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Thiohydroxamic esters

A new class of polymerization regulator

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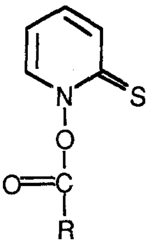
Summary

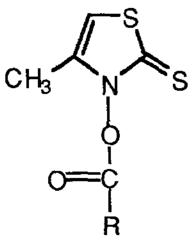
N-Hydroxypyridine-2-thione derivatives **Ia-c** and N-hydroxy-4-methylthiazole-2(3H)-thione derivatives **IIa-b** act as chain transfer agents in free radical polymerizations of methyl methacrylate (C_x = 0.6-4.3), styrene (C_x = 0.32-3.9), methyl acrylate (C_x = 3.1-20), and vinyl acetate (C_x = 9.7-80) at 60 °C. Some retardation occurs with vinyl acetate and methyl acrylate. **Ib** also has the property of initiating the polymerization of methyl methacrylate photochemically, while **IIb** acts as a thermal initiator. The chain transfer constants of **IIb** make it particularly suitable for regulating molecular weight in batch polymerizations of methyl methacrylate and styrene.

Introduction

The regulation of molecular weight in free radical polymerizations is frequently accomplished by the addition of a chain transfer agent (1). We have recently been investigating new classes of chain transfer agents that act *via* novel addition-fragmentation sequences (2-4). In certain applications, these chain transfer agents have more favorable chain transfer constants than thiols, which are the most widely used type of molecular weight regulator. This paper describes our experiments with N-hydroxypyridine-2-thione derivatives **Ia-c** and N-hydroxy-4-methylthiazole-2(3H)-thione derivatives **IIa-b** as chain transfer agents for free radical polymerizations.



Ia R = $C_{15}H_{31}$
Ib R = $C_6H_5CH_2$
Ic R = C_6H_5



IIa R = $C_{15}H_{31}$
IIb R = $C_6H_5CH_2$

These thiohydroxamic esters have been investigated by Barton and Critch (5-9) as sources of alkyl radicals *via* a chain process that is illustrated in Scheme 1 for the N-hydroxypyridine-2-thione derivative **Ia**. N-Hydroxy-4-methylthiazole-2(3H)-thione

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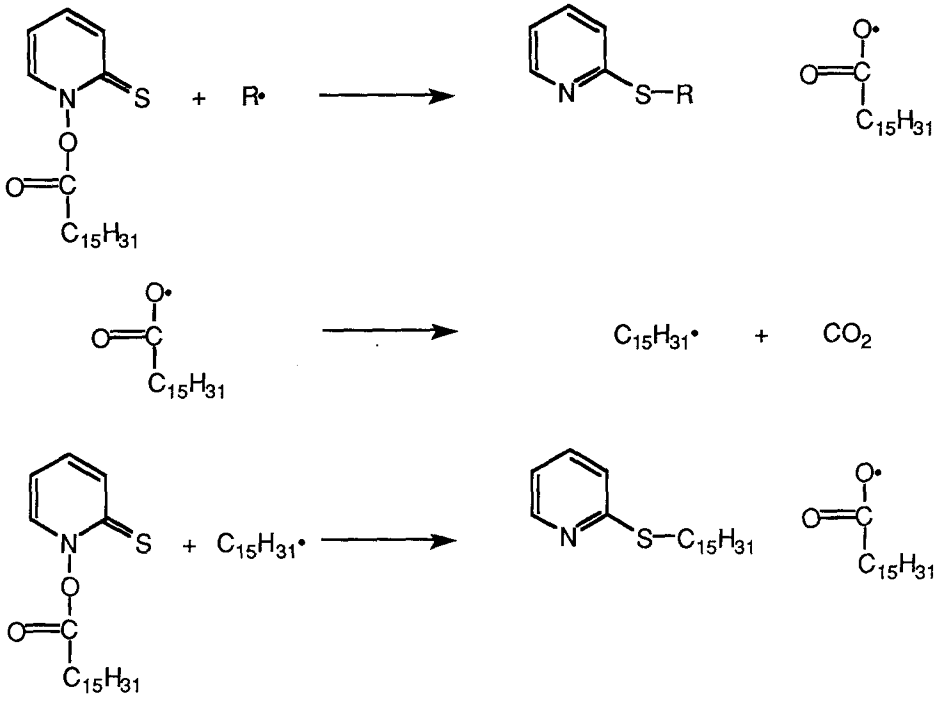
*To whom offprint requests should be sent derivatives **IIa-b** are believed to react in a similar manner. The first step of this chain reaction is the addition of initiating radicals to the carbon-sulfur double bond; this is followed by fragmentation of the weak N—O bond. A driving force for this fragmentation appears to be the generation of the aromatic pyridine or thiazole system. The expelled carboxyl radical then undergoes decarboxylative fragmentation to generate the alkyl radical, $C_{15}H_{31}\bullet$. This radical then re-enters the cycle.

