Conformational and Dielectric Studies on Polysulfides with Pyridine Groups in the Main Chain

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ABSTRACT: Procedures are described to synthesize and characterize linear and cyclic oligomers of poly(2,6-pyridinediyl sulfide) (PPyS). Three-dimensional order that is well developed in bromo-terminated oligomers with a number of repeating units $x \leq 3$ decreases as the molecular weight increases so that chains with 12 repeating units are totally amorphous. Low molecular weight cyclic oligomers do not crystallize from the melt. A rotational isomeric state model is stated that describes the conformational statistics of linear and cyclic PPyS chains. The model predicts energy minima about C^{ar}–S bonds located at ±100°, the $g^{\pm}g^{\mp}$ states having slightly higher energy than the alternative $g^{\pm}g^{\pm}$ ones. Dielectric results in a relatively narrow interval of temperature are reported for some PPyS compounds, specifically the bromo-terminated linear dimer P3PyS, the cyclic P3PySC trimer, and the linear chain of 12 repeating units P13PyS. Whereas the linear dimer exhibits a well-developed relaxation in the vicinity of room temperature, this relaxation is weak for both P3PySC and P13PyS, suggesting that this process is mainly associated with molecular motions in the crystalline structure. The conductivity of the linear dimer is nearly 2 orders of magnitude higher than that of the other two compounds. In the vicinity of 60 °C, P3PyS has a conductivity close to that of semiconductors, but it is an insulating material at room temperature.

Introduction

Polythioethers with structural unit $-(CH_2)_x-S-$ are interesting and simple substances whose physical properties are strongly dependent on the number of methylene groups of the repeating unit of the chains.[1-3] These polymers can schematically be obtained from polyethers with repeating unit $-(CH_2)_x-O-$ by substituting a sulfur atom for an oxygen atom. Important changes in the conformational characteristics of polysulfides occur as a consequence of the fact that the C–S bond length is ca. 30% larger than the C–O bond length and the C–S–C bond angle is nearly 10° smaller than the C–O–C bond angle.[4] Moreover, the sulfur atom has a van der Waals radius ca. 20% larger than that of the oxygen atom.

In general polysulfides have higher conformational versatility than the corresponding polyoxides in the sense that they have fewer skeletal bonds highly constrained to particular rotational states. In spite of this, the members of the family of the polysulfides have higher melting points than their polyoxide counterparts partially due to the larger intermolecular interactions of the chains in the crystal, caused by the higher polarizability of the sulfur atom compared to the oxygen atom, that overcome the higher flexibility of polysulfide chains.[5]

Owing to their simplicity, polysulfides and polyoxides have traditionally been used as models to study the conformational characteristics of polymer chains.[6,7] Pursuant to the objective of gaining a deeper insight into the influence of the structure on the properties of polythioethers, attention is paid in this work to the synthesis and characterization of poly(2,6-pyridinediyl sulfide) (PPyS), a polymer that schematically can be obtained from poly(methylene sulfide) (PMS) by substituting a methylene group in these chains for a pyridine group.

It is expected that the presence of a bulky group in PPyS as a part of the main chain will provide rigidity to the chains and will alter in a significant way its conformational space with respect to that of PMS. It is also expected that these polymers will have a significantly higher dipole moment than PMS chains where rotations of the same sign that place the dipole moment associated with the C–S–C bond in antiparallel direction are strongly favored.[3] Unfortunately, PPyS chains are soluble only in polar solvents that alter the internal field in a significant way, thus precluding the experimental determination of their dipole moments in solution. However, the theoretical interpretation of the dipole moments of molecular compounds whose structure resembles that of these chains will facilitate the development of a rotational state scheme that permits prediction of the conformational characteristics of these apparently intractable polymers.

The dielectric response in an alternating field and the dc conductivity of linear and cyclic PPyS oligomers is also studied in the neighborhood of room temperature with the aim of obtaining more information on the influence of structure on the conducting properties of organic compounds.

