Physical-Chemical Studies of Polyhexene-1. Some Dilute Solution Properties*

F. C. LIN, S. S. STIVALA, and J. A. BIESENBERGER, *Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, New Jersey 07030*

Synopsis

This work is a study of some dilute solution properties of polyhexene-1. Results with the following experimental measurements are reported: osmotic pressure, phase equilibrium, viscosity, light scattering, molecular weight, molecular weight distribution, and degree of chain extension. Three good solvents were used, cyclohexane, tetrahydrofuran, and toluene, and one poor solvent, phenetole, in order to obtain theta conditions. The properties of polyhexene-1 are compared with those of other α-olefin polymers reported in the literature.

INTRODUCTION

The properties of a polymer are controlled by the monomeric constituents and the manner in which these monomer units are linked together. Polyolefins are almost completely saturated hydrocarbon molecules, and the only dissimilarities among the various polymers are the molecular weights, the small amount of unsaturation present in the chains, and the number of tertiary carbon atoms or branch points in the hydrocarbon chain. Measurements of dilute solution from light scattering, osmotic pressure, phase equilibrium, and viscosity are used to establish some molecular parameters, e.g., molecular weight (MW), molecular weight distribution (MWD), size, and shape. Unfortunately, relatively few detailed data have been published for the *n*-alkyl series of the poly-α-olefins. Accordingly, it is the primary objective of this study to explore some solution properties of one member of this series in some detail, namely polyhexene-1.

Polyhexene-1 is a rubbery polymer which is soluble in most organic solvents at room temperature. The dynamic mechanical properties of this polymer were studied by Kurath, Passaglia, and Pariser.[1] The work of Cooper and Gilbert[2] on the effect of ionizing radiation on polyhexene-1 showed that the polymer forms a crosslinked network. Polyhexene-1 is amorphous at room temperature[3,4] and has the lowest softening point ($-55°C$) among the series.[5] Nuclear magnetic resonance[6] and x-ray

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* Abstracted from dissertation submitted by F. C. Lin in partial fulfillment for the Ph.D. degree at Stevens Institute of Technology.

studies[7,8] of this polymer were also reported.   Recently, Tu, Biesenberger, and Stivala[9] reported on the kinetics of hexene-1 polymerization in cyclohexane solvent using the catalytic system of α-TiCl$_3$–AlClEt$_2$.

It is the intent of this work to examine some equilibrium and nonequilibrium properties in solution.   Among these are osmotic pressure phase equilibria, viscosity, and light scattering in assessing thermodynamic properties of the polymer solution, MW, MWD, and average extension of the chains in toluene and cyclohexane.

A subsequent paper will examine hydrodynamic behavior of polyhexene-1 in several solvents in terms of various dilute solution theories.

EXPERIMENTAL

Purification and Fractionation

Polyhexene-1 was prepared by polymerizing the hexene-1 monomer in cyclohexane in the presence of TiCl$_3$–Al(isobutyl)$_3$, according to the procedure described by Tu, Biesenberger, and Stivala.[9]

The polymer was purified by dissolution in cyclohexane followed by centrifugation at 20,000 rpm for 20 min and finally recovered by freeze drying. The purified polymer was a white, tacky, rubbery material.

The polymer was fractionated by fractional precipitation at 25°C, using cyclohexane as solvent and acetone as nonsolvent.   A 28.8-g portion of original purified polymer was dissolved in 1500 ml of cyclohexane to which solution acetone was added gradually until incipient turbidity was observed. The original 28.8 g polyhexene-1 was separated into 32 fractions.   The fractionated polymers were recovered and dried to constant weight by freeze drying and the weights of the polymer fractions recorded.

Osmometry

The number-average molecular weights ($\bar{M}_n$) of the polymer fractions were determined at 37°C in cyclohexane, toluene, and tetrahydrofuran (THF) with a Mechrolab Model 501 high-speed membrane osmometer. Nonaqueous Schleicher and Schuell Type 0–8 membranes, made of deacetylated acetyl cellulose, were used.   They were conditioned to the desired solvents according to the manual supplied by the company.[10]   Data were taken at four or five different concentrations and graphical extrapolations were made of π/c-versus-c plots to zero concentration, where π is the osmotic pressure and c is the concentration.   The instrument was calibrated with a National Bureau of Standards (NBS) polystyrene sample ($\bar{M}_w$ = 6.7×10^5 and $\bar{M}_w/\bar{M}_n$ = 1.15) before use.

Phase Equilibria

Liquid–liquid phase equilibria studies were made in the vicinity of the critical miscibility temperature for the fraction of polyhexene-1 in ethyl phenyl ether (phenetole).   The precipitation temperatures were deter-

mined as a function of concentration by visual observation of the appearance of turbidity of the polymer–diluent mixture upon cooling. The precipitation temperature of the most concentrated solution was determined first, and subsequent determinations of lower concentrations were made by dilution.

The critical miscibility temperatures, T_c, corresponding to the maximum point of each curve, then were treated in accordance with the relation

$$\frac{1}{T_c} = \frac{1}{T_\theta}\left[1 + \frac{1}{\psi_1}\left(\frac{1}{x^2} + \frac{1}{2x}\right)\right]$$ (1)

where T_θ and ψ_1 are the theta temperature and entropy parameter, respectively, and x is the degree of polymerization. The theta temperature is obtained by plotting $1/T_c$ against $(1/x^2 + 1/2x)$ and extrapolating the linear curve to infinite molecular weight.

