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Investigations into the AIBN initiation steps in the free radical polymerisation of acrylonitrile by the aminoxyl trapping technique

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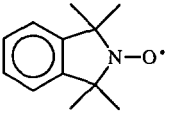
Summary

A modification of the radical trapping technique employing the stable nitroxide 1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindol-2-yloxyl, has been used to study the reaction of cyanoisopropyl radicals with acrylonitrile. By keeping the concentration of the aminoxyl radical very low (strategically added *via* a syringe pump), the addition of acrylonitrile to cyanoisopropyl radicals becomes competitive with radical trapping. Thus, sufficient quantities of alkoxyamines produced by the trapping of 'second generation' carbon-centred radicals (cyanoisopropyl plus one monomer unit), and even 'third generation' carbon-centred radicals were obtained for identification by HPLC / MS techniques. Trapping by traces of adventitious oxygen was also competitive and the various peroxy radicals thus formed, underwent addition to acrylonitrile followed by further reaction or trapping by the aminoxyl.

Introduction

The early stages of free radical polymerisation involve the reaction between an initiating radical (often an oxygen-centred radical) and a monomer, to produce a carbon-centred radical, which then adds to a second molecule of monomer to produce a 'second generation' carbon-centred radical, which then adds to a third monomer molecule and so on. The radical trapping technique, employing aminoxyl radical **1**, developed by the CSIRO (1), has been very successful in identifying the structures of the first-formed ('first generation') carbon-centred radicals (2-5), produced by the addition of one monomer unit to an oxygen-centred radical. This success has been due in part to the very efficient scavenging (rates close to diffusion-controlled (6-7)) of carbon-centred radicals by **1**, and, in general, the lack of reaction between **1** and oxygen-centred initiator radicals.



1 ≡ $R_2NO^{\bullet}$

Our most recent developments in the use of the radical trapping technique have been to demonstrate that it can also be employed to study initiation by sulfur-centred radicals (8-9) and phosphorus-centred radicals (10). We have also reported (5,11) that the syringe pump modification of the radical trapping technique can be used to study 'second generation' carbon-centred radicals in special cases.

This paper reports the application of this technique to study the initiation stages in the polymerisation of acrylonitrile by the common free radical initiator, AIBN (azobis(isobutyronitrile) or 2,2'-azobis(2-methylpropionitrile)). The 'first generation'

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carbon-centred radicals in polymerisations using AIBN as initiator are the cyanoisopropyl radicals, produced directly from decomposition of the initiator. Under the normal conditions used for radical trapping experiments, the large excess of **1** would prevent the formation of any 'second or higher generation' carbon-centred radicals by efficient trapping. By minimising the concentration of **1** to that necessary to prevent the formation of polymer over the course of the reaction, the addition of monomer to cyanoisopropyl radicals becomes competitive with radical trapping and allows the products from the trapping of 'second and possibly higher generation' carbon-centred radicals to be identified.

