

# Dithioester Functionalization of Poly(cyclohexene oxide) and Its Application To Obtain Block Copolymers

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**ABSTRACT:** A new method of introducing dithioester groups into the polymer chain of poly(cyclohexene oxide) is reported. It includes the use of diaryliodonium salt and an aromatic dithioacid as a redox couple to initiate the cationic polymerization of cyclohexene oxide. It was found that the dithioacid by itself cannot start the polymerization of cationic polymerizable monomers; however, in combination with a diaryliodonium salt, an exothermic reaction was produced, yielding a thiocarbonylthio-functionalized polyether. Thermal profiles of the redox polymerizations were determined by means of optical pyrometry. A preliminary study showed that when the poly(cyclohexene

oxide) functionalized with dithioester groups was introduced into the radical polymerization of styrene, the polystyryl growing radicals reacted with the dithioester-functionalized polyether to form a block polymer. The amount of polyether actually incorporated into the block copolymer was calculated to be 70% of the initial amount of poly(cyclohexene oxide)/dithiobenzoic acid charged into the reactor. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 598–605, 2008

**Key words:** block copolymers; cationic polymerization; radical polymerization; redox polymers

## INTRODUCTION

The development of functionalized polymers and their use as intermediate species in the synthesis of block copolymers is one of the most important synthetic routes. The introduction of a reactive functional group during the polymerization of a given monomer can result in a functionalized polymer that can then be further copolymerized with a new monomer either with the same polymerization technique or with a different method. Pan et al.<sup>1</sup> used such a technique to prepare a miktoarm ABC star copolymer with poly(ethylene oxide), polystyrene (PS), and poly(L-lactide) via the reaction of poly(ethylene oxide) with maleic anhydride followed by coupling with dithiobenzoic acid (DTBA) to obtain a dithiobenzoate-functionalized poly(ethylene oxide). Their work involved the introduction of styrene to the poly(ethylene oxide) chain by means of reversible addition–fragmentation chain-transfer polymerization (RAFT polymerization) through the pendant dithiobenzoate groups. The L-lactide was then introduced to the chain by ring-opening polymerization in the final reaction step. In another study, dendrimer-star polymers and block copolymers were prepared similarly.<sup>2</sup> In a first step, a dendritic polyester with 16 surface dithiobenzoate groups was synthesized to pro-

duce a dendritic transfer agent, which was then further polymerized with styrene by means of the RAFT polymerization to yield the desired copolymers.

This study involved two different sequential methods of polymerization, namely, the redox cationic polymerization of cyclohexylene epoxy monomers and the radical polymerization of vinyl monomers. Thus, the purpose of this research was to develop a new method to obtain a variety of copolymers composed of vinylic and nonvinylic monomers.

Crivello and Lam<sup>3</sup> first reported the cationic polymerization of epoxy monomers induced by a redox reaction between ascorbic acid and its derivatives with diaryliodonium salts in the presence of catalytic amounts of copper(I) salts. It was found that even though ascorbic acid was a very effective reducing agent of the onium salts, its poor solubility limited its use as a component of a redox couple. Other compounds with better reducing properties were investigated. For instance, benzoin displayed better solubility than ascorbic acid derivatives, showing enhanced reactivity.<sup>4</sup> Crivello and Lee<sup>4</sup> proposed a mechanism involving the reduction of diaryliodonium salt by ascorbic acid derivatives, generating a strong Brønsted acid that initiated the polymerization of epoxy monomers (see Scheme 1).

Onen and Yagci<sup>5</sup> realized the effectiveness of redox cationic polymerizations, using ascorbyl 6-hexadecanoate and *N*-ethoxy-2-methyl pyridinium as the redox couple. Their studies with model compounds demonstrated that the pyridinium salt was reduced

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Where M is cationically polymerizable monomer

**Scheme 1** Mechanism of cationic polymerization by means of a redox reaction between a diaryliodonium salt and a reducing agent (R–H).

by the action of the hexadecanoate. This reduction was confirmed because 2-methyl pyridine was found in the analyses of the photolysis products of the photoinitiator by gas chromatography/mass spectrometry (GC–MS).

Kampmeier and Nalli<sup>6</sup> investigated the redox radical-chain reaction of diaryliodonium halides with cationic polymerizable monomers such as tetrahydrofuran and 1,3-dioxolane. In their study, those monomers acted as hydrogen atom donors, generating a radical by the action of azobisisobutyronitrile (AIBN). The derived monomer radical then reduced the iodonium salt, generating in this way a Brønsted acid that polymerized the monomers.

This article reports the results of the polymerizations of cyclohexene oxide (CHO) with a new redox couple formed by an aromatic dithioacid and a diaryliodonium salt. Four different aromatic dithioacids promoted a vigorous exothermic polymerization of CHO when mixed with a diaryliodonium salt to yield functionalized poly(cyclohexene oxide)s (PCHOs). The course of the cationic polymerizations was monitored by means of optical pyrometry, and the obtained polymers were characterized by gel permeation chromatography (GPC), ultraviolet–visible (UV–vis), and NMR. Then, functionalized polyethers were incorporated into styrene free-radical polymerization to form block copolymers.