Viscosity

All viscosity measurements were made with a Cannon-Ubbelohde semimicrotype viscometer. The intrinsic viscosities were determined in cyclohexane, toluene, and tetrahydrofuran (THF) at 25°C ± 0.01°C, and ethyl phenyl ether (phenetole) at 61.3°C. Solvent time of the viscometer was between 150 sec and 300 sec. Data were taken at four or five different concentrations, C, in grams per deciliter, and graphical extrapolations were made of both η_{sp}/c versus c and $(\ln \eta)/c$ versus c to zero concentration to obtain the intrinsic viscosity $[\eta]$. The usual precautions to prevent precipitation of polymer were undertaken when viscosity measurements were performed at the theta temperature (61.3°C).

The effect of shear rate on the viscosity was investigated by using a five bulb Ubbelohde-type viscometer.[11] Solutions were prepared, filtered, and diluted in the conventional manner. In determining the relative viscosity, the apparent relative viscosities for each concentration at several rates of shear, corresponding to different bulbs, are determined and plotted. Extrapolation to zero rate of shear, corresponding to different bulbs, are determined and plotted. Extrapolation to zero rate of shear gives the values used in subsequent evaluation of intrinsic viscosity.

Light Scattering

Eight fractions were used in obtaining light scattering data either in toluene or in cyclohexane, at 25°C. Measurements were made with a 1000-Series Brice-Phoenix light scattering photometer. Cylindrical cells and unpolarized light of wavelength 436 mμ (4360 Å) were used. The photometer assembly was calibrated in two ways: one with the measurement of Rayleigh ratio of pure toluene, and the other with the measurement of a standard NBS polystyrene sample of known molecular weight (see osmometry). The solvents and solutions to be examined were clarified by centrifugation at 20,000 rpm for 1 hr, followed by filtration through 0.45-μ Milli-

pore filter paper directly into the cylindrical cell. Data were taken at four or five different concentrations and in the range of angle of 45° to 135°. Zimm plots were constructed in treating the data.

The specific refractive index increment dn/dc of the polymer solutions was measured with a Brice-Phoenix differential refractometer.[12] The refractometer was calibrated previously with aqueous sucrose solution. The refractive index increments for polyhexene-1 in toluene and cyclohexane at 25°C and wavelength of 436 mμ were −0.042 and −0.063 ml/g, respectively.

RESULTS

Fractionation Data

The polyhexene-1 sample was fractionated from dilute cyclohexane solution into 32 fractions. The last fraction was liquid material, which may have been low molecular weight species. Of the 28.8 g of polymer fractionated, a total of 28.1 g was obtained for a recovery of 97.6%. Table I summarizes the results from successive fractionation.

Osmotic Pressure

Plots of π/c versus c were constructed from the osmotic pressure data, where π is osmotic pressure in centimeters of solvent and c is the polymer concentration in g/l. The number-average molecular weights $\bar{M}_n$ and the osmotic second virial coefficients B were obtained from the ordinate intercepts and slopes of the linear curves, respectively. The $\bar{M}_n$, $[\eta]$, and B values are shown in Table II, for the various fractions in cyclohexane, toluene, and THF. As expected, the $\bar{M}_n$ for any given fraction is independent of solvent, though the $[\eta]$ and B are solvent dependent, e.g., see fractions 7 and 27 in Table II.

The relationship between number-average molecular weight and osmotic second virial coefficient was established by plotting B and $\bar{M}_n$ on log–log coordinates. Linear relationships were obtained from which the exponents and the coefficients in eqs. (2), (3), and (4) were derived from the slopes and intercepts, respectively.

In cyclohexane at 37°C,

$$B = 2.98 \times 10^{-2} \bar{M}_n^{-0.28}. \tag{2}$$

In THF at 37°C,

$$B = 4.74 \times 10^{-3} \bar{M}_n^{-0.15}. \tag{3}$$

In toluene at 37°C,

$$B = 1.02 \times 10^{-3} \bar{M}_n^{-0.04}. \tag{4}$$

TABLE I
Fractionation Data

Fraction no.	Weight, g	Cumulative Weight, g	Weight Fraction w_i[a]	Cumulative Weight Fraction $C(M_i)$[b]
32	1.6733	1.6733	0.0595	0.0298
31	0.1249	1.7982	0.0044	0.0617
30	0.1604	1.9686	0.0057	0.0668
29	0.2912	2.2498	0.0104	0.0748
28	0.4349	2.6847	0.0155	0.0878
27	0.8082	3.4929	0.0287	0.1099
26	0.1194	3.6123	0.0043	0.1264
25	0.4074	4.0197	0.0145	0.1358
24	0.2993	4.3190	0.0106	0.1483
23	0.4263	4.7453	0.0152	0.1612
22	0.4396	5.2849	0.0192	0.1784
21	0.9519	6.0368	0.0267	0.2014
20	0.5571	6.5939	0.0198	0.2246
19	0.5086	7.1025	0.0181	0.2436
18	0.5666	7.6691	0.0201	0.2627
17	0.3934	8.0625	0.0140	0.2797
16	0.6320	8.6945	0.0225	0.2980
15	1.1777	9.8724	0.0419	0.3302
14	0.4397	10.3121	0.0156	0.3589
13	1.1864	11.4985	0.0422	0.3878
12	1.2640	12.7625	0.0449	0.4314
11	0.8209	13.5834	0.0292	0.4724
10	0.8523	14.4358	0.0303	0.5022
9	1.7152	16.1482	0.0609	0.5478
8	1.5648	17.7130	0.0556	0.6060
7	1.9423	19.6553	0.0691	0.6684
6	1.9004	21.5557	0.0676	0.7367
5	1.0052	22.5609	0.0357	0.7884
4	1.4405	24.0014	0.0512	0.8318
3	1.5610	25.5624	0.0555	0.8852
2	1.1977	26.7601	0.0426	0.9342
1	1.3566	28.1167	0.0482	0.9796

[a] w_i = Weight fraction = weight of each fraction/total weight of sample.

