Macromolecules 1988, 21, 918-923

$$\sum_{m=0}^{\infty}\left\{\left[\left(\frac{\alpha}{a}\right)^2+\frac{K_2}{D_2}+\omega_m^2\right]b_m^{(2)}(\alpha)-\frac{K_1}{D_2}b_m^{(1)}(\alpha)\right\}\cos\omega_m z=0 \qquad \text{(A20)}$$

Since the cos $\omega_m z$ is an orthogonal function, eq A20 can only be satisfied when the coefficient in brackets is identically zero. This leads to the relation

$$b_m^{(2)}(\alpha)=\frac{\dfrac{K_1}{D_2}b_m^{(1)}(\alpha)}{\left[\left(\dfrac{\alpha}{a}\right)^2+\dfrac{K_2}{D_2}+\omega_m^2\right]}$$

$$=\frac{\dfrac{K_1}{D_2}\left[\dfrac{(-1)^m 4I}{D_1 L\alpha J_1(\alpha)}\right]}{\omega_m\left[\left(\dfrac{\alpha}{a}\right)^2+\dfrac{K_1}{D_1}+\omega_m^2\right]\left[\left(\dfrac{\alpha}{a}\right)^2+\dfrac{K_2}{D_2}+\omega_m^2\right]} \qquad \text{(A21)}$$

where we have used eq A18.

The equation for $P_3(z,r)$ in eq 3 is of exactly the same form as that for $P_2(z,r)$, except that P_3 replaces P_2 while P_2 replaces P_1. The steps leading to the first equation in eq A21 can therefore be repeated with the result

$$b_m^{(3)}(\alpha)=\frac{\dfrac{K_2}{D_3}b_m^{(2)}(\alpha)}{\left[\left(\dfrac{\alpha}{a}\right)^2+\dfrac{K_3}{D_3}+\omega_m^2\right]} \qquad \text{(A22)}$$

and eq A21 may be substituted into this result. Continuing in this manner out to the equation for $P_j(z,r)$, we arrive at

$$b_m^{(j)}(\alpha)=\left[\frac{(-1)^m 4I}{D_1 L\alpha J_1(\alpha)}\right]\left[\frac{\prod_{i=1}^{j-1}(K_i/D_{i+1})}{\omega_m\prod_{i=1}^{j}\left[\left(\dfrac{\alpha}{a}\right)^2+\dfrac{K_j}{D_i}+\omega_m^2\right]}\right] \qquad \text{(A23)}$$

Substitution of this result back into eq A1 gives $P_j(z,r)$ in eq 7 in the body of the text. Thus the problem of the distribution is solved. It is evident that the series in eq 7 is rapidly convergent, because both α and ω_m increase rapidly, in sequence, and the squares of these quantities appear in the denominators of the terms in the series. Furthermore, as j increases the convergence is even more rapid since j square bracket factors appear in the denominators.

Registry No. $C_6H_5CH{=}CH_2$, 100-42-5.

References and Notes

(1) El Shall, M. S.; Bahta, A.; Rabeony, H.; Reiss, H. *J. Chem. Phys.* **1987**, *87*, 1329.

(2) Private communication to the authors from Professor John Schmitt, University of Missouri at Rolla. Professor Schmitt has been conducting measurements on the steady-state distribution of polymeric radicals in styrene vapor, using the high-precision expansion cloud chamber developed at Rolla. Preliminary results (as with the experiments of ref 1) provide definitive evidence of the self-initiated polymerization of styrene in the gas phase. The results also indicate that a time on the order of 10 min is required to set up the steady-state distribution, after the larger polymers are removed by adiabatic expansion and nucleation. Preliminary data, kindly supplied to the authors by Professor Schmitt, when substituted into the formulas of the present paper, suggest that the thermal rate of generation of initiating free radicals is of the order of 1.0 $cm^{-3}\ s^{-1}$.

(3) Unpublished experimental studies, in progress at UCLA, due to M. S. El Shall and the authors.

(4) Reiss, H.; Rabeony, H. M.; El Shall, M. S.; Bahta, A. *J. Chem. Phys.* **1987**, *87*, 1315.

(5) Arfken, G. *Mathematical Methods for Physicists*; Academic: New York, 1968; Chapter 11.

(6) Reference 5, p 511.

