Study of the Dilute Solution Properties of Poly(Acrylamide-*Co*-Methyl Methacrylate)

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STUDY OF THE DILUTE SOLUTION PROPERTIES OF POLY(ACRYLAMIDE-*co*-METHYL METHACRYLATE)

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ABSTRACT

A random $(r_1r_2 = 1)$ hydrophilic/hydrophobic copolymer of methyl methacrylate and acrylamide has been prepared and characterized. Fractions prepared by the fractional precipitation method are characterized in terms of molecular weight, second virial coefficient, intrinsic viscosity, and diffusion coefficient. Equivalent hard sphere radii are calculated, and the ratios between different radii are compared to those of homopolymers. Molecular weight dependencies of the second virial coefficient, intrinsic viscosity, and diffusion coefficient are also examined. The results indicate that random copolymers made of very different comonomers behave similarly, in their scaling behavior, to homopolymers, although these results are somewhat inconclusive due to the narrow range and relatively low values of molecular weight investigated.

INTRODUCTION

Dilute solution properties of flexible chain polymers, such as radius of gyration (R_G), second virial coefficient (A_2), diffusion coefficient (D_0), and intrinsic viscosity $([\eta])$, have been the subject of much theoretical consideration and experimental measurement [1, 2]. These properties reflect the polymer size in the solution.

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R_G is the root-mean-square distance of the segments of the polymer chain from the chain's center of gravity; A_2 is proportional to an effective volume excluded by a macromolecule to other molecules in solution; D_0 is related to the apparent hydrodynamic size of a molecule as it moves through a solvent; and $[\eta]$ is a measure of the polymer molecule's hydrodynamic volume influencing the rate of energy dissipation during shear flow of the polymer solution.

Scaling theory predicts that, in the nondraining self-avoiding limit, dilute solution properties exhibit power scaling laws against molecular weight (M) given by [3]

$$R_G \approx M^\nu, A_2 \approx M^\beta, D_0 \approx M^{-\nu}, [\eta] \approx M^\alpha \tag{1}$$

where ν is a characteristic exponent and $\alpha = 3\nu - 1$, $\beta = 3\nu - 2$. The hydrodynamic radius (R_H) can be calculated from D_0 and the Stokes–Einstein equation:

$$D_0 = kT/6\pi\eta_0 R_H \tag{2}$$

where k is the Boltzmann constant, T is the absolute temperature, η_0 is the solvent viscosity, and R_H is the hydrodynamic radius. Because D_0 is proportional to $M^{-\nu}$, R_H should be proportional to M^ν.

In good solvents the characteristic exponent ν was initially estimated by Flory to be 0.6 [4, 5]. A more rigorous treatment by renormalization group theory predicts a slightly smaller value: 0.588 [6]. However, the Flory value 0.6 for three dimensions can be considered exact for most practical applications [5]. Below the asymptotic limit, where the molecular weight is not large enough or where the solvent is only fairly good, the ν value is expected to lie below 0.6, but larger than 0.5, which is the value of ν in the θ-state [1].

In addition to the scaling law expressions, theory also predicts [3], in the nondraining self-avoiding limit, universal ratios between the dilute solution properties which are independent of the chemical details of the polymer chain. These ratios are

$$U_{\eta s} = \frac{M[\eta]}{N_A R_G^3} = 4.078 \tag{3}$$

$$U_{A\eta} = \frac{(A_2 M)}{[\eta]} = 1.196 \tag{4}$$

$$U_{fs} = \frac{D_0}{\eta_0 R_G kT} = 12.067 \tag{5}$$

$$U_{\eta f} = \left(\frac{M[\eta]}{N_A}\right)^{\frac{1}{3}} \frac{\eta_0 kT}{D_0} = 0.1297 \tag{6}$$

In the above equations, kT takes its usual meaning and N_A is Avogadro's number. These universal ratios are frequently represented in terms of the ratios between equivalent solid sphere radii. The universal ratios of these radii have been calculated as $R_G:R_V:R_T:R_H = 1.56:1.12:1.02:1.00$ [3].

Experimental results from various homopolymer systems show good agreement with the theoretically predicted values [3, 7–13]. On the other hand, copolymers have rarely been used for comparison with theory. One exception is alternating copolymers of ethylene and tetrafluoroethylene [14, 15]. For these copolymers the

exponents obtained from the molecular weight dependence of dilute solution properties show good agreement with the theoretically predicted values. This should cause little surprise since the alternating copolymers might be viewed as homopolymers with repeating units consisting of pairs of consecutive alternating comonomers.

In the present work we study the dilute solution properties of a copolymer composed of two monomers with very different polarities. Molecular weight dependencies of these properties and the equivalent hard sphere sizes calculated are examined, and the results are compared with those for homopolymers. The copolymer employed in this work is the random copolymer of methyl methacrylate and acrylamide. Acrylamide is a very hydrophilic monomer which is freely miscible with water. On the other hand, methyl methacrylate is a hydrophobic monomer which is insoluble in water. The dilute solution properties of this copolymer are studied in an amphiphilic solvent, *N*-methylformamide.

