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The Phenyl Thiyl Radical as Initiator in Vinyl Polymerizations. Investigations into the Initiation Step by the Aminoxyl Trapping Technique

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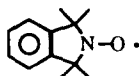
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Abstract: The reactions of phenyl thiyl radicals with styrene, methyl methacrylate, methacrylonitrile, and vinylacetate in the presence of an aminoxyl radical scavenger have been studied. Two main products were formed: diphenyl disulfide, and the expected product formed by addition of the thiyl radical to the double bond of the monomer followed by trapping by the aminoxyl radical. The relative reactivity of the monomers towards addition of phenyl thiyl radicals at 60°C was: VA : MAN : MMA : STY = 1 : 50 : 100 : 500.

Introduction

Since its discovery, and much later formulation as a free-radical chain reaction, the anti-Markownikoff addition of thiols to unsaturated compounds has been the subject of many reviews¹. It has been found that in radical polymerisations, thiyl radicals are less reactive as initiators than carbon- and oxygen-centred radicals² under the same conditions. Thiyl radicals can be generated by photolysis of thiols or disulfides, or by hydrogen atom abstraction from thiols³. Recently allylic sulfides⁴ have been used as chain-transfer agents in radical polymerisations. The propagating polymer chain adds to the double bond of the chain-transfer agent which 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. Thus the molecular weight of the polymer and the nature of end groups⁵ can be controlled.

The initiation step in the free radical polymerisation of vinyl monomers can be conveniently studied using the aminoxyl radical trapping technique⁶⁻⁹ developed by Rizzardo and Solomon¹⁰. The aminoxyl radical **1** (1,1,3,3-tetramethyl-2,3-dihydro-1H-isoindol-2-yloxy)¹¹



1 = R₂NO•

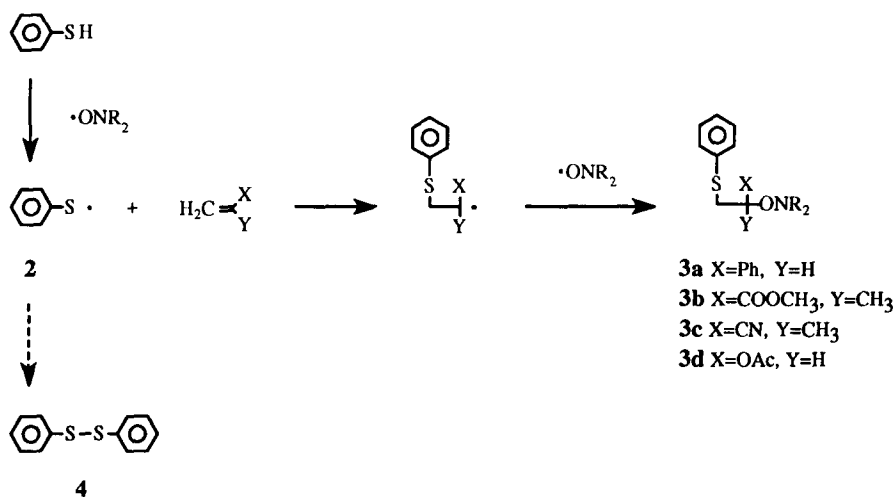
is known to scavenge carbon¹²- and phosphorus¹³-centred radicals at almost diffusion-controlled rates (10⁷-10⁹ l mol⁻¹s⁻¹), but it is unreactive towards oxygen-centred radicals. Thus most work in this field has been done with oxygen-centered radicals as initiating species. However, we have recently shown that the

reaction of phosphorus¹³- and sulfur¹⁴-centred radicals can also be investigated by this technique. In this paper we describe the use of the aminoxyl trapping technique to study reactions of phenyl thiyl radicals **2** with vinyl monomers.

