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Polythioamide Synthesis through Chemical Modification of Polyamides

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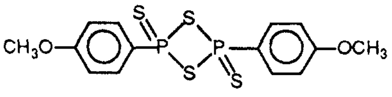
The chemical modification of polyamides has been the subject of numerous studies by R. C. Schulz and coworkers, the results of which may support some important applications. We have noted (a) the formation of *N*-chloropolyamides, which may be used either as chlorinating agents[1] or as free-radical generators via reduction with ferrous ions,[2] (b) the N-acylation with trifluoroacetyl anhydride,[3] which provides *N*-trifluoroacetylpolyamides (such polymers become soluble in common solvents and are then suitable for NMR analysis and molecular weight determinations[4] and may be used as acylation reagents for low molecular weight alcohols, amines, and aminoesters[5] or eventually for activation of anionic polymerization of lactams[6]), (c) the metalation of polyamides followed by alkylation,[7] and (d) the reduction to polyamines with the aid of borane–dimethyl sulfide.[8]

Chemical transformation of amides to thioamides (a particular example of the so-called thionation reaction) was for a long time obtained through heating with diphosphorus pentasulfide in refluxing xylene, but recently soluble sulfur-containing phosphorus derivatives have proved to be more efficient and their use is now well-established. Particularly, 2,4-bis(4-methoxyphenyl)-2,4-dithioxo-1,3-dithiadiphosphetane, readily prepared from anisole and P_2S_5 (Lawesson reagent, 1), is well adapted to the specific thionation of amides:[9] yields are often nearly quantitative. Other 2,4-dithioxodithiadiphosphetane have been described and found to be convenient for other thionation reactions[10] but give low yields in the conversion of amides into thioamides. These reagents are supposed to react with carbonyl groups according to a Wittig reaction-like mechanism via a sulfur–phosphorus ylide (Scheme I). We report here the results of some tests to prepare polythioamides from polyamides, as all the previously known polythioamides were obtained from bis(dithioesters) and diamines.[11] We were interested in preparing polythioamides from polyamides to obtain either new polymers from commercial ones or statistical amide–thioamide copolymers. Common polyamide solvents (formic acid, sulfuric acid, phenols, low molecular weight amides) are not convenient for thionation reactions using reagents such as the Lawesson reagent. Therefore, polyamide thionation reactions were attempted in heterogeneous conditions in a polyamide nonsolvent, such as toluene, tetrahydrofuran, and 1,2-dimethoxyethane.[12] The best results were obtained in toluene with the Lawesson reagent, just as for the thionation of low molecular weight amides.



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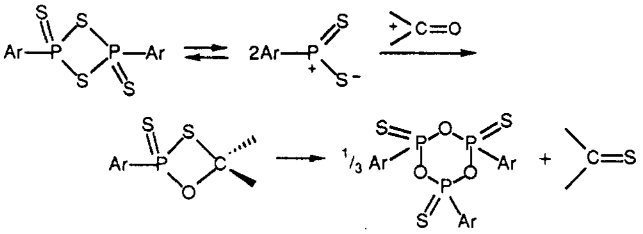
Experimental Section

Diamines and dithioesters: 4,9-dioxa-1,12-diaminododecane, $H_2N(CH_2)_3O(CH_2)_4O(CH_2)_3NH_2$; 4,7,10-trioxa-1,13-diaminotridecane, $H_2N(CH_2)_3O(CH_2)_2O(CH_2)_2O(CH_2)_3NH_2$; ethyl hexanedithioate, $CH_3(CH_2)_4C(S)SC_2H_5$; didodecyl 1,12-dodecanebis(dithioate), $RS(S)C(CH_2)_{10}C(S)SR$; didodecyl 4,7-dioxa-1,10-decanebis(dithioate), $RS(S)C(CH_2)_2O(CH_2)_2O(CH_2)_2C(S)SR$ ($R = n\text{-}C_{12}H_{25}$). (Dioxa- and trioxadiamine samples were obtained from BASF, France.)

