Eur. Polym. J. Vol. 19, No. 10/11, pp. 1075–1079, 1983
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0014-3057/83 $3.00 + 0.00

OPTICALLY ACTIVE VINYL POLYMERS—XXVI

THE UNPERTURBED DIMENSIONS OF POLY-(S)-4-METHYL-1-HEXENE AND POLY-4-METHYL-1-PENTENE

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Abstract—The unperturbed dimensions of isotactic, optically active poly-(S)-4-methyl-1-hexene and isotactic poly-4-methyl-1-pentene were estimated from viscosity data. The characteristic ratio $\bar{h}_0^2/nl^2$ for the optically active polymer is remarkably higher than that of the structurally analogous poly-4-methyl-1-pentene. The results support, at least qualitatively, the previously outlined model for the conformation of isotactic, optically active poly-α-olefin chains in solution.

1. INTRODUCTION

A preliminary evaluation of the conformational characteristics of branched poly-α-olefins on the basis of statistical mechanics of chain molecules [1] as described by Flory [2], Volkenstein [3] and Birshstein and Ptitsyn [4] predicted surprisingly large differences between the dimensions of isotactic, optically active poly-(S)-4-methyl-1-hexene (PS4MH)* and those of the structurally analogue, isotactic, optically inactive poly-4-methyl-1-pentene (P4MP)*.

The characteristic ratio $\bar{h}_0^2/nl^2$ and its temperature coefficient would be much higher for the optically active polymer than for the optically inactive one [5]. Thus the macromolecular chain of isotactic PS4MH in the unperturbed state is considered to have left- and right-handed helical sections [6]. The helical sections of opposite senses would be in a diastereometric relationship to each other, due to inherent asymmetry of the helical conformations and to the asymmetry of the side-chains. The difference in conformational energy of a monomeric unit containing in the lateral chain an asymmetric carbon atom with (S) absolute configuration inserted in a left- or right-handed section is expected to lead to left-handed sections of greater average length with respect to the average length of right-handed sections. In the P4MP which does not contain asymmetric carbon atoms in the lateral chains, the left- and right-handed helical sections are of course in enantiomeric relationship to each other and their average lengths should be equal and smaller compared to the left-handed helical sections in PS4MH. The above difference should generate smaller average chain dimensions in P4MP than in PS4MH [5].

The aim of this work is the experimental investigation of the unperturbed dimensions of isotactic PS4MH and P4MP in order to test qualitatively the validity of the proposed model [6]. The experimental results could also be very useful for further improvement of the described model, leading to a better understanding of the conformational properties of these poly-α-olefins in solution.

2. CHARACTERIZATION OF THE POLYMERS

In a previous paper [7] the syntheses and the fractionation of PS4MH and P4MP according to stereoregularity and molecular weight by extraction with boiling solvents and by fractional precipitation from a solvent–non solvent system were reported. The polymer fractions were characterized by $\langle M \rangle_n$ and $\langle M \rangle_w$ and the intrinsic viscosities were measured in several solvents. Although the molecular weight distribution width decreased on fractionation, the best fractions remained polydisperse, $\langle M \rangle_w/\langle M \rangle_n$ ranging from 2 to 6. Gel permeation chromatography was used for further qualitative investigation of the molecular weight distributions of the polymer-fractions and it was concluded that the fractions had unimodal molecular weight distributions and most of them conformed well to the logarithmic normal distribution [7]. The degree of stereoregularity of the polymers was evaluated by i.r. and ^{13}C-NMR spectroscopy [8].

The meso dyad content [8] of all the fractions for the present investigation exceeded 95%. The constants K and a_η of the Mark–Houwink equation (1),

$$[\eta] = \mathrm{K} \cdot M^{a_\eta} \tag{1}$$

(Table 1), were calculated for PS4MH in methylcyclopentane at 0°, methylcyclohexane at 60°, *o*-dichlorobenzene at 133°, α-chloronaphthalene at 165° and α-methoxynapththalene at 233°. For P4MP the following solvents were used: methylcyclohexane at 60°, chlorobenzene at 100° and α-chloronaphthalene at 205°. The solution properties [7] of the fractions used in the present investigation are shown in Tables 2 and 3.

