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LETTERS

Tetrathiophosphoric acid tri(1-phenylethyl) ester and 1-phenylethyl-diphenylphosphinodithioate as controlled radical polymerization agents

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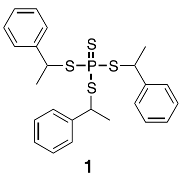
Abstract—Polystyrene and polystyrene-b-polyvinylacetate have been prepared in presence of either tetrathiophosphoric acid tri(1-phenylethyl) ester **1** or 1-phenylethyl-diphenylphosphinodithioate **2** under radical conditions. From kinetic studies performed with or without **1** or **2**, it was shown that the polymerization presents the criteria of living/controlled polymerization. © 2003 Elsevier Science Ltd. All rights reserved.

1. Introduction

During the last decade living radical polymerization has emerged as one of the most efficient routes to well-defined polymers. Several approaches have been reported such as nitroxide-mediated or alkoxyamine-initiated polymerization (NMP), atom transfer radical polymerization (ATRP) and more recently the reversible addition–fragmentation chain transfer (RAFT) process based on dithioesters, dithiocarbamates or xanthates.[1–4] None of these techniques is universal and each presents its own advantages and drawbacks. In a constant effort to find new controllers for radical polymerization we have decided to prepare tetrathiophosphoric acid tri(1-phenylethyl) ester **1** and 1-phenylethyl-diphenylphosphinodithioate **2** and to evaluate their potential as controllers in living polymerization.



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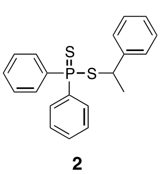

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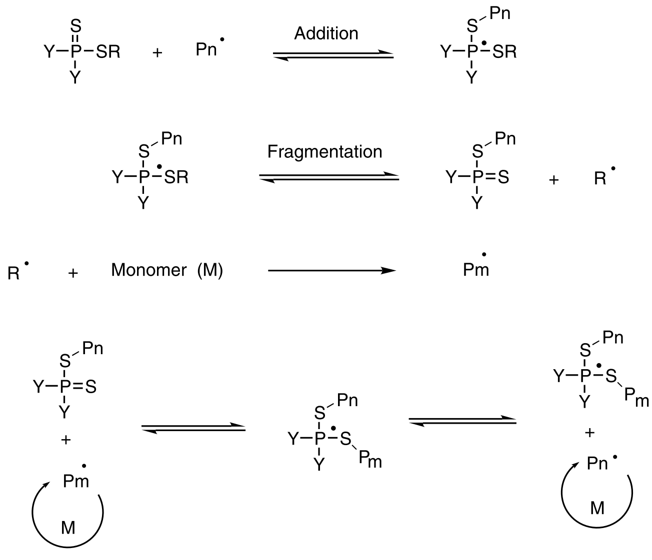
The interest of these compounds relies on the preparation of a functionalized polymer or of multi-branched materials. Like in the RAFT process, the concept of polymerization in the presence of compounds **1** and **2** involves a series of reversible addition–fragmentation steps (Scheme 1). Addition of a propagating radical (Pn•) to the sulfur atom of the P=S double bond leads to a phosphoranyl radical which can fragment to gener-



Scheme 1. Proposed mechanism for radical polymerization of various monomers in presence of compounds **1** or **2**.

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ate a phosphorus-capped polymer and a new propagating radical.

Reaction then proceeds with growing polymer chains reacting alternatively to the sulfur atoms of the P=S bond of the polymeric phosphorus compound.

To test their efficiency as controller agents, compounds **1** and **2** were used in the synthesis of homopolystyrene and polystyrene-b-polyvinylacetate.

2. Experimental

2.1. Reagents

Compound **1** has been prepared by the reaction of phosphorus pentasulfide with 1-phenylethanol according to Vlasova's procedure.[5] Compound **2** has been obtained by esterification of diphenyl-phosphinodithioic acid with 1-bromo-ethyl benzene following the method of Hopkins[6] for the preparation of alkyl diphenylphosphinodithioates.

2.2. Polymerizations

Typically **1** or **2**, 2,2′-azobisisobutyronitrile (AIBN) and styrene were added in a Schlenk flask. The medium was then thoroughly purged with nitrogen. Bulk polymerizations were conducted at 65°C. Samples were withdrawn under nitrogen and analyzed by size exclusion chromatography (SEC). Polystyrene-b-polyvinylacetate was prepared by polymerization of a vinyl acetate solution, containing AIBN and polystyrene prepared in presence of **1**. The reaction mixture was heated to 65°C and thoroughly degassed by freeze pump–thaw cycles before polymerization.