Scheme I
Thionation Reaction Mechanism



Polyamides. Commercial polyamides were obtained from ATOCHEM: PA-6, $[NH(CH_2)_5CO-]_n$; PA-11, $[NH(CH_2)_{10}CH-]_n$; PA-12, $[NH(CH_2)_{11}CO-]_n$; poly(ether-*block*-amide) (PEBA), $[-\{O(CH_2)_4-\}_xOCORCO\{NH(CH_2)_{11}CO-\}_yNHRCO-]_n$ (25% w/w PA-12, 75% poly(tetramethylene oxide), PEBAX 3533). Other polyamides (PA-12.10, PA-dioxa12.10, and PA-trioxa13.10) were prepared, respectively, from sebacoyl chloride and 1,12-diaminododecane (**2**), 4,9-dioxa-1,12-diaminododecane (**3**), and 4,7,10-trioxa-1,13-diaminotridecane (**4**).

PA-dioxa12.10 and PA-trioxa13.10. To the ice-cooled solution of 12.5 mmol of diamine and 27.25 mmol of triethylamine in 25 mL of dimethylformamide (DMF) is added 12.5 mmol of sebacoyl chloride in 10 mL of DMF. After 5 h of stirring at room temperature, the mixture is poured into 250 mL of methanol; the precipitate was washed with methanol, 1 N HCl, water, and acetone and then dried.

PA-dioxa12.10: $[-NH(CH_2)_3O(CH_2)_4O(CH_2)_3NHCO(CH_2)_8CO-]_n$ $(C_{20}H_{38}N_2O_4)_n$. Yield: 80%. DSC: $T_m = 147$ °C; T_g = nd. IR (KBr): 3310, 1640, 1535, 1110 cm^{-1}.

PA-trioxa13.10: $[-NH(CH_2)_3O(CH_2)_2O(CH_2)_2O(CH_2)_3NHCO(CH_2)_8CO-]_n$ $(C_{20}H_{38}N_2O_5)_n$. Yield: 82%. DSC: $T_m = 127$ and 137 °C; T_g = nd. IR (KBr): 3310, 1645, 1573, 1115 cm^{-1}.

Diamides. Model diamides were prepared from diamines and hexanoyl chloride: 20 mmol of hexanoyl chloride in 10 mL of DMF is added slowly into the stirred ice-cooled solution of 10 mmol of diamine and 20 mmol of triethylamine in 15 mL of DMF. The mixture is stirred at room temperature for 5 h and then poured in excess water; the precipitate is washed with water, 1 N HCl, water, and cold acetone and dried.

***N,N'*-Dihexyldodecanediamide ($C_{24}H_{48}N_2O_2$)**: white crystals. Yield: 73%. Mp: 132 °C. ^{1}H NMR (CDCl$_3$): δ 0.88 (t, 6 H), 1–2 (32 H), 2.13 (m, 4 H), 3.22 (m, 4 H), 5.56 (br, 2 H). IR (KBr): 3310, 1630, 1535 cm^{-1}.

***N,N'*-Dihexyl-4,9-dioxadodecanediamide ($C_{22}H_{44}N_2O_4$)**: white crystals. Yield: 70%. Mp: 88 °C. ^{1}H NMR (CDCl$_3$): δ 0.85 (t, 6 H), 1–2 (20 H), 2.01 (m, 4 H), 3.35 (m, 12 H), 6.15 (br, 2 H). ^{13}C NMR (CDCl$_3$): δ 13.88, 22.38, 25.51, 26.60, 29.49, 31.53, 36.73, 36.78, 37.85, 69.57, 70.83, 173.14. IR (KBr): 3310, 1630, 1545, 1120 cm^{-1}.

Lawesson Reagent. Diphosphorus pentasulfide is boiled in anisole (10-fold excess) until the end of gas evolution (H_2S may be conveniently trapped by concentrated NaOCl solution or "bleach"). Cooling the filtered solution at room temperature affords yellow crystals, which are filtered off, washed with chloroform, and dried in vacuo. Yield: 70%.

Thionation Reaction. Model diamides were submitted to reaction with the Lawesson reagent in toluene: 0.5 mmol of diamide and 0.5 mmol of Lawesson reagent in 25 mL of toluene are heated at 100 °C for 1 h. After filtration and cooling, the solution is concentrated and the thioamide isolated. Identical compounds were prepared from diamines and excess ethyl dithiohexanoate (reaction in toluene at room temperature).

***N,N'*-Dihexyldodecanedithioamide ($C_{24}H_{48}N_2S_2$)**: white crystals. Yield: 93% from dithioester. Mp: 110 °C. ^{1}H NMR (CDCl$_3$): δ 0.93 (t, 6 H), 1–2 (32 H), 2.70 (m, 4 H), 3.73 (m, 4 H), 7.33 (br, 2 H). IR (KBr): 3210, 1540 cm^{-1}. MS: m/e^+ 428 (M = 428.79).

