Macromolecules 1983, *16*, 925–929

(3) Fixman, M. *J. Chem. Phys.* **1978**, *69*, 1527, 1538.
(4) Weber, T. A. *J. Chem. Phys.* **1978**, *69*, 2347; **1979**, *70*, 4277.
(5) Evans, G. T.; Knauss, D. C. *J. Chem. Phys.* **1980**, *72*, 1504. Evans, G. T. *Ibid.* **1981**, *74*, 4621.
(6) Simon, E. M.; Zimm, B. H. *J. Stat. Phys.* **1969**, *1*, 41.
(7) Levy, R. M.; Karplus, M.; McCammon, J. A. *Chem. Phys. Lett.* **1979**, *65*, 4.
(8) McCammon, J. A.; Northrup, S. H.; Karplus, M.; Levy, R. M. *Biopolymers* **1980**, *19*, 2033. Pear, M. R.; Northrup, S. H.; McCammon, J. A.; Karplus, M.; Levy, R. M. *Ibid.* **1981**, *20*, 629.
(9) Mandell, M. *J. Chem. Phys.* **1972**, *57*, 4858.
(10) Shore, J. E.; Zwanzig, R. *J. Chem. Phys.* **1975**, *63*, 5445.
(11) Mansfield, M. *J. Polym. Sci., Polym. Phys. Ed.*, in press.
(12) Clark, M. B.; Zimm, B. H. In "Dielectric Properties of Polymers"; Karasz, F. E., Ed.; Plenum Press: New York, 1972; pp 45–72. Clark, M. B. *Ibid.*, pp 73–97.
(13) Weiner, J. H.; Pear, M. R. *Macromolecules* **1977**, *10*, 317.
(14) Perchak, D., private communication.
(15) Skinner, J. L.; Wolynes, P. G. *J. Chem. Phys.* **1980**, *73*, 4015, 4022.
(16) Helfand, E. *J. Chem. Phys.* **1979**, *71*, 5000. Chandler, D.; Berne, B. J. *Ibid.* **1979**, *71*, 5386. Pechukas, P. *Ibid.* **1980**, *72*, 6320. Helfand, E.; Wasserman, Z. R.; Weber, T. A.; Skolnick, J.; Runnels, J. H. *Ibid.* **1981**, *75*, 4441. Fixman, M. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 3050; see also ref 2.
(17) Chandresekhar, S. *Rev. Mod. Phys.* **1943**, *15*, 1.
(18) Zwanzig, R. *Annu. Rev. Phys. Chem.* **1965**, *16*, 67.
(19) Numerical tabulations of the simulation-generated correlations are available from R.C.
(20) Shore, J. E. Ph.D. Thesis, University of Maryland, 1974.
(21) Williams, G.; Watts, D. C. *Trans. Faraday Soc.* **1970**, *66*, 80. Williams, G.; Watts, D. C.; Dev, S. B.; North, A. M. *Ibid.* **1971**, *67*, 1323.

Characteristic Ratios of Atactic Poly(vinylethylene) and Poly(ethylethylene)

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ABSTRACT: The characteristic ratios of atactic poly(vinylethylene) and poly(ethylethylene) have been determined by combining intrinsic viscosity and weight-average molecular weight measurements on a series of near-monodisperse samples. The poly(vinylethylenes) were prepared by the anionic polymerization of 1,3-butadiene while the poly(ethylethylene) samples were the product of the hydrogenation of the poly(vinylethylene) materials. The characteristic ratio for poly(ethylethylene) of 5.3, although not in accord with available experimental values, is in excellent agreement with the predictions of Flory, Mark, and Abe.

Introduction

In a series of studies, the rotational isomeric state (RIS) model has been used[2-12] to evaluate the configurational characteristics of polymethylene, poly(methylethylene), and poly(ethylethylene). For the α-olefinic polymers,[4-12] the unperturbed random-coil configurations were treated on the basis of three rotational states for each backbone bond. Each state was weighed according to the interactions between the methylene, methine, and substituent groups that were separated by either three or four C–C bonds. The treatment was applied to chains having various tacticities for the calculation of the characteristic ratios. More recently, Suter and Flory[13] have examined the conformational energy and configurational statistics of poly(methylethylene) by the use of five rotational states for the chain bonds.