[b] Standard Schulz's method, for ith fraction, i.e., $c(M_i) = \frac{1}{2}w_i + \sum_{j=i+1}^{32} w_j$.

Molecular Weight Distribution

The cumulative weight fractions $C(M_i)$ in the last column of Table I were calculated according to the procedure of Schulz.[13] Figure 1 shows the integral distribution curve plotted from the $C(M_i)$ and $\bar{M}_n$ data of Tables I and II.

The data were found to fit the empirical distribution function of Tung,[14]

$$W(M) = yz \exp(-yM^z) M^{z-1} \tag{5}$$

TABLE II.   Osmotic Pressure and Viscosity of Polyhexene-1 Fractions

Frac-tion	$\bar{M}_n \times 10^{-4}$			$[\eta]$, dl/g				$B \times 10^4$, mole-cc/g²		
	Cyclohexane	THF	Toluene	Cyclohexane	THF	Toluene	Phenetole	Cyclohexane	THF	Toluene
32										
31	0.883			0.13				1.347		
30										
29			1.43			0.14				6.812
28										
27	2.71	2.71		0.30	0.24	0.31	0.155	17.54	10.44	
26										
25			4.15				0.190			6.977
24										
23	6.86		6.31	0.65		0.42	0.240	14.52		10.787
22		7.44			0.53				9.12	
21						0.48				
20			8.47			0.54				7.307
19			8.73			0.56				6.693
18	10.76			0.87		0.66	0.340	10.34		
17			12.2[a]			0.77				
16		13.2								
15			14.7	1.14	0.89	0.92	0.365		7.54	5.864
14										
13	19.56		19.56	1.50	1.09	1.12	0.525	9.193	6.17	7.058
12		20.60	20.60		1.44					6.668
11			23.77							6.356
10			24.72			1.56	0.640			6.204
9			29.15	2.28	1.92	1.70				6.26
8			34.72							
7	42.0	42.0		3.06	2.38	2.15	0.822	8.676	7.69	
6			49.35	3.80		2.70	1.06			6.472
5			59.40			3.10	1.16			7.650
4			77.30		3.71	3.32				7.573
3	97.4[a]			5.75						
2			114.7[a]			5.32				
1	193.1[a]			10.10						

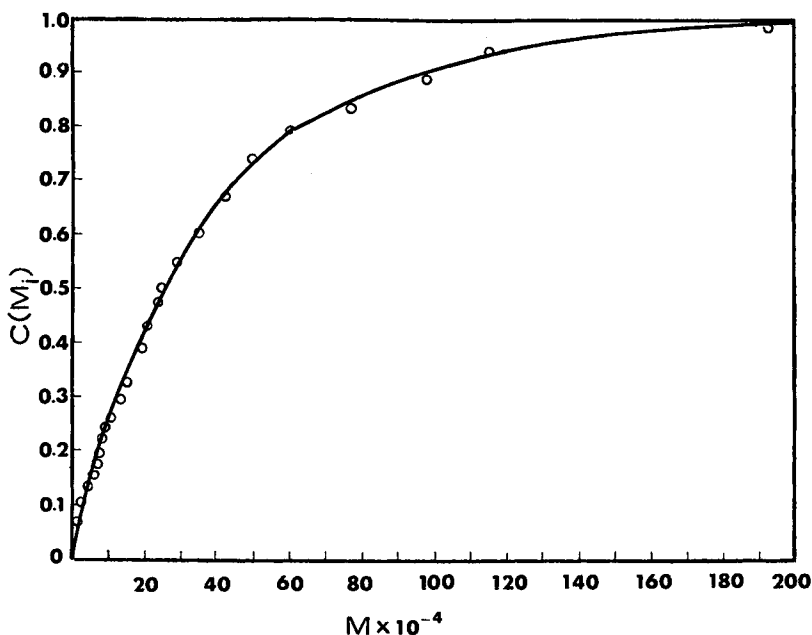[a] Calculated from Mark–Houwink equations.