EXPERIMENTAL SECTION

Polymer Samples

Copolymers were prepared by free radical polymerization in pure ethanol solution at 70°C in the presence of 3.8×10^{-4} mol/L azobisisobutyronitrile. The total monomer concentration was held constant at 3.2 mol/L, and the ratio of acrylamide and methyl methacrylate in the feed was 3:1. All reagents and solvents used in the polymerization reaction were purified prior to use. Ethanol was introduced into the reaction flask under argon pressure using a long transfer needle. The reaction mixture was degassed and flushed with argon gas. After reaction, the copolymer was precipitated in ethyl ether and recovered by filtration using a fritted glass filter. Copolymer purification was carried out by repeating three times the cycle of dissolving in *N*-methylformamide and precipitation in ethyl ether. The purified copolymer was dried in a vacuum oven at 60°C overnight and stored in the dark in a dessicator at room temperature. Polymerization was stopped before 9% completion in order to minimize compositional drift. The composition of the copolymers was determined by elemental analysis.

Determination of Reactivity Ratio

Copolymers from feeds of five different comonomer concentrations were prepared by the procedure described above. The total concentration of monomers was held constant at 0.8 mol/L ethanol. The initiator was used at a concentration of 2 g/L ethanol. Reactivity ratios were calculated by both the Fineman–Ross and the Kelen–Tüdös methods [16, 17].

Fractionation

Polymer fractionation was performed in an *N*-methylformamide (solvent)–ethanol (precipitant) mixture under argon at 26 ± 0.05°C. The concentration of the polymer in the solution was 0.2–0.05% (w/v). Ten fractions were obtained. Only seven fractions, numbers 4 to 10, were used in further studies due to the high

polydispersity of the first three fractions (estimated from the cumulant analysis of dynamic light-scattering data); these are denoted by S-1 (4th fraction), S-2 (5th fraction), etc. Because random copolymer molecules can differ from each other in both molecular weight and composition, we cannot assume that fractionation will be based solely on molecular weight differences. We will argue below, however, that compositional variations in long polymers are probably negligible, and the fractionations are, to a good approximation, based on molecular weight [18, 19].

Static Light-Scattering Measurements

Molecular weights and second virial coefficients were obtained with a BI-200SM motorized goniometer and detection system (Brookhaven Instrument Co.). The light employed was a vertically polarized 488 nm blue line from a Lexel Model 95-2 argon ion laser. The calibration of the system was carried out using benzene, and the Rayleigh ratio value used for benzene was 3.8×10^{-5} cm^{-1} [20, 21]. At 25°C and $\lambda = 488$ nm, the refractive index of N-methylformamide (n_0) is 1.4309 [22] and the refractive index increment of the sample (dn/dc) is 0.0848 cm^3/g, determined by a refractometer (C. N. Wood, Model RF-600). For each copolymer sample, 4 to 6 solutions of different concentrations were prepared from a stock solution of N-methylformamide. The solutions were filtered into the measuring cell directly, using a 0.22-μm Millipore Teflon filter. For the highest molecular weight fraction (S-1), measurements were made at each of the following angles (θ): 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, and 140. Because the values of (count rate) $\times$ sin θ were independent of angle, intramolecular interference could be ignored. Hence, in all fractions, only data measured at 90° were used. Because of the lack of intramolecular interference, the radius of gyration could not be determined. All measurements were made at 25 $\pm$ 0.05°C.

Static light-scattering data were analyzed according to the equation [23]

$$Kc/R_\theta = 1/M_w + 2A_2c + \cdots \tag{7}$$

where K is the optical constant of the system [$K = 2\pi^2 n_0 (dn/dc)^2/\lambda^4 N_A$], c is the concentration in g/mL, R_θ is the excess Rayleigh ratio, M_w is the weight-average molecular weight, and A_2 is the second virial coefficient.

Dynamic Light-Scattering Measurements

The same light-scattering system used in the determination of molecular weight was used to measure intensity autocorrelation functions. The signal from the photomultiplier tube was sent to the DI-2030 Digital correlator with 136 channels (Brookhaven Instrument Co.) and stored. The concentration of the solutions measured was in the range $0.05c^*$ to $0.25c^*$, where c^* is the polymer coil overlap concentration [5], estimated as $[\eta]^{-1}$. Between three and seven measurements were made for every sample at 25 $\pm$ 0.05°C and at $\theta = 90°$. The viscosity of the solvent (N-methylformamide) was obtained from the literature [24].

The electric field autocorrelation function $g^{(1)}(\tau)$ is given by [25]

$$\ln g^{(1)}(\tau) = \tfrac{1}{2} \ln (1/b) + \tfrac{1}{2} \ln \{G^{(2)}(\tau)/B - 1\} \tag{8}$$

where τ is the delay time, b is a constant that is a function of the detecting electron-

ics, $G^{(2)}(\tau)$ is the intensity autocorrelation $<I(0)I(t)>$, and B is the baseline of the intensity autocorrelation function. For a polydisperse solution, the electric field autocorrelation function consists of a sum or distribution of single exponentials [26]:

$$g^{(1)}(\tau) = \int_0^\infty G(\Gamma) \exp (-\Gamma\tau)d\Gamma \qquad (9)$$

where $G(\Gamma)$ is the normalized distribution function of the decay rates and $\Gamma = Dq^2$. Here D is the translational diffusion coefficient and q is the magnitude of the scattering vector given by

$$q = (4\pi n_0/\lambda) \sin \left(\frac{\theta}{2}\right) \qquad (10)$$

The experimental electric autocorrelation function $g^{(1)}(\tau)$ was first fitted to a second-order cumulant using weighted least-squares [27]:

$$\ln g^{(1)}(\tau) = -\Gamma_{ave}\tau + \frac{1}{2} \mu_2\tau^2 \qquad (11)$$

where Γ_{ave} is the mean of decay constant Γ and μ_2/Γ_{ave}^2 is a measure of the width of the distribution in Γ. The experimental autocorrelation function was also analyzed using CONTIN (Version 2DP) [28], and the results were compared with the results by the cumulant method. The diffusion coefficient at zero concentration (D_0) was determined according to the equation [29]

$$D_c = D_0(1 + k_d c) \qquad (12)$$

where D_c is a diffusion coefficient measured at a finite concentration and k_d represents the first-order concentration dependence of the diffusion coefficient. D_0 values were determined from the intercepts of D_c versus concentration plots. The k_d values for these samples were determined from the slope. D_0 values for Samples S-5, S-6, and S-7 were estimated from theoretically estimated k_d values and a D_c measured at a sufficiently high concentration. The coefficient k_d was estimated from [29]

$$k_d = 0.8A_2M - [\eta]/2.5 - v_2 \qquad (13)$$

The partial specific volume v_2 is about 1 mL/g or less and was neglected in the calculation of k_d [30]. The hydrodynamic radius (R_H) was calculated from the Stokes–Einstein equation.

Viscosity Measurement

Measurements were made in *N*-methylformamide solution in a 25 $\pm$ 0.05°C bath using an Ostwald viscometer. Flow rates were chosen such that kinetic energy corrections were negligible. Intrinsic viscosity $[\eta]$ and Huggins' constant (k') were obtained from the intercept and slope of the plot of η_{red} against concentration, according to Huggins' equation

$$\eta_{sp}/c = [\eta] + k'[\eta]^2c \qquad (14)$$

Shear rate effects were negligible because the molecular weights of the samples were low.

RESULTS

Reactivity Ratios

The reactivity ratio values determined by the Fineman–Ross method were $r_{MMA} = 3.17 \pm 0.10$ and $r_{AA} = 0.32 \pm 0.04$. The values determined by the Kelen–Tüdös method were $r_{MMA} = 3.20 \pm 0.20$ and $r_{AA} = 0.31 \pm 0.02$. Figure 1 shows the Kelen–Tüdös plot. Both methods agree satisfactorily, so we may be quite confident of the r_1 and r_2 values. The results indicate random polymerization since the $r_1 r_2$ product is very close to unity.

Static Light-Scattering

In general, light scattering of copolymers must be analyzed differently from that of homopolymers because compositional heterogeneity leads to different values of (dn/dc) for every molecule [1]. However, it has been demonstrated that heteroge-

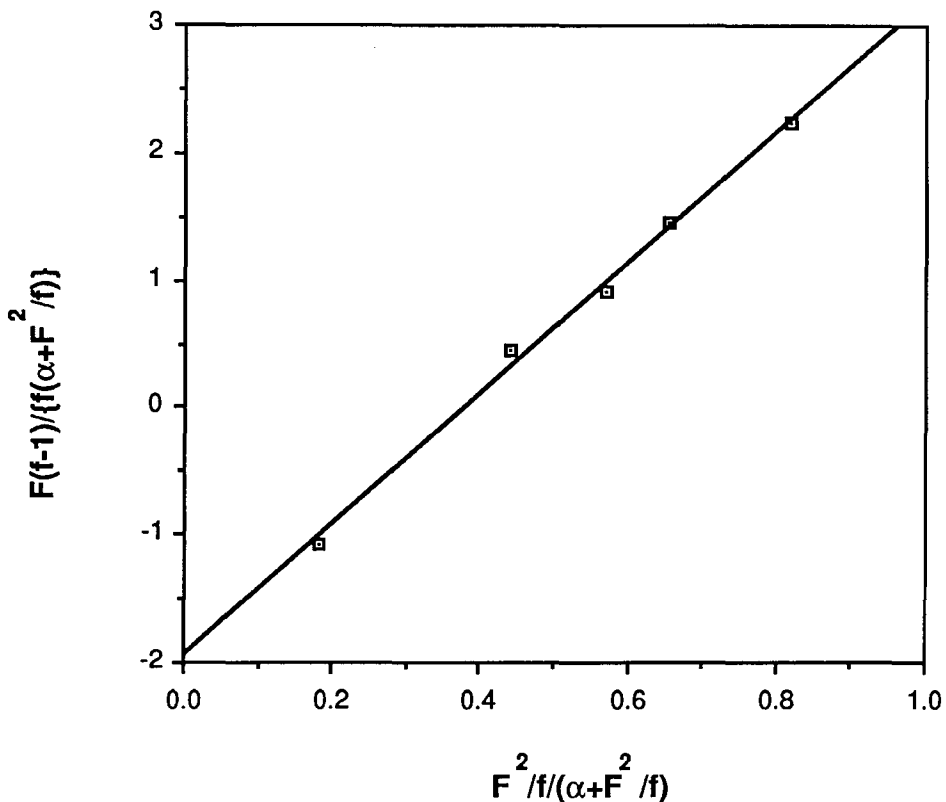FIG. 1.   Kelen–Tüdös plot for the determination of reactivity ratios of MMA and AA. F is the ratio of MMA (M_1) to AA (M_2) mole concentrations in the feed and f is the ratio of MMA to AA mole fractions in the copolymer. α is $(H_M H_m)^{0.5}$, where H_M is the highest value of F^2/f and H_m is the lowest value of F^2/f. The slope is $(r_1 + r_2/\alpha)$ and the intercept is $-r_2/\alpha$.