Experimental results for the case of polymethylene[2,14-19] have shown the essential correctness and success of the RIS approach. However, disagreement does exist between experiment[20,21] and theory[7] for the case of atactic poly(ethylethylene) [poly(1-butene)]. Some of these experimental results were based[20] on intrinsic viscosity measurements on samples of apparently unknown polydispersity.

Various bulk polymer properties, e.g., elasticity and optical properties, are dependent upon chain configuration. Recently, Graessley and Edwards[22] have related the plateau modulus of a polymer to its characteristic ratio. Hence, knowledge of this parameter is of value for an understanding of properties other than just the dilute solution unperturbed posture of a polymer chain.

It has been reported[23-25] that the anionic polymerization of butadiene can be carried out to yield virtually 100% 1,2 enchainment. The resulting near-monodisperse poly(vinylethylene) can be then converted by hydrogenation to poly(ethylethylene). This approach was used for the samples examined in this study, which reports our findings regarding the characteristic ratios for the atactic forms of poly(vinylethylene) and poly(ethylethylene). To the best of our knowledge, the RIS approach has not yet been used to calculate the characteristic ratio of the former polymer.

Experimental Section

The polymerization, under vacuum, of 1,3-butadiene was carried out with purified, by distillation, *sec*-butyllithium with cyclohexane as the solvent. The polymerization temperatures were between 10 and 20 °C while the duration of the reactions ranged from 24 to 48 h. Termination was carried out by the addition of methanol. The general procedures followed in these polymerizations have been described elsewhere.[26]

Until recently, it was not possible to prepare virtually 100% poly(vinylethylene) via homogeneous anionic polymerization systems involving the alkali metals. However, the use of bis(piperidinyl)ethane as a "promoter" in concert with butyllithium has been reported[23-25] to lead to the near-quantitative conversion of 1,3-butadiene to poly(vinylethylene). Thus bis(piperidinyl)ethane was used to control the microstructure of the polymers examined in this work. The ratio of promoter to active-center concentration was about 5.

The poly(vinylethylene) polymers were converted to poly(ethylethylene) via hydrogenation. The catalyst was palladium on calcium carbonate.[27] After the change brought about by hy-

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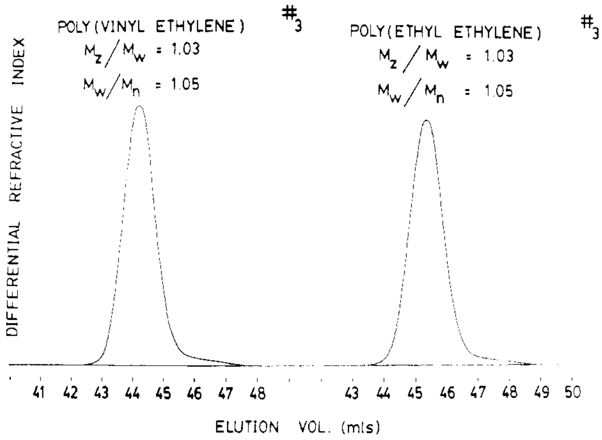

Figure 1. Chromatograms of poly(vinylethylene) and poly(ethylethylene).

Table I
Specific Refractive Index Increments (dn/dc, mL g^{-1}) for Poly(vinylethylene) and Poly(ethylethylene) in Cyclohexane at 30 °C

polymer	λ, nm 436	546	633
poly(vinylethylene)	0.0988	0.0919	0.0873
poly(ethylethylene)	0.0696	0.0679	0.0672

drogenation was taken into account, the weight-average molecular weights measured before and after hydrogenation were, within experimental error, identical.

The analyses of the poly(vinylethylenes) and poly(ethylethylenes) by size exclusion chromatography (GPC) revealed that the samples possessed near-monodisperse molecular weight distributions and that hydrogenation did not cause any detectable chain branching or degradation. Representative chromatograms are shown in Figure 1. These chromatograms were obtained with a Waters 150C GPC equipped with six μ-Styragel columns having a porosity range of 10^6–10^2 Å. Supplemental measurements were made with a Waters Ana-Prep instrument having seven 4-ft Styragel columns. The porosity range of this column set ranged from 10^6 to 10^3 Å. Purified tetrahydrofuran was the carrier solvent at a flow rate of 1 mL min^{-1}. The temperature of measurement was 30 °C. Both the poly(vinylethylene) and poly(ethylethylene) samples were found to adhere to a universal calibration,[28] which was generated by using near-monodisperse polystyrene samples. It should also be mentioned that the small low molecular weight tails seen in these chromatograms were also observed in the other samples used in this work. This can be taken as an indication that a very limited amount of active-center termination occurs during these polymerizations.

