Effects of the Wavelength and the Matrix on the Photopolymerization of 2,5-Distyrylpyrazine and Its Related Compounds and on Their Photodepolymerization*

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The solution photopolymerization of 2,5-distyrylpyrazine (DSP) and its related compounds with the general formula of Ar–CH=CH–Ar′–CH=CH–Ar, where Ar and Ar′ represent aryl and arylene groups respectively, have been investigated. All diolefines were converted in good yields into amorphous oligomers with cyclobutane in the main chain on the exclusive excitation of the monomer molecules, while, in the crystalline state, only DSP and 1,4-bis[β-pyridyl-(2)-vinyl] benzene are known to yield highly crystalline oligomers under the same light. All the oligomers were found to be photodepolymerized to the original monomers in the solution on the excitation of the terminal groups of these oligomers. In consequence, a photoreverse scheme has been demonstrated between the diolefinic monomer and the oligomer, depending on the excitation wavelength. Poly-DSP was photodepolymerized into the monomer in trifluoroacetic acid solution, while amorphous poly-DSP in film was readily photooxidized in the air under sunlight. From the photochemical behavior of DSP, oligo-DSP, and poly-DSP, it was found that chemically the same substance, oligo-DSP, behaved in three ways, photopolymerization, photodepolymerization and no photoreaction, according to the physical state. Such a matrix effect is discussed from the point of view of topochemical reaction.

Various kinds of diolefinic compounds have been known to photopolymerize in the crystalline state into highly crystalline polymers with cyclobutane in the main chain.[1–3] Among a series of diolefinic compounds with the general formula of Ar–CH=CH–Ar′–CH=CH–Ar (where Ar and Ar′ represent aryl and arylene groups respectively), 2,5-distyrylpyrazine(DSP) and 1,4-bis-[β-pyridyl-(2)-vinyl]benzene (P2VB) have been reported to be photopolymerized in the crystalline state.[3] Furthermore, photooligomerization on DSP, P2VB, and other types of diolefinic compounds in the crystalline state has been reported in a preceding paper.[4]

On the other hand, the attempted solution photopolymerization of DSP has been reported in the earlier paper not to produce the polymer.[5] In the present work, it was found that the oligomer of DSP and other related diolefinic compounds were obtained by the irradiation of the light with a wavelength that excites monomer molecule exclusively.

Contrary to the exclusive monomer excitation, all the oligomers obtained were found to be photodepolymerized to the monomer in the solution when terminal groups of these oligomers were excited. In addition, a photooxidative degreadation which is not observed in the solution has been investigated preliminarily on amorphous film of poly-DSP.

In the present paper, the photooligomerization of DSP and related compounds and their photodepolymerization will be described. The results for these diolefinic monomers will be discussed in comparison with the reaction in the crystalline state and with reactivity of the corresponding monoolefines.

Experimental

Preparation of Monomers. DSP,P2VB, and three other monomers, 1,4-bis[β-pyridyl-(3)-vinyl] benzene (P3VB), 1,4-bis[β-pyridyl-(4)-vinyl]benzene(P4VB), and 1,4-distyrylbenzene(DSB), were prepared as has been described in an earlier paper.[3]

Preparation of Oligo-DSP in the Solution. DSP was dissolved in tetrahydrofuran(THF) which had been distilled over calcium hydride. The solution (1.41×10^{-2} mol/l, 50 ml) was irradiated with filtered light of a wavelength longer than 380 mμ for 48 hr at room temperature. The filtered light was produced by using a cut-off filter(Corning. 3—75) on a 500-W xenon lamp. After irradiation, the solvent was removed *in vacuo*; a pale yellow oil was thus obtained. A few milliliters of ethyl alcohol were added to the oil, the mixture was stirred overnight, and the precipitated powder was filtered off, and then dried *in vacuo*. The oligomer structure of the product with cyclobutane and a terminal olefinic double bond was confirmed by NMR and IR spectroscopies. The average molecular weight was about 900 (as determined by vapor-pressure osmometry). The final yield of oligo-DSP was 0.12 g (60%).