TABLE 1.   Molecular Weights and Second Virial
Coefficients (A_2) of the Copolymer Samples. The
Error Is the Standard Error of the Mean

Sample	Molecular weight ± SE, g/mol	A_2 ± SE × 10^4, mL/g
S-1	166,500 ± 1,600	4.15 ± 0.06
S-2	138,600 ± 4,500	4.37 ± 0.21
S-3	116,700 ± 1,300	4.84 ± 0.07
S-4	101,600 ± 4,600	5.14 ± 0.35
S-5	88,800 ± 3,500	5.23 ± 0.15
S-6	56,200 ± 1,100	5.69 ± 0.17
S-7	36,400 ± 1,200	6.22 ± 0.30

neity effects can be ignored for copolymers with $r_1 r_2$ close to unity [31]. The molecular weights and second virial coefficients obtained are listed in Table 1. The standard errors are relatively small ($< 5\%$) except for S-4, which shows about 5% standard error for molecular weight and 7% for second virial coefficient.

Viscosity

Intrinsic viscosities and Huggins' coefficients obtained from the intercept and slope of the plot of η_{red} against concentration are listed in Table 2. The Huggins' constant k' for flexibly coiled polymers in good solvents usually has a value between 0.3 and 0.5 and is approximately constant for any given polymer–solvent combination. The values obtained in this work, with an average of 0.41, lie well within this range.

Dynamic Light-Scattering

Table 3 shows the results of data analyses by both the cumulant and CONTIN methods. The polydispersity index [μ_2/Γ_{ave}^2] is also listed. In general, the hydrodynamic radii obtained by both methods are in good agreement, although the sizes

TABLE 2.   Intrinsic Viscosity and Huggins' Constant
of Each Sample. The Error Is the Standard Error of
the Mean

Sample	MW, g/mol	[h] (mL/g) ± SE	k'
S-1	166,500	59.6 ± 1.1	0.44
S-2	138,600	52.9 ± 0.4	0.41
S-3	116,700	46.7 ± 0.5	0.42
S-4	101,600	42.3 ± 0.1	0.42
S-5	88,800	37.9 ± 0.4	0.40
S-6	56,200	28.7 ± 0.2	0.38
S-7	36,400	21.6 ± 0.3	0.43

TABLE 3.   Hydrodynamic Radius (R_H) and Diffusion Coefficient (D_c) of Each Sample at Several Concentrations. The Data in Parentheses Are Obtained by the CONTIN Method. The Error Is the Standard Error of the Mean

Sample	Concentration, mg/mL	Size (R_H), nm	Diffusion coefficient (D_c) ($\times 10^{+7}$), cm^2/s	μ_2/Γ^2_{ave}
S-1	1.0	10.8 (10.9)	1.219 ± 0.002 (1.210 ± 0.003)	0.17 ± 0.00
	2.0	10.3 (10.5)	1.282 ± 0.016 (1.254 ± 0.016)	0.09 ± 0.04
	3.0	10.1 (10.2)	1.313 ± 0.016 (1.298 ± 0.042)	0.10 ± 0.03
	4.0	9.6 (9.9)	1.375 ± 0.003 (1.331 ± 0.000)	0.08 ± 0.05
S-2	2.0	9.5 (9.8)	1.391 ± 0.017 (1.349 ± 0.048)	0.13 ± 0.03
	3.4	9.5 (9.5)	1.396 ± 0.016 (1.398 ± 0.035)	0.12 ± 0.01
	5.1	9.3 (9.2)	1.421 ± 0.005 (1.445 ± 0.023)	0.13 ± 0.02
	6.4	9.3 (9.0)	1.433 ± 0.010 (1.475 ± 0.016)	0.16 ± 0.02
S-3	2.5	8.1 (8.5)	1.635 ± 0.021 (1.551 ± 0.024)	0.10 ± 0.03
	5.1	8.0 (8.0)	1.654 ± 0.075 (1.652 ± 0.050)	0.08 ± 0.02
	7.1	7.6 (7.7)	1.733 ± 0.005 (1.722 ± 0.054)	0.08 ± 0.03
	10.1	7.7 (7.3)	1.716 ± 0.047 (1.793 ± 0.059)	0.08 ± 0.03
S-4	2.0	6.9 (7.7)	1.924 ± 0.093 (1.710 ± 0.037)	0.17 ± 0.02
	3.3	6.8 (7.4)	1.942 ± 0.010 (1.787 ± 0.007)	0.12 ± 0.02
	5.0	6.8 (7.1)	1.941 ± 0.017 (1.859 ± 0.021)	0.10 ± 0.01
	10	6.7 (7.1)	1.964 ± 0.004 (1.865 ± 0.008)	0.09 ± 0.01
S-5	2.6	6.8 (7.0)	1.945 ± 0.014 (1.909 ± 0.190)	0.24 ± 0.02
S-6	2.7	5.3 (5.6)	2.496 ± 0.055 (2.347 ± 0.178)	0.17 ± 0.05
S-7	11.4	4.3 (4.2)	3.089 ± 0.007 (3.114 ± 0.022)	0.19 ± 0.01

obtained by the CONTIN method are usually slightly larger than those calculated by the cumulant method. The difference is usually within 5% except for the S-4 samples at low concentrations, which show differences of 8–10%. The μ_2/Γ^2_{ave} values are highly variable from run to run. Except for S-4, μ_2/Γ^2_{ave} becomes smaller as concentration increases, probably because the quality of scattering data is better at higher concentrations. Sample S-5, S-6, and S-7 show fairly large values of μ_2/Γ^2_{ave}. Since scattering intensity is proportional to the square of the molecular weight for a Rayleigh scatterer, this may be due to the weak scattering from these small molecular weight samples. D_0 and k_d values obtained are shown in Table 4. Theoretically calculated k_d values are in good agreement with the measured k_d values. Similar k_d values are observed for the polystyrene-tetrahydrofuran system [13] where the k_d values are 14, 32, and 36 mL/g for samples with weight-average molecular weights of 51,000, 110,000, and 180,000, respectively.