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***N,N′*-Dihexyl-4,9-dioxadodecanedithioamide** ($C_{22}H_{44}N_2O_2S_2$): white crystals. Yield: 95%. Mp: 60 °C. ^{1}H NMR ($CDCl_3$): δ 0.85 (t, 6 H), 1–2 (20 H), 2.60 (m, 4 H), 3.52 (m, 12 H), 8.10 (br, 2 H). ^{13}C NMR ($CDCl_3$): δ 13.93, 22.42, 22.65, 27.86, 28.89, 31.17, 45.65, 47.37, 70.51, 71.07, 205.04. IR (KBr): 3210, 1540, 1120 cm^{-1}. MS: m/e^+ 432 (M = 432.74).

***N,N′*-Dihexyl-4,7,10-trioxatridecanedithioamide** ($C_{22}H_{44}N_2O_3S_2$): pale yellow liquid (after column chromatography on silica gel, elution in cyclohexane/chloroform). Yield: 80%. ^{1}H NMR ($CDCl_3$): δ 0.9 (t, 6 H), 1–2 (16 H), 2.67 (m, 4 H), 3.71 (m, 16 H), 8.70 (br, 2 H). ^{13}C NMR ($CDCl_3$): δ 13.95, 22.41, 27.69, 28.99, 31.12, 44.92, 46.98, 70.25, 70.40, 205.07. IR (KBr): 3210, 1540, 1120 cm^{-1}. MS m/e^+ 448 (M = 448.74).

Polyamide thionations were carried out in toluene (25 mL of solvent/g of polymer) at 100 °C, preferentially onto finely divided samples. As soon as the polymer–solvent dispersion temperature is reached, the reagent is added at once: dissolution of the reagent is observed, and heating is maintained for 2 h. Except for PEBA, polymers remain insoluble and are filtered off from the hot solution.

Purification was carried out by dissolution in DMF and precipitation in water (PA-12.10) or in chloroform/methanol (others). Modified PEBA becomes at least partly soluble in hot toluene: precipitation in methanol followed by dissolution/precipitation in chloroform/methanol.

Degrees of substitution (DS) for thionation of polyamides are estimated from IR spectra: amide carbonyl bands disappear (see below). DS near 100% were observed for finely divided samples of PA-12.10, PA-dioxa12.10, and PA-trioxa13.10. The same polythioamides (PTA) were also obtained from *n*-dodecyl decanebis(dithioate) and the corresponding diamines.

PTA-12.10: poly(*N,N′*-didecyldodecanedithioamide). Already described.[11] IR (KBr): 3220 and 1540 cm^{-1}. DSC: T_m = 147 °C.

PTA-dioxa12.10: (*N,N′*-didecyl-4,9-dioxadodecanedithioamide). IR (KBr): 3210, 1542, 1125 cm^{-1}. DSC: T_m = 93 °C. η_{inh} = 21 mL·g^{-1} (DMF, 1.5 g·L^{-1}; obtained from PA-12.10 through thionation reaction). η_{inh} = 32–105 mL·g^{-1} (DMF, 1.5 g·L^{-1}; in condensation reactions according to reaction times).

PTA-trioxa13.10: poly(*N,N′*-didecyl-4,7,10-trioxatridecanedithioamide). IR (KBr): 3210, 1545, 1125 cm^{-1}. DSC: no melting or glass transition above room temperature. η_{inh} = 108 mL·g^{-1} ($CHCl_3$, 1.5 g·L^{-1}) Satisfactory analyses were obtained for all these thioamides (models and polymers).

Results

Homopolyamides. Only finely divided samples of polyamides react completely in the conditions used; pellets remain apparently unchanged. So only laboratory-made samples gave modified polymers. However, some superficial reaction may have occurred on bulk materials, and this is now under investigation.

PA-12.10, PA-dioxa12.10, and PA-trioxa13.10 were completely modified when Lawesson reagent was used in toluene at 100 °C at a ratio of 1.1 g/g of polyamide. Particularly meaningful is the complete disappearance of the amide carbonyl group absorptions near 1630 cm^{-1}. Amide N–H stretching deformation is shifted from 3310 cm^{-1} in amides to 3210–3220 cm^{-1} in thioamides.

