over an average of 35 folds, the fold length can be estimated to be ~100 Å, which is consistent with the transmission electron micrographs. These findings are not surprising since polymers generally crystallize from solution by chain folding with a characteristic fold length of ~100 Å.[21,22] It should be noted that Lieser et al.[18] have previously proposed the concept of chain folding with respect to polyacetylene. Such a crystal structure may also explain the room-temperature isomerization reflected in Figure 1; that is, it derives from amorphous material present at the fold surfaces.

Many polymers are known to crystallize in helical conformations, including the polydienes,[23] which are structurally related to polyacetylene, and Natta and Corradini[24] have empirically derived a set of principles concerning the crystallization of such macromolecules. In particular, they have shown that the conformation in a crystal approaches that corresponding to the minimum potential energy of the isolated helical chain. Recently, Cernia and D'Ilario[25] have made potential energy calculations for isolated *cis*-polyacetylene chains and concluded that this molecule should assume a distorted cis-cisoid helical conformation, similar to the one we have assigned to our crystals. We suggest that prior to crystalization the *cis*-polyacetylene in PS_{100}–PA existed in solution as such a helix.

What then accounts for the dramatic difference between the previously reported crystal structure of *cis*-polyacetylene[17-19] and that described above? We propose the following explanation.

Although both crystal packing modes exhibit nearly the same density (see above), the hexagonal structure contains 36% more (00*l*) surface area per unit cell than those previously published. Chain folding also increases the effective (00*l*) crystal surface area per molecule so that decreasing the fold length results in an increase in the interfacial surface area per polyacetylene chain. It is this (00*l*) crystal plane that must accommodate the polystyrene blocks, and we believe that the cis-transoid crystal structure cannot provide a sufficient (00*l*) surface area to permit the formation of a stable crystalline phase in sample PS_{100}–PA. For the same reasons PS_{200}–PA and PI_{200}–PA, which contained twice the carrier polymer molecular weight, were found to be soluble. As stated, it is our contention that the equilibrium conformation of isolated *cis*-polyacetylene is a distorted cis-cisoid helix and not planar cis-transoid, although it is the latter form that appears to be produced by Ziegler–Natta polymerization.

In the case of the Shirakawa synthesis, polymerization is followed by immediate crystallization which dictates a crystal structure based upon the planar cis-transoid conformation. On the other hand, crystallization of initially formed PS_{100}–PA is inhibited by packing restrictions associated with the carrier block and this, we believe, allows the polyacetylene block to attain an equilibrium helical conformation in solution. Crystallization can then occur with a hexagonal crystal structure because this permits accommodation of the carrier polystyrene.

In conclusion, we have demonstrated for the first time a method of preparing single crystals of polyacetylene. In particular, the *cis*-polyacetylene moiety of a polyacetylene–polystyrene diblock copolymer has been shown to crystallize from solution by chain folding into a hexagonal structure. We propose that these crystals consist of helical polyacetylene chains in a distorted cis-cisoid conformation and that this reflects an equilibrium helical conformation in solution.

Forthcoming reports will address the properties of single-crystalline *cis*- and *trans*-polyacetylene in more detail.

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Registry No. Acetylene–styrene copolymer, 84824-32-8.

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Do Scaling Laws Apply in Moderately Concentrated Polymer Solutions?[†]

In spite of an enormous amount of experimental work on semidilute polymer solutions, no critical experiment has been performed that can differentiate between competing

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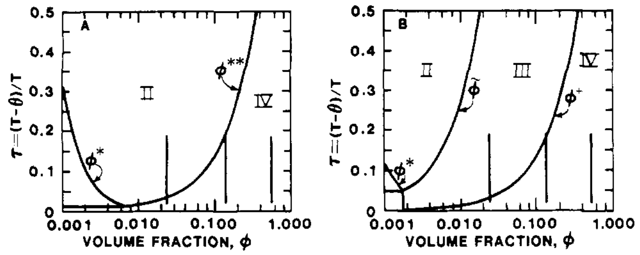

Figure 1. *T–C* diagram according to DJ (A) and SJP (B). Diagrams are plotted assuming $\chi_S = 0.15$. Procedures for developing the diagrams are found in ref 3. Bold vertical lines show the region covered by experiments reported in Figure 2. Θ is the theta temperature.

Table I
Power Laws for ξ_ρ

regime	DJ	SJP
II, good	$\phi^{-3/4}\tau^{-1/4}$	$\phi^{-3/4}\tau^{-1/4}$
III, marginal		$\phi^{-1/2}\tau^{-1/2}$
IV, Θ	ϕ^{-1}	ϕ^{-1}

models for the structure of these solutions. The models in question are summarized by the temperature–concentration (*T–C*) diagrams given by Daoud and Jannink (DJ)[1] and by Schaefer, Joanny, and Pincus (SJP).[2,3] These diagrams are shown in slightly modified form in Figure 1. Although these models differ in their predicted power-law exponents for various observables, experimentalists have been forced to work in concentration regimes in which the models are indistinguishable. In this report, small-angle X-ray scattering results are reported for the polystyrene/cyclopentane (PS/CP) system. The measured exponents for the temperature dependence of the static correlation range ξ_ρ are consistent only with the SJP model.

