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The t-Butylthiyl Radical as Initiator in Vinylpolymerizations.

Investigations into the Initiation Step by the Aminoxyl Trapping Technique

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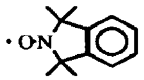
Abstract: The reactions of t-butylthiyl radicals with methyl methacrylate, methacrylonitrile, vinylacetate and styrene were studied by using an aminoxyl radical scavenger. The product **4** (thiyl radical **2** trapped by the aminoxyl **1**) was the main product in all monomers except styrene. Products formed by addition of the thiyl radical to the double bond of the monomer were observed in vinyl acetate, methacrylonitrile and methyl methacrylate. Surprisingly, in styrene no products arising from addition of thiyl radicals were observed. The ratio of the rate of addition of t-butyl thiyl radicals to monomer is: VA : MAN : MMA = 1 : 5 : 8.

Introduction

The aminoxyl radical (nitroxide) trapping technique developed by CSIRO[1] has been successfully used to provide information about the initiation step in radical polymerisations of vinylmonomers[2-5]. The aminoxyl radical 1 (1,1,3,3-tetramethyl-2,3-dihydro-1H-isoindol-2-yloxyl)[6] is known for scavenging carbon-centred radicals at almost diffusion-controlled rates (10^7-10^9 $\mathrm{lmol^{-1}s^{-1}}$)[7]. So far mainly benzoyloxyl and tert-butoxyl radicals have been used as initiating radicals in aminoxyl trapping experiments, taking advantage of the feature that the aminoxyl radical does not react with oxygen-centred radicals.



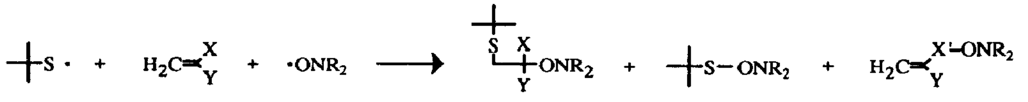
1 = • $\mathrm{ONR_2}$

In polymerizations, chain-transfer agents such as allylic sulfides[8] have been used to control the molecular weight of the polymer and the nature of end groups[9]. The propagating polymer chain adds to the double bond of the chain-transfer agent which, in the case of allylic sulfides, fragments to give a polymer with a functional end group and a thiyl radical. The thiyl radical is then capable of initiating new polymer chains. In this paper we describe the use of the aminoxyl trapping technique to investigate the reaction of thiyl radical 2 with various vinylmonomers.

Results and Discussion

Hewitt et al.[10] have observed that the aminoxyl 1 can abstract hydrogen from benzenethiol to yield benzenethiyl radicals. In our experiments we employed 2-methyl-2-propanethiol and the aminoxyl 1, assuming that aminoxyl 1 would similarily abstract hydrogen from the thiol to give thiyl radicals 2. The single monomer experiments were carried out in vacuum for 270 min at 50°C in neat monomer. Reaction mixtures contained 1 eq. 2-methyl-2-propanethiol (e.g. $9\mathrm{x}10^{-2}$mol $\mathrm{l^{-1}}$), 2.2 eq. aminoxyl 1 (e.g. $2\mathrm{x}10^{-1}$mol $\mathrm{l^{-1}}$) and monomer (1 ml, $8.7\mathrm{x}10^{-6}$-$1.2\mathrm{x}10^{-5}$ mol). Monomers employed were methyl methacrylate, vinyl acetate, methacrylonitrile and styrene. The competition experiments were carried out at 60°C for 90 min with two monomers present in the ratio of 1:1. The products were isolated by reverse phase HPLC and characterized by nmr spectroscopy and mass spectrometry.

The reaction pathway for vinyl acetate, methacrylonitrile and methyl methacrylate is shown in Scheme 1. The main product observed was **4** which is formed by trapping of thiyl radical **2** by aminoxyl **1**. It is interesting to note that aminoxyl 1 reacts with sulfur-centred radicals, whereas it does react with oxygen-centred radicals. The products **3a**, **3b** and **3c** were formed by addition of thiyl radical **2** to the double bond of vinyl acetate, methacrylonitrile and methyl methacrylate, respectively, followed by trapping by aminoxyl **1**. The relative product yields at $50^{o}C$ are shown in Table 1 (relative product yields are temperature dependant).


2 **1** **3a** X=OAc, Y=H **4** **5a** X'=OCOCH$_2$

3b X=CN, Y=CH$_3$

3c X=COOCH$_3$; Y=CH$_3$

Scheme 1

In vinyl acetate, a small amount of hydrogen abstraction product **5a** was observed. This is not surprising as hydrogen abstraction by aminoxyl radicals has been described previously[11].

Table 1. Relative Product Yields after 270 min at $50^{o}C$ in neat monomer

Monomer	Product 4	Addition (Product 3)	H-abstraction (Product 5)
Methylmethacrylate (MMA)	46	54	-
Methacrylonitrile (MAN)	56	44	-
Vinylacetate (VA)	66	26	9

The relative reactivity of thiyl radical **2** to the monomers follows the order VA<MAN<MMA (see Table 1). In competition experiments at $60^{o}C$ the relative reactivity of thiyl radical **2** to the monomers was determined to be VA:MAN:MMA=1:5:7.

The experiments with styrene gave a different, unexpected result. Neither addition products nor trapped thiyl radicals (product **4**) were formed. The absence of product **4** suggests that the formation of thiyl radicals (hydrogen abstraction from the thiol by aminoxyl **1**) does not take place in styrene. In support of this idea, in a mixed monomer experiment (styrene and methacrylonitrile or methyl methacrylate, 1:1) neither **3b** or **3c** nor **4** were formed, and yet the products were formed in the absence of styrene. In contrast, the analogous reaction of benzenethiol to benzenethiyl in styrene has been observed[10]. Further investigations are being carried out in an attempt to clarify these observations. However, addition of thiyl radical **2** to the double bond of styrene has been observed in different systems[12].

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