## EXPERIMENTAL

### Materials and equipment

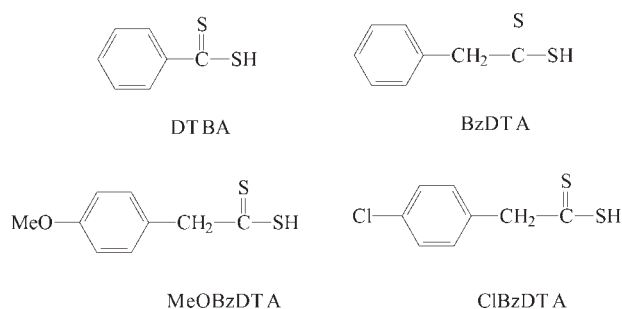
Benzyl bromide, bromobenzene, 4-methoxybenzyl chloride, 4-chlorobenzyl chloride, Grignard-grade magnesium powder, carbon disulfide, and CHO, all reagent-quality, were purchased from Aldrich Chemical Co. (Milwaukee, WI) and used as received. Tetrahydrofuran and diethyl ether were dried with sodium with the benzophenone–sodium complex as an indicator. Styrene was purified by being washed with sodium hydroxide to remove the inhibitors, dried with  $\text{CaH}_2$  and distilled under a nitrogen atmosphere. AIBN was recrystallized twice from ethanol. The onium salts, cationic photoinitiators

(4-*n*-decyloxyphenyl) phenyliodonium hexafluoroantimonate (DPPI  $\text{SbF}_6$ ) and (4-*n*-decyldiphenyl) phenyl triarylsulfonium hexafluoroantimonate (DPPTS  $\text{SbF}_6$ ), were prepared as described by Crivello and coworkers.<sup>7,8</sup>  $^1\text{H-NMR}$  spectra were obtained with a JEOL (Peabody, MA) 300-MHz NMR spectrometer at room temperature. Routine IR spectra were performed on a Magna (Middleton, WI) Nicolet 550 IR spectrometer. UV–vis spectra were analyzed in a Hewlett–Packard (Palo Alto, CA) 8452 A spectrometer with a diode array. The molecular weights of the polymers were determined in a Hewlett–Packard HPLC series 1100 with two detectors, a UV detector with a diode array (HP series 1100) and a differential refractometer (HP 1047 A). Three Ultrastaygel columns with pore sizes of  $10^6$ ,  $10^5$ , and  $10^3$  Å were used. An unmodified Omega OS552-V1-6 industrial IR thermometer from Omega Engineering, Inc. (Stamford, CT), was used in these studies. This instrument has a sensitivity of  $1^\circ\text{C}$  within an operating temperature range of  $-18$  to  $538^\circ\text{C}$ .

### Synthesis of DTBA

The synthesis of this compound was carried out according to the method reported by Aycock and Jurch.<sup>9</sup> Into a 250-mL, three-necked, round-bottom flask provided with a magnetic stirrer, argon inlet, addition funnel, and thermometer was placed 2.32 g (0.095 mol) of Grignard-grade magnesium powder. The reaction system was subjected to three vacuum–heating cycles to eliminate humidity. Afterwards, 100 mL of dried tetrahydrofuran was introduced into the system. Then, 15 g (0.095 mol) of bromobenzene dissolved in 30 mL of dried tetrahydrofuran was added dropwise to the mixture. This mixture was heated to reflux for 3 h, and after this time, the mixture was allowed to cool to room temperature. Then, 8 g (0.1045 mol) of carbon disulfide was added to the formed Grignard reagent. The temperature was slowly raised to the boiling point and held for 3 h. The mixture was then poured into 200 mL of distilled water and extracted three times with 50 mL of dried ether. The aqueous phase was acidified to pH 1 with hydrochloric acid. Then, the reaction mixture was placed in a separation funnel, and the aqueous phase was extracted again with ethyl ether. The ether extracts were dried over anhydrous sodium sulfate. After the evaporation of the solvent, 7.79 g (53% theory) of a purple, dense liquid identified as DTBA was obtained.

To prepare 2-phenyl dithioacetic acid (BzDTA), 4-methoxyphenyl dithioacetic acid (MeOBzDTA), and chlorophenyl dithioacetic acid (ClBzDTA), the same procedure was used, bromobenzene being replaced with benzyl bromide, 4-methoxybenzyl chloride, or 4-chlorobenzyl chloride, respectively (see Scheme 2 for the chemical structures).



**Scheme 2** Different dithioacids used in this study.

#### Characterization of DTBA

Fourier transform infrared (FTIR) in a KBr disc: 2545 (S—H); 1582 (C—C aromatic);  $1050\text{ cm}^{-1}$  (C—S).  $^1\text{H-NMR}$  in  $\text{CDCl}_3$  with tetramethyl silane (TMS): 8.0 (1H, d, Ar—H), 7.5 (2H, t, Ar—H); 7.35 ppm (2H, t, ArH).