Preparation of Other Oligomers in the Solution. The oligomerization of other monomers was carried out in a similar way. However, a 0—51 filter was used in place of the 3—75 filter for the oligomerization of DSP in order to filter out the light shorter than 360 mμ. A mixture of petroleum ether and ethyl ether was used as a precipitant for the oily products. The final yield, the irradiation conditions, and the average molecular weight of the oligomers are summarized in Table 1.

The Attempted Dimerization of Stilbene and 2-Styrylpyridine in the Solution. Stilbene was dissolved in THF which had been distilled over calcium hydride. The solution (2.22×10^{-2} mol/l, 50 ml) was irradiated with filtered light of wavelengths longer than 300 mμ for 48 hr at room temperature. The filtered light was produced by using a cut-off filter(0—54) on a 500-W xenon lamp. After irradiation, the solvent was removed *in vacuo*; an oily product was thus obtained. The oil was dissolved in 0.8 ml of deuterochloroform and then submitted to NMR spectroscopy. Aromatic and vinyl-(*trans*- and *cis*-types) protons and the remaining THF were found in the NMR spectrum. The dimerization of 2-styrylpyridine was attempted under the same reaction conditions as were used in the stilibene. Only a *cis*-*trans* isomerization reaction was observed by NMR spectroscopy.

Photodepolymerization of the Oligomers. The oligomer

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was dissolved in chloroform or THF at a suitable concentration for UV measurement. The solution was then irradiated with the monochromatic light from a spectroirradiator(Jasco) equipped with a 2000-W xenon lamp as the light source and a gration monochromater. The reaction was followed by UV spectrometry.

Photodecomposition of Poly-DSP in the Solution and in Amorphous Film. Since crystalline poly-DSP is insoluble in the usual organic solvent, trifluoroacetic acid was used as the solvent of poly-DSP. The trifluoroacetic acid solution of poly-DSP (0.5 mg/40 ml) was irradiated with the light of 300 mμ from the spectroirradiator and the reaction was followed by UV spectrometry.

An amorphous poly-DSP film was made by casting on the glass plate from the trifluoroacetic acid solution. After the solvent had been removed *in vacuo*, the film was washed with triethylamine and then with ethyl alcohol. The poly-DSP film in the glass tube was degassed by means of a vacuum line and replaced by helium gas. After this procedure had been repeated three times, the tube was sealed. The tube was then exposed to sunlight through window glass for 80 days. The film sample thus exposed to the sunlight was subsequently compared with a sample which had been exposed to the sunlight in the air by means of IR spectroscopy. The sample stored in the dark in the air was prepared in a wrapped tube with aluminum foil. After 80 days, the contents were checked by studying the IR spectrum.

Results and Discussion

Solution Photooligomerization of DSP and Related Compounds. Figure 1 shows the UV spectral change in DSP when 0.5 ml of DSP in THF(6.09×10^{-3} mol/l) was irradiated by monochromatic light of 395 mμ. The absorption maximum of DSP at 385 mμ decreased gradually with the irradiation, and finally the absorption spectrum was changed to the f spectrum. This spectrum coincides with that of the oligo-DSP obtained by the photooligomerization of DSP in the crystalline state[4] when the remaining monomer of 19%, which was estimated from the absorption ratio of a and f 385 mμ, is subtracted from the f spectrum; then the concentration of the resulting spectrum was adjusted to the concentration at the spectral measurement of oligo-DSP(g) from the crystalline-state photoreaction. The NMR spectrum of the oligomer through solution photoreaction is shown in Fig. 2. A broad peak at 4.9 ppm due to the aryl cyclobutane[6] and a peak at 7.2—7.9 ppm of aromatic hydrogen-overlapping olefinic hydrogen may be seen in Fig. 2. Furthermore, terminal double bond in the oligomer chain was observed at both 970 and 1630 cm^{-1} in the IR absorption spectrum. From these spectral results, it was concluded that DSP was oligomerized in the solution by means of irradiation with the selected wavelength.

