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A Critical Look at Measurements of the ν Exponent for Polymer Chains in Two Dimensions[†]

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

Physique de la Matière Condensée, Collège de France, 11, place Marcelin-Berthelot, 75231 Paris, Cedex 05, France. *Received December 12, 1987;*
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ABSTRACT: We have performed extensive surface-pressure measurements on monolayers of atactic poly(methyl acrylate) (PMA) and poly(methyl methacrylate) (PMMA) chains spread at the air–water interface. The value of the ν exponent, which characterizes the molecular weight dependence of the 2D radius of gyration $R_{F2} \propto N^{\nu}$, is derived from the power law dependence of the surface pressure π versus polymer surface concentration C in the high-pressure range. For PMA, we obtain $\pi \propto C^{2.80}N^0$, independent of temperature between 5 and 30 °C. This corresponds to a ν value of 0.78 ± 0.01, characteristic of excluded-volume behavior for flexible polymers in two dimensions. This result contradicts earlier reports by Takahashi et al. (*Macromolecules* **1982**, *15*, 1196; **1983**, *16*, 956), who had observed for PMA a sharp transition from good solvent to Θ solvent behavior around 18.2 °C. For atactic PMMA, we obtain $\pi \propto C^{16.5}N^0$, corresponding to a ν value of 0.53. This value is significantly lower than our previous determination of $\nu = 0.56$ (Vilanove, R. et al. *Phys. Rev. Lett.* **1980**, *45*, 1502). Moreover, we have been able to observe that the second virial coefficient measured in the low-concentration regime is not zero but slightly negative. This indicates that PMMA chains are in a conformation intermediate between the collapse and the Θ state at the air–water interface. The observed value of $\nu = 0.53$ sets therefore a lower limit to the ν_Θ value for chains at the Θ state in two dimensions. This limit seems to exclude the value $\nu_\Theta = 0.505$ proposed by field theory and ϵ-expansion methods and is more in agreement with the value $\nu_\Theta = 0.57$ recently suggested by several authors.

Introduction

The determination of the scaling exponents that govern the properties of flexible polymer chains in two dimensions has provoked a flurry of activity among theoreticians during recent years. Almost all the newest methods of theoretical physics have been used to calculate the value of the exponent ν relating the chain radius of gyration R_{F2} to the polymerization index N, $R_{F2} \propto N^{\nu}a$ (a is the monomer length). The consistency between the different approaches has, however, been unequal for excluded-volume chains and tricritical chains corresponding to the good and Θ solvent cases, respectively.

For 2D chains in good solvents, the theoretical predictions are narrowly centered around the mean-field value of 0.75.[1] The best ϵ-expansion calculations by Le Guillou and Zinn-Justin[2] gave a ν value of 0.77. Exact numerations of self-avoiding walks (SAW) on triangular lattices for short chain lengths ($N < 18$) gave $\nu = 0.7500 \pm 0.0025$.[3,4] Monte Carlo simulations, which can be performed on much longer chains, predict $\nu = 0.753 \pm 0.004$.[5] However, this result is also approximate since the Monte Carlo approach implies an averaging on a limited number of SAWs. Numerical results by Derrida obtained by the matrix-transfer method on strips yield $\nu = 0.7503 \pm 0.0002$.[6] Finally, there is a growing body of evidence in favor of the Nienhuis conjecture[7] that the exact ν value is 0.75. This result is accidently equal to the mean-field prediction, although this latter result was originally obtained through the fortunate cancellation of two errors.[1]

In the case of Θ chains, the situation is much less clear. The predictions fluctuate widely for reasons that are related to the very special nature of the Θ point in two dimensions. The mean-field value ν_Θ is $^2/_3$ when only ternary interactions are considered. The ideal random walk value is $^1/_2$ and is identical in two dimensions ($d = 2$) with the exponent for collapsed chains $R_G \propto N^{1/d}$. This raises the question of which order in the monomer–monomer interactions has to be retained in the calculations. Early Monte Carlo simulations, in which only nearest neighbors interactions were incorporated, have suggested $\nu_\Theta = 0.51$.[8] On the other hand, Birshtein et al.,[9] working with a different algorithm, have obtained $\nu_\Theta = 0.59$. This rather high value was independently confirmed by Kremer and Lyklema.[10] Using an indefinitely growing self-avoiding walk (IGSAW) on a 2D square lattice with $N = 100$ steps, these authors have obtained $\nu = 0.567 \pm 0.003$. It was shown later by Coniglio et al.[11] that the IGSAW was actually equivalent, in what concerns ν, to a SAW with attractive interactions for nearest neighbors and some of the next nearest neighbors, and that the exponent ν_Θ could be identified with the expansion exponent ν of the IGSAW. Field theory provides a radically different approach to the calculation of the ν exponent in the vicinity of the Θ point. It relies on an analogy with tricritical points of gas–liquid or magnetic systems discovered by de Gennes,[12] which has been used by several different groups.[13–15] The calculated value for $d = 2$ is $\nu_\Theta = 0.505$,[16,17] remarkably close to the collapse exponent $\nu_{\text{coll}} = 0.50$. Unfortunately, this value is obtained through an $\epsilon = 3 - d$ expansion which is known to be poorly convergent in the vicinity of tricritical points.[18,19] Real space renormalization[20–22] suggests much higher values, typically up to 0.59, while transfer-matrix data[23] suggest $\nu_\Theta = 0.55$. The most recent attempt is due to Duplantier and Saleur.[24] Using a new SAW model on the honeycomb lattice with vacancies, they have proposed that the *exact* value of ν_Θ should be $^4/_7$, i.e., very close to the 0.57 value already found by several other techniques. To say the least, and despite all the efforts described above, the theoretical situation is still unclear in the Θ solvent case.

Curiously, the experimental situation parallels the theoretical one in the sense that the ν values derived from surface-pressure data on polymer monolayers spread at an air–water interface are fairly consistent between the different experimentalists for polymer chains in good solvents but differ widely in the Θ case. The studies are still too few, but it seems that poly(vinyl acetate),[25] poly(methyl acrylate) (in the high-temperature range),[26] poly(oxyethylene),[27] and poly(tetrahydrofuran)[27] are good arche-

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[†] Laboratoire associé au CNRS (U.A. no. 792).

[*] To whom correspondence should be addressed at Laboratoire de Structure et Réactivité aux Interfaces, Université Paris VI, 4, place Jussieu, 75231 Paris, France.