#### Characterization of BzDTA

FTIR in a KBr disc: 2530 (S—H); 1602 (C—C aromatic);  $1024\text{ cm}^{-1}$  (C—S).  $^1\text{H-NMR}$   $\text{CDCl}_3$  with TMS: 7.4 (5H, m, Ar—H), 4.25 ppm (2H, s, Ar—CH<sub>2</sub>).

#### Characterization of MeOBzDTA

FTIR in a KBr disc: 2540 (S—H); 1608 (C—C aromatic); 1248 (C—O);  $1029\text{ cm}^{-1}$  (C—S).  $^1\text{H-NMR}$  in  $\text{CDCl}_3$  with TMS: 7.2 (2H, d, Ar—H), 6.8 (2H, d, Ar—H); 4.2 (2H, s, Ar—CH<sub>2</sub>); 3.8 ppm (3H, s, CH<sub>3</sub>O—Ar).

#### Characterization of ClBzDTA

FTIR in a KBr disc: 2532 (S—H); 1602 (C—C aromatic);  $1020\text{ cm}^{-1}$  (C—S).  $^1\text{H-NMR}$  in  $\text{CDCl}_3$  with TMS: 7.2 (4H, m, Ar—H); 4.7 ppm (2H, s, Ar—CH<sub>2</sub>).

#### Redox polymerization of CHO

In vials fitted with caps was placed 0.136 g ( $1.0 \times 10^{-4}$  mol) of (4-*n*-decyloxyphenyl) phenyliodonium (DPPI) dissolved in 1 g (0.010 mol) of CHO previously cooled to 0°C. Then, 0.031 g ( $1.0 \times 10^{-4}$  mol) of DTBA was dissolved in 1 g of cold CHO and added to the previous dissolution of DPPI in CHO. The reaction mixture was flushed with nitrogen, sealed, and allowed to react in a water bath at room temperature. A vigorous exothermic reaction took place when CHO reached 25°C. The water bath functioned to dissipate the released heat. After 2 h, the polymerizations were terminated by the injection of a methanolic solution of NH<sub>4</sub>OH into the reaction mixtures. The polymer was dissolved in hexane and precipitated in methanol. The obtained polymer was

reprecipitated three times to eliminate traces of free dithioacid. The following analysis techniques, NMR, IR, GPC, and UV-vis, were used to characterize the obtained functionalized PCHO. The same procedure was performed with the three BzDTA, ClBzDTA, and MeOBzDTA dithioacids.

#### Analysis of the products from the reaction between the dithioacid and the diaryliodonium salt

DPPI (0.136 g,  $1.0 \times 10^{-4}$  mol) was placed together with 0.031 g ( $1.0 \times 10^{-4}$  mol) of DTBA in dry dichloromethane in a two-necked, 50-mL, round-bottom flask with an argon inlet and magnetic stirring. The reaction mixture was analyzed after 3 h of stirring at room temperature. Unreacted DPPI was precipitated with hexane, and the remaining mixture was separated by column chromatography. The isolated products were characterized by IR, NMR, and GC-MS.

#### Studies by optical pyrometry of the rates of the cationic polymerization initiated by a redox reaction

Crivello et al.<sup>10</sup> designed a very simple and reliable method to monitor the course of photopolymerizations by measuring the increase in the temperature as a result of the heat released during the highly exothermic photopolymerization reactions. This method, using an optical pyrometer, was used to follow the extent of the redox cationic polymerizations studied in this research. The configuration of the system used in this study and the preparation of the samples have been described elsewhere.<sup>10</sup> Cationic polymerizations were conducted at ambient temperatures. In all cases, the samples were allowed to equilibrate and establish a flat baseline for 20 s before the contents of the vials were mixed with the dithioacids and diaryliodonium salts in CHO. Temperature data were collected at a rate of one measurement per second and directly recorded to a computer.

#### RESULTS AND DISCUSSION

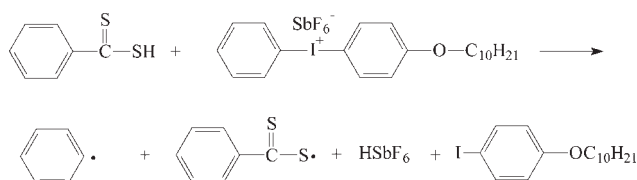
The objective of this study was to combine two distinct methods of polymerization to obtain block copolymers. In the first method, a diaryliodonium salt was used as the photoinitiator in the presence of a dithioacid to photopolymerize cationic polymerizable monomers, such as CHO, to produce a dithioester-functionalized polyether. In the second method, this polyether could react in a second stage as a reversible chain-transfer agent for radical polymerizations of styrenic or acrylic monomers.

The photopolymerization of CHO was carried out in the presence of the aromatic dithioacid. There was a spontaneous polymerization reaction even before any UV irradiation when DTBA was added to CHO with DPPI  $\text{SbF}_6$  as a photoinitiator at 1 mol %. These results deserved a deeper investigation into this apparently redox polymerization.

