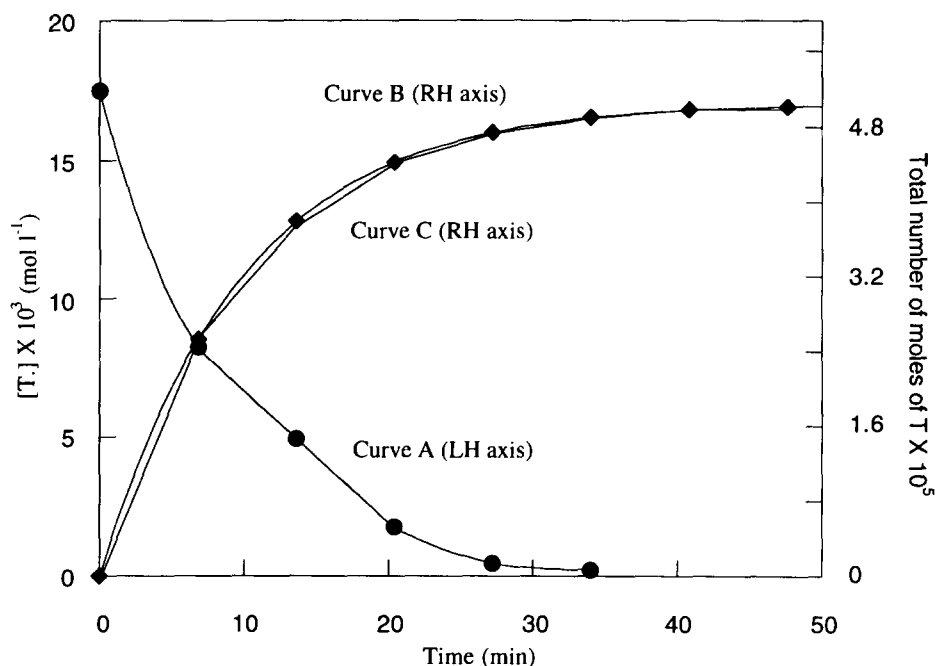


Figure 1 Nitroxide trap decay monitored at 417 nm

that styrene reacts with a styryl end group from 1.6 to 4 times slower than acrylonitrile depending on the penultimate unit<sup>13</sup>. Thus, since RSAT is observed, we would expect to also observe RSST (a stronger chromophore) at low concentration. We therefore favour the assignment of products **8** and **9** to RSST.

There is the possibility that RSAT could be produced by the reaction between R· and a 1 : 1 'charge transfer complex' (Scheme 4).

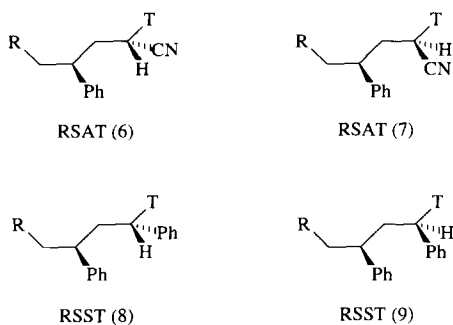
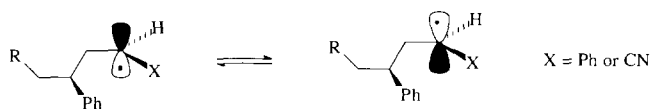
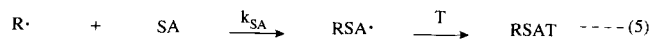
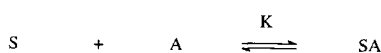


Figure 2 The dimeric products formed at low T concentrations. (Products **8** and **9** are unconfirmed)



Scheme 3



Scheme 4 The charge transfer complex mechanism

If the product RSAT was formed solely by the 'charge transfer complex' mechanism, then the yield of RSAT compared with RST would be independent of the concentration of T and only dependent on the monomer concentrations, that is, where K is the equilibrium

$$\frac{RST}{RSAT} = \frac{k_S[S]}{k_{SA}[SA]} = \frac{k_S}{k_{SA}K[A]}$$

constant for the formation of the 'charge transfer complex' SA. The product percentages as a function of T concentration are given in Table 2. RST/RSAT is clearly dependent on the concentration of T, see Figure 3, showing that a 'charge transfer complex' plays little or no part in the initiation step in the copolymerization of styrene and acrylonitrile. A similar conclusion was obtained by Busfield *et al.*<sup>8</sup> for the copolymerization of vinyl acetate with acrylonitrile. Thus, the present data support the 'free monomer' mechanism shown in Scheme 5.

