

# Solution Properties of Poly(thiocarbonates)

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## Synopsis

Poly(thiocarbonates) with alkyl side chains have been prepared, and the solution properties of these polymers were studied in different solvents. Comparison with other poly(thiocarbonate) analogues and poly(carbonates) shows that the conformational parameter ( $K_\theta$ ) and rigidity factor increase as the volume of the side chain increases. The effect of the side-chain structure on the solution properties is analyzed.

## INTRODUCTION

In a previous paper<sup>1</sup> we reported the solution properties, chain flexibility, and conformational behavior of poly(thiocarbonates) derived from bisphenol A. These polymers are a new family of amorphous polymers that present very interesting properties from fundamental and industrial points of view.<sup>2</sup> Because of their particular structure poly(thiocarbonates) show very interesting phenomena: The rigidity factor  $\sigma$  [ $\sigma = (\langle r^2 \rangle_o / \langle r^2 \rangle_{of})^{1/2}$  where  $\langle r^2 \rangle_o^{1/2}$  and  $\langle r^2 \rangle_{of}^{1/2}$  are the root-mean-square end-to-end distance for the unperturbed chain and for a chain consisting of free-bond rotation, respectively] and the conformational parameters are lower than that of the corresponding poly(carbonate) analogues. This behavior has been interpreted in terms of the different contributions to double bonds between CO—O and CS—O caused by their partial double-bond character and the difference in electronegativity between sulfur and oxygen. The calorimetric study of a series of poly(thiocarbonates) with aliphatic, aromatic, and cycloaliphatic side groups shows a marked dependence of the glass transition temperature  $T_g$  on the side chain structure.<sup>3</sup> The bulkiness, flexibility, and polarity of the pendant group attached to polymer main chain exert important influence in the magnitude of  $T_g$ . When comparing the magnitude of  $T_g$  for this series of poly(thiocarbonates) with the corresponding poly(carbonates) analogues, a general decrease in  $T_g$  values is observed.<sup>3</sup> If we take into account that  $T_g$  represents the onset of long-range cooperative chain motion in the solid polymer sample, we can expect that the conformational parameters and chain flexibility should reflect this behavior from dilute solution measurements.

The aim of this work is the comparative study of the solution properties of a series of poly(thiocarbonates) with different side-chain structures. Described here are the solution properties in several solvents and chain flexibility of poly[oxythiocarbonyloxy-1,4-phenylene-2,2-butyl-1,4-phenylene] (PMET) and poly[oxythiocarbonyloxy-1,4-phenylene-(4-methyl)-2,2-pentyl-1,4-phenylene] (PMiBT), and a comparison of these properties with those of

poly(thiocarbonates) (PPhTC) and poly(carbonates) (PPhC) derived from bisphenol A previously described.<sup>1</sup>

## EXPERIMENTAL

### Polymer Preparation

Poly[oxythiocarbonyloxy-1,4-phenylene-2,2-butyl-1,4-phenylene] (PMET) was obtained from 2,2-*bis*(4-hydroxyphenyl)butane and thiophosgene under phase transfer conditions, using tetrabutylammonium bromide as catalyst and dichloromethane as solvent.<sup>4</sup>

Poly[oxythiocarbonyloxy-1,4-phenylene-(4-methyl-2,2-pentyl-1,4-phenylene)] (PMiBT) was synthesized in the same way, starting from 2,2-*bis*(4-hydroxyphenyl)-4-methylpentane.

### Intrinsic Viscosity Measurements

Intrinsic viscosity  $[\eta]$  measurements at  $298 \pm 0.02$  K were performed by using a Desreux-Bischoff<sup>5</sup> dilution viscometer in tetrahydrofuran (THF), dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), dioxane, chloroform ( $\text{CHCl}_3$ ), and one binary mixture (chloroform/cyclohexane). The kinetic energy correction was not necessary for the conditions used.

### Molecular Weight Determination

The weight-average molecular weights ( $\bar{M}_w$ ) of the fractions were determined by size exclusion chromatography (SEC), using a Perkin-Elmer high-performance liquid chromatograph (HPLC) equipped with a 6000-psi pump, a Perkin-Elmer differential refractometer model LC-25, and an injector of 175  $\mu\text{L}$ . Three Waters Associated UltraStyragel<sup>TM</sup> columns ( $10^3$  Å,  $10^4$  Å,  $10^5$  Å) in series were used. For samples of very low molecular weight, a Shodex A-803 column was used.