The *T–C* diagram of Daoud and Jannink is shown in Figure 1A. These authors use analogies with magnetic critical phenomena[4] to derive the power laws for the concentration and temperature dependence of various quantities. Different exponents are found in regimes separated by lines in the *T–C* diagram. Below the volume fraction ϕ^* the system is dilute and not of concern here. Between ϕ^* and ϕ^{**} DJ find asymptotic scaling exponents for ξ_ρ. The predicted power-law exponents for ξ_ρ are summarized in Table I. Region II is the good-solvent regime, in which it is generally agreed that scaling should work. The critical feature of the DJ diagram, however, is the direct crossover near ϕ^{**} to a "Θ-like" regime (IV).

The SJP *T–C* diagram differs from DJ in the existence of a "marginal" regime III, where scaling laws fail but where two-body monomer contacts still dominate the solution thermodynamics. A tuned-up version[3] of the SJP diagram is shown in Figure 1B. To develop this diagram, scaling arguments are used in region II exactly following DJ. Around $\tilde{\phi}$, however, scaling laws break down because of the nearly Gaussian structure of strands on a small length scale.[3] For concentrations exceeding $\tilde{\phi}$ linear response theory[5,6] in the mean-field approximation leads to the power-law exponents found in Table I. The marginal regime covers most experiments reported to date. Above $\phi^\dagger$ (region IV), the SJP model is again identical with DJ in that scaling theory and perturbation theory give identical results. In this regime the system is sufficiently concentrated that three-body monomer contacts dominate the thermodynamics.

The extent of the marginal regime is directly related to the ratio of the second and third osmotic virial coefficients.[3] In certain cases (e.g., completely flexible chains) regime III may disappear and Figure 1B would collapse into Figure 1A. Figure 1B is plotted for a flexibility index[3] $n = 1.67$, which is appropriate to PS.

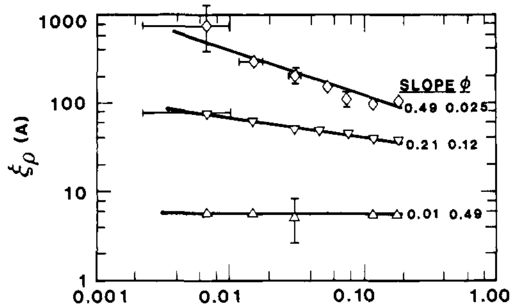

Figure 2. Temperature dependence of the correlation range at three concentrations for PS/CP. Molecular weights used are $M_n = 2 \times 10^6$ for $\phi = 0.025$, $M_n = 2.3 \times 10^5$ for $\phi = 0.12$, and $M_n = 1.7 \times 10^4$ for $\phi = 0.49$.

Although the DJ and SJP formulations differ substantially, essentially every experimental measurement available can be explained with either model. This situation arises because most experimental data are taken near $\phi \sim 0.05$ and $\tau \sim 0.1$. In this regime SJP expect a crossover from marginal to Θ behavior and apparent exponents are fortuitously close to the scaling predictions for region II.

A clear example of confusion in interpretation is found in the measurements of Cotton et al.[7] of the concentration and temperature dependence of ξ_ρ and PS/cyclohexane near the Θ temperature. Although these authors interpret the data assuming a direct ϕ^{**} crossover, Okano et al.[8] show that the data are equally consistent with the $\phi^\dagger$ crossover in Figure 1B.

Problems also arise in the interpretation of dynamic data as illustrated by the PS/benzene (BZ) system. Here, light scattering data[9,10] seem to agree with the interpolation formulas of DJ,[11] assuming a direct crossover between scaling formulas. Schaefer and Han,[12] on the other hand, claim that the PS/BZ system is far from the asymptotic limits required by scaling and interpret the data as reflecting a $\phi^\dagger$ crossover.

The list of nondefinitive experiments could be extended to include measurements of osmotic pressure, radii-of-gyration, viscosity, self-diffusion, etc. In all cases, experimental data do not adjudicate between the models.

The data reported here show clear-cut evidence in favor of the SJP model. The temperature and concentration dependence of ξ_ρ was measured for the PS/CP system. This system was chosen because of excellent X-ray contrast, because it has a convenient Θ temperature, and because dilute solution measurements[13] indicate that the *T* dependence of swelling is very strong (i.e., the reduced residual partial molar entropy parameter χ_S is small, $\chi_S \simeq 0.15$).

Experiments were performed with the Kratky system at the National Center for Small Angle Scattering at Oak Ridge National Laboratory. The data were analyzed[14] by using a slit-smeared Ornstein–Zernike structure factor. Samples were prepared from Pressure Chemical standards, with CP purified following Saeki et al.[15] We find a Θ temperature of 20.5 °C but are aware of reported values from 20 to 24 °C.

