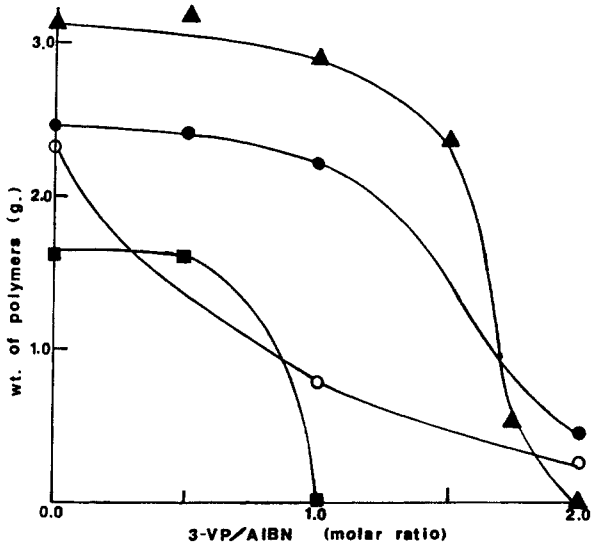


Figure 1. Effect of 3VP on the inhibition of the polymerizations of (▲) styrene, (●) methyl methacrylate, (○) 4-vinylpyridine, and (■) vinyl acetate. Reaction conditions. All the inhibition reactions were carried out under identical conditions except that the amount of inhibitor was varied: 25 mmol of the purified monomer was refluxed with 0.1 mmol of AIBN and the specified amount of 3VP or perylene in 7.0 mL of benzene for 12 h under N_2. Polystyrene was precipitated by ethanol, poly(4-vinylpyridine) precipitated during the reaction, and the other two polymers were obtained by the removal of solvent in vacuo at 60 °C.

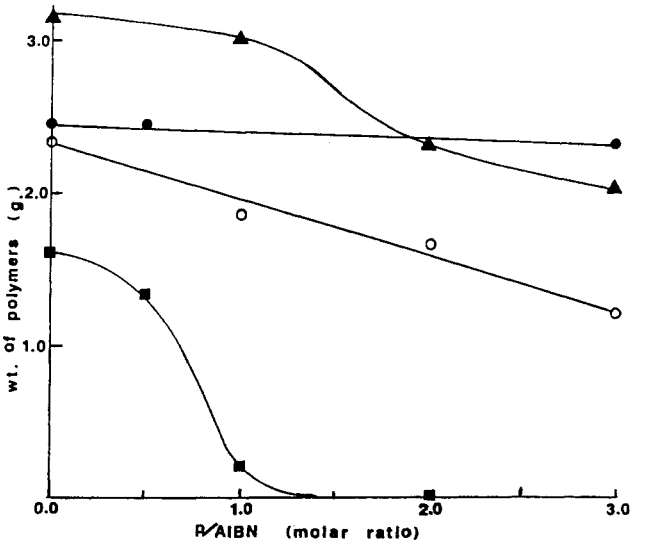
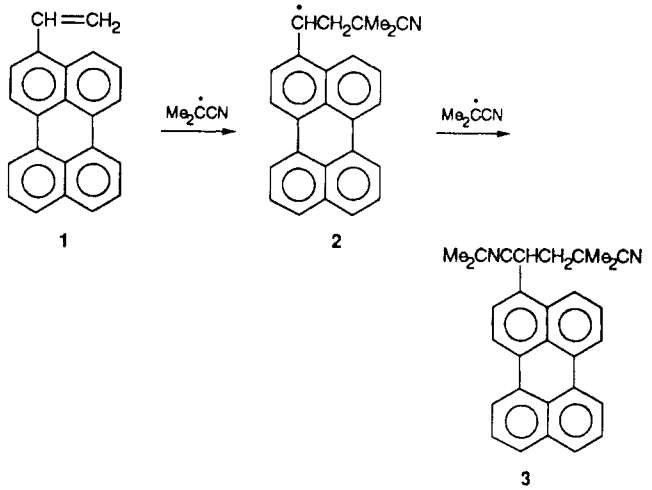


Figure 2. Effect of perylene on the inhibition of the polymerizations of (▲) styrene, (●) methyl methacrylate, (○) 4-vinylpyridine, and (■) vinyl acetate. Reaction conditions were the same as in Figure 1.