The initial step of this investigation was to determine if DTBA itself was promoting the cationic polymerization of CHO. To do this, experiments were carried out at different concentrations of DTBA (from 0.5 to 2.5 mol %), in the presence of CHO with no photoinitiator, while the temperature was varied. The reactions were carried out at 50°C and kept for 2 days at that temperature, which was subsequently increased to 70°C for 6 h. None of the results showed any evidence of polymerization of CHO.

Then, a study to determine the interactions between the dithioacid and the diaryliodonium salt was performed. After DPPI  $\text{SbF}_6$  was mixed with DTBA in stoichiometric ratio in dry dichloromethane, the products formed in this reaction were separated by a chromatographic column and analyzed by IR, NMR, and GC-MS. One of the isolated products was 4-iodophenyl decyl ether, a product resulting from the reduction of DPPI  $\text{SbF}_6$ . The reduction was clearly indicative of a redox reaction between DTBA and DPPI  $\text{SbF}_6$ . The results agreed with the mechanism originally proposed by Crivello and Lam,<sup>3</sup> that is, a redox reaction between diaryliodonium and a reducing agent occurred, as shown in the first step of Scheme 1. The results therefore substantiated that DTBA promoted the reduction of DPPI  $\text{SbF}_6$ , releasing the superacid  $\text{HSbF}_6$  to form the aforementioned phenyl decyl ether (see Scheme 3).

Results of the bulk polymerization of CHO using four different dithioacids in conjunction with the diaryliodonium salts are shown in Table I. The number-average molecular weight ( $M_n$ ) of the obtained PCHO polymeric products was about 6000 g/mol. All the different samples of PCHO were colored by the effect of the attachment of the dithioacid to the backbone of the polyether. The color remained even after the third dissolution-precipitation purification process. The PCHO derived from the redox reaction of DTBA and DPPI had a strong pink color, whereas the PCHO from ClBzDTA was yellow.



**Scheme 3** Proposed mechanism for the redox reaction between the diaryl iodonium salt and a dithioacid.

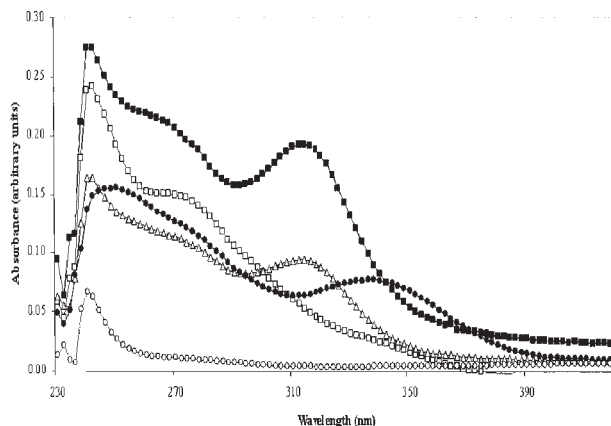
**TABLE I**  
Characterization of the Obtained Polyethers by GPC

Sample	$M_n$	Polydispersity index	Color of PCHO
PCHO-DTBA	5535	2.74	Pink
PCHO-BzDTA	6010	2.68	Orange
PCHO-MeOBzDTA	5235	2.81	Mauve
PCHO-ClBzDTA	5617	2.72	Yellow

CHO (1 g) was polymerized in the presence of 1 mol % DPPI  $\text{SbF}_6$  and 1 mol % dithioacid.

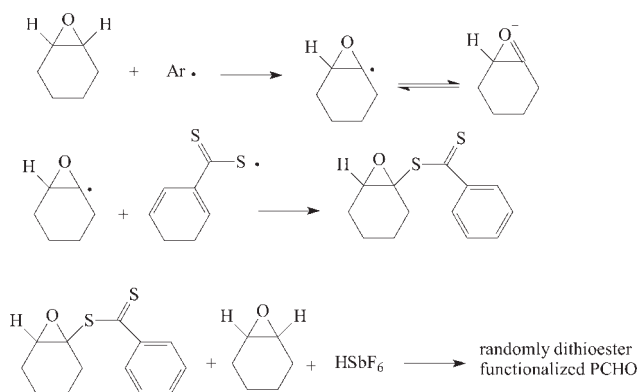
The UV spectra of the PCHO polymeric products showed that in all cases there was a functionalization of each PCHO with the dithioester moiety. Figure 1 shows that pure PCHO did not exhibit absorption in the range of 260–390 nm, but absorption was observed for the PCHO polymers from the redox polymerization of CHO. The proposed mechanism to obtain the functionalized PCHO is depicted in Scheme 4. It is known that the hydrogen atoms bonded to the epoxide group can be easily abstracted by radicals.<sup>11</sup> As such, the subsequent attack of the dithiyl radical would result in the formation of the dithioester-functionalized cyclohexane epoxide. This compound could then copolymerize with CHO in the presence of superacid  $\text{HSbF}_6$  to yield PCHO. The  $^1\text{H-NMR}$  spectrum of a PCHO prepared in the presence of DTBA is shown in Figure 2. This spectrum reveals the signals for the aromatic protons of the aromatic dithioester in the range of 7–8 ppm. From the integral of these signals and the ratio with the signals corresponding to  $-\text{CH}-\text{O}$  in PCHO at 3.4 ppm, it was calculated that the number of dithioester groups by chain was 0.019.