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types of the 2D excluded-volume chain behavior. In all these systems the measured ν values are close to one another and support the prediction of $\nu = 0.75$. On the other hand, poly(methyl methacrylate) and poly(methyl acrylate) (in the low-temperature range), which have both been claimed to be good examples of 2D Θ chains, display widely different ν values. Vilanove and Rondelez have proposed $\nu = 0.56 \pm 0.01$ for poly(methyl methacrylate) at 16 °C,[28] while Takahashi et al. using the same analysis technique but on poly(methyl acrylate) have reported a much lower value of 0.51.[26] In addition, they have apparently observed a sharp transition between Θ and excluded-volume behaviors when varying the temperature of the poly(methyl acrylate) monolayer between 18 and 25 °C.

In view of the discrepancy between the results of these last two experimental groups and of the long-lasting dispute between the theoreticians, we have decided to redo all the measurements published in the literature on 2D polymer monolayers in the Θ state, using the same samples as in the previous works plus some new ones. To our surprise, we have not been able to reproduce the low-temperature data of Takahashi et al. on poly(methyl acrylate).[26,30] This polymer seems to be in the good solvent case for all temperatures at the air–water interface, and the measured exponent is always $\nu = 0.78 \pm 0.01$. On the other hand, experiments on a monodisperse fraction of atactic poly(methyl methacrylate) with a particularly low molecular weight allows us to demonstrate that this polymer is not exactly at its Θ point when spread in monolayers at the air–water interface. Working with the same samples as in our earlier work but with an improved trough design, we have obtained $\nu = 0.530 \pm 0.005$, markedly lower than our previous report of $\nu_\Theta = 0.56 \pm 0.01$. This value of $\nu = 0.53$ has been confirmed on several narrow fractions of poly(methyl methacrylate) of controlled tacticity and ranging from 3300 to 1 600 000 in molecular weight. On all PMMA samples, we have observed that the surface-pressure measurements are independent of temperature over a 30 °C interval. This observation also differs from earlier results by Jaffé et al.[29]

Samples

The poly(methyl acrylate) samples were a generous gift from A. Takahashi, at Mie University in Japan. The PMA-2 (M_w = 4200) and PMA-4 (M_w = 12 000) fractions were the same as previously used by Takahashi et al. in ref 26 and 30. Their polydispersity M_w/M_n was 1.1. They were used as received, but for reasons that will become clear in the following, we checked by proton NMR that the material was indeed PMA, by comparing the positions of the various peaks CH–C, $-CH_2-$, and $O-CH_3$ with those of a polydisperse commercial sample (EGA, 7924, Steinheim, West Germany). Taking trimethylsilane as a reference, the peaks came at 1.7 ppm for the methylene group, 2.3 ppm for the CH–C group, and 3.7 ppm for the methoxy group. The solvent was chloroform, and it shows up as a narrow peak at 7.25 ppm. The poly(methyl methacrylate) samples were obtained from two different sources, both commercial and noncommercial (Polymer Laboratories, Loughborough, United Kingdom, and Ecole Nationale Supérieure de Chimie de Mulhouse, courtesy of M. Riess). The range of molecular weights was between 3300 and 1 600 000, with a typical polydispersity of $M_w/M_n < 1.2$. The chain stereoregularity was checked by ^{1}H and ^{13}C high-resolution NMR,[31] with tetrachloroethane at 130 °C as the solvent The chains were mainly atactic with a small, inevitable, percentage of isotactic triads and pentads. The degree of isotacticity was generally around 2–4%.

Polymer solutions were prepared by weighing small amounts of polymer material and dissolving them in known volumes of chloromethylene, which is a good solvent of poly(methyl methacrylate) and poly(methyl acrylate). This solvent spreads easily on the water surface. Because of its low boiling point, it also evaporates quickly, leaving the polymer chains pinned onto the interface by their carbonyl bonds. Typical volumes of solution used for an experiment were $\simeq 30\ \mu$L at a concentration of 5×10^{-3} g cm^{-3}. Single-drop deposition was favored because it allows an accurate and reproducible control of the average area occupied by each molecule, to within one part in 10^4. All that is required is the exact determination of the surface of the trough and the mass of polymer deposited on the interface.

A glass trough ($19 \times 5 \times 1$ cm^3) covered with a thin layer of octadecyltrichlorosilane to make the surface hydrophobic was used rather than the classical Teflon trough because it is less prone to surface contamination and is easier to clean. The bottom of the trough was clamped on a thick aluminum plate in which grooves had been made to allow circulation of water coming from a thermostat. The temperature of the water subphase just below the monolayer was measured with a platinum resistance thermometer. Temperatures could be varied between 1 and 40 °C, to an accuracy of ±0.05 °C. The whole trough equipment was enclosed in a thick Lucite box, the temperature of which was individually controlled. Air currents and water evaporation were thus avoided as much as possible. A moving barrier allowed to continuously compress the monolayer following initial deposition. Its motion (position and displacement speed) was driven by a stepping motor, itself controlled by a microcomputer.

The surface pressures of the spread polymer monolayers were measured by the Wilhelmy hanging plate technique.[32] The plate was made of platinum and had a length of 2 cm, a width of 1 cm, and a thickness of 0.01 cm. It was carefully brought to a red-hot temperature with a small gas burner before contacting the water surface to remove all traces of organic contaminants. The plate was attached by a thin platinum wire to the moving core of a differential transformer which acted as a sensitive force transducer. The electrical signal was amplified in a sensitive phase-lock amplifier and sent to a digital voltmeter and an $X(t)$ recorder. The sensitivity was 1 μN/m^{-1}, and the drift was usually less than 16 μN m^{-1} h^{-1}. Typical noise levels were 4 μN m^{-1}. Before the polymer monolayer was formed at the air–water interface, the trough surface was completely swept by the moving barrier and the surface pressure recorded. The water surface was considered free of surface-active impurities if the pressure rise following compression did not exceed 5–10 μN m^{-1} for a 100% decrease in the trough area. The polymer monolayer was compressed between 150 and 15 Å^2 molecule^{-1} over a total time period of about 60 min. The surface pressure was monitored at all times, and the barrier motion was stopped every time the instantaneous pressure change exceeded 10 μN m^{-1}. The motion was resumed only after complete mechanical relaxation was established within the monolayer, as indicated by a pressure variation limited to the inevitable thermal drift.