Scheme I



molar ratio of 3VP to AIBN suffices to inhibit the vinyl acetate while a double molar ratio is needed for the inhibitation of the other three monomers.

In support of this interpretation, 2,5-dimethyl-2,5-dicyano-3-(3-perylenyl)hexane (**3**) (16.1%) was obtained as orange crystals, mp = 240–242 °C, when 3VP was refluxed with 3 mol of AIBN in benzene under N_2 for 24 h. Anal. Calcd for $C_{30}H_{26}N_2$: C, 86.92; H, 6.32; N, 6.76. Found: C, 86.58; H, 6.28; N, 6.19.

It was previously reported that perylene (P) inhibits the AIBN-initiated polymerization of vinyl acetate at molar ratios of P:AIBN of 2.03.[3] The authors calculated that perylene has the largest delocalization energy among a dozen polynuclear aromatic compounds and documented that perylene could capture active radicals. However, the exact mechanism was not defined. Moreover, Kamogawa[4] was able to succesfully polymerize various perylene-containing vinyl monomers in which the vinyl group was not directly conjugated with the perylene ring. This underlines the special stabilization of the perylenylmethyl radical.

We have examined the effect of perylene on the four monomers studied above and present the results in Figure 2. Clearly, vinyl acetate is the only monomer that perylene can inhibit. Because vinyl acetate is the least reactive monomer, the corresponding radical, itself poorly conjugated, is probably reactive enough to attack perylene to give an unreactive species, thus inhibiting the polymerization. The polymerization of vinyl acetate is known to be sensitive to impurities in low concentrations.[5]

Registry No. **3**, 119696-18-3; 3VP, 77003-70-4; AIBN, 78-67-1; styrene, 100-42-5; methyl methacrylate, 80-62-6; 4-vinylpyridine, 100-43-6; vinyl acetate, 108-05-4.

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Dimension of a Single Polymer in a Good Solvent

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Long ago Flory[1,2] calculated the scaling of the root-mean-square (rms) end-to-end distance with chain length, N, for a single chain in a good (athermal) solvent in three dimensions with mean-field theory. His method can also be used for other dimensions, d, than three:[2] $\langle r^2 \rangle^{1/2} = N^{\nu}$, $\nu = 3/(d + 2)$, $d \leq 4$. This scaling relation has been ob-

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tained more rigorously with renormalization theory.[3,4] In two dimensions Flory's result seems to be correct,[5] but for three dimensions a slightly smaller value for the exponent than predicted by Flory has been found,[6] i.e., $\nu = 0.5880 \pm 0.0015$. Careful extrapolation of exact enumerations yields a similar value,[7] $\nu = 0.5875 \pm 0.0015$, and two recent Monte Carlo calculations[8,9] yielded $\nu = 0.5745 \pm 0.0143$ and $\nu = 0.592 \pm 0.003$. The renormalization group is now clearly the method of choice to calculate long-wavelength properties of polymer chains.[4]

However, the Flory result remains a useful estimate for the scaling exponent. In fact, for $d = 3$ or $d = 2$ it is a much better estimate than that obtained by first-order renormalization group calculations.[4] Flory has calculated a mean-field excluded volume, $v_0N^2R^{-d}$, which tends to swell the chain (v_0 is the excluded-volume parameter describing the interactions between two segments, and R is the chain radius) and an elastic force (entropy term), R^2N^{-1}, which tends to contract the chain, and he determines the chain radius by finding the minimum in free energy.[2] (This simple description of the Flory theory follows de Gennes.[2] See Freed[4] for a discussion of the family of Flory theories and the work of Edwards.[10]) Both terms overestimate the correct value considerably, but the errors approximately cancel each other. de Gennes[11] has shown that the overestimation is $N^{2\nu-1}$ for the first term and $N^{\gamma-1}$ for the second term, where γ is a critical exponent connected to the entropy of the self-avoiding chain.[2] Obukhov[12] discusses the approximations further and gives an error estimate for the scaling exponent, i.e., $\delta\nu/\nu$ is smaller than 10% for $4 > d \geq 1$. He also points out that Flory type theories give incorrect results near $d = 4$, where the error terms given by de Gennes should cancel each other.