Samples were eluted with THF and the flow rate was 1.0 mL/min. The columns were first calibrated with standard polystyrene samples of narrow molecular weight distribution.

A Knauer Model 11.00 digital vapor pressure osmometer equipped with a universal thermistor probe was used for determination of number-average molecular weight ( $\bar{M}_n$ ) in chlorobenzene solutions at  $333 \pm 0.001$  K.

### Calorimetric Measurements

$T_g$  measurements were performed with a Perkin-Elmer differential calorimeter model DSC-1B with heating rates between  $16^\circ\text{C}/\text{min}$  and  $32^\circ\text{C}/\text{min}$  under  $\text{N}_2$ . Regular calibration of the instrument was carried out using metal standards.

Before measuring the  $T_g$ , all samples were first heated to the upper limit (500 K) and quenched to the starting temperature in order to minimize differences in thermal history. The glass transition was located as baseline shift on the thermogram and  $T_g$  was estimated from the point of intersection of the sloping portion of the curve resulting from the baseline shift.<sup>3</sup>

TABLE I  
Solvents and Nonsolvents for PMET and PMiBT and the Solubility  
Parameters for Different Media

Solvent	$\delta^a$ (cal/cm <sup>3</sup> ) <sup>1/2</sup>	Solubility	
		PMET	PMiBT
Hydrocarbon solvents			
<i>n</i> -Hexane	7.3	i	i
Cyclohexane	8.2	i	i
Toluene	8.9	s	s
Benzene	9.2	s	s
Chlorinated hydrocarbons			
Carbon tetrachloride	8.6	s	s
Chloroform	9.3	s	s
Chlorobenzene	9.5	s	s
Dichloromethane	9.7	s	s
<i>O</i> -Dichlorobenzene	10.0	s	s
Dichloroethane	10.2	s	s
Oxygenated solvents			
Tetrahydrofuran	9.1	s	s
Acetone	9.9	i	i
1,4-Dioxane	9.9	s	s
Dimethylformamide	12.1	s	s
Methanol	14.5	i	i

<sup>a</sup> From Ref. 6.

Abbreviation: s: soluble; i: insoluble.

### Solubility and Fractionation of Polymers

The solubility of poly(thiocarbonates) was tested in various organic solvents at room temperature (see Table I). Polymers were fractionated using chloroform as solvent and methanol as nonsolvent. Some fractions were chosen for this study.

### RESULTS AND DISCUSSION

Table I lists the solvents and nonsolvents for PMET and PMiBT and the solubility parameters  $\delta$  for different media. These polymers show a more extended range of solubilities than the corresponding methyl derivative, namely, (PPhTC).<sup>1</sup> From Table I we have chosen four single solvents: dioxane, THF, chloroform, and dichloromethane, and one binary mixture, cyclohexane-chloroform, for the study of the dilute solution properties of poly(thiocarbonates). These solvents were selected to compare the solution properties of these polymers with that of the first member of the series previously described.<sup>1</sup> Table II summarizes the  $[\eta]$  values,  $\bar{M}_n$  (determined by VPO),  $\bar{M}_w$  (determined by multiplying  $\bar{M}_n$  from VPO by  $\bar{M}_w/\bar{M}_n$  from SEC).

The polydispersity indexes of the fractions determined by SEC are also summarized in Table II. We have calculated the polydispersity index of the fractions taking for  $\bar{M}_w$  and  $\bar{M}_n$  the values obtained by SEC and osmometry.

From these results we have determined the Mark-Houwink-Sakurada (MHS) equations at 298 K in the four solvents studied. Figure 1 shows the double

TABLE II  
 Intrinsic Viscosity  $[\eta]$ , Weight-Average Molecular Weight  $\bar{M}_w$  (SEC), and Number-Average  
 Molecular Weight  $\bar{M}_n$  for Poly(thiocarbonates) PMET and PMIBT