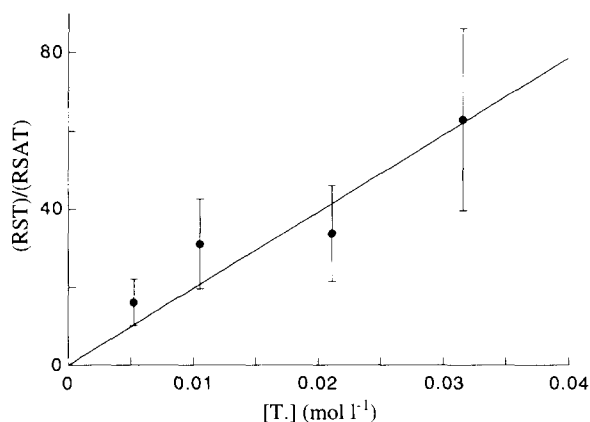
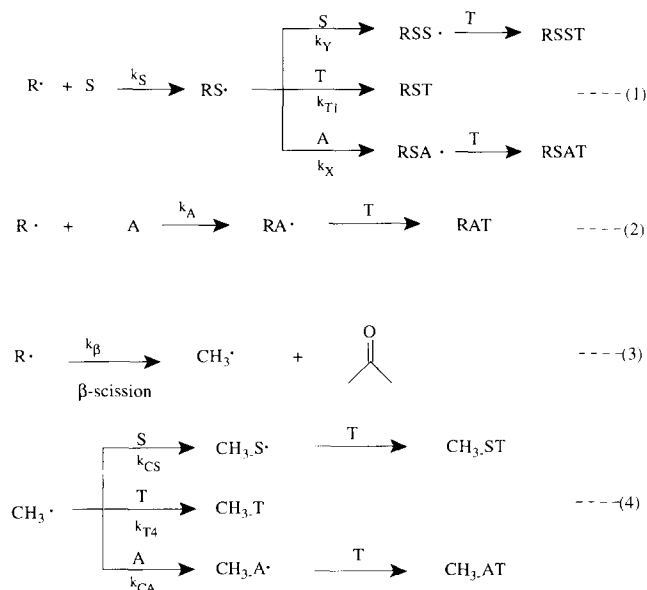
Details of the reactant concentrations and the relative product yields obtained for the reactions of varying monomer ratios and constant trap concentration are shown in Table 3.

These data, which are more extensive than those in Table 1, confirms the relative reactivities of both *t*-butoxyl and methyl radicals towards S and A. That is, according to Scheme 5, a graph of the ratio of yields (RST + RSAT + RSST)/RAT vs. [S]/[A] gives a slope,  $k_S/k_A$  (see Figure 4), and a graph of the ratio of yields MeST/MeAT vs. [S]/[A] gives a slope,  $k_{CS}/k_{CA}$  (see Figure 5). If we assume the graphs are linear, the rate constant ratios are:  $k_S/k_A = 5.2$ ;  $k_{CS}/k_{CA} = 0.31$ . However, the points in Figure 5 indicate a disproportionately high rate of formation of MeST at low S concentration.

