Physicochemical Studies of Poly(hexene-1). III. Application of Dilute Solution Theories

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Synopsis

Experimental data on dilute solutions of poly(hexene-1), obtained from viscosity, osmometry, and light scattering in various solvents, previously reported, were treated and compared with various hydrodynamic theories of linear polymers. It was found that poly(hexene-1) can best be described by the model of Flory-Fox. Furthermore, the data were found to conform to the treatment of Kinsinger and Ballard for nonpolar polymers in the α-olefin series in the unperturbed state.

INTRODUCTION

Various dilute solution properties of poly(hexene-1) in a number of solvents were previously reported[1] by the authors on fractionated samples studied from phase equilibria, osmometry, viscometry, and light scattering. Molecular weight distribution functions were determined, Mark-Houwink relationships in good and poor solvents established, and weight-average root-mean-square end-to-end distances, $(\bar{r}^2)_w^{1/2}$, of the poly(hexene-1) fractions, corrected for polydispersity, were calculated from light scattering data.

It is the purpose of this paper to treat the experimental data obtained on poly(hexene-1) fractions previously reported by us in terms of various dilute solution theories. The unperturbed chain dimensions are estimated according to these theories both in good and theta solvents, and compared with those calculated by assuming free rotation from fixed bond length (1.54 Å) and bond angle (109.5°). Finally, the unperturbed dimensions of poly(hexene-1) are compared with those of other poly(α-olefins) in attempting to establish the effect of the pendent groups of poly(α-olefins) on the unperturbed dimensions.

EXPERIMENTAL

Experimental procedures for fractionation, osmometry, viscometry, phase equilibria, and light scattering of poly(hexene-1) were described in an earlier paper.[1]

RESULTS

Intrinsic viscosities $[\eta]$ in cyclohexane, tetrahydrofuran (THF), toluene, and phenetole, and weight-average molecular weights $\bar{M}_w$ obtained from light scattering were reported in an earlier paper.[1] Table I summarizes the

TABLE I
Molecular Weights $\bar{M}_w$ and Intrinsic Viscosities of
Poly(hexene-1) Fractions

| Frac-tion no. | $\bar{M}_w \times 10^{-4}$ | $[\eta]$, dl/g | | | | $(\alpha_\eta)_{tol}$ |
		Cyclohexane	THF	Toluene	Phenetole	
4	143	4.50	3.71	3.32	1.16	1.42
6	90.9	3.80	2.95	2.70	0.975	1.40
7	62.5	3.06	2.38	2.15	0.822	1.38
9	39.7	2.28	1.92	1.70	0.680	1.36
13	21.7	1.50	1.30	1.09	0.525	1.28
15	15.9	1.14	0.89	0.92	0.365	1.36
18	11.9	0.87	2.95	0.66	0.340	1.25
21	8.13	0.665	0.53	0.48	0.265	1.22

$[\eta]$ and $\bar{M}_w$ values for several fractions pertinent to the discussion of this paper. The following Mark-Houwink relationships were established by the method of least squares[1]:

In cyclohexane, 25°C,

$$[\eta] = 2.05 \times 10^{-4}\bar{M}_w^{0.72} \tag{1}$$

In THF, 25°C,

$$[\eta] = 2.32 \times 10^{-4}\bar{M}_w^{0.69} \tag{2}$$

In toluene, 25°C,

$$[\eta] = 2.28 \times 10^{-4}\bar{M}_w^{0.69} \tag{3}$$

In phenetole, 61.3°C,

$$[\eta]_\theta = 9.57 \times 10^{-4}\bar{M}_w^{0.5} \tag{4}$$

DISCUSSION

In our earlier paper,[1] the universal constant Φ was calculated from viscosity and light scattering data. An average value of 2.71×10^{21} was obtained, which is in good agreement with the accepted average value of 2.65×10^{21} from both experimental and theoretical calculations. The value of Φ obtained in this work establishes poly(hexene-1), in the solvents studied, as a random coil. Thus, the data can be treated in accordance with various hydrodynamic theories of linear polymers in dilute solution.