Theoretical Background

Let us recall briefly how the surface pressure π of the polymer monolayer can be related to the monomer surface concentration C, over the whole concentration range, by using scaling law arguments. At very low surface concentration, the surface pressure π, which is nothing but a two-dimensional osmotic pressure, is simply proportional to the number of polymer *chains* times the temperature T:

$$\pi_d = CRT/M \tag{1}$$

The subscript d indicates that one is dealing with a dilute regime where the chains are noninteracting and behave as isolated two-dimensional "pancakes" of size $R_{F2} \propto N^\nu a$. R is the gas constant. If a virial expansion is used to account for the residual chain–chain interactions, one can write to first order

$$\pi_d = RT[(C/M) + A^c{}_{22}(T)C^2 + ...] \tag{2}$$

$A^c{}_{22}$ is the second virial coefficient where the double subscript stands for a $d = 2$ space, and the superscript recalls that the concentration is expressed in units of mass per unit of surface. The equation for the osmotic pressure can also be written in terms of the chain concentration $\Gamma = C/(Nm_0)$, where m_0 is the monomer molecular weight:

$$\pi_d = RT[\Gamma + A^{\Gamma}_{22}\Gamma^2 + ...] \tag{3}$$

with $A^{\Gamma}_{22} = A^{c}_{22}M^2$. The Γ superscript recalls that here the concentration is expressed in moles per unit of surface.

The second virial coefficient A^{Γ}_{22} is large in good solvents and is identically zero in Θ solvents. In the vicinity of the Θ temperature θ, it is generally assumed that A^{Γ}_{22} varies linearly with temperature. Hidden subtleties in the definition of Θ have been stressed by several workers in the field. de Gennes in particular[1] has made clear the distinction between the so-called bare θ temperature at which the second virial coefficient between *monomers* vanishes and the renormalized $\tilde{\theta}$ temperature at which the second virial coefficient between two *chains* vanishes. Experimentally, surface-pressure measurements are sensitive to the second virial coefficient between chains. Therefore, when A^{Γ}_{22} is found to be equal to zero, that means that the polymer-interface system is at the temperature $\tilde{\theta}$. Rigorously speaking, $\tilde{\theta}$ is a function of N, but this is a weak effect: in practice the chains can be considered as infinite as soon as the chain molecular weight exceeds 100 monomer units.

Starting from the tricritical approach to the polymer Θ point, Daoud and Jannink[33] have proposed a scaling law for the second virial coefficient A^{Γ}_{2} as a function of the chain length N and of the reduced temperature $\tau = 1 - \theta/T$. Their expression, $A^{\Gamma}_{2} = N^{\nu d}\tau^{d(\nu-\nu_\Theta)/\varphi_t}$, has also been obtained later by renormalization group methods.[34,35] Here φ_t is a crossover exponent dependent on the space dimensionality d. According to Stephen,[13] $\varphi_t = {}^1/_2$ for $d = 3$, while $\varphi_t = 0.6$ for $d = 2$. The exponents ν and ν_Θ take their usual values $\nu = {}^3/_5$ and $\nu_\Theta = {}^1/_2$ for $d = 3$, $\nu = {}^3/_4$, and $\nu_\Theta = 0.505$–0.57 for $d = 2$. For two-dimensional chains in good solvent conditions, it is therefore predicted that A^{Γ}_{22} should scale with molecular weight as $N^{3/2}$. It must be noted that this expression holds true *only* when the concentration is expressed in number of chains per unit surface.[34,35] When it is expressed in mass per unit surface, A^{c}_{2} scales as $N^{\nu d-2}$, i.e., $A^{c}_{23} \propto N^{-0.20}$ for $d = 3$ ($\nu = {}^3/_5$) and $A^{c}_{22} \propto N^{-0.50}$ for $d = 2$ ($\nu = {}^3/_4$).[36] Daoud and Jannink[33] have also discussed the width of the Θ region, that is to say, the temperature domain ΔT over which the chains can be characterized by Θ exponents. They predicted that ΔT should follow a power law $\Delta T \propto N^{-\varphi_t}$. The coefficient of proportionality is not universal and depends on the particular system investigated. At this point it is important to note that ΔT decreases when the chain molecular weight increases. On the other hand, there are experimental indications that even with chains of very high molecular weight, ΔT can be quite large. Recent data in bulk polystyrene solutions and for several organic solvents have shown $\Delta T \simeq 30$ °C for $N = 10^5$ monomer units.[37]

As the surface concentration is kept increasing, a new regime is gradually entered in which the polymer chains cease to behave as impenetrable objects but rather interact through smaller segments, the blobs, of characteristic size $\xi < R_F$.[1] For $d = 3$, this regime where the chains start to interpenetrate is well defined. For $d = 2$, it is not as easy to picture how two different chains can entangle while keeping all their monomers strictly in the interfacial plane. To stress this difficulty, it may be more appropriate to speak of the intermediate regime rather than of the semidilute regime. At any rate, the main physical idea is that since the characteristic interaction length ξ is smaller than the global chain size R_{F2}, the osmotic pressure π should depend only on the monomer density and not on the chain length. This assumption has been proved to be indeed correct in bulk solutions and is therefore probably true in monolayers also.

Applying a scaling law argument, one can tentatively write

$$\pi_i \propto C^y \tag{4}$$

where y is an unknown exponent to be determined and the subscript i stands for the intermediate regime. This expression applies for all concentrations larger than the concentration of first overlap C^*. Moreover, the surface-pressure variation must be continuous over the whole concentration range. Especially one should have $\pi_d = \pi_i$ at $C = C^*$. The final expression of the surface pressure in the intermediate regime should therefore be

$$\pi_i = \pi_d^*(C/C^*)^y \tag{5}$$

where π_d^* is the value of π_d taken at $C = C^*$. The crossover concentration C^* is calculated by using the physical argument that at C^* the macroscopic surface density is approximately equal to the internal chain density, $C_{int} \propto N/R_{F2}{}^2$. This leads to

$$C^* \propto N^{1-2\nu} \tag{6}$$

The value of the exponent y can then be easily derived by imposing the condition π_i independent of N. We obtain

$$y = 2\nu/(2\nu - 1) \tag{7}$$

Experimentally, surface-pressure data for polymers of various molecular weights will be plotted on log–log scales as a function of surface monomer concentration C. For C smaller than C^*, one expects the data points to fall on a series of straight lines of slope unity, one for each molecular weight. For C larger than C^*, one expects all data points to condense on a single curve, which should be a straight line of slope y. The crossover between these two regimes occurs at C^*, which decreases as molecular weight increases. The dilute regime should thus be observed over a wider concentration range with polymeric chains of low molecular weight. According to eq 3, it is convenient to plot $(\pi/RT)(1/\Gamma)$ as a function of Γ. At low concentrations, one expects to observe a linear variation with an initial slope equals to A^{Γ}_{22}, the second virial coefficient. For $\Gamma \rightarrow 0$, the intercept with the ordinate axis should be equal to unity if the molecular weight of the polymer chain has been correctly measured independently. For polymers chains of nonzero polydispersity, the relevant molecular weight to use is the mass average molecular weight M_n.