The weight-average molecular weights were measured with the Chromatix KMX-6 low-angle photometer. This instrument was equipped with a helium–neon laser and operates at a wavelength of 633 nm. Cyclohexane was the solvent.

The specific refractive index increments of poly(vinylethylene) and poly(ethylethylene) were measured with Brice-Phoenix and Chromatix KMX-16 refractometers. Linear relationships were obtained for the dn/dc values at 30 °C, as a function of wavelength. These values are given in Table I.

The number-average molecular weights of the poly(vinylethylene) samples were measured with a Hewlett-Packard 503 osmometer equipped with S and S membranes. Toluene was used as the solvent at a temperature of 37 °C.

The Θ temperatures for poly(vinylethylene) and poly(ethylethylene) were determined in purified 2-octanol, using a Sofica photometer set at an angle of 90°. The second virial coefficients were determined as a function of temperature. The temperatures at which $A_2 = 0$ were taken as the Θ temperatures for these two substituted polyethylenes. For both polymer types, the two lowest molecular weight samples were used in the Θ temperature measurements.

The dilute solution viscosities in tetrahydrofuran and 2-octanol were measured in Cannon-Ubbelohde semimicroviscometers having no appreciable kinetic energy corrections. The Wescan 221 automatic timing device was used for the solvent and solution flow time measurements. The intrinsic viscosities were obtained by the conventional extrapolation to zero concentration of the η_{sp}/c and $\ln \eta_{rel}/c$ vs. c plots.

The glass transition temperatures of poly(vinylethylene) and poly(ethylethylene) were determined with the DuPont 990 DSC. Mercury and indium were used to calibrate the instrument. Heating rates of 2, 5, 10, and 20 °C min^{-1} were used, with the glass transition temperature determined by the conventional approach of extrapolating to the 0 °C min^{-1} heating rate. The glass transition temperatures thus determined were −4 °C for poly(vinylethylene) and −30 °C for poly(ethylethylene). The only transition found for both polymers was the glass transition temperature. No secondary transitions were found over the temperature range of ca. −100 to +150 °C. This indicates that both polymer types can be considered to be amorphous; e.g., the melting point for syndiotactic poly(ethylethylene) is reported[29] to be 127 (±1) °C.

The poly(vinylethylene) microstructure was analyzed by ^{1}H NMR (Varian 300 MHz) and ^{13}C NMR (Varian CF-20) spectroscopy. The solvent was $CDCl_3$ while the temperature of measurement was 30 °C. The poly(ethylethylene) samples were also analyzed in this manner. These measurements showed that the poly(vinylethylenes) contained between 1 and 2% of the 1-butenylene (1,4-butadiene) unit.

The extent of hydrogenation in the poly(vinylethylene) samples was measured by IR and ^{13}C NMR spectroscopy. There were no indications that residual vinyl groups were present in the poly(ethylethylene) materials. ^{13}C NMR measurement showed that the configurational sequences (the meso 1,2–1,2 dyads and the racemic 1,2–1,2 dyads) were found for the poly(vinylethylenes) to occur in a Bernoullian fashion as did the dyad repeat units in the poly(ethylethylene) samples. Both types of dyads were found to occur in nearly equal proportions. The assignments used to interpret these spectra are those given elsewhere.[30,31] Thus the polymers used in this work can be classified as atactic.

It should also be noted that both the ^{1}H NMR and ^{13}C NMR spectra did not reveal the presence of the 1,2-disubstituted 4-vinylcyclopentane unit in the poly(vinylethylenes). This cyclic structure has been found[32,33] to be formed under conditions of slow chain propagation such as occurs when monomer is added slowly over the course of a polymerization reaction modified by the presence of a bidentate base such as *N,N,N′,N′*-tetramethylethylenediamine. The polymerizations conducted in this work can be described as batch processes where the total amount of monomer was present at the beginning of the reaction.