Debye and Bueche[2] introduced the pearl-necklace model in which the polymer chain may be regarded as a sequence of beads connected to each

TABLE II
Comparison of $(\bar{r}_w^2)^{1/2}$ of Poly(hexene-1) Fractions
Calculated in Accordance with Various Theories

| Fraction no. | $(r_w^2)^{1/2}$ (root-mean-square end-to-end distance in toluene at 25°C), Å | | | | |
	Experimental	Debye-Bueche	Kirkwood-Riseman	Peterlin	Flory-Fox ($\Phi = 2.65 \times 10^{21}$)
4	1192.5	1013.3	1354.2	1309.5	1222.4
6	937.4	813.3	1086.8	1044.1	981.1
7	816.3	665.3	889.1	865.8	802.6
9	610.5[a]	528.9	706.7	690.0	638.0
13	446.9	372.8	496.7	501.1	448.5
15	371.9[a]	317.7	424.5	436.6	383.3
18	310.2	276.7	339.7	377.8	306.7
21	258.5[a]	204.5	274.3	312.2	247.5

[a] Calculated from $(\bar{r}_w^2)^{1/2} = 0.56 \times \bar{M}_w^{0.54}$.

other by a string, in which hydrodynamic resistance to the flow of solvent is offered by the beads but not the string. The model assumes spherical symmetry.

Kirkwood and Riseman[3] used basically the same model as Debye and Bueche, with the added refinement that the polymer segments were no longer considered to be distributed evenly throughout the volume of the sphere, but were statistically distributed about the center of mass.

Peterlin[4] used a purely statistical coil made up of chain elements such that the orientation of one element was independent of the orientation of neighboring elements.

Flory and Fox[5,6] treated the polymer molecules as hydrodynamic equivalent spheres. They assumed that both the density distribution with respect to the center of gravity and the distribution of the end-to-end distance are Gaussian and that spherical symmetry exists.

Table II shows experimental values for $(\bar{r}_w^2)^{1/2}$ in toluene at 25°C, together with values calculated in accordance with the Flory-Fox theory using 2.65×10^{21} for Φ. Also appearing in this table are the values of $(\bar{r}_w^2)^{1/2}$ calculated from the other hydrodynamic models mentioned above. It is evident that the experimental and calculated values are in good agreement and that the Flory-Fox model appears to best represent poly(hexene-1) in toluene at 25°C.

The unperturbed chain dimension can be calculated from the perturbed one by using the relation

$$\alpha = [(\bar{r}^2)/(\bar{r}^2)_0]^{1/2} \tag{5}$$

where α is the statistical expansion factor. It is the ratio of root-mean-square (rms) end-to-end distance in a good solvent to the corresponding

TABLE III
Values of $(\bar{r}_w{}^2)_0{}^{1/2}$ and $[(\bar{r}_w{}^2)_0/\bar{M}_w]^{1/2}$ as Determined by
Light Scattering in Toluene at 25°C

Fraction no.	$\bar{M}_w \times 10^{-4a}$	$\bar{M}_n \times 10^{-4a}$	$\bar{M}_w/\bar{M}_n$	$(\bar{r}_z{}^2)_,{}^{1/2}$ Å	$(\alpha_\eta)_{tol}$	$(\bar{r}_w{}^2)_0{}^{1/2}$, Å	$[(\bar{r}_w{}^2)_0/\bar{M}_w]^{1/2} \times 10^{10}$
4	143	77.3	1.85	1440.8	1.42	839.8	70.23
6	90.9	49.35	1.84	1131.3	1.40	669.6	70.23
7	62.5	42.0	1.49	940.1	1.38	591.5	74.82
9	39.7	29.15	1.36	—	1.36	448.9	71.24
13	21.7	19.56	1.11	468.5	1.28	349.1	74.95
15	15.9	14.70	1.08	—	1.36	273.5	68.60
17	11.9	10.76	1.11	352.2	1.25	248.2	71.94
21	8.13	7.44	1.09	—	1.22	211.9	74.32
						average	72.04

[a] Experimental values from reference 1.