	F <sub>1</sub>	F <sub>2</sub>	F <sub>3</sub>	[ $\eta$ ] dL/g of fractions				F <sub>7</sub>
				F <sub>4</sub>	F <sub>5</sub>	F <sub>6</sub>		
<b>PMET</b>								
Dioxane	0.38 <sub>6</sub>	0.29 <sub>6</sub>	0.23	0.17	0.13	—	—	—
Dichloromethane	0.32	0.27	0.22	0.15 <sub>5</sub>	0.12 <sub>5</sub>	0.11	—	—
THF	0.31 <sub>5</sub>	0.26 <sub>5</sub>	0.21	0.15	0.12 <sub>5</sub>	0.11	—	—
Chloroform	0.31	0.25	0.20 <sub>5</sub>	0.15	0.12	0.10 <sub>5</sub>	—	—
Chloroform/Cyclohexane (76.5/23.5 by vol) ( $\theta$ )	0.19	0.17 <sub>5</sub>	0.14 <sub>8</sub>	—	0.08 <sub>3</sub>	—	—	—
$\bar{M}_w \times 10^{-4}$	2.40	2.20	1.40	0.80	0.54	0.51	—	—
$\bar{M}_n \times 10^{-4}$	1.78	1.41	1.00	0.63	0.45	0.40	—	—
$\bar{M}_w/\bar{M}_n$	1.35	1.56	1.40	1.11	1.20	1.28	—	—
<b>PMIBT</b>								
Dioxane	0.51	0.35 <sub>5</sub>	0.30	—	—	0.16 <sub>5</sub>	—	0.14 <sub>5</sub>
Dichloromethane	0.51	0.37	0.31	0.25	0.19 <sub>5</sub>	—	—	0.14
THF	0.61 <sub>5</sub>	0.41 <sub>5</sub>	0.35 <sub>5</sub>	—	0.21	0.18 <sub>5</sub>	—	0.16 <sub>5</sub>
Chloroform	0.58	0.40	0.33 <sub>5</sub>	—	0.20	0.18	—	0.16
Chloroform/cyclohexane (19.95/80.05 by vol) ( $\theta$ )	—	0.26 <sub>7</sub>	—	0.19 <sub>7</sub>	0.15 <sub>7</sub>	0.14	—	0.12 <sub>9</sub>
$\bar{M}_w \times 10^{-4}$	3.50	2.00	1.55	1.04	0.70	0.54	—	0.47
$\bar{M}_n \times 10^{-4}$	2.82	1.58	1.26	0.89	0.63	0.50	—	0.40
$\bar{M}_w/\bar{M}_n$	1.24	1.27	1.23	1.17	1.11	1.08	—	1.18

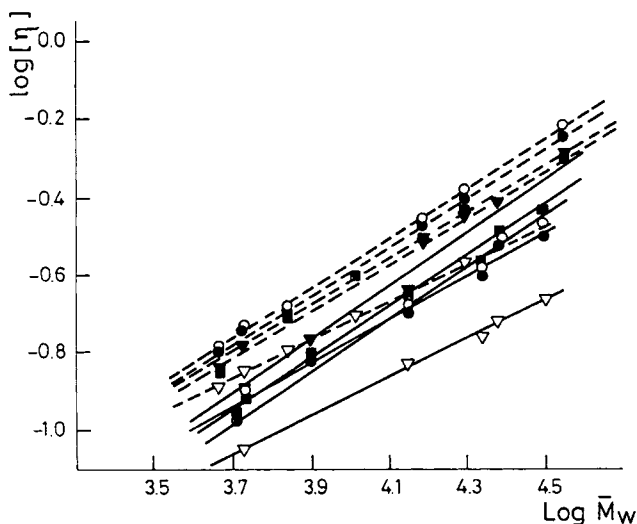


Fig. 1. Intrinsic viscosity-molecular weight relation for PMET (—) and PMiBT (---) in: THF (○);  $\text{CH}_2\text{Cl}_2$  (■);  $\text{CHCl}_3$  (●); dioxane (▼) and chloroform/cyclohexane (▽) (theta condition).

logarithmic plot of  $[\eta]$  and  $\bar{M}_w$  for PMET and PMiBT in dioxane, dichloromethane, THF, chloroform, and one binary solvent cyclohexane/chloroform ( $\theta$  condition). Good straight lines are obtained, from which the  $K_\alpha$  and  $\alpha$  parameters as intercept and slope are determined.

Table III summarizes the MHS constants,  $K_\alpha$  and  $\alpha$ , obtained for these polymers in different media at 298 K and the corresponding values for PPhTC reported previously.<sup>1</sup>

The  $\alpha$  exponent in the poor binary solvent chloroform/cyclohexane (76.5/23.5 by volume for PMET and 19.95/80.05 by volume for PMiBT) at 298 K ( $\theta$  condition) is 0.50 as is expected for theta condition. According to the  $\alpha$  values summarized in Table II, THF is the best solvent for PPhTC and PMiBT and dioxane for PMET, although the solvents studied here have approximately the same strength for the three polymers.