ANALYSIS OF DATA

Intrinsic viscosity (Table 2) and second virial coefficient (Table 1) values are plotted as a function of molecular weight in Figs. 2 and 3. In the molecular weight range studied, the data can be described by

TABLE 4.   Diffusion Coefficient at Zero Concentration (D_0) and k_d Values. Hydrodynamic Radius (R_H) is Calculated from the Stokes–Einstein Equation. The Error is the Standard Error of the Mean

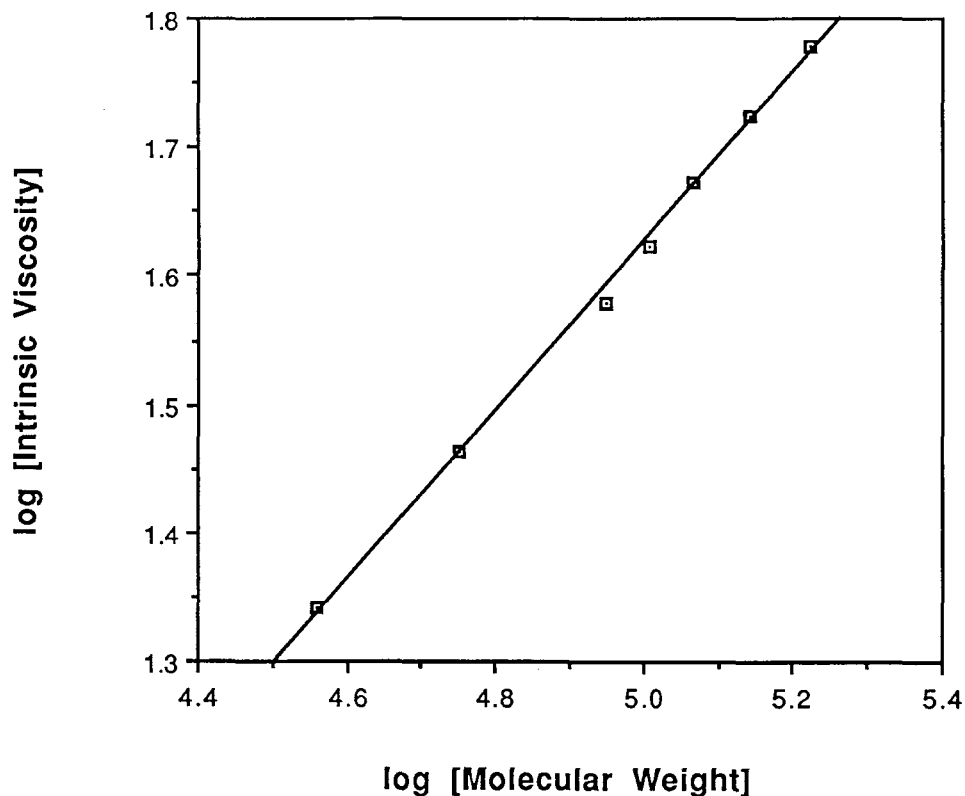| Sample	MW, g	Size (R_H), nm	$D_0 \times 10^7$, cm^2/s	k_d, mL/g
S-1	166,500	11.3	1.171 ± 0.005	34.7 ± 1.7 (31.3)
S-2	138,600	10.2	1.296 ± 0.008	22.0 ± 1.5 (27.3)
S-3	116,700	8.9	1.482 ± 0.019	21.5 ± 2.0 (26.4)
S-4	101,600	8.0	1.643 ± 0.030	24.2 ± 4.3 (25.0)
S-5	88,800	7.4	1.797	(22.0)
S-6	56,200	5.8	2.262	(14.0)
S-7	36,400	4.7	2.825	(9.3)