distance in a theta solvent. An alternate form for the expansion factor has been defined as follows:

$$\alpha_\eta = [\eta]/[\eta]_\theta. \tag{6}$$

Flory and Fox[6] proposed a relation between α_η and α:

$$\alpha_\eta = \alpha^3. \tag{7}$$

Table III shows the unperturbed dimension $(\bar{r}_w{}^2)_0{}^{1/2}$ and $[(\bar{r}_w{}^2)_0/\bar{M}_w]^{1/2}$ calculated from light scattering data of poly(hexene-1) fractions in dilute toluene solution. An average value of 72.04×10^{-10} was obtained for the characteristic ratio $[(\bar{r}_w{}^2)_0/\bar{M}_w]^{1/2}$. This ratio could also have been calculated from K in the Mark-Houwink equation under theta conditions. However, this method is often limited by the difficulty in finding appropriate theta solvents. It is, therefore, highly desirable to use a method for estimating the unperturbed dimension without the need for theta solvent experiments. Several methods have been proposed in the literature for this purpose. Flory, Fox, and Schaefgen[6,7] were the first to put forward such a method: their equation was

$$[\eta]^{2/3}M^{-1/3} = K^{2/3} + K^{5/3}C_T M[\eta]^{-1}. \tag{8}$$

A plot of $[\eta]^{2/3}M^{-1/3}$ versus $M[\eta]^{-1}$ should yield a linear relationship from which K may be obtained from the intercept and C_T, from the slope. The unperturbed root-mean-square end-to-end distance $(\bar{r}^2)_0{}^{1/2}$ can then be obtained using the following equation[8]:

$$K = \Phi[(\bar{r}^2)_0/M]^{3/2}. \tag{9}$$

An alternate method, applicable to polymers dissolved in "good" and "poor" solvents, was proposed by Kurata and Stockmayer[8] based on the solution theory of Kurata, Stockmayer, and Roig.[9] Their relationship is

$$[\eta]^{2/3}M^{-1/3} = K^{2/3} + 0.36\Phi_0 B\{g(\alpha_\eta)M^{2/3}[\eta]^{-1/3}\} \tag{10}$$
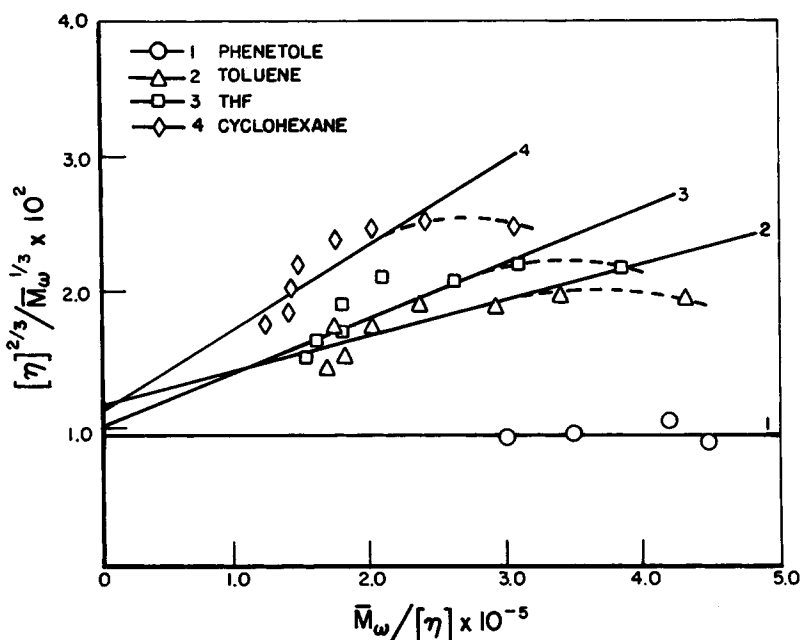
Fig. 1. Flory-Fox-Schaefgen plots (eq. 8) for polyhexene-1 fractions in various solvents.