To evaluate the dimensions of these poly(thiocarbonates) we have determined the conformational parameter  $K_\theta$  by using the Stockmayer-Fixman theory.<sup>7</sup> The short-range interaction parameter  $K_\theta$  is related to the unperturbed dimensions  $\langle r^2 \rangle_o^{1/2}$  by the well known relation:  $K_\theta = (\langle r^2 \rangle_o / M)^{3/2} = [\eta]_\theta / M^{1/2}$ , where  $[\eta]_\theta$  is the intrinsic viscosity under  $\theta$  conditions. This parameter can be obtained from  $[\eta]$  data by the Stockmayer-Fixman<sup>7</sup> equation

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

where  $[\eta]$  is the intrinsic viscosity in good and theta solvents, and  $\bar{M}_w$  is the weight-average molecular weight,  $\Phi_o$  is the Flory constant, and  $B$  the long-range interaction parameter. For the  $\Phi_o$  Flory constant, we have used two values,  $\Phi_o = 2.2 \times 10^{21}$  (cgs) and  $2.5 \times 10^{21}$  (cgs). The first value is that suggested for sharply fractionated polymers<sup>8</sup> and is the value used for

TABLE III  
Mark-Houwink-Sakurada Constants for PPhTC, PMET and PMiBT  
in Different Solvents at 298 K

Solvent	Polymer	$K_{\alpha} \times 10^4$	$\alpha$	$B \times 10^{28}$ ( $\text{cm}^3 \text{mol}^2 \text{g}^{-2}$ )	Ref.
THF	PPhTC	3.89	0.67	—	1
	PMET	6.88	0.60	38.10	a
	PMiBT	7.33	0.64	60.38	a
$\text{CH}_2\text{Cl}_2$	PPhTC	10.70	0.55	—	1
	PMET	5.57	0.62	42.55	a
	PMiBT	7.39	0.63	42.55	a
$\text{CHCl}_3$	PPhTC	8.32	0.59	—	1
	PMET	6.0	0.61	36.36	a
	PMiBT	7.83	0.63	51.95	a
Dioxane	PPhTC	7.24	0.60	—	1
	PMET	4.58	0.65	58.82	a
	PMiBT	8.78	0.60	34.48	a
$\text{CH}/\text{CHCl}_3^b$ ( $\sim \theta$ )	PPhTC	25.1	0.50	—	1
	PMET	13.0	0.50	0.0	a
	PMiBT	19.0	0.50	0.0	a

<sup>a</sup>This work.

<sup>b</sup>The mixture composition  $\text{CH}/\text{CHCl}_3$  is 76.5/23.5 by vol for PPhTC and PMET and 19.95/80.05 by vol for PMiBT, and  $[\eta]$  in  $\text{dL g}^{-1}$ .

poly(carbonates) of similar structure in the literature;<sup>10</sup> the second, is that considered as the best experimental value established from viscosity and light scattering measurements.<sup>10</sup>

Table III also summarizes the values of the thermodynamic interaction parameter  $B$ , obtained from Stockmayer-Fixman theory. The values of conformational parameter  $K_{\theta}$  (corrected by polymolecularity) evaluated from these plots are summarized in Table IV. In this table we also list the  $K_{\theta}$  values obtained in theta solvents. The polymolecularity correction factor was calculated using the Sutter-Kuppel<sup>11</sup> and Bareiss<sup>6</sup> methods assuming a Schulz-Zimm<sup>12,13</sup> distribution for each fraction. The values of  $K_{\theta}$  so obtained are rather similar to that obtained from the MHS equation in theta condition (see Table IV), nevertheless, the uncertainty in the Stockmayer-Fixman plots is not eliminated.

