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Louis M. Leung^a; W. H. Chan^a; Sew Koo Leung^a; Siu Ming Fung^a

^a Department of Chemistry, Hong Kong Baptist College, Kowloon, Hong Kong

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SYNTHESIS OF ALIPHATIC AND AROMATIC POLY(S-DITHIOCARBONATES) USING A PHASE-TRANSFER CATALYST

LOUIS M. LEUNG*, W. H. CHAN, SEW KOO LEUNG, and SIU MING FUNG

Department of Chemistry
Hong Kong Baptist College
224 Waterloo Rd., Kowloon, Hong Kong
FAX: 852-338-8014

Key Words: Poly(*S*-dithiocarbonate); Poly(xanthate ester); Sulfur-containing polymer; Phase-transfer catalyst; Dixanthate anion

ABSTRACT

A series of aliphatic and aromatic polydithiocarbonates was prepared using a novel low temperature “one-pot” synthetic procedure employing a phase-transfer catalyst. The starting reagents were a dihalide, a diol, and an excess of carbon disulfide. The effects of the phase-transfer catalyst and reaction conditions on yield are reported. The structure and composition of the polymers were determined from infrared and ultraviolet spectroscopy and elemental analyses. The polymers were further characterized by viscosity measurement and thermogravimetric analysis.

INTRODUCTION

It is well known that sulfur-containing polymers have a wide temperature range of application and excellent resistance to chemicals and solvents. The sulfur-based polymers that have been studied extensively in the past include polythioester [1], polyphenylene sulfide (PPS) [2], polythiophene [3], polythiocarbonate [4–7],

etc. Some of these polymers with overlapping π -electrons such as the PPS and polythiophene have also been reported to possess semiconducting electrical properties. For all the sulfur-containing polymers studied, very little data have been provided on polymers containing the oxythiocarbonylthio or xanthate ester ($-\text{O}-\text{CS}-\text{S}-$) moiety. The poly(*S*-dithiocarbonate) is of particular interest because the xanthate groups are important synthetic intermediates in olefin preparation through the Chugaev reaction [8] as well as in the synthesis of thiols, *S*-activated carbanion, photosensitizers for vinyl monomers [9], etc. The dithiocarbonate polymers are also known to possess biological activity and have been used as anions in metal exchange resins [10].

The synthesis of polythiocarbonates, including the trithiocarbonate ($-\text{S}-\text{CS}-\text{S}-$) [11], thiocarbonylthio ($-\text{S}-\text{CO}-\text{S}-$) [6, 7], oxycarbonylthio ($-\text{O}-\text{CO}-\text{S}-$) [5, 7], and oxythiocarbonyloxy ($-\text{O}-\text{CS}-\text{O}-$) [4], has been reported in the literature. Their synthetic schemes usually involve a multistep process and require the use of toxic and expensive chemicals such as phosgene or thiophosgene. Most of these reactions only lead to products with symmetrical carbonyl or thiocarbonyl group. The synthesis of asymmetric dithiocarbonate has also been reported in the past [1, 9], but a multistep process was also required.

Recently, a phase-transfer catalyzed (PTC) process has been reported to produce trithiocarbonate [12], dithiocarbonate [13], or dithiocarbamate [14] moieties in a one-step reaction process using inexpensive carbon disulfide (CS_2) as the only sulfur nucleophile. The synthesis of a series of aliphatic and aromatic polytrithiocarbonate employing this PTC method was reported earlier [15]. In this study, a series of aliphatic and aromatic poly(*S*-dithiocarbonate)s using the same PTC method was prepared. In this one-pot polymerization process, a stoichiometric ratio of a diol and a dihalide and an excessive amount of carbon disulfide are mixed with an aqueous strong base solution at room temperature. The phase-transfer catalyst employed has the function of transferring the dixanthate or alkoxide anion across the aqueous/organic interface in order for the anions to have a stepwise nucleophilic substitution reaction with the dihalide. The reaction conditions required as well as the relationship of the chemical composition on some physical properties of the poly(*S*-dithiocarbonate) polymers are reported.