Dedicated to Professor Dr Oto Wichterle on the occasion of his 70th birthday.

*Systematic nomenclature: PS4MH = poly[(S)-1-(2-methylbutyl)ethylene] and P4MP = poly[1-isobutylethylene].

Table 1. Constants of the Mark–Houwink equation for PS4MH and P4MP in various solvents

Polymer	Solvent	T (°C)	K (dl/g)	a_η
PS4MH	Methylcyclopentane	0	$7.73 \cdot 10^{-6}$	0.93
PS4MH	Methylcyclohexane	60	$1.35 \cdot 10^{-5}$	0.88
PS4MH	*o*-Dichlorobenzene	133	$1.15 \cdot 10^{-3}$	0.50
PS4MH	α-Chloronaphthalene	165	$8.88 \cdot 10^{-4}$	0.50
PS4MH	α-Methoxy-naphthalene	233	$3.36 \cdot 10^{-4}$	0.52
P4MP	Methylcyclohexane	60	$1.86 \cdot 10^{-5}$	0.85
P4MP	Chlorobenzene	100	$7.09 \cdot 10^{-5}$	0.73
P4MP	α-Chloronaphthalene	205	$2.06 \cdot 10^{-4}$	0.60

3. ATTEMPTS TO EVALUATE UNPERTURBED DIMENSIONS OF PS4MH AND P4MP

Several methods can be used to evaluate unperturbed dimensions for polymers in solution [9–14]. For the above evaluation it would be desirable to use monodisperse fractions and to perform all investigations at theta conditions. In the case of PS4MH and P4MP, this evaluation becomes particularly difficult because it has not been possible to obtain monodisperse fractions of these polymers and the evaluated degree of stereoregularity by i.r. and NMR must be considered as an average value. Macromolecules with slightly different, but very high degrees of stereoregularity, are probably present in our polymer fractions.

Theta conditions for PS4MH were determined in α-methoxynaphthalene. By plotting the precipitation temperature of the polymer solution against the volume fraction of the dissolved polymer, the maximum of the precipitation temperature curve, T_p, does not precisely correspond to the critical temperature, T_c, which is needed to obtain the theta temperature by the Schultz–Flory [15] equation (2), since T_p is usually slightly higher than T_c [16].

$$1/T_c = \frac{1}{\theta}\left(1 + \frac{1}{\psi_1}\left(\frac{1}{\sqrt{X}} + \frac{1}{\sqrt{2X}}\right)\right) \qquad (2)$$

For non-monodisperse samples, the use of T_p instead of T_c [16] results in a slight error in the estimation of the theta temperature. In the case of PS4MH in α-methoxynaphthalene, a_η was 0.52 instead of the theoretical value 0.5 at 233°. The precipitation curves and relationship between T_p^{-1} and $\bar{X}_n$ instead of X of equation 2, are shown in Figs 1 and 2, $\bar{X}_n$ being the number-average degree of polymerization.

In the cases of *o*-dichlorobenzene and α-chloronaphthalene, theta conditions were estimated by variation of the solution temperatures until by iterating $[\bar{\eta}]$ vs $\bar{M}_\eta$ (obtained by equation 1 and 11 of Ref. [34]) the parameter a_η was found to be 0.5 (Table 1).

No attempts have been made to evaluate theta conditions for P4MP. The values of α_η in different solvents at different temperatures, shown in Table 1, indicate that the solution properties of P4MP at the highest temperature is within the range of the applicability of the following equations. Evaluation of the unperturbed dimensions have been made for both PS4MH and P4MP by using intrinsic viscosity, light scattering and osmometry data and by cor-