Results and Discussion

The evaluation of C_∞ is most conveniently accomplished by the combined measurements of weight-average molecular weights and intrinsic viscosities. The latter parameter can be measured in either thermodynamically good solvents or an ideal solvent, i.e., under Θ conditions. Both types of solvent, tetrahydrofuran and 2-octanol, were used in this work. Measurements under Θ conditions directly yield the unperturbed chain dimensions while measurements in good solvents require the application of extrapolation to zero molecular weight as shown in the procedures of Burchard[34] and Stockmayer and Fixman.[35]

From the values of intrinsic viscosity, the ratio $\langle r^2\rangle_0/\bar{M}_w$ can be determined from the relation[36,37]

$$[\eta]_\Theta = \Phi(\langle r^2\rangle_0/\bar{M}_w)^{3/2}\bar{M}_w^{1/2} = K_\Theta M_w^{1/2} \qquad (1)$$

where $\langle r^2\rangle_0$ represents, as usual, the mean-square unperturbed end-to-end distance (in square centimeters), $[\eta]$ is intrinsic viscosity in deciliters per gram, and Φ is the constant of proportionality[37-39] known as the Flory constant. The experimental value of Φ is 2.5 (±0.1) × 10^{21}. This value, which is based on measurements of $[\eta]_\Theta$ and $\langle S^2\rangle_z$ of narrow molecular weight distribution polystyrenes[40-42] and polyisoprenes,[43] is the one predicted by Flory in 1953.[44]

Table II
Molecular Characteristics of Poly(vinylethylene)

sample	$\overline{M}_n \times 10^{-4}$	$\overline{M}_w \times 10^{-4}$	$[\eta]^{30\,°C}_{THF}$, dL g^{-1}	k_H	$[\eta]^{32.8\,°C}_{2\text{-octanol}}$, dL g^{-1}	k_H	M_w/M_n[a]	M_w/M_n[b]	M_z/M_w[b]
5	1.20	1.22	0.21_1	0.40	0.13_0	0.63	1.02	1.03	1.02
1	2.53	2.57	0.35_3	0.36	0.19_0	0.78	1.02	1.04	1.02
3	6.58	7.06	0.72_8	0.38	0.31_8	0.81	1.07	1.05	1.03
2	10.0	10.6	0.96_8	0.34	0.38_7	0.91	1.06	1.05	1.03
4[c]	20.5	23.1	1.92_7	0.35	0.58_3	1.27	1.13	1.13	1.09
8	31.5	34.6	2.65_4	0.29	0.71_9	1.38	1.10	1.06	1.04
7	48.0	52.0	3.48_4	0.22	0.84_5	1.37	1.08	1.10	1.05
6	47.4	52.1	3.48_3	0.26	0.86_3	1.25	1.10	1.12	1.06

[a] Absolute measurements. [b] Via Waters 150 and Ana-Prep instruments. The values shown are averages from the two instruments. [c] This sample contained ca. 6% of doublet (coupled) chains. This coupling reaction will occur during termination if oxygen is present.[45,46]

Table III
Molecular Characteristics of Poly(ethylethylene)

sample	$\overline{M}_w \times 10^{-4}$[a]	$[\eta]^{25\,°C}_{THF}$, dL g^{-1}	k_H	$[\eta]^{23.6\,°C}_{2\text{-octanol}}$, dL g^{-1}	k_H	M_w/M_n[b]	M_z/M_w[b]
1	2.66	0.19_0	0.45	0.12_9	0.51	1.03	1.02
3	7.35	0.39_7	0.30	0.20_2	0.78	1.05	1.03
2	10.2	0.52_2	0.37	0.25_3	1.02	1.05	1.03
8	36.0	1.34_6	0.37	0.49_0	1.17	1.06	1.04
7	52.6	1.80_8	0.31	0.60_0	0.93	1.10	1.04
6	55.0	1.85_4	0.31	0.60_6	1.20	1.11	1.05

[a] Via light scattering. [b] Via Waters 150 GPC.