From a consideration of this reaction scheme for generating alkyl radicals, and noting the possibility that R• could be a growing polymer chain, we considered that there was potential for thiohydroxamic esters, such as **Ia-c** and **IIa-b**, to be useful chain transfer agents in free radical polymerizations, provided the rate constants of the steps in Scheme 1, particularly that of the first step (i.e. the reaction of the macroradical with the thione), were sufficiently high to be competitive with propagation in the polymerization.

Scheme 1:



Results and Discussion

When methyl methacrylate was polymerized (AIBN; 60 °C) in the presence of the thiohydroxamic ester **Ia** there was a marked lowering of the molecular weight compared with a polymerization carried out in its absence. The conversion of the polymerization was not affected, even when sufficient **Ia** was added to effect a 50-fold decrease in molecular weight. This supports a mechanism involving true chain *transfer* rather than termination of polymer chains without reinitiation (retardation). The chain transfer constant (C_x in Table 1), calculated from the Mayo equation (10) using 3 concentrations of **Ia** and a control without added chain transfer agent, was 4.0.

Table 1. Chain transfer constants (C_x) of thiohydroxamic esters **Ia-c** and **IIa-b** determined at 60 °C.

Chain transfer agent	methyl methacrylate	styrene	methyl acrylate	vinyl acetate
Ia	4.0	3.8	20	36
Ib	4.3	3.9		80
Ic	2.8			
IIa	0.64	0.32	3.1	9.7
IIb	1.0	0.97		18

It is also noteworthy that **Ia** itself initiated polymerization (no AIBN present at 25 °C) when the mixture was irradiated with the light of a 75 W incandescent desk lamp. At a distance of 25 cm, an irradiation time of 1 h, and a concentration of **Ia** of 55 mM in neat methyl methacrylate, a polymer of $\bar{M}_n = 3600$ was obtained at a conversion of 5%. After 6 h of irradiation, the conversion to polymer was 26%. Control experiments established that there was no polymerization in the dark or in the absence of **Ia**. **Ia** was not an effective thermal initiator of methyl methacrylate polymerizations at 60 °C. The ^1H NMR spectrum of a sample of poly(methyl methacrylate) prepared with **Ia** (AIBN initiation) showed signals at δ 7.15, 7.55 and 8.38 ppm, which were indicative of the presence of the thiopyridine end group predicted from Scheme 1. Such a group may be useful for further modification (e.g., quaternization to give a hydrophilic head-group) or may be the basis of ionic association with polymers containing acid groups (11).

The N-hydroxypyridine-2-thione derivative **Ia** also lowered the molecular weight in styrene, methyl acrylate, and vinyl acetate polymerizations. The chain transfer constants are listed in Table 1. Although this thiohydroxamic ester was useful for regulating the molecular weight in styrene polymerizations, the chain transfer constants with methyl acrylate and vinyl acetate were too high to give narrow distributions of molecular weight in batch polymerizations taken to high conversion (12). Moreover, there was significant retardation (e.g. a 46-fold reduction of molecular weight was accompanied by a 19-fold drop in the yield of polymer) in vinyl acetate polymerizations, indicating that with this monomer chain termination without reinitiation competed with true chain transfer.