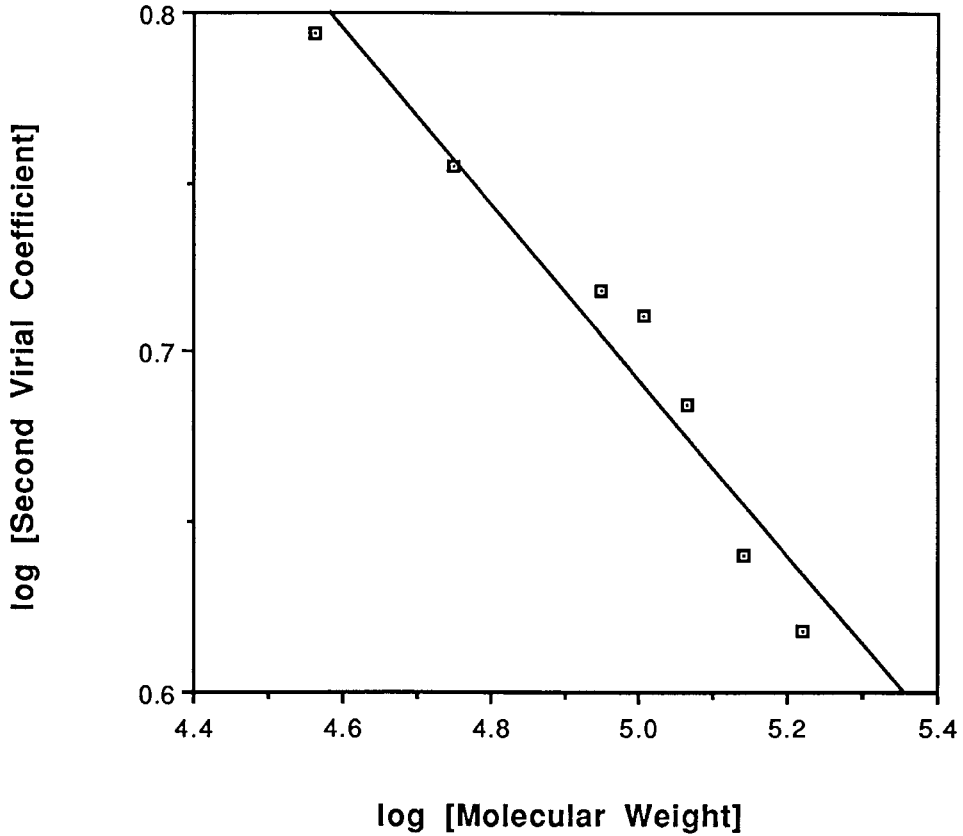FIG. 2.   Plot of the molecular weight dependence of intrinsic viscosity.

FIG. 3.   Plot of the molecular weight dependence of second virial coefficient.

$$[\eta] = 2.06 \times 10^{-2} \, M^{0.662 \pm 0.014} \, \text{mL/g} \tag{15}$$

$$A_2 = 0.98 \times 10^{-2} \, M^{-0.260 \pm 0.029} \, \text{mL/g} \tag{16}$$

Polymer molecules in good solvents are usually treated as impenetrable hard spheres in both hydrodynamic and thermodynamic models [4]. For a hard sphere, R_V and R_T are given by [1]

$$R_V = 5.41 \times 10^{-9} \, ([\eta]M)^{1/3} \, \text{nm} \tag{17}$$

$$R_T = 4.63 \times 10^{-9} \, (A_2 M^2)^{1/3} \, \text{nm} \tag{18}$$

Substituting for $[\eta]$ from Eq. (15) and for A_2 from Eq. (16), Eqs. (17) and (18) become the following scaling expressions:

$$R_V = 1.48 \times 10^{-2} \, M^{0.554 \pm 0.005} \, \text{nm} \tag{19}$$

$$R_T = 0.99 \times 10^{-2} \, M^{0.580 \pm 0.010} \, \text{nm} \tag{20}$$

In Fig. 4, values of hydrodynamic radius are plotted as a function of molecular weight. The data can be described by a power law:
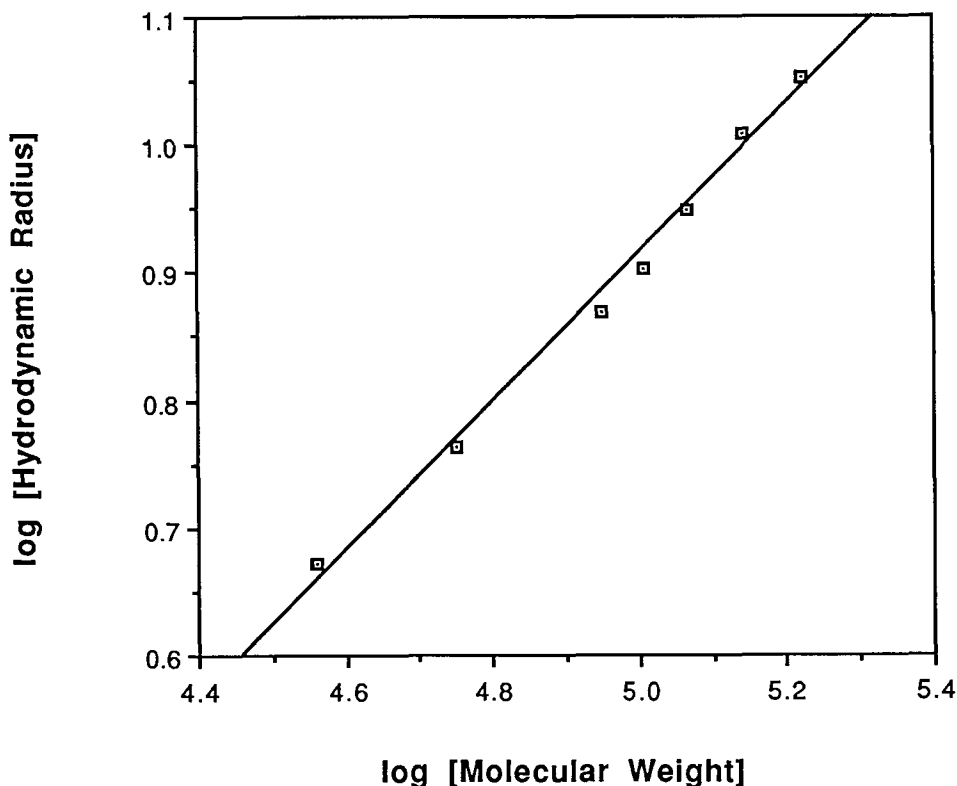
FIG. 4. Plot of the molecular weight dependence of hydrodynamic radius.

$$R_H = 1.01 \times 10^{-2} M^{0.582} \text{ nm} \qquad (21)$$

with an uncertainty in the exponent of ± 0.023. The values of R_V, R_T, and R_H are collected in Table 5. Ratios between the various radii are also listed.