Experimental Results

We have first studied the variation of the surface pressure π with the surface concentration C (in mg m^{-2}) in the case of poly(methyl methacrylate) (PMMA) samples. The results obtained at 25 °C and with molecular weights of 7800 and 1 600 000 corresponding to the two extremes of the investigated range have been plotted in logarithmic scales in Figure 1. Above $C = 0.8 \times 10^{-3}$ mg m^{-2}, all the data points align on a single straight line of slope $y = 16.5 \pm 1.0$. The surface-pressure data are thus molecular weight independent at high concentrations. At low concentrations, on the contrary, the data points become molecular weight dependent. The deviation from the straight line behavior in Figure 1 occurs sooner and is more prominent for the lowest molecular weight sample.

All the above experiments have been repeated at various temperatures between 1 and 35 °C. Within experimental accuracy, we have been unable to observe any changes in the data, in both the high- and the low-concentration regimes. For instance, the slope y has been measured to be 18, 16.5, 16, 17, 18, and 12 at 1, 5.3, 9.5, 15, 26, and 35 °C,

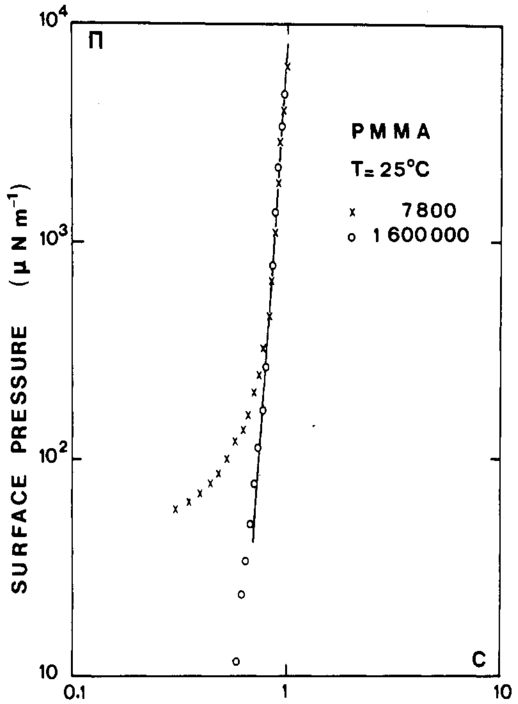

Figure 1. Logarithmic plot of surface pressure π versus surface concentration C for poly(methyl methacrylate) chains spread at the air–water interface (T = 25 °C). Sample molecular weights are M_w = 7800 and 1 600 000, respectively.

respectively, in the case of the M_w 1 600 000 sample. The slightly lower value of y at the most elevated temperature is probably an artifact due to monolayer contamination by impurities released from the trough inner surfaces. A control experiment at 31 °C gave a value of 16.7, totally consistent with the data obtained at lower temperatures. At low surface concentrations, we have also checked that the absolute values of the surface pressure stay the same when the temperature is varied. It is therefore clear that the surface-pressure data are independent of temperature, at least in the temperature range investigated. Most of the experiments on PMMA have therefore been performed at the single temperature of 25 °C.

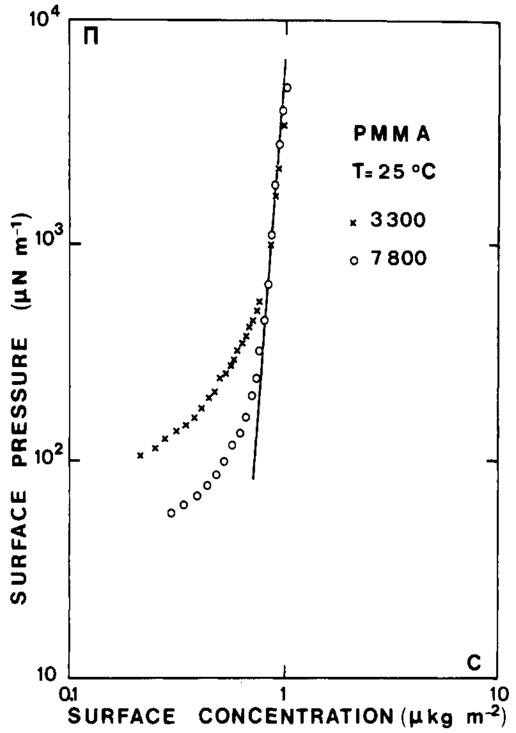

Figure 2. Same as Figure 1 but for M_w = 3300 and 7800.

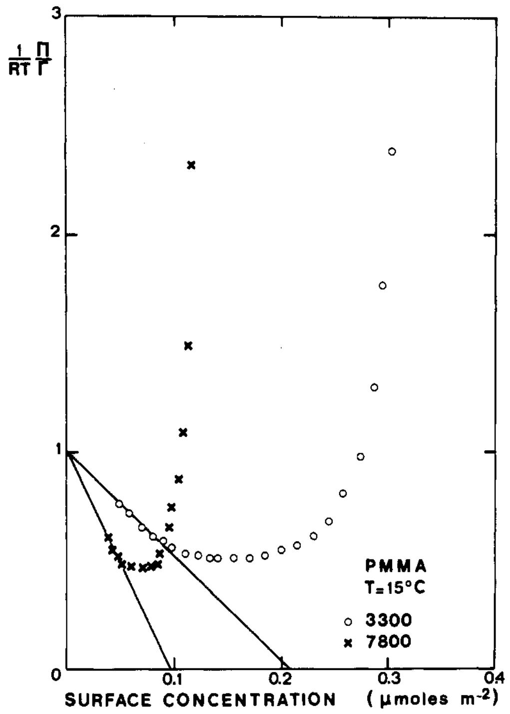

Figure 3. Linear plot of $(1/RT)(\pi/\Gamma)$ versus surface concentration Γ expressed in mol m^{-2} for poly(methyl methacrylate) chains spread at the air–water interface (T = 15 °C). Sample molecular weights are identical with those of Figure 2. The solid lines are an educated guess to calculate the second virial coefficient A^{Γ}_{22} between chains.