The phenylacetyl thiohydroxamate **Ib** had similar chain transfer constants to **Ia**, except with vinyl acetate, where the activity of **Ib** was approximately twice as high. It is should be noted, however, that the determination of very high chain transfer constants by the Mayo equation, even at polymerization conversions of only a few percent, leads to inaccurate results. As might be anticipated, since the reinitiating species derived from **Ib** is the resonance stabilized benzyl radical, **Ib** retards the polymerization of vinyl acetate significantly more than does **Ia**. There was, however, only very mild retardation with styrene and methyl methacrylate, confirming that these monomers are much more effectively reinitiated with benzyl radical. The benzoyl thiohydroxamate **Ic** also had significant chain transfer activity in methyl methacrylate polymerizations (Table 1); it was not, however, examined further.

The N-hydroxy-4-methylthiazole-2(3H)-thione derivative **IIa** also displayed activity as a chain transfer agent with methyl methacrylate ($C_x = 0.64$), styrene ($C_x = 0.32$), methyl acrylate ($C_x = 3.1$) and vinyl acetate ($C_x = 9.7$). No retardation was detected with methyl methacrylate or styrene; however, surprisingly, there was a slight increase in the conversions of methyl acrylate polymerizations carried out in the presence of **IIa**. Vinyl acetate polymerizations were mildly retarded in the presence of **IIa**.

The phenylacetyl ester **IIb** had a chain transfer constant of 1.0 with methyl methacrylate. This value is the optimum for obtaining narrow distributions of molecular weight in batch polymerizations taken to high conversion (12). It was noted, however, that the conversion of the polymerization was dependent on the amount of **IIb** added; at concentrations required to produce an approximate 20-fold decrease in molecular weight (88 mM), there was an increase in conversion of almost 300%. Accordingly, we examined the potential of **IIb** to initiate polymerization of its own accord. Substantial amounts (32% conversion) of low molecular weight poly(methyl methacrylate) ($\overline{M}_n$ = 12000) were obtained when **IIb** (75 mM) was heated in methyl methacrylate at 60 °C for 4 h in the absence of AIBN initiator. A control experiment carried out without **IIb** or AIBN yielded no polymer. **IIb** does not, however, initiate polymerization to any significant extent when irradiated with a tungsten lamp at ambient temperatures (75 W; 25 cm; 1 h). This was an interesting contrast, since unlike **Ib**, with **IIb** autoinitiation occurs under thermal, and not with visible light. Similar observations have been made by Barton and coworkers (5,8) for the radical rearrangements of **Ia** and **IIa**.

The phenylacetyl ester **IIb** also displayed almost optimal activity in styrene polymerizations (C_x = 0.97), although again there was an increase in the conversion of the polymerization at high concentrations of **IIb** because of thermal autoinitiation. In contrast, **IIb** retarded vinyl acetate polymerizations; the apparent chain transfer constant was 18.

In summary, the above results highlight the efficiency of thiohydroxamic esters, particularly **IIb**, for regulating the molecular weight of styrene and methyl methacrylate polymerizations.

Experimental

N-hydroxypyridine-2-thione, palmitoyl ester **Ia**

Palmitoyl chloride (2.8 g) was added to a suspension of 2-mercaptopyridine-N-oxide, sodium salt (2.8 g) (Aldrich) in dichloromethane (50 mL) and the mixture was stirred at ambient temperature for 2 h. It was then filtered and the solvent was removed. The crude product (85% yield) was rapidly subjected to chromatography on a short column of silica gel (eluent: dichloromethane/petroleum spirit 3:1) to afford a yellow solid m.p. 68.5-69 °C. ^{1}H NMR spectrum: ($CDCl_3$) δ 0.87 (3H, t, J = 6 Hz), 1.0-2.0 (26H, m), 2.7 (2H, t, J = 7 Hz), 6.60 (1H, m), 7.18 (1H, m), 7.6 (2H, m).