At low trap concentration, acrylonitrile competes successfully with trap in the reaction with styryl radicals, see Scheme 5, set (1). The ratio of the yields of products RST and RSAT allows the evaluation of the ratio of the

**Table 2** Percentages of products with a constant monomer ratio of S : A = 0.1 and increasing T concentration

[T] × 10 <sup>-3</sup>	MeAT 4	MeT 1	RAT 5	MeST 2	RSAT 6	RSAT 7	RST 3	RSST <sup>a</sup> 8	RSST <sup>a</sup> 9
5.26	8.9	4.1	57.3	0.6	0.8	0.9	27.2	0.1	0.1
10.53	4.6	6.2	50.0	0.7	0.5	0.7	37.0	0.1	0.2
21.10	5.8	6.4	54.6	1.1	0.4	0.5	31.0	0.1	0.2
31.60	3.7	6.9	53.4	0.2	0.3	0.3	35.2	0.1	0.1

<sup>a</sup>RSST is an unconfirmed structure**Figure 3** Dependence of the product ratio on the concentration of T at a molar ratio of 1 : 10 for S : A**Scheme 5** Normal kinetic control in the copolymerization of styrene and acrylonitrile initiated with *t*-butoxyl radicals

rate constants,  $k_{T1}/k_X$ , for the two reactions. *Figure 6* shows a graph of the ratio of yields,  $(\text{RSAT}/\text{RST})[\text{T}]$  vs.  $[\text{A}]$ ; the points are close to linear and the slope gives  $k_{T1}/k_X = 4.3 \times 10^4$ . The trapping of a primary carbon centered radical with T has been reported<sup>11,12</sup> to be under diffusion control with a rate constant,  $k_T$ , close to  $1 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$  at 18°C. This is unlikely to vary much up to 60°C and therefore, suggests a value of the order of  $2 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$  at 60°C for  $k_X$ . It is of interest to compare  $k_X$  with the rate constant for the addition of

acrylonitrile to a long chain copolymer with a styryl radical chain end. The S/A copolymer system is known to be governed by penultimate unit effects<sup>13</sup> with reactivity ratios  $k_{SSS}/k_{SSA} = 0.23$  and  $k_{ASS}/k_{ASA} = 0.63$ . Taking the average value for this rough comparison (0.43) and the rate constant for homopolymerization of S as  $1761 \text{ mol}^{-1} \text{ s}^{-1}$  at 60°C<sup>14</sup> evaluated from 'pulsed laser photolysis', the rate constant for addition of A to a styryl radical chain end is on average about  $400 \text{ l mol}^{-1} \text{ s}^{-1}$ . It seems totally unrealistic that this value should be 50 times less than  $k_X$ , and we must conclude that  $k_{T1}$  is significantly less than  $1 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$  and may in fact be under kinetic rather than diffusion control.

The nitroxide trap also competes for methyl radicals with both S and A to give three products MeT, MeAT and MeST. However, the amounts are small and quantitative comparisons are accompanied by relatively large experimental error. If the graph of the ratio of yields  $(\text{MeAT}/\text{MeT})[\text{T}]$  vs.  $[\text{A}]$  in *Figure 7* is assumed to be linear, the slope gives  $k_{T4}/k_{CA} = 1.2 \times 10^3$ . Making the same assumption as above (i.e.  $k_{T4} = 1 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ ),  $k_{CA}$  would have a value of the order of  $10^6 \text{ l mol}^{-1} \text{ s}^{-1}$  at 60°C. Earlier it was shown that  $k_{CS}/k_{CA} = 0.31$ , thus  $k_{CS}$  would have a value of the order of  $0.3 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$  at 60°C.