Experimental Section

α,ω-Dibromooligothioethers as well as the cyclic trimer were prepared by polycondensation of 2,6-dibromopyridine (2,6-DBPy) with sodium sulfide, using solid–liquid phase transfer catalysis conditions.[8] The following procedure was used for the preparation of the linear oligomer ($x = 12$):

$$(x+1)\text{Br–Py–Br} + x\text{Na}_2\text{S} \rightarrow \text{Br–Py[S–Py]}_x\text{–Br} + 2x\text{NaBr} \quad (1)$$

2,6-DBPy (23 mmol), Na_2S (20 mmol), and the phase transfer catalyst, i.e, 15-crown-5 (2.3 mmol), were stirred in dry DMF (5 mL) at 120 °C for 6 h under nitrogen. After cooling at room temperature, the reaction mixture was extracted with chloroform (50 mL). The organic phase was washed twice with an aqueous solution of sulfuric acid (pH 3.5) and then five times with water. After drying on Na_2SO_4, most of the solvent was evaporated and

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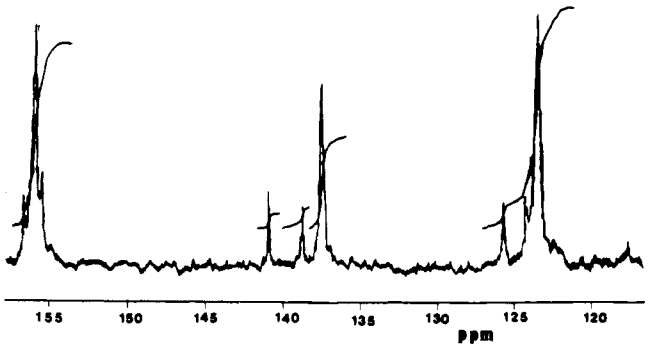

Figure 1. ^{13}C NMR spectrum of bromo-terminated linear poly(2,6-pyridinediyl sulfide) with 12 repeating units in the chain (P12PyS).

Table I
Chemical Shifts with Respect to TMS of the Carbons of Linear (x = 1 and x = 12) and Cyclic (x = 3) Oligomers in $CDCl_3$ and $CDCl_2/CDCl_2$, Respectively

	δ (ppm)		
no. of C	x = 1	x = 12	cyclic trimer
1	140.77	140.94	
2	125.53	125.64	
3	138.58	138.74	
4	124.26	124.20	
5	155.64	major peak at	
6	156.38	156.03	154.64
7	123.32	123.43	124.36
8	137.65	137.47	136.72

the polymer was recovered by precipitation in hexane and dried under vacuum. With Na_2S containing around 25% water, the products thus obtained are mainly linear oligomers. The yield of polythioether, calculated from the amount of NaBr formed and eq 1, was found to be 61%.

Analysis of the polymer, performed by TLC on alumina with DMAc/$CHCl_3$ (1/1, v/v), showed the absence of cyclic products. The composition of the polythioethers was determined by elemental analysis. The bromine content allowed an evaluation of the number average molecular weight by assuming that the structure of eq 1 is valid. The values found for the different elements are in excellent agreement with the proposed structure. Anal. Calcd for x = 12 (M_n = 1550): C, 50.6; H, 2.5; N, 11.8; S, 25.0; Br, 10.1. Found: C, 50.5; H, 2.8; N, 11.6; S, 25.4; Br, 10.0. The polymer was also characterized by ^{13}C NMR[8] (see Figure 1 and Table I). By adding chromium acetylacetonate (0.025 mol/L) to the polymer solution in $CDCl_3$, it was possible to determine x from the ratio of the surfaces corresponding to the C–Br and C–S peaks (M_n = 1550).

The same procedure was used for the preparation of cyclic oligomers with the important exception that in this case carefully dried Na_2S (containing only 5% water) was used instead of Na_2S containing 25% water. This is the key point which leads either to the cyclic or to the linear products. The reaction mixture was treated with $CHCl_3$ (5 mL) in order to isolate the linear oligomer because the cyclic ones are poorly soluble in this solvent. The residue was then extracted with tetrachloroethane (50 mL), and the two organic phases were treated in a manner similar to that described in the case of linear oligomers. A 50% yield of cyclic compounds, mostly composed of the cyclic trimer as checked by gas chromatography and mass spectroscopy performed on similar samples, was obtained. Elemental analysis gives a good agreement between the values found for the different elements and those calculated for a cyclic oligomer. Anal. Calcd for $(C_5H_3SN)_3$: C, 55.1; H, 2.8; N, 12.8; S, 29.3. Found: C, 56.1; H, 2.1; N, 12.3; S, 28.9. This cyclic trimer was characterized by ^1H and ^{13}C NMR spectroscopy in $CDCl_2/CDCl_2$ (see Table I for the comparison of the ^{13}C NMR spectra of linear and cyclic oligomers). ^1H NMR: 7.18 (H_{C7}, d), 7.45 ppm (H_{C8}, t, J_{AB} = 7.5 Hz).

