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Solvent Effects on Intramolecular Photocycloaddition of Poly(1-vinylnaphthalene)

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Photocycloaddition reaction of naphthalene side groups in poly(1-vinylnaphthalene) was studied in cyclohexane, benzene, and dichloromethane. In cyclohexane the reaction proceeds following the first order kinetics to a high conversion of 70%, while in dichloromethane the reaction levels off at a very low conversion of 20%. The reaction behavior in benzene is intermediate between cyclohexane and dichloromethane. Quenching and sensitizing experiments proved that a triplet mechanism is predominant in cyclohexane, while in dichloromethane a singlet mechanism, presumably excimer mechanism, takes place. The solvent effect was interpreted by the formation of ground state dimer due to the conformational change of the polymer chain in poor solvents.

Photocycloaddition of aromatic compounds, in particular anthracene and acenaphthylene, is of interest from photochemical and photophysical points of view.[1] It has been assumed that the excimer state is the intermediate state in the formation of cyclodimers of anthracene derivatives.[2] Recently, experimental evidence of the mechanism has accumulated by use of a single crystal of the anthracene dimer[3] or the bichromophoric systems.[4]

In the case of photocycloaddition of acenaphthylene, however, other schemes have been proposed in addition to the singlet excimer mechanism[1f] *e.g.* bimolecular reaction between triplet state and ground state molecules, and pseudounimolecular photo-reaction of a ground state associated dimer. Although the latter unimolecular mechanism has attracted little attention[1e] because of the absence of the spectroscopic evidence of the postulated ground state dimer, it is worthwhile to reconsider this mechanism since several non-conjugated bichromophoric systems have recently been reported to undergo intramolecular cycloaddition *via* excitation of ground state complexes.[4,5]

In a previous paper[6] a report was given on spectroscopic evidence for the formation of a ground state dimer in poly(1-vinylnaphthalene) and 1,3-di-1-naphthylpropane in fluid and solid cyclohexane, respectively. This paper deals with the cycloaddition mechanism of naphthalene side groups in poly(1-vinylnaphthalene), especially the effect of solvent on the reaction, and a consideration on the role of the ground state dimer in the cycloaddition reaction. The intramolecular cyclodimerization of 1,3-di-1-naphthylpropane was also carried out as a model system of the polymer. These studies are expected to give valuable information on the precursors of the cycloaddition process of naphthalene and its homologes.[7]

Experimental

Preparation and purification methods of poly(1-vinylnaphthalene) have been described.[6] Cyclohexane and dichloromethane were of spectrograde. All samples were degassed by the freeze-pump-thaw-cycles under a reduced pressure less than 10^{-5} mmHg in the dark.

A super high pressure mercury lamp (1 kW) was used as a radiation source. Wavelengths longer than 280 nm were selected with a Toshiba UV-29 filter. Absorption and emission spectra were measured with a Shimadzu UV-200 spectrophotometer and a Hitachi MPF-2A spectrofluorometer, respectively.

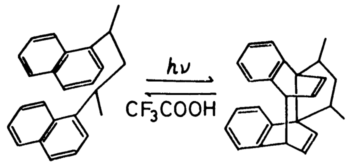
Quantum yields of the cycloaddition reaction were determined with a chemical actinometer of potassium ferioxalate system. The mercury line of 297 nm was isolated with a grating monochrometer (Ritsu MC-20), the initial concentration being so controlled as to make the absorbance at 297 nm less than 0.1.

Results and Discussion

Photocycloaddition in Solutions. Poly(1-vinylnaphthalene) exhibits monomer, dimer, and excimer emissions in dichloromethane, while in cyclohexane a dimer emission becomes predominant, the excimer emission not being discerned.[6,8] This indicates that the dimer conformation is stable even in the excited state in cyclohexane, though the excimer conformation is favorable in dichloromethane. The absorption spectrum in cyclohexane also notably differs from the spectrum in dichloromethane, indicating the formation of the ground state dimer in a cyclohexane solution.[6] The conformation of the polymer in poor solvents is conceived to be more rigid as compared to conformation in good solvents, the conformational change in the excited state being restricted. On the other hand, higher mobility of the chain in good solvents makes it possible to attain the most stable conformation, an excimer conformation, in the excited state.