DISCUSSION

Copolymer molecules can differ from each other not only in their molecular weight but also in the relative content of each type of monomer unit, i.e., in their chemical composition. The chemical composition distribution can arise from two sources; the statistical nature of the formation of copolymers (statistical distribution) and the change in the feed comonomer ratio at various stages of the copolymerization reaction. Compositional distribution due to drift in the feed comonomer composition at low conversion ($< 10\%$) is usually negligible [18], and we can assume that there is only statistical distribution of chemical composition. The magnitude of the statistical distribution depends on the size of the copolymer molecules. The dependence of the distribution breadth on the size of the molecules can be determined by the theoretical expression for the variance of chemical composition [19], where σ^2 is expressed as $\sigma^2 = w_{av}(1 - w_{av})k/P_n$ {w_{av} is average composition, P_n is

TABLE 5.   Size of the Molecules Determined by Various Methods and the Ratios between Different Radii

Sample	MW, g	R_V, nm	R_T, nm	R_H, nm	R_V/R_H	R_T/R_H	R_V/R_T
S-1	166,500	11.7	10.4	11.3	1.04	0.92	1.13
S-2	138,600	10.5	9.4	10.2	1.03	0.92	1.12
S-3	116,700	9.5	8.7	8.9	1.07	0.98	1.09
S-4	101,600	8.8	8.1	8.0	1.10	1.01	1.09
S-5	88,800	8.1	7.4	7.4	1.10	1.00	1.09
S-6	56,200	6.4	5.6	5.8	1.10	0.97	1.14
S-7	36,400	5.0	4.3	4.7	1.07	0.92	1.16
				Average:	1.07	0.96	1.12
			Standard error:		± 0.03	± 0.04	± 0.03
				Predicted:	1.12	1.02	1.10

the number-average chain length, and $k = [1 - 4w_{av}(1 - w_{av})(1 - r_1 r_2)]^{1/2}$ where r_1 and r_2 are the reactivity ratios of each monomer}. For a random copolymer, $r_1 r_2 = 1$, and this formula gives $\sigma^2 = w_{av}(1 - w_{av})/P_n$. The breadth of the distribution becomes smaller as P_n increases, and it becomes zero for a copolymer with infinite molecular weight. When the chain length is 100, the distribution is rather broad with normalized standard deviation 5%. As chain length increases, the distribution becomes narrower. When the chain length is 420, which is approximately the case of the lowest molecular weight sample used, about 95% of molecules fall within $\pm 5\%$ of the mean. A fractionation procedure with the accuracy to separate within this level of compositional heterogeneity does not exist. Assuming that statistical fluctuation in composition can be ignored, we postulate that fractionations are only by molecular weight.

The exponents obtained in this work should be treated qualitatively rather than quantitatively because the molecular weights of the samples range over only one decade and are not large enough to observe the asymptotic behavior of various physical and transport properties. Another reason for the qualitative interpretation of the exponents obtained is that the samples used are not monodisperse. Finally, we make the assumption that the fractions are exclusively based on molecular weight, although we do expect a small distribution due to compositional heterogeneity.

The exponent α obtained for intrinsic viscosity is 0.662. A large amount of data indicates that α is 0.5 in θ-solvents and that α takes values between 0.5 and 0.8 in non-θ-solvents. Generally, α for a given polymer is larger for a better solvent [32]. In good solvents, α is usually found to lie between 0.7 and 0.8. The theoretically predicted good solvent limiting value of α is 0.8 for the Flory theory and 0.764 based on the renormalization group calculation. The α-value obtained in this work is rather smaller than the values usually obtained in good solvents for other polymers. Actually, the data points obtained in this work follow a curve slightly bent upward at molecular weight 88,800 (S-5), above which they follow a straight line with a slope of $\alpha = 0.728$. This α-value is closer to the limiting value in a good solvent than the value $\alpha = 0.662$ obtained by using the whole set of data points.

Similar behavior has been reported in the polystyrene–benzene system by Einaga et al. [33].

The exponent β of Eq. (16) is usually in the range 0.2–0.3, although the asymptotic value is predicted to be 0.2 [1, 4]. However, it has been observed that log M vs log A_2 plots show an upward curvature in the low molecular weight region [8, 11]. Fujita [34] suggests that, in general, β should be considered as a function of molecular weight. Figure 3 shows the plot of log M vs log A_2 for the data obtained in this work. The value of β obtained, 0.26, is well within the usual range of β observed for homopolymers.

A more careful look at the data points of A_2 and R_H reveals that there is a slight deviation for the two highest molecular weight samples. This deviation may originate from the molecular weight heterogeneity of these high molecular weight samples. It is also possible that the asymptotic behavior is being approached as the molecular weight increases, as discussed in the previous paragraph.

