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Initiation mechanisms in radical polymerization: reaction of cyanoisopropyl radicals with styrene

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Summary

The reaction of styrene with AIBN in the presence of the aminoxyl scavenger 1,1,3,3-tetramethyl-1,3-dihydro-1*H*-isoindol-2-yloxyl is reported. By keeping the concentration of the aminoxyl radicals very low, the addition of cyanoisopropyl radicals to styrene becomes competitive with radical trapping. Traces of adventitious oxygen give rise to some unusual reactions and products.

Introduction

The radical trapping technique, employing the stable aminoxyl radical 1,1,3,3-tetramethyl-1,3-dihydro-1*H*-isoindol-2-yloxyl (TMIO) developed by the CSIRO (1, 2), has been used to study the details of the initiation steps in free radical polymerization. Some examples from this laboratory include initiation by oxygen-centred radicals (3-6), sulfur-centred radicals (7-8) and phosphorus-centred radicals (9). Until recently, the study of initiation by carbon-centred radicals has proved elusive, as these radicals are rapidly and efficiently scavenged by TMIO. However, by using a syringe pump to maintain a low aminoxyl concentration during the course of the reaction, the technique can be used to study 'second or higher generation' carbon-centred radicals (6, 10). The success of this syringe pump modification of the radical trapping technique has been demonstrated by our most recent work on the reaction of AIBN with acrylonitrile (11) where it was found that traces of adventitious oxygen led to the formation of alkoxy and alkylperoxy end-groups.

In this paper, we wish to report the results obtained from reaction of AIBN with styrene in the presence of TMIO.

Results and Discussion

Under the controlled conditions employed in our previous report (11), the five alkoxyamines **2**, **5**, **6**, **7** and **8** (Figure 1) were identified in the reaction of cyanoisopropyl radicals with styrene in the presence of TMIO. A mechanism for the formation of products is presented in Scheme 1 while the relative amounts of the products are given in Table 1. It can be seen from Table 1, column (**a**), that less than half (38.7%) of the initiating (first-formed carbon-centred) radicals were directly trapped by the aminoxyl to form compound **2**. More than half (55.0%) of the initiating radicals added to styrene and were subsequently trapped by the aminoxyl radicals to form compound **7**. This is quite surprising given than carbon-centred radicals react with TMIO at close to diffusion-controlled rates (12) but demonstrates that radical trapping and the addition of radicals to monomer are very competitive when the concentration of aminoxyl radicals is sufficiently low. There was evidence for the formation of a 'third generation' carbon-centred radical. Approximately 0.5% of the initiating cyanoisopropyl radicals added to styrene and this styryl radical then added to a second molecule of styrene to generate a

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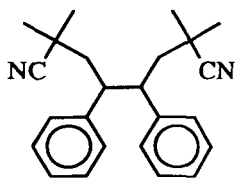
'third generation' carbon-centred radical which was then trapped by the aminoxyl to form compound **6**. In addition to the expected products **2**, **6** and **7**, two unexpected products, **5** and **8**, were also observed. These products result from the presence of trace amounts of adventitious oxygen and are only observed in experiments where the concentration of aminoxyl is kept extremely low. As expected, the relative concentration of **5** and **8** increased when the concentration of oxygen was increased (see Table 1, columns **a**, **b** and **c**). The relative amounts formed are consistent with the suggestion (13) that aminoxyl radicals are about 20 times less effective than oxygen in trapping carbon-centred radicals.

Interestingly the peroxystyryl radical **4** (Scheme 1) was not trapped by TMIO [in contrast to the analogous peroxyl radical formed from acrylonitrile (11)] suggesting that its lifetime is very short. Internal cyclization of the peroxystyryl radical **4** to give the cyanoisopropoxyl radical and styrene oxide is consistent with a mechanism proposed by Watanabe *et al.* (14-15).

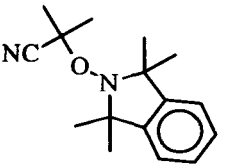
The formation of the intermediate styrene oxide and reaction pathway to compound **5** was confirmed by the results of two independent reactions which were carried out under the same conditions (2.5 hr, 75 °C): (i) reaction of styrene oxide with aminoxyl radicals; (ii) reaction of styrene oxide with AIBN in the presence of aminoxyl radicals. The first reaction produced several products but not compound **5**. In contrast, the second reaction produced several products including compound **5**. (Compound **5** was detected and isolated by HPLC. Its structure was determined by NMR and mass spectrometry.) This evidence suggests that styrene oxide was formed and subsequently underwent hydrogen abstraction by AIBN followed by ring opening to give the benzoylmethyl radical then trapping by TMIO to give **5** (see Scheme 1).