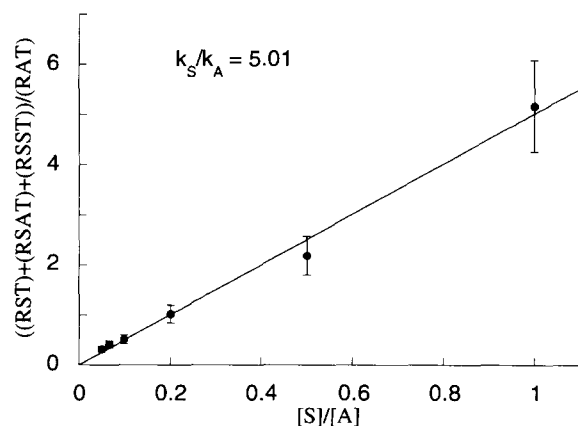
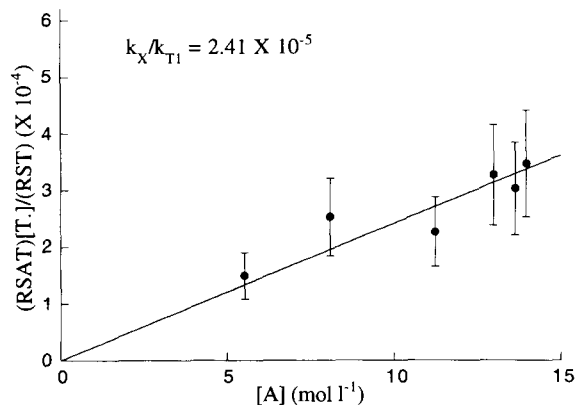
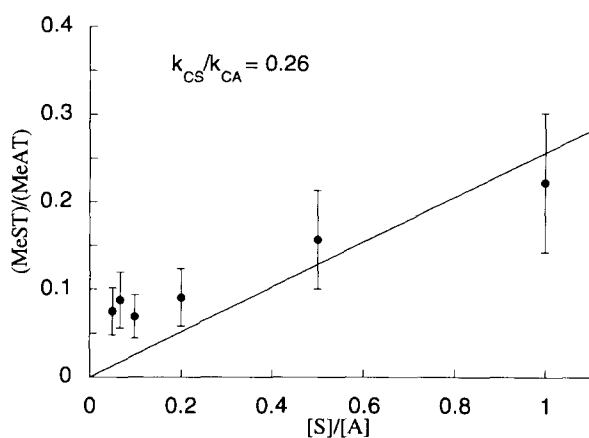
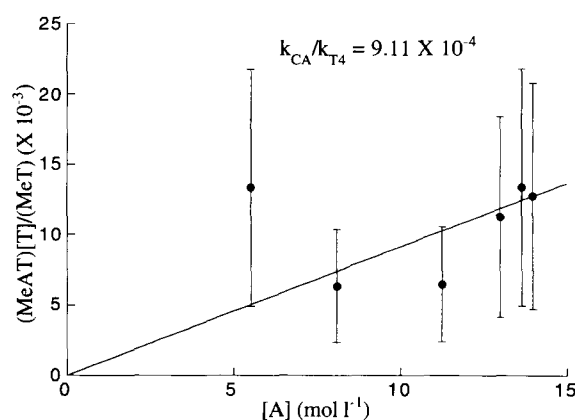
Solvent effects have been observed in many reactions involving free radicals. We have carried out this reaction in solvents cyclohexane and acetonitrile with a 1 : 1 molar mixture of S and A. The solvents were selected on the basis of their similar polarity to monomers S and A, respectively. Dielectric constants are recorded in *Table 4* along with the values of  $k_S/k_A$  derived from experiments in bulk monomer as solvent and in solvents (90% v/v). There is certainly a solvent effect, but it is clearly not just due to solvent polarity. The,  $k_S/k_A$  values for the two non olefinic solvents are similar but contrast markedly with the value in bulk. One possibility is that there is preferential solvation of the *t*-butoxyl radicals by styrene, such that, normal kinetic behaviour is not observed in the bulk system. Therefore, addition of a non-complexing solvent diminishes this preferential solvation by dilution, and normal kinetic control applies.

This explanation is similar to that known as the bootstrap effect<sup>15</sup>, which suggests preferential partitioning of monomer about the polymer coil to explain solvent effects in homopolymerization and copolymerization.

The reaction has also been carried out in *t*-butanol, a typical H-bonding solvent. H-bonding solvents have frequently been observed to have a pronounced effect on radical reactions and copolymerization<sup>16</sup>. The ratio of  $k_S/k_A$  increased markedly compared with the value in non H-bonding solvents (see *Table 4*). The result suggests