Here I want to note that the Flory result can be derived by considering only the excluded-volume term. The idea behind the derivation is the following. A polymer in solution is affected by the excluded volume only if its length exceeds a certain number of Kuhn persistence lengths. I estimate how the persistence length has to scale as a function of chain length to keep the excluded volume independent of the chain length and propose that the real chain scales like such an invariant persistent chain.

A persistent random-walk (PRW) chain with N segments of length unity where α segments point in the same direction is considered. Such a chain has the same Gaussian distribution function as a random-walk chain with N/α segments of length α and its end-to-end distance is therefore[2]

$$\langle r^2\rangle^{1/2} = (N\alpha)^{1/2} \tag{1}$$

In the calculation of the mean-field excluded volume for the PRW chain, the equivalence to the RW chain with N/α independent segments of length α is used. Since the probability of two segments intersecting is proportional to their volume (hypervolume in d dimensions) and since the volume of each of the N/α segments is proportional to α, the excluded-volume parameter for these segments is αv_0. The excluded volume for the PRW is then

$$\mathrm{EV}(\alpha,N,d) = (\alpha v_0)(N^2\alpha^{-2}R^{-d}) \tag{2}$$

where the first factor is the excluded-volume parameter and the second factor is the square of the number of segments (of length α) divided by the volume of the chain. The chain radius, R, of the PRW scales with N and α like the rms end-to-end distance in eq 1, and the excluded volume therefore scales as

$$\mathrm{EV}(\alpha,N,d) \sim v_0N^{2-d/2}\alpha^{-d/2-1} \tag{3}$$

where the proportionality factor between radius and end-to-end distance has been ignored.

For $d \geq 4$ the excluded volume decreases or stays constant with increasing chain length, and the chain scales like an ideal random-walk chain. For $d < 4$ the persistence length is calculated as a function of N such that eq 3 is independent of N:

$$\alpha \sim N^{(4-d)/(d+2)} \tag{4}$$

With eq 1, the Flory result follows for the scaling relation of the rms end-to-end distance; see above.

Flory's calculating the radius by balancing the excluded volume term by the elastic force and finding the minimum energy is therefore equivalent to dividing his excluded volume by the persistence length and requiring that the excluded volume is independent of chain length; see eq 3. Using the mean-field result for the scaling exponent, the persistence length in eq 4 is equal to the correction term for the excluded volume given by de Gennes,[11] $N^{2\nu-1}$ and it seems to be an approximate measure of the correlations that arise because of the connectivity of the chain. The constant excluded volume calculated here is (with the mean-field exponent) therefore equal to de Gennes's[11] corrected excluded volume, $N^{3-\nu(d+2)}$. By requiring the latter to be independent of N, the Flory result can be obtained without having to use the entropy term.

The presented derivation is a blob theory (where the persistence length is equal to the blob size) which uses additionally the concept of invariance familiar from renormalization group calculations. Blob theory calculations have been used for calculating the crossover from the good solvent limit to the Θ state or from the dilute chain solution to more concentrated solutions. In these calculations the blob size for the athermal isolated chain is kept constant and taken to be equal to the whole chain in the former case and equal to a segment in the latter, quite different from the approach used here. Blob theories work best in the good solvent limit and have been critically compared to the renormalization group method by Douglas and Freed.[13] The present theory can be used only for the athermal chain and has the same range of applicability as do the other Flory theories.[12]

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