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analysis will be developed in detail in a forthcoming paper.[19]

It should be noted that the agreement between the microscopic results and the SAXS measurements is very good. Even for PS/PMMAD, the large anomalous long-period value measured by SAXS (528 Å) is confirmed.

Conclusion

SIMS has been used to investigate the surface-induced orientation of symmetric, diblock PS/PMMA copolymers. It has been shown that films cast from toluene solutions, while microphase separated, are randomly oriented with respect to the surface of the film. Annealing the copolymers at 170 °C for 24 h produces films with a strong orientation of the copolymer microdomains parallel to the surface. The effect of surface ordering is found to persist through the entire thickness of the film. It was found that PS and PMMA domains of ca. one-half the width of the domains in the film interior were located at the air/copolymer and copolymer/Si wafer interfaces, respectively. This ordering was found in films as thick as 5×10^3 Å. The period of the ordered morphology was found to be in good agreement with results from small-angle X-ray scattering and interference microscopy. Due to the large area of the specimen probed by the ion beam (80-μm diameter) these results suggest that there is extensive lateral coherence of the copolymer microdomains. Finally, interference microscopy studies have shown the formation of steps on the surface of the annealed copolymer films. The heights of these steps correspond to precisely one period characteristic of the microdomain morphology.

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Registry No. (S)(MMA) (block copolymer), 106911-77-7.

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Polythioamide and Poly(1,3,4-thiadiazole) Synthesis from Dimethyl Tetrathioterephthalate

Isabelle Delfanne

Centre de Recherche CERDATO, ATOCHEM, 27470 Serquigny, France

Guy Levesque*

Laboratoire de Chimie des Composés Thioorganiques (associé au C.N.R.S.), Institut des Sciences de la Matière et du Rayonnement, Université de Caen, 5 rue d'Edimbourg, 14032 CAEN, France.

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ABSTRACT: Dimethyl tetrathioterephthalate (DMTT) was synthesized in a one-pot procedure from 1,4-bis(chloromethyl)benzene and sulfur. Condensation of DMTT with various aromatic and aliphatic diamines was explored mainly in order to get high molecular weight polythioamides (A). Best results were obtained in heterogeneous conditions; it must be noted that fairly polar solvents such as chloroform sometimes gave better results than did amide solvents. Hydrazine and DMTT reacted in propylene carbonate to yield poly(*p*-phenylene-1,3,4-thiadiazole) (D).

Introduction

Developing mild and efficient methods for the synthesis of condensation polymers remains a significant aspect of synthetic polymer chemistry. Some polythioamides were obtained by Ogata et al. from bis(thionester)s and diamines at room temperature but in low yields and either were insoluble or presented very low molecular weights.[1]

Levesque and Gressier have prepared many aliphatic polythioamides from bis(dithioester)s and diamines[2] and some aromatic and semiaromatic polythioamides from tetrathioterephthalates and phenylene bis(dithioacetate)s;[3] most of these condensations occurred rapidly between 0 and 30 °C in dimethylformamide–toluene solutions. They have also investigated the relations between polyamides and polythioamides from the point of view of their thermal behavior.[2] Generally, polythioamides afford lower melting and glass transition temperatures than do homologous polyamides.[2,3]

Semiaromatic and fully-aromatic polythioamides were obtained mainly as low molecular weight samples and from

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hardly accessible thio-organic monomers. Aromatic polythioamides are potentially interesting materials if they can provide lowered melting and glass transition temperatures and enhanced solubilities with respect to homologous polyamides.

This paper describes new attempts to prepare aromatic polythioamides (A) from dimethyl tetrathioterephthalate (DMTT) whose synthesis was studied. Condensation reaction between dithioesters and amines is now being studied kinetically with some detail,[4] and although the solvent influence is not correctly understood, particularly in the case of polymerization occurring with phase separation, some molecular weight improvements were obtained by varying the solvent nature or attempting to condense a diamine and DMTT without solvent.

Both aromatic and cycloaliphatic amines were reacted with DMTT, but hydrazine was also used as well as 1,6-diamino hexane in order to compare molecular weights in these new reaction conditions with previously obtained values. Thermal analysis was applied to study some interesting polythioamide samples.

Experimental Section

^{1}H NMR spectra were recorded on a Varian EM 360 apparatus at 60 MHz and ^{13}C NMR spectra on a Bruker UP80SY3 at 20.15 MHz. Chemical shifts are in parts per million downfield from TMS. UV–visible spectra were recorded on a Perkin-Elmer Lambda 15 spectrometer and IR spectra on a Perkin-Elmer 684 apparatus.