EXPERIMENTAL

Materials

All chemicals and solvents used were reagent grade unless otherwise specified. The monomers (from Fluka, Switzerland, and Aldrich, USA) tried and their abbreviations are the following. The dihalide monomers used were 1,2-dibromoethane (C2), 1,4-dibromobutane (C4), 1,6-dibromohexane (C6), α, α' -dichloro-*p*-xylene (p-DCX), and α, α' -dibromo-*p*-xylene (p-DBX). The diols used were ethylene glycol (C2), 1,4-butanediol (C4), 1,6-hexanediol (C6), 1,4-benzodimethanol (p-BDM), and 1,4-cyclohexanediol (p-CHD). All monomers were used "as received" and without any further purification. The phase-transfer catalyst employed for all reactions was tetrabutylammonium hydrogen sulfate (TBAHS).

Polymerization Procedures

A typical polymerization procedure is as follows. Ten milliliters of 33–50% (by weight) aqueous sodium hydroxide solution was added to a round-bottom flask followed by 1 mmol of the phase-transfer catalyst, an excess of carbon disulfide (20 mL), and 4 to 10 mmol each of the diol and dihalide. The mixture was stirred vigorously and allowed to react for 4–20 hours at room temperature or at $\sim 40^{\circ}\text{C}$ (which is below the reflux temperature of CS_2 at 46°C). The polymer was obtained by reprecipitation (if not already precipitated out from the reaction solution) using methanol and then washed with methanol/water and diethyl ether several times to remove the impurities. For some of the polymers that cannot be readily reprecipitated into the fine powder form, an electric blender filled with hot water was used to reduce the size of the pieces. Finally, the polymers were dried in a vacuum oven for days.

Characterization

Elemental analysis on the polymers was performed at the Shanghai Institute of Organic Chemistry of the Chinese Academy of Sciences, People's Republic of China. An Ostwald viscometer and a thermostat-controlled water bath was used for the viscosity measurements. Thermal analysis was performed on a thermogravimetric analyzer (Shimadzu TGA-40) scanning at $5^{\circ}\text{C}/\text{min}$ from room temperature to 550 to 600°C under a nitrogen purge. The chemical structure of the polymers and the reaction side-products was characterized by using an infrared spectrophotometer (Hitachi Model 270-30 with data processor) with samples in the format of either KBr pellets or polymer thin films, a double-beam UV-visible spectrophotometer (Shimadzu UV-240 with optional interface OPI-1), and a 60 MHz ^1H -NMR (Jeol JNM-PMX 60SI) using CDCl_3 as solvent and tetramethylsilane (TMS) as internal reference.

RESULTS AND DISCUSSION

The *S*-dithiocarbonate polymers were all yellowish in color. The repeating unit structures of the various aliphatic and aromatic poly(*S*-dithiocarbonates) synthesized are given in Fig. 1. The abbreviated symbols used for the dithiocarbonate polymers will be according to the abbreviation given for their monomers in the order of diol/dihalide. As an example, C2/C6 represents a poly(*S*-dithiocarbonate) derived from a C2 diol and a C6 dihalide monomer.

Mechanism

The polymerization reaction was initiated by the formation of alkoxide ($^-\text{OR}'\text{O}^-$) and then dixanthate ($^-\text{S}(\text{CS})\text{OR}'\text{OS}(\text{CS})\text{S}^-$) anions at the aqueous side of the aqueous/organic interface. The conversion of the diols into dixanthate anions in the aqueous phase was evidenced by the color of their products which were blood red in color. In some polymerization reactions the color did not appear until a later