The linear low molecular weight molecules Br–Py[S–Py]$_x$–Br ($x \leq 3$) were prepared as follows: A mixture of 0.084 mol of DBP and 0.010 mol of Na_2S with 45% water in 40 mL of DMSO was stirred at 120 °C for 3 h and then poured into 50 mL of distilled water. The oligomers were filtered, washed with water, and then dried under high vacuum in the presence of P_2O_5. They were dissolved in chloroform and separated by chromatography on a silica gel column (70–230 mesh), using this solvent as eluent, with the following yields for the crude products: 33%, 6%, and 1.2% for x = 1, 2, 3, respectively. The chemical analysis for the dimer gives the following results. Anal. Calcd: C, 39.6; H, 2.0; N, 9.2; S, 14.1; Br, 35.1. Found: C, 39.1; H, 1.8; N, 8.8; S, 13.9; Br, 36.4. The small discrepancies observed between the experimental and calculated values may be attributed to the presence of ~10% of the oligomer with x = 1. This is confirmed by the ^{13}C NMR spectrum in which the intensities of the peaks corresponding to the carbons of the bromopyridine moieties, i.e., C_1, C_2, C_3, and C_4, are slightly higher than those of the carbon central unit, namely, C_7 and C_8.

DSC experiments carried out on the oligomers show a sharp melting peak for P3PyS whose onset is located at 92 °C; crystallinity is rapidly developed for this oligomer from the melt at relatively low undercoolings. Crystallinity is not developed in the linear oligomer compound P13PyS. Several experiments carried out on the cyclic trimer at different undercoolings also seem to suggest that this compound does not crystallize from the melt.

Dielectric measurements were carried out with a capacitance bridge (General Radio, type 1689 M) operating in the frequency range 0.1–10 kHz. The measurements were performed on pellets obtained by pressing the compounds under 5 × 10^8 Pa. The electric conductivity of the pellets used in the dielectric measurements was measured with an HP-4329 A electrometer coupled with a Guildline 6500 Teraohmeter. Both the dielectric and conductivity experiments were performed in the interval 273–350 K.

Table II
Geometrical Parameters Used in the Calculations of Conformational Energies (Taken from Sybyl[10] Database)[a]

bond length (Å)	bond angle (deg)
C^{ar}–H = 1.08	H–C^{ar}–N = 119.4
C^{ar}–Br = 1.85	Br–C^{ar}–N = 119.4
C^{ar}–N = 1.349 (1.335)	S–C^{ar}–N = 119.4 (117.7)
C^{ar}–S = 1.77 (1.780)	C^{ar}–N–C^{ar} = 121.5 (116.7)
C^{ar}–C^{ar} = 1.398 (1.376)	N–C^{ar}–C^{ar} = 120.4 (123.5)
	H–C^{ar}–C^{ar} = 120.4
	C^{ar}–C^{ar}–C^{ar} = 119.2 (118.6)
	C^{ar}–S–C^{ar} = variable[b] (101.9)

[a] Values given in parenthesis represent the values obtained by X-ray analysis in ref 11. [b] Averaged value for conformations around the minima: θ = 97.4°.

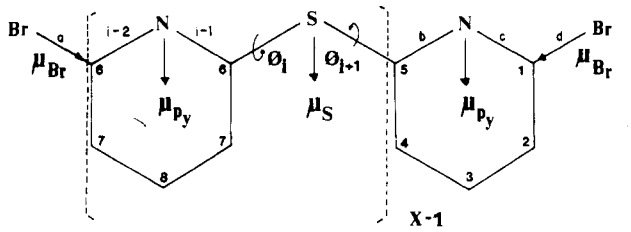

Figure 2. Linear bromo-terminated poly(2,6-pyridinediyl sulfide) in an all-trans conformation.