Results and Discussion

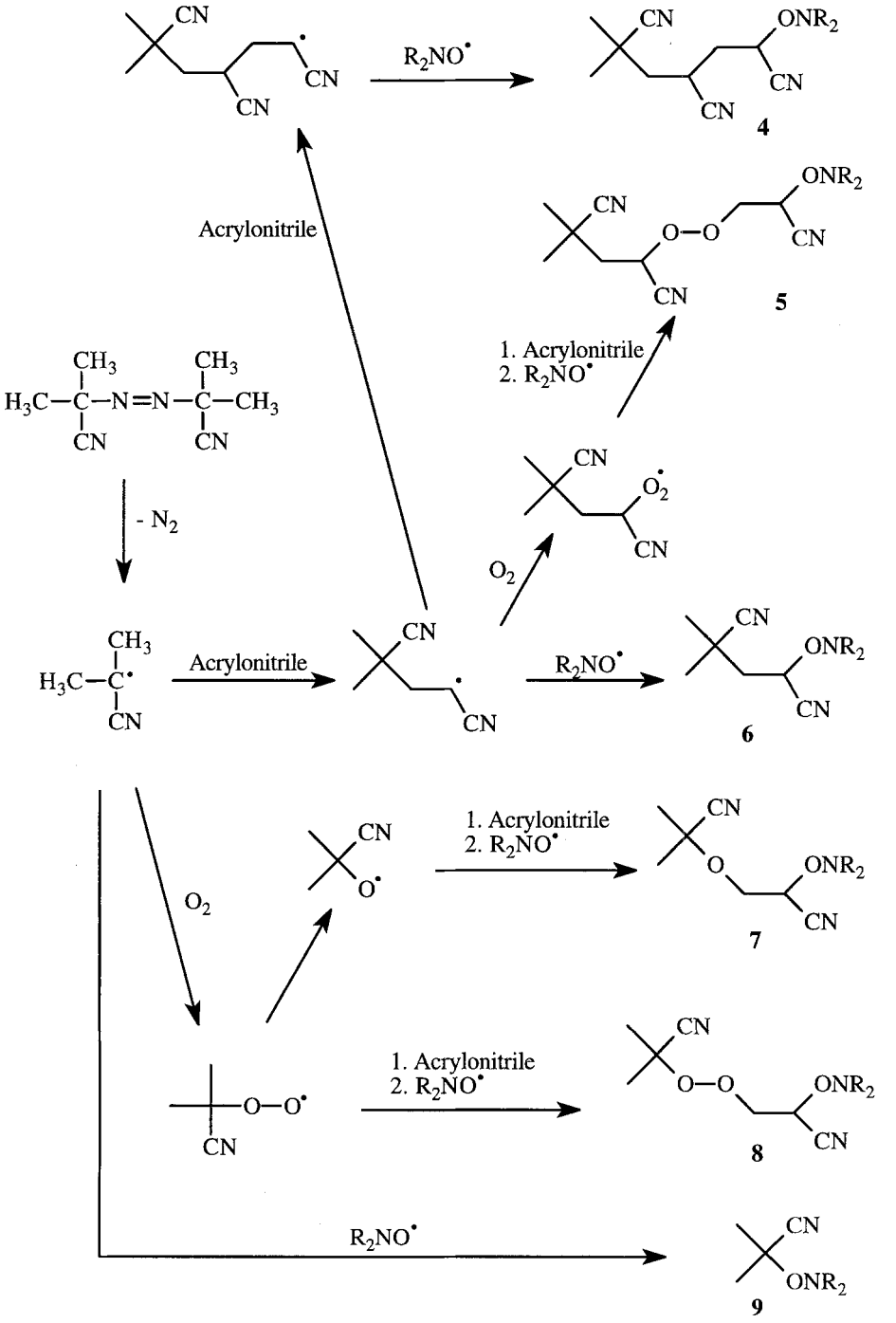
Typically, a solution of AIBN (7.7 mg, 4.74 x 10^{-2} mmol) in acrylonitrile (3 ml) was placed in a reaction vessel fitted with a 1000 microliter syringe containing a solution of 1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindol-2-yloxyl, **1**, (4.5 mg, 2.37 x 10^{-2} mmol) in acrylonitrile (1 ml). After degassing the solutions by successive freeze-thaw cycles on a high vacuum line, the reaction vessel was filled with nitrogen 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 (12) (see Table 1). The reaction mixture was cooled, concentrated and the residue taken up in 75% methanol / water (2 ml). The alkoxyamines were separated and identified by HPLC / electrospray mass spectrometry and are listed in Table 2 in order of increasing retention time. Among these alkoxyamine products, compounds **8** and **9** were isolated and their identities confirmed by NMR.