Poly(S-Dithiocarbonate)		Monomer	
$\left[\text{S} - \overset{\text{S}}{\parallel} \text{CO} - \text{R}' - \text{O} - \overset{\text{S}}{\parallel} \text{C} - \text{S} - \text{R} \right]_n$			
Aliphatic		Diol	Dihalide
R' = $\text{---}(\text{CH}_2)_6\text{---}$	R = $\text{---}(\text{CH}_2)_2\text{---}$	C6	C2
$\text{---}(\text{CH}_2)_6\text{---}$	$\text{---}(\text{CH}_2)_6\text{---}$	C6	C6
$\text{---}(\text{CH}_2)_4\text{---}$	$\text{---}(\text{CH}_2)_2\text{---}$	C4	C2
$\text{---}(\text{CH}_2)_4\text{---}$	$\text{---}(\text{CH}_2)_6\text{---}$	C4	C6
$\text{---}(\text{CH}_2)_2\text{---}$	$\text{---}(\text{CH}_2)_2\text{---}$	C2	C2
$\text{---}(\text{CH}_2)_2\text{---}$	$\text{---}(\text{CH}_2)_6\text{---}$	C2	C6
Aromatic			
R' = $\text{---}(\text{CH}_2)_6\text{---}$	R = $\text{---CH}_2\text{---}$  $\text{---CH}_2\text{---}$	C6	<i>p</i> -DBX/ <i>p</i> -DCX
$\text{---}(\text{CH}_2)_4\text{---}$	$\text{---CH}_2\text{---}$  $\text{---CH}_2\text{---}$	C4	<i>p</i> -DCX
$\text{---}(\text{CH}_2)_2\text{---}$	$\text{---CH}_2\text{---}$  $\text{---CH}_2\text{---}$	C2	<i>p</i> -DBX
$\text{---CH}_2\text{---}$  $\text{---CH}_2\text{---}$	$\text{---}(\text{CH}_2)_2\text{---}$	<i>p</i> -BDM	C2
$\text{---CH}_2\text{---}$  $\text{---CH}_2\text{---}$	$\text{---}(\text{CH}_2)_4\text{---}$	<i>p</i> -BDM	C4
$\text{---CH}_2\text{---}$  $\text{---CH}_2\text{---}$	$\text{---}(\text{CH}_2)_6\text{---}$	<i>p</i> -BDM	C6
$\text{---CH}_2\text{---}$  $\text{---CH}_2\text{---}$	$\text{---CH}_2\text{---}$  $\text{---CH}_2\text{---}$	<i>p</i> -BDM	<i>p</i> -DBX/ <i>p</i> -DCX
---  ---	$\text{---CH}_2\text{---}$  $\text{---CH}_2\text{---}$	<i>p</i> -CHD	<i>p</i> -DBX

FIG. 1. Repeating unit structure for the various aliphatic and aromatic poly(S-dithiocarbonates) and abbreviations for the diols and dihalide monomers used.

time, suggesting an alternation to the mechanism in which the alkoxide was extracted first into the organic phase before converting to the dixanthate anion. The route a diol took to convert to the dixanthate anion species is determined by the solubility of the diols. For a highly soluble diol, alkoxides were easily formed and likely to be extracted into the organic phase before reacting with a carbon disulfide to produce the dixanthate anion. The suggested reaction mechanism is presented in Fig. 2.

As shown in Fig. 2, the alkoxide and dixanthate anions have their solubility in the organic phase increased after coupling with the PTC cations (Q^+). A nucleophilic substitution reaction was effected by the extracted dixanthate anions and the dihalides in the organic phase, suggesting a stepwise polymerization mechanism. The consumed PTC cation was then returned to the aqueous phase together with a halide anion in order to maintain a charge balance in both phases. The recycled

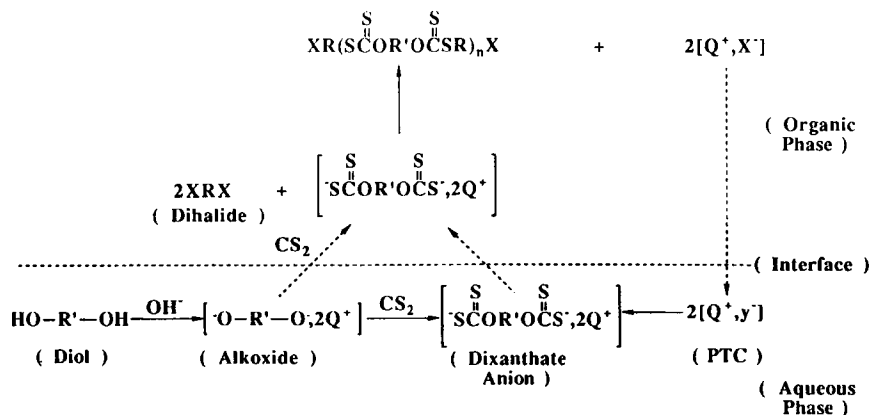


FIG. 2. Reaction mechanism for the PTC-aided stepwise polymerization of poly(S-dithiocarbonate).