Fig. 1. Integral molecular weight distribution for polyhexene-1.

where y and z are adjustable parameters. The z value varies inversely with the breadth of the distribution; y together with z determines the average molecular weights of the above distribution function which can be integrated analytically to the integral distribution form

$$C(M) = \int_0^M W(M)dM = 1 - e^{-yM^z}. \tag{6}$$

A plot of log $[1/1 - C(M)]$ versus M on log–log coordinates should yield a straight line, from which the parameters z and y are obtained from the slope and intercept, respectively. Figure 2 shows such a plot where y and z were found to be 0.8517×10^{-5} and 0.907, respectively. The differential distribution function $W(M)$ calculated according to eq. (5) is shown in Figure 3. Tung's distribution function applies well to many condensation and vinyl polymers. The application of eqs. (5) or (6) to the fractionation data of a sample of high-density polyethylene yielded values of $z = 0.890$ and $y = 5.23 \times 10^{-5}$.[15]

Phase Equilibria

The precipitation temperatures T_p of six fractions of polyhexene-1 in phenetole were plotted against the weight percentage of polymer in solution from which the critical miscibility temperature T_c of each of the fractions was obtained. The theta temperature was obtained by plotting $1/T_c$ versus $(1/\bar{M}_n^{1/2} + 1/2\bar{M}_n)$ and extrapolating to infinite molecular weight.
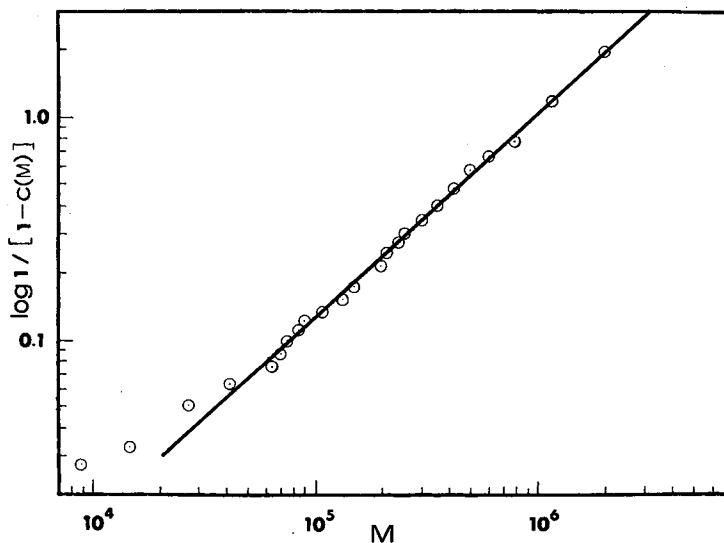
Fig. 2. Logarithmic plot for determination of Tung parameters y and z.

From the intercept of Figure 4, $T_\theta = 61.3°C$ and ψ_1, the entropy parameter, has a value of 0.729, obtained from the slope.

Viscosity

The viscosities of ten fractions of polyhexene-1 were measured at the theta condition, i.e., in phenetole at 61.3°C. The double plots of η_{sp}/c versus c and $(\ln \eta_r)/c$ versus c were used to determine the intrinsic viscosities. Intrinsic viscosities of polymer fractions were also obtained in cyclohexane, THF, and toluene at 25°C. All the values of intrinsic viscosities are shown in Table II.

Shear rate dependence of intrinsic viscosity was measured for two high molecular weight fractions. The horizontal nature of the plots of relative viscosity versus several rates of shear indicates that they are shear rate independent. The intrinsic viscosities thus obtained by plotting $(\eta_{sp}/c)_{\gamma=0}$ versus c and extrapolating to zero concentration were within 5% of that determined before by using semimicro dilution type viscometer.

Light Scattering

The literature values of the Rayleigh ratio, R_{90}, for toluene at 436 mμ are in the range of $(55.3-60.3) \times 10^{-6}$ cm^{-1}. The theoretical value of 58.09×10^{-6} cm^{-1}, calculated from the Einstein-Cabannes equation,[16,17] was selected. Accordingly, a multiplicative correction factor of 58.09/(experimental R_{90}) has been introduced throughout the light scattering data. Zimm plots were constructed from the data to obtain weight-average molecular weight $\bar{M}_w$, z-average root-mean-square end-to-end distance $(\bar{r^2})^{1/2}$ (calculated from the radii of gyration R_G), and the second virial coefficient
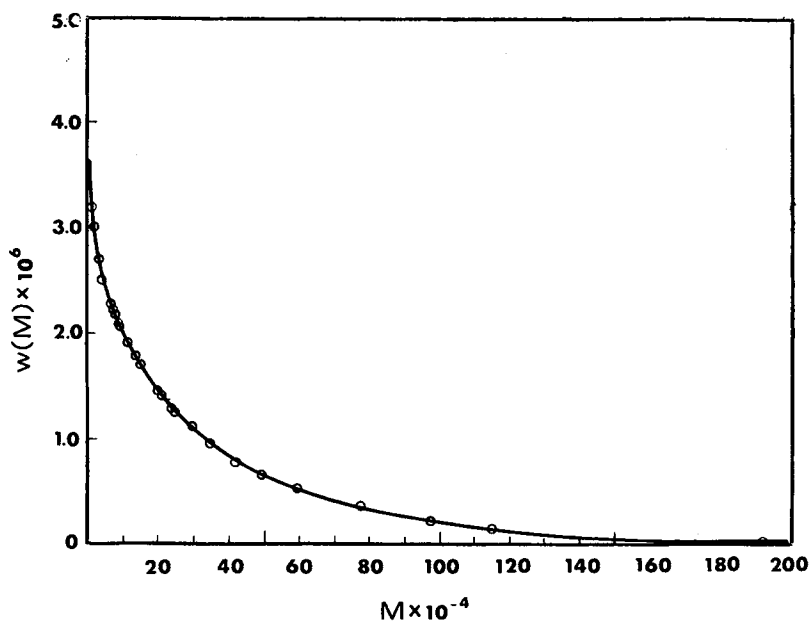
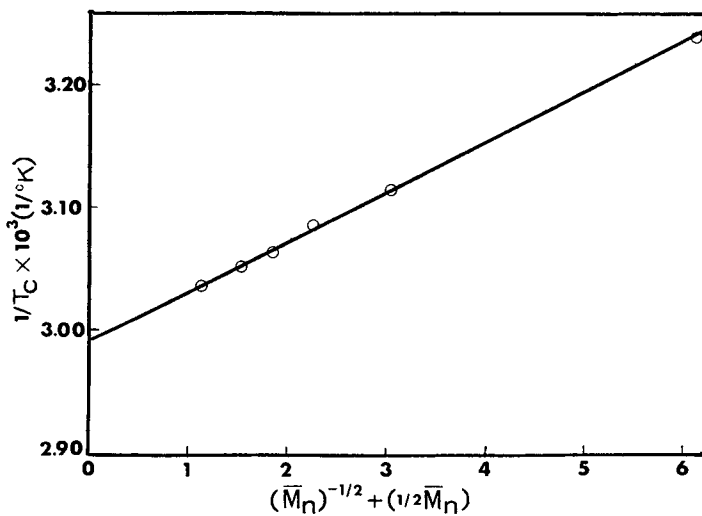Fig. 3. Differential molecular weight distribution for polyhexene-1.