Dimethyl Tetrathioterephthalate (DMTT). Sodium methoxide (0.40 mol) is placed under nitrogen in 600 mL of anhydrous methanol together with 0.40 mol of elemental sulfur in a 1-L reactor fitted with a mechanical stirrer, a reflux condenser a gas inlet, and a dropping funnel. Refluxing for 150 min gives an orange solution with some dispersed sulfur. Then 0.10 mol of 1,4-bis(chloromethyl)benzene is introduced in 30 min; the solution is refluxed for 7 h. The red sodium tetrathioterephthalate solution is cooled to room temperature and 0.205 mol of dimethyl sulfate is added rapidly. The mixture is refluxed for 8 h and cooled: the precipitate is extracted (Kumagawa) with three 500-mL portions of hexane. Crystalline DMTT is isolated after cooling, filtered off, and dried in vacuo. Yield 53%, mp = 134.5–135.5 °C.

Anal. ($C_{10}H_{10}S_4$) (258.43) found (calcd): C, 46.66 (46.48); H, 3.88 (3.90); S 49.41 (49.62). UV–visible (CH_2Cl_2) $\lambda_{max}(\epsilon)$: 323 (34 400 mol^{-1}·L·cm^{-1}), 506 nm (500 mol^{-1}·L·cm^{-1}). ^{1}H NMR ($CDCl_3$) δ: 2.81 (s, 6 H, CH_3S), 8.10 (s, 4 H, phenyl ring). ^{13}C NMR ($CDCl_3$) δ: 20.6 (CH_3S), 126.8 (unsubstituted aromatic carbons), 147.2 (substituted aromatic carbons), 227.5 (CS_2).

Dibenzyl Tetrathioterephthalate. The same procedure using benzyl chloride as alkylating agent gives a similar yield of dibenzyl tetrathioterephthalate, mp = 126–128 °C. Anal. ($C_{22}H_{18}S_4$) (410.64) found (calcd): S, 31.25 (31.23). UV (CH_2Cl_2) $\lambda_{max}(\epsilon)$: 330 nm (34 900 mol^{-1}·L·cm^{-1}). ^{1}H NMR ($CDCl_3$) δ: 4.60 (s, 4 H, CH_2S), 7.31 (m, 10 H, benzyl ring hydrogens), 8.10 (s, 4 H, tetrathiophtalic ring hydrogens). ^{13}C NMR ($CDCl_3$) δ: 42.4 (CH_2S); 126.9, 127.9, 128.8, 129.3 (unsubstituted aromatic carbons); 134.8, 147.0 (substituted aromatic carbons); 225.8 (CS_2).

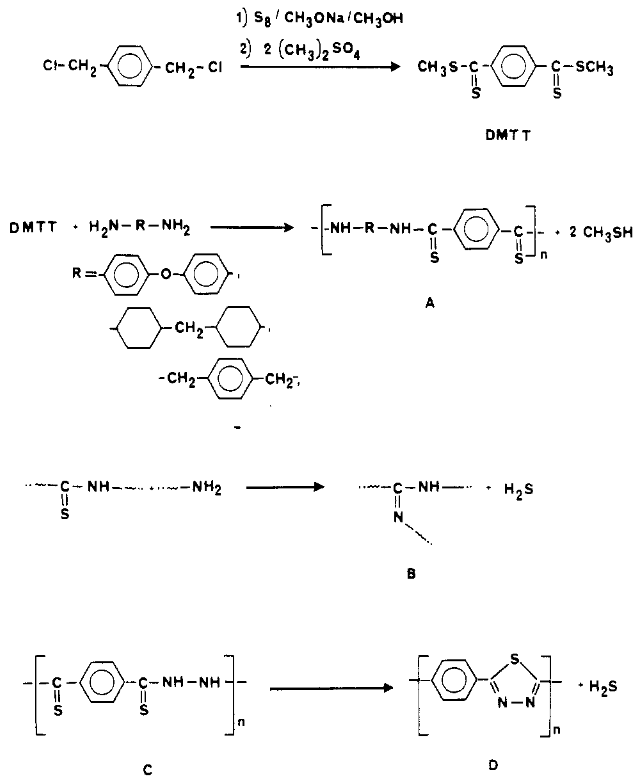
Polythioamide Synthesis. Polycondensation conditions are indicated in the tables: ca. 1 g of DMTT and an equivalent amount of diamine were heated in 5 mL of solvent under nitrogen. Raw polymers were thoroughly washed with methanol. Solubilization in NMP/DMAC/LiCl (47.5/47.5/5) was used when possible to purify the polymer; precipitation and washings were done with methanol, followed by drying at 80 °C in vacuo. Absence of residual solvent was checked via infrared spectroscopy.

