

SOLUTION PROPERTIES AND RANDOM COIL DIMENSIONS OF POLY(3,3'-DIMETHYLTHIETANE)

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Abstract—Poly(3,3'-dimethylthietane) synthesized by anionic polymerization was studied with regard to its dilute solution properties. Several fractions were isolated by fractional precipitation, with benzene/methanol at 25°. Osmotic and viscometric measurements were performed. The (intrinsic viscosity)/(molecular weight) relationship $[\eta](\text{dl/g}) = 1.10 \times 10^{-4} \bar{M}_n^{0.79}$ was obtained for tetrahydrofuran at 25°. The unperturbed dimension of the chain, as expressed by the characteristic ratio $\langle r_0^2 \rangle / (nl^2)$ is 5.0, in excellent agreement with theoretical predictions. Intrinsic viscosities and the Flory-Huggins interaction parameter were used to determine the cohesive energy density. The assigned solubility parameter is $\delta = 8.6 \text{ cal}^{1/2} \text{ cm}^{-3/2}$. Comparisons with other polysulphides and polyoxides help to elucidate the effects of the size of the heteroatom and substituents on the properties.

INTRODUCTION

Polythietanes form a group of polymers having the four bond structural unit (S-C-C-C-). They can be considered as derived from a four-methylene unit, where one methylene has been replaced by one sulphur heteroatom. From a physical point of view, this structural modification involves changes in bond lengths, angles and polarizability. Consequently, the conformational energies of the neighbouring bonds are modified. It is expected that conformation-dependent properties, like unperturbed chain dimensions, vary with these changes. Thus, in a previous paper [1], it has been shown that the characteristic ratio of polythietane, PTS, has a small value, which is nearly half that exhibited by the polymethylene chain [2] at the same temperature. This is a drastic reduction of the chain extension, brought about by the insertion of a sulphur atom every three methylene groups, and shows the great increment produced in the flexibility of the chain by the presence of this heteroatom.

From the viewpoint of studying the effect of the chemical modification of a chain on properties, the substitution of two hydrogens by methyl groups at the β position of the structural unit of polythietane alters the conformational energies of the neighbouring bonds [3]. An understanding of the behaviour of the polythietane series is at least dependent on the ability to relate their equilibrium configuration properties with their structure. For this purpose, it is quite convenient to have knowledge of the dilute solution properties of these polymers. In preceding papers [4, 5] we reported some of the properties of poly(3,3'-dimethylthietane), PDMT, mainly in the solid state. In this paper the dilute solution properties of PDMT are evaluated from number-average molecular weights, \bar{M}_n , and intrinsic viscosities, $[\eta]$, in a good solvent. The derived unperturbed dimensions are compared with the theoretical values and together with the cohesive energy density, CED, are used to explain some of the properties of this polymer.

EXPERIMENTAL

The monomer, 3,3'-dimethylthietane, was prepared by the method described by Searles *et al.* [6] and purified by distillation in a vacuum line several times from sodium-mirror and then from butyl lithium at temperatures below 0°. 3,3'-Dimethylthietane was stored in tubes equipped with teflon stopcocks.

Poly(3,3'-dimethylthietane) was prepared by anionic polymerization with sodium naphthalene as the initiator in tetrahydrofuran (THF) at -78°. The reaction mixture was dropped onto methanol and, after recovering, it was dried in vacuum.

The ¹H-NMR spectrum was determined at 90 MHz in CDCl₃ with tetramethylsilane as internal reference. The spectrum shows two absorptions: a single peak at 1.05 ppm and another at 2.65 ppm, due to the methyl and methylene protons, respectively. The intensity ratio was 6:4, which corresponded to the structural unit. The ¹³C-NMR (off-resonance) spectrum shows three absorptions: a multiplet at 1.15 ppm, a single peak at 1.57 ppm and a triplet at 1.98 ppm due to the methylene, tetrasubstituted and methyl carbons respectively.