Photoresponsive Vinyl Polymer Bearing Norbornadiene as a Pendant Group

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ABSTRACT: The synthesis of a novel class of photoresponsive polymers is reported. The norbornadiene unit in the polymer was found to be converted in the film state under nitrogen atmosphere to a quadricyclane unit reversibly with irradiation by UV light of two different wavelengths. Polymers bearing norbornadiene units having carboxylate and/or substituted amide groups at the 2- and 3-positions and having a vinyl group at the end of the 2-substituent were prepared by the polymerization of respective monomers. Polymers bearing an amide substituent at the 2-position indicated a much higher photosensitivity in the film state as well as a larger red shift in the absorption spectrum than those bearing a carboxylate substituent.

Introduction

In a previous study,[1] we reported the first synthesis together with photosensitivity of a vinyl polymer bearing a norbornadiene unit as a pendant group.

In the present study, the carboxylate and/or carboxamide groups bearing a vinyl double bond have been substituted at the 2,3-positions of norbornadiene, and the photosensitivity of the films made of the polymerization products of the resulting vinyl monomers was investigated.

The synthesized monomers were shown in Chart I. Monomers **1a–j** were polymerized to afford respective polymers which gave transparent films from solutions. The polymers thus prepared were irradiated either in solution or in film with UV light under nitrogen atmosphere and

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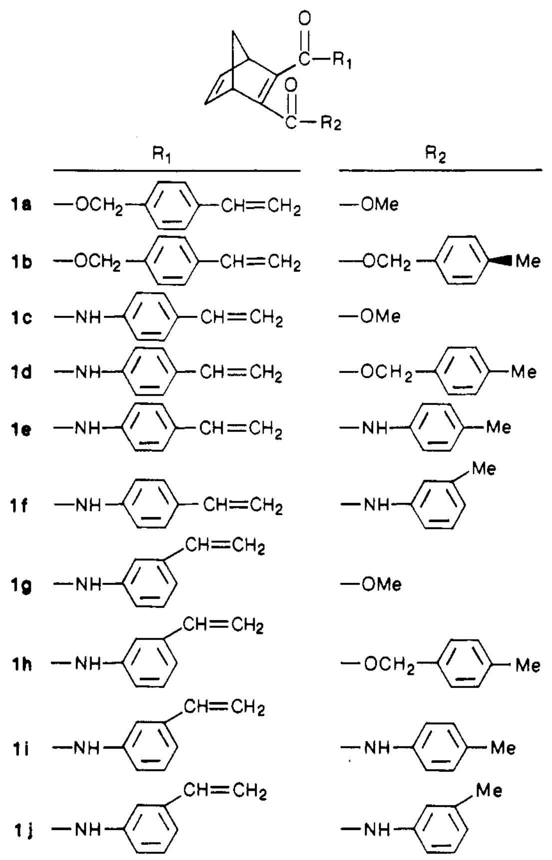
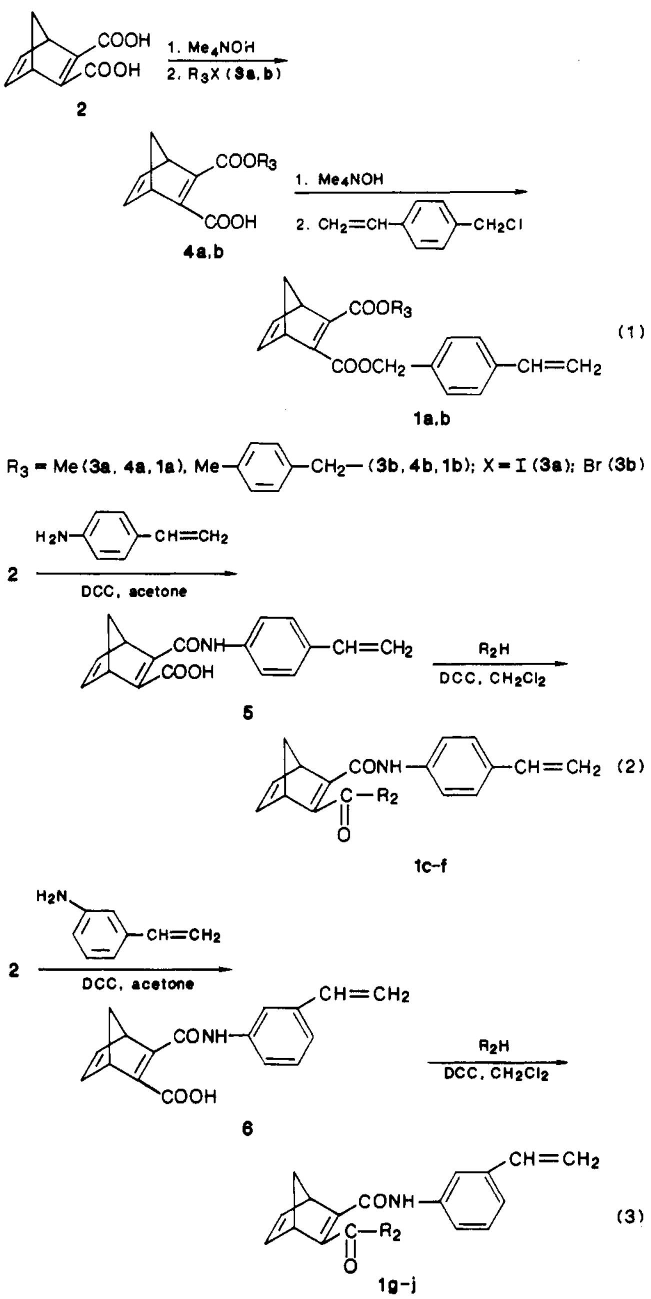
Chart I