where $\alpha_\eta = \{[\eta]/[\eta]_\theta\}^{1/3}$, $g(\alpha_\eta) = 8\alpha_\eta{}^3(3\alpha_\eta{}^2 + 1)^{-3/2}$, and B is parameter measuring the polymer–solvent interactions. A method which appears to be simpler was proposed by Burchard[10] and by Stockmayer and Fixman.[11] The latter authors suggested that the equation

$$[\eta]M^{-1/2} = K + 0.51\Phi_0 B M^{1/2} \tag{11}$$

would be useful for all solvent–polymer systems. Inagaki, Suzuki, and Kurata[12] arrived at the following expression:

$$[\eta]^{4/5}M^{-2/5} = 0.786K^{4/5} + 0.950K^{4/5}k^{2/3}M^{1/3} \tag{12}$$

where $k = 0.33B\,[M/(\bar{r}^2)_0]^{3/2}$. These authors point out that their equation is a good method for determining K for polymers in good solvent systems. A modified form of an equation proposed by Bohdanecky[13] was suggested by Cowie.[14] The equation

$$[\eta]M^{-1/2} = \Phi(\epsilon)\Phi_0{}^{-1}K + 0.9166\Phi(\epsilon)\Phi_0{}^{-1}Kk^{7/10}M^{1/2} \tag{13}$$

having a solvent-dependent factor modifying K should be valid both in good and theta solvent. Here, $\Phi(\epsilon) = \Phi_0(1 - 2.63\epsilon + 2.86\epsilon^2)$; and ϵ is given by $\bar{r}^2 = K_r M^{1+\epsilon}$ and is related to 'a,' the exponent in the Mark-Houwink equation, by $a = [(1 + 3\epsilon)/2]$. Thus, $\Phi_0 = \Phi(\epsilon)$ in a theta solvent.

Figures 1 through 5 show the plots of these methods. It can be seen from these plots that our theta-solvent data agree with the proposed expressions over the range examined. However, for good solvents devia-
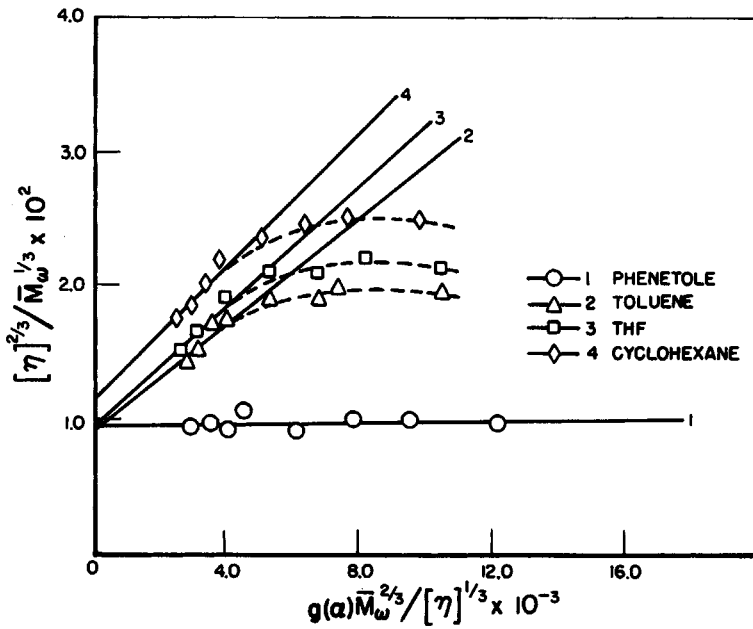
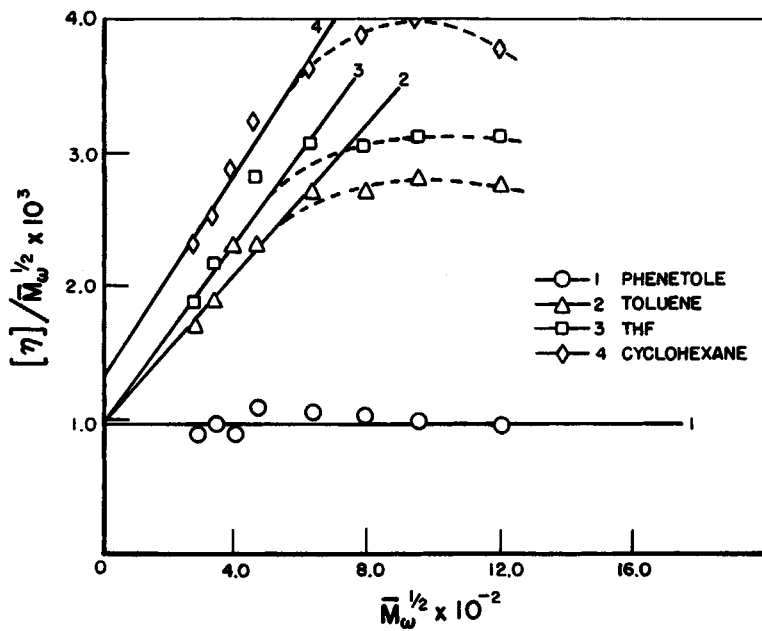Fig. 2. Kurata-Stockmayer plots (eq. 10) for polyhexene-1 fractions in various solvents.