The whole polymer was fractionated by precipitation at 25° with benzene-methanol. Polymer molecular weight characterization was performed by membrane osmometry and gel permeation chromatography. The number-average molecular weights of the fractions were measured in a Mechrolab high-speed membrane osmometer model 502. The membranes were ultracellafilter grade finest, and were conditioned from 1-propanol to THF. The data were obtained at 25° in THF. Seven fractions were measured in the range from 3.8×10^4 to 1.29×10^5 .

Gel permeation chromatography measurements were performed in THF at 25° using a Waters Associates apparatus model 150 C. A set of 6 microstyragel columns with nominal exclusion sizes of 10^6 , 10^5 , 10^4 , 10^3 , 10^2 and 10^1 Å was used. The molecular weight averages were obtained by the universal calibration procedure [7], where the Mark-Houwink-Sakurada relation utilized for polystyrene in THF at 25° was $[\eta](\text{dl/g}) = 6.82 \times 10^{-5} \bar{M}_w^{0.766}$ and the $[\eta] - M$ relation used for PDMT was that developed in this work.

The solution viscosity measurements were made at 25° using a capillary viscometer of the Ubbelohde type. The intrinsic viscosity, $[\eta]$, was determined by extrapolating two

Table 1. Viscometric and osmotic results for poly(3,3'-dimethyl thietane) in tetrahydrofuran at 25°

Fraction	$ \eta $ (dl/g)	$\bar{M}_n \times 10^{-4}$ (g/mol)	$A_2 \times 10^3$ (cm ³ mol/g ²)
I	1.27	12.86	0.699
II	1.05	10.40	0.664
III	0.89	7.43	0.671
IV	0.81	7.43	0.702
V	0.80	7.31	0.794
VI	0.62	5.22	0.936
VII	0.47	3.82	0.985

types of viscosity-concentration plots, i.e. η_{sp}/c and $\ln(\eta_r)c$ vs c , so as to yield a common intercept at $c = 0$; the kinetic energy correction was applied. The density of amorphous PDMT was measured by dilatometry at 25° yielding a value of 1.053 g/ml.

RESULTS AND DISCUSSION

The dilute solution characterization results are given in Table 1 for 7 fractions of PDMT, covering the range of \bar{M}_n from 3.8×10^4 to 1.29×10^5 . The experimental data of osmotic measurements in THF at 25° are shown in Fig. 1. The significant value of the third virial coefficient is shown by the curvature of the π/c vs c plot. The data are better analyzed according to the equation [9]:

$$(\pi/c)^{1/2} = (RT/\bar{M}_n)^{1/2} + (RT\bar{M}_n)^{1/2} A_2 c/2, \quad (1)$$

where π is the osmotic pressure, c the polymer concentration, R the gas constant, \bar{M}_n the number-average molecular weight, T the temperature and A_2 the second virial coefficient.

It is shown in the framework of the two parameter theory of dilute solutions that the second virial coefficient decreases on raising the molecular weight [10]. The experimental data follow this trend and they fit the expression $A_2 = CM^{-\epsilon}$ with ϵ equal to -0.26 . The value of the exponent is slightly higher than the maximum value suggested by Kurata and Stockmayer for synthetic polymers [11].

The solution intrinsic viscosities and the molecular weights give the following relationship for THF at 25°:

$$|\eta| = 1.10 \times 10^{-4} \bar{M}_n^{0.79}, \quad (2)$$

where $|\eta|$ is expressed in dl/g. The value of the exponent is in the usual range 0.5–0.8 observed for polymers conforming to the random coil configuration. The high value of the exponent is in accordance with the thermodynamic goodness of the solvent.

Another equation, for benzene at 25°, has been published [12] but it was based on unfractionated samples synthesized by cationic ring-opening polymerization of 3,3'-dimethylthietane via the sulphonium ion. As is well known, in this kind of polymerization, transfer from the growing ion to the polymer chain occurs, giving branched structures through the formation of tertiary sulphonium ions of low reactivity. These species are very stable, and they remain unchanged after precipitation of the polymer with methanol [12]. On the contrary, the PDMT used in this work was synthesized via anionic poly-

merization using sodium naphthalene as initiator. Under appropriate experimental conditions, the polymerization is "living" without any transfer reactions, with the possibility of obtaining polymers with very narrow molecular weight distribution [13].