Vertical lines in Figure 1 show the domain covered. Based on the two *T–C* diagrams, one expects the power-law exponent for the temperature dependence of ξ_ρ to differ by a factor of 2 at the lowest concentration ($\phi = 0.025$) studied. Both diagrams predict temperature independence at the highest concentration ($\phi = 0.49$). At the intermediate concentration ($\phi = 0.12$), "apparent" exponents re-

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flect interpolation between the respective regimes.

The *T* dependence of ξ_p at the three concentrations is plotted in Figure 2. These data are *T* independent at the highest concentration as expected from both models. At the lowest concentration the data follow a power law that is close to the SJP entry in the table but differs by a factor of 2 from the DJ prediction.

The data at the intermediate concentration show an exponent consistent with the scaling prediction for region II, but it is clear that this result is due to crossover and is not evidence for scaling laws.

The data presented demonstrate that scaling behavior is not found in the region of the *T–C* diagram usually studied by experimentalists. In addition, a reasonable explanation is provided for the observation of "apparent" scaling exponents in the crossover near $\phi^\dagger$, which separates the marginal and Θ regimes.

Registry No. Polystyrene, 9003-53-6; cyclopentane, 287-92-3.

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Singlet Energy Migration of Anthracene Polymers in Polystyrene

Effective transformation of light into chemical energy is a subject that has received much attention of late.[1] One of the problems encountered in such work is the necessity for efficient collection of photonic energy at a site where complex chemistry can take place. For this to occur, photon harvesters, or "antennas", must be designed to facilitate energy transfer to the reaction center, which, on a molecular level, may be far removed from the original point of light absorption.[2]

Recently, Faulkner and Renschler[3] have estimated the degree to which singlet excitation energy may migrate between diphenylanthracene (DPA) sites when these are dispersed in a film of polystyrene (PS) and tetrabromo-*o*-quinone (TBBQ) is used as an acceptor. Values of up to 55 Å for the diffusion length of excitation energy (*D*), through hopping from one DPA site to another by a Förster energy-transfer mechanism, were obtained.[4] Since the rate of such transfer increases dramatically with decreasing distance between the sites,[5] it might be feasible to increase the extent of diffusion by chromophore polymerization rather than by increasing the small-molecule concentration. Polymer-bound chromophores may also be more compatible with a host film. Furthermore, the problem of site loss from the film, because of leaching, would then be severely curtailed. Energy migration in dilute polymer solutions has been invoked to explain various characteristics of macromolecular photophysics.[6]

Table I
Characteristics of the Polymers

polymer[a] (PPA-*co*-PS)	mole fraction[b]	τ,[c] ns
1	0.016	6.9
2	0.021	6.2
3	0.039	5.3
4	0.051	5.2

[a] Molecular weight (M_w) of each copolymer is 13 500 (PD = 1.5). [b] Mole fraction of phenylanthracene units in the copolymers (calculated from visible absorption spectroscopy). [c] Fluorescence lifetimes of neat films.

We have synthesized (10-phenyl-9-anthryl)methyl methacrylate[7] and copolymerized it with varying amounts of styrene (copolymers PPA-*co*-PS, 1–4). Table I lists the essential features of these polymers. Polystyrene films containing one of the copolymers, or the saturated monomer equivalent (PA), with or without quencher (TBBQ), were cast by dropping a benzene solution of the components onto a glass slide rotating at approximately 6000 rpm on a Headway Research Inc. (Model EC101) spin-casting apparatus. Mole ratios of the components in solution were retained on the slide. Films cast by allowing the solvent to evaporate slowly were not used in this study because visible inspection of the films, facilitated by the red color of the quencher, showed nonhomogeneity. Fluorescence decay curves, obtained by excitation of the phenylanthracene chromophore at 355 nm using a Nd:YAG laser, were digitized on a fast transient recorder (Tektronix Model 7912). The decay curves of the films could be fit satisfactorily to a single exponential over the time range $t = 1.5$ ns to $t = 10$ ns, over which time the emission had decreased about sevenfold. $t = 0$ was taken as the maximum of the decay curve. Mirroring Faulkner's work,[3] we then estimated the extent of singlet energy migration that occurs on irradiation when these copolymers are either dispersed in polystyrene or utilized as neat films and compared the results with those of the saturated monomer (PA) under identical conditions.

The occurrence of energy migration between PA sites in a polystyrene matrix is demonstrated by the dependence of γ, the Förster quenching parameter,[5] on fluorophore concentration. Extrapolation of a plot of γ vs. [PA] to zero fluorophore concentration yields a value of 0.43 for γ. From this value, R_0, the critical transfer distance between PA and TBBQ sites, is estimated to be ~25 Å. Faulkner cites a value of 28 Å for DPA–TBBQ pairs using this method, which agrees well with the value of R_0 obtained from theoretical considerations.[3]

The Yokota–Tanimoto theory[8] has been widely cited and used as a means of measuring *D* in those systems in which energy diffusion plays a significant part. Figure 1

0024-9297/83/2216-1017$01.50/0