Unperturbed Chain Dimensions of Poly(4-methyl-pentene-1) in Theta Solvents

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ABSTRACT: The unperturbed mean-square end-to-end distance $\langle R_0^2 \rangle$ and its temperature variation $d\ln\langle R_0^2 \rangle/dT$ for isotactic poly(4-methyl-pentene-1) have been estimated from limiting viscosity data in three theta solvents, *i.e.*, diphenyl, diphenyl ether, and diphenyl methane. Measurements were made at the theta temperatures as determined from precipitation temperature measurements. The characteristic ratios, $\langle R_0^2 \rangle/nl^2$, where n is the number of bonds of length l in the main chain, evaluated by assuming $\Phi = 2.5 \times 10^{21}$, are 13.1 in diphenyl methane (at $\theta = 176.6^\circ\text{C}$), 12.7 in diphenyl (at $\theta = 194.6^\circ\text{C}$), and 13.2 in diphenyl ether (at $\theta = 210.0^\circ\text{C}$). These values lead to the temperature coefficient $d\ln\langle R_0^2 \rangle/dT \approx 0$. The results obtained were in support of the theoretical calculation reported by Abe.

KEY WORDS Poly(4-methyl-pentene-1) / Unperturbed Chain Dimensions / Precipitation Temperature / Phase Diagram /

The unperturbed chain dimension and its temperature variation for linear polyethylene and stereoregular poly- α -olefins have been theoretically investigated by Nagai,¹ Flory *et al.*,^{2,3} and Abe.⁴ Experimentally, these quantities were estimated on linear polyethylene,⁵ iso-polypropylene,⁶ iso-polybutene-1,⁷ and isopentene-1.⁸ In particular, the experimental results on iso-polypropylene reported by us⁶ were supported by Abe's theoretical results⁴ on poly- α -olefins having taken into account the effect of side chains attached to the α -carbons. The side chains of poly(4-methyl-pentene-1) (P4MP1) are larger than those of polypropylene, and thus may effect the unperturbed chain dimensions more markedly in comparison with polypropylene.

The aim of this report is to determine the unperturbed chain dimensions in several theta solvents, and to compare the experimental results with the calculations given by Abe.⁴

EXPERIMENTAL

Polymer Samples

The monomer, 4-methyl-pentene-1, purified

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through molecular sieve, was polymerized⁹ for 3 hr at 50°C with a Ziegler-Natta catalyst consisting of $\text{Al}(\text{C}_2\text{H}_5)_3/\text{TiCl}_4 = 2.6$ in *n*-heptane. The polymer obtained was extracted with boiling *n*-hexane to remove stereoirregular molecular species. About 50% of the polymer remained after the extraction. This highly isotactic residual sample was dissolved in decalin containing 100-ppm *N,N'*-di- β -naphthyl-*p*-phenyl diamine (a stabilizer to prevent chain degradation at elevated temperature). Then to obtain different molecular weights, the sample was separated into ten fractions by successive precipitations at 130°C by adding the non-solvent ethyl cellosolv. Five fractions chosen from these fractions were further purified by reprecipitation from xylene, and used for the experiments.

The isotacticity of these fractions was kindly investigated by Dr. Fujiwara of Kuraray Co. According to his estimation from NMR spectra, the isotacticity of the fractions is expected to be *ca.* 0.90-0.94.

Viscosity Measurements

The limiting viscosity numbers of the fractions were determined in decalin at 130°C , and in the three theta solvents at their theta temperatures, *i.e.*, in diphenyl methane at 176.6°C , in diphenyl

at 194.6°C, and in diphenyl ether at 210.0°C. Viscosity measurements were carried out with a modified Ubbelohde dilution viscometer manufactured by us.⁵ Decalin used as the solvent was a mixture of *cis*(70.2%)-and *trans*(29.8%)-decalin, and its density was 0.806 at 130°C. For measurements at 130°C in decalin, 100-ppm *N,N'*-di- β -naphthyl-*p*-phenyl diamine was added to the solutions. For measurements at theta temperatures, the concentration of this stabilizer in solutions was about 0.2%. Freshly prepared solutions containing the stabilizer were used for viscosity measurements so as to eliminate the possibility for chain scission in solutions at elevated temperature.

Osmotic Pressure Measurements

The number-average molecular weights of these five fractions were determined from the osmotic pressure in tetralin at 130°C. A high-speed membrane osmometer equipped with a UCF-super dense semipermeable membrane was used for the measurements. Polymer solutions in tetralin were stabilized with 0.2-% 2,6-di-*tert*-butyl-*p*-cresol to prevent chain degradation. The stabilizer was also added to the solvent side of the apparatus.