Analysis of poly(*p*-phenylen-1,3,4-thiadiazole) $(C_8H_4N_2S)_n$ $(160.2)_n$ found (calcd): N, 18.4 (17.50); S, 19.9 (20.02).

Monomer Synthesis

Dithioesters were first obtained in low yield by Houben from Grignard reagents and carbon disulfide in diethyl ether.[5] Marvel et al. have proposed one of the best dithioester synthesis from nitriles;[6] we used it to get bis(dithioester)s from dinitriles[2] but it doesn't work for glutaric and succinic dithioesters which were obtained by Hoffman and Hartke from bis(thioamide)s.[7]

Scheme I



Monofunctional dithioacids and -esters are accessible in fair to good yields from Grignard reagents through reaction of CS_2 in tetrahydrofuran;[8] this method is of limited value to prepare bis(dithioester)s.[4] Various methods derived from Friedel–Crafts reaction[9] are no more convenient for the synthesis of bis(dithioester)s, whereas some phenylene bis(dithioacetate) derivatives could be obtained via bis(thioamide)s,[10] more easily prepared from diacylbenzene through a Willgerodt-Kindler reaction.[11]

Tetrathioterephthalic esters have been prepared, either from the dinitrile[3] or from the aldehyde.[12] Ueno et al.,[13] from 1,4-bis(chloromethyl)benzene, have prepared the piperidinium salt of tetrathioterephthalic acid. Such piperidinium salts are powerful nucleophiles,[14] although to a lesser degree than tetraalkylammonium salts,[15,16] and were used to give tetrathioterephthalic esters.[13,14,17]

We have synthetised DMTT in a one-pot procedure and obtained reproducible yields in the range 45–50% by reacting 1,4-bis(chloromethyl)benzene with elemental sulfur in methanol (600 mL/0.1 mol of dichloride) and alkylating the sodium salt with dimethyl sulfate (Scheme I). Yields are lowered if less solvent is used. Dibenzyl tetrathioterephthalate was prepared similarly.

Synthesis of Polythioterephthalamides: Influence of the Solvent Nature. Condensation of primary and secondary amines with dithioesters and thioesters has been known for a long time to give mainly thioamides,[18] but aromatic amines do not usually react at room temperature, unless the leaving group allows some assistance to deprotonation of the nitrogen atom as in carboxymethyl dithiocarboxylate we have already used.[3]

The reaction between dithioesters and amines is quite specific and usually thioamides are obtained in very high yield. In some cases, however, secondary reaction may occur: 1,2-diaminoethane and dithioesters give rise to

Table I
Synthesis of Polythioamides A from DMTT and Various Diamines

diamine[a]	solvent[b]	reactn time, h	temp, °C	η_{sp}/c, mL/g
DAPO	HMPA	200	190	6[c]
	PPC	24	150	12[c]
	DMF	24	100	16[c,d]
	DMPU	24	100	24[c]
DACM	HMPA	100	80	19[e]
	PPC	24	100	20[e]
	sulfolane	20	80	12[e]
	DMA	100	80	16[d,e]
	FPD	100	80	25[e]
	DMSO	240	80	16[e]
	NFP	100	80	25[e]
	BZA	72	80	36[e]
	MCR	3	80	38[e]
	$CHCl_3$	144	60	33[e]
	none	0.2	180	insol[f]
BAMB	$CHCl_3$	215	60	83[e]
HDZ	HMPA	24	80	17[e]
D	$CHCl_3$	24	60	7[c]
	PPC	48	60	42[c]

[a] DAPO = bis(4-aminophenyl) oxide; DACM = bis(4-aminocyclohexyl)methane; BAMB = 1,4-bis(aminomethyl)benzene; HDZ = hydrazine. [b] HMPA = hexamethylphosphotriamide; PPC = propylene carbonate; DMF = *N*,*N*-dimethylformamide; DMPU = *N*,*N*′-dimethylpropyleneurea; DMA = *N*,*N*-dimethylacetamide; DMSO = dimethyl sulfoxide; FPD = *N*-formylpiperidine; BZA = benzyl alcohol; MCR = *m*-cresol. [c] Measured at 1.5 g/L in 96% H_2SO_4. [d] Other noncyclic amide solvents gave similar results. [e] Measured at 1.5 g/L in *N*-methylpyrrolidone (47.5%) + DMA (47.5%) + LiCl (5%). [f] Many attempts were made to react DMTT and an aromatic or cycloaliphatic diamine without solvent above the monomer melting point, but in a few minutes the mixture became so viscous that stirring was no longer possible and the polymer was insoluble in all tested solvents, including H_2SO_4 and oleum.