The intrinsic viscosity measurements for both polymers were done with tetrahydrofuran and 2-octanol. The $[\eta]$ and $\bar{M}_w$ data in Table II yield the following relations for poly(vinylethylene):

$$[\eta]^{30\,°C}_{THF} = 1.59 \times 10^{-4} \bar{M}_w^{\,0.76} \tag{2}$$

$$[\eta]^{32.8\,°C}_{2\text{-octanol}} = 1.20 \times 10^{-3} \bar{M}_w^{\,0.50} \tag{3}$$

while the hydrogenated product, poly(ethylethylene), yielded the following equations (Table III):

$$[\eta]^{25\,°C}_{THF} = 8.24 \times 10^{-5} \bar{M}_w^{\,0.76} \tag{4}$$

$$[\eta]^{23.5\,°C}_{2\text{-octanol}} = 6.05 \times 10^{-4} \bar{M}_w^{\,0.52} \tag{5}$$

Clearly, the temperature of 23.5 °C initially measured for poly(ethylethylene) in 2-octanol is higher than the true Θ temperature. However, the exponent of 0.52 shows that the intrinsic viscosity measurements were done under near-Θ conditions. The respective molecular weights and intrinsic viscosity values for the poly(vinylethylenes) and poly(ethylethylenes) are given in Tables II and III.

The unperturbed dimension $\langle r^2 \rangle_0$ can be determined by using Flory's equation:

$$K_\Theta = \Phi(\langle r^2 \rangle_0 / \bar{M}_w)^{3/2} \tag{6}$$

Thus for poly(vinylethylene) (in Å)

$$\langle r^2 \rangle_0^{1/2} = 0.783 \bar{M}_w^{\,1/2} \tag{7}$$

while the corresponding relation for poly(ethylethylene) is

$$\langle r^2 \rangle_0^{1/2} = 0.667_6 \bar{M}_w^{\,1/2} \tag{8}$$

Following Flory,[47] the characteristic ratio, C_∞, can be used for a comparison of the average dimensions of unperturbed random coils:

$$C_\infty = \lim_{n \to \infty} \left[\frac{\langle r^2 \rangle_0}{n l^2} \right] \tag{9}$$

Table IV
Unperturbed Chain Parameters for Poly(vinylethylene) and Poly(ethylethylene)

	poly(vinylethylene)	poly(ethylethylene)
$K_\Theta \times 10^3$[a]	1.20	0.74_4[b]
C_∞	7.0	5.3

[a] Determined from intrinsic viscosity measurements done under Θ or near-Θ conditions. [b] Determined by the extrapolation procedure of Burchard[34] and Stockmayer and Fixman.[35]

where n denotes the number of backbone chain bonds and l the bond length. For these substituted polyethylenes n is 2 per repeat unit and l is taken as 1.54 Å. The values of C_∞ (Table IV) show that the conversion of the pendant vinyl group to the ethyl unit causes C_∞ to decrease. The same trend can be seen in the chromatograms of Figure 1, where the poly(ethylethylene) sample exhibits a longer retention time in the μ-Styragel columns than its poly(vinylethylene) "parent". This relative elution behavior is a demonstration that poly(ethylethylene) is a more flexible chain than poly(vinylethylene), a conclusion that is also supported, in a qualitative fashion, by the respective values of the glass transition temperatures.

The value of 7.0 for the poly(vinylethylene) is slightly less than that for polymethylene; i.e., $C_\infty = 7.6$.[48] It is recognized that the internal rotational angle ϕ about the polymethylene skeletal backbone bonds, as measured from the trans position, may take the discrete values of ϕ(trans), ϕ(gauche, g) and ϕ(gauche bar, $\bar{g}$),[49] where the gauche conformers are less stable than the trans conformer. Furthermore, the occurrence of either the $g\bar{g}$ or $\bar{g}g$ for two consecutive bonds is energetically unstable as a consequence of steric interference, i.e., nonbonded interactions resulting from rotations about more than two consecutive backbone bonds. Thus the alteration of the polymethylene C_∞ occasioned by the introduction, in an atactic fashion, of either a vinyl or an ethyl group should be rationalized within the scope of this framework.

Clearly, the presence of either of these side groups leads to C_∞ values lower than that exhibited by the parent polymethylene chain. This effect can, at least in part, be explained by an increase in the population of the more compact gauche conformations at the expense of the more extended trans form. Thus the introduction of the vinyl and ethyl substituent groups cause, in part, the energy minima for the rotation potentials of the carbon–carbon single bond leading to the g or $\bar{g}$ conformers to become more favorable relative to the trans form as compared to those observed for polymethylene. It must also be mentioned that neighbor correlations must also be taken into account.