Measurements of Precipitation Temperature

Diphenyl methane, diphenyl, and diphenyl ether were used as the theta solvents. The polymer fraction was added to the diluent containing 0.5-% 2,6-di-*tert*-butyl-*p*-cresol, and the mixture was sealed in a glass tube under a nitrogen atmosphere. The contents were heated to dissolve the polymer completely, then slowly cooled down to determine the precipitation temperature T_p by observing the appearance of turbidity. The critical precipitation temperature T_c for each fraction was determined as the maximum temperature of the precipitation temperature vs. polymer concentration curve.

RESULTS AND DISCUSSION

Molecular Weight—Limiting Viscosity Number Relationship

The molecular weights obtained from the osmotic pressures and the limiting viscosity numbers in decalin at 130°C were plotted on a double logarithmic scale in Figure 1. A straight

Figure 1. Limiting viscosity number—molecular weight relationship for poly(4-methyl-pentene-1) in decalin at 130°C.

line obtained by the least-squares method leads to the equation:

$$[\eta] = 1.95 \times 10^{-4} M^{0.75}, \text{ in Decalin at } 130^\circ\text{C} \quad (1)$$

Determination of Theta Temperature

In Figures 2—4, the precipitation temperatures, T_p , are plotted against the volume fractions, v_2 , of polymer. The maximum point of the curve corresponds to the critical temperature, T_c . The reciprocal critical temperatures, $1/T_c$, were plotted against the reciprocals of the root molecular weights, $1/M^{1/2}$, for the three solvent systems in Figure 5. From this plot the theta temperatures θ for these solvent systems were determined in accordance with the well-known Flory-Schulz equation:¹⁰

$$\begin{aligned} 1/T_c &= 1/\theta(1 + b/M^{1/2}), \\ b &= (V_s/\bar{v})^{1/2}/\phi_1 \end{aligned} \quad (2)$$

Figure 2. Phase diagram for four poly(4-methyl-pentene-1) fractions in diphenyl methane. Molecular weights of A, B, C, and D are 228600, 190000, 169600, and 137400, respectively.

Figure 3. Phase diagram for four poly(4-methyl-pentene-1) fractions in diphenyl. Molecular weights of fractions are given in Figure 2.

Figure 4. Phase diagram for four poly(4-methyl-pentene-1) fractions in diphenyl ether. Molecular weights of fractions are given in Figure 2.

Figure 5. Plots of the reciprocal critical temperature against the reciprocal of the root molecular weight for poly(4-methyl-pentene-1) in diphenyl methane (A), diphenyl (B), and diphenyl ether (C).

where, V_s is the molar volume of the solvent, $\bar{v}$ the partial specific volume of the polymer, and ϕ_1 is the entropy parameter. The θ values obtained were shown in Table I, together with the results on the chain dimensions.

Limiting Viscosity Number at the Theta Temperature

The limiting viscosity numbers at the theta temperature $[\eta]_\theta$ for P4MP1 fractions in diphenyl methane (176.6°C), diphenyl (194.6°C), and diphenyl ether (210.0°C) are plotted against the molecular weight M on a double logarithmic scale in Figures 6, 7, and 8, respectively. The polymer concentration c in g/dl units was determined from the weight concentrations by

Figure 6. Double logarithmic plot of the limiting viscosity number in diphenyl methane at its theta temperature (176.6°C) against the molecular weight for poly(4-methyl-pentene-1).

Figure 7. Double logarithmic plot of the limiting viscosity number in diphenyl at its theta temperature (194.6°C) against the molecular weight for poly(4-methyl-pentene-1).

Table I. Characteristic ratios of P4MP1 in three theta solvents

Solvent	θ temp, °C	$K_\theta \times 10^3$	$\langle R_0^2 \rangle / nl^2$	$d \ln K_\theta / dT$
Diphenyl methane	176.6	1.60	13.1	$\cong 0$
Diphenyl	194.6	1.52	12.7	
Diphenyl ether	210.0	1.58	13.2

Figure 8. Double logarithmic plot of the limiting viscosity number in diphenyl ether at its theta temperature (210.0°C) against the molecular weight for poly(4-methyl-pentene-1).

using the densities of the polymer and the solvents as a function of temperature. The density of polymer as a function of temperature was taken from Rånby's results.¹¹ With respect to solvents, densities in g/ml units were determined as a function of temperature. They were: $\rho(\text{diphenyl methane}) = 1.026 - 8.18 \times 10^{-4}T$, $\rho(\text{diphenyl}) = 1.056 - 8.60 \times 10^{-4}T$, and $\rho(\text{diphenyl ether}) = 1.097 - 9.13 \times 10^{-4}T$, in which T is in °C units.