In order to describe the dilute solution properties of a long flexible polymer such as PDMT, the two parameter scheme is useful. One of these is a measure of the unperturbed dimensions and the other describes the polymer-solvent interactions. One parameter of the first kind is the characteristic ratio, and of the second, the linear expansion factor and the polymer-solvent interaction parameter. To obtain these quantities for PDMT, intrinsic viscosities and osmotic data are used. In order to characterize the spatial extension, a convenient parameter is the unperturbed mean-square end-to-end distance, $\langle r_0^2 \rangle$, from which the conformation factor can be calculated. Thus, valuable information concerning the structure of PDMT is obtained.

The most straightforward way to obtain unperturbed dimensions is from measurements in θ solvents, through the relationship [2]:

$$|\eta| = \Phi_0 (r_0^2/M)^{3/2} M^{1/2}, \quad (3)$$

where the symbols have the usual meaning and Φ_0 is Flory's constant. Alternatively, under non- θ conditions, the chains have perturbed dimensions and the above equation should be modified as:

$$|\eta| = K_\theta M^{1/2} \alpha^3, \quad (4)$$

with $K_\theta = \Phi_0 (\langle r_0^2 \rangle / M)^{3/2}$. The expansion factor, α , is an increasing function of the excluded volume parameter, but the effect vanishes for short chains. For

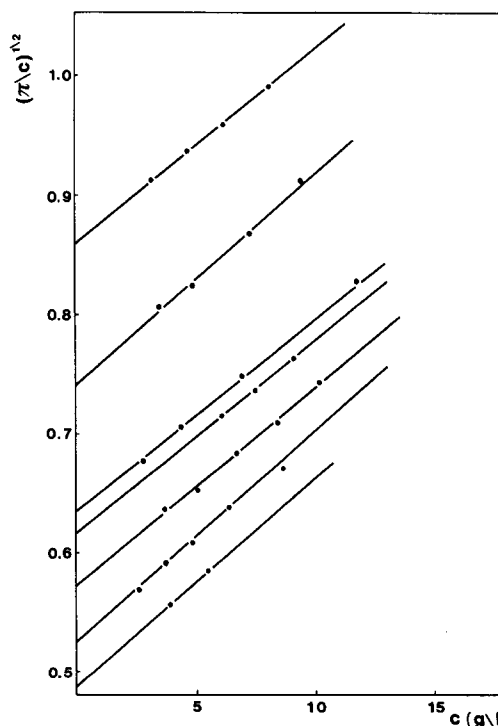


Fig. 1. Plot of $(\pi/c)^{1/2}$ vs c for PDMT fractions in tetrahydrofuran at 25°.

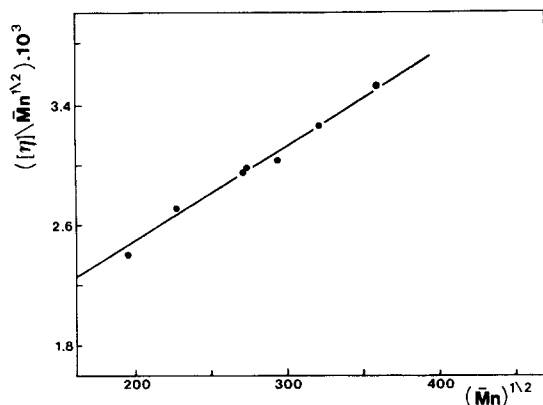


Fig. 2. Burchard-Stockmayer-Fixman plot of PDMT.

