(5) Flory, P. J.; Ronca, G. *Mol. Cryst. Liq. Cryst.* **1979**, *54*, 311.
(6) Roviello, A.; Sirigu, A. *Gazz. Chim. Ital.* **1977**, *107*, 333.
(7) Asrar, J.; Toriumi, H.; Watanabe, J.; Krigbaum, W. R.; Ciferri, A. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 1119.
(8) Vasilenko, S. V.; Khokhlov, A. R.; Shibaev, V. P. *Macromolecules* **1984**, *17*, 2270.
(9) Boehm, R. E.; Martire, D. E.; Madhusudana, N. V. *Macromolecules* **1986**, *19*, 2329.
(10) Warner, M.; Flory, P. J. *J. Chem. Phys.* **1980**, *73*, 6327.
(11) Aden, T. A.; Bianchi, E.; Ciferri, A.; Conio, G. *Macromolecules* **1984**, *17*, 2010.
(12) Krigbaum, W. R.; Hakemi, H.; Ciferri, A.; Conio, G. *Macromolecules* **1985**, *18*, 973.
(13) Bianchi, E.; Ciferri, A.; Conio, G.; Krigbaum, W. R. *Polymer* **1987**, *28*, 813.
(14) Ciferri, A.; Marsano, E. *Gazz. Chim. Ital.* **1987**, *117*, 567.
(15) Krigbaum, W. R.; Hakemi, H.; Kotek, R. *Macromolecules* **1985**, *18*, 965.
(16) Flory, P. J. *Macromolecules* **1978**, *11*, 1141.
(17) Khokhlov, A. R.; Semenov, A. N. *Physica A: (Amsterdam)* **1981**, *108A*, 546.
(18) Krigbaum, W. R.; Tanaka, T. *Macromolecules* **1988**, *21*, 743.
(19) Ciferri, A. *Trans. Faraday Soc.* **1961**, *57*, 853.
(20) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents: Physical Properties and Methods of Purification*, 4th ed.; Wiley: New York, 1986.
(21) Yamakawa, H.; Fujii, M. *Macromolecules* **1974**, *7*, 128.
(22) Herman, B.; Flory, P. J.; Hummel, J. P. *Macromolecules* **1980**, *13*, 484.
(23) Pauling, L. C. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University: Ithaca, NY, 1960.
(24) Bohdanecky, M. *Macromolecules* **1983**, *16*, 1483.
(25) Saito, M. *Polym. J. (Tokyo)* **1983**, *15*, 213.
(26) Krigbaum, W. R.; Brelsford, G. *Macromolecules* **1988**, *21*, 2502.
(27) Reddy, G. V.; Bohdanecky, M. *Macromolecules* **1987**, *20*, 1393.
(28) Laivins, G. V.; Gray, D. G. *Macromolecules* **1986**, *18*, 1746.
(29) Yamakawa, H.; Yoshizaki, T. *Macromolecules* **1982**, *15*, 1444.
(30) Ronca, G.; Yoon, D. Y. *J. Chem. Phys.* **1984**, *80*, 930.
(31) Ciferri, A.; Hoeve, C. A. J.; Flory, P. J. *J. Am. Chem. Soc.* **1961**, *83*, 1015.
(32) Flory, P. J.; Irvine, P. A. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 1807.

Molecular Weight Dependence of the Second Virial Coefficient for Flexible Polymer Chains in Two Dimensions

D. Poupinet, R. Vilanove, and F. Rondelez*

Laboratoire de Physique de la Matière Condensée,† Collège de France, 11 Place Marcelin-Berthelot, 75231 Paris, Cedex 05, France, and Laboratoire de Structure et Réactivité aux Interfaces, Université Paris VI, 4 Place Jussieu, 75231 Paris, Cedex 05, France. *Received June 24, 1988; Revised Manuscript Received November 23, 1988*

ABSTRACT: Detailed surface pressure measurements have been performed in the dilute regime for Langmuir monolayers of atactic poly(methyl methacrylate) chains spread at the air–water interface. Marked deviations from the ideal gas law give clear evidence for attractive interactions between the two-dimensional polymer chains. The second virial coefficient is negative and scales with the chain molecular weight as $A_{22}^{\Gamma} \propto M^{2\nu}$ when the concentration is measured in units of the number of chains $\Gamma = c/M$. For chains with molecular weights between 3250 and 18600, we obtain $\nu = 0.57 \pm 0.03$ for the Flory exponent describing the single-chain conformation $R_G \propto N^{\nu}$. This new, and independent, derivation of the ν exponent in two dimensions is in complete agreement with the value based on the concentration dependence of the surface pressure in the semidilute regime. This is the first time that the molecular weight dependence of the second virial coefficient is clearly established for polymer chains in two dimensions.