Eight alkoxyamines were identified in the reaction of AIBN, acrylonitrile and aminoxyl **1**. A mechanism for the formation of these products is presented in *Scheme 1.* As expected, most (84.8%) of the initiating ('first generation') radicals were directly trapped by the aminoxyl to form compound **9**. This reflects the very fast trapping reaction (~10^9 M^{-1} s^{-1}) compared with the much slower addition of these radicals to acrylonitrile (~10^2 M^{-1} s^{-1}). However, under the controlled conditions employed (Table 1), it was possible to observe the addition of cyanoisopropyl radicals to acrylonitrile to form the 'second generation' carbon-centred radicals which were subsequently trapped by the aminoxyl **1** to produce alkoxyamine **6** in almost 10% yield. We were also able to observe the formation of a small amount (2.1%) of the 'third generation' radical, trapped as **4**. Most surprising, was the formation of the minor products **5** (0.7%), **7** (0.2%) and **8** (0.4%). These were attributed to the presence of traces of adventitious oxygen, which is also a very efficient trap for carbon-centred radicals. It has been suggested that aminoxyl radicals are about 20 times less effective than oxygen in trapping carbon-centred radicals (13). With the much higher concentrations of **1** normally employed, these products have not been

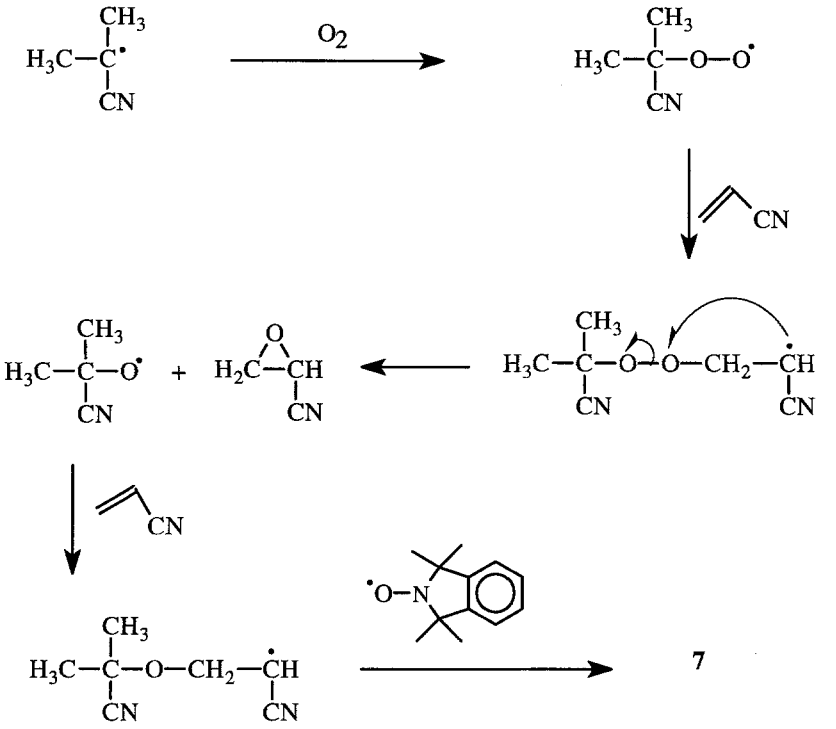
Table 1: Injection rate of aminoxyl solution into reaction mixture

Reaction time min	Injection rate		Reaction time min	Injection rate	
	µl/min	10^{-6} mol/min		µl/min	10^{-6} mol/min
0	5.5	0.130	60	5.8	0.137
1	6.0	0.142	65	5.6	0.133
2	6.5	0.154	70	5.4	0.128
3	7.0	0.166	75	5.2	0.123
4	7.5	0.178	80	5.0	0.118
10	8.0	0.189	85	4.8	0.114
15	8.5	0.201	90	4.6	0.109
25	8.0	0.189	95	4.4	0.104
30	7.7	0.182	100	4.2	0.099
35	7.4	0.175	105	4.0	0.095
40	7.1	0.168	110	3.8	0.090
45	6.8	0.161	115	3.6	0.085
50	6.5	0.154	120	3.4	0.080
55	6.1	0.144	125	3.2	0.076

Scheme 1: Reaction pathways of the early stages of AIBN-initiated polymerisation of acrylonitrile.