Photoillumination of poly(1-vinylnaphthalene) in the two solvents, cyclohexane and dichloromethane, results in a photochemical reaction of the naphthalene side groups. The photochemical reaction was followed by measurements of the absorption spectra of the naphthalene side groups in the 250—350 nm region (Figs. 1 and 2). In both cases the intensity of the absorption decreases with photoillumination.

Addition of a trace amount of trifluoroacetic acid to the illuminated sample restores the initial absorbance.[7a] The recovery indicates that the decrease in absorbance induced by photoillumination is due to the photocycloaddition of the naphthalene side groups as shown in the following:



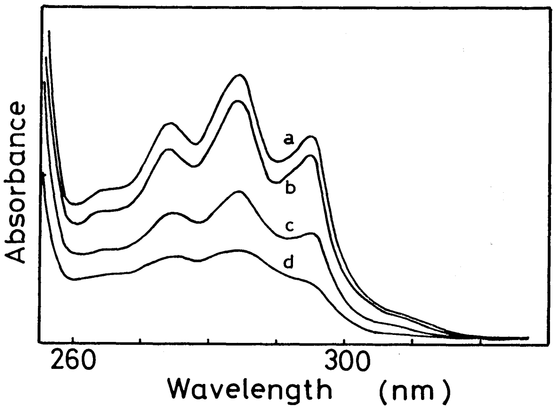


Fig. 1. Absorption spectra of poly(1-vinylnaphthalene) in cyclohexane before and after photoillumination by the light passed through Toshiba UV-29 filter ($\lambda >$ 280 nm) at 20 °C. Illumination times are (a) 0, (b) 0.2, (c) 11 and (d) 36 min. Initial concentration of poly(1-vinylnaphthalne) is 5×10^{-5} M.

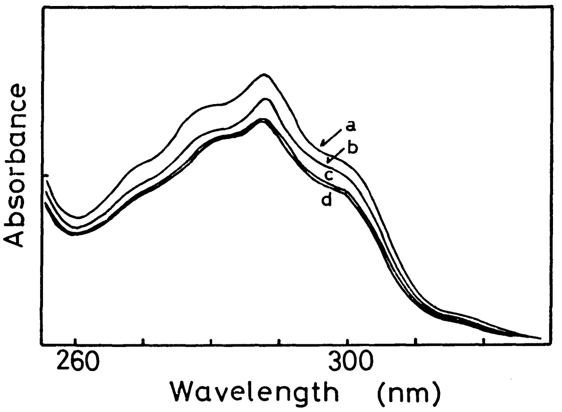


Fig. 2. Absorption spectra of poly(1-vinylnaphthalene) in dichloromethane before and after photoillumination at 20 °C. Illumination times are (a) 0, (b) 0.5, (c) 4 and (d) 20 min. Initial concentration of poly(1-vinylnaphthalene) is 5×10^{-5} M.

In order to confirm the cycloaddition reaction, NMR spectra of the sample were measured before and after photoillumination (Fig. 3). The intensity ratio of aromatic and vinyl protons to the alkyl proton is 2.23 before photoillumination, while it decreases to 1.64 after illumination for 3 h. The corresponding theoretical values before and after the cycloaddition should be 2.33 and 1.50, respectively. Although the values include some errors even before photoillumination probably due to chain end groups, the value after illumination is located between the initial and theoretical values. In addition to the above ratio the NMR spectrum after illumination shows a new peak at 6.1 τ attributable to methine proton.[7c)] These results indicate that the photochemical reaction of poly(1-vinylnaphthalene) corresponds to the cycloaddition.