The experimental points shown in Figures 6—8 are approximately fitted by a straight line with a slope of 1/2 as predicted theoretically by

$$[\eta]_\theta = K_\theta M^{0.5} \quad (3)$$

The values of K_θ obtained were given in Table I. *Unperturbed Chain Dimension and Its Temperature Variation*

The K_θ is related to the unperturbed mean-square end-to-end distance $\langle R_0^2 \rangle$ by

$$K_\theta = \Phi [\langle R_0^2 \rangle / M]^{3/2} \quad (4)$$

where Φ is a constant. Accordingly, the characteristic ratio $\langle R_0^2 \rangle / nl^2$ is written as

$$\langle R_0^2 \rangle / nl^2 = [K_\theta / \Phi]^{2/3} M / nl^2 \quad (5)$$

in which n and l are the number of C—C bonds in a chain and the length of a C—C bond, respectively. For P4MP1, $M/n = 42$ and $l = 1.54 \text{ \AA}$. The characteristic ratio calculated by using the value $\Phi = 2.5 \times 10^{21}$ is given in Table I.

The temperature variation of the unperturbed chain dimension is given by

$$\frac{d \ln \langle R_0^2 \rangle}{dT} = \frac{2}{3} \frac{d \ln K_\theta}{dT} \quad (6)$$

From the values of K_θ for the three solvents at their theta temperatures, we obtain $d \ln \langle R_0^2 \rangle / dT \cong 0$.

The unperturbed mean-square end-to-end distance $\langle R_0^2 \rangle$ of a chain molecule composed of n C—C bonds is mathematically represented by the following equation.

$$\langle R_0^2 \rangle = nl^2 + 2 \sum_{i < j} \langle \mathbf{l}_i \cdot \mathbf{l}_j \rangle \quad (7)$$

where, $\mathbf{l}_i$ is the i th C—C bond vector, l the bond length of a C—C bond, and $\langle \mathbf{l}_i \cdot \mathbf{l}_j \rangle$ the average of the scalar product $\mathbf{l}_i \cdot \mathbf{l}_j$ over all available chain conformations.

Conformation calculations for P4MP1 were developed by Abe⁴ in his report on the unperturbed chain dimensions of poly- α -olefins, $\text{H} - [\text{CH}_2 - \text{CHR}]_{n/2} - \text{CH}_3$. By taking into consideration the effect of the side chain (—R) on the backbone chain conformations, *i.e.*, the four-bond interactions due to side chain configuration, Abe introduced the statistical weight factors τ^* and ω'' respectively for the tt and g^+g^- (or g^-g^+)-conformations (t and $g^\pm$ denote *trans* and *gauche* conformations, respectively) of the adjoining skeletal bonds $i-1$ and i joined by the C atom of the CHR residue. These factors τ^* and ω'' were normalized to unity for the stable helical conformation, and related to the conformational energies E_{τ^*} and $E_{\omega''}$ by $E_{\tau^*} = -RT \ln \tau^*$, and $E_{\omega''} = -RT \ln \omega''$, respectively. Abe assigned the following values for

polypropylene ($R=CH_3$), poly-butene-1 ($R=CH_2\cdot CH_3$), and poly(4-methyl-pentene-1) ($R=CH_2\cdot CH(CH_3)_2$).

R	E_{τ^*}/RT	$E_{\omega''}/RT$
CH_3	0	4
$CH_2\cdot CH_3$	1.4	5
$CH_2\cdot CH(CH_3)_2$	5	5

On the basis of the statistical weight matrix expressions for the stereochemical arrangements, Abe⁴ used eq 7 to carry out a Monte Carlo calculation on the unperturbed chain dimensions of a 100 monomer units P4MP1 Monte Carlo chain, which was generated in a computer as a function of stereoregularity p_r , wherein p_r de-

notes the probability of an isotactic dyad placement.

The curves obtained are reproduced in Figures 9 and 10. Our experimental value, $\langle R_0^2 \rangle / nl^2 \cong 13$, is in agreement with the theoretical value at $p_r \approx 0.94$. This value of p_r does not conflict with the isotacticity $p_r = 0.90-0.94$ estimated for our samples from NMR spectra. From Figure 10, it is pointed out that the experimentally obtained temperature variation $d \ln \langle R_0^2 \rangle / dT \cong 0$ is also supported by the calculation.

The final point to add is that P4MP1 is not dissolved in any solvent at temperatures below *ca.* 100°C, hence various measurements with solutions had to be carried out at rather high temperatures and, at the same time, in the presence of the stabilizer to prevent chain degradation. Some scatters of data points seems to have been unavoidable.

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Figure 9. Characteristic ratio against isotacticity p_r for poly(4-methyl-pentene-1). The experimentally obtained value is shown by a horizontal bar. The curve was cited from Abe's paper.⁴

Figure 10. Temperature coefficient of the characteristic ratio as a function of isotacticity for poly(4-methyl-pentene-1), cited from Abe's paper.⁴

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