Theoretical Conformational Studies

The Tripos[9] force field and the Sybyl Molecular Modelling software[10] were used to compute the conformational energies of 2,2′-thiobispyridine (TBP) as a function of rotational angles over C–S (ϕ_i) and S–C (ϕ_{i+1}) bonds using the bond angles and bond lengths summarized in Table II where, for comparative purposes, the values obtained from X-ray experiments on the cyclic trimer are also shown.[11] The structure of this compound can be derived schematically from Figure 2 by taking x = 1 and replacing the initial and final bromine atoms by hydrogens; therefore, TBP can be considered a low molecular weight analogue of poly(2,6-pyridinediyl sulfide). The energy of any given

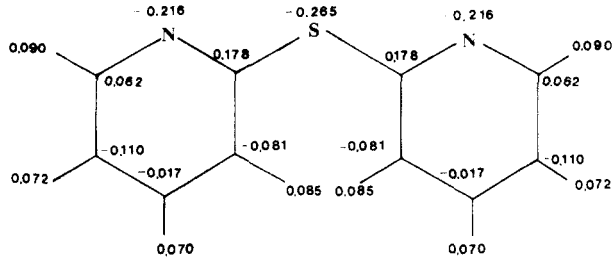

Figure 3. Charge distribution of 2,2′-thiobispyridine.

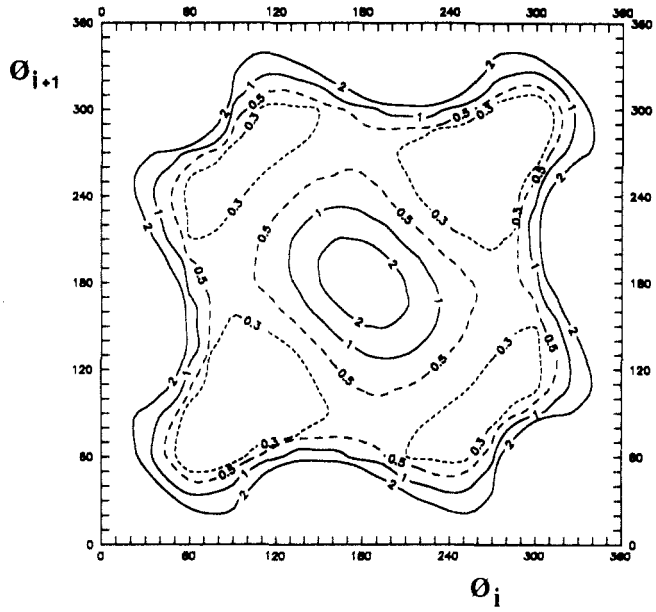

Figure 4. Conformational energy map for 2,2′-thiobispyridine.

conformation strongly depends on the value assigned to the C–S–C bond angle, and consequently, this parameter was taken as variable so that the energy of each conformation (i.e., each combination of ϕ_1 and ϕ_2 rotational angles) was minimized with respect to the bond angles.

An exploratory calculation without Coulombic interactions was performed in order to obtain the approximate location of the conformation of minimum energy. The result of this exploration gave $\phi_1 = \phi_2 = 72°$ and θ(C–S–C) = 96.9°. The charge distribution of a molecule of TBP having this conformation was then computed with MNDO[12] and written as the point charge distribution shown in Figure 3 which reproduces both modulus and orientation of the dipole moment computed by MNDO. This point charge distribution and an effective dielectric constant $\epsilon = 4$ were used to calculate Coulombic interactions thereafter. However, it is noteworthy to indicate that these interactions have very little effect on the final values of total conformational energies.

The results of conformatinal energy as a function of rotations ϕ_1 and ϕ_2 are shown in Figure 4 where the isoenergetic contours of the whole conformational space of the molecules are drawn. The minimum energy is obtained for the conformations $\phi_1 = \phi_2 = \pm 70°$; all the values indicated in the conformational map were normalized with respect to the energy of these minima that was arbitrarily taken as zero. As Figure 4 indicates, the energy is large when at least one of the rotational angles is close to zero, the maximum (E = 51 kcal mol^{-1}) being obtained with $\phi_1 = \phi_2 = 0$ where the hydrogens attached to the C(7) atom force the C–S–C bond angle to open up to $\theta = 135°$. There is a second maximum, E = 3.3 kcal mol^{-1} for the $\phi_1 = \phi_2 = 180°$, $\theta = 103.9°$ conformation, where the strongest contribution to the energy comes from