, Fig. 4. Plot for determination of theta temperature for polyhexene-1 in phenetole.

A_2.   Table III summarizes these calculations from measurements made at 25°C in toluene and cyclohexane for several polyhexene-1 fractions.

Mark-Houwink Constants

Intrinsic viscosity–number-average molecular weight relationships were established by plotting data of viscosity against number-average molecular

TABLE III

Light Scattering Results in Toluene and Cyclohexane at 25°C

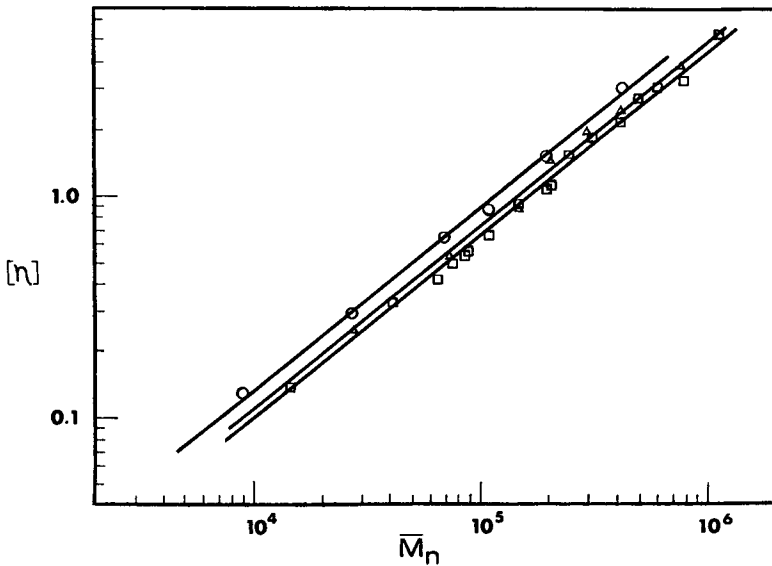| Frac-tion	$\bar{M}_w \times 10^4$		$A_2 \times 10^4$		$(\bar{R}_G^2)^{1/2}$, Å		$(\bar{r^2})_z^{1/2}$, Å	
	Toluene	Cyclohexane	Toluene	Cyclohexane	Toluene	Cyclohexane	Toluene	Cyclohexane
21		8.13		10.78		150.3		368.2
18	11.9		7.56		132.8		325.2	
15		15.9		9.40		321.8		788.3
13	21.7		6.58		191.3		468.5	
9		39.7		11.8		320.1		784.2
7	62.5		5.65		384.2		941.0	
6	90.9	90.9	6.78	11.4	461.5	543.0	1131.3	1330.1
4	143.0		5.30		588.2		1440.8	

Fig. 5. Mark-Houwink plots for polyhexene-1 in cyclohexane, toluene, and tetrahydro-
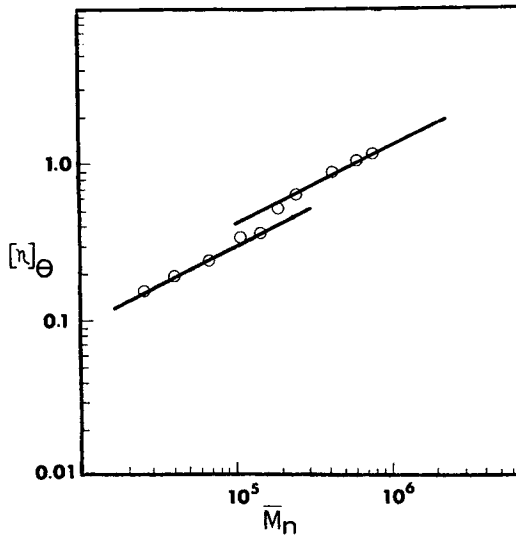furan at 25°C.