The formation of significant amounts of **5** and **8** (total amount approximately 0.5%, 6.8% and 11.7% in reactions (**a**), (**b**) and (**c**), respectively) suggests that unless oxygen is rigorously excluded, there will be significant polymer molecules with either ether or keto end groups formed during the polymerization of styrene using AIBN as initiator. Also, the appreciable hydrogen abstraction observed from styrene by cyanoisopropyl radicals suggests that benzylic hydrogen abstraction from the polystyrene backbone could be an important side-reaction during the polymerization of styrene. We are currently investigating this possibility using appropriate model compounds.

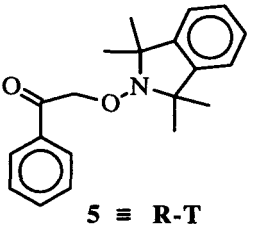
Figure 1: Products obtained from the reaction of AIBN with styrene in the presence of aminoxyl radicals.



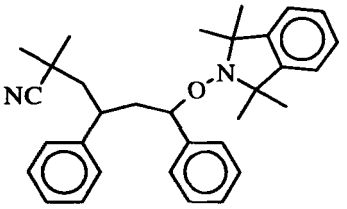
1 ≡ I-S-S-I



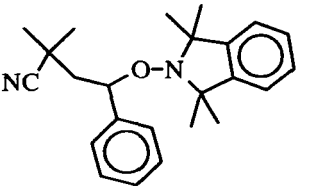
2 ≡ I-T



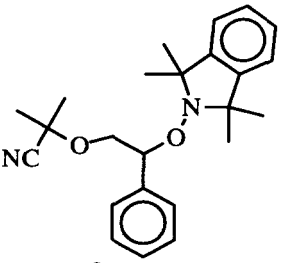
5 ≡ R-T



6 ≡ I-S-S-T

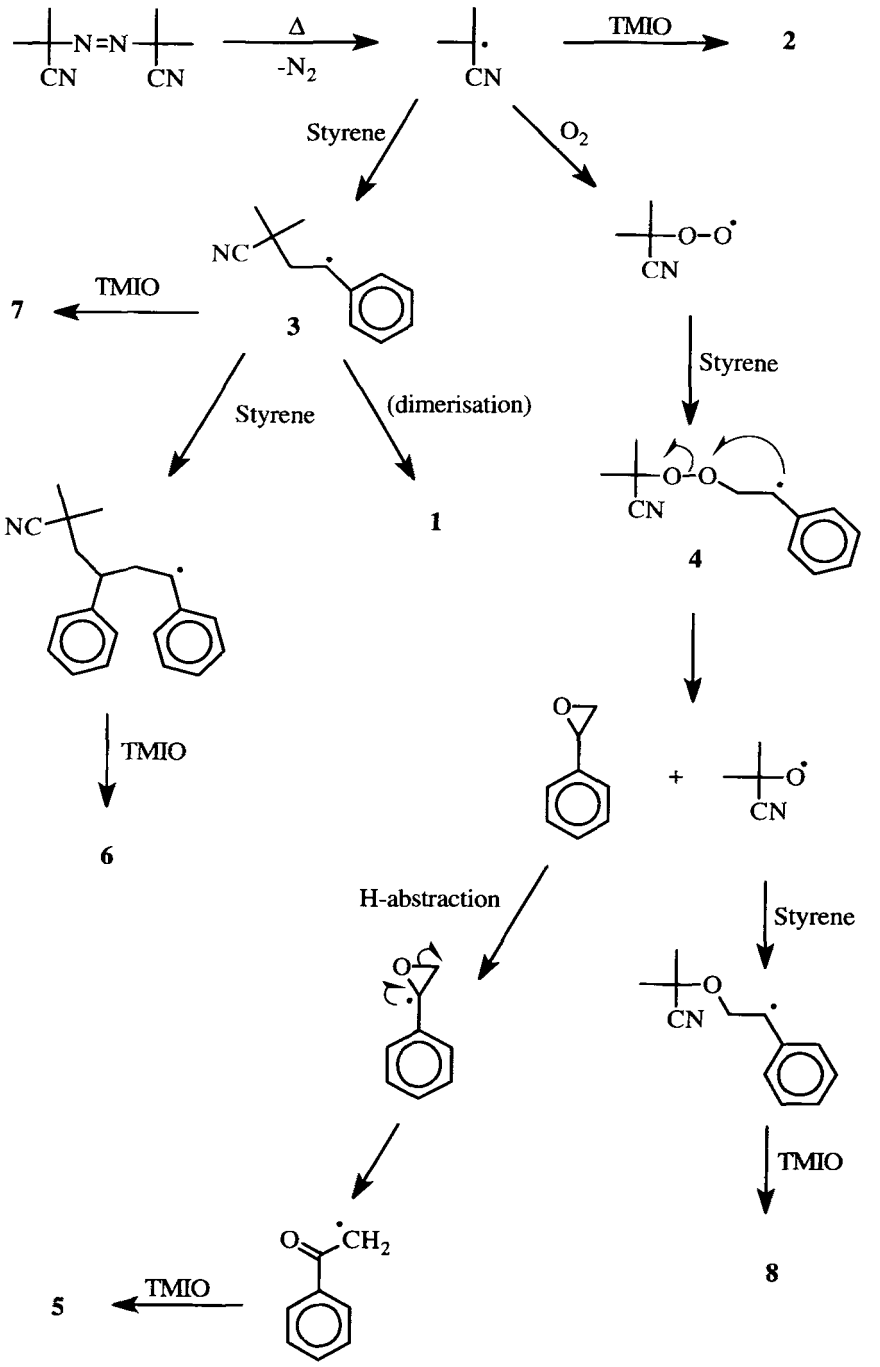


7 ≡ I-S-T



8 ≡ I-O-S-T

Scheme 1: Reaction pathways of AIBN-initiated polymerization of styrene.



The only non-alkoxyamine product identified was the apparent dimer **1**. This was a minor product and insufficient material was available for complete characterisation by NMR. The tentative structure **1** is based on the molecular weight, the fact that the precursor radical **3** is one of the major species produced, and the percentage yield of **1** decreases with increasing oxygen concentration parallelling a similar decrease in the percentage of **7** (Table 1). The formation of **1** is presumably a consequence of the very low concentrations of TMIO and oxygen, the relatively low rate constant for the addition of the styryl radical **3** to styrene, and possibly to a cage effect (two cyanoisopropyl radicals formed simultaneously, in close proximity within a solvent cage of styrene might be expected to give rise to a high local concentration of **3**). The formation of small but not insignificant amounts of **1** suggests that this product may be present as a low molecular weight impurity when styrene is polymerized using AIBN as an initiator.