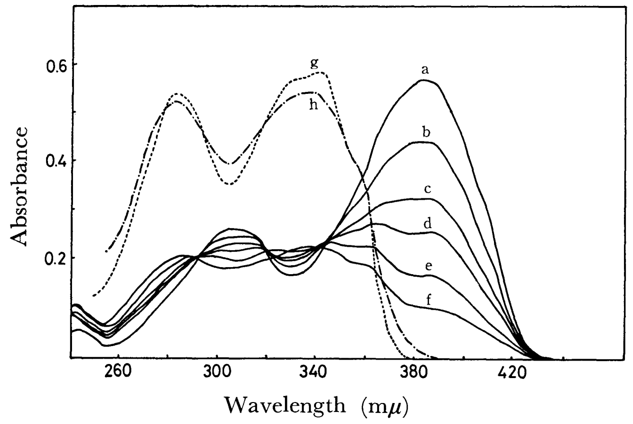


Fig. 1. UV spectral change during the oligomerization of DSP in THF by the irradiation with the light of 395 mμ. a: spectrum of DSP, b—f: after irradiation for 5, 10, 30, 45 and 60 min, respectively, g: oligo-DSP obtained from the crystalline photooligomerization in THF (1.07×10^{-2} g/l), h: spectrum of oligo-DSP estimated from f.

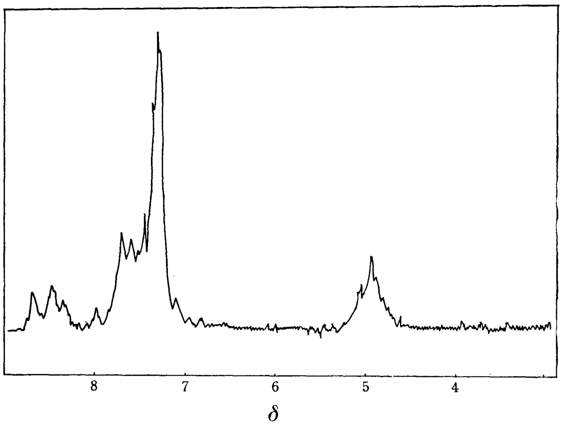


Fig. 2. NMR spectrum of oligo-DSP obtained from solution photooligmerization.

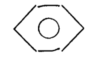
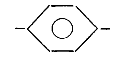
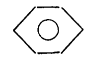
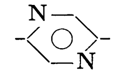
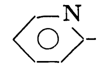
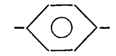
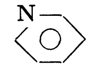
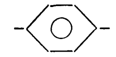
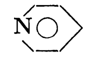
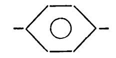
Oligo-DSP was obtained in a 60—80% yield in preparative scale and showed the average molecular weight of 600—900, corresponding to that of the dimer or trimer as is shown in Table 1.

The successful oligomerization of DSP can be explained in terms of two side reaction, the photoreaction of olefinic compound with the solvent[7] and the photocleavage of the resulting cyclobutane in the oligo-DSP, as will be discussed in a later section, being suppressed by interrupting the light shorter than 380 mμ. Another side reaction, the formation of phenanthrene- or azaphenanthrene-type derivatives as photoproducts, can be assumed because of their *cis*-form.[8,9] However, in the present work, such photoproducts were not detected in the oligomerization reaction of any diolefinic compound.

The wavelength of the light for the oligomerization reaction of DSP was chosen from the UV-absorption-spectrum difference between DSP and oligo-DSP. Since the longer-absorption end of oligo-DSP is 380 mμ in the THF solution, an irradiation wavelength longer than 380 mμ excites only DSP, not the terminal olefinic group of the oligomer.