Fig. 6. Mark-Houwink plots for polyhexene-1 fractions with molecular weight greater
than 1.96×10^5 and less than 1.47×10^5 at the theta condition.

weight (see Table II) on log–log coordinates, Figures 5–7.   The following
relationships were obtained by the least-squares method.

In cyclohexane at 25°C,

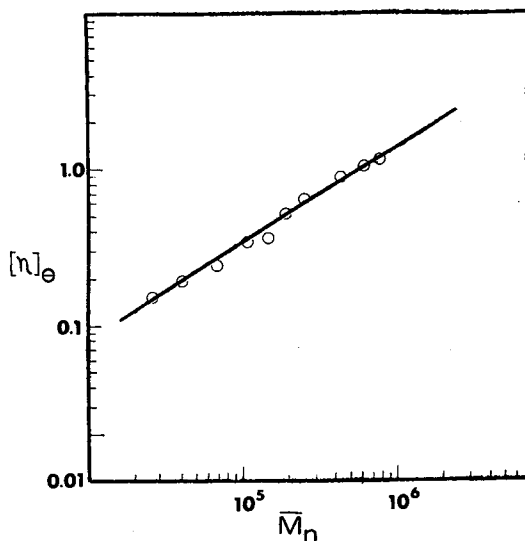$$[\eta] = 6.14 \times 10^{-5} \ \bar{M}_n^{0.83}. \tag{7}$$

Fig. 7. Mark-Houwink plot for polyhexene-1 fractions in the molecular weight range
2.71×10^4 to 7.73×10^5 at the theta condition.

THF, 25°C,

$$[\eta] = 4.99 \times 10^{-5} \ \bar{M}_n^{0.83}. \tag{8}$$

Toluene, 25°C,

$$[\eta] = 4.32 \times 10^{-5} \ \bar{M}_n^{0.84}. \tag{9}$$

Phenetole, 61.3°C,

for $\bar{M}_n$ in the range of 2.71×10^4 to 7.73×10^5,

$$[\eta]_\theta = 2.36 \times 10^{-4} \ \bar{M}_n^{0.63} \tag{10}$$

for $\bar{M}_n > 1.96 \times 10^5$,

$$[\eta]_\theta = 1.33 \times 10^{-3} \ \bar{M}_n^{0.5} \tag{11}$$

for $\bar{M}_n < 1.47 \times 10^5$,

$$[\eta]_\theta = 0.94 \times 10^{-3} \ \bar{M}_n^{0.5} \tag{12}$$

Using the method of least squares, the following weight-average molecu-
lar weight–intrinsic viscosity relationships for polyhexene-1 were also ob-
tained in various solvents and at the temperature indicated (Fig. 8).

In cyclohexane at 25°C,

$$[\eta] = 2.05 \times 10^{-4} \ \bar{M}_w^{0.72}. \tag{13}$$

In THF at 25°C

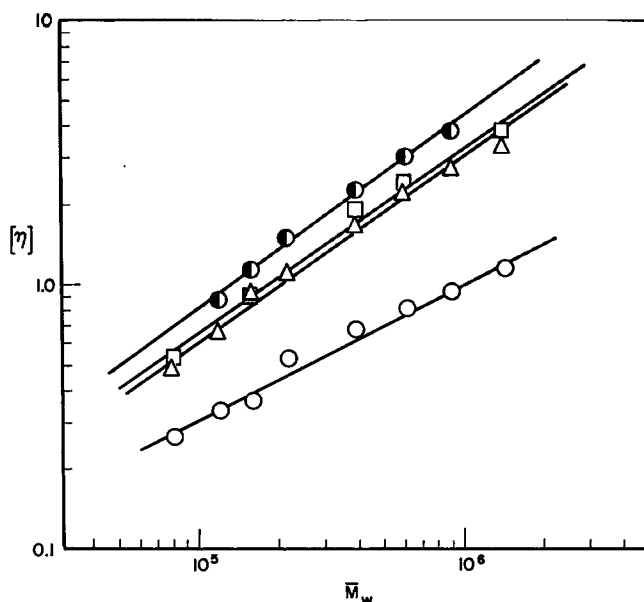$$[\eta] = 2.32 \times 10^{-4} \ \bar{M}_w^{0.69}. \tag{14}$$

Fig. 8. Intrinsic viscosity–weight-average molecular weight relationship for polyhexene-1 in cyclohexane (◐), THF (□), toluene (△), and phenetole (○).

In toluene at 25°C,

$$[\eta] = 2.28 \times 10^{-4} \, \bar{M}_w^{0.69} \tag{15}$$

In phenetole at 61.3°C,

$$[\eta]_\theta = 9.57 \times 10^{-4} \, \bar{M}_w^{0.50} \tag{16}$$

Chain Dimension and Polydispersity

The dimensions of the polyhexene-1 fractions obtained from the Zimm plots were z-averages and accordingly were converted to weight-average dimension by use of the relation (17):

$$(\overline{r^2})_w^{1/2} = (\overline{r^2})_z^{1/2} \, [(h+1)/(h+2)]^{1/2} \tag{17}$$

where h is a parameter characterizing the molecular weight distribution and is given by

$$h = \left[\left(\frac{\bar{M}_w}{\bar{M}_n} \right) - 1 \right]^{-1}. \tag{18}$$

Table IV summarizes the conversion factors used along with molecular weights, chain dimensions, and dispersity $\bar{M}_w/\bar{M}_n$ for several fractions.