Fig. 3. Stockmayer-Fixman plots (eq. 11) for polyhexene-1 fractions in various solvents.
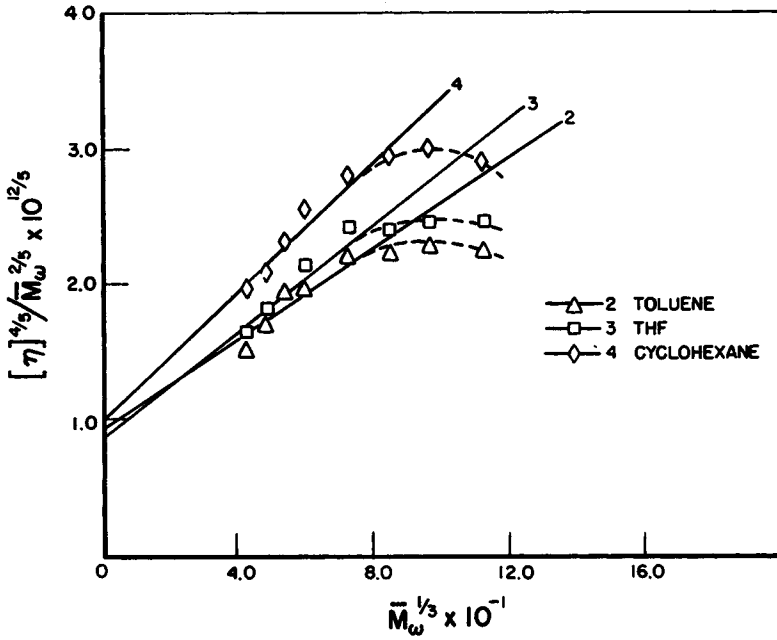
Fig. 4. Inagaki-Suzuki-Kurata plots (eq. 12) for polyhexene-1 fractions in various solvents.
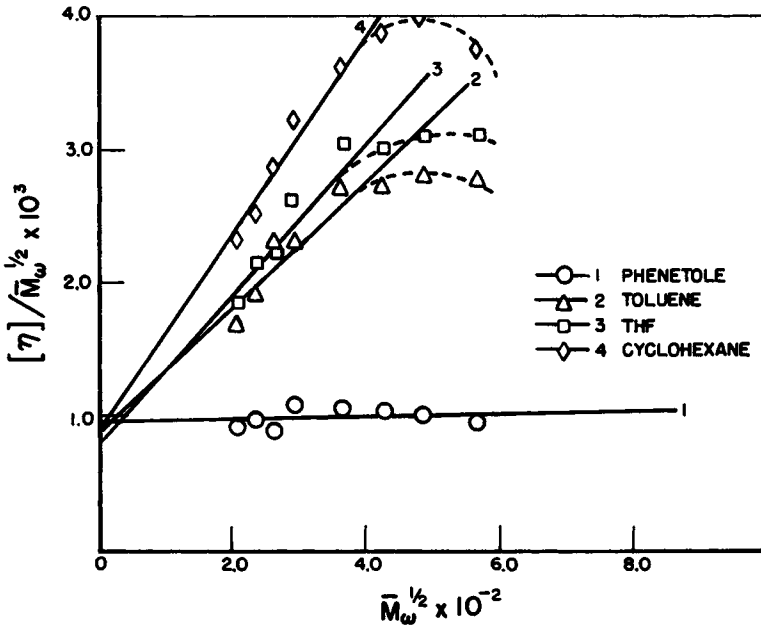

Fig. 5. Modified Bohdanecky plots (eq. 13) for polyhexene-1 fractions in various solvents.