The oligomerization technique of DSP was also extended to other diolefines, P2VB, P3VB, P4VB, and DSB. An irradiation wavelength longer than 360 mμ was decided on for the same reason as in the case of DSP. As a result, all the diolefines examined here gave the same type of oligomers as oligo-DSP, which has a structure with a cyclobutane ring in the main chain. The experimental conditions, the oligomer yield, and their average molecular weights are shown in Table 1.

Table 1. Solution photooligomerization of DSP and its related compounds

Monomers Ar	 Ar′		Irradiated wavelength (mμ)	Reaction time (hr)	Concentration of the monomers in THF (mol/l)	Yield of the oligomer (%)	Molecular weight
		DSB	≥360	48	1.42×10^{-2}	100	634
		DSP	≥380	48	1.40×10^{-2}	60	900
		P2VB	≥360	48	1.40×10^{-2}	29	814
		P3VB	≥360	48	1.40×10^{-2}	94	1074
		P4VB	≥360	48	1.40×10^{-2}	74	682

The degree of polymerization of the obtained oligomers ranges from 2 to 4, and the yields are relatively high except for the case of oligo-P2VB.

It should be noticed that all the diolefinic compounds attempted were converted to the oligomers, while among this type of compounds only DSP and P2VB are photooligomerized or photopolymerized in the crystalline state. These results indicate that the cycloaddition reaction ability on this type of diolefinic compound does not depend on its chemical structure.

A study of the wavelength dependency on the photochemical behavior in solution was carried out for the corresponding to monoolefines, stilbene, and 2-strylpyridine for the sake of comparison. However, neither of these two compounds dimerized under experimental condition similar to those of the oligomerization; exclusive excitation of the monoolefines in the highly-concentrated solution suppressed the photocleavage of resulted cyclobutane and isomerization reaction. It can be assumed from the results that, in a solution, the ability of cyclobutane formation of the monoolefines is lower than that of the corresponding diolefines, although the formation of a small amount of a photodimer has been reported in the case of stilbene in benzene by means of long irradiation with an ultraviolet lamp.[6] Although such a difference in reactivity between mono- and di-olefines can not be explained at present, if a unimolecular side reaction, the *cis-trans* isomerization of monoolefines, is presumed to be more striking than that of diolefines, and if cyclobutane is presumed to be produced only from *trans*-olefines, the observed difference in reactivity may be understood.

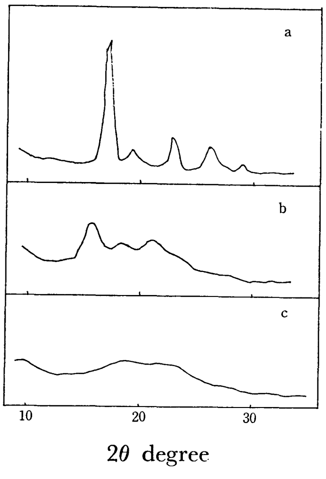
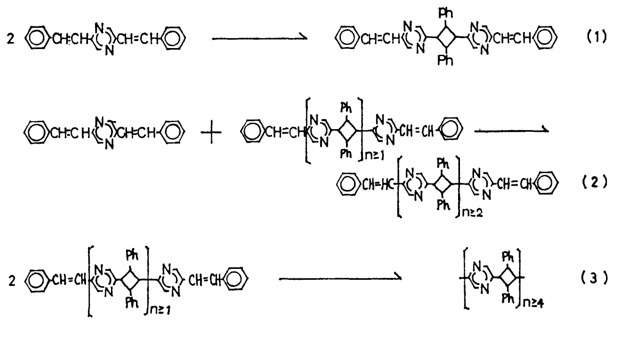


Fig. 3. X-ray diffraction diagrams of oligo-DSP. a: as-polymerized oligomer, b: recrystallized oligomer, c: amorphous oligomer.