The following relationship was also obtained, using least squares, from a log–log plot of $(\overline{r^2})_w^{1/2}$ versus $\bar{M}_w$.

In toluene at 25°C,

$$(\overline{r^2})^{1/2} = 0.56 \times \bar{M}_w^{0.54}. \tag{19}$$

TABLE IV

Conversion Factor for Polymer Dimensions due to Polydispersity
in Toluene at 25°C

Frac-tion	$\bar{M}_w \times$ 10^{-4}	$\bar{M}_n \times$ 10^{-4}	$\bar{M}_w/\bar{M}_n$	h	$[(h+2)/$ $(h+1)]^{1/2}$	$\overline{(r^2)_z}^{1/2}$	$\overline{(r^2)_w}^{1/2}$
21	8.13	7.44	1.09	12.00	1.0408		
18	11.9	10.76	1.11	9.0909	1.0484	325.2	310.2
15	15.9	14.70	1.08	12.50	1.0364		
13	21.7	19.56	1.11	9.0909	1.0484	468.5	446.9
9	39.7	29.15	1.36	2.7778	1.1246		
7	62.5	42.0	1.49	2.0408	1.1528	941.0	816.3
6	90.9	49.35	1.84	1.1905	1.2069	1131.3	937.4
4	143.0	77.3	1.85	1.1765	1.2081	1440.8	1192.5

Flory Universal Constant Φ

According to Flory[19,20] and Fox,[21] the intrinsic viscosity of random coil chains in solution should be proportional to the ratio of the volume occupied by the chain to its molecular weight. If the volume is conveniently chosen as the third power of the $(\overline{r^2})^{1/2}$, then it was shown that

$$[\eta] = \Phi(\overline{r^2})^{3/2}/M \tag{20}$$

where Φ is a constant which should be the same for all polymers irrespective of solvent, provided of course that the molecules conform to the random coil model. According to some of the most precise light scattering experiments critically interpreted,[22,23] the value of Φ applicable at or near the θ-point is $(2.5 \pm 0.1) \times 10^{21}$. A value close to 2.80×10^{21} has the support of many theoreticians.[24] An intermediate value of 2.65×10^{21} will be adopted here for further calculations.

Equation (20) suggests at once a means of establishing the value of the universal constant Φ if $\overline{r^2}$ has been determined from light scattering measurements or by some other means. Table V shows such a calculation

TABLE V

The Universal Constant Φ Determined from Light Scattering Data
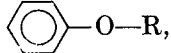of Polyhexene-1 in Toluene at 25°C

Frac-tion	$\bar{M}_w \times 10^{-4}$	$[\eta]$	$M_w[\eta] \times 10^5$	$\overline{(r_w^2)}_{exp}^{1/2}$	$\overline{(r_w^2)}_{exp}^{3/2}$ $\times 10^{-6}$	$\Phi \times 10^{-21}$
4	143.0	3.32	47.476	1192.5	1695.8	2.80
6	90.0	2.70	24.543	937.40	823.7	2.98
7	62.5	2.15	13.438	816.3	543.9	2.47
9	39.7	1.70	6.749	610.5[a]	224.2	3.01
13	21.7	1.09	2.387	446.9	89.25	2.67
15	15.9	0.92	1.463	371.9[a]	51.44	2.84
18	11.9	0.66	0.785	310.2	29.85	2.63
21	8.13	0.48	0.390	258.5[a]	17.27	2.26
					average	2.71

[a] Calculated from eq. (19).

where an average value of 2.71×10^{21} for Φ was obtained, which agrees well with the adopted value mentioned before. This agreement indicates that the polyhexene-1 is of the random coil conformation in solution and as such can be treated in accordance with standard theories of dilute solutions of linear polymers, as will be reported in a later paper.
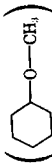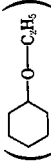
DISCUSSION

In the determination of the theta temperature, the value of the degree of polymerization, x, was calculated from $\bar{M}_n$ rather than $\bar{M}_w$. It can be shown that when $\bar{M}_w$ is used to calculate the value of x, a small change of intercept is noted which is well within the range of experimental error. Table VI summarizes the results of phase equilibria studies, reported by others, on some other polyolefins arranged in order of increasing number of carbon atoms in the side chain, starting with polyethylene, which has none.

The theta solvents are all phenyl ether derivatives, $\langle\bigcirc\rangle$—O—R, where R is C_6H_5—, CH_3—, and C_2H_5— in diphenyl ether, anisole, and phenetole, respectively. These solvents are essentially similar chemically. Further, since both polyethylene and polyisobutylene do not contain asymmetric carbon atoms, these polymers have no tacticity. The tacticity of the polyhexene-1 used in this investigation is not known but is discussed in some detail later. It is noted from Table VI that as the number of carbon atoms increases in the side chain, the theta temperature decreases for both atactic and isotactic species. Also, the amorphous polyisobutylene has $T_\theta = 86.0°C$. It is further noted that the absolute temperature differential ΔT for polypropylene, polybutene-1, and polypentene-1 is 8.5, 3.0, and 0, respectively. If this trend is essentially correct, then the theta temperature of polyhexene-1 and the higher n-alkyl series for both isotactic and atactic species should be the same. Thus, $T_\theta = 61.3°C$ obtained in this study for polyhexene-1 should be independent of tacticity. Further, one might assign $T_\theta = 50.4°C$ for the isotactic polyoctene-1 based on the value reported experimentally for the atactic species. The observed $T_\theta = 61.3°C$ in this work for polyhexene-1 follows the decreasing trend of T_θ with increasing carbon in the side chain of the polyolefin in chemically similar solvents.