The values of the  $B$  parameter are in good agreement with the  $\alpha$  values obtained from MHS equation, that is, in the best solvent  $B$  and  $\alpha$  are higher than in the poor solvent. From these results it is possible to conclude that the behavior of PMET is normal in the sense that these polymers behave as linear flexible polymer.<sup>14</sup>

Following the same treatment of the data for PPhTC<sup>1</sup> we have determined the steric hindrance parameter  $\sigma$  which is defined by the relation:

$$\sigma = \left( \langle r^2 \rangle_o / \langle r^2 \rangle_{of} \right)^{1/2} \quad (2)$$

where  $\langle r^2 \rangle_{of}$  is the mean-square end-to-end distance of the freely rotating chain. Therefore,  $\sigma$  can be evaluated from the experimentally determined

$(\langle r^2 \rangle_o/M)^{1/2}$  and the theoretically calculated  $(\langle r^2 \rangle_{of}/M)^{1/2}$ . The value of  $\langle r^2 \rangle_{of}$  can be evaluated from the basic structure of the chain. For poly(carbonates) and poly(thiocarbonates) with four bonds per repeat unit,  $\langle r^2 \rangle_{of}$  should be given by<sup>1,9</sup>

$$\frac{\langle r^2 \rangle_{of}}{M} = (4l^2/M_u)[(1 - \cos \theta)/(1 + \cos \theta)] \quad (3)$$

where  $l$  and  $\theta$  are average values for bond length and valence angle, respectively, and  $M$  is the molecular weight of the repeat unit. Therefore,  $\sigma$  can be expressed by<sup>1,8</sup>

$$\sigma = (K_\theta/\phi)^{1/3} \{ (M_u/4l^2)[(1 + \cos \theta)/(1 - \cos \theta)] \}^{1/2} \quad (4)$$

From these equations we calculate  $\sigma$  for poly(thiocarbonates). These calculated values and those for poly(carbonates) and poly(thiocarbonates) derived from bisphenol A, reported in the literature,<sup>1,10,15</sup> are summarized in Table IV.

The  $K_\theta$  values reported in Table IV, have been obtained from the Stockmayer-Fixman equation,<sup>7</sup> in good solvents, in theta condition, and from the Kamide-Moore (KM)<sup>16</sup> relationship which is expressed by:

$$\ln \left[ 2 \{ (\alpha - 0.5)^{-1} - 2 \}^{-1} + 1 \right] - \ln K_\alpha = (\alpha - 0.5) \ln M_o - K_\theta \quad (5)$$

where  $K_\alpha$  and  $\alpha$  are the MHS constants and  $M_o$  is the molecular weight of the monomer unit. We have used the  $K_\alpha$  and  $\alpha$  values of Table III. Figure 2 shows the Kamide-Moore<sup>16</sup> plots and the extrapolation to  $\alpha = 0.5$ .

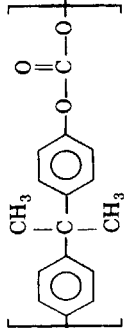
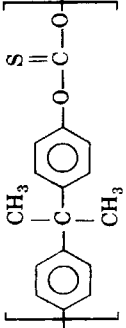
From this extrapolation we obtain  $K_\theta = 13.2 \times 10^{-2}$  and  $K_\theta = 18.0 \times 10^{-2}$  ( $\text{cm}^3 \text{g}^{-3/2} \text{mol}^{1/2}$ ) for PMET and PMiBT, respectively, with polymolecularity correction. These  $K_\theta$  values are rather similar to those obtained from the Stockmayer-Fixman plot in good solvents and in theta condition. By using the  $K_\theta$  value obtained from SF and KM representation, we have determined the steric factor  $\sigma$  (see Table IV). The  $K_\theta$  values so obtained are close to that of PPhTC.<sup>1</sup> These results seem to indicate that poly(thiocarbonates) behave as flexible polymers. It is interesting to note that  $K_\theta$  and  $\sigma$  increase as the volume of the side chain structure of the poly(thiocarbonates) increases.

The values of the steric factor  $\sigma$  are similar to that observed for aromatic heterocyclic polymer.<sup>6,17</sup> However, one may also use the term  $K_\theta M_u^{3/2}$  to compare the chain rigidity. Table IV shows these values for the different polymers studied. We can see that this term ( $K_\theta M_u^{3/2}$ ) increases in the same sense as  $\sigma$ . It has been pointed out<sup>18</sup> that the best parameter to compare the conformational structure of polymers is the characteristic ratio  $C_\infty$ .<sup>18</sup> This parameter has been calculated from experimental values of  $\langle r^2 \rangle_o/M$  by means of