Figure 4 shows the relative changes in absorbance of naphthalene side groups in cyclohexane, dichloromethane and benzene during the course of photolysis. The photocycloaddition of 1,3-di-1-naphthylpropane in cyclohexane is also shown for the sake of comparison with the corresponding polymer system. In this experiment the concentrations of the polymer and 1,3-di-1-naphthylpropane were so controlled as to have the same absorbance at 297 nm. In cyclohexane the reaction proceeds following the first order kinetics except in the very early stage. The behavior is similar to the reaction of 1,3-di-1-naphthylpropane.[7c)] This suggests that the cycloaddition of naphthalene side groups in cyclohexane occurs between the isolated dimer pairs, which are formed stably in the ground state. A statistical calculation predicts the degree of pairing of the side groups to be 84.46% when the side groups make a pair randomly.[9)] In a real polymer system, however, the degree of pairing is naturally less than the theoretical prediction due to the conformational restriction. Thus, the conversion of 70% is explained by the dimerization of the naphthalene pairs formed in the ground state independent of each other.

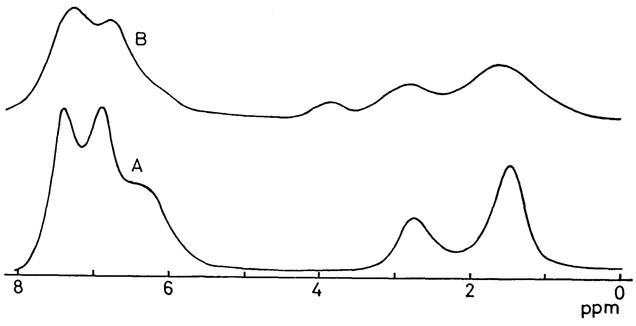


Fig. 3. NMR spectra of poly(1-vinylnaphthalene) (A) before and (B) after photoillumination for 3 h in benzene at 20 °C. $CDCl_3$ was used as a solvent.

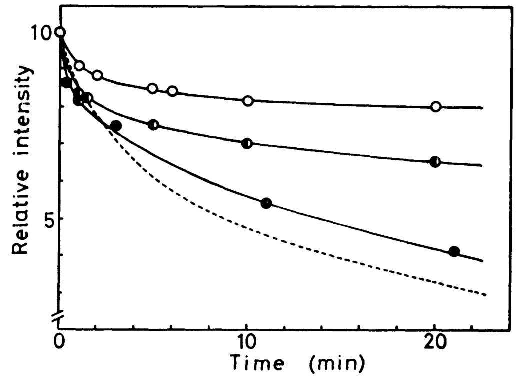


Fig. 4. Photocycloaddition of poly(1-vinylnaphthalene) in (○) dichloromethane, (◐) benzene and (●) cyclohexane and of 1,3-di-1-naphthylpropane (---) in cyclohexane at 20 °C. The reaction was followed by measurements of absorbance at 295 nm.

On the other hand, in dichloromethane the reaction levels off at a very low conversion of *ca.* 20%. The flexibility of the polymer chain in dichloromethane makes the reaction possible between nonadjacent naphthalenes.[5)] The reaction between the nonadjacent molecules presumably produces the macro-ring to make the polymer chain rigid. The regidity thus formed is considered to prevent the reaction between the residual side groups, giving rise to the low conversion.

The reaction behavior in benzene is intermediate between cyclohexane and dichloromethane. The

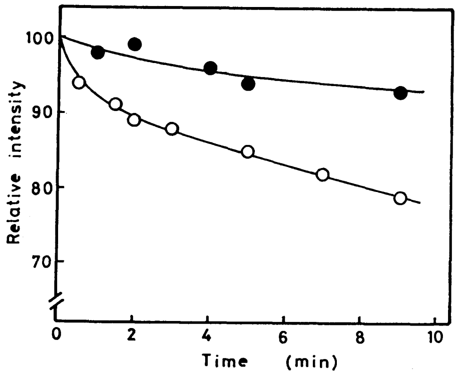


Fig. 5. Photocycloaddition reaction of poly(1-vinylnaphthalene) in cyclohexane in the absence (○) and in the presence (●) of 5×10^{-4} M of 1,3-pentadiene at 20 °C.

cycloaddition reaction proceeds up to 40% conversion but after that it levels off. The intensity of the dimer absorption in benzene is weaker than that in cyclohexane, though it is much higher than in dichloromethane. The higher conversion in benzene is attributable to the photo-reaction of the ground state dimers.