this reason, K_θ can be obtained by extrapolation from the dependence of the intrinsic viscosity on molecular weight. Several graphical methods of extrapolation have been published. An approximate equation widely used in the relation between viscosity, molecular weight and solvent quality is due to Burchard, Stockmayer and Fixman [14,15]. This BSF equation is given by:

$$[\eta]/M^{1/2} = K_\theta + 0.51 B \Phi_0 M^{1/2}, \quad (5)$$

with the parameter B given by:

$$B = \bar{v}_2^2 (1 - 2\chi) / (v_1 N), \quad (6)$$

where v_1 is the solvent molar volume, \bar{v}_2 the polymer partial specific volume, N the Avogadro number and χ the polymer-solvent interaction parameter. The BSF plot applied to PDMT, represented in Fig. 2, gives an intercept $K_\theta = 1.2 \times 10^{-3} \text{ dl mol}^{1/2} \text{ g}^{-3/2}$. Since in this equation average molecular weights were used, the value of K_θ is quite sensitive to the molecular weight distribution. To have a knowledge of this parameter, GPC measurements were performed on the fractions of PDMT. The polydispersity index, \bar{M}_w/\bar{M}_n , is for all the fractions close to 1.3. Assuming the Schulz-Zimm exponential function for the molecular weight distribution, the value of the correction factor q is 1.13 [16]. By using this number, the value $(\langle r_0^2 \rangle / \bar{M}_n)^{1/2} = (K/\Phi_0)^{1/3} = 7.44 \times 10^{-9} \text{ cm mol}^{1/2} \text{ g}^{-1/2}$ is deduced.

To compare the average dimensions of random coil chains, a useful parameter is the characteristic ratio, $\langle r_0^2 \rangle / (nl^2)$, which relates the unperturbed mean-square end-to-end distance to the value of that quantity for the freely jointed chain. It is expressed in terms of the number of the chain bonds, n , equal to $4 \bar{M}_n / M_0$, and the square of the average bond lengths, being $l_{C-C} = 1.53 \text{ \AA}$ and $l_{C-S} = 1.815 \text{ \AA}$. This dimensionless ratio serves as a measure of the unperturbed spatial extension of a polymer chain and the resulting value for PDMT is $\langle r_0^2 \rangle / (nl^2) = 5.0$. This value is in good agreement with the 5.1 previously calculated from the rotational isomeric state treatment [3], which considered the unperturbed random coil configuration of PDMT on the basis of three rotational states for each backbone bond.

The interaction parameter coefficient of PDMT in THF is obtained from the slope of the BSF plot and

equation (6). A value of 0.361 results, when using the experimental specific volume of the polymer, $0.950 \text{ cm}^3/\text{g}$. The thermodynamic interaction parameter is an important measure of polymer solubility and, in the absence of specific polymer-solvent interactions, it can be related to the solubility parameter as follows [17]:

$$\chi = 1/z + V(\delta_s - \delta_p)/(RT), \quad (7)$$

where z is the coordination lattice number and δ_s and δ_p the solubility parameters of solvent and polymer respectively. Assuming $1/3$ for the reciprocal of the lattice number and considering $9.1 \text{ cal}^{1/2} \text{ cm}^{-3/2}$ for the solubility parameter of THF, the value $\delta_p = 8.7 \text{ cal}^{1/2} \text{ cm}^{-3/2}$ is obtained. The solubility parameter of PTS, as measured from the polymer-solvent interaction coefficient, was reported previously [1]. It is $\delta = 10.0 \text{ cal}^{1/2} \text{ cm}^{-3/2}$, i.e. 13% higher than for the dimethyl derivative. At least in part, it corresponds to larger intermolecular forces due to a change of density, which increases about 10% on passing from PDMT to PTS.

The solubility parameter of PDMT is also obtained by viscometry measurements in several solvents. A plot of the intrinsic viscosities vs solubility parameters of the solvents is shown in Fig. 3. The smooth curve drawn through the points shows the maximum polymer-solvent interaction at $\delta = 8.6 \text{ cal}^{1/2} \text{ cm}^{-3/2}$. The solubility parameter is also calculated using the empirical Small method [18], $\delta = \rho \Sigma F_i / M_0$, where M_0 is the molecular weight of the repeating unit, ρ the density of the amorphous polymer and F_i the bond attraction constant of the group i . The density of amorphous PDMT at 25° is