PTC cations therefore guaranteed a continuous supply of the dioxanthate anions to allow the oligomers to propagate into high molecular weight polymers. A different anion species, the trithiocarbonate (CS_3^{2-}) anion, has also been reported to be generated in a similar reaction mixture containing CS_2 and a strong base [15]. The trithiocarbonate anion, which is also blood red in color, can lead to the formation of trithiocarbonate polymer instead of the dithiocarbonate moiety as expected. An earlier study [13], however, did not show evidence of abundant trithiocarbonate formation in a reaction involving an alcohol, a halide, and CS_2 under identical reaction conditions. Whether the dioxanthate or the trithiocarbonate anion has been produced or extracted is related to the relative solubility of the diol and CS_2 in the aqueous phase. For the reactions studied in this report, the formation of dioxanthate anion was preferred to the trithiocarbonate anion. The evidence of any trithiocarbonate moieties in the polymer chain will be discussed in a later section when spectroscopic data and results from elemental analysis are examined.

Reaction Conditions

The effectiveness of the various types of PTC were discussed in a recent publication on the synthesis of polytrithiocarbonate [15]. A PTC suitable for this type of reaction usually has a reasonable size (or carbon number) cation with a large extraction constant. For the purpose of this study, a tetrabutylammonium cation was found to be sufficient. According to a previous study [15], the properties of the PTC anion was suggested to be more crucial than the cation in affecting the reaction. The PTC anion employed should have a lower affinity to the PTC cation than the dioxanthate anion so that only the dioxanthate anion will be extracted across the boundary of the aqueous/organic interface. For reaction at a higher temperature, a phosphonium-based PTC was found to have better thermal stability than the ammonium salt used [16].

The yields for the various aliphatic and aromatic poly(*S*-dithiocarbonates) prepared under a series of reaction conditions are listed in Table 1. For polymers with the same diol unit, a smaller carbon number dihalide gave a higher yield. It was also found that the diol has little or no definite bearing on the yield obtained, suggesting the rate-determining step is the propagation step. In most cases the aliphatic products have a slightly higher yield than the aromatic products with the same diol structure. The yield is also related to the purity of the monomer and the PTC selected for the process. Increasing the reaction time from 4 to 20 hours at room temperature did not show any drastic improvement on the product yield which was due to the dithiocarbonate polymers precipitating from the reaction mixture as soon as they attained a certain high molecular weight. The employment of a solvent that dissolves the dithiocarbonate polymer may increase the yield as well as the molecular weight of the product, but it may also affect the efficiency of the PTC. This is because the dissociation constant for the different cation/anion complexes varies with different dielectric media. The efficiency of the PTC is also

TABLE 1. Synthesis Conditions and Results for Poly(*S*-Dithiocarbonate)

Poly(<i>S</i> -dithiocarbonate)		Reaction conditions, temperature in °C/hours ^a	Yield, ^b %	Intrinsic viscosity (dL/g) and solvent used ^c
Diol	Dihalide			
Aliphatic				
C6	C2	rt/4	89	0.230/CHCl ₃
	C6	rt/4	65	0.220/CHCl ₃
C4	C2	rt/4	91	0.018/CHCl ₃
	C6	rt/4	71	0.043/CHCl ₃
C2	C2	rt/4	84	0.013/CHCl ₃
	C6	rt/4	75	0.017/CHCl ₃
Aromatic				
C6	p-DBX	rt/4	73	0.043/DMF
	p-DCX	rt/12	80	0.091/NMP
	p-DCX	40/8	89	0.043/NMP
	p-DCX	40/8 ^d	38	0.198/NMP
C4	p-DCX	40/8	74	0.155/NMP
C2	p-DBX	rt/20	74	0.083/NMP
p-BDM	C2	rt/4	75	0.039/DMF
	C4	40/8	65	0.119/NMP
	C6	rt/20	68	0.250/NMP
	p-DCX	rt/20	66	0.044/NMP
	p-DBX	rt/4	61	0.018/DMF
p-CHD	p-DBX	rt/20	71	0.041/NMP

^a"rt" indicates reaction at room temperature (18–20°C).

^bPercentage yield calculated based on weight % of reactants converted to final product.

^cIntrinsic viscosity measured: NMP/25°C, CHCl₃/20°C, DMF/20°C.

^dp-DCX added dropwise over a 2-hour period in CS₂.

dependent on the pH factor. The concentration of the base employed for the reaction studied, however, was found to be sufficiently high so that the alkoxide intermediates were produced at a reasonably high rate and at the same time allowed proper performance of the PTC.