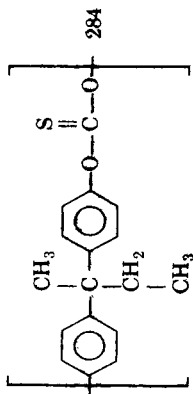
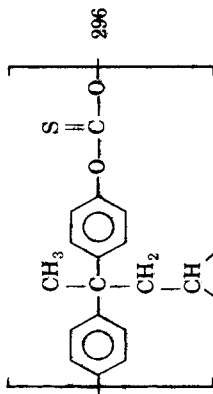
$$C_\infty = (\langle r^2 \rangle_o/M)_\infty (M_b/l^2) \quad (6)$$

where  $M_b$  is the mean molecular weight per skeletal bond. The results are also listed in Table IV. In the previous paper<sup>1</sup> we have reported that poly(thio-

TABLE IV  
 Conformational Parameters  $K_\theta$ , Unperturbed Dimensions, Flexibility Factor  $\sigma$ , and  $K_\theta M_u^{3/2}$ , Characteristic Ratio  $C_\infty$ , and  $T_g$   
 for Poly(carbonate) (PPhC) and Poly(thiocarbonates), PPhTC, PMET, and PMiBT

	$M_u$	$K_\theta \times 10^{-2}$ , $\text{cm}^3 \text{g}^{-3/2} \text{mol}^{1/2}$	$K_\theta M_u^{3/2}$	$(\langle r^2 \rangle_0 / M)^{1/2}$ , Å	$(\langle r^2 \rangle_0 / M)^{1/2}$ , Å	$\sigma$	$C_\infty$	$T_g$ , K	Ref.
 <p style="text-align: center;">I</p>	254	18.0	7.29	0.683	0.943 <sup>e</sup> 0.896 <sup>f</sup>	1.38 <sup>e</sup> 1.31 <sup>f</sup>	4.53 <sup>e</sup> 4.10 <sup>f</sup>	422 429.5	(15, 18) (1)
	 <p style="text-align: center;">II</p>	270	13.2 <sup>b</sup> 17.1 <sup>c</sup>	5.86 <sup>b</sup> 5.59 <sup>c</sup>	0.673	0.843 <sup>e</sup> 0.808 <sup>f</sup> 0.919 <sup>e</sup> 0.881 <sup>f</sup>	1.25 <sup>e</sup> 1.20 <sup>f</sup> 1.37 <sup>e</sup> 1.31 <sup>f</sup>	3.84 <sup>e</sup> 3.53 <sup>f</sup> 4.57 <sup>e</sup> 4.19 <sup>f</sup>	429.5



 <p style="text-align: center;">III</p>	284	12.7 <sup>b</sup>	6.08 <sup>b</sup>	0.656	0.833 <sup>e</sup>	1.27 <sup>e</sup>	3.94 <sup>e</sup>	375.0	ε
		13.2 <sup>c</sup>	6.32 <sup>c</sup>		0.798 <sup>f</sup>	1.22 <sup>f</sup>	3.62 <sup>f</sup>		
		13.4 <sup>d</sup>	6.41 <sup>d</sup>		0.843 <sup>e</sup>	1.29 <sup>e</sup>	4.04 <sup>e</sup>		
 <p style="text-align: center;">IV</p>	296	19.6 <sup>b,d</sup>	9.98 <sup>b</sup>	0.643	0.962 <sup>e</sup>	1.59 <sup>e</sup>	5.48 <sup>e</sup>	401	ε
		18.0 <sup>c</sup>	9.17 <sup>c</sup>		0.922 <sup>f</sup>	1.43 <sup>f</sup>	5.03 <sup>f</sup>		
					0.935 <sup>e</sup>	1.45 <sup>e</sup>	5.18 <sup>e</sup>		
					0.896 <sup>f</sup>	1.39 <sup>f</sup>	4.76 <sup>f</sup>		

<sup>a</sup>With polymolecularity correction. 6, 11, 12

<sup>b</sup>From Stockmayer-Fixman.

<sup>c</sup>From Kamide-Moore.

<sup>d</sup>From data in theta solvents.

<sup>e</sup>Calculated with  $\phi_0 = 2.2 \times 10^{21}$  (cgs).

<sup>f</sup>Calculated with  $\phi_0 = 2.5 \times 10^{21}$  (cgs).

<sup>g</sup>This work.