The interactions between flexible chains in dilute polymer solutions of finite concentration are generally described by the so-called virial coefficients. Numerous theoretical expressions have been proposed for the second-order virial coefficient A_2, which describes the average interactions between two polymeric chains. A pioneering approach by Yamakawa[1] describes all the dilute solution properties in terms of combinations of three parameters: the unperturbed dimension of the chain, the two-body excluded volume, and finally the three-body interactions between chain segments. His calculations are performed to first order with respect to the binary and ternary interactions. On the other hand, since a very long polymer chain is also a critical object,[2] the renormalization techniques developed in field theory are also applicable. Different schemes have been used. For example, Freed and his co-workers[3] have selected the cut-off regularization and the dimensional regularization to extend the perturbation calculations to values of the ternary interactions that were previously unaccessible. Their two separate approaches give an accurate treatment of the second and third virial coefficients for linear and branched polymers. Their expressions for A_2 and A_3 include important prefactors and apply to all dimensionalities, d, higher than 2. Similar calculations, but limited to $d = 4$, have been performed by Kosmas and Kosmas.[4] Witten and Schäfer[5] and des Cloizeaux,[6,7] working independently, have used direct renormalization, which makes no reference to the analogy between polymer chains and magnetic systems. They have performed $\epsilon = 4 - d$ expansions to calculate A_2 to first[5,6] and second[7] order in ϵ. Since these authors were mainly considering swollen chains in goods solvents, only binary interactions were taken into account. Some years earlier, Daoud and Jannink[8] had taken a simpler approach, based on the magnetic analogy, and used scaling arguments to derive the asymptotic dependence of A_2 on temperature and molecular weight. Their results are therefore only valid in the limit of infinite molecular weight samples. This first-step approach is interesting, however, in so far it allows us to make predictions in the entire temperature–concentration phase diagram of the polymer solution and can readily be tested experimentally. Moreover, the values of the power law exponents are not system dependent and should be solely defined once the space dimensionality and the universality class are specified. When polymer concentration is expressed as the number of chains per unit volume, Γ, the predicted scaling law is $A_2^{\Gamma} \propto N^{\nu d}$, where ν is the well-known Flory exponent and N is the chain degree of polymerization. When the polymer concentration is expressed in units of mass per unit volume, $c = M\Gamma$, where M is the chain molecular weight,

† Laboratoire associé au CNRS (U.A. No. 792).

0024-9297/89/2222-2491$01.50/0

a slightly different expression is obtained, namely $A_2^c \propto N^{\nu d-2}$. Measurements of the N dependence of A_2 for a given polymer–solvent system therefore give access to the ν exponent, describing the conformation of a single chain, $R_G \propto N^{\nu} l$, where R_G is the coil radius of gyration and l the monomer length.

Experimental data in bulk solutions ($d = 3$) have confirmed the above predictions. Osmotic pressure[9] and static light scattering[10,11] measurements have shown that $A_2^c \propto N^{-0.20}$ for polystyrene of large molecular weight dissolved in toluene. This value is in good agreement with the mean-field value $\nu = {}^3/_5$ for chains in good solvents[2] and also with the estimate $\nu = 0.5885$ obtained from renormalization group methods.[12] In addition, it has been shown by Fujita and Norisuye[13] that for molecular weights lower than 10^5, the variation of A_2 with M is larger than $A_2 \propto N^{-0.20}$. This is entirely consistent with the fact that ν approaches the ${}^3/_5$ value only in the asymptotic limit of $N \to \infty$.

In principle, measurements of A_2 for chains in two dimensions could also be performed. Indeed the surface pressure, π, exerted by a polymeric monolayer deposited at the liquid–vapor interface of a Langmuir trough is the two-dimensional equivalent of osmotic pressure.[14] A nonlinear dependence of the surface pressure with surface concentration gives, therefore, access to the virial coefficients of polymer monolayers. For two-dimensional chains in good solvents, the predicted ν exponent is ${}^3/_4$ for mean-field theory or 0.76 ± 0.03 for renormalization group theory.[12] Therefore, one expects $A_{22}^{\Gamma} \propto N^{3/2}$ and $A_{22}^c \propto N^{-1/2}$. (The second subscript indicates the space dimensionality.)

Despite several experimental attempts,[15-17] these power laws have never been confirmed in the literature. The main reason is that meaningful A_{22} measurements have to be performed in the dilute regime, where the chains behave as individual objects. This regime corresponds to extremely low polymer surface concentrations, especially in the case of good solvents, and therefore to exceedingly low surface pressures. The nonrespect of this basic rule by early workers in this field has led to erroneous results. Most previous experiments have actually been performed in the semidilute regime of surface concentration, where the chains overlap and entangle. This explains, for instance, why Llopis and Subirana have observed an anomalous A_{22}^c increase (instead of the expected decrease) with polymer molecular weight in the case of poly(methyl acrylate) chains spread at the air–water interface.[15]

In this paper, we present what we think are the first consistent measurements of the second virial coefficient for two-dimensional polymer chains in the dilute surface concentration regime. We investigate the power law variation of A_{22} with molecular weight, $A_{22}^{\Gamma} \propto N^a$, and compare the power law exponent $a = 2\nu$ with the two-dimensional Flory exponent ν obtained independently from the concentration dependence of the surface pressure in the semidilute regime. The agreement between both determinations is found to be very good.

To achieve this goal, it has been compulsory to select polymer systems with dilute regimes encompassing the widest possible concentration range. The crossover surface concentration, c^*, marks the limit between the dilute regime and the semidilute regime. In the low-concentration region ($c < c^*$), colligative properties such as the surface pressure, π, are best described by a virial expansion in increasing powers of the surface concentration, c,

$$\pi_{dil} = RT\frac{c}{M}(1 + A_{22}^c cM + A_{32}^c c^2 M + ...) \quad (1)$$

or equivalently

$$\pi_{dil} = RT\Gamma(1 + A_{22}^{\Gamma}\Gamma + A_{32}^{\Gamma}\Gamma^2 + ...) \quad (2)$$

with c in kg·m^{-2} and $\Gamma = c/M$ in mol·m^{-2}.