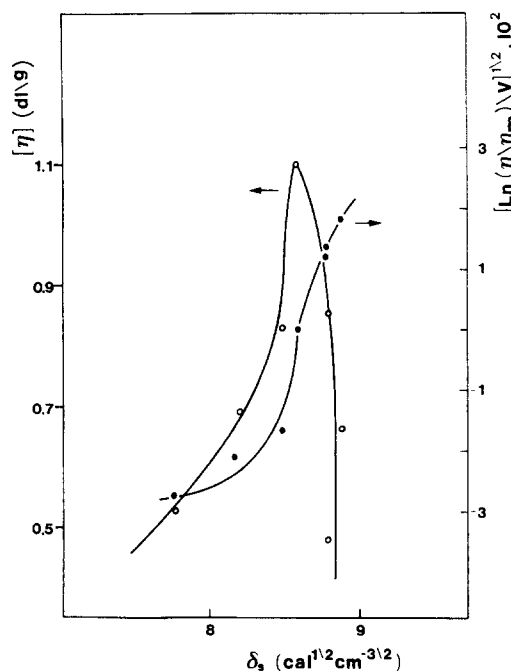


Fig. 3. Plot of PDMT intrinsic viscosity, $[\eta]$, in several solvents (○) and $[\ln([\eta]/[\eta]_m)/V]^{1/2}$ (●) vs solvent solubility parameter, δ_s , where $[\eta]_m$ is the highest value of $[\eta]$ and V the solvent molar volume.

Table 2. Characteristic ratio, cohesive energy density and three-dimensional solubility parameter of polythietane, PTS, poly(3,3'-dimethylthietane), PDMT, polyoxetane, PTO and poly(3,3'-dimethyloxetane), PDMO

Polymer	$\langle r_0^2 \rangle / (nl^2)$	CED (cal cm ⁻³)	δ_d (cal ^{1/2} cm ^{-3/2})	δ_p (cal ^{1/2} cm ^{-3/2})	δ_h
PTS	4.0 ^a	100 ^a	9.2 ^a	2.9 ^a	2.4 ^a
PDMT	5.0	74	8.0	2.5	2.0
PTO	3.9 ^b	88 ^c	8.7 ^c	1.2 ^c	2.0 ^c
PDMO	4.2 ^b	62 ^c	7.5 ^c	1.2 ^c	2.0 ^c

^aRef. [1]. ^bRef. [23]. ^cRef. [24]. ^dRef. [25].

1.05 g/ml, which gives a value of $\delta = 8.5 \text{ cal}^{1/2} \text{ cm}^{-3/2}$, in good agreement with the experimental result.

The solubility parameter or the related cohesive energy density can be considered as a measure of the interaction forces in the amorphous state. A better knowledge of the nature of these forces can be obtained using the three dimensional concept of the solubility parameter. According to Hansen [19–21], the interaction energy, E , is the result of dispersion (E_d), dipole (E_p), and hydrogen bonding, (E_h) energies. The original Hildebrand solubility parameter [22] is related to these by the expression $\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$, where $\delta = (E/V)^{1/2}$, V being the molar volume. In three dimensional space, the polymer is represented by a point placed at the centre of a sphere which encloses all the solvents of the polymer. A test of solubility was performed in order to find this central point for PDMT. Thus, the polymer is soluble in aromatic hydrocarbons, chlorinated solvents and cyclic ethers and insoluble in aliphatic hydrocarbons. These facts are reflected in the three obtained components of the solubility parameter, quoted in Table 2. Semi-empirical relationships between the dispersion component and some physical properties of polymers have been described. For polyoxetanes, a class of polymers structurally similar to polythietanes, it was found that the dispersive component of the solubility parameter is related to the refractive index and molar volume, through the equation $\delta_d = 11.4 n_D / V^{1/6}$ [24]. Substitution of the values estimated for PDMT, $n_D = 1.55$ and $V = 96.8 \text{ cm}^3/\text{mol}$, gives $\delta_d = 8.3 \text{ cal}^{1/2} \text{ cm}^{-3/2}$, a result which is close to the experimental value.