PEBA. This block copolymer becomes soluble in hot toluene as the reaction proceeds. Pellets can be used without difficulty, and it seems likely poly(tetramethylene oxide) sequences may act as a solvent for the reagent; moreover, the sample used contained only 25% polyamide in weight. This copolymer is prepared through condensation of dihydroxypoly(tetrahydrofuran) and carboxy-terminated polyamide so that the links are ester groups. Ester groups are very slowly affected by the Lawesson reagent, and in the conditions used, it is quite probable that no modification of ester links is realized, so we assumed the PEBA thionation reaction to be

$$[-\{\mathrm{O(CH_2)_4}-\}_x\mathrm{OCOR}\mathit{CO}\{\mathrm{NH(CH_2)_{11}}\mathit{CO}-\}_y\mathrm{NHRCO}-]_n$$
$$\rightarrow [-\{\mathrm{O(CH_2)_4}-\}_x\mathrm{OCOR}\mathit{CS}\{\mathrm{NH(CH_2)_{11}}\mathit{CS}-\}_y\mathrm{NHRCO}-]_n$$

This affords a convenient means to estimate the degree of substitution (DS): both unreacted and totally modified PEBA were available, and we have postulated the ester carbonyl absorption (at 1735 cm^{-1}) remained constant whereas amide group absorption (near 1640 cm^{-1}) decreased linearly while DS was growing (Figure 1). In this particular case, partial modifications with total dissolution were possible by varying the reagent to polymer ratio. In Figure 2, degrees of substitution (DS) are reported versus this ratio (in grams of reagent per grams of PEBA). It appears by extrapolation that total modification could be expected for 0.14 g of reagent/g of PEBA.

This ratio after correction for PEBA composition indicates three amide groups react with 1 mol of Lawes-

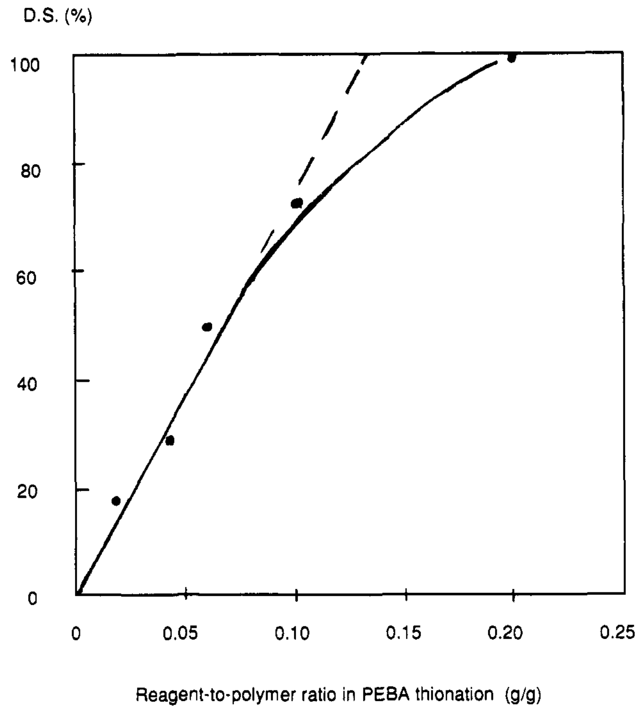

Figure 1. Degree of substitution (DS) vs the reagent-to-polymer ratio in poly(ether-*block*-amide) thionation reaction in toluene.

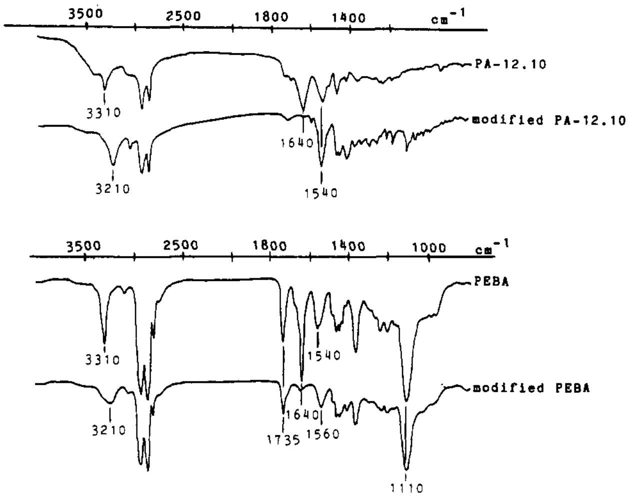

Figure 2. Infrared spectra of some thionation-modified polyamides: ν(N–H) shifts from 3310 to 3210 cm^{-1} whereas ν(C=O) at 1640 cm^{-1} disappears. In poly(ether-*block*-amide), however, the ester carbonyl absorption at 1735 cm^{-1} remains unchanged.