Table 2. Molecular weight averages and solution properties of PS4M fractions

Fraction	$\langle M \rangle_w$	$\langle M \rangle_n$	$\langle M \rangle_w / \langle M \rangle_n$	I.R.-stereoregularity index*	$[\eta]$‡ (dl/g)	$[M]_D^{25}$†
PS4MH 1	$1.2 \cdot 10^7$	ND	—	0.78	>5	285
PS4MH 2	$5.5 \cdot 10^6$	ND	—	0.84	>5	303
PS4MH 3	2,000,000	297,000	6.23	0.85	4.58	285
PS4MH 4	1,610,000	236,000	6.82	0.86	3.37	310
PS4MH 5	1,100,000	207,000	5.31	0.76	2.59	280
PS4MH 6	690,000	200,000	3.45	0.75	1.81	285
PS4MH 7	435,000	126,000	3.45	0.76	1.24	285
PS4MH 8	350,000	92,900	3.76	0.75	0.97	289
PS4MH 81	770,000	207,000	3.72	0.90	2.20	295
PS4MH 82	909,000	196,000	4.64	0.85	2.26	280
PS4MH 83	588,000	204,000	2.88	0.73	1.47	271
PS4MH 84	276,000	118,000	2.34	0.67	0.79	268
PS4MH 85	136,000	67,100	2.03	0.71	0.58	269

*$D_{995\text{cm}^{-1}}/D_{964\text{cm}^{-1}}$ for PS4MH. †In benzene at 25°. ‡In methylcyclohexane at 60°.

Table 3. Molecular weight averages and solution properties of P4MP fractions

Fraction	$\langle M \rangle_w$	$\langle M \rangle_n$	$\langle M \rangle_w / \langle M \rangle_n$	I.R.-stereoregularity index*	$[\eta]$† (dl/g)
P4MP 1	660,000	92,900	7.10	0.37	1.68
P4MP 2	1,000,000	118,000	8.47	0.36	2.25
P4MP 3	1,200,000	161,000	7.45	0.35	2.36
P4MP 4	730,000	115,000	6.17	0.35	1.78
P4MP 5	435,000	61,000	7.13	0.37	1.15
P4MP 6	183,000	24,300	7.53	0.28	0.52
P4MP 3H‡	154,000	20,400	7.75	n.d.	0.45

*$D_{995\text{cm}^{-1}}/D_{917\text{cm}^{-1}}$ for P4MP. †In methylcyclohexane at 60°. ‡Polymer obtained by polymerization in H_2 atmosphere.

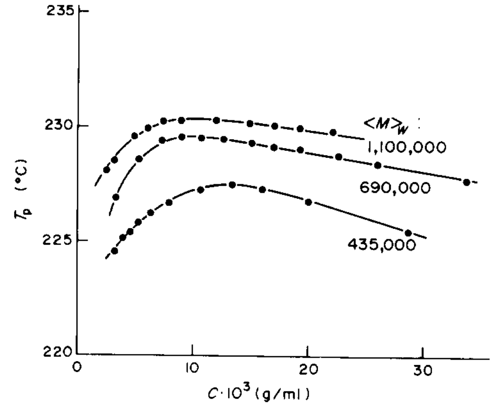

Fig. 1. Cloud point tritration of PS4MH in α-methoxynaphthalene.

recting the results for polydispersity and, when necessary, for conditions different from the theta condition, as described in the literature.

(a) *Unperturbed dimensions of PS4MH and P4MP from intrinsic viscosity measurements*

Application of Philippoff's rule (equation 3) for the intrinsic viscosity of polydisperse samples [17] with a logarithmic normal distribution [18] to the Mark–Houwink equation gives

$$[\bar{\eta}] = \sum_{1}^{i} w_i [\bar{\eta}]_i \tag{3}$$

$$[\eta]_i = \mathrm{K} \cdot M_i^a \tag{4}$$

$$[\bar{\eta}]_\theta = \mathrm{K}_\theta \cdot \langle M^{1/2} \rangle_w = \mathrm{K}_\theta \cdot \langle M \rangle_w^{1/2} \cdot \left(\frac{\langle M \rangle_w}{\langle M \rangle_n} \right)^{-1/8}$$
$$= \mathrm{K}_\theta \cdot \bar{M}_w^{1/2} \cdot q_{\mathrm{SFB}} \tag{5}$$

The polymolecularity correction factor q_{SFB} is given in Ref. [19] for the logarithmic normal distribution and the Schulz–Zimm distribution. The polymolecularity correction factor q_{SFB} decreases from 1 to ~0.9 in the range of $1 < \langle \bar{M}_w / \bar{M} \rangle_n < 2$ but mostly remains unaffected when $\langle M \rangle_w / \langle M \rangle_n > 2$.