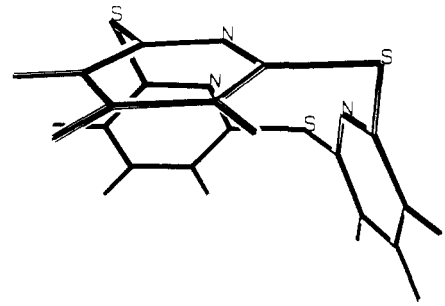

Figure 5. Lowest energy conformation for the cyclic trimer P3PySC.

interactions between nitrogen atoms that are separated by a distance of 2.38 Å. There are four relatively large areas in which the energy is smaller than 0.3 kcal mol^{-1}; averaged values of the conformational parameters were computed over these areas by using the familiar expressions

$$\langle \phi_k \rangle = \sum\sum \phi_k \exp(-E(\phi_j,\phi_k)/\kappa T) / \sum\sum \exp(-E(\phi_k,\phi_j)/\kappa T) \quad (2)$$

and

$$\langle E \rangle = \sum\sum E(\phi_j,\phi_k) \exp(-E(\phi_j,\phi_k)/\kappa T) / \sum\sum \exp(-E(\phi_j,\phi_k)/\kappa T) \quad (3)$$

The results obtained were $\langle \phi_1 \rangle = \langle \phi_2 \rangle = \pm 99°$, $\langle \theta \rangle = 97.3°$ and $\langle \phi_1 \rangle = -\langle \phi_2 \rangle = \pm 102°$, $\langle \theta \rangle = 97.4°$. The average energy of the latter conformations is 0.15 kcal mol^{-1} higher than that of the former ones. Therefore, a two-state conformational model with rotational angles located at ca. ±100°, bond angle $\theta = 97.4°$, and energy $E_\gamma \approx 0.15$ kcal mol^{-1} for the $\phi_1 = -\phi_2$ conformations should give a good account of the conformational statistics of both TBP and the repeating unit of the polymer.

Preliminary calculations carried out using these findings showed that the development of the cyclic trimer can only be attained by the rotations of different sign about the consecutive skeletal C–S–C bonds forming the cycle. Any other combination of rotations producing a closed structure would entail a much larger energy. Minimization of the energy carried out with Sybyl shows that rotations of ±111° and skeletal bond angles of 97° intervene in the conformation of minimum energy that forms the cyclic trimer, these results being in reasonable agreement with the values of 100° and 97.4° found, respectively, for these quantities in the linear chains. The conformation corresponding to these results, represented in Figure 5, resembles a chair. This conformation together with those obtained by symmetry is presumably the most important conformation intervening in the formation of the cyclic trimer. The small conformational versatility of the cycle probably decreases the packing of the chains in the crystal, thus hindering the development of three-dimensional order in this compound.

Comparison between Theoretical and Experimental Results

The experimental dipole moments summarized in Table III were used to obtain contributions of skeletal bonds or groups of bonds for both TBP and the bromo-terminated oligomers. The analysis of pyridine and the three isomers of bromopyridine suggests a contribution for the ring of $\mu_{py} = 2.2$ D with a direction pointing from N to C(8), i.e., with the center of negative charge close to the N atom, and a second contribution for the Br–C bond of $\mu_{Br} = 1.4$ D (slightly smaller than the experimental dipole moment

Table III
Experimental Dipole Moments[13] for Several Compounds Related to Poly(pyridinediyl sulfide)

compound	empirical formula	dipole moment (D)
pyridine	C_5H_5N	2.2
2-bromopyridine	C_5H_4NBr	3.01–3.22
3-bromopyridine		2.0
4-bromopyridine		0.8
2,2′-thiobispyridine	$C_{10}H_8N_2S$	3.50 at 25 °C 3.53 at 45 °C
bromobenzene	C_6H_5Br	1.55 ± 0.05
diphenyl sulfide	$C_{12}H_{10}S$	1.5 ± 0.1

of bromobenzene) pointing from Br to C atoms. The dipole moments computed by straight addition of these two vectors are 2.2, 3.14, 1.93, and 0.38 D for pyridine and 2-bromo-, 3-bromo-, and 4-bromopyridine, respectively, all of them in excellent agreement with the experimental results given in Table III.[13]

The contribution of the C–S–C group was represented by a dipole μ_S having a modulus of 1.5 D (the experimental dipole moment of diphenyl sulfide[13]), located in the bisector of the C–S–C bond angle and having the negative end at the S atom. The location of this contribution was checked by using MNDO to compute the charge distribution of diphenyl sulfide in the conformation of minimum energy ($\phi_1 = \phi_2$, θ(C–S–C) = 96.9°). The results of this calculation suggest that the strongest contribution (i.e., about 94% of the total dipole moment of the molecule) can be represented by the vector just described.