Table 1: Relative yields of products obtained from the reactions of AIBN and styrene under 1 atm. pressure of (a) argon, (b) a mixture of 10% air in argon and (c) 100% air in the presence of aminoxyl radicals .

No.	Compound	MW	Relative yield / %		
			(a)	(b)	(c)
1	I-S-S-I	344	3.6	1.3	0.6
2	I-T	258	38.7	50.5	59.9
5	R-T	309	<0.1	0.6	0.7
6	I-S-S-T	466	0.5	0.0	0.0
7	I-S-T	362	55.0	39.3	22.6
8	I-O-S-T	378	0.5	6.2	11.0
*	Unassigned		1.7	2.1	5.2

Note:
(*) Unknown by-products, I = cyanoisopropyl radical, T = TMIO (aminoxyl radical), R= benzoylmethyl radical, S = Styrene.

Experimental

Materials
The aminoxyl radicals were generated as previously described (2). Styrene and styrene oxide were purchased from Aldrich Chemical Co Inc.. Styrene was purified by distillation and stored in a refrigerator and styrene oxide was used without purification. AIBN was purified by recrystallization from ethanol and dried under vacuum.

General procedure
Typically, a solution of AIBN (28.0 mg, 17.1 x 10^{-2} mmol) in a mixture of styrene (1.5 ml) in dry benzene (3.0 ml) was placed in a reaction vessel (10 ml) fitted with a 1000 microliter syringe containing a solution of 1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindol-2-yloxyl (20.0 mg, 10.5 x 10^{-2} mmol) in dry benzene (1.2 ml). After degassing the solutions by successive freeze-thaw cycles on a high vacuum line, the reaction vessel was filled with argon to 1 atm and immersed in an oil-bath at 75°C. The aminoxyl solution was injected over 2.5 hr *via* a syringe pump into the reaction mixture at a rate approximating the rate of production of cyanoisopropyl radicals [see previous report (11), and Table 2]. The reaction mixture was cooled, concentrated and the residue taken up in 67% acetonitrile / water (2 ml) for analysis.