The exponent α in the Mark-Houwink equation for random coil chains at the theta condition has the value of 0.5. In plotting the $\bar{M}_n$ and $[\eta]$ of polyhexene-1 fractions in the theta solvent phenetole at the theta temperature of 61.3°C on log–log coordinates (Fig. 7), the exponent α was found to be 0.63, eq. (10). This value, which deviates from 0.5 by 0.13, was obtained by the least-squares method. In closely examining the points in Figure 7, it was noted that two linear relationships could be drawn, each having slopes (exponent α) of 0.5 and K values of 1.33×10^{-3} and 0.94×10^{-3} for $\bar{M}_n > 1.96 \times 10^5$ and $\bar{M}_n < 1.47 \times 10^5$, respectively (see eqs. (11) and (12) and Fig. 6). It has been reported[27,31] that, in general,

TABLE VI
Theta Conditions for Several Poly-α-olefins

Polymer	Solvent	Theta temperature T_θ, °C					Reference
		Atactic	Isotactic	Nontactic	Unknown tacticity	ΔT	
Polyethylene	diphenyl ether, bp 259°C			161.4–163.9			25
Polypropylene	diphenyl ether, bp 259°C	153.8	145.3			8.5	26
Polybutene-1	anisole, bp 155°C	86.3	89.3			3.0	27
Polyisobutylene	phenetole, bp 172°C			86.0			28
Polypentene-1	phenetole, bp 172°C	64.0	64.0			0	29
Polyhexene-1	phenetole, bp 172°C	(61.3)[a]	(61.3)[a]		61.3		this work
Polyoctene-1	phenetole, bp 172°C	50.4	(50.4)[a]				30

[a] Values assumed based on trend of decreasing theta temperature differential between atactic and isotactic isomers, assuming $\Delta T = 0$ beyond polypentene-1.

the same Mark-Houwink expression applies for both atactic and isotactic species in thermodynamically good solvents but that differences may be observed between the stereoregular and random polymer in poor solvents, as manifested in the small differences between the K values. It would seem that during the course of fractionation in the present study, the first portions (higher molecular weights) of the polyhexene-1 fractions are stereo-block polymers dominated by predominantly isotactic sequences having lower solubility and higher molecular weight while others (later portions) are dominated by predominantly atactic sequence in the stereoblock polymer having higher solubility and lower molecular weight.

Tu, Biesenberger and Stivala[9] attempted to assess some tacticity in polyhexene-1 by examining two fractions (of low and high molecular weight) using infrared spectroscopy and the polarizing microscope. They found no significant differences between the two fractions examined. It is interesting to note that differences in a thermodynamic parameter of mixing was reported for atactic and isotactic polypropylene.[26] Consequently, the theta temperature was found to be different for these isomers. A similar difference, but of lesser magnitude, was reported for atactic and isotactic polybutene-1.[27] It is now apparent from Figure 4 that separate extrapolation of the first three points (high molecular weight fractions) and the last three points (lower molecular weights) could have given slightly different values of T_θ compared to 61.3°C for extrapolation of all the six points, i.e., $T_\theta = 61.3$°C may be slightly lower than what it should be for isotactic-dominated fractions and higher than those of atactic-dominated fractions. This would be true in poor solvents, i.e., at the theta condition. Another explanation for this phenomenon may be due to differences in polydispersity of these fractions. As shown in Table IV, the high molecular weight fractions were found to be more dispersed than those fractions with lower molecular weight, and weight-average molecular weights are preferred for determining the constant in the Mark-Houwink equation for polydisperse polymer, since $\bar{M}_v$ is nearer to $\bar{M}_w$ than to $\bar{M}_n$. This was confirmed when $\bar{M}_w$ was used instead of $\bar{M}_n$ to establish the relationship between molecular weight and intrinsic viscosity. A single line with slope of 0.5 was obtained, as noted in Figure 8.

The Mark-Houwink constant α obtained by using number-average molecular weight in thermodynamically good solvents is higher, as expected. The high values of α for all three solvents reflect their behavior as thermodynamically good solvents.

According to the theory of Flory and Fox,[32] the exponent α in the Mark-Houwink equation must lie between the limits 0.5 and 0.8 for linear flexible chains without draining effects. The lower limit is for rather tightly coiled chains in theta solvent, and the upper limit, for highly swollen polymer in very good solvents. A violation of this upper limit must be interpreted as evidence for the draining effect. Furthermore, this violation is also usually regarded as evidence for high "stiffness" of chains, since the draining effect should be greater for more highly extended molecules.

On the other hand, according to the theory of Kurata and Stockmayer,[33] the upper limit of α for nondraining molecules was extended to 1.0. They show that violations of the upper Flory-Fox limit are by no means confined exclusively to cellulose derivatives or other natural polymers, but are also found on occasion for polymers conventionally and justifiably regarded as flexible chains. It seems unlikely that the large α-values can be interpreted in terms of abnormal chain stiffness. It is believed that the high value of α in the $\bar{M}_n$-[η] relationships of polyhexene-1 were also partially due to the difference in polydispersity of fractions as mentioned above.

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