The intrinsic viscosity, which is also an indication of the molecular weight of the polymers prepared, is also shown in Table 1. The highest intrinsic viscosity was obtained for polymers containing a flexible repeating unit structure such as the C6 diol or C6 dihalide. The flexible polymer chains have better solubility in the organic phase and allowed the propagation reaction to continue until the polymer precipitated from the solution. An example is the p-BDM/dihalide series in which the intrinsic viscosity is at a maximum for the p-BDM/C6 polymer. A higher reaction temperature also improved the intrinsic viscosity due to better solubility of the polymer and a higher reaction rate. A different reaction condition was employed to improve the molecular weight of the product. The dihalide monomer was added in a dropwise fashion during the reaction (for example, see C6/p-DCX in Table 1). The high intrinsic viscosity obtained for this reaction was most likely due to the limited amount of low molecular weight oligomers formed. The same process, however, also resulted in a very low yield (at 38%).

Properties

The polymers collected were either yellowish powders or pellets. The structure of each polymer was identified by IR and UV spectroscopy. IR absorption in the 1040 to 1080 cm^{-1} range is due to C=S stretching, and the absorption in the 1250

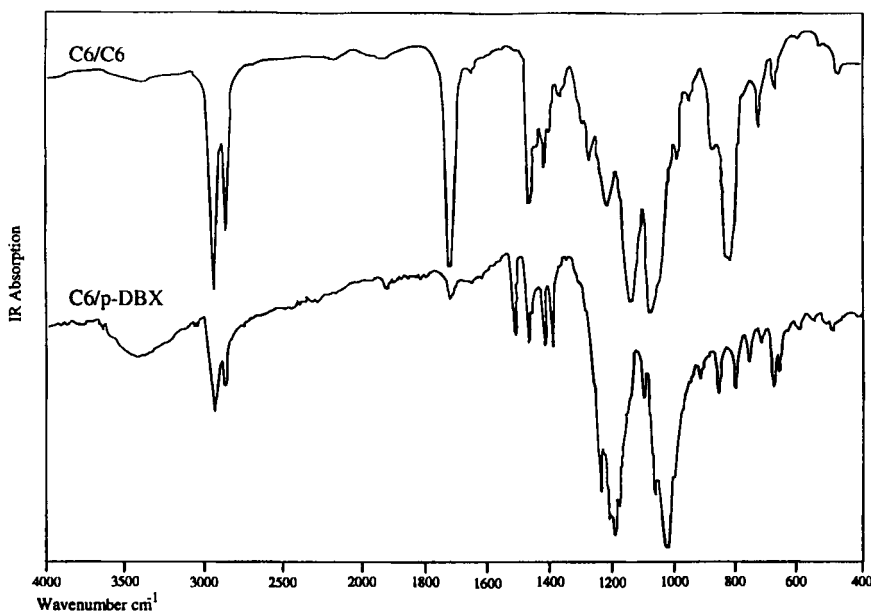


FIG. 3. IR absorption (relative) spectrum for an aliphatic (C6/C6) and an aromatic (C6/p-DBX) dithiocarbonate polymer using solvent-cast thin film.

to 1140 cm^{-1} range is related to C—O stretching. A typical IR spectrum for an aliphatic and an aromatic dithiocarbonate polymer is given in Fig. 3. The UV spectrum for a dithiocarbonate polymer shows a strong absorption peak at 315 nm, similar to the spectrum of polytrithiocarbonate from an earlier study [15].

Elemental analysis has been performed on selected dithiocarbonate polymers, and the results are given in Table 2. The elements analyzed were C, H, S, and the halogen (either Br or Cl). The difference between the total amount of the four elements detected and 100% is assigned to O. In general, the structural formula calculated from the analysis is in agreement with their assigned repeating unit structure. The number-average number of repeating unit for the polymer (\bar{X}_n) was estimated based on the ratio of the C and halogen elements by assuming both ends of the polymer chain remained a bis(halomethyl) group. In the case of only one halogen per polymer chain, the calculated \bar{X}_n is halved. The \bar{X}_n calculated followed the trends of the viscosity measured, with slight variations due to polymers with different chemical structures which might affect their chain conformation in solution. Comparison of the experimentally determined sulfur content in the polymers with the theoretically calculated value is also presented in Table 2. A high experimental value indicated the possibility of having a trithiocarbonate moiety in the polymer chain. A lower than experimental value, however, was obtained for the C2/p-DBX polymer. This unusual result is probably due to the highly soluble C2 diol leading to polymers with high polydispersity and to the possibility that unreacted xanthate groups may be present at the polymer chain ends.