In the semidilute concentration region ($c > c^*$), surface pressure obeys a power law versus surface concentration and is independent of molecular weight, M. The π behavior is characterized by a single critical exponent, y,

$$\pi_{int} = c^y \quad (3)$$

It has been postulated earlier[18] that y is directly connected to the ν exponent relating the radius of gyration of an isolated two-dimensional polymer chain to its polymerization index, N, $R_{G2} \propto N^{\nu} l$. One has

$$y = \frac{2\nu}{2\nu - 1} \quad (4)$$

Since the crossover concentration, c^*, varies inversely with N as

$$c^* \propto \frac{N}{R_{G2}{}^2} \propto N^{1-2\nu} \quad (5)$$

it is advisable to work with low molecular weight samples in order to obtain the widest possible range for the dilute regime. It is also preferable to select thermodynamic conditions such that the exponent $1 - 2\nu$ is much smaller than unity. Theoretical predictions for chains in two dimensions are that ν is equal to ${}^3/_4$, ${}^4/_7$, and ${}^1/_2$ for good solvent,[11] Θ solvent,[19] and bad solvent[11] conditions, respectively. Accordingly, c^* will scale as $N^{-0.50}$ for $2d$ excluded-volume chain behavior, $N^{-0.13}$ for $2d$ Θ chains, and N^0 for collapsed chains. For a given N, c^* will therefore be higher for Θ chains than for excluded-volume chains and higher for collapsed chains than for Θ chains. On the other hand, it is not possible to study the molecular weight dependence of A_{22} in the case of Θ chains since, by definition, $A_{22}(\Theta) \equiv 0$ for all M at the Θ point. With these limitations in mind, we have chosen to work on a polymer–solvent system that is in a slightly less than Θ condition. It affords a c^* value that is relatively high, but still smaller than $c^* \simeq l^{-2}$, characteristic of collapsed $2d$ chains. For surface densities close to maximum compacity, polymeric monolayers are most probably in their glassy state and equilibrium thermodynamic conditions become difficult to reach experimentally.

In an earlier publication,[20] we have studied atactic poly(methyl methacrylate) (PMMA for short) spread in monolayers at the air–water interface and around room temperature. It was shown that surface pressure data in the semidilute regime were characterized by an exponent $y = 16.5 \pm 1.0$, from which a ν value of 0.530 ± 0.005 was calculated for high molecular weight samples. This ν value was intermediate between the predictions for collapsed and Θ chains, suggesting that PMMA monomer–monomer interactions are attractive in this case. This latter point was confirmed by preliminary observations of negative values for the second virial coefficient, A_{22}^{Γ}. For PMMA of molecular weight 10^4, the crossover concentration, c^*, was estimated to be 0.4 mg·m^{-2}. At this surface concentration, the surface pressure was found to be of the order of 100 μN·m^{-1}.

The main characteristic of the particular poly(methyl methacrylate) samples used for the present study is that they are of low molecular weight. Their specifications are given in Table I. They were obtained from two commercial sources (Polymer Laboratories, Church Strelton SY6 6AX, U.K.; and Polymer Standard Services, Postfach

Table I
Molecular Weights and Tacticity Contents of Our Poly(methyl methacrylate) Samples

		NMR triads, %			NMR diads, %	
M_n, g/mol	M_w/M_n	iso	hetero	syndio	meso	racemic
3250	1.15	3.8	27.4	68.8	17.5	82.5
6000	1.08	3.5	41.1	55.4	24.0	76.0
6440	1.14	3.0	20.1	76.9	13.1	86.9
7400	1.10	2.9	41.9	55.2	23.9	76.1
9400	1.07	4.0	52.5	43.5	30.3	69.7
17000	1.30	3.9	23.8	72.3	15.8	84.2
18600	1.09	1.6	47.3	51.1	25.2	74.8