**Table 3** Reactant ratios and percentages of products at a constant  $[T]$  of  $5.26 \times 10^{-3}$  M

[S] M	[A] M	MeAT 4	MeT 1	RAT 5	MeST 2	RSAT 6	RSAT 7	RST 3	RSST <sup>a</sup> 8	RSST <sup>a</sup> 9
5.52	5.52	2.8	1.1	15.5	0.6	1.0	1.2	76.9	0.2	0.6
4.05	8.10	3.3	2.7	29.4	0.5	1.4	1.5	60.7	0.2	0.3
2.25	11.25	5.0	4.0	45.0	0.5	0.9	0.9	43.5	0.1	0.1
1.30	12.99	8.9	4.1	57.3	0.6	0.8	0.9	27.2	0.07	0.1
0.91	13.64	8.5	3.4	61.6	0.8	0.7	0.7	24.0	0.05	0.1
0.70	13.97	8.8	3.6	65.8	0.7	0.7	0.7	19.7	0.02	0.02

<sup>a</sup> RSST is an unconfirmed structure**Figure 4** Relative rates of addition of *t*-butoxyl radicals to styrene and acrylonitrile as a function of monomer concentration**Figure 6** Relative rate of addition of acrylonitrile to styryl radicals to nitroxide trapping as a function of acrylonitrile concentration**Figure 5** Relative rates of addition of methyl radicals to styrene and acrylonitrile as a function of monomer concentration**Figure 7** Relative rate of addition of acrylonitrile to methyl radicals to nitroxide trapping as a function of acrylonitrile concentration

that 'complexation' between the *t*-butanol solvent and *t*-butoxyl radical increases the reactivity of *t*-butoxyl radicals toward S.

## CONCLUSION

In summary, this work has shown that *t*-butoxyl radicals add to styrene five times more rapidly than to acrylonitrile, whereas methyl radicals add to acrylonitrile about four times more rapidly than to styrene. This is probably due to the strongly differing electrophilic nature of the two radicals. The ratio of *t*-butoxyl addition to styrene and acrylonitrile is reduced in both

cyclohexane and acetonitrile solvents and enhanced in *t*-butanol solvent in comparison with neat monomer as solvent. This is thought to be due to a change in the electrophilic nature of *t*-butoxyl radicals, caused by loss of preferential solvation with monomer by dilution in the case of non-olefinic solvents and by H-bond complexation producing a gain with *t*-butanol.

We have also shown that by using a specially designed injection system for keeping the nitroxide trap concentration low and constant during the reaction, second monomer addition products can be accumulated and characterized in favourable cases. The addition of acrylonitrile to styryl radical end groups has a rate constant  $2.3 \times 10^{-5}$  that of the nitroxide radical trapping

**Table 4** The effect of solvent on the rate constant ratio  $k_S/k_A$  for reaction of *t*-butoxyl radicals with equimolar S/A mixtures

Monomer	$k_S/k_A$	Dielectric constant <sup>d</sup>
Bulk	5.16	2.43 (25) to 37.5 (20)
Acetonitrile	2.23	33.0 (20)
Cyclohexane	2.86	2.02 (25)
<i>t</i> -Butanol	14.0	17.8 (20)

<sup>a</sup> The values in parentheses are the temperatures in °C

<sup>b</sup> The dielectric constant for the bulk system will lie between the values for styrene and acrylonitrile

of the styryl radical. The comparable figure for acrylonitrile adding to methyl radicals compared to trapping of methyl radicals is  $10^{-3}$ . These figures suggest that the trapping of carbon centered radicals by the nitroxide radical T may not have a rate constant as high as previously reported, and is possibly under kinetic control.

## EXPERIMENTAL

### Materials

Acrylonitrile (Aldrich) was fractionally distilled and stored over 4A Sieves. Styrene (Aldrich) was passed twice through neutral alumina before distillation at reduced pressure. Monomer storage was at 4°C. Acetonitrile was AJAX h.p.l.c. grade. Cyclohexane and *t*-butanol were fractionally distilled. Di-*t*-butyl peroxyoxalate<sup>17</sup> and the nitroxide trap<sup>18</sup> were prepared according to literature procedures.