The quantum yields of cycloaddition by the mercury line of 297 nm were measured to be 0.04 and 0.02 in cyclohexane and dichloromethane, respectively, at 20 °C. The yield in dichloromethane is the value in the initial stage at 2×10^{-5} M, since it decreases with time and finally becomes very small after prolonged illumination. The higher value in cyclohexane indicates that the rigid dimer conformation is favorable to the cycloaddition reaction in comparison with the mobile conformation in dichloromethane.

Reaction Mechanism. The difference in the reaction behavior in cyclohexane and dichloromethane was further confirmed by quenching and sensitizing experiments. Figure 5 shows the effect of the addition of 1,3-pentadiene upon the cycloaddition reaction in cyclohexane. The reaction is suppressed by 1,3-pentadiene in cyclohexane. In this experiment very low concentration of 1,3-pentadiene (5×10^{-4} M) was adopted in order to avoid the addition reaction between the naphthalene side groups in the excited singlet state and 1,3-pentadiene.[10] In dichloromethane, however, no noticeable difference was observed in the reaction even in the presence of the same concentration of 1,3-pentadiene.[11] The quenching experiment confirmed that the solvent alters the reaction mechanism. In cyclohexane a triplet excited state is mainly responsible for the reaction. The reaction was suppressed not only by 1,3-pentadiene but also by oxygen which is a typical triplet quencher. Ineffectiveness of 1,3-pentadiene in dichloromethane suggests a singlet mechanism, since the triplet state of naphthalene is known to be effectively quenched by 1,3-pentadiene.

In order to substantiate the triplet mechanism in cyclohexane, the triplet sensitization by benzophenone was carried out as shown in Fig. 6. The reaction was followed by the fluorescence intensity of the naphthalene moiety. Decrease in intensity was observed even when the excitation wavelength was restricted to the absorption of benzophenone (λ>390 nm). The decrease is not due to the reaction between a naphthyl side group and benzophenone, since the fluorescence of 1-methylnaphthalene retains the same intensity even after prolonged photoillumination in the presence of benzophenone. The result provides unambiguous evidence that the cycloaddition reaction in cyclohexane occurs in the triplet excited state.

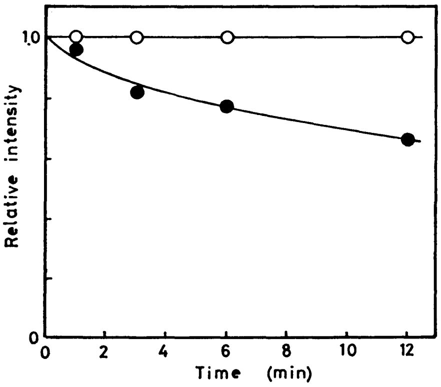


Fig. 6. Photosensitized cycloaddition of poly(1-vinylnaphthalene) in (●) cyclohexane and (○) dichloromethane in the presence of benzophenone by excitation wavelengths longer than 340 nm at 20 °C. The reaction was followed by measurements of the fluorescence intensity of the naphthalene moiety. The areas of the whole spectra plotted against wave number scale were compared.

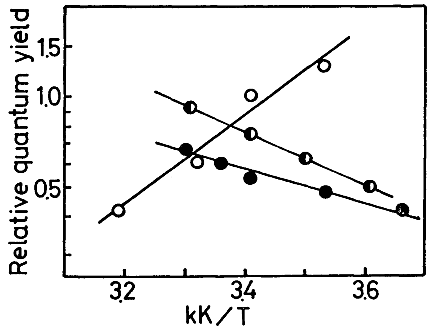


Fig. 7. Temperature dependence of relative quantum yields of photocycloaddition of poly(1-vinylnaphthalene) in (○) cyclohexane and (●) dichloromethane and of 1,3-di-1-naphthylpropane in cyclohexane(◐).

On the other hand, the fluorescence intensity shows no decrease in a dichloromethane solution by photosensitization with benzophenone under identical conditions. The result confirms the singlet mechanism, presumably excimer mechanism, of the cycloaddition reaction in dichloromethane.