Figure 2 shows the same plot as in Figure 1, but for samples with molecular weights 7800 and 3300. The deviation from the straight line behavior occurs at a concentration of 0.86 mg m^{-2} for the M_w 3300 sample. The interest of using low molecular weight polymer chains is the ability to extend the measurements to very low concentrations and therefore to study the dilute regime in detail. This is done in Figure 3, where the data points of Figure 2 have been plotted as $(1/RT)(\pi/\Gamma)$ versus Γ, where Γ is the surface concentration expressed in mol m^{-2} and is therefore equal to $C/(Nm_0)$. In such a representation, all curves must start from unity on the ordinate axis for $\Gamma = 0$, and the initial slope is the second virial coefficient A^{Γ}_{22} between chains. Examination of Figure 3 shows that the values for $(1/RT)(\pi/\Gamma)$ are less than unity up to Γ^* = 0.105 μmol m^{-2}, and Γ^* = 0.28 μmol m^{-2} for the M_w 7800 and 3300 samples, respectively. This means unambigously that the initial slope and therefore A^{Γ}_{22} have negative values. As Γ becomes lower and lower, there is a gradual upturn of the data points. Ultimately they should reach unity, but it has not been possible to work at low enough concentrations with the present force-measuring system. The two solid lines are our best guesses for the data variation in the limit of zero surface concentration. The calculation of the corresponding second virial coefficient yield $A^{\Gamma}_{22} = -12 \pm 1$ m^2 μmol^{-1} and $A^{\Gamma}_{22} = -4.8 \pm 0.5$ m^2/μmol^{-1} for the 7800 and 3300 molecular weight samples, respectively.

To complete our data on PMMA samples, we decided to repeat the experiments performed in our previous publication[28] on samples with molecular weights 10 000, 280 000, and 659 000, respectively. To keep experimental conditions as identical as possible, we used the same temperature of 16.5 °C, although we are convinced that the

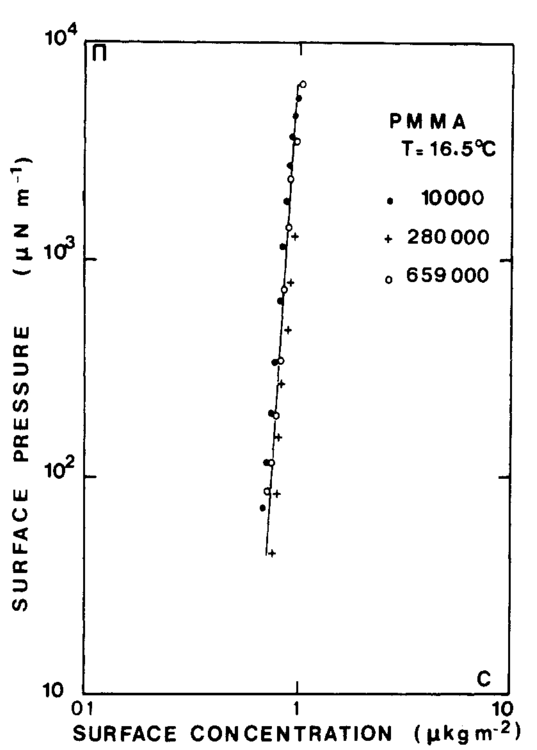

Figure 4. Same as Figure 1 but for the poly(methyl methacrylate) samples used in our previous publication[28] (T = 16.5 °C). Samples molecular weights are 10 000, 280 000 and 659 000.

data certainly do not change with temperature between 16.5 and 25 °C. The results are shown on Figure 4 for the high-concentration regime only. All points fall on a straight line with a slope $y = 16.5 \pm 1.0$. According to eq 7, this corresponds to a ν value of 0.530 ± 0.005. Comparison with the data of Figure 1 shows a perfect superposition except for a slight systematic shift by a few percent along the surface concentration scale for the M_w 250 000 sample, which may be due to an error in dilution during sample preparation.

We then turned to a similar investigation for the poly(methyl acrylate) samples. The results for samples of molecular weights 12 000 and 4200 at a temperature of 15 °C are shown in Figure 5. As for the PMMA samples, we observe a linear variation of π versus C at large concentrations, when plotted in logarithmic scales. The slope y is 2.80 ± 0.05 for both samples, corresponding to a ν value of 0.77 ± 0.01. At lower concentrations, typically below 0.15 mg m^{-2} for the longest PMA chain and below 0.20 mg m^{-2} for the shortest one, there is a marked upward deviation of the data points relative to the straight line. This low-concentration range is better analyzed in Figure 6, where $(1/RT)(\pi/\Gamma)$ has been plotted as a function of Γ, the surface concentration in chains, expressed in units of mol m^{-2}. The points corresponding to each molecular weight align on a straight line that intersects the ordinate axis at unity. This latter fact is a confirmation of the molecular weight of the samples used in these experiments. Were the nominal value different from the real one, the intercept would have been the ratio of these two values. The slopes of the straight lines drawn in Figure 6 yield the value of the second virial coefficient A^{Γ}_{22} between chains. Both values are positive. For M_w = 12 000, we obtain $A^{\Gamma}_{22} = 188 \pm 10$ μmol^{-1} m^2 while $A^{\Gamma}_{22} = 28 \pm 5$ μmol^{-1} m^2 for M_w = 4200. It is to be noted that the experiments shown in Figure 6 have been performed at two temperatures, namely, 15 and 25 °C. All data are superimposed, provided they correspond to the same molecular weight. We have confirmed this absence of temperature dependence by performing several independent experiments between 5 and 30 °C in both the low- and high-concentration regimes.