To evaluate the unperturbed dimensions from systems not corresponding to theta conditions, equation (6) proposed by Stockmayer, Fixman [20] and Burchard has been used

$$[\eta]_i / M_i^{1/2} = \mathrm{K}_\theta + c' \cdot \mathrm{K}_\theta \cdot M_i^{1/2} \quad c' = \text{constant} \tag{6}$$

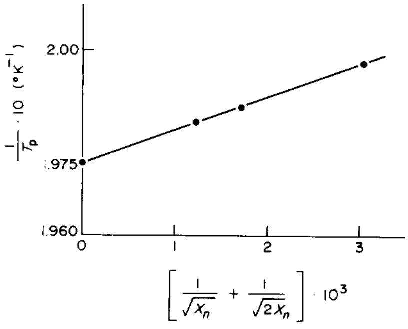

Fig. 2. Estimation of the θ-temperature of PS4MH in α-methoxynaphthalene.

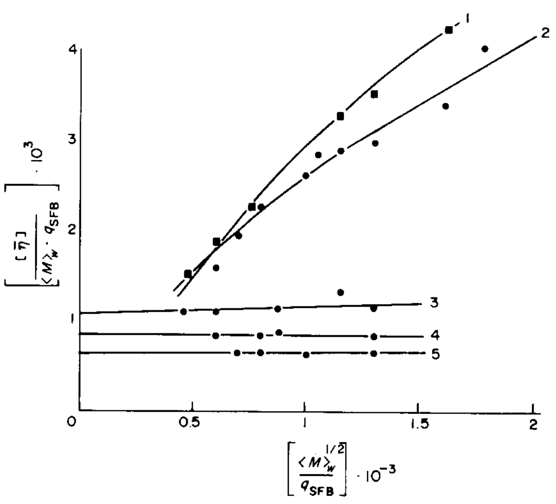

Fig. 3. The Stockmayer–Fixman–Burchard plot for PS4MH in various solvents: (1) Methylcyclopentane 0°; (2) Methylcyclohexane 60°; (3) *o*-Dichlorobenzene 133°; (4) α-Chloronaphthalene 165°; (5) α-Methoxynaphthalene 233°.

This equation may be easily extended to polymolecular systems' equation (7), the polymolecularity correction factors being the same as in equation (5). Most of the other methods proposed [12] for evaluation of the unperturbed dimensions give laborious expressions for polydisperse systems without offering any great advantage over equation (6).

$$[\bar{\eta}] / \langle M \rangle_w^{1/2} \cdot q_{\mathrm{SFB}} = \mathrm{K}_\theta + c' \cdot \mathrm{K}_\theta \cdot \langle M \rangle_w^{1/2} / q_{\mathrm{SFB}} \tag{7}$$

K_θ can be obtained (Figs 3 and 4) from equation (7). However, as shown in these Figures, equation (7) works for the polymer solutions close to or at theta conditions. In fact, as reported for other polymer solutions, in thermodynamically very good solvents [12] ($a_\eta > 0.7$), the experimental values deviate strongly from linearity required according to equation (7). This result clearly shows the limited range of application of equation (7) as of the many other methods suggested which relate the expansion factor α to the molecular weight [12].

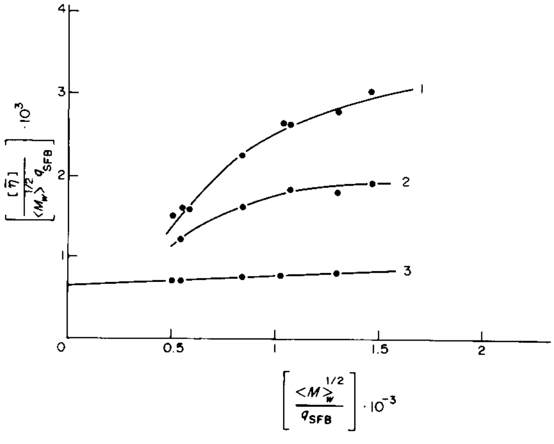

Fig. 4. The Stockmayer–Fixman–Burchard plot for P4MP in various solvents: (1) Methylcyclohexane 60°; (2) Chlorobenzene 100°; (3) α-Chloronaphthalene 205°.