The contribution of permanent dipoles to the cohesive energy density can be evaluated from the equation which relates the dipole moment with the dipolar component, $\delta_p = 50.1 \langle \mu \rangle / V^{3/4}$ [26]. It has been reported that the dipole moment ratio of PDMT, $\langle \mu^2 \rangle / (nm^2)$ is 0.61 [2], where n is the number of skeletal bonds and m^2 the average of skeletal bond moments, m , calculated from $m^2 = 1/4(2m_{C-C}^2 + 2m_{C-S}^2)$. By using $m_{C-C} = 0 \text{ D}$ and $m_{C-S} = 1.21 \text{ D}$, a value of $\langle \mu \rangle = 1.34 \text{ D}$ is obtained and hence $\delta_p = 2.2 \text{ cal}^{1/2} \text{ cm}^{-3/2}$. The hydrogen bonding component is determined from the relationship $\delta_h = 360/V$ [24] and therefore $\delta_h = 1.9 \text{ cal}^{1/2} \text{ cm}^{-3/2}$.

The characteristic ratio obtained for PDMT is compared with that reported for poly(trimethylene sulphide) in Table 2. As can be seen, the spatial extension of PDMT is about 25% larger than that of the unsubstituted PTS. This cannot be attributed to an effect of steric repulsions of consecutive methyl pendant groups, because they are four bonds apart.

Thus, the alteration of the poly(trimethylene sulphide) dimensions resulting from the introduction of two methyl substituents in the β -position should be rationalized in terms of the stability of different conformers. Clearly the presence of these two side groups leads to a higher characteristic ratio than that exhibited by the parent poly(trimethylene sulphide). This situation is opposite to that observed in some vinyl polymers. Thus, when polyethylene, $\langle r_0^2 \rangle / (nl^2) = 7.6$ [21], and poly(1,1-dimethylethylene), $\langle r_0^2 \rangle / (nl^2) = 6.5$ [27], are compared, the conclusion is that the substitution favours the coiling of the chain. The theoretical conformational analysis indicates that the PTS conformation of minimum intramolecular energy has gauche rotational configurational state in all the bonds [28]. However, the energy differences between gauche and *trans* states are very small. The presence of dimethyl substituents in PDMT, due to nonbonded interaction between the methyl groups and the methylene separated by 3 bonds, favours the more extended *trans* conformation around the C–S bonds, while the other two C–C bonds show preference for gauche conformations [3]. Consequently, the more extended unperturbed dimension of PDMT as compared with PTS is due to a higher proportion of bonds in the higher extended *trans* conformation.

Concerning the solubility parameter, this concept, based on the geometric mean rule, can only be considered on the assumption that the energy of interaction between molecules of different kinds is the geometric average of the interaction energy between molecules of the same kind. Another limitation involves the assumption of ideal entropy of mixing which is also not valid for real polymer systems. In spite of these limitations, this concept has been extensively used for its predictive capacity and simplicity. As can be observed in Table 2, the single solubility parameter as well as each of their components are higher for PTS than for PDMT. This situation is similar to that observed in polyoxetane, PTO, and poly(3,3'-dimethyl oxetane), PDMO. The effect of the substituents on the CED is quantitatively more important in polyoxetanes than in polysulphides, especially in connection with the polar component. This is probably due to the fact that in the dimethyl derivatives there is a higher proportion of $g^\pm g^\pm$ conformations in the 2 bonds flanking the central carbon of the repeating unit. This conformation places the dipoles of the 2 consecutive carbon-heteroatom bonds in antiparallel position, cancelling their dipole moments.

Finally, intermolecular forces and chain flexibility are useful in relation to thermal properties. By comparing the two members of the polythietane series, the glass transition temperature is observed to follow the order PDMT > PTS [29, 4]. Qualitatively, the T_g of PDMT supports the fact that PDMT has a less flexible chain than PTS, as indicated by the characteristic ratio results. The different CED values in the polymers do not seem to play any important role on the location of T_g . The melting temperature of PTS is higher than that for PDMT and this result suggests a reverse dominant influence of both parameters on this thermodynamic property. It has been shown [30] that the low enthalpy of fusion is the main reason for

the low melting temperature of PDMT, while the entropy of fusion, associated with chain flexibility, is of comparatively minor importance in fixing this transition.

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