3. Results and discussion

The kinetic behaviors of polymerization of styrene, in presence of either AIBN or AIBN plus **1** or **2** were compared. The living character of styrene polymerization carried out with **1** is illustrated in Figures 1 and 2. As shown in these figures, the plots of $\ln(1/(1-X))$ versus time is linear, moreover, the variation of Mn versus conversion (X) is increasing with monomer conversion.

In a similar manner, the living character of styrene polymerization in the presence of compound **2** is illustrated in Figure 3.

A polystyrene transfer agent (Mn = 112400 g mol^{-1}) prepared as described above, was then used (Table 1) to synthesize a block copolymer polyvinylacetate-b-polystyrene. A concomitant increase with time of conversion and number average molecular weight was observed. This behavior suggests a living character for the polystyrene transfer agent and the formation of the block copolymer.

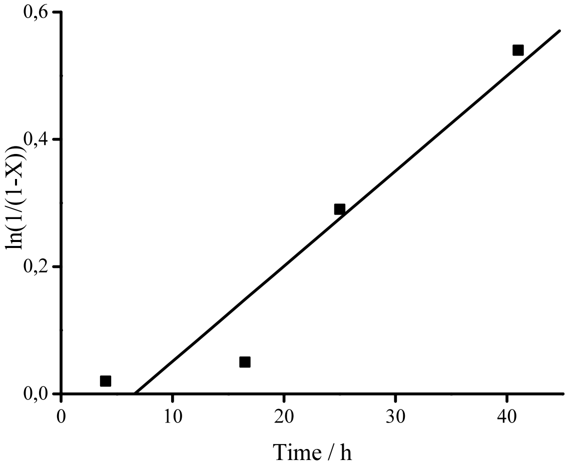

Figure 1. Semilogarithmic plots of conversion for bulk polymerization of styrene (60 ml) initiated by AIBN (17.3 mg) with **1** (22 mg).

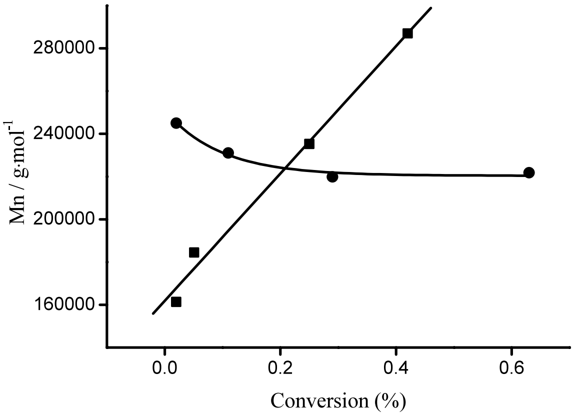

Figure 2. Evolution of number-average molecular weight (Mn) versus monomer conversion for the bulk polymerization of styrene (60 ml) initiated by AIBN (17.3 mg) with (22 mg) (■) and without (●) **1** at 65°C.

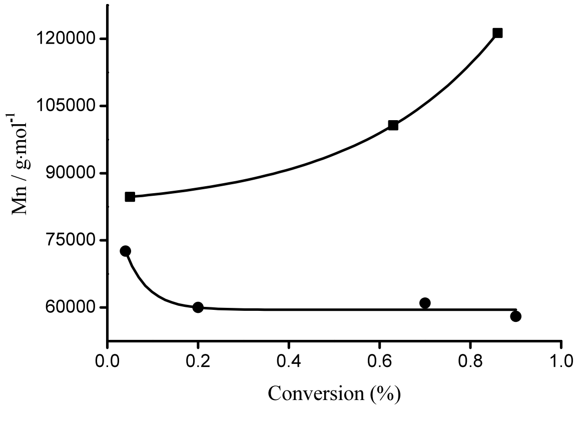

Figure 3. Evolution of molecular weight with conversion for the bulk polymerization of styrene (15 ml) initiated by AIBN (28 mg) with (121 mg) (■) and without (●) **2** at 65°C.

Table 1. Evolution of number-average molecular weight of block copolymer PS-b-PVAc versus conversion of vinyl acetate (VAc) monomer

Time (min)	Conversion	Mn (g mol^{-1})
0	0	112400
15	0.15	171200
30	0.39	182400

4. Conclusion

These preliminary results indicate that compounds **1** and **2** can exert a control on the radical polymerization of styrene and vinyl acetate in presence of AIBN. Work is in progress to study the efficiency of such molecules for polymerization of various monomers.

Acknowledgements

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