Table 4. Comparison of experimental and calculated characteristic ratios of PS4MH and P4MP at various temperatures

Polymer	$\bar{h}_0^2/nl^2$ experimental values	$\bar{h}_0^2/nl^2$ calculated values [26]
PS4MH‡	11.2 (133°)	13.2 (27°)
PS4MH‡	9.4 (165°)	10.1 (127°)
PS4MH‡	8.1 (233°)	7.8 (227°)
P4MP‡	6.7 (205°)	6.7 (227°)
PS4MH*	10.8 (80°)	
P4MP†	13.2 (210°)	

*From light scattering measurements in methylcyclohexane at 80°. †From viscosity measurements, see Ref. [25]. ‡From viscosity measurements, present investigation.

The unperturbed dimensions of isotactic PS4MH and P4MP, using the K_θ values obtained by extrapolating the straight lines shown in Figs 3 and 4, are reported in Table 4. The Fox–Flory constant, ϕ, used was $2.83 \cdot 10^{23}$ (cgs).

(b) *Unperturbed dimensions from light scattering measurements*

Baumann [21] derived equation (10) using the expansion factor α and Fixman's model of the molecular weight dependence of α [20].

$$\alpha^3 - 1 = c'' M^{1/2} \quad c'' = \text{constant} \tag{9}$$

$$(\bar{r}_i^2/M_i)^{3/2} = K_\theta + c'' K_\theta \cdot \bar{M}_i^{1/2} \tag{10}$$

Equation (10), which is valid for monodisperse systems, can be extended according to Sutter and Kuppel [22] to polydisperse systems. Equation (11) contains the experimentally accessible averages $\langle \bar{r}^2 \rangle_z$ and $\langle M \rangle_w$ and the corresponding polymolecularity correction factors $q_{B,r}$ and $q_{B,M}$. In the case of the logarithmic normal distribution, the simple expressions of equations (12a) and (13a) may be obtained from the general expression of equations (12) and (13) with (16).

These correction factors are listed in Refs [19] and [23] for the logarithmic normal distribution and the Schulz–Zimm distribution.

$$(\langle \bar{r}^2 \rangle_z \cdot q_{B,r}/\langle M \rangle_w \cdot q_{B,M})^{3/2} = K_\theta^{3/2} + b \cdot (\langle M \rangle_w \cdot q_{B,M})^{1/2} \quad b = \text{const.} \tag{11}$$

$$q_{B,r} = ((\langle M^2 \rangle_z)^2/(\langle M^{3/2} \rangle_z)^{8/3} \times ((\langle M^{(3/2+3\epsilon/2)} \rangle_z)^{2/3}/\langle M^{(1+\epsilon)} \rangle_z) \tag{12}$$

$$q_{B,r} = (\langle M \rangle_w/\langle M \rangle_n)(\epsilon^2/4 + \epsilon/2 + 5/4) \tag{12a}$$

$$q_{B,M} = (\langle M^2 \rangle_z)^2/\langle M \rangle_w \cdot (\langle M^{3/2} \rangle_z)^2) \tag{13}$$

$$= (\langle M \rangle_w/\langle M \rangle_n)^{9/4} \tag{13a}$$

The value of a_r in equations (12) and (13) can be obtained from equation (14) ($a_\eta = 0.88$ for PS4MH in methylcyclohexane at 80°)

$$a_r = 1 + \epsilon = \tfrac{2}{3}(1 + a_\eta) \tag{14}$$

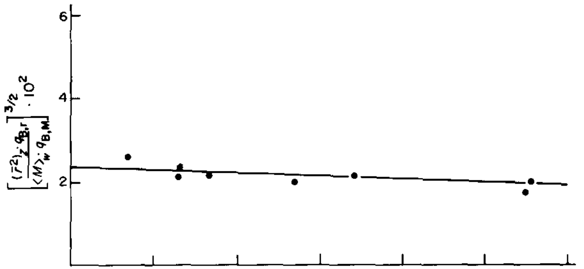

Fig. 5. The Baumann plot for PS4MH in methylcyclohexane at 80°.