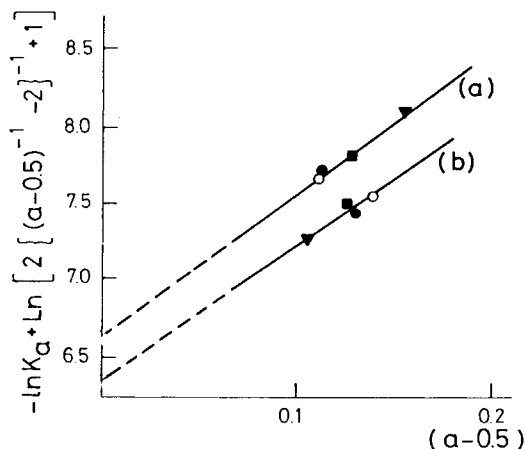


Fig. 2. Kamide-Moore plot according to eq. (5) for PMET and PMiBT in various solvents: THF (○); CH<sub>2</sub>Cl<sub>2</sub> (■); CHCl<sub>3</sub> (●); dioxane (▼) and chloroform/cyclohexane (▽) (theta condition).

carbonates) are more flexible than poly(carbonates) and we have explained this behavior taking into account the differences because of the introduction of sulfur instead of oxygen in the polymer chain. According to Table IV the structures II and III are more flexible than the corresponding poly(carbonate), but structure IV shows a larger rigidity than the other members of the series. These results agree with those obtained in the solid state, where the  $T_g$  values of several poly(thiocarbonates) are noticeably affected by the differences in the side chain structure,<sup>3</sup> that is,  $T_g$  increases as the volume of the side chain increases and decreases as spacer groups are inserted in the side chain.

Following the same procedure as that reported for PPhTC,<sup>1</sup> we have determined  $\sigma$  by using Eq. (2). Therefore the values of  $\sigma$  were calculated considering  $\bar{l} = 4.19$  Å and  $\theta = 68^\circ$ .<sup>15</sup> These values were the average of the four bond lengths and angles of the repeat unit, respectively.<sup>15</sup> It is interesting to note that in the calculation of the free rotation dimensions for these kinds of polymers, it is necessary to take into account that the conformation of ester groups are planar and preponderantly *trans*. Also the CO—O bond presents a partial double-bond character, which is manifested by a shortening of these bonds from 1.44 (or 1.43) to 1.3 Å in the case of the ester.<sup>10,18</sup>

Our results, dealing with the flexibility of poly(thiocarbonates) are in good agreement with those obtained from  $T_g$  measurements for poly(thiocarbonates).<sup>3,6</sup> We always found that poly(thiocarbonates) show a slight decrease in flexibility (see  $\sigma$  and  $C_\infty$  values in Table IV). This effect can be explained taking into account the differences in electronegativity between sulfur and oxygen. This behavior is manifested as a lower contribution to the double-bond in case of CS—O as compared to CO—O. However, the small values of  $\sigma$  are in good agreement with that obtained for poly(ethylene terephthalate). This can be interpreted as a reduction of the hindrance to internal rotation because of the introduction of aromatic rings in the backbone.<sup>19</sup>

We have determined the characteristic ratio  $C_\infty$  to verify the experimental results dealing with the polymer structure. For this reason we have calculated  $C_\infty$  from intrinsic viscosity data in good solvents and used the  $K_\theta$  values listed in Table IV.

These polymers, being polycondensates, contain functional groups —OCO— along the chain; because of the partial double bond character of these groups,<sup>18</sup> they can exert two opposing effects if they are incorporated into a polymethylene chain. Owing to their length and/or stiffness, they make the chain more extended (Effect I). At the same time they reduce the hindrance to rotation about the nearby bonds (Effect II). As the latter effect predominates, the result is a decrease of the unperturbed dimensions.<sup>20</sup> From  $K_\theta$  values listed in Table IV we have determined the  $p$  parameter defined by Bohdanecky and Simek<sup>20</sup> as the fraction of bonds which are expected to participate in Effects I and II.

The  $p$  values obtained for all poly(thiocarbonates) are about 0.33. These values fit well with the theoretical curve of  $p$  vs.  $C_\infty$  giving a lower value than other aromatic polymers showing a more flexible chain.<sup>1,7,16</sup>

Finally, we can conclude that poly(thiocarbonates) are more flexible than the corresponding poly(carbonates) analogues, and the introduction of different side chains attached to the main chain affects the flexibility of the polymer.

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