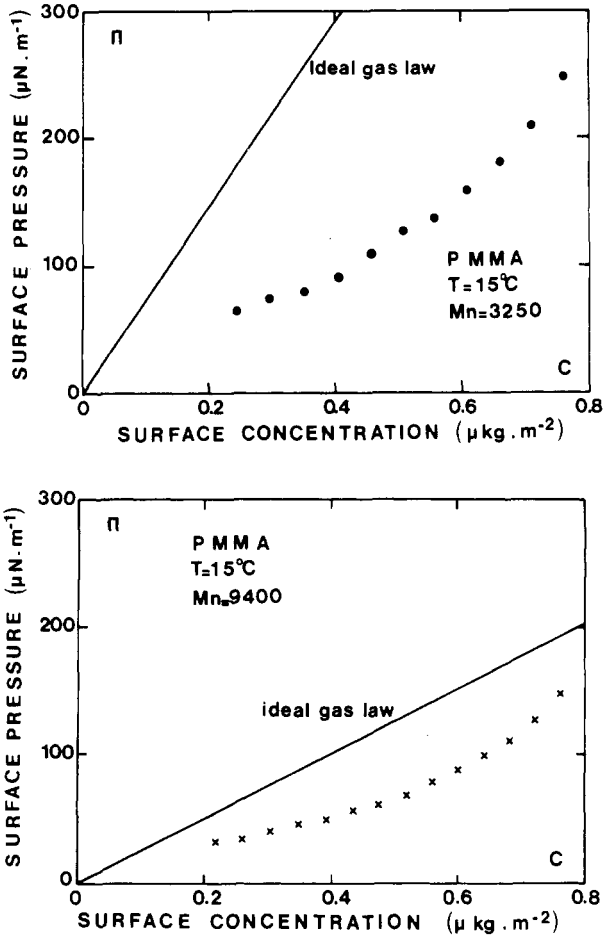

Figure 1. (a, top) Surface pressure (π) of poly(methyl methacrylate) monolayers versus surface concentration (c) expressed in unit mass per unit area. Sample molecular weight is M_n = 3250. Temperature is 15 °C. Note the marked deviation between the experimental data points and the ideal gas pressure law $\pi = (cRT)/M_n$, indicated by the straight solid line. (b, bottom) Same as above but for poly(methyl methacrylate) chains of molecular weight M_n = 9400.

3368, 6500 Mainz, W.G.) and used as received, without further purification. Number-average molecular weights, M_n, were between 3250 and 18600. Gel permeation chromatograms showed that their polydispersity, M_w/M_n, was always less than 1.14. All experiments have therefore been performed on narrow polymer fractions. The chain tacticity was investigated by high-resolution ^{1}H NMR, and the results are presented in Table I both in percentages of iso (i), hetero (h) and syndio (s) triads and in percentages of meso (m) and racemic (r) diads. A diad is called meso if the two successive methyl methacrylate side groups are on the same side of the polymer backbone and racemic if they are on alternate sides. Diad and triad contents are related by the formulas m = i + h/2 and r = s + h/2. We observed from Table I that all samples used have predominantly atactic chains, with an isotatic triad fraction not exceeding 4%.

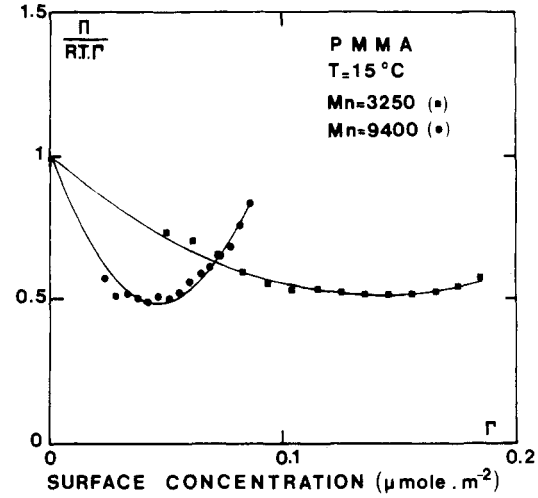

Figure 2. Same data points as in Figure 1 but plotted as $\pi/(RT\Gamma)$ versus Γ, where Γ is the surface concentration expressed in moles per unit surface and R is the gas constant. In this representation, the intercept with the ordinate axis is unity, independent of chain molecular weight and the initial slope for $\Gamma \rightarrow 0$ is the second virial coefficient (A_{22}^{Γ}). The solid line is the result of a least-squares fit between eq 2 and the data points. The values used for A_{22}^{Γ} and A_{32}^{Γ} in the adjustment procedure are reported in Table II for the various molecular weight samples.

Polymer monolayers were formed in the usual way by depositing a droplet of dilute solution in a volatile solvent at the air–water interface of a Langmuir trough.[14] Surface pressures were measured by the Wilhelmy hanging plate using a temperature-controlled force transducer system with excellent long-term stability. The setup enabled us to measure surface pressure down to 10 μN·m^{-1} with a sensitivity of 1 μN·m^{-1}. Experimental details will be published elsewhere.[21] Surface concentration was continuously varied using a movable Teflon barrier, the displacement of which was computer controlled. Special care was taken to stay as close as possible to thermodynamic equilibrium and to avoid reaching metastable states of the polymer chains within the monolayer. Surface pressure versus surface concentration measurements were repeated at least 3 times for each polymer sample. Reproducibility of the data was better than 5%.

The surface pressure, π, has been measured as a function of polymer surface concentration, c, for seven PMMA samples in both the dilute and the semidilute regimes. Two typical curves for the dilute regime of concentration are shown in parts a and b of Figure 1 for M_n = 3250 and 9400, respectively. All experiments were performed at a single temperature of 15 °C since we have already established that the surface pressure data for PMMA monolayers are independent of temperature, at least in the range 2–35 °C.[20] In Figure 1, the surface pressure is clearly an increasing function of surface concentration and shows a marked upward curvature. It is also important to note that, in the range between 0.2 and 0.8 mg·m^{-2}, the pressure data are systematically lower than the corresponding values for an ideal gas of polymer chains using the number-average molecular weight, M_n, measured by gel permeation chromatography. The straight lines in Figure 1 correspond to the ideal gas equation $\pi = (RTc)/M_n$. The same data have been replotted in Figure 2 in a form that reveals that the second virial coefficient, A_{22}, is clearly negative in the case of these PMMA monolayers. The ordinate axis is $(1/(RT))(\pi/\Gamma)$, while the abscissa axis is $\Gamma = c/M_n$. In this representation, the intercept with the

Table II
Second and Third Virial Coefficients for Two-Dimensional Chains of Poly(methyl methacrylate) at the Air-Water Interface

M_n, g/mol	A_{22}^{Γ}, m^2·μmol^{-1}	A_{32}^{Γ}, m^4·μmol^{-2}	Γ^*,[a] μmol·m^{-2}
3250	−6.6 ± 0.5	22.3 ± 3.0	0.282 ± 0.005
6000	−13 ± 1	163 ± 15	0.110 ± 0.003
6440	−18 ± 3	142 ± 36	0.125 ± 0.010
7400	−14.5 ± 1.3	181 ± 28	0.103 ± 0.002
9400	−22.5 ± 1.0	244 ± 17	0.095 ± 0.002
17000	−31.5 ± 10	~650	0.046 ± 0.003
18600	−53 ± 10	~1200	0.038 ± 0.002

[a] Γ^* is the crossover concentration between the dilute and the semidilute regimes.