As Flory, Mark, and Abe[7] have pointed out, the presence of an articulated side group (ethyl), in which the group β to the chain backbone is of a size equivalent to the methylene unit, can be readily accommodated if one or both of the backbone bonds adjacent to the methine carbon has a gauche conformation. This avoidance of steric repulsions is much more limited for the case when both of the adjacent bonds possess the trans conformations. Thus the change in C_∞ brought about by the presence of the ethyl group on a polyethylene backbone is the anticipated effect. In a similar vein, the presence of the relatively unarticulated vinyl group would not be expected to lead to a large decrease in C_∞ since the population of the trans conformers would not be decreased by a substantial extent.

It is also germane to note that our value of C_∞ for the poly(ethylethylene) is in agreement with the predictions of Flory, Mark, and Abe.[7,8] Among the parameters used in their calculations were $\Delta\phi$ and τ^*, where $\Delta\phi$ denotes the change in rotation angle for the t, g, and $\bar{g}$ states and τ^* the statistical weight factor for the occurrence of a t–t pair of bonds on either side of the methine carbons in the chain backbone. Our evaluation of C_∞ allows a refinement of the values for these two parameters.

Thus for the case where $\Delta\phi$ is zero, the value of τ^* ranges from about 0.08 to 0.22. If, though, the presence of the substituent group causes a perturbation, via three- and four-bond interactions, then the value of τ^* assumes a value within the range of about 0.30 to 0.36 for the case where $\Delta\phi = 20°$. This latter case may well represent a more realistic assessment since nonbonded interactions would be expected to alter the rotational angles in atactic poly(ethylethylene). It is, though, presently not possible to refine the values of $\Delta\phi$ without further insight into the value of τ^*, which in effect denotes the frequency of the occurrence of the t–t bond pair, associated with the methine carbons, along the chain backbone. It is also to be recalled that the foregoing values refer to those used[7] in the three rotational state model, which is recognized to be approximate.[47,50,51] More elaborate calculations involving the five rotational state approach may lead to different, and more refined, values for $\Delta\phi$ and τ^*.

It should also be noted that our value for the poly(ethylethylene) of 5.3 is not in agreement with the values of 7.2[20] and 6.6,[21] which are available elsewhere. Suffice it to note that those values are based on intrinsic viscosity measurements of polydisperse samples, with no corrections made for polydispersity.[52] Additional suppositions regarding the reasons for the differences in the previously reported C_∞ experimental values and our value would not be in order.

In conclusion, it is also noted that the Huggins constants show trends similar to that observed for near-monodisperse polyisoprenes under Θ conditions and in a good solvent.[53] Our results for k_H in tetrahydrofuran are in accord with the predictions[54-58] that $k_H < 0.4$ for linear polymers in good solvents.

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References and Notes

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(2) Ciferri, A.; Hoeve, C. A. J.; Flory, P. J. *J. Am. Chem. Soc.* **1961**, *83*, 1015.

(3) Hoeve, C. A. J. *J. Chem. Phys.* **1961**, *35*, 1266.

(4) Mark, J. E.; Flory, P. J. *J. Am. Chem. Soc.* **1965**, *87*, 1423.

(5) Flory, P. J.; Mark, J. E.; Abe, A. *J. Polym. Sci., Part B* **1965**, *3*, 973.

(6) Abe, A.; Jernigen, R. L.; Flory, P. J. *J. Am. Chem. Soc.* **1966**, *88*, 631.

(7) Flory, P. J.; Mark, J. E.; Abe, A. *J. Am. Chem. Soc.* **1966**, *88*, 639.

(8) Abe, A. *Polym. J.* **1970**, *1*, 232.

(9) Heatley, F. *Polymer* **1972**, *13*, 218.

(10) Boyd, R. J.; Breitling, S. M. *Macromolecules* **1972**, *5*, 279.

(11) Biskup, U.; Cantow, H. J. *Macromolecules* **1972**, *5*, 546.

(12) Allegra, G.; Calligaris, M.; Randaccio, L.; Moraglio, G. *Macromolecules* **1973**, *6*, 397.

(13) Suter, U. W.; Flory, P. J. *Macromolecules* **1975**, *8*, 765.