One of the most striking features of the step-by-step solution photooligomerization in the present work originates in the monomer structure, in which two reactive double bonds are mutually conjugated through the 1,4-position of an aromatic ring. In such a structure of the monomers, the photocycloaddition step consists of three kinds of addition, as is represented in the case of DSP below:



Under the reaction conditions where only the monomer is excited, only Steps(I) and (2) proceed in the solution. Furthermore, these two elementary processes do not proceed after the monomer has been exhausted. The average molecular weight of the oligomers should be determined by the reaction velocity ratio of the two elementary processes, Steps(I) and (2). The actual ratio does not take any extreme values(infinitude or zero), since more of the oligomer mixture than dimer is obtained in the preparative experiment. These are the reasons why all the monomers here can not grow into high polymers in a solution, whereas, for example, bismaleimide derivatives are polymerized by photocycloaddition into high polymers through a step-by-step photoreaction.[10]

Configuration of Oligomers. The oligomers obtained through the solution photooligomerization are distingunished from the oligomers of DSP and P2VB through crystalline-state photooligomerization, which established the following two points. First, the oligomer from the solution is shown to be amorphous by x-ray analysis, as is shown in Fig. 3, while the oligomer obtained through crystalline-state oligomerization shows a high crystallinity. Second, the amorphous oligomers of DSP and P2VB in the solid state do not grow into high polymers on irradiation with the light of 340 mμ, which excites the terminal group of the oligomer.

The first difference suggests that the oligomers obtained through solution photooligomerization consist of mixed structures of cyclobutane units in the oligomers, while the as-polymerized oligomers of DSP are known from the results of x-ray crystal analysis to consist of a single steric configuration of 1,3-*trans*-type cyclobutane.[11,12] However, by NMR analysis, we could not observe the definite differences between these two types of oligomers because of poor spectrum resolution. The second difference in photoreactivity between amorphous and as-polymerized crystalline oligomers suggests that, in the case of the crystalline oligomer, residual terminal olefinic groups face each other in the crystal intermolecularly, but this is not the case with amorphous oligomers of DSP and P2VB.

Photodepolymerization of the Oligomers. In order to study further the photochemical behavior of the oligomers in a solution, a chloroform solution(1 mg/40 ml) of oligomer of DSP, which had been prepared by solution photooligomerization, was irradiated with the monochromatic light of 340 mμ and the reaction was monitored by UV spectroscopy, as is shown in Fig. 4. The peak which appeared at 385 mμ was identified with that of DSP by comparison with the UV spectrum (e in Fig. 4) in chloroform. When oligo-DSP in a chloroform solution (4.85×10^{-3} mol/l) is irradiated with a light longer than 340 mμ, the molecular weight of the oligomer is depressed from the 954 of the original to 475 after irradiation. Accordingly, in the solution unimolecular photodepolymerization reaction is considered to overcome a bimolecular-chain growth reaction(Step (3)), if any. Another type of oligo-DSP obtained through crystalline-state photooligomerization has been confirmed to be photodepolymerized in the solution in the same manner.

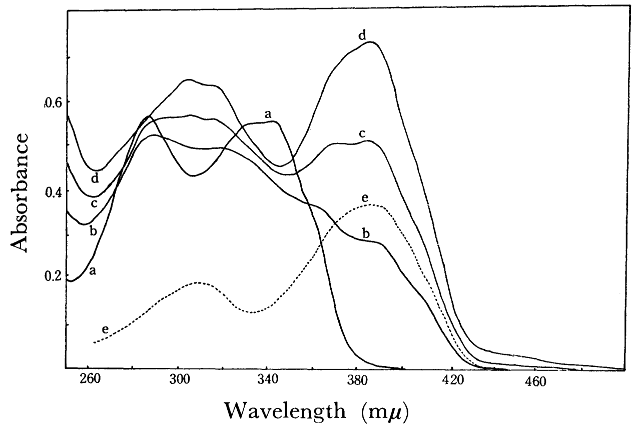


Fig. 4. UV spectral change during the photodepolymerization of oligo-DSP in chloroform by the irradiation with the light of 340 mμ. a: oligo-DSP, b—d: after irradiation for 15, 30 and 60 min, respectively, e: DSP (0.7×10^{-5} mol/l).