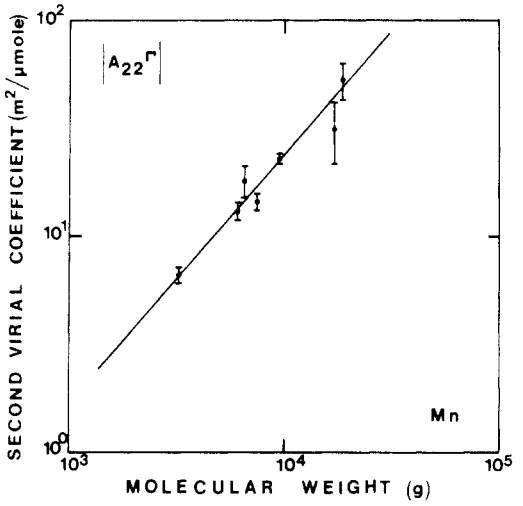

Figure 3. log–log plot of the experimental values for the second virial coefficient (A_{22}^{Γ}) versus the chain molecular weight (M_n). $|A_{22}^{\Gamma}|$ is observed to obey a power law behavior $|A_{22}^{\Gamma}| \propto M_n^a$ with $a = 1.14 \pm 0.06$. Negative values for A_{22}^{Γ} indicate that chain–chain interactions are attractive. According to theory, a is equal to νd, where $d = 2$ is the space dimensionality.

ordinate axis is unity, independent of M_n, and the initial slope of the curve is A_{22}^{Γ}. We have performed a least-squares fitting of the data with eq 2. We can thus derive meaningful data points not only for A_{22}^{Γ} but also for the third virial coefficient, A_{32}^{Γ}. The solid lines in Figure 2 correspond to the best fits, using A_{22}^{Γ} and A_{32}^{Γ} as adjustable parameters. The accuracy in A_{22}^{Γ} is ±10%, while the accuracy in A_{32}^{Γ} is somewhat poorer, of the order 20%. Results for all molecular weights are compiled in Table II. The second virial coefficient, A_{22}^{Γ}, is always negative, and its absolute value increases with molecular weight. Plotting the data on logarithmic scales (Figure 3) shows that A_{22}^{Γ} obeys a power law relationship $|A_{22}^{\Gamma}| \propto M_n^a$ with $a = 1.14 \pm 0.06$. The third virial coefficient, A_{32}^{Γ}, is always positive. It increases markedly with molecular weight. However, the scattering of the A_{32}^{Γ} values even between samples of similar molecular weights was too large to attempt checks for a possible scaling law. We surmise that A_{32}^{Γ} may be sensitive to details in the chain tacticity content.

Measurements have also been extended to surface concentrations well into the semidilute regime. In this range, the surface pressure, π, is a strong function of surface concentration, c. According to eq 3, π should scale with c as $\pi \propto c^y$ and be independent of molecular weight. The results for two PMMA samples of molecular weight 3250 and 9400, respectively, are shown in logarithmic scales in Figure 4. For a given molecular weight, the data points align on a straight line of slope y above a concentration of about 0.9×10^{-6} kg·m^{-2}. The y values is 11 for M_n = 3250 and 13.5 for M_n = 9400. Both values are somewhat

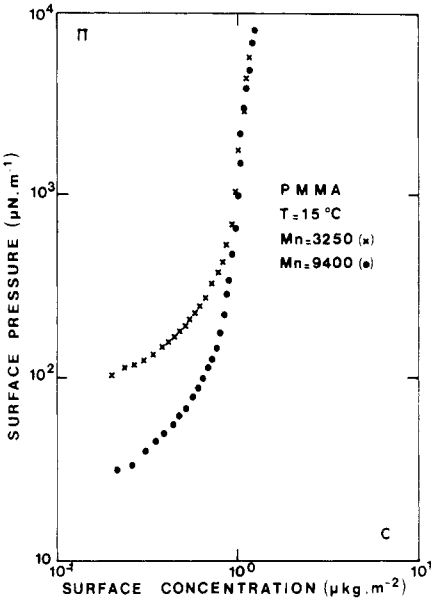

Figure 4. Surface pressure (π) for poly(methyl methacrylate) monolayers as a function of the surface concentration (c) in logarithmic scales. Samples molecular weights are M_n = 3250 and 9400, respectively. Temperature of the experiment is 15 °C.