(14) Chiang, R. *J. Phys. Chem.* **1965**, *69*, 3109.

(15) Chiang, R. *J. Phys. Chem.* **1966**, *70*, 2348.

(16) Stacy, C. J.; Arnett, R. L. *J. Phys. Chem.* **1965**, *69*, 3109.

(17) Nakajima, A.; Hamada, F.; Hayashi, S. *J. Polym. Sci., Part C* **1966**, *15*, 285.

(18) Inagaki, H.; Miyamoto, T.; Ohta, S. *J. Phys. Chem.* **1966**, *70*, 3420.

(19) Wagner, H. L.; Hoeve, C. A. J. *J. Polym. Sci., Part C* **1976**, *54*, 327.

(20) Moraglio, G.; Bianotti, G.; Canusso, F. *Eur. Polym. J.* **1967**, *3*, 251.

(21) Krigbaum, W. R.; Kurz, J. E.; Smith, P. *J. Am. Chem. Soc.* **1961**, *65*, 1984.

(22) Graessley, W. W.; Edwards, S. F. *Polymer* **1981**, *22*, 1329.

(23) Halasa, A. F.; Schulz, D.; Tate, D. P.; Mochel, V. D. *Adv. Organomet. Chem.* **1980**, *16*, 55.

(24) Halasa, A. F.; Lohr, D. F.; Hall, J. E. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1357.

(25) Worsfold, D. J.; Bywater, S.; Schuê, F.; Sledz, F.; Marti-Collet, V. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 239.

(26) Morton, M.; Fetters, L. J. *Rubber Rev.* **1975**, *48*, 359.

(27) Rachapudy, H.; Smith, G. G.; Raju, V. R.; Graessley, W. W. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1211.

(28) Grubisic, Z.; Rempp, P.; Benoit, H. *J. Polym. Sci., Part B* **1967**, *5*, 753.

(29) Wang, J.-S.; Porter, R. S.; Knox, J. R. *Polym. J.* **1978**, *10*, 619.

(30) Clague, A. D. H.; van Broekhouen, J. A. M.; Blaauw, L. P. *Macromolecules* **1974**, *7*, 348.

(31) Makino, K.; Ikeyama, M.; Takeuchi, Y.; Tanaka, Y. *Polymer* **1982**, *23*, 287, 413.

(32) Quack, G.; Fetters, L. J. *Macromolecules* **1978**, *11*, 369.

(33) Luxton, A. R.; Burrage, M.; Quack, G.; Fetters, L. J. *Polymer* **1981**, *22*, 383.

(34) Burchard, W. *Makromol. Chem.* **1960**, *50*, 20.

(35) Stockmayer, W. H.; Fixman, M. *J. Polym. Sci., Part C* **1963**, *1*, 137.

(36) Flory, P. J. *J. Chem. Phys.* **1949**, *10*, 51.

(37) Flory, P. J.; Fox, T. G *J. Am. Chem. Soc.* **1951**, *73*, 1904.

(38) Fox, T. G; Flory, P. J. *J. Phys. Colloid Chem.* **1949**, *53*, 197.

(39) Flory, P. J.; Fox, T. G *J. Polym. Sci.* **1950**, *5*, 745.