Calculations of the square root of the mean-square dipole moment of TBP, $\langle\mu^2\rangle^{1/2}$, were performed with the dipolar contributions indicated before as a function of E_γ, the energy of $g^\pm g^\mp$ conformers with respect to that of the alternative $g^\pm g^\pm$ ones. The theoretical calculations indicate that $\langle\mu^1\rangle^{1/2}$ decreases as E_γ increases as a consequence of the fact that there is a decrease in the population of conformers that place the dipoles of the pyridine groups forming small angles between them. A decrease of E_γ from +0.5 to −0.5 kcal mol^{-1} increases the dipole moment of the compound from 3.24 to 3.99 D. By using $E_\gamma = 0.15$ kcal mol^{-1}, the average energy obtained from the analysis of the conformational map of Figure 4, the value of $\langle\mu^2\rangle^{1/2}$ amounts to 3.51 and 3.52 D at 25 and 45 °C, respectively, in very good agreement with the experimental results[13] of 3.50 and 3.53 D obtained at these respective temperatures. The critical interpretation of the dipole moment of TBP suggests that a 2 × 2 rotational state scheme is a suitable model to describe the conformational properties of bromo-terminated poly(2,6-pyridinediyl sulfide) polymers. The statistical weight matrices used for bonds a–d in Figure 2 are

$$\mathbf{U}_a = (1 \quad 0) \qquad \mathbf{U}_{i-2} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \tag{4}$$

$$\mathbf{U}_{i-1} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \quad \mathbf{U}_i = \begin{pmatrix} 1 & 1 \\ 0 & 0 \end{pmatrix} \quad \mathbf{U}_{i+1} = \begin{pmatrix} 1 & \gamma \\ \gamma & 1 \end{pmatrix} \tag{5}$$

$$\mathbf{U}_b = \begin{pmatrix} 1 & 0 \\ 1 & 0 \end{pmatrix} \quad \mathbf{U}_c = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \quad \mathbf{U}_d = \begin{pmatrix} 1 \\ 1 \end{pmatrix} \tag{6}$$

Values of the dipole moment for bromo-terminated poly(2,6-pyridinediyl sulfide) were calculated as a function of the degree of polymerization at 25 and 45 °C using standard matrix multiplication methods described in detail elsewhere.[6,14] The partition function for a chain of x repeating units is given by

$$Z = \mathbf{U}_a[\mathbf{U}_{i-2}\mathbf{U}_{i-1}\mathbf{U}_i\mathbf{U}_{i+1}]^{x-1}\mathbf{U}_b\mathbf{U}_c\mathbf{U}_d$$

The results expressed in terms of the ratio of the mean-square dipole moment to the degree of polymerization are shown in Table IV, where it can be seen that $\langle\mu^2\rangle/x$ decreases as x increases, tending to an asymptotic value of 6.5 D^2/repeating unit. An increase in temperature will increase the population of higher polarity conformers, and therefore the dipole moments of the chains will exhibit a positive temperature coefficient. This explains why the experimental dipole moment of TBP is higher at 45 °C than at 25 °C. Linear poly(2,6-pyridinediyl sulfide) has a polarity much higher than poly(methylene sulfide) for which the value of $\langle\mu^2\rangle/x$ lies in the vicinity of 0.8 D^2. It should be pointed out that the polysulfides of structural unit $(-SCH_2)_x-$ have, in general, dipole ratios lower[7] than 1.