Product Analysis
Alkoxyamine products were separated and identified by HPLC / electrospray mass spectrometry. Reaction samples were injected onto a reverse phase HPLC column using 67% acetonitrile / water as eluent (Dynamax 60A, C18 analytical column, UV detector set at 270 nm) and each of the separated compounds was then identified by electrospray

ionisation. (Single quadrupole VG platform 2 spectrometer with MassLynx Version 1 used for Data acquisition.)
Relative yields were determined from HPLC peak areas based on the extinction coefficients of the chromophoric groups present. Peak areas were obtained from the HPLC chromatograms.
Alkoxyamine product **5** was isolated from a blank reaction by HPLC with a Dynamax 60A, C18, preparative column using 75% MeOH / H_2O as eluent. Alkoxyamine product **7** was isolated by HPLC with a Dynamax 60A, C18, semipreparative column using 67% CH_3CN / H_2O as eluent. Both products **5** and **7** were characterised by ^1H, ^{13}C and ^1H-^{13}C correlation NMR.
^1H and ^{13}C NMR spectra were recorded on Varian Gemini 200 or 400 MHz spectrometers, with deuterated chloroform as solvent. Chemical shifts for ^1H NMR spectra are relative to residual $CHCl_3$, (δ7.24 ppm) and for ^{13}C NMR spectra are relative to the central peak of the triplet resonance due to the solvent ($CDCl_3$, δ77.0 ppm).

Table 2: Injection rate of aminoxyl solution (8.75 x 10^{-2} M) into reaction mixture.

Reaction time / min	Injection rate		Reaction time / min	Injection rate	
	10^{-3}ml / min	10^{-6}mol /min		10^{-3}ml / min	10^{-6}mol / min
0	6.0	0.525	45	8.0	0.700
1	6.5	0.569	50	7.8	0.682
2	7.0	0.612	55	7.4	0.647
3	7.5	0.656	60	7.0	0.612
4	8.0	0.700	65	6.6	0.577
5	8.5	0.744	75	6.2	0.542
6	9.0	0.787	85	5.8	0.507
10	9.5	0.831	95	5.6	0.490
20	9.0	0.787	105	5.4	0.472
25	8.8	0.770	115	5.2	0.455
30	8.6	0.752	125	5.0	0.437
35	8.4	0.735	130	4.8	0.420
40	8.2	0.717	140	4.4	0.385

Alkoxyamine Products

2,2,7,7-Tetramethyl-2,5-diphenyloctanedinitrile, **1**.
Mass spectrum: Found: *m/z* 367 $(M+Na)^+$, 345 $(M+H)^+$. $C_{24}H_{28}N_2$ requires: *m/z* 367 $(M+Na)^+$, 345 $(M+H)^+$.

2-Methyl-2-(1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindol-2-yloxy)propanenitrile, **2**.
Mass spectrum: Found: *m/z* 281 $(M+Na)^+$, 259 $(M+H)^+$. $C_{16}H_{22}N_2$ requires: *m/z* 281 $(M+Na)^+$, 259 $(M+H)^+$.

1-Phenyl-2-(1,1,3,3-tetramethyl-3,4-dihydro-1*H*-isoindol-2-yloxy)ethan-1-one, **5**.
Mass spectrum: Found: *m/z* 332 $(M+Na)^+$, 316 $(M+Li)^+$, 310 $(M+H)^+$. $C_{20}H_{23}NO_2$ requires: *m/z* 332 $(M+Na)^+$, 316 $(M+Li)^+$, 310 $(M+H)^+$. ^1H NMR (400 MHz, $CDCl_3$) δ1.5 (s, 12 H, 4 $C\underline{H}_3$), 5.3 (s, 2 H, $C\underline{H}_2$), 7.1 (m, 2 H, isoindol ring), 7.2 (m, 2 H, isoindol ring), 7.5 (t, 2 H, J = 7.7 Hz, *meta* H, phenyl ring), 7.6 (t, 1 H, J = 7.7 Hz, *para* H, phenyl ring), 7.9 (d, 2 H, J = 7.7 Hz, *ortho* H, phenyl ring). ^{13}C NMR (50 MHz) δ14.1 (2 C, $\underline{C}H_3$), 29.7 (2 C, $\underline{C}H_3$), 67.7 (2 C, C1&C3, isoindol ring), 80.9 (1 C, $\underline{C}H_2$) 121.5 (2 C, C5&C6, isoindol ring), 127.4 (2 C, C4&C7, isoindol ring), 128.2