The comparison of the thermal profiles of the four polymerizations of CHO is detailed in Figure 3.



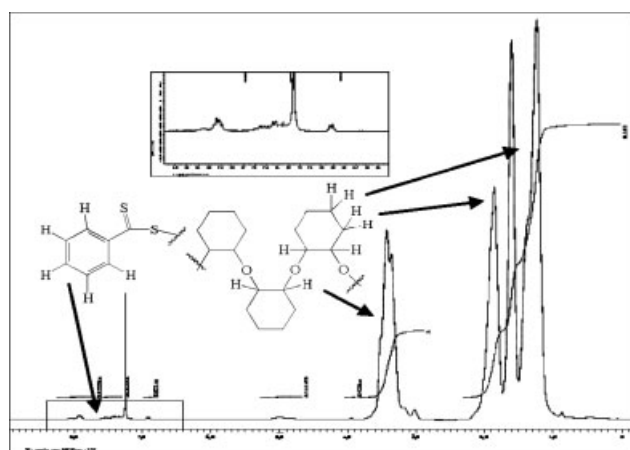
**Figure 1** UV spectra of samples of PCHO in  $\text{CHCl}_3$ , at  $1 \times 10^{-4} \text{ M}$ , functionalized with different dithioacids at 1 mol %: (○) pure PCHO, (□) DTBA, (■) BzDTA, (●) MeOBzDTA, and (△) ClBzDTA.



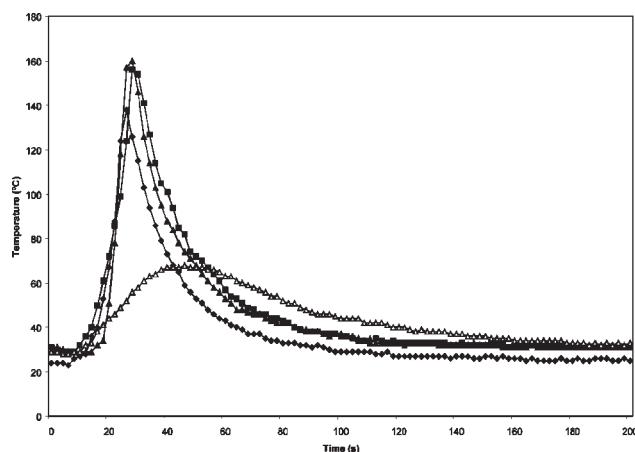


**Scheme 4** Redox cationic polymerization of CHO with a diaryliodonium salt and DTBA.

These profiles are the results from polymerization reactions of CHO with four different dithioacids in the presence of diaryliodonium salt DPPI  $\text{SbF}_6$  as the initiating species (both at 1 mol %). The results clearly show that the extent of the polymerization with the two phenyl dithioacetic derivatives BzDTA and ClBzDTA was higher than that with DTBA. In the two former cases, the maximum temperature reached  $160^\circ\text{C}$ , whereas it was  $140^\circ\text{C}$  for the latter case. Each temperature was obtained when two drops of the solution of dithioacid in CHO at 1 mol % were mixed with another two drops of the solution of the diaryliodonium salt also at 1 mol % in the same monomer. In the case of MeOBzDTA, the profile measured by optical pyrometry was not as sharp as in the other cases of dithioacids. It reached only  $65^\circ\text{C}$ . The decrease in the rate of the cationic polymerization for MeOBzDTA could be due to the slight basicity of the methoxy group, which could compete to a certain extent with the oxirane ring of CHO, for the released superacid from the diaryliodonium salt. The thermal profiles confirmed that all the dithioacids promoted the redox polymerization, even



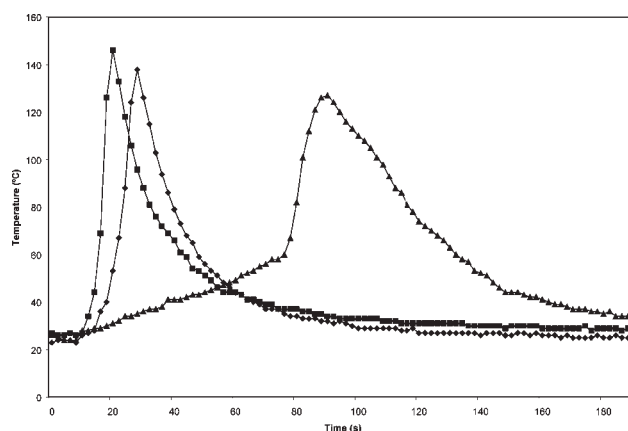
**Figure 2**  $^1\text{H-NMR}$  spectrum of PCHO functionalized with DTBA.