2-alkylimidazolines,[19] and aromatic amines, if reacted at elevated temperatures, may produce *N*,*N*′-diaryl amidines.[20] Other dithioester reactions are related to their easy enolization, which is excluded in aromatic ones such as DMTT.

DMTT was reacted with some aromatic and cycloaliphatic diamines: bulk condensation at or above monomer melting temperature resulted always in cross-linked insoluble material, which was correlated with the evolution of both methanethiol and hydrogen sulfide. The high temperature needed to melt the monomers may have caused the insolubility as the result of branching through amidine formation (B). When the condensation was achieved in the presence of various solvents (Table I), very long reaction times were used in order to obtain high molecular weights, which were estimated through viscosimetric measurements. Molecular weight evolution was followed as a function of reaction time for the condensation of DMTT and diaminodicyclohexylmethane (DACM) in chloroform (Figure 1): after 5 h the mixture became heterogeneous and the specific viscosity increasing rate was then considerably lowered.

From the results reported in Table I, it is clear that polythioamide molecular weights remained generally low, the main exception being the polymer derived from the nonconjugated bis(aminomethyl)benzene (BAMB). DACM is another nonconjugated amine, the amino group of which is bore on a rather bulky group, and this may account for the intermediate behavior of this amine.

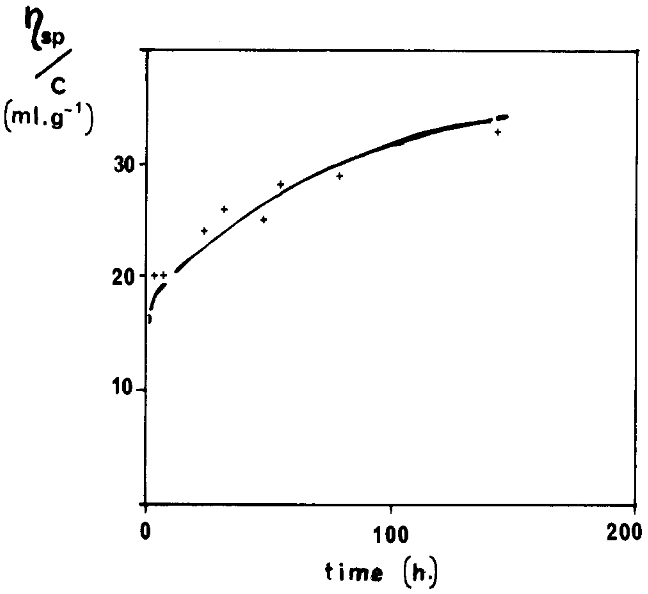


Figure 1. Viscosity of polythioamides prepared from DACM and DMTT as a function of reaction time ($CHCl_3$, 60 °C).

Surprisingly the best solvents for condensing DMTT and diamines were rarely amides, which are yet often used in polyamides synthesis. Some of the highest molecular weights were found when the reaction was conducted in chloroform, i.e., under evidently heterogeneous conditions. Similar results were obtained with benzyl alcohol or *m*-cresol, which are solvents of poly(diaminodicyclohexylmethaneterephthalamide) under heating. This unusual behavior might be a consequence of the characteristics of bis(dithioester)s which are nonpolar in nature, whereas polythioamides are highly polar materials: the best condensation conditions might be a compromise between the polymer swelling ability of the solvent and the monomer solubility in this solvent. As a consequence of the absence of hydrogen bonding in thioamides, a moderately polar solvent which is also a poor donor in H-bonding might be more effective than an amide solvent (in which dithioesters are nearly insoluble).

Reaction between DMTT and hydrazine hydrate (HDZ) gave interesting results in propylene carbonate as a solvent. As will be postulated below, the so-obtained polymer was no longer a polythioamide (C) but a poly(*p*-phenylene-1,3,4-thiadiazole) (D). Similar polymers have been described as poly(1,3,4-oxadiazole)s:[21] their synthesis took place by reacting dicarboxylic acids and hydrazine in a phosphorous pentoxide/methanesulfonic acid solvent.

Some low molecular weight thiadiazoles were previously obtained by reacting hydrazine and dithioesters[18] but it is necessary to optimize the condensation reactions of aromatic dithioesters.

Polymer Characterization

All polythioamides are yellow to orange powders; characterization was realized on the samples which offered the highest molecular weights. Viscosimetric data were collected mainly as η_{sp}/c measured at 1.5 g/L. Intrinsic viscosity was determined for some samples and the two determinations showed only slight differences (Figure 2).