(40) McIntyre, D.; Wims, A.; Williams, L. C.; Mandelkern, L. *J. Phys. Chem.* **1962**, *66*, 1932.
(41) Berry, G. C. *J. Chem. Phys.* **1967**, *46*, 4886.
(42) Miyaki, Y.; Einaga, Y.; Fujita, H.; Fukada, M. *Macromolecules* **1980**, *13*, 588.
(43) Hadjichristidis, N.; Xu, Z.; Fetters, L. J.; Roovers, J. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 743.
(44) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, NY, 1953; p 617.
(45) Fetters, L. J.; Firer, E. M. *Polymer* **1977**, *18*, 306.
(46) Yasuda, H.; Walczak, M.; Rhine, W.; Stucky, G. *J. Organomet. Chem.* **1975**, *90*, 123.
(47) Flory, P. J. "Statistical Mechanics of Chain Molecules"; Wiley: New York, 1969; p 35-39.
(48) This corrected value (to 30 °C) for the polymethylene C_∞ is based on the values listed in Table I, p 40, of ref 47, which were measured over the temperature range 138-142 °C and by the use of the temperature coefficient -1.1×10^{-3} deg^{-1} as is given in Table 2, p 45, of ref 47.
(49) Flory, P. J.; Sundararajan, P. R.; DeBolt, L. C. *J. Am. Chem. Soc.* **1974**, *96*, 5015.
(50) Flory, P. J. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *11*, 621.
(51) Flory, P. J. *Macromolecules* **1974**, *7*, 381.
(52) Bareiss, R. E. "Polymer Handbook", 2nd ed.; Brandrup, J., Immergut, E., Eds.; Wiley: New York, 1974; p IV-115.
(53) Hadjichristidis, N.; Quack, G.; Bauer, B. J.; Fetters, L. J., to be submitted.
(54) Riseman, J.; Ullman, R. *J. Chem. Phys.* **1951**, *19*, 578.
(55) Yamakawa, H. *J. Chem. Phys.* **1961**, *34*, 1360.
(56) Imai, S. *Proc. R. Soc. London, Ser. A* **1969**, *308*, 497.
(57) Freed, K. F.; Edwards, S. F. *J. Chem. Phys.* **1975**, *62*, 4032.
(58) Muthukumar, M.; Freed, K. F. *Macromolecules* **1977**, *10*, 899.

Molecular Weight Distribution for Molecules Requiring Rotational Diffusion Prior to Reaction

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ABSTRACT: The molecular weight distributions have been calculated for rigid rods that must rotate into a collinear conformation prior to reaction. The underlying assumptions include bimolecular reaction without byproduct formation and a rotary diffusion parameter that is proportional to molecular length through the term $i^{-N} + j^{-N}$, where i and j are rod lengths and N is an arbitrary parameter. To reduce the number of simultaneous differential equations that must be solved, an empirical scaling law is introduced which is independent of chain length. Essentially asymptotic values are obtained for number-average molecular weights greater than 10.

Introduction

In 1939 Flory announced the principle of equal reactivity of polymer chains.[1] The principle maintains that the ability of a chain molecule to form larger molecules is independent of the chain length. The argument was very significant at that time for two reasons: First, the existence of high molecular weight polymers was considered by some to be improbable. These proponents argued that the high molecular weight species must have a higher diffusion constant, relative to the lower molecular weight species, which would eventually limit the extent of polymerization. Studies on condensation-type polymers with random coils demonstrated the general validity of the principle of equal reactivity.[2] The second significant result was that the distribution of molecular weights could be readily calculated from kinetic parameters that were independent of chain length.

The major significant deviations from this principle seem to occur only with very low molecular weight species where inductive or polarization effects can be transmitted across a small molecule. Indeed, Lenz[3] cites a number of cases where the reactivity of a functional group on a difunctional monomer depends on whether or not the other functional group has reacted. Challa[4] showed a similar effect on the rate of polymerization of poly(ethylene terephthalate), where the reactivity of the "monomer" bis(β-hydroxyethyl) terephthalate differs from that of higher oligomers and polymer. Peebles and Wagner[8] examined the transesterification kinetics of dimethyl terephthalate and ethylene glycol in the presence of a catalyst. They concluded that the second transesterification reaction was some 3 times faster than the first transesterification reaction. The overall transesterification of the terephthalate monomer must somehow involve some type of molecular transition state containing the catalyst because attempts to verify the faster transesterification reaction with the partly transesterified material resulted in absolutely no reaction.[6] Thus, the documented "violations" of the principle of equal reactivity seem to be restricted to very small chain segments of random coil molecules.

Several calculations have been made to determine how departures from the principle of equal reactivity would influence the molecular weight distribution of a polymer. Nanda and Jain[7] assumed that the second-order reaction constant for a condensation polymer was proportional to the molecular weight of the formed polymer through the relation $k(1 + \xi i)$, where k and ξ are constants, and i is the number of monomers in a chain of length i, to obtain an analytical solution for the molecular weight distribution. Maget[8] developed simultaneous integral equations for stepwise polymerizations without termination for a number of conditions where the rate constant for propagation varied with chain length. His approaches are limited, however, in that the precise polymerization conditions must be specified before the equations can be evaluated.

A new series of stiff rodlike polymers[9] has recently been synthesized and characterized with a repeating unit of the form

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