N-hydroxypyridine-2-thione, phenylacetyl ester **Ib**

This compound was obtained from phenylacetyl chloride and 2-mercaptopyridine-N-oxide, using the procedure described above. It was a viscous yellow oil that crystallized on standing (mp 79-82 °C from CH_2Cl_2/petroleum spirit). ^{1}H NMR spectrum: ($CDCl_3$) δ 4.02 (2H, s), 6.57 (1H, "t"), 7.0-7.8 (8H, m).

N-hydroxypyridine-2-thione, benzoyl ester **Ic**

This compound, mp 106-107 °C, was prepared in 87% yield in a similar manner from 2-mercaptopyridine-N-oxide, sodium salt and benzoyl chloride. ^{1}H NMR spectrum: ($CDCl_3$) δ 6.62 (1H, t), 6.9-7.9 (6H, m), 8.2 (2H, m).

4-Methyl-3-palmitoyloxythiazol-2(3H)-thione **IIa**

This compound, mp 54-54.5 °C [lit. (5) mp 54 °C], was prepared by the sequence described by Barton et al. (5).

4-Methyl-3-(phenylacetoxy)thiazol-2(3H)-thione **IIb**

This compound, mp 79-81 °C, was prepared from 3-hydroxy-4-methylthialzole-2(3H)-thione and phenylacetyl chloride by a procedure similar to that described by Barton and coworkers (5) for 4-methyl-3-palmitoyloxythiazol-2(3H)-thione. ^{1}H NMR spectrum: ($CDCl_3$) δ 1.97 (3H, s), 3.98 (2H, s), 6.17 (1H, "s"), 7.1-7.5 (5H, m).

Procedure for carrying out polymerizations

Azobisisobutyronitrile (34.9 mg) was dissolved in freshly distilled styrene (25 ml). Aliquots (5.0 ml) were removed and added to ampoules containing various amounts of the chain transfer agent. Generally, for a given chain transfer agent/monomer combination, polymerizations were carried out with four different concentrations of the chain transfer agent. The mixtures were then degassed by three freeze-evacuate-thaw cycles and sealed under vacuum (10^{-3} Torr). After the polymerization (1 h at 60 °C), the contents of the ampoules were poured into methanol and the precipitated polymers were collected and dried *in vacuo* overnight. A small portion of each polymer was examined by gel permeation chromatography (GPC) using a Waters Instrument connected to six μ-Styragel columns (10^6, 10^5, 10^4, 10^3, 500, and 100 Å pore size). Tetrahydrofuran was used as the eluent at a flow rate of 1 ml/min and the system was calibrated using narrow distribution polystyrene standards (Waters).

Polymerizations of methyl methacrylate were carried out similarly for 1 h at 60 °C. Azobisisobutyronitrile (48.2 mg) was dissolved in freshly distilled methyl methacrylate (25 ml). Aliquots (2.0 ml) were removed and added to ampoules containing weighed amounts of the chain transfer agent. After the polymerization, the contents of the ampoules were then poured into hexane and the precipitated polymers were collected, dried, and examined as before.

Polymerizations of methyl acrylate were carried out using a stock solution prepared from azobisisobutyronitrile (9.1 mg) and freshly distilled methyl acrylate (25 ml). Aliquots (2.0 ml) were removed and added to ampoules containing thiophene-free benzene (8.0 ml) and weighed amounts of the chain transfer agent. After degassing, the mixtures were polymerized at 60 °C for 1 h. The volatiles were then removed and the polymers were dried in vacuo to constant weight and examined by GPC.

Vinyl acetate polymerizations were carried out *in vacuo* at 60 °C for 1 h using the following procedure. Azobisisobutyronitrile (8.0 mg) was dissolved in freshly distilled vinyl acetate (50 ml). Aliquots (10 ml) were removed and added to ampoules containing weighed amounts of the chain transfer agent. After the polymerization, the volatiles were removed and the polymers were dried and examined as before.

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