(2 C, *ortho* carbons, phenyl ring), 128.7 (2 C, *meta* carbons, phenyl ring), 133.4 (1 C, *para* carbon, phenyl ring), 134.8 (1 C, *ortho* C-C-CO, phenyl ring), 144.8 (2 C, C8&C9, isoindol ring), 196.3 (1 C, CO).

2,2-Dimethyl-4,6-diphenyl-4-(1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindol-2-yloxy)hexanenitrile, **6**.
Mass spectrum: Found: *m/z* 489 $(M+Na)^+$, 467 $(M+H)^+$. $C_{32}H_{38}N_2O$ requires: *m/z* 489 $(M+Na)^+$, 467 $(M+H)^+$.

2,2-Dimethyl-4-phenyl-4-(1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindol-2-yloxy)butanenitrile, **7**.
Mass spectrum: Found: *m/z* 385 $(M+Na)^+$, 363 $(M+H)^+$. $C_{24}H_{30}N_2O$ requires: *m/z* 385 $(M+Na)^+$, 363 $(M+H)^+$. ^1H NMR (200 MHz, $CDCl_3$) δ1.1 (s, 3 H, CH_3), 1.2 (s, 3 H, CH_3), 1.42 (s, 3 H, CH_3), 1.44 (s, 3 H, CH_3), 1.5 (s, 3 H, CH_3), 1.6 (s, 3 H, CH_3), 2.1 (dd, 1 H, J = 13.8, 9.5 Hz, CH_2), 2.5 (dd, 1H, J = 13.8, 4.3 Hz, CH_2), 4.9 (dd, 1 H, J = 9.5, 4.3 Hz, CH_2-CH(Ar), 6.9-7.3 (m, 5 H, ArH), 7.3-7.5 (m, 4 H, isoindol ring protons). ^{13}C NMR (50 MHz, $CDCl_3$) δ25.3 (1 C, CH_3), 25.9 (1 C, CH_3), 27.5 (1 C, CH_3), 28.2 (1 C, CH_3), 29.1 (1 C, CH_3), 30.5 (1 C, CH_3), 45.6 (1 C, CH_2), 67.1 (2 C, C1&C3 isoindol ring), 68.0 (1 C, C(CH_3)$_2$CN), 84.4 (1 C, CH_2CH), 121.4 (2 C, phenyl ring), 121.6 (2 C, phenyl ring), 124.4 (1 C, C-CN), 127.1 (1 C, phenyl ring), 128.3 (2 C, isoindol ring), 128.8 (2 C, isoindol ring), 142.0 (2 C, isoindol ring).

2-(2-Cyano-prop-2-yloxy)-1-phenyl-1-(1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindol-2-yloxy)ethane, **8**.
Mass spectrum: Found: *m/z* 401 $(M+Na)^+$, 379 $(M+H)^+$. $C_{24}H_{30}N_2O_2$ requires: *m/z* 401 $(M+Na)^+$, 379 $(M+H)^+$.

Conclusions

The syringe pump modification of the aminoxyl radical trapping technique, combined with HPLC / electrospray mass spectrometry is a powerful technique for the study of both major and minor pathways in the initiation stages of free radical polymerization, and is applicable to initiation by carbon-centred radicals.
The results obtained in the present study show the importance of rigorously excluding air from the polymerization system. Even traces of air will lead to efficient trapping of the cyanoisopropyl radicals to give peroxyl radicals which then undergo addition to the monomer. The resulting carbon-centred radical subsequently decomposes to give an oxygen-centred radical and styrene oxide. The later molecule undergoes hydrogen abstraction by initiator followed by rearrangement to produce a new radical. Thus, polymerization of styrene using AIBN as initiator in the presence of traces of oxygen would produce a polymer with some ether end-groups (analogous to **8**) or some keto-end groups (analogous to **5**) but probably not peroxy end-groups.
Further studies on this and other initiator / monomer systems are in progress.

Acknowledgments

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