Scheme 2: The proposed mechanism for the formation of compound **7**.



observed previously. It is only under the conditions employed here, with strategically maintained low concentrations of **1** [at that crucial point where to lower the concentration of **1** further would result in polymerisation] that trapping by the minute amounts of oxygen present becomes competitive. The level of these products increased significantly when the reaction was carried out in air (see Table 2). Conversely, when the reaction was carried out under an oxygen atmosphere, the level decreased. Apparently, at these higher levels of oxygen concentration, most radicals are trapped by oxygen rather than aminoxyl **1** and the extent of other reactions increases, e.g. products **2** and **3**, Table 2. It is known (14-16) that carbon-centred radicals rapidly add to oxygen to form peroxy-radicals. These radicals do not react with aminoxyl **1** but can add to monomers to generate the 'second and third generation' carbon-centred radicals which can then be trapped to form compounds **8** and **5**, respectively. There are two possible structures for compound **5** which has only been identified by its mass spectrum. The alternative to that shown in Table 2, results from the trapping of the radical formed by the addition of two monomer units to the cyanoisopropylperoxyl radical, i.e. RO_2M_2T. The yield of this product would be expected to be significantly less than that of **8**, e.g. the ratio of the yields of products **4** and **6** is 0.22. Since the yield is almost twice that of **8**, we suggest that compound **5** is more likely to have the structure shown in Table 2. The formation of compound **7**, apparently derived from addition of monomer to the cyanoisopropoxyl radical, is intriguing. Although this compound could in principle be derived from product **8** (17-19), an internal cyclisation of the intermediate peroxyl radical to give the cyanoisopropoxyl radical and acrylonitrile peroxide (*Scheme 2*) seems more likely and is consistent with a mechanism proposed by Watanabe *et al.* (17).

Table 2: Relative yields of alkoxyamine products obtained from the reaction of AIBN with acrylonitrile in the presence of **1**.

No	Compound [1]	MW [2]	Relative Yields [3] (%)		
			(a)	(b)	(c)
2	HO-M-T [4]	260		6.0	44.4
3	H-M-T [4]	244	2.3	3.3	11.6
4	R-M_2-T	364	2.1		
5	R-M-O_2-M-T [5]	396	0.7	15.1	19.8
6	R-M-T	311	9.5		
7	R-O-M-T	327	0.2	0.1	4.7
8	R-O_2-M-T	343	0.4	22.3	10.2
9	R-T	258	84.8	53.2	9.3

Notes:

1. Products listed in order of elution by reverse phase HPLC. R = cyanoisopropyl; M= acrylonitrile; T = nitroxide.
2. Molecular weights
3. Yields from experiments carried out under: (a) nitrogen with (presumably) adventitious oxygen, (b) air, (c) oxygen.
4. Secondary products (structures tentative) formed by uncertain mechanism.
5. An alternative possible structure is R-O_2-M_2-T.

Experimental

Product Analysis

Alkoxyamine products were separated and identified by HPLC / electrospray mass spectrometry. Reaction samples were injected onto a reverse phase HPLC column using 60% acetonitrile / water as eluent (Dynamax 60A, C18 analytical column, UV detector set at 270 nm) and each of the separated compounds were 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 observation that alkoxyamines containing the isoindoline group and no other UV chromophores have almost identical molar absorption coefficients at 270 nm (20). Peak areas were obtained from the HPLC chromatograms.

Alkoxyamine products **8** and **9** were isolated by semi-preparative scale HPLC and characterised by NMR. ^{1}H and ^{13}C NMR spectra were recorded on Varian Gemini 200 or 400 spectrometers, with deuterated chloroform as solvent. Chemical shifts for ^{1}H NMR spectra are relative to residual C**H**Cl_3, (δ7.24 ppm) and for ^{13}C NMR spectra are relative to the central peak of the triplet resonance due to the solvent ($CDCl_3$, δ77.0ppm).