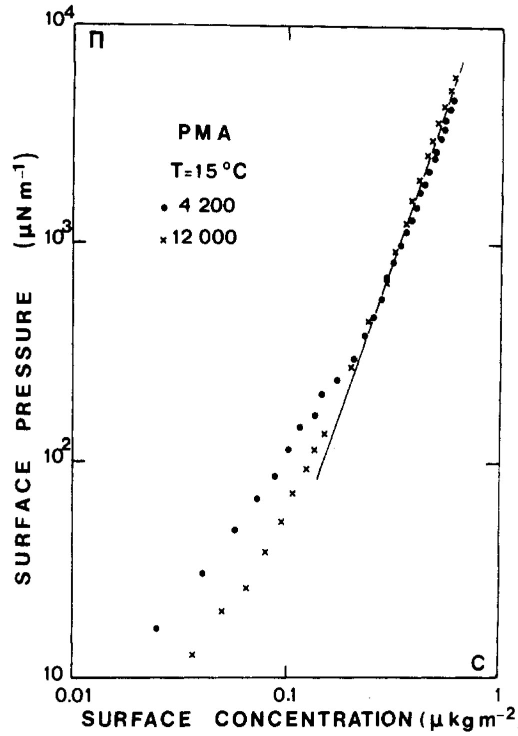

Figure 5. Logarithmic plot of surface pressure π versus surface concentration C for poly(methyl methacrylate) chains spread at the air–water interface (T = 15 °C). Sample molecular weights are M_w = 4200 and 12 000, respectively.

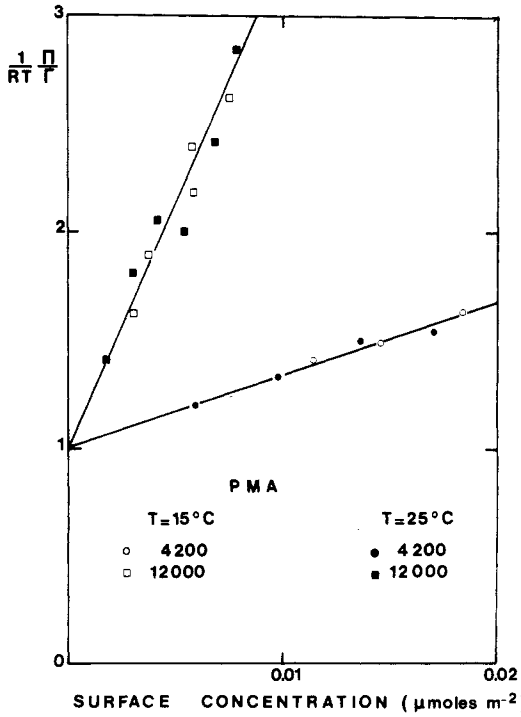

Figure 6. Linear plot of $(1/RT)(\pi/\Gamma)$ versus surface concentration Γ expressed in mol m^{-2} for poly(methyl acrylate) chains spread at the air–water interface (T = 15 and 25 °C). Sample molecular weights are the same as Figure 5. The solid lines show a linear variation of the data points at low concentrations. Their slopes yield the second virial coefficient A^{Γ}_{22}.

Discussion

The present data on poly(methyl methacrylate) and poly(methyl acrylate) confirm the existence of two different concentration regimes in monolayers of amphiphilic polymers spread at an air-water interface.

At low concentrations, the chains are only weakly interacting, and one has the analogue of a gaseous phase which is described by the ideal gas law. The polymer molecular weight derived from the extrapolation of the surface-pressure data points to zero concentration is in perfect agreement with the nominal molecular weight. This proves that the macromolecular chains are molecularly dispersed and do not form clusters or aggregates. The statement of course can be made more strongly for PMA than for PMMA. Indeed as shown in Figure 6 for PMA, the extrapolation of the results to zero surface concentration leaves little doubt that the best fit to the data is a straight line intersecting the ordinate axis at unity. On the contrary, for the PMMA data shown in Figure 3, extrapolation of the results is more problematic and one can only try an educated guess. The deviation from ideality at finite, yet very low, concentrations give access to the second virial coefficient. For the PMMA samples of molecular weights 3300 and 7800, A^{Γ}_{22} is definitely negative, and therefore the air–water interface must be considered as a "less than Θ" solvent, contrary to what was said in our initial report.[28] The zero value of the second virial coefficient in ref 28 was obtained on a sample of slightly larger molecular weight, namely, 10 000. Since these measurements require work at lower and lower concentrations and also at lower and lower surface pressures (for a given concentration), as the molecular weight is increased, it is not too surprising that an error could have been made in our early data. The present observation of an increase of the A^{Γ}_{22} value with molecular weight is entirely consistent with the theoretical prediction of Daoud and Jannink, $|A^{\Gamma}_{22}| \propto N^{\nu d}$.[33] Since ν is of the order of 0.53 for the PMMA chains investigated here, νd is positive, $\simeq 1.06$. Systematic measurements are currently under way to check this power law dependence more precisely. It is interesting to compare our best estimate of $A^{\Gamma}_{22} = -12 \pm 1$ μmol^{-1} m^2 for PMMA chains of molecular weight 7800 with the results obtained by Granick on monolayers of poly(dimethylsiloxane) (PDMS).[38] Analysis of Figure 6 of ref 38 yields $A^{\Gamma}_{22} = -13.4$ μmol^{-1} m^2 at 20 °C for PDMS chains of molecular weight 730. Using the Daoud–Jannink relationship and taking ν experimental to be $\simeq 0.51$ for PDMS, we calculate that A^{Γ}_{22} should be $\simeq -148$ μmol^{-1} m^2 for PDMS chains of molecular weight 7700. This is a factor 15 times higher than the A^{Γ}_{22} value measured here for the PMMA chains of same M_w. The PDMS chains are therefore in a much more collapsed state at the air-water interface than the PMMA chains.

For PMA, A^{Γ}_{22} is positive, which shows that the polymer chains are in an extended configuration at the air-water interface. Here also, we have observed that A^{Γ}_{22} increases with chain molecular weight by as much as a factor of 6 for a molecular weight change of 2.8:1. Theoretically one expects $A^{\Gamma}_{22} \propto N^{\nu d}$, i.e., $A^{\Gamma}_{22} \propto N^{1.54}$, using our experimental determination for ν. This would correspond to an increase by a factor of 4.9 between the two polymer samples. The agreement is satisfactory.

Our results, obtained at temperatures between 1 and 35 °C, show rather unambiguously that the surface-pressure data for both PMMA and PMA monolayers do not depend on temperature. Such an observation is very important because it contradicts several reports of the early literature on this subject.[26,29,30,39,40] We believe that the variations observed in most of the previous works are due to the leaching-out of surface-active impurities from the trough inner surfaces. The data taken at elevated temperatures are the most prone to be affected by this surface contamination. It is striking, for instance, to observe that the data of Llopis and Subirana on PMA,[39] when plotted as $(\pi/RT)(1/\Gamma)$ versus Γ, are independent of temperature between 25 and 30 °C but start to increase markedly above 30 °C and up to 50 °C. A similar observation can be made on the data of Jaffé et al. for atactic PMMA.[29,40] Our own experience is that reliable measurements become difficult to achieve above 35 °C, even though our fused silica trough could be cleaned thoroughly and had a low probability of releasing organic contaminants.