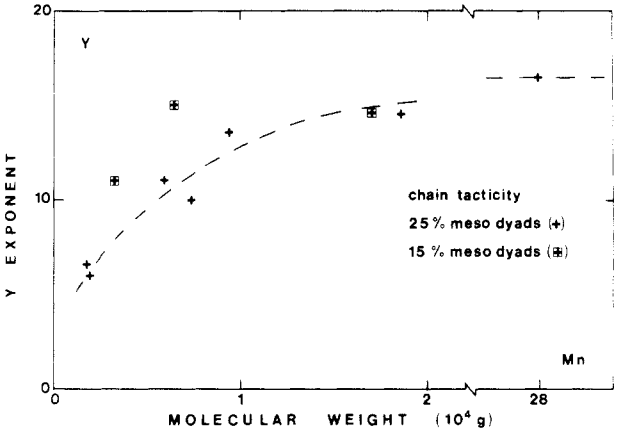

Figure 5. Values of the exponent y characterizing the surface pressure dependence on surface concentration in the semidilute regime, $\pi \propto c^y$. The exponent reaches an asymptotic value $y = 16.5 \pm 1$ for molecular weight samples larger than approximately 20000. The dotted line is just a guide for the eye and is of no physical significance. Chains with two different stereoregularity, as characterized by their content in meso diads, have been investigated.

smaller than the value of $y = 16.5 \pm 1$ previously measured on much higher molecular weight samples.[20] Figure 5 shows the molecular weight dependence of y for all our samples. We definitely observe that the y exponent reaches its asymptotic value only for PMMA samples with M_n values higher than about 20000. On the other hand, chains with less than 200 monomeric units deviate from the infinitely long chain limit. It should come as no surprise that calculations that neglect all end effects break down with too short chains. This phenomenon is well documented in bulk solutions.[13,22] On the contrary, the surprise comes from the fact that predictions made for infinitely long chains hold true in two dimensions down to extremely low molecular weights.

Finally we have tried to make an experimental estimate of the crossover concentration, c^*, betweeen the dilute and the semidilute regimes. Somewhat arbitrarily, we have defined c^* as the polymer surface concentration at which the measured surface pressure rejoins the calculated value

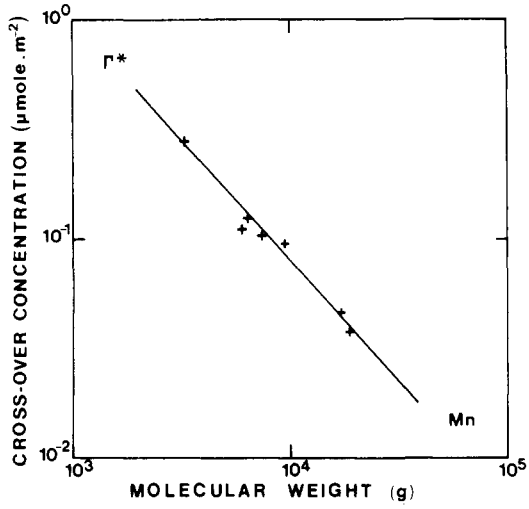

Figure 6. Crossover concentration $\Gamma^* = c^*/M_n$ separating the dilute from the semidilute regime in the polymer monolayer as a function of sample molecular weight. The data points fall on a straight line (on log scales) with slope $b = -1.10 \pm 0.04$. According to theory, b is equal to $-\nu d$, where $d = 2$ is the space dimensionality.

for an ideal gas of polymeric chains. At this point, the concentration has become large enough for the third-order correction term to the virial expansion to counterbalance the negative contribution of the second-order term. The monolayer is no longer in its highly dilute limit. On the other hand, the surface pressure is still sufficiently low to justify that the chains are not overlapping strongly. The criterion used here is analogous to the one proposed by des Cloizeaux and Jannink[23] for polymer solutions in good solvents. In that case, the second virial coefficient is positive, and these authors have suggested to define c^* as the concentration for which the experimental osmotic pressure is twice that of the ideal gas law. From plots such as shown in Figure 2, we obtain c^* values ranging from 0.40 to 0.65 mg·m^{-2} for molecular weights between 3250 and 18600. According to eq 5, c^* should scale with molecular weight as $c^* \propto N^{1-2\nu}$. Consequently, $\Gamma^* = c^*/M$ should scale as $\Gamma^* \propto N^{-2\nu}$. The data points for Γ^* have been plotted on logarithmic scales in Figure 6 as a function of M_n. They align on a straight line of slope $b = -1.10 \pm 0.04$.

The key point of the present experiments is that the use of relatively low molecular weight samples and the selection of slightly worse than Θ thermodynamic conditions have enabled us to perform accurate surface pressure measurements in both the dilute and the semidilute regimes. From these two sets of data, we have access independently to the ν exponent, which characterizes the chain conformation in two dimensions. The power law exponent a of the second virial coefficient, A_{22}^{Γ}, versus polymer molecular weight in the dilute regime is equal to 2ν, while the power law exponent y of the surface pressure, π, versus polymer surface concentration in the semidilute regime is equal to $2\nu/(2\nu - 1)$. Using the y value of 12 ± 2 for chains with molecular weights between 3250 and 18600, we obtain an estimate for ν of 0.545 ± 0.010. On the other hand, the measured value for exponent a centers around 1.14 ± 0.06, which yields $\nu = 0.57 \pm 0.03$. Within experimental accuracy, it seems reasonable to say that the two independent approaches give identical estimates for ν. A third confirmation of the value for ν is given by the molecular weight dependence of Γ^*. Since the slope $b = -2\nu$ is equal to -1.10 ± 0.04, we obtain $\nu = 0.55 \pm 0.02$, in good agreement with the above estimations.