The value of a_r was also calculated with the help of a least squares best fit algorithm [24] relating $\langle \bar{r}^2 \rangle_z$ to $\langle M^{a_r} \rangle_z$ (equations 15 and 16).

$$\langle \bar{r}^2 \rangle_z = K_r \cdot \langle M^{a_r} \rangle_z^{2_r} \tag{15}$$

$$\langle M^{a_r} \rangle = \langle M \rangle_w^{[(a_r^2 + 3a_r)/2]} \cdot \langle M \rangle_n^{-[(a_r^2 + a_r)/2]} \tag{16}$$

A value of $a_r = 0.96$ was obtained in this way. The experimental results of the light scattering measurements of PS4MH in methylcyclohexane are shown in Fig. 5. The characteristic ratio $\bar{h}_0^2/nl^2$ for PS4MH in methylcyclohexane at 80° was found to be 10.8. We believe that the value for $\bar{h}_0^2/nl^2$ obtained by this method is less accurate than those obtained by the viscosity method, since the $\bar{r}_z^2$ averages are used. The differences in the values of a_r as estimated by equation (14) or (15) and (16) introduce inaccuracy into the correction factors $q_{B,M}$ and $q_{B,r}$. This fact is shown in the slope of the straight line in Fig. 5 which is expected to be positive for a polymer in a good solvent and which is close to zero in the experimental results.

4. COMPARISON OF THE UNPERTURBED DIMENSIONS OF DIFFERENT POLY-α-OLEFINS

Table 4 shows some experimental values of the unperturbed dimensions of poly-α-olefins with branched side-chains and Fig. 6 shows these values as a function of the temperature. For comparison with our results, some published results are recalculated by

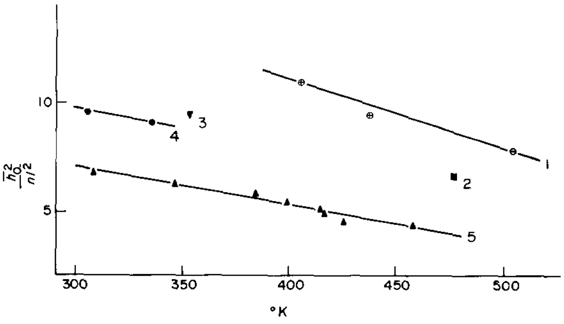

Fig. 6. The characteristic ratios of different poly-α-olefins vs temperature: (1) PS4MH in chlorobenzene 133° (⊕), α-chloronaphthalene 165° (⊗) and α-methoxynaphthalene 233° (⊖); (2) P4MP in α-chloronaphthalene 205° (■); (3) Polybutene-1 (▼); (4) Polypentene-1 (●) re-calculated values from Lit. 29–31; (5) Polypropylene (▲).

using the parameter $\phi_r = 2.87 \cdot 10^{23}$ (cgs). It is evident that the characteristic ratio $\bar{h}_0^2/nl^2$ of optically active, isotactic PS4MH, obtained from the molecular weight and viscosity measurements at theta conditions, are distinctly greater than those of the optically inactive isotactic P4MP or isotactic polypentene-1, polybutene-1 and polypropylene at comparable temperatures. The results obtained by Nakajima *et al.* [25] for P4MP (see Table 4) differ greatly from those obtained in this work. The difference could be explained by the fact, that only $\langle M \rangle_n$ values were used to obtain the unperturbed dimensions and no corrections were made for polydispersity. The results for polypropylene reveal that in this particular case the tacticity of the polymer has no great influence on the unperturbed dimensions for polymers with meso-dyad contents between 50 and 98%.

DISCUSSION

It is evident that the unperturbed dimensions of the isotactic optically active PS4MH are distinctly greater than those of the optically inactive P4MP and all the other poly-α-olefins. This supports at least qualitatively the previously outlined model.

The results of very recent theoretical calculations [26] of the unperturbed dimensions of our polyolefins are included in Table 4. This type of calculation, based on Flory's statistical mechanics of chain molecules, has already been successfully applied to polypropylene [27]. The agreement between our experimental results and the theoretical calculations is very good and it will be used as the basis for a more detailed quantitative description of the conformational characteristics of isotactic poly-α-olefins in solution.

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