son reagent instead of the usual two groups (Lawesson reagent might theoretically substitute four sulfur atoms for oxygen). This may be correlated with the reaction occurring by diffusion of the reagent into the (only slightly swollen) poly(ether-*block*-amide) copolymer as compared to reaction between small molecules in (diluted) solution.

PEBA analysis confirmed total reactions when no amide carbonyl group absorption was present (found: N, 1.62%; S, 4.07%; S/N, 2.5 ± 0.4 (calcd S/N, 2.3)). These polymer samples are very convenient to study as they are well soluble in common solvents such as chloroform. ^{1}H and ^{13}C NMR spectra were recorded and confirmed the persistence of ester carbonyl group ($\delta(^{13}C) = 173.86$ ppm) and the presence of two thioamide groups ($\delta(^{13}C) = 204.66$ (minor) and 205.47 (major). As it appears in the postulated formula of modified PEBA, two different thiocarbonyl groups are formed in the thionation reaction of PEBA and may be detected if the chain length of the R group is small enough).

In UV–visible spectra, thionated PEBA offered the thioamide absorptions, respectively, at 269 nm ($\pi \rightarrow \pi^*$, intense) and 340 nm ($n \rightarrow \pi^*$, weak) (in chloroform).

Different methods were tested in order to find out if some polymer degradation may have occurred during the thionation reaction. However, molecular dimensions are subjected to both polymer–polymer and polymer–solvent interactions and may appear to change as thionation suppresses the H-bonding donor character of amide groups. Only a complete molecular weight and dimensions study could answer to the question of degradation during thionation reaction. Nevertheless, viscosimetric and size-exclusion chromatographic (SEC) determinations indicate low degradation, if any, has taken place.

We have used inherent viscosity instead of intrinsic viscosity after examining the Huggins and Krämer constants (respectively, 0.60 and −0.03) for modified PEBA in chloroform. There is practically no difference between the values of intrinsic and inherent viscosities (measured at 1.5 g/L).

SEC in *N*-methylpyrrolidone at 85 °C of modified PEBA (DS = 100) gave M_n = 19 000 and M_w = 51 400 (in polystyrene units) in comparison to, respectively, 38 300 and 84 100 for original PEBA, and it seems likely that each average chain broke once. However, this sample of modified PEBA had an inherent viscosity, $\eta_{inh} = 118$ mL·g^{-1} (in chloroform) as the thionation reaction was conducted without drying of the PEBA. After reaction on thoroughly dried PEBA samples, inherent viscosities were observed in the range 140–160 mL·g^{-1}. So we can suspect that chain breaking occurs during the thionation reaction of PEBA only when water is present. The phosphorus oxide like byproducts may act as a catalyst to induce some ester links hydrolysis producing chain scission in this particular block copolymer.

In conclusion, it appears that some polyamides have been successfully transformed into polythioamides by using Lawesson reagent (1) in toluene at 100 °C. However, the modification reaction needed finely divided polymer samples except for an ether–amide block copolymer for which pellets could be used for partial modifications. With respect to the particular properties of thioamides (alkylation, oxidation to free radicals), this reaction opens a door toward chemical grafting into polyamides.

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Registry No. **1**, 19172-47-5; (**3**)(sebacoyl chloride) (copolymer), 129217-06-7; (**3**)(sebacoyl chloride) (SRU), 59060-67-2; (**4**)(sebacoyl chloride) (copolymer), 129217-07-8; (**4**)(sebacoyl chloride) (SRU), 129217-09-0; PEBAX 3533 (copolymer), 108548-63-6; $C_{24}H_{48}N_2O_2$, 58982-05-1; $C_{22}H_{44}N_2O_4$, 129217-01-2; $C_{24}H_{48}N_2S_2$, 129217-02-3; $C_{22}H_{44}N_2O_2S_2$, 129217-03-4; $C_{22}H_{44}N_2O_3S_2$, 129217-04-5.