That measurements in both the dilute and the semidilute regimes yield the same ν value should help cool off a current debate between monolayer experimentalists on the actual possibility of using the high surface concentration regime to measure single-chain properties. We fully agree that the physical significance of a semidilute regime for polymer monolayers is not entirely clear. It is hard to envision how polymer chains could overlap in two dimensions as they do in bulk solutions. Therefore, it is quite normal to question the validity of eq 4. What is given in the present work is an experimental proof that the ν values derived at high concentrations, i.e., in a regime of surface pressures that are large and therefore easy to measure, are consistent with the ν estimates derived from second virial coefficient measurements in a much more dilute range of concentrations.

To conclude, we have presented here the first experimental evidence for the molecular weight dependence of the second virial coefficient in dilute solutions of two-dimensional polymeric chains. In the case of atactic poly(methyl methacrylate), A_{22}^{Γ} is negative, indicating attractive forces between the chains. The second virial coefficient scales with molecular weight as $A_{22}^{\Gamma} \propto M^{-1.14}$. This result is in fair agreement with the theoretical predictions $A_{22}^{\Gamma} \propto M^{-2\nu}$, where ν is the Flory exponent of the radius of gyration, taking for ν the value 0.545 ± 0.010 derived from surface pressure measurements in the semidilute concentration regime. The fact that the ν values measured from dilute solution properties agree with that latter value justifies a posteriori the semidilute method which has become a standard for measuring the ν exponent of polymer chains spread in monolayers. The measured A_{22}^{Γ} values seem independent of the precise chain stereotacticity for atactic chains with an isotacticity content less than 4%. On the other hand, the third virial coefficient, A_{32}, seems to depend on the percentage of meso diads in the chain. This could be a subject of further investigation. Finally we want to reemphasize that the present experiments have been performed on chains with relatively low molecular weights, while the scaling predictions are always derived in the limit of infinite molecular weights. The absolute values of the ν exponent indicated here are most probably 4–5% higher than the asymptotic limit, as can be seen by comparison with the results of ref 20 obtained with high molecular weight samples.

Registry No. PMMA, 9011-14-7.

References and Notes

(1) Yamakawa, H. *J. Chem. Phys.* **1966**, *45*, 2606.
(2) de Gennes, P. G. *J. Phys. Lett.* **1975**, *36*, 55. See also *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(3) Douglas, J. F.; Cherayil, B. J.; Freed, K. F. *Macromolecules* **1985**, *18*, 2455. Cherayil, B. J.; Douglas, J. F.; Freed, K. F. *J. Chem. Phys.* **1987**, *87*, 3089. See also: Freed, K. F. *Renormalization Group Theory of Macromolecules*; Wiley: New York, 1987 .
(4) Kosmas, M. K.; Kosmas, A. M. *Polymer* **1986**, *27*, 1359.
(5) Witten, T. A.; Schäfer, L. *J. Phys. A: Math Gen.* **1978**, *14*, 1978.
(6) des Cloizeaux, J. *J. Phys., Lett.* **1980**, *41*, 151.
(7) des Cloizeaux, J. *J. Phys. (Les Ulis, Fr.)* **1981**, *42*, 635.
(8) Daoud, M.; Jannink, G. *J. Phys. (Les Ulis, Fr.)* **1976**, *37*, 973.
(9) Krigbaum, W. R.; Flory, P. J. *J. Am. Chem. Soc.* **1953**, *75*, 1775.
(10) Miyaki, Y.; Einaga, Y.; Fujita, H. *Macromolecules* **1978**, *11*, 1180.
(11) Huber, K.; Bantle, S.; Lutz, P.; Burchard, W. *Macromolecules* **1985**, *18*, 1461.
(12) Le Guillou, J. C.; Zinn-Justin, J. *J. Phys., Lett.* **1977**, *39*, 95; *J. Phys., Lett.* **1985**, *46*, 137.
(13) Fujita, H.; Norisuye, T. *Macromolecules* **1985**, *18*, 1637.
(14) Gaines, G. L. *Insoluble Monolayers at Liquid–Gas Interfaces*; Wiley: New York, 1966.

(15) Llopis, J.; Subirana, J. A. *J. Colloid Sci.* **1961**, *16*, 618.
(16) Jaffé, J.; Berliner, C.; Lambert, M. *J. Chem. Phys.* **1967**, *64*, 499.
(17) Kawaguchi, M.; Yoshida, A.; Takahashi, A. *Macromolecules* **1983**, *16*, 956.
(18) Vilanove, R.; Rondelez, F. *Phys. Rev. Lett.* **1980**, *45*, 1502.
(19) Duplantier, B.; Saleur, H. *Phys. Rev. Lett.* **1987**, *59*, 539.
(20) Vilanove, R.; Poupinet, D.; Rondelez, F. *Macromolecules* **1988**, *21*, 2880.
(21) Poupinet, D.; Dêtry, D.; Vilanove, R.; Rondelez, F., to be submitted for publication.
(22) Weill, G.; des Cloizeaux, J. *J. Phys. (Les Ulis, Fr.)* **1979**, *40*, 99.
(23) des Cloizeaux, J.; Jannink, G. Les Polymères en Solution. *Editions de Physique*; 1987.