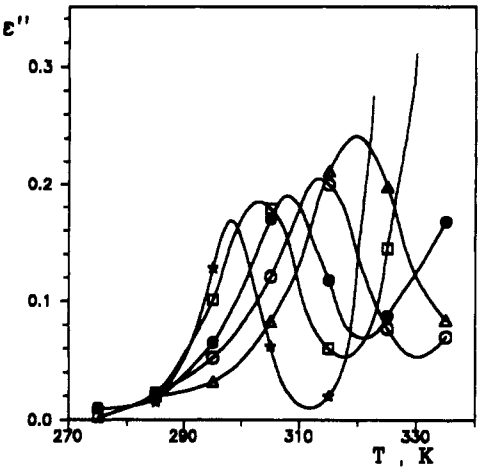

Figure 6. Dielectric loss ϵ'' dependence on temperature for the linear bromo-terminated dimer P3PyS, at several frequencies: (*) 0.1, (□) 0.5, (●) 2, (○) 10, and (△) 50 kHz.

Table IV
Dependence of the Dipole Moment, $\langle\mu^2\rangle^{1/2}$, and the Dipole Ratio, $\langle\mu^2\rangle/x$, on the Degree of Polymerization, x, at 25 °C

x	$\langle\mu^2\rangle^{1/2}$ (D)	$\langle\mu^2\rangle/x$ (D^2)	x	$\langle\mu^2\rangle^{1/2}$ (D)	$\langle\mu^2\rangle/x$ (D^2)
2	4.284	9.176	10	8.367	7.001
3	5.013	8.376	12	9.103	6.905
4	5.605	7.866	15	10.106	6.808
5	6.157	7.581	20	11.586	6.712

The polarity of the cyclic trimer in the conformation of minimum energy was determined in two ways: (a) via MNDO and (b) by addition of the dipoles associated with the polar groups intervening in the formation of the cycle. In the first case the dipole moment was found to be 6.47 D, in fairly good agreement with the value of 7.42 D obtained by the second method. Therefore, these results suggest that the polarity of the cyclic trimer is somewhat larger than the polarity of its linear counterpart.

Dielectric Relaxation and Conductivity

The dielectric relaxation spectrum of bromo-terminated P3PyS, represented in Figure 6, exhibits a well-developed absorption centered at 300 K at 0.2 kHz. A plot of the natural logarithm of the frequency against the reciprocal of the absolute temperature associated with the maximum of the peak gives a straight line with correlation coefficient $\rho = 0.9987$. Therefore, the absorption obeys Arrhenius behavior with an activation energy of 54.2 kcal mol^{-1}. In order to investigate the effects of the structure on the

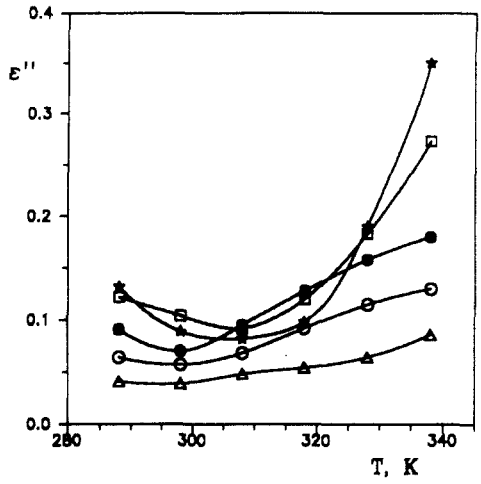

Figure 7. Variation of the dielectric loss ϵ'' with temperature for the cyclic trimer P3PySC, at several frequencies: (*) 0.2, (□) 0.5, (●) 2, (○) 10, and (△) 50 kHz.

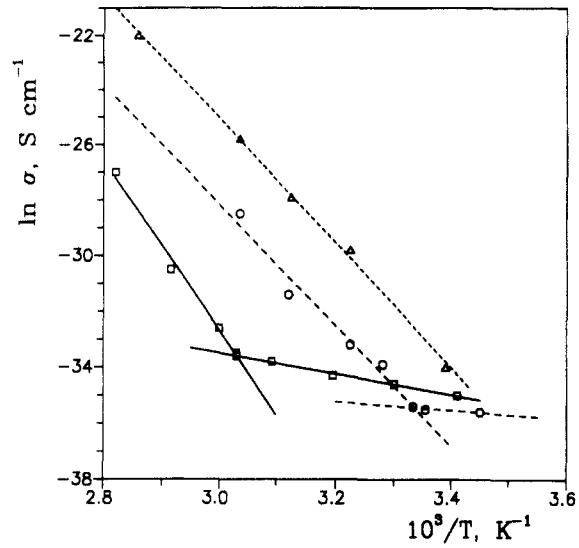

Figure 8. Arrhenius plot for the electric conductivity σ of the cyclic trimer P3PySC (□), the bromo-terminated chains P3PyS (△), and P12PyS (○).

relaxation spectrum, dielectric investigations were also conducted on the cyclic trimer P3PySC. The spectrum of this compound, represented in Figure 7, only shows a weak relaxation that overlaps with conductivity effects. Similar behavior appears in the bromo-terminated oligomer with 12 repeating units in the chains.