Thermal Analysis

In Table 3 the onset degradation temperature and the percent weight loss associated with each of the weight loss steps determined from TGA are tabulated

TABLE 2. Results of Elemental Analysis of Poly(*S*-Dithiocarbonate)

Poly(<i>S</i> -dithiocarbonate)		Mole % of elements				Weight % of sulfur		\bar{X}_n^c
Diol	Dihalide	C	H	S	X ^a	Exptl.	Theo. ^b	
C2	p-DBX	45.4	38.4	11.4	0.13	35.3	40.3	58
p-BDM	C6	37.7	46.3	11.6	0.13	39.2	34.2	42
p-BDM	p-DCX	44.8	38.5	11.1	0.23	34.6	32.3	21
p-CHD	p-DBX	40.0	41.8	10.0	0.12	33.4	32.2	38

^aMolar percentage of elements determined from elemental analysis. "X" is the halogen used in the dihalide compound. The remainder is assumed to be oxygen.

^bTheoretical weight percentage of sulfur in the polymer having \bar{X}_n number of repeating units.

^cNumber-average number of repeating unit for the polymer calculated from carbon assuming both ends of the polymer chain remain a halogenated compound.

Table 3. Thermogravimetric Analysis of Poly(*S*-Dithiocarbonate)

Poly(<i>S</i> -dithiocarbonate)		Reaction conditions, temperature in °C/hours	TGA degradation steps: ^a onset temperature (°C) and % weight loss
Diol	Dihalide		
Aliphatic			
C6	C2	rt/4	157/86%
	C6	rt/4	289/90%
C4	C2	rt/4	173/76%
	C6	rt/4	207/74%
C2	C2	rt/4	168/93%
	C6	rt/4	271/73%
Aromatic			
C6	p-DBX	rt/4	150/24%, 230/44%
	p-DCX	rt/12	138/12%, 234/44%
	p-DCX	40/8	117/23%, 274/41%
	p-DCX	40/8 ^b	121/18%, 279/59%
C4	p-DCX	40/8	154/21%, 271/44%
C2	p-DBX	rt/20	136/10%, 260/48%
	p-BDM	C2	rt/4
p-BDM	C4	40/8	153/25%, 273/47%
	C6	rt/20	128/7%, 250/85%
	p-DCX	rt/20	129/12%, 277/67%
	p-DBX	rt/4	136/8%, 250/51%
p-CHD	p-DBX	rt/20	202/63%, 264/13%

^aTGA results presented are the onset degradation temperature and % weight loss associated with each degradation step at a heating rate of 5°C/min under nitrogen atmosphere.

^bp-DCX added dropwise over a 2-hour period in CS₂.

for the various aliphatic and aromatic dithiocarbonate polymers. In general, the aliphatic products exhibited only a single but broad degradation loss step with a high percentage weight loss. The thermal stability was found to relate to the structure of the dihalide monomer rather than that of the diol. All aliphatic poly(*S*-dithiocarbonates) prepared from a C6 dihalide monomer have an onset degradation temperature above 200°C, whereas for polymers prepared from a C2 dihalide monomer, their onset degradation temperatures were reduced to 150 to 170°C. All the aromatic polymers have two distinct degradation steps. The one at the lower temperature has a low percentage weight loss. Volatile residue was suspected for some of the aromatic polymers. The second degradation step for the aromatic polymers was usually above 200°C. Again, the diol structure was found to have little or no effect on the thermal stability of the aromatic polymers as indicated by the aliphatic diol/p-DCX polymer series. But for the p-DBM/C6 to C2 series, the polymer prepared from a C2 dihalide has the lowest thermal stability compared to polymers prepared from a C4 or C6 dihalide. Optimum thermal stability was obtained for the p-CHD/p-DBX polymer among all the aromatic polymers studied.

CONCLUSION

A series of aliphatic and aromatic poly(*S*-dithiocarbonates) or poly(xanthate esters) was prepared using a novel "one-pot" phase-transfer catalyzed reaction procedure. Carbon disulfide was the only sulfur nucleophile required. The stepwise reaction was regulated by the transport of the dixanthate or alkoxide anions into the organic phase, the propagation rate of the nucleophilic substitution reaction with the dihalide, and the solubility of the resulting polymers in CS₂. The structure of the dihalide monomer was found to have a more significant influence on the product yield, solution viscosity, and thermal stability of the polymers than did that of the diol.

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