In Table 5 the various calculated radii (R_V, R_T, and R_H) are listed. For sufficiently long flexible chains in good solvents, these radii are expected to differ from one another, but to vary with molecular weight in the same way:

$$radius \propto M^\nu \tag{22}$$

Despite the low molecular weights of the samples examined, except for R_V, the exponents obtained in this work are close to the predicted values (0.588 or 0.6).

The ratios between sizes measured by different methods are shown in Table 5. The value of R_V/R_H varies between 1.03 and 1.10 with an average value of 1.07. The value of R_T/R_H varies between 0.92 and 1.01 with an average value of 0.96. The value of R_V/R_T varies between 1.09 and 1.16 with an average value of 1.12. Theoretical ratios of R_V/R_H, R_T/R_H, and R_V/R_T for self-avoiding coils are listed in Table 6 along with the results obtained in the studies of other polymer systems in good solvents. R_G/R_H values are also listed for comparison.

The values of R_T/R_H, R_V/R_H, and R_V/R_T obtained in this work are in good agreement with the theoretical values. Even the values for the lowest molecular weight sample ($M_w = 36,400$) are close to the predicted values. Similar results have been reported by various investigators. The results of Davidson et al. [7] for polyisoprene in cyclohexane show that R_T/R_H values for samples with molecular weight 15,200 and 23,400 are 0.92 and 0.93, respectively, indicating that they are already close to the asymptotic value. The results of Cotts et al. [35] and Selser [36] show that the R_T/R_H values reach that typical of very high molecular weight samples, probably the asymptotic value, at $M_w \approx 30,000$. The results of Huber et al. [11] also show that the R_T/R_H ratio reaches its asymptotic value at molecular weight as low as 10,000. Similar results were also obtained for R_V/R_H [7].

The central result of the present work is that, within the somewhat narrow molecular weight regions we studied, the various scaling laws applied to homopolymers also seem to be valid for copolymers whose comonomers are very different in polarity. {Acrylamide is freely soluble in very polar solvent such as water [$\delta = 23.4$ $(cal/cm^3)^{1/2}$] and methanol, but methyl methacrylate [$\delta = 8.8$ $(cal/cm^3)^{1/2}$] dissolves primarily in nonpolar solvents [32]}. It should be noted, however, that the copolymer/solvent system chosen for study may favor this result compared with other systems. First, we chose a random copolymer with nearly identical composition of the polar and nonpolar moieties. For such a copolymer, stretches of exclusively

TABLE 6. Theoretical and Experimental Ratios between Various Radii

Sample	Solvent	R_V/R_H	R_T/R_H	R_V/R_T	R_G/R_H	Reference
Self-avoiding coils	Good solvent	1.12	1.02	1.10	1.56	8, 9
Polystyrene	Toluene	1.04	0.98	1.06	1.47	11, 12
	Benzene	1.03	1.02	1.01	1.55	8, 10, 34
	Ethylbenzene	1.21	1.07	1.13	1.61	13
	Tetrahydrofuran	1.00	1.00	1.00	1.35	39, 40
Poly(α-methylstyrene)	Toluene	1.09	0.94	1.16	1.50	35, 36, 41–43
Polyisoprene	Cyclohexane	1.11	0.94	1.18	1.39	7
	N-Methylformamide	1.06	0.97	1.09	1.50	44
Poly(MMA-co-AA)		1.07	0.96	1.11		This work

polar or exclusively nonpolar character will be rare. Typical stretches along the chains will have polarities fluctuating around a mean polarity. One can therefore treat the copolymer as if it were a homopolymer with this average polarity. Such a simplification would not be appropriate for block copolymers, which are known to form polar and nonpolar domains. These points can be further supported by the fact that the homopolymers of the comonomers do not dissolve in MFA. The second feature of our system which favors homopolymerlike behavior is the use of an amphiphilic solvent. N-Methylformamide contains both polar and nonpolar regions which can make energetically favorable contacts with the acrylamide and methyl methacrylate monomers, respectively. Actually, both of these comonomers are soluble in MFA.

Although not studied here, the behavior of polar/nonpolar copolymers in a nonamphiphilic solvent such as water might be of considerable interest. Globular proteins are known to consist of polar and nonpolar amino acids. Apparently the stability of the protein globule depends on the sequestration of hydrophobic amino acids in the core, with a polar "coating." To a good approximation, the stability of the globule relative to an unfolded denatured state is determined by the length of the chain and the relative abundance of polar and nonpolar residues. This observation is the basis for a statistical mechanical theory of protein folding due to Dill [37]. The polar/nonpolar copolymers studied here might therefore be an interesting model system for studying protein collapse and denaturation, and for testing Dill's theory. We attempted to do this, but were hampered by the formation of aggregates whose scattering intensity overwhelmed that of the single chains. Recently a theory for copolymer aggregation has appeared by Fields et al. [38]. Based on the hydrophobicity of methyl methacrylate, the composition of our copolymers, and the lengths of our polymer fractions, it appears from this theory that aggregation was predictable. Further efforts to use polar/nonpolar copolymers to test Dill's theory should use copolymers whose length and composition are such that no aggregation should occur. It should be noted that Dill and Fields et al. predict that aggregation phenomena are extremely sensitive to composition: conditions exist in which the change of a single monomer from polar to nonpolar, or vice versa, can induce or prevent denaturation and/or aggregation. Therefore, if one is to use a random copolymer system, care must be taken to make sure that one is safely away from phases boundaries, and that composition is as homogeneous as possible. In particular, the statistical fluctuation in composition discussed above should be suppressed, and this may require alternative synthesis methods.

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