### Procedure

(a) *Experiments with high (normal) trap concentration.* Initiator (I, 56 mg,  $0.0138 \text{ mol l}^{-1}$ ) and nitroxide trap (T, 115 mg,  $0.031 \text{ mol l}^{-1}$ ) were dissolved in 20 ml of monomer or mixed monomer for preparative scale reactions. The solution was degassed by several freeze-thaw cycles and evacuated to better than  $10^{-4}$  mm Hg before reaction at 60°C for at least three half lives (21 min). The reaction mixtures were concentrated under reduced pressure, dissolved in methanol, filtered and the reaction components separated on a preparative h.p.l.c. column using methanol/water (methanol 70–90%) for elution and 270 nm for u.v. detection. Analytical scale reactions were similar, however, the concentration step was omitted and the reaction mixture (after cooling) was injected directly into an analytical reverse phase h.p.l.c. column. Peak areas were determined by Shimadzu-C-R6A Chromatopac Peak Integrator. Products containing only nitroxide trap moiety as u.v. chromophore were assumed to have identical extinction coefficients (molar proportions equal area proportions). The extinction coefficients of products containing additional u.v. chromophoric groups are given in Table 5.

(b) *Experiments with low trap concentration (syringe pump technique).* Typically, a 1 ml syringe containing T (90 mg) dissolved in 1 ml of the monomer mixture was injected by the syringe pump into a solution of I (56 mg), T (10 mg) in 30 ml of monomer mixture in a reaction vessel at 60°C under argon. The mixtures had previously been de-oxygenated by bubbling argon through them. The rate of injection kept the concentration of T in the vessel constant over the period of the

**Table 5** Extinction coefficients of alkoxyamine products containing an additional u.v. chromophore

Product	$\epsilon$ ( $\text{l mol}^{-1} \text{ cm}^{-1}$ )	Log $\epsilon$
T·	616.4	2.7
RST	1339.9	3.1
RSAT <sup>a</sup>	1339.9	3.1
RSST <sup>a</sup>	1849.2	3.3

<sup>a</sup> Products RSAT and RSST were not isolated in sufficient quantity for measurement of  $\epsilon$ , it was assumed RSAT was identical to that for RST, and that RSST was three times that for T

reaction by the method described. Thereafter, the procedure was as described in (a).

## PRODUCT CHARACTERIZATION

<sup>1</sup>H and <sup>13</sup>C n.m.r. spectra (both proton and off resonance decoupled); DEPT and COSY experiments were used for characterization. The instruments used were Bruker NM-250; Bruker CXP-300; Varian Gemini-200 and Varian Unity-400 spectrometers.

Mass spectra were run at the University of Queensland on a Kratos MS 25 RFA instrument.

The compounds (in order of elution) **4** (MeAT), **1** (MeT), **5** (RAT), **2** (MeST), **3** (RST) have all been observed previously. They were identified by comparing their proton n.m.r. spectra with those published<sup>1,3</sup>.

*New compounds.* New alkoxyamine products were characterized by spectroscopic data listed below. *J* values are given in Hz, ring CH<sub>3</sub> refers to methyl substituents on isoindole. Connectivities of protons were confirmed by 2D COSY n.m.r., and coupling constants were confirmed using the PANIC simulation program.

