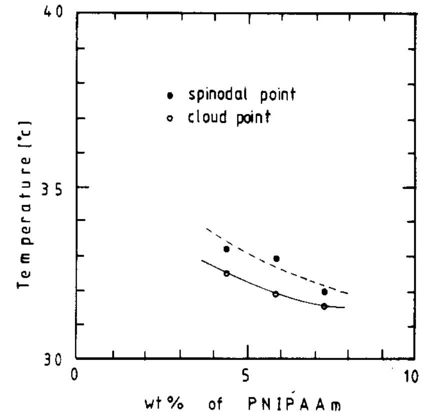

Figure 1. Cloud points and spinodal points for the aqueous solution of poly(*N*-isopropylacrylamide).

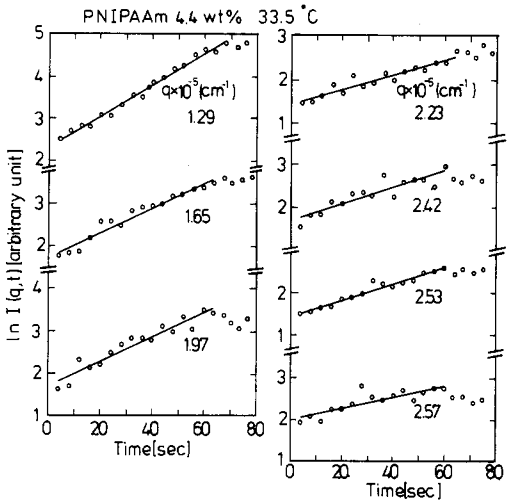

Figure 2. Time dependence of scattered light intensity from a 4.4 wt % solution at 33.5 °C.

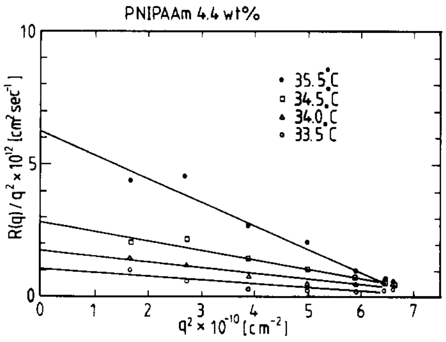

Figure 3. Plots of $R(q)/q^2$ vs q^2 for 4.4 wt % solutions at various temperatures.

The Cahn's theory, the following formula of $R(q)$ was derived:

$$R(q)/q^2 = D_{\mathrm{app}} - 2KMq^2 \qquad (3)$$

where D_{app} is the apparent diffusion coefficient, M mobility, and K a constant representing surface energy effect. To obtain the values of D_{app}, the experimental data of $R(q)/q^2$ were plotted against q^2. Some examples of such plots are shown in Figure 3.

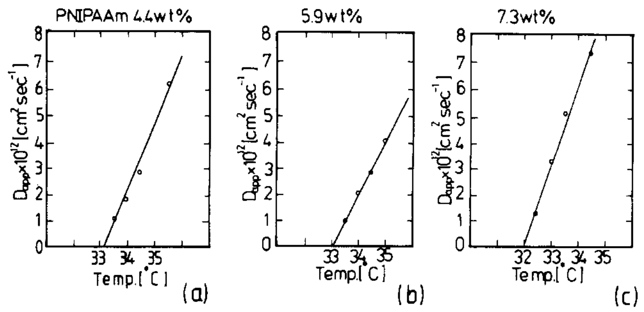

Figure 4. Temperature dependence of the apparent diffusion coefficient: (a) 4.4 wt % solution; (b) 5.9 wt % solution; (c) 7.3 wt % solution.

All the values of D_{app} obtained for each polymer concentration are presented in Figure 4. This figure clearly shows that the extrapolation method can be adopted to determine a spinodal point at which the apparent diffusion coefficient equals zero. The determined spinodal points are shown in Figure 1. The spinodal point for each polymer concentration is slightly higher than the corresponding cloud point.

Thus in the present work, the occurrence of spinodal decomposition was confirmed for the aqueous solution of poly(*N*-isopropylacrylamide).

Registry No. Isopropylacrylamide, 25189-55-3.

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3-Vinylperylene: A Powerful Radical Trap

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3-Vinylperylene (3VP) has been previously prepared,[1] but there is no report of its polymerization or attempted polymerization in the literature. We now find that it cannot be polymerized or copolymerized (with styrene and maleic anhydride) and further that it strongly inhibits the radical polymerization of reactive monomers.

3VP was prepared from perylene via perylenecarboxaldehyde by Vilsmeier[2] and Wittig[1] reactions: mp = 162-164 °C (lit.[1] mp 153-154 °C); yield (overall) 62.0%. Anal. Calcd for $C_{22}H_{14}$: C, 94.93; H, 5.07. Found: C, 94.58; H, 5.07.