The relaxation described above could be caused by intramolecular motions of the molecules in the compounds, intermolecular interactions, or both. The conformational map of TBP shows a maximum in the conformational energy when the two rotational angles are zero due to repulsive interactions between neighbor hydrogen atoms. The fact that this energy is 51 kcal mol^{-1}, a value close to the activation energy of the process, suggests that conformational changes about C–S–C bonds might produce the relaxation observed in these compounds. On the other hand, the relatively high intensity of the spectrum of P3PyS also suggests that an important contribution to the relaxation must come from motions about S–C bonds within the crystal; in support of this assumption we should point out that the intensity of this relaxation is in comparison very small for the totally amorphous P13PyS oligomer and the cyclic trimer.

Overlapping of the π orbitals of the pyridine rings with the p orbitals of the sulfur atom can produce molecular orbitals in which the highest filled levels and the lowest unoccupied levels are separated by an energy gap low enough so that electrons can be thermally promoted from the former to the latter level. This, together with structural regularity, would be a prerequisite for the appearance of electronic conductance.[15] In order to test the capability of –S–Py– structures for the development of conducting polymers, conductivity experiments were carried out on linear and cyclic trimers and on P13PyS. The natural logarithm of the conductivity, σ, of these compounds is plotted against the reciprocal of the temperature in Figure 8. The Arrhenius plots for P3PySC and P13PyS present two straight lines with high and low slopes at the high and low temperature sides, respectively; the changes in slope occur at 323 and 300 K for the former and the latter compounds, respectively. However, the slope of the Arrhenius plot for P3PyS does not change in the interval of temperature 20–77 °C.

The conductivity is an activated process with an activation energy above the room temperature of about 40 kcal mol^{-1} for the linear compounds and 60 kcal mol^{-1} for the cyclic trimer. The activation energy is much smaller in the low temperature interval. Comparisons in conductivity made in terms of σ at the reference temperature of 30 °C indicate that the value of this parameter for the linear dimer (5.9×10^{-14} S cm^{-1}) is nearly 2 orders of magnitude higher than the values of σ for the cyclic trimer (7.2×10^{-16} S cm^{-1}) and for P13PyS (4.5×10^{-16} in the same units). The enhanced conductivity of the linear dimer must be connected with the molecular order in this compound. In any case, all the compounds have conductivities smaller than 10^{-10} S cm^{-1} and therefore can be considered insulating materials.

Conductivity studies on poly(2,6-pyridinediyl sulfide) have been earlier reported by Laakson et al.[16] on samples that do not have a well-defined chemical structure as suggested by the experimental C/S ratio (3.8) given by these researchers that is too small compared with the theoretical value (5.0). A striking difference between their results and ours is that they find a conductivity of 2.1×10^{-11} S cm^{-1} (the temperature of measurement is not given) that is almost 3 orders of magnitude higher than the value found in our experiments at room temperature. In fact, our results predict conductivities of the order of 10^{-11} S cm^{-1} at 60 °C for the linear dimer and much larger for the other compounds.

Conclusions

The synthesis and characterization of linear and cyclic poly(2,6-pyridinediyl sulfide) is thoroughly described, indicating that the percentage of water in sodium bisulfide conditions the structure, linear or cyclic, of the chains. A two rotational state model has been developed that gives a good account of the conformational statistics of poly(2,6-pyridinediyl sulfide) chains. The relaxation behavior of these compounds in the vicinity of room temperature is strongly dependent on the crystallinity. Overlapping of π orbitals of the pyridine ring with the p orbitals of the sulfur atoms does not seem to produce a noticeable increase in the conductive properties of these materials at room temperature. However, the high temperature dependence of the conductivity, σ, suggests that the linear dimer becomes a semiconductor at temperatures somewhat lower than its melting temperature. Therefore, doping of these compounds could enhance in a significant way their conductivity.

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