At high concentrations, one enters a new regime where the chains are strongly interacting. In this regime intermediate between the dilute and the compact monolayer, the surface pressure increases sharply with surface concentration but no longer depends on molecular weight. More precisely, π is observed to obey a power law with an exponent y. If one accepts the analogy between this intermediate regime in 2D monolayers and the semidilute regime in 3D solutions, y can be related to the ν exponent describing the molecular weight dependence of the 2D radius of gyration R_{F2}. Markedly different results are obtained for the two types of polymer chains investigated here. For PMA, $y = 2.80 \pm 0.05$, and, with use of eq 7, this yields a ν value of 0.78 ± 0.01. For PMMA, $y = 16.5 \pm 1.0$, leading to a ν value of 0.530 ± 0.005. These results are temperature independent, and therefore the chains stay in the same configuration over at least a 30 °C temperature range around room temperature. It is clear, from the good agreement between the experimental value and the predicted value for self-avoiding walk behavior, that the PMA chains are in an extended configuration and that the air–water interface behaves as a good solvent for this type of polymer chain. This statement is confirmed by our observation of a positive second virial coefficient in the low-concentration range.

On the contrary, the PMMA chains are in a "less than Θ" state at the air-water interface, as evidenced from a negative second virial coefficient. However, the chains are still not totally collapsed since a dense compact state imposes that $\nu = 0.50$ (for $d = 2$), whereas our experimental value for the ν exponent is 0.53. This latter value can be used to set a lower limit for the characteristic ν exponent of a 2D polymeric chain in the Θ state. The present experiments are therefore inconsistent with the approximate value $\nu_{\Theta} = 0.505$ obtained from field theory and ϵ-expansion methods.[16] We mentioned in the Introduction that several theories based on Monte Carlo simulations,[8,10] real space renormalization group,[20] and transfer matrix analysis[23] seem to converge toward a prediction of $\nu_{\Theta} \simeq 0.57$.[24] Our new data on PMMA are certainly compatible with this prediction, although they can by no means constitute a definitive proof. In that respect we have to reemphasize that our previous estimation of $\nu_{\Theta} = 0.56 \pm 0.01$ made in ref 28 was erroneous. It was based on measurements performed at 16.5 °C on PMMA samples with molecular weights 10 000, 280 000, and 659 000. We surmise that the method of deposition of the monolayer by successive additions onto the air–water interface (1) does not allow control of the surface concentration to a high enough degree of accuracy, (2) offers no protection against the possibility of solvent retention within the monolayer, and (3) supposes that the monolayer is able to reach mechanical equilibrium quickly and that there is no trapped entanglements between the chains. Any one of these difficulties can explain why the y exponent of the power law $\pi \propto C^y$ in the intermediate was found to be $y = 10$ instead of $y = 16.5$ as in the present investigation.

For chains in the Θ state, another value of $\nu = 0.51$ has been proposed by Takahashi et al.[26,30] on the basis of their experiments on PMA monolayers at the air–water interface. Working at various temperatures between 16.5 and 45 °C, they did report a dramatic transition from excluded-volume to Θ behavior and even to collapse. This was apparently supported by their data in both the high-concentration and low-concentration regimes. For instance, the slope y of the power law dependence at large surface pressure changes from 2.85 ± 0.05 at 25–45 °C to 35 ± 5 at 18.2 °C, corresponding to ν values of 0.77 ± 0.01 and 0.51 ± 0.005, respectively. The second virial coefficient was measured at low concentrations: A^{c}_{22} changed from positive (above 25 °C), to zero (at 18.2 °C), to negative (at 16.5 °C) values. These experiments look therefore like the perfect demonstration of a temperature-induced crossover between Θ and excluded-volume statistics for two-dimensional chains. Unfortunately, we believe that the Takahashi et al. measurements have been plagued by an unknown experimental artifact. Indeed, we have been unable to reobserve their strong temperature dependence, although both experiments were performed on the same samples. The possibility of chemical degradation can be ruled out since the experimentally measured molecular weights agree quite well with the nominal values. Moreover, our experiments have been repeated over a two-year period with various experimental arrangements and several different troughs. The temperature dependence of the surface-pressure isotherms is not the only point of disagreement between the two sets of experiments. In ref 26, surface pressures in excess of 10 dyn cm^{-1}, which are typical of very compact monolayers, were reached as early as 0.35 mg m^{-2}, whereas in the present experiments, such high values are not obtained before 0.70 mg m^{-2}. The difference is strikingly large and may again indicate contamination by a surface-active impurity, which could in turn induce a phase separation in the monolayer. This maximum value of 0.35 mg m^{-2} just before monolayer collapse also does not agree with data obtained with other polymeric materials such as poly(vinyl acetate)[25] and poly(tetrahydrofuran).[27] If one compares the data points for PMA, M_w 12 000, at 20 °C plotted in Figure 1 of ref 26 with our data points of Figure 5, our surface-pressure measurements increase much more gradually. Our results are, on the other hand, consistent with the Llopis and Subirana data on a PMA sample of molecular weight 17 000 at 25 °C.[39]

There are at least two other indirect arguments against the possibility of a transition from good solvent to Θ solvent behavior, over a narrow span of temperature, that are worth mentioning here. The first one is derived from similar attempts made by one of us[37] on 3D solutions of flexible coils in organic solvents. Experimental evidence for the crossover between Gaussian and excluded-volume single chain could be observed only under very stringent conditions. First, the complete transition requires one to work with chains of very high molecular weight (e.g., $M_w > 10^7$ in the case of polystyrene). Second, the complete transition could never be followed in a single solvent, even over temperature spans of 35 °C. It was necessary to use a range of solvents to artificially vary the temperature of the experiment between θ and $\theta + 200$ °C. The relevant parameter to describe the transition is the product $M\tau^2$, where $\tau = (T - \theta)/\theta$. If $M\tau^2 = 1$, the chain is Gaussian. It was experimentally proven that to reach the asymptotic excluded-volume regime for both static and dynamic properties, the product $M\tau^2$ has to be larger 10^5. It is hard to see why the situation would be radically different when working with polymer monolayers. In the best case the product $M\tau^2$ in Takahashi experiment is a low 16.