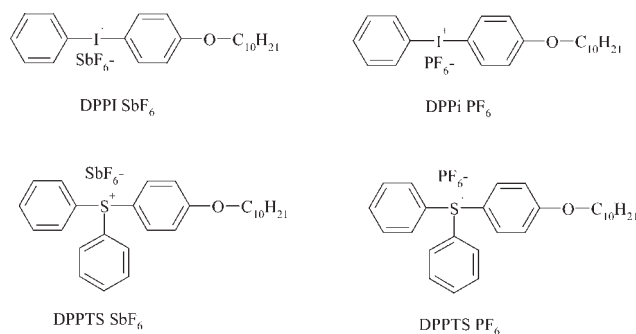
**Figure 3** Thermal profiles of the redox polymerization of CHO with DPPI  $\text{SbF}_6$  at 1 mol % in the presence of different dithioacids: (♦) DTBA, (▲) BzDTA, (■) ClBzDTA, and (△) MeOBzDTA.

though there was not a defined pattern of the effect of the substituents in the aromatic ring of the dithioacids.

Figure 4 shows the results acquired when the concentration of DPPI was varied at a fixed concentration of DTBA of 1 mol %. At the DPPI concentration of 0.5 mol %, the polymerization of CHO started very slowly, and after about 100 s, the temperature increased rapidly to  $125^\circ\text{C}$ . These observations could be considered proof that stoichiometric ratios of both reactants must be used. This was confirmed when equal ratios of both reactants were used and a very steep peak was observed at about 30 s. When the concentration of DPPI was doubled, the maximum temperature reached  $150^\circ\text{C}$ , which was  $10^\circ\text{C}$  higher than when stoichiometric ratios were used. This could be due to the thermal decomposition of the excess of the diaryliodonium salt resulting in a higher amount of initiating species.

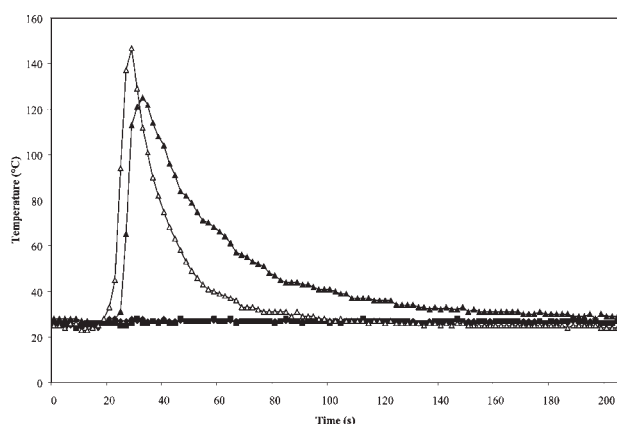


**Figure 4** Thermal profiles of the polymerizations of CHO with DTBA at 1 mol % and various amounts of DPPI  $\text{SbF}_6$ : (▲) 0.5, (♦) 1, and (■) 2.0 mol %.



**Scheme 5** Different diaryliodonium and triarylsulfonium salts used in this study.

It was of interest to determine whether other types of onium salts could participate in the proposed redox mechanism. The ability of diaryliodonium salts as oxidizing agents is well known.<sup>12–14</sup> Thus, we wanted to determine the effect of using triaryl sulfonium salts, whose oxidation potential ( $E_{1/2} = -1.01$  to  $-1.46$  V) is higher than that of the diaryliodonium salts ( $E_{1/2} = -0.2$  V).<sup>15</sup> Four different onium salts (see Scheme 5 for the chemical structures) were used as oxidizing agents in the evaluation. The results, as shown in Figure 5, confirmed that only the diaryliodonium salts were able to promote the redox polymerization; the triarylsulfonium salts produced a very slow polymerization rate. From the results, the diaryliodonium salts proved to possess greater ability to participate in a redox reaction and, therefore, could be considered validation in favor of the proposed mechanism. The differences in reactivity of both diaryliodonium salts could be due to the nature of the anion. As the hexafluoroantimonate anion is a larger anion than the hexafluorophosphate, it is more loosely bound to the cation, and hence, the cationic propagating species are more reactive.



**Figure 5** Thermal profiles of the polymerizations of CHO with 1 mol % DTBA and different onium salts at 1 mol %: (Δ) DPPI SbF<sub>6</sub>, (▲) DPPI PF<sub>6</sub>, (■) DPPTS SbF<sub>6</sub>, and (●) DPPTS PF<sub>6</sub>.

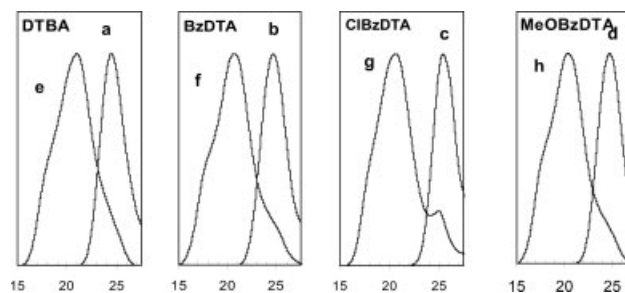
Besides CHO, other monomers such as 4-vinylcyclohexene dioxide and 3,4-epoxycyclohexyl-3',4'-epoxycyclohexancarboxylate also polymerized with the dithioacid/diaryliodonium salt redox couple. However, CHO is generally much preferred as its polymerization results in linear polymers more soluble in either organic solvents or certain monomers. This is particularly important when radical polymerizations of styrene or methyl methacrylate are intended.