After attempts to polymerize or copolymerize 3VP under the normal free radical conditions failed, we investigated the effects of small quantities of added 3VP on the AIBN-initiated polymerizations of styrene, methyl methacrylate, 4-vinylpyridine, and vinyl acetate. The results are shown in Figure 1: the polymerization of vinyl acetate is completely inhibited when the 3VP molar concentration equals that of the initiator. For the other three monomers, the polymerization is strongly retarded by a concentration of 3VP double that of the initiator and completely stopped by three times the concentration.

Our results suggest that 3VP reacts with the initiator radicals as shown in Scheme I. The reactive vinyl group of 3VP traps $\mathrm{Me_2\dot{C}CN}$ radicals, either immediately on their release from AIBN or in the early growth of the polymer chain, with the formation of radical **2**. **2** is insufficiently reactive to initiate polymerization. As further $\mathrm{Me_2CCN}$ is released, it reacts faster with radical **2** (to give **3**) than with the unreactive monomer vinyl acetate, but slower than with reactive monomers, such as styrene. Hence, an equal

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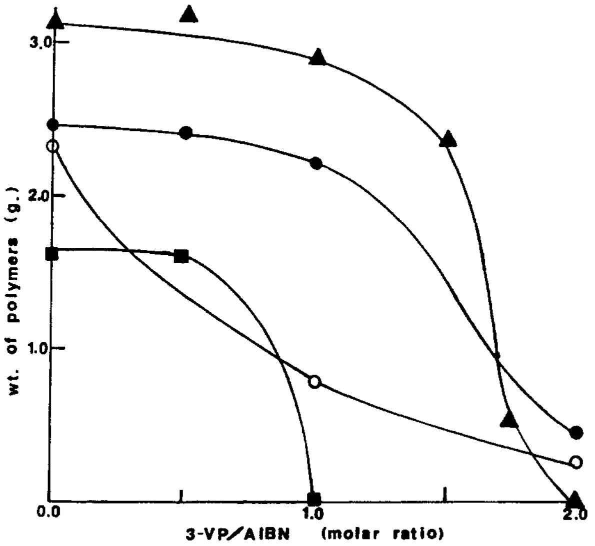
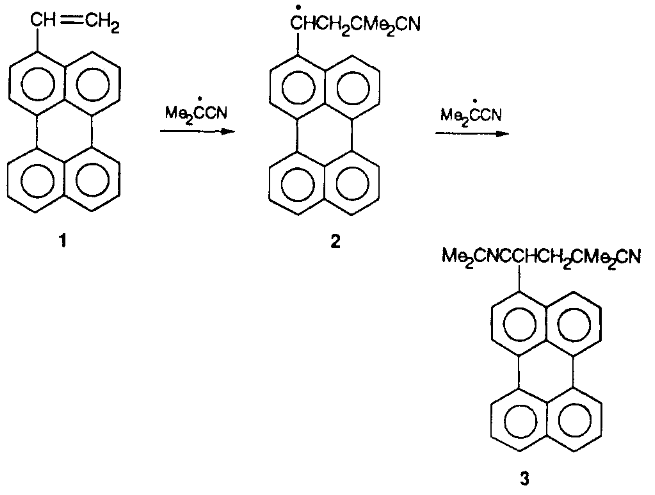


Figure 1. Effect of 3VP on the inhibition of the polymerizations of (▲) styrene, (●) methyl methacrylate, (○) 4-vinylpyridine, and (■) vinyl acetate. Reaction conditions. All the inhibition reactions were carried out under identical conditions except that the amount of inhibitor was varied: 25 mmol of 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.

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.

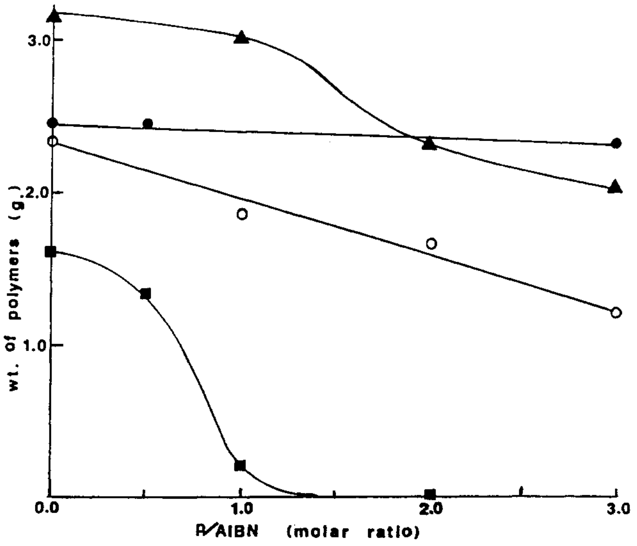


Figure 2. Effect of perylene on the inhibition of the polymerizations of (▲) styrene, (●) methyl methacrylate, (○) 4-vinylpyridine, and (■) vinyl acetate. Reaction conditions were the same as in Figure 1.

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] $\langle r^2\rangle^{1/2} = N^{\upsilon}$, $\upsilon = 3/(d + 2)$, $d \leq 4$. This scaling relation has been ob-

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