Results and Discussion

Thiyl radicals can be formed by hydrogen atom abstraction from thiols by the aminoxyl **1**^{14,15}. In our experiments we employed phenyl thiol and the aminoxyl **1** to produce thiyl radicals **2**. The single monomer experiments were carried out in vacuum for 90 min at 60°C in neat monomer. Reaction mixtures contained 1 eq. phenyl thiol (e.g. 9×10^{-2} mol l⁻¹), 2.2 eq. aminoxyl **1** (e.g. 2×10^{-1} mol l⁻¹) and monomer (8.7×10^{-3} - 1.2×10^{-2} mol l⁻¹). The monomers employed were styrene, methyl methacrylate, methacrylonitrile and vinyl acetate. A series of competition experiments was also carried out at 60°C for 90 min with two monomers present as a 1:1 molar mixture. The products were isolated by reverse phase HPLC and characterized by ¹H and ¹³C nmr spectroscopy and mass spectrometry.

The reaction pathway for the various monomers is shown in Scheme 1. Two main products were identified. Addition of thiyl radicals **2** to the double bond of styrene, methyl methacrylate, methacrylonitrile and vinyl acetate followed by trapping by the aminoxyl **1** gave the products **3a** - **3d**, respectively. As expected¹, no Markownikoff-addition products were observed. The other main product in all reactions was diphenyl disulfide (**4**). The relative product yields at 60°C are shown in Table 1.



Scheme 1

In reactions of methacrylonitrile and of vinyl acetate, small amounts of another product were also observed. We have tentatively assigned the structure **5** to this product, corresponding to a similar product **6** formed in the analogous reaction with *t*-butyl thiol^{15,16}. ¹H and ¹³C nmr data were consistent with the structure **5**, however, both the CI and electrospray mass spectra failed to give a parent ion. An ion corresponding to M-CH₄ (*m/e*= 283.1029, C₁₈H₂₁NOS - CH₄ requires M⁺=283.1031) supports the presence of sulfur, oxygen and nitrogen. Strangely, **5** was not formed in a 'blank' reaction when phenyl thiol and the aminoxy **1** were heated in benzene for 90 mins at 60°C. The only product formed was product **4**. However, the product **5** does not appear to be important in the initial stage of the reaction, since after a short reaction time (10 mins), in the case of methacrylonitrile, the main products **3c** and **4** were present but the product **5** was not observed (whereas after 90 mins, the relative yield of product **5** had increased to 12% in the reaction mixture). It is clear then, that **5** is formed as a result of secondary reactions. It also appears to be quite stable as heating the reaction mixture overnight showed no change in the ratio of **4** : **5**, although the relative amount of **3c** decreased slightly.



Table 1. Relative Product Yields after 90 min at 60°C in neat monomer

Monomer	Diphenyl disulfide (Product 3)	Addition (Product 4)	Product 5
Styrene (STY)	4	96	--
Methylmethacrylate (MMA)	11	89	--
Methacrylonitrile (MAN)	22	66	12
Vinylacetate (VA)	90	9	1

The relative reactivity of the monomers towards addition of thiyl radical **2** follows the order VA<MAN<MMA<STY (see Table 1), which is the same order found in addition reactions of *t*-butyl thiyl radicals¹⁵ and *t*-butoxyl radicals (in contrast to benzoyloxyl, methyl and phenyl radicals, for which the monomers follow a different order)¹⁷. Attempts have been made to relate the Q and e values of vinyl monomers to their reactivities towards radicals. In the case of *t*-butoxyl radicals the suggestion was made that the radicals are controlled not only by the polar nature but also by the resonance effect of the monomers¹⁷. Considering our results this could also be applicable to the addition of thiyl radicals. In competition experiments at 60°C the relative reactivity of the monomers towards the thiyl radical **2** was

determined to be VA:MAN:MMA:STY= 1 : 50 : 100 : 500, which is a much larger variation than that found under the same conditions for t-butyl thiyl radicals (VA:MAN:MMA= 1 : 5 : 8)¹⁵. Presumably steric effects are important in the case of the t-butyl thiyl radical in the monomers methacrylonitrile and methyl methacrylate.

Conclusion

Exclusive tail addition of the phenyl thiyl radical to the monomers styrene, methyl methacrylate, methacrylonitrile, and vinyl acetate were obtained. Head addition was not observed. The relative reactivity of styrene, methyl methacrylate, methacrylonitrile, and vinyl acetate towards addition of the phenyl thiyl radical was found to be 500 : 100 : 50 : 1, respectively. In radical polymerisations of less reactive monomers such as vinyl acetate, the phenyl thiyl radical would be a relatively inefficient initiator.

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