### 5-*t*-Butoxy-4-Phenyl-2-(1,1,3,3-tetramethyl-2,3-dihydro-1H-isoindol-2-yloxy)pentronitrile (RSAT) **6**

(Found: M 420.2789. C<sub>27</sub>H<sub>36</sub>N<sub>2</sub>O<sub>2</sub> requires 420.2776.)  
 $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 1.10, s, 9H, C(CH<sub>3</sub>)<sub>3</sub>; 1.26, s, 9H, 3 × ring methyls; 1.52, s, 3H, 1 × ring methyl; 2.22, ddd, 1H, <sup>2</sup>*J* = 13.82 Hz, <sup>3</sup>*J* = 9.2 Hz, <sup>3</sup>*J* = 5.62 Hz, CNC(CH<sub>2</sub>)CHPh; 2.44, ddd, 1H, <sup>2</sup>*J* = 13.82 Hz, <sup>3</sup>*J* = 9.4 Hz, <sup>3</sup>*J* = 4.85 Hz, CNC(CH<sub>2</sub>)CHPh; 3.02, m, 1H, <sup>3</sup>*J* = 9.2 Hz, <sup>3</sup>*J* = 8.08 Hz, <sup>3</sup>*J* = 4.94 Hz, <sup>3</sup>*J* = 4.85 Hz, CNC(CH<sub>2</sub>)CHPh; 3.42, dd, 1H, <sup>2</sup>*J* = 8.87 Hz, <sup>3</sup>*J* = 8.08 Hz, (CH<sub>3</sub>)<sub>3</sub>COCH<sub>2</sub>; 3.49, dd, 1H, <sup>2</sup>*J* = 8.87 Hz, <sup>3</sup>*J* = 4.94 Hz, (CH<sub>3</sub>)<sub>3</sub>COCH<sub>2</sub>; 4.34, dd, 1H, <sup>3</sup>*J* = 9.4 Hz, <sup>3</sup>*J* = 5.63 Hz, CHCN; 7.01, m, 5H, CHPh; 7.04, m, 2H, H4 & H7; 7.20, m, H5 & H6.  $\delta_{\text{C}}$  (CDCl<sub>3</sub>) 15.1, s, 2 × ring methyls; 17.5, s, C(CH<sub>3</sub>)<sub>3</sub>; 20.9, s, 2 × ring methyls; 28.0, CHCH<sub>2</sub>CH; 36.0, PhCH; 64.5, CH<sub>2</sub>OC(CH<sub>3</sub>)<sub>3</sub>; 66.2, s, C1 & C3; 72.2, OC(CH<sub>3</sub>)<sub>3</sub>; 73.6, CNCH; 128.4, CN; 130.5, C4 & C7; 137.3, C2'; 137.6, C5 & C6; 138.0, C4'; 139.1, C3'; 154.2, C1'; 158.0, C3a & C7a.

### 5-*t*-Butoxy-4-phenyl-2-(1,1,3,3-tetramethyl-2,3-dihydro-1H-isoindol-2-yloxy)pentronitrile (RSAT) **7**

(Found: MH<sup>+</sup> 421.2855. C<sub>27</sub>H<sub>36</sub>N<sub>2</sub>O<sub>2</sub>H<sup>+</sup> requires 421.2876.)

$\delta_{\text{H}}$ (CDCl<sub>3</sub>) 1.09, s, 9H, C(CH<sub>3</sub>)<sub>3</sub>; 1.24, s, 9H, 3 × ring methyls; 1.56, s, 3H, 1 × ring methyl; 2.16, ddd, 1H, <sup>2</sup>*J* = 14.26 Hz, <sup>3</sup>*J* = 7.73 Hz, <sup>3</sup>*J* = 8.01 Hz, CHCH<sub>2</sub>CH; 2.46, ddd, 1H, <sup>2</sup>*J* = 14.26 Hz, <sup>3</sup>*J* = 7.37 Hz,

$^3J = 6.78$  Hz,  $\text{CHCH}_2\text{CH}$ ; 3.13, 1H,  $^3J = 4.69$  Hz,  $^3J = 9.07$  Hz,  $^3J = 7.37$  Hz,  $^3J = 7.73$  Hz,  $\text{PhCH}$ ; 3.34, 1H,  $^2J = 8.18$  Hz,  $^3J = 9.07$  Hz,  $\text{CH}_2\text{OC}(\text{CH}_3)_3$ ; 3.47, dd, 1H,  $^2J = 8.18$  Hz,  $^3J = 4.69$  Hz,  $\text{CH}_2\text{OC}(\text{CH}_3)_3$ ; 4.72, dd, 1H,  $^3J = 8.01$  Hz,  $^3J = 6.79$  Hz,  $\text{CHCN}$ ; 6.9–7.2, m, 9H, aromatic protons.  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 14.9, s,  $2 \times$  ring methyls; 17.4,  $\text{C}(\text{CH}_3)_3$ ; 20.6, s,  $2 \times$  ring methyls; 28.6,  $\text{CHCH}_2\text{CH}$ ; 36.0,  $\text{PhCH}$ ; 64.7,  $\text{CH}_2\text{OC}(\text{CH}_3)_3$ ; 66.3, s, C1 & C3; 72.3,  $\text{OC}(\text{CH}_3)_3$ ; 73.1,  $\text{CNCH}$ ; 128.5,  $\text{CN}$ ; 130.5, C4 & C7; 137.1, C2'; 137.6, C5 & C6; 138.3, C4'; 139.0, C3'; 154.6, C1'; 158.3, C3a & C7a.