The temperature dependence of the quantum yield of cycloaddition is shown in Fig. 7. The slope in dichloromethane gave an activation energy of 2.0 kcal/mol, which is smaller than the value 4.3 kcal/mol for 1,3-di-1-naphthylpropane. The difference suggests that in this temperature range polymer chains assist the cycloaddition reaction. The enthalpy change associated with the excimer formation is conceived to be similar both in the polymer and 1,3-di-1-naphthylpropane, while the activation energy necessary to attain the excimer conformation or dimer conformation is considered to depend on the chain length. The low activation energy in the polymer system indicates that the naphthyl side groups, which are in a favorable conformation to make the cyclodimer, react in the initial stage of the reaction in dichloromethane.

The temperature dependence in cyclohexane, on the other hand, gave a negative value of −5.7 kcal/mol. The reaction scheme in cyclohexane can be expressed as follows:

$$\begin{array}{lll} \mathrm{N} + \mathrm{N} \rightleftharpoons (\mathrm{N{\cdot}N}) & \begin{array}{l} k_{\mathrm{d}} \\ k_{\mathrm{m}}, \end{array} & (1) \\ (\mathrm{N{\cdot}N}) \xrightarrow{h\nu} {}^1(\mathrm{N{\cdot}N})^* & I_0, & (2) \\ {}^1(\mathrm{N{\cdot}N})^* \longrightarrow {}^3(\mathrm{N{\cdot}N})^* & k_{\mathrm{ISC}}, & (3) \\ {}^1(\mathrm{N{\cdot}N})^* \longrightarrow \mathrm{N} + \mathrm{N} & k_{\mathrm{f}} + k_{\mathrm{n}}, & (4) \\ {}^3(\mathrm{N{\cdot}N})^* \longrightarrow \mathrm{N{-}N} & k_{\mathrm{D}}, & (5) \\ {}^3(\mathrm{N{\cdot}N})^* \longrightarrow \mathrm{N} + \mathrm{N} & k_{\mathrm{p}} + k_{\mathrm{n}}'. & (6) \end{array}$$

Here, N, (N·N) and N–N are a naphthalene side group, an associated dimer and a photodimer, respectively. Equations 4 and 6 involve all deactivation processes in the excited singlet and triplet states, respectively. Using the steady-state approximation, the quantum yield of the cycloaddition reaction, Φ_{D}, is given by

$$\Phi_{\mathrm{D}} = k_{\mathrm{ISC}} \cdot k_{\mathrm{D}} \cdot \tau_1 \cdot \tau_3 \cdot \frac{k_{\mathrm{d}} \bar{\varepsilon}_{\mathrm{d}}}{k_{\mathrm{d}} \bar{\varepsilon}_{\mathrm{d}} + k_{\mathrm{m}} \bar{\varepsilon}_{\mathrm{m}}},$$

where τ_1 and τ_3 are lifetimes of singlet and triplet excited states, respectively, $\bar{\varepsilon}_{\mathrm{d}}$ and $\bar{\varepsilon}_{\mathrm{m}}$ average extinction coefficients of dimer and monomer, respectively, at the excitation wavelength. The negative activation energy is attributable to τ_3 and $k_{\mathrm{d}}\bar{\varepsilon}_{\mathrm{d}}/(k_{\mathrm{d}}\bar{\varepsilon}_{\mathrm{d}}+k_{\mathrm{d}}\bar{\varepsilon}_{\mathrm{m}})$, since other terms are insensitive or have positive temperature coefficient. The increase in the mobility of polymer chain at higher temperatures is considered to cause the decrease of the triplet state lifetime due to the increase in the rates of non-radiative deactivation processes and prevent the formation of cyclodimer, giving a low quantum yield.

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8) Monomer emission signifies the fluorescence from isolated naphthalene side groups excited to its first excited singlet state. Dimer emission is the fluorescence emitted from an excited dimer produced by excitation of the associated dimer of the side groups with its conformation in the ground state essentially unchanged. Excimer signifies a kind of excited dimer the conformation of which is suitable for strong interaction in the excited state between the side groups but repulsive in the ground state. This conformation clearly differs from that of the associated dimer formed in the ground state.

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11) External heavy atom effect of the solvent is negligible. Dichloromethane scarcely alters the triplet lifetime of the polymer. Conversely, low viscosity of dichloromethane increases the collision frequency between the polymer and the quencher.