Other oligomers, oligo-DSB, -P2VB, -P3VB, and -P4VB, were also found to be photodepolymerized with oligo-DSP in a similar way, as is represented by oligo-DSB in Fig. 5. From these results, it may be concluded that these oligomers are photodepolymerized to the monomers when the terminal groups are excited in the solution. In consequence, a photoreverse scheme has been found between diolefinic monomers and the oligomers, depending on the different excitation wavelength. Such a photodepolymerization reaction results in the irradiation-wavelength effect of the solution oligomerization of these monomers.

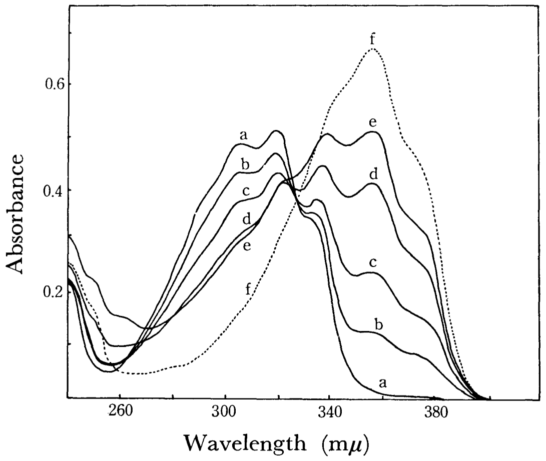


Fig. 5. UV spectral change during the photodepolymerization of oligo-DSB in THF by the irradiation with the light of 277 mμ. a: oligo-DSB, b—e: after irradiation for 1, 3, 12 and 40 min, respectively, f: DSB (1.2×10^{-5} mol/l).

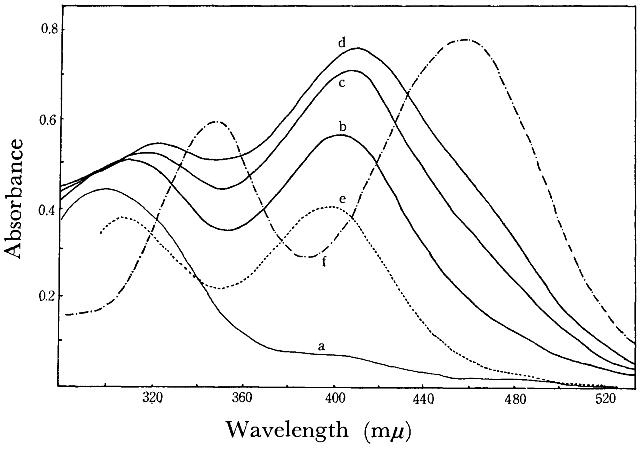


Fig. 6. UV spectral change during the photodepolymerization of poly-DSP in trifluoroacetic acid by the irradiation with the light of 300 mμ. a: poly-DSP, b—d: after irradiation for 20, 120 and 200 sec, respectively, e: oligo-DSP, f: DSP.

Photodegradation of Poly-DSP. In a previous paper, it has been reported that poly-DSP is thermally depolymerized to the monomer in a high yield.[1] In the course of the photochemical study of cyclobutane derivatives, the photodepolymerization of poly-DSP was also examined. Fig. 6 shows the UV spectral change when the trifluoroacetic acid solution of poly-DSP was irradiated with the light of 300 mμ. In comparision with the spectra of DSP and oligo-DSP in the same solvent, the spectrum obtained was confirmed to be a mixture of the monomer and the oligomer of DSP. From these results, it may be concluded that the photodepolymerization of poly-DSP proceeds at random in the polymer chain under the present experimental conditions.

The photochemical behavior of poly-DSP was also examined in amorphous film. The poly-DSP film did not show any change in IR spectroscopically when the film was stored for eighty days in helium gas in the dark. On the other hand, hydroxy and carbonyl groups appeared vigorously in the IR spectrum when poly-DSP film was stored in the air under the sunlight, as is shown in Fig. 7. Moreover, the photoirradiation of the film by sunlight in helium resulted in little change in the IR spectrum. Although no photoproducts have been isolated from the degrated film, it is obvious that amorphous film of poly-DSP is photooxidized, while the poly-DSP in the solution is mostly photodepolymerized to the monomer. Such an extreme difference in the reactivities between amorphous and solution states of the same polymer is unique in polymeric materials.