Elemental analysis was particularly useful in the case of polymer derived from hydrazine hydrate: nitrogen and sulfur contents (as well as spectroscopic data) are consistent only with the formation of poly(*p*-phenylene-1,3,4-thiadiazole).

The presence of a thioamide group was attested by infrared spectroscopy: all polymers (but those obtained from HDZ) offered a wide absorption band near 3210 cm^{-1} (N–H stretching) and a fairly intense absorption band at 1530 cm^{-1} (amide II). Moreover, IR spectra are useful in order to ascertain the solvent elimination because it was previously established that polythioamides retain very

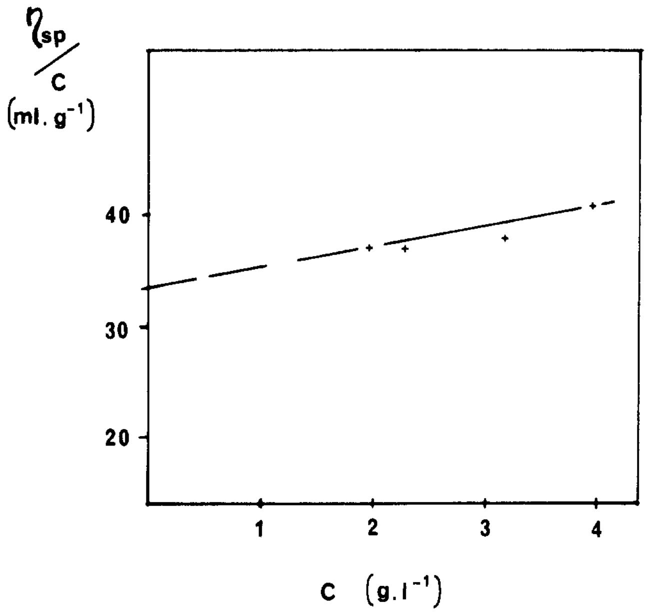


Figure 2. Intrinsic viscosity determination for a polythioamide derived from DACM and DMTT.

Table II
Solubility of Polymers Issued from Diamines and Dimethyl Tetrathioterephthalate[a]

diamine[b]	DAPO	DACM	BAMB	HZD
solvent				
96% H_2SO_4	+	++	+	+
NMP		±		
NMP/DMA/LiCl (47.5/47.5/5)		+	±	
phenol		+	±	
HFIP[c]		+		

[a] ++, soluble at room temperature; +, soluble under heating; ±, partially soluble. All polymers insoluble in other tested solvents: e.g., formic acid, acetic acid, DMF, DMA, DMSO, *m*-cresol, benzyl alcohol. [b] See footnote *a* in Table I. [c] HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol.

Table III
Thermal Analysis of Polymers Obtained from DMTT and Diamines

diamine[a]	DAPO	DACM	BAMB	HZD
T_g, °C[b]	208 (220)	247 (226)	229 (191)	
T_m °C[c]	302 (273)	303 (312)	345 (344)	200

[a] See footnote *a* in Table I. [b] Values in parentheses calculated according to Van Krevelen[22] and Gressier and Levesque[2,3] for the molar contribution of thioamide group to the glass transition temperature. [c] Values in parentheses calculated according to Van Krevelen[22] and Gressier and Levesque[2,3] for the molar contribution of thioamide group to the melting temperature.

strongly most polar solvents.[2]

Although the molecular weights of these polymers seem to be low, they are only slightly soluble in a very few solvents (Table II). Attempts to acetylate them with trifluoroacetic anhydride were complicated by the evolution of nauseous volatile sulfur compounds and in no case it was possible to get stable polymeric derivatives, whose solubility would have been enhanced in respect to the initial polythioamides.

Registry No. DMTT, 46321-75-9; (DMTT)(H_2NNH_2) (copolymer), 119529-45-2; A (R = 4,4′-$C_6H_4OC_6H_4$, copolymer), 119529-42-9; A (R = 4,4′-$C_6H_4OC_6H_4$, SRU), 80159-27-9; A (R = 4,4′-$C_6H_{10}CH_2C_6H_{10}$, copolymer), 119529-43-0; A (R = 4,4′-$C_6H_{10}CH_2C_6H_{10}$, SRU), 80162-96-5; A (R = 4-$CH_2C_6H_4CH_2$, copolymer), 119529-44-1; A (R = 4-$CH_2C_6H_4CH_2$, SRU), 119529-41-8; D, 26023-47-2; S, 7704-34-9; 4-$ClCH_2C_6H_4CH_2Cl$, 623-25-6; 4-$C_6H_5CH_2SC(S)C_6H_4C(S)SCH_2C_6H_5$, 119529-40-7.

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