Materials

The nitroxide **1** was prepared as previously described (21). Acrylonitrile was purchased from Aldrich Chemical Co Inc.. It was purified by distillation and stored in a refrigerator. AIBN was obtained from Aldrich. It was purified by recrystallisation from ethanol and dried under vacuum.

Alkoxyamine Products

4,6-Dicyano-6-methyl-2-(1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindol-2-yloxy)-heptanenitrile , **4**.

Mass spectrum: $(M+Na)^+$, *m/z:* 387, $(M+H)^+$, *m/z:* 365.

1,3-Dicyano-3-methylbutyl 2-cyano-2-(1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindol-2-yloxy)ethyl peroxide, **5**.

Mass spectrum: $(M+Na)^+$, *m/z:* 419, $(M+H)^+$, *m/z*: 397.

4-Cyano-4-methyl-2-(1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindol-2-yloxy)pentanenitrile, **6**.
Mass spectrum: $(M+Na)^+$, *m/z:* 334, $(M+H)^+$, *m/z:* 312.
3-(2-Cyano-prop-2-yloxy)-2-(1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindol-2-yloxy)-propanenitrile, **7**.
Mass spectrum: $(M+Na)^+$, *m/z:* 350, $(M+H)^+$, *m/z*: 328.
2-Cyano-prop-2-yl 2-cyano-2-(1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindol-yloxy)ethyl peroxide, **8**.
Mass spectrum: $(M+Na)^+$, *m/z:* 366, $(M+H)^+$, *m/z:* 344.
^{1}H NMR (400 MHz, $CDCl_3$) δ1.4 ($2CH_3$), 1.5 ($2CH_3$), 1.6 ($2CH_3$), 4.5 (d, J6Hz, CH_2CH), 5.0 (t, J6Hz, CH_2CH), 7.1 (m, 2ArH), 7.3 (m, 2ArH).
2-Methyl-2-(1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindolol-yloxy)propanenitrile, **9**.
Mass spectrum: $(M+Na)^+$, *m/z:* 281, $(M+H)^+$, *m/z:* 259.
^{1}H NMR (200 MHz, $CDCl_3$) δ1.4 ($2CH_3$), 1.6 ($2CH_3$), 1.7 ($2CH_3$), 7.1 (m, 2ArH), 7.3 (m, 2ArH). ^{13}C (50 MHz, $CDCl_3$) δ25.7 ($2CH_3$), 27.3 ($2CH_3$), 30.7 ($2CH_3$), 68.8 (C1&C3), 74.4 ($(CH_3)_2CCN$), 121.7 (C4&C7), 122.9 (CN), 127.6 (C5&C6).

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 polymerisation, and can be used to study initiation by carbon-centred radicals, at least in selected cases.
The results obtained in the present study are generally consistent with the accepted 'text-book' mechanism for polymerisation of acrylonitrile using AIBN as initiator (i.e. normal head - to - tail addition, as there was no evidence for any minor isomeric products arising from head - addition of the initiator etc.) except that they show the importance of rigorously excluding air from the polymerisation 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 polymer would thus contain a source of built - in instability, namely a peroxy end group (analogous to **5**). There may be potential for the production of macroinitiators. There will also be small amounts of ether end groups (analogous to **7**).
Further studies on this and other initiator / monomer systems are in progress.

Acknowledgments

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12. This was estimated using the rate constant for the thermal decomposition of AIBN in benzene. The data given in Table 1 are the conditions under which the yields of the products derived from the 'second and third generation' carbon-centred radicals were optimal. Lower concentrations of aminoxyl **1** resulted in polymerisation; higher concentrations led almost exclusively to a single product, **9**.
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