Once the polyethers were prepared and characterized in the first stage, they were used in the second stage as chain-transfer agents for the radical polymerization of vinyl monomers. Reaction results with the four functionalized polyethers are presented next.

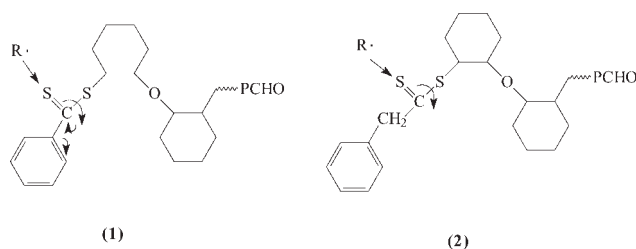
### PS-PCHO block copolymers

In the first series of experiments, all four differently functionalized PCHOs were evaluated as macro chain-transfer agents in the RAFT polymerization as developed by the Commonwealth Scientific & Industrial Research Organization group.<sup>16</sup> Each polyether was dissolved separately in styrene at a concentration of 15% (w/w) containing AIBN, and then from this solution, a second solution was prepared with a styrene/AIBN/PCHO molar ratio equal to 190 : 1 : 1. Each resulting mixture was then degassed and heated for 15 h at 60°C. The reaction mixtures were precipitated in methanol and analyzed by size exclusion chromatography (SEC). Figure 6 shows the SEC traces for each product collated with its respective initial polyether.

The results show that in the case of the styrene polymerization in which PCHO-DTBA and PCHO-BzDTA were used as macro transfer agents, the polyethers were incorporated completely into the structure of the PS. This was not the case with MeOBzDTA and ClBzDTA; after their purification,



**Figure 6** Chromatograms of polymers obtained by the free-radical polymerization of styrene in the presence of 15% polyether prepared with (a) PCHO derived from DTBA, (b) PCHO derived from BzDTA, (c) PCHO derived from ClBzDTA, (d) PCHO derived from MeOBzDTA, and (e–h) PS copolymerized with PCHO.



**Scheme 6** Ability of dithiobenzoic ester and phenyldithioacetic ester to generate stable transient radicals.

part of the polyether could be detected mixed with the PS. In fact, for ClBzDTA, the PCHO was not incorporated totally into the PS at all.

It has been reported that RAFT chain-transfer agents that involve benzyl dithioesters do not impart good control of the molecular weight because they induce lateral reactions. The benzyl group in the macro-RAFT agents, represented by structure **2** in Scheme 6, influences the stability of the intermediate radicals and modifies the reactivity of the C=S double bond toward radical addition. In comparison with a phenyl group (**1**), which is recognized to activate and stabilize the transient free radical (**I**), producing a narrow molecular weight distribution,<sup>17</sup> the benzyl group has relatively poor radical stabilization ability and reduces the chain-transfer constant. This may cause the formation of broad molecular weight distribution and bimodal polymers.<sup>18</sup> This effect can be worsened when the benzyl group is substituted with electron-withdrawing substituents such as chloro or nitro in the para position. Thus, it is not surprising that a fraction of the initial PCHO functionalized with benzyl groups still remained in the SEC traces. Comparatively, the PCHO prepared with DTBA yielded a product in which a major part

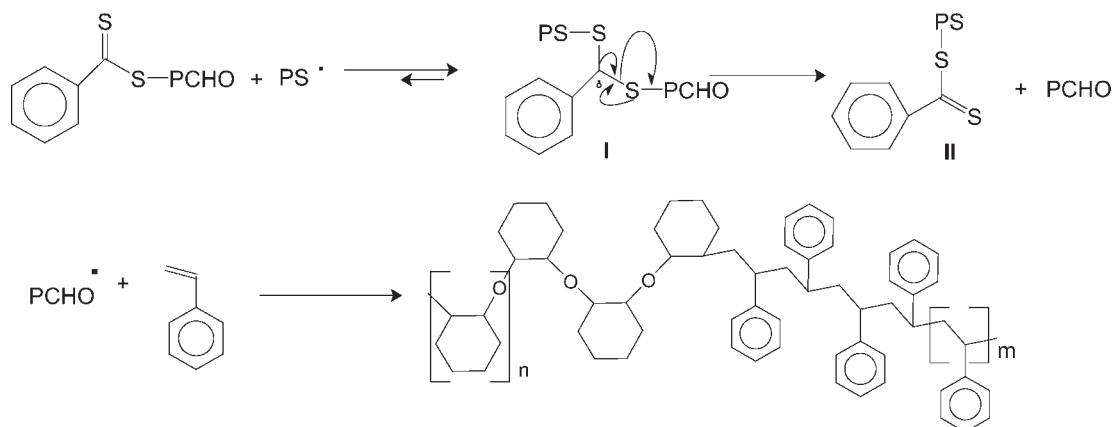
of the macromolecular chain-transfer agent was incorporated, forming a block copolymer.