TABLE IV

Comparison of $[(\bar{r}_w{}^2)_0/\bar{M}_w]^{1/2}$ for Poly(hexene-1) in Different Solvents in Accordance with Various Theories

Method	Solvent	$K \times 10^3$	$[(\bar{r}_w{}^2)_0/\bar{M}_w]^{1/2} \times 10^{10}$	T, °C	Remarks
Peterlin	phenetole	—	70.53	61.3	
Flory-Fox	phenetole	0.957	71.21	61.3	
Flory-Fox-Schaefgen	phenetole	0.955	71.17	61.3	
	toluene	1.25	77.85	25.0	
	THF	1.05	73.23	25.0	
	cyclohexane	1.22	77.14	25.0	
Stockmayer-Fixman	phenetole	0.981	71.83	61.3	
	toluene	0.999	72.37	25.0	
	THF	0.919	70.25	25.0	
	cyclohexane	1.27	78.31	25.0	
Kurata-Stockmayer	phenetole	0.963	70.24	61.3	use corrected value of 2.78×10^{21}
	toluene	0.899	68.64	25.0	
	THF	0.906	68.81	25.0	
	cyclohexane	1.24	76.41	25.0	
Inagaki-Suguki-Kurata	phenetole	—	—	61.3	not applicable
	toluene	1.23	77.33	25.0	
	THF	1.16	75.82	25.0	
	cyclohexane	1.32	79.29	25.0	
Modified Bohdanecky	phenetole	0.963	71.37	61.3	
	toluene	1.23	77.33	25.0	
	THF	1.12	75.03	25.0	
	cyclohexane	1.31	79.13	25.0	
Experimental	toluene		72.04	25.0	Table III

TABLE V

Comparison of Unperturbed Dimensions $(\bar{r}_w{}^2)_0{}^{1/2}$ of Poly(hexene-1) Fractions in Phenetole as Determined by Various Dilute Polymer Solution Theories[a]

	Fraction no. $(\bar{r}_w{}^2)_0{}^{1/2}$, Å							
	4	6	7	9	13	15	18	21
Experimental[b]	839.8	699.6	591.5	448.9	349.1	273.5	248.2	211.9
Debye-Bueche	564.2	457.9	381.8	308.1	231.1	184.7	163.6	132.7
Kirkwood-Riseman	832.6	675.6	563.3	454.6	342.5	272.3	241.5	195.7
Peterlin	843.4	672.4	557.6	444.4	328.5	281.2	243.4	201.1
Flory-Fox	851.5	678.9	653.0	448.7	331.7	283.9	245.7	203.0
Flory-Fox-Schaefgen	851.1	678.5	562.7	448.4	331.5	283.8	245.5	202.9
Stockmayer-Fixman	858.9	684.8	567.9	452.6	334.6	286.4	247.8	204.8
Kurata-Stockmayer	839.9	669.7	555.3	442.6	327.2	280.0	242.3	200.3
Modified Bohdanecky	853.4	680.4	564.3	449.7	332.4	284.6	246.2	203.5

[a] For weight-average molecular weights of fractions, see Table I.

[b] Calculated from equation $(\bar{r}_0{}^2)^{1/2} = \dfrac{1}{\alpha} (\bar{r}^2)^{1/2}$.