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

sample	$10^{-3}M_w$	M_w/M_n	NMR triads, % iso	 hetero	 syndio
Polysciences	3.3	1.15	3.8	27.4	68.8
Polysciences	7.8	1.15	3	20.1	76.9
Mulhouse 1	10.0	1.2	2	24.2	72.8
Mulhouse 2	280	1.2	5.9	37.5	56.6
Mulhouse 3	659	1.2	9.8	39.9	50.3
Polysciences	1600	1.3	4	37	59

The second argument is related to the width of the Θ regime, which has been estimated by Daoud and Jannink[33] to be $\Delta T/\theta \propto N^{-0.6}$. With low molecular weight samples such as used in the monolayer experiments ($N < 140$), we can calculate that the chains will not change their θ configuration over a temperature range of at least 10 °C. Although we have arbitrarily set the prefactor to be equal to unity, this is already larger than the 7 °C range over which the crossover from the Θ state to the excluded-volume regime is totally completed in the work by Takahashi et al.[30] A more satisfactory theoretical estimate of the extension of the Θ domain can be derived from the Monte Carlo results of Birhstein et al.[9] Using Figure 12 of ref 9, we have calculated ΔT to be about 60 °C for chains with a molecular weight of 10^4 and 23 °C for chains with a molecular weight of 10^5.

One last point is worth mentioning. It is known since the pioneering work of Beredjick[41] that surface-pressure data of poly(methyl methacrylate) monolayers are a strong function of the chain stereoregularity. The isotactic form takes a swollen conformation at the air–water interface, while the syndiotactic form is much more condensed. As a consequence, surface pressure for a given concentration can be 10 times higher in the first case than in the second. The pressure variation with surface concentration is also different. Surface-pressure measurements have actually been used to determine the fraction of isotactic triads for PMMA chains of unknown stereoregularity.[29] It is therefore compulsory to specify the stereoregular composition of the chains when one tries to measure critical exponents such as ν. This is done in Table I for all our PMMA samples. The ν value of 0.53 proposed in the present work corresponds to mostly atactic chains, the isotactic fraction being generally less than 5% with the exception of the 659 000 molecular weight sample, which has a 9% isotactic fraction.

Conclusion

The present results moderate our previous claim that poly(methyl methacrylate) chains spread at the air–water interface could be a good archetype for polymer chains at the Θ state in two dimensions. We now believe that atactic PMMA chains are in a less than Θ state in the temperature range between 1 and 35 °C. The second virial coefficient measured in the low-concentration regime is negative, and the characteristic ν exponent as measured from data in the intermediate regime is $\nu = 0.53$. This result sets a lower limit for the value of the ν_Θ exponent in the Θ state. The proposed limit excludes the value $\nu_\Theta = 0.505$ predicted by field theory and ϵ-expansion methods, which are known to converge poorly in two dimensions. On the opposite, it is consistent with the value $\nu_\Theta \simeq 0.57$ obtained by real space renormalization transfer matrix, Monte Carlo simulations, and Coulomb gas methods.

Our measurements on PMA monolayers show that the PMA chains take an excluded-volume conformation at the air–water interface. The value of the ν exponent is 0.78,

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in close agreement with the theoretical predictions and previous experimental data on other polymer monolayers. Contrary to an earlier report by Takahashi et al., the chain configuration is not affected by temperature variations in the range 5–30 °C. Consequently, the experimental value of $\nu_\Theta = 0.51$ proposed in ref 26 and 30 cannot be considered as reliable.

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Registry No. PMA, 9003-21-8; PMMA, 9011-14-7.

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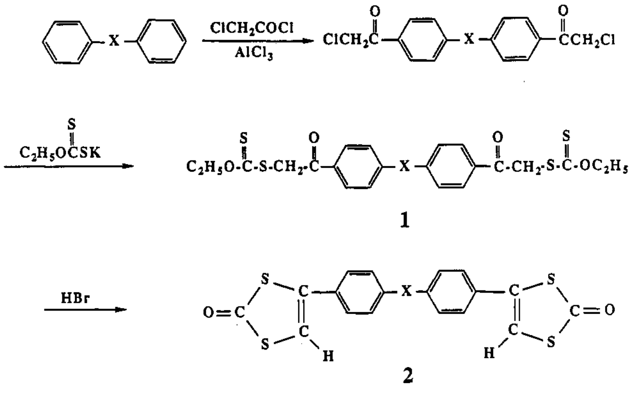
Communications to the Editor

Soluble and Electroactive Nickel Bis(dithiolene) Complex Polymers

Considerable effort has been devoted to the synthesis and understanding of transition-metal bis(dithiolenes)[1] and structurally related complexes[2] which possess interesting electrochemical, optical, magnetic, liquid crystalline,[3] electrically conductive, and superconductive[4] properties. A number of polymers and oligomers based on the square-planar MS_4 center have also been prepared that are electroactive and conductive. These include poly(metal tetrathiooxalates),[5] poly(metal ethylenetetrathiolates),[6] poly(metal tetrathiosquarates),[7] poly(metal tetrathiafulvalenetetrathiolates),[8,9] poly(metal tetrathianaphthalenes),[10] and poly(metal benzenetetrathiolates).[11] Most of these metal complex polymers are insoluble and infusible solids due to their ribbonlike rigid structure. During synthesis some of these systems possess solubility that can be attributed to the high charge density along the polymer backbone, but precipitation to amorphous powders prohibits resolubilization.

Scheme I



We report here on the synthesis and properties of a new metal complex polymer, poly[[1,1′-oxybis[4-(1,2-dithiolatoethenyl)benzene]]nickel(II)] (PBOSD-Ni) which, in the reduced form, is *aqueous* and *organic* solvent soluble and exhibits electrochemical properties analogous to the transition-metal bis(dithiolenes).

Bis[4-(2-oxo-1,3-dithiolyl)phenyl] oxide (BSDTO) was the required monomer precursor for this study. The synthesis of this compound was carried out in three steps as shown in Scheme I. Starting with diphenyl ether (X = O), Friedel–Crafts acylation with chloroacetyl chloride in the presence of $AlCl_3$ led to bis[4-(chloroacetyl)phenyl] oxide. Bromoacetyl bromide and bromoacetyl chloride were also used as acylating reagents, but low yields of product were obtained. Bis[4-(chloroacetyl)phenyl] oxide was reacted with the potassium salt of *O*-ethyl xanthate

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