According to the mechanism already established for the RAFT polymerization, it is proposed that in our case, a thiocarbonylthio-functionalized polyether can act as a macro chain-transfer agent (see Scheme 7). Once the AIBN decomposes thermally, the generated radical can react with the monomer, styrene in this case, forming propagating radicals. The growing free radicals can then undergo an addition reaction with the carbon–sulfur double bond to create a transient radical (**I**), which is readily transformed to the thiocarbonylthio-containing compound (**II**). As a result of this addition–fragmentation process, a free radical localized in the structure of the PCHO is created, which becomes available to reinitiate styrene polymerization, forming block copolymers.

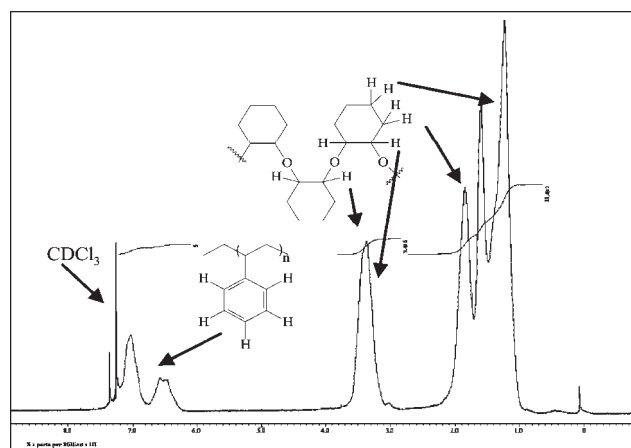
However, in this series of experiments, it was unclear that the desired copolymers were produced. Therefore, a new experiment was performed that focused on a DTBA-functionalized polyether. Because the low molecular weight of the PCHO–DTBA made it easier to assess the formation of a block copolymer, it was decided to use a PCHO with  $M_n = 1280$  g/mol, and consequently, the styrene/PCHO–DTBA molar ratio was also decreased.

The new experiment involved dissolving the pink-colored polyether into a mixture of benzene/styrene (50% v/v) containing AIBN, which was accurately degassed, heated, and maintained at 60°C. The styrene/polyether/AIBN molar ratio was calculated to be 28 : 2 : 1. The reaction was discontinued after 16 h. At this time, the conversion of styrene determined gravimetrically was 81%.

The obtained product was dissolved in a minimum amount of THF and then poured into a large amount of hexane. Slowly, a styrene-rich fraction



**Scheme 7** Formation of a block copolymer in a RAFT polymerization mediated with functionalized thiocarbonylthio polyethers.



**Figure 7**  $^1\text{H-NMR}$  spectrum of the block polymer obtained after purification with dithioester-functionalized PCHO in the polymerization of styrene. The styrene/polyether/AIBN molar ratio was 28 : 2 : 1.

([PS] = 93%, [PCHO] = 7%) produced a precipitate that was recovered by filtration, whereas a major fraction formed a stable emulsion favored by the distinct solubility of polyether and PS in hexane. Evaporation of hexane from this emulsion yielded an amount of polymer that represented 78% of the total. The SEC  $M_n$  value of this fraction, referenced to PS standards, was calculated to be 2620 g/mol, which agreed with the calculated theoretical value of 2580 g/mol. Further fractionation of this product using cold hexane was unsuccessful, and this suggested that the polyether and the PS formed a copolymer in accordance with Scheme 6. The polyether block efficiency, which is defined as the ratio of the polyether actually incorporated into the block copolymer to the initial amount of PCHO–DTBA charged into the reactor, was calculated to be 71%, and the PCHO content calculated from the  $^1\text{H-NMR}$  spectrum in Figure 7 was 79 mol %.

In light of these observations, it can be said that cationic polymerization induced with the redox couple DTBA/DPPI  $\text{SbF}_6$  produced a functionalized polyether–DTBA that was able to participate in a chain-extension reaction in a free-radical polymerization of styrene through the RAFT mechanism. This is likely due to the dithioester moiety attached to PCHO.

Further studies are ongoing to determine more extensively the mechanism involved in the formation of the copolymer as well as the nature of the free radical generated in the PCHO when it is copolymerized with vinyl monomers. Also, other monomers, either epoxide or vinyl, would be used to determine the generality of the method.

## CONCLUSIONS

A novel methodology to functionalize polyethers is reported. This methodology is based on the redox polymerization of CHO initiated by the couple dithioacid/diaryliodonium salt. A vigorous exothermic polymerization takes place when the dithioacid, dissolved in CHO (1 mol %), is mixed with a solution of a diaryliodonium salt in CHO (also at 1 mol %). Preliminary results have revealed that it is possible to obtain block copolymers when the functionalized PCHO is used as a chain-transfer agent in the RAFT polymerization of styrene. The formation of a copolymer using the PCHO–DTBA polyether shows the feasibility of preparing a wide family of polyether/polyvinyl block copolymers with the combined cationic and free-radical polymerizations.

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