TABLE VI
Values of $[(\bar{r}_w{}^2)/(\bar{r}_w{}^2)_{0f}]^{1/2}$ and $[(\bar{r}_w{}^2)_0/(\bar{r}_w{}^2)_{0f}]^{1/2}$ of Poly(hexene-1)

Fraction no.	$[(\bar{r}_w{}^2)_{0f}/\bar{M}_w]^{1/2}$	$(\bar{r}_w{}^2)_{0f}{}^{1/2}$	$(\bar{r}_w{}^2)_0{}^{1/2}$	$(\bar{r}_w{}^2)^{1/2}$	$[(\bar{r}_w{}^2)_0/(\bar{r}_w{}^2)_{0f}]^{1/2}$	$[(\bar{r}_w{}^2)/(\bar{r}_w)_{0f}]^{1/2}$
4	0.3361	401.9	839.8	1192.5	2.09	2.97
6	0.3361	320.4	669.6	937.4	2.09	2.93
7	0.3361	265.7	591.5	816.3	2.23	3.07
9	0.3361	211.8	448.9	610.5	2.12	2.88
13	0.3361	156.6	349.1	446.9	2.23	2.85
15	0.3361	134.0	273.5	371.9	2.04	2.78
18	0.3361	116.0	248.2	310.2	2.14	2.67
21	0.3361	95.8	211.9	258.5	2.21	2.70
				average	2.14	2.86

tions from linearity occur at high values of the abscissae. The extrapolations were carried out by a least-squares method, and results for K are listed in Table IV together with characteristic ratios $(\bar{r}_0{}^2/M)^{1/2}$. These ratios were calculated according to eq. (9) by using a value of 2.65×10^{21} for Φ, except in the case of Kurata and Stockmayer[8] for which the value of 2.78×10^{21} was applied to reflect the heterogeneity of the polymer fraction. Excellent agreement was found among various theories in the theta solvent phenetole (see Table IV). In good solvent, the characteristic ratios are within 10% of each other. Table V shows the comparison of experimental and calculated values of unperturbed chain dimensions of some poly(hexene-1) fractions in phenetole along with the values calculated from Debye-Bueche and Kirkwood-Riseman theories. It is interesting to compare $(\bar{r}_w{}^2)_0{}^{1/2}$ with $(r_w{}^2)_{0f}{}^{1/2}$, calculated by assuming free rotation of the bond of length 1.54 Å and the fixed bond angle 109.5°. Accordingly, Table VI shows such comparison along with the values of $[(\bar{r}_w{}^2)/(r_w{}^2)_{0f}]^{1/2}$. It can be seen that the root-mean-square end-to-end distances for poly(hexene-1) are 2.86 times as large in a nonideal solvent, toluene, and 2.14 as large in an ideal solvent, phenetole.

It is also of interest to compare the unperturbed chain dimensions of poly(hexene-1) with several other poly(α-olefins). A comparison was made using the ratio of $(\bar{r}_w{}^2)_0{}^{1/2}$ to the square root of the degree of polymerization. Table VII shows the results of this comparison. These calculations indicate that the dimensions are dependent on the pendent group and are proportional to their size. Thus, with respect to the pendent group, the unperturbed average end-to-end dimensions fall in the order phenyl > hexyl > butyl > propyl > ethyl > dimethyl > methyl, if we ignore the value of polypropylene obtained by Danusso and Maraglio[23] but accept that found by Kinsinger and Hughes[22] in diphenyl ether.

Kurata and Stockmayer[8] have found a smooth correlation between $\sigma = [(\bar{r}_w{}^2)/(\bar{r}_w{}^2)_{0f}]^{1/2}$, the ratio of root-mean-square (rms) unperturbed dimensions to the rms freely rotating dimension, and the molar volume V_x of the pendent group. For nonpolar polymer in the α-olefin series, this is a