*2[4-(t-butoxy)-1,3-diphenyl-1-butoxy]-1,1,3,3-tetramethyl-2,3-dihydro-1H-isoindol* (**8** and **9**, suspected of being isomers of RSST)

Products **8** and **9** were produced in only very minor yield (always < 1%) and insufficient quantities were isolated for conclusive identification. Two peaks appeared on the h.p.l.c. chromatogram with elution times typical of dimonomeric species. N.m.r indicated the presence of *t*-butyl, aromatic and isoindol moieties. Mass spectrometry analysis was inconclusive and there was insufficient material for a  $^{13}\text{C}$  n.m.r. spectrum of **8**.

#### ACKNOWLEDGEMENTS

We gratefully acknowledge continued helpful advice from Ezio Rizzardo and San Thang of CSIRO Chemicals and Polymers Division. Financial assistance from ARC is also acknowledged.

#### REFERENCES

- 1 Busfield, W. K., Jenkins, I. D., Thang, S. H., Rizzardo, E. and Solomon, D. H. *J. Chem. Soc. Perkin Trans I* 1988, 485
- 2 Busfield, W. K., Grice, I. D., Jenkins, I. D. and Monteiro, M. J. *J. Chem. Soc., Perkin Trans. 2* 1994, 1071
- 3 Griffiths, P. G., Rizzardo, E. and Solomon, D. H. *Tetrahedron Lett.* 1982, **23**, 1309
- 4 Avilia, D. V., Brown, C. E., Ingold, K. U. and Luszyk, J. J. *Am. Chem. Soc.* 1993, **115**, 466
- 5 Moad, G., Rizzardo, E. and Solomon, D. H. *Aust. J. Chem.* 1983, **36**, 1573
- 6 Tedder, J. M. and Walton, J. C. *Tetrahedron* 1980, **36**, 710
- 7 Giese, B. *Angew. Chem. Int. Ed. Engl.* 1983, **22**, 753
- 8 Busfield, W. K., Grice, I. D. and Jenkins, I. D. *Polym. Int.* 1992, **27**, 119
- 9 Griffiths, P. G., Rizzardo, E. and Solomon, D. H. *J. Macromol. Sci. Chem.* 1982, **A17(1)**, 45
- 10 Griffiths, P. G., Moad, G., Rizzardo, E. and Solomon, D. H. *Aust. J. Chem.* 1983, **36**, 397
- 11 Bowry, V. W. and Ingold, K. U. *J. Am. Chem. Soc.* 1992, **114**, 4992
- 12 Beckwith, A. L. J., Bowry, V. W. and Ingold, K. U. *J. Am. Chem. Soc.* 1992, **114**, 4893
- 13 Hill, D. J. T., O'Donnell, J. H. and O'Sullivan, P. W. *Macromolecules* 1982, **15**, 960
- 14 Dean, J. A. 'Lange's Handbook of Chemistry', 14th Edition, McGraw-Hill, 1992
- 15 Harwood, H. J. *Macromol. Chem., Macromol. Symp.* 1987, **10/11**, 331
- 16 (a) Ito, T. and Otsu, T. *J. Macromol. Sci.-Chem.* 1969, **A3**, 197; (b) Chapiro, A. and Perec-Spitzer, L. *Eur. Polym. J.* 1975, **11**, 59; (c) Cameron, G. G. and Esslemont, G. F. *Polymer* 1972, **13**, 435; (d) Busfield, W. K. and Low, R. B. *Eur. Polym. J.* 1975, **11**, 309
- 17 Bartlett, P. D., Benzing, E. P. and Pincock, R. E. *J. Am. Chem. Soc.* 1960, **82**, 1762
- 18 Rizzardo, E., Serelis, A. K. and Solomon, D. H., *Aust. J. Chem.* 1982, **35**, 2013