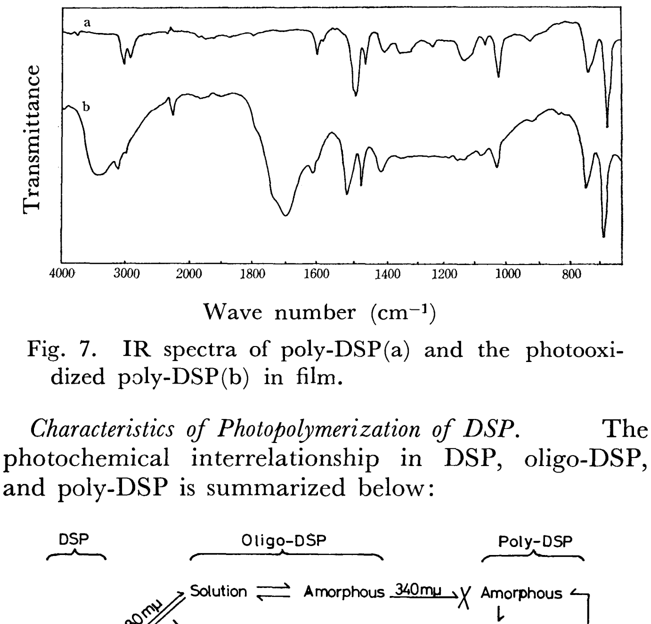
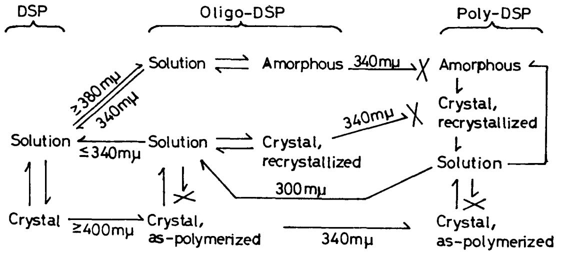


Fig. 7. IR spectra of poly-DSP(a) and the photooxidized poly-DSP(b) in film.

Characteristics of Photopolymerization of DSP. The photochemical interrelationship in DSP, oligo-DSP, and poly-DSP is summarized below:



This experiment demonstrates that the DSP molecule in the crystal reacts only with a intermolecularly-facing double bond under the steric control of the crystalline lattice (a topochemical process) to give a thermodynamically metastable polymer (as-polymerized crystalline polymer). As a matter of course, such a metastable polymer crystal can never be reproduced after it has been dissolved, but the thermodynamically-stable polymer crystal with a different form (a recrystallized crystalline polymer) is obtained from a polymer solution.[13]

According to the same explanation, oligo-DSP does not grow further into a high polymer without such topotactic assistance (crystal lattice control) as is presented in the case of the as-polymerized crystalline oligo-DSP. Therefore, the oligo-DSP retains two different reaction paths which are entirely the reverse of each other, cyclobutane formation in the crystalline state and its cleavage in the solution, under the same irradiation light. In other words, the direction of the reaction depends principally on its physical reaction states(matrix effect). Such a matrix effect is also revealed on amorphous and recrystallized oligo-DSP. That is, neither of the oligomers grows into a polymer in the solid state, while both are photodepolymerized to the monomer in a solution. It is interesting that chemically the same substance, the oligomer, behaves in three extremely different ways, photopolymerization, no photoreaction, and photodepolymerization, according to the physical state (in the as-polymerized, amorphous or recrystallized, and solution states). Such a multiplicity of reactivity is clear-cut example of a matrix effect originating in a topochemical process and has been demonstrated for the first time in the organic field.

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