TABLE VII

Comparison of $[(\bar{r}_w^2)_0/D.P.]^{1/2}$ for Atactic Poly(α-olefins)

| Polymer	Structure unit	Temp., °C	Solvent	$K \times 10^4$	$[(\bar{r}_w^2)_0/M_w]^{1/2}$ $\times 10^{10}$	$[(\bar{r}_w^2)_0/$ D.P.$]^{1/2}$ $\times 10^{10}$	Reference
Polystyrene	—CH₂—CH— / C₆H₅	34.8	cyclohexane	8.2	67.64	6.90	16
	Cl—(CH₂)ₙ—H	32.8		8.4	68.18	6.95	17
	diethyl malonate	35.9		8.7	68.98	7.03	18
				7.8	66.52	6.78	18
				7.7	66.23	6.75	18
Poly(octene-1)	—CH₂—CH— / C₆H₁₃	50.4	phenetole	6.54	62.72	6.64	15
Poly(hexene-1)	—CH₂—CH— / C₄H₉	61.3	phenetole	9.57	71.22	6.53	In this work
Poly(pentene-1)	—CH₂—CH— / C₃H₇	32.5	isobutyl acetate	10.0	72.26	6.13	19
Poly(pentene-1)		64	phenetole	9.77	71.70	6.08	19
		85	anisole	9.86	71.93	6.10	19
		149	phenyl ether	9.44	70.89	6.02	19
Poly(butene-1)	—CH₂—CH— / C₂H₅	86.2	anisole	12.3	77.42	5.79	20
Polyisobutene	—CH₂—C— / (CH₃)₂	105	anisole	9.1	70.03	5.24	21
		24	benzene	10.7	73.91	5.53	21
		86	phenetole	9.1	70.03	5.24	21
Polypropylene	—CH₂—CH— / CH₃	74	α-chloronaphthalene	18.2	88.23	5.72	22
		92	cyclohexane	17.2	86.58	5.61	22
		34	Isoamyl acetate	16.85	85.99	5.57	23
		153	diphenyl ether	12.0	76.79	4.98	22
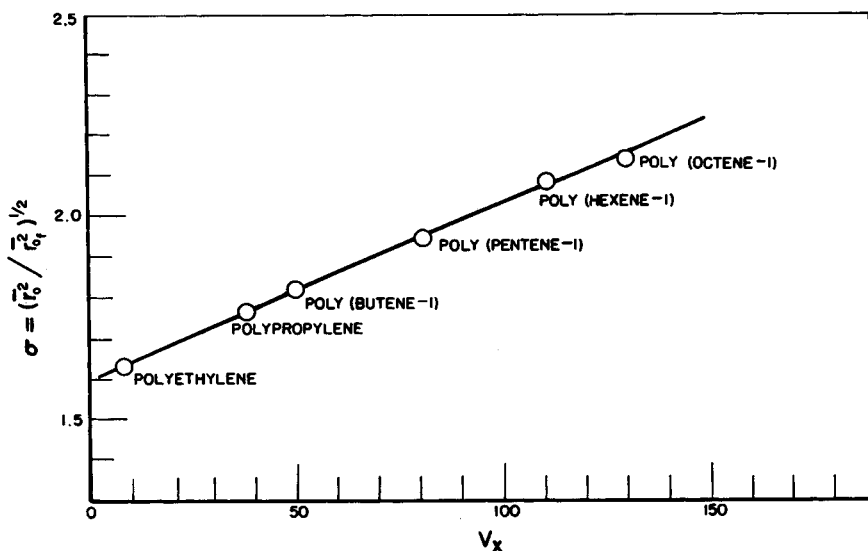
Fig. 6. Plot of steric factor σ vs. molar volume of pendent group V_x, at T_θ for some poly-(α-olefins).

monotonically increasing curve in σ as V_x increases. Kinsinger and Ballard[15] showed that the σ-value obtained for poly(octene-1) is in excellent agreement with the extrapolated limiting curve for the nonpolar, linear poly(α-olefins). Reproducing the plot of Kinsinger and Ballard, we see that the poly(hexene-1) falls on this line in accordance with Kurata and Stockmayer's calculation, using the computed values of $\sigma = 2.09$ and $V_x = 111$ for poly(hexene-1) polymer (Fig. 6). Included also is the point for poly(pentene-1),[19] with computed values $\sigma = 1.95$ and $V_x = 82$. This suggests that the large groups cause the polymer to be more extended due to a higher probability of chain interference, i.e., more hindrance to free rotation, so that the dimensions of poly(α-olefins) are proportional to the size of the bulky group on the side chain.

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