Solution Properties of Amine-Cured Epoxy Resins Based on Triglycidyl Isocyanurate: Semidilute Solutions

E. Wachenfeld-Eisele and W. Burchard*

Institute of Macromolecular Chemistry, Stefan-Meier-Strasse 31, University of Freiburg, 7800 Freiburg i.Br., Federal Republic of Germany. *Received August 8, 1988; Revised Manuscript Received November 30, 1988*

ABSTRACT: The properties of epoxy resins, prepared by the curing reaction of triglycidyl isocyanurate (TGI) with hexamethylenediamine (HMDA), have been studied in semidilute solution. Because of its ambiguity, the commonly used definition of the coil overlap concentration c^* is avoided, and the thermodynamically clearly defined parameter $X = A_2M_wc$ is instead used as a scaling parameter. The reduced osmotic modulus $(M_w/RT)(\partial\pi/\partial c) = M_wKc/R_{\theta=0}$ of four high molecular weight samples was obtained by extrapolation to $\theta = 0$. The lowest molecular weight sample shows behavior between that of flexible random coils and hard, impenetrable spheres, as was expected, but the curves are shifted toward smaller X values the larger the molecules. This unexpected behavior is tentatively explained by the strong decay of A_2 with growing cluster size and extreme polydispersity. The four curves form, however, asymptotically one common line when $c[\eta]$ is used as a scaling parameter. Similarly a master curve is found for the zero shear rate viscosity when $c[\eta]$ is used. The final exponent $n = 2.4 \pm 0.1$ agrees very satisfactorily with the general relationship $na = 0.75$ that was recently predicted for randomly branched materials, where $a \simeq 0.30$ is the exponent in the Mark-Houwink equation. This exponent is close to 0.375 as was predicted by the percolation theory. The concentration dependence of the translational diffusion coefficient $D(c)$ is significantly weaker than that for impenetrable spheres. $D(c)$ contains a thermodynamic part and a counteracting frictional part. Since the thermodynamic part was measured by static light scattering, the frictional contribution is considered separately. The strongly increasing friction of these randomly branched samples is much more pronounced than for spheres. Because of the lack of theory, even for hard spheres, these phenomena cannot so far be quantitatively interpreted.

Introduction

Reaction of triglycidyl isocyanurate (TGI, Figure 1) with 1,6-hexanediamine (HMDA) yields statistically branched epoxy resins with a high branching density and a very broad molecular weight distribution. The dilute solution properties of these resins have been discussed in previous papers.[1,2] This paper deals with static (SLS) and dynamic (DLS) light-scattering and viscosity measurements of *semidilute solutions* of TGI/HMDA resins with weight-average molecular weights M_w of about 2×10^6–5×10^6 g/mol.

During the past few years much experimental work has been carried out with light scattering from semidilute solutions, mainly on linear chains.[3-9] Recently other studies on different architectures[9-14] have also been performed. A characteristic feature of semidilute solutions of linear chains is that all properties become molecular weight independent.[8] However, recent studies with other types of polymers reveal that the properties depend on the architecture.[9] Theoretical predictions exist so far only for flexible, linear chains in marginal to good solvents and for hard spheres at high concentrations. These theories are not discussed in detail here because of their complexity, and we refer to the literature.[15-20] Since no theory exists for randomly branched polymers, the results of the measurements are compared to these two theories. The discussion is subdivided into five parts: (i) osmotic modulus, (ii) M_w dependence of the second virial coefficient, (iii) viscosity measurements, (iv) diffusion coefficient, and (v) anomalies at high concentration.

Experimental Section

1,6-Hexanediamine from Sigma was used without further purification. Triglycidyl isocyanurate (Araldit PT 810 from Ciba Geigy) is a mixture of two enantiomer pairs (RRS/SSR or α-TGI and RRR/SSS or β-TGI). The less symmetric α-TGI, which was used for the synthesis of the epoxy resins, was obtained by fractional crystallization from this mixture.

Crystallization of α-TGI. A mixture of α- and β-TGI was refluxed in methanol (TGI:methanol 1:4 by weight) for 10 min and filtered hot over a hot Buchner funnel. α-TGI separates from the filtrate as fine white crystals when the solution is cooled to 0 °C. The crystalline α-TGI was filtered off, washed with cold methanol, and then dried in vacuo for 2–3 days at room temperature. The resulting product had a melting point of 105–106 °C (lit.[21] mp 106 °C).

Synthesis of the Resins. All resins were prepared in dimethylformamide (DMF) solution in calibrated flasks. The concentration was chosen so that 1.7 mmol monomer was diluted in 1 mL of DMF. To make resins of different molecular weight, the composition was changed slightly. The appropriate amount of TGI was placed in a calibrated flask, and DMF was added. The flask then was immersed in an oil bath of 70 °C and TGI dissolved. With a pipet the necessary amount of HMDA (in DMF) was added. Then the solution was maintained at 70 °C for 20 h, cooled to room temperature, and filled to the marker with DMF.

Refractive Index Increment. The refractive index increments were measured in DMF at 20 °C with a Brice Phoenix differential refractometer.

Light-Scattering Measurements. Static and dynamic light scattering (SLS and DLS) was measured simultaneously in DMF at 20 °C with an automatic goniometer and a structurator/correlator ALV-3000 by ALV-Langen. The blue line ($\lambda_0 = 488$ nm) of an argon ion laser Model 2000 by Spectra Physics was used

0024-9297/89/2222-2496$01.50/0