Scheme I



the resulting changes in absorption spectra were investigated.

Results and Discussion

The monomer synthesis was carried out in two steps without isolating the intermediate products according to Scheme I. R_2's have the same meaning as those in monomer 1. In sequence 1, 2,3-norbornadienedicarboxylic acid (2), synthesized from cyclopentadiene and acetylenedicarboxylic acid[2] and neutralized with Me_4NOH, was treated with alkyl halide (R_3X) in DMF to afford the monoester,[4a,b] which was further neutralized with Me_4NOH and treated with *p*-vinylbenzyl chloride to provide the product[1a,b] in 33–34% yields.

In sequence 2, **2** and *p*-vinylaniline, synthesized by the alkaline dehydration of p-(2-hydroxyethyl)aniline,[3] were stirred in acetone in the presence of *N,N'*-dicyclohexylcarbodiimide (DCC) to yield the monoamide **5**, which was again stirred with DCC and R_2H in CH_2Cl_2 to give **1c–f** in 21–64% yields.

The reaction of sequence 3 was essentially the same as that of (2) except for the use of *m*-vinylaniline, synthesized from *m*-aminoacetophenone via *m*-(1-hydroxyethyl)aniline, the reduction product with $NaBH_4$,[4] instead of *p*-vinylaniline. Yields of 21–76% were obtained. Purifications of the monomers **1a–j** thus synthesized were carried out by silica gel column chromatography. All monomers thus purified indicated a single spot by TLC. Analytical data were also satisfactory.

Monomers **1a–j** were polymerized in THF at 50 °C for 72 h by using α,α'-azobis(isobutyronitrile) (AIBN) as initiator. Table I indicates the obtained results. Gel formation took place when the monomer concentration was high, presumably due to the participation of the 5,6-double bond of the norbornadiene unit in the polymerization of the vinyl double bond. However, at the concentration in Table I no gel formation was observed. Although conversions were moderate and the values of $[\eta]$ were low, transparent films 0.01 mm in thickness were obtained when the solution of each polymer in THF (CH_2Cl_2 for polymers **1a,b**) was spread over a quartz plate and the solvent was evaporated. This fact may indicate that at a

Table I
Polymerization Behavior of Monomers 1a–j[a]

monomer	conv, %	polymer $[\eta]$,[b] dL/g	appearance
1a	52	0.02	white solid
1b	38	0.01	white solid
1c	54	0.04	slight yellow solid
1d	47	0.04	slight yellow solid
1e	51	0.06	slight yellow solid
1f	48	0.05	slight yellow solid
1g	48	0.04	slight yellow solid
1h	29	0.03	slight yellow solid
1i	69	0.04	slight yellow solid
1j	66	0.04	slight yellow solid

[a] Monomer, 0.4 g; AIBN, 0.02 g; THF, 2 mL; 50 °C, 72 h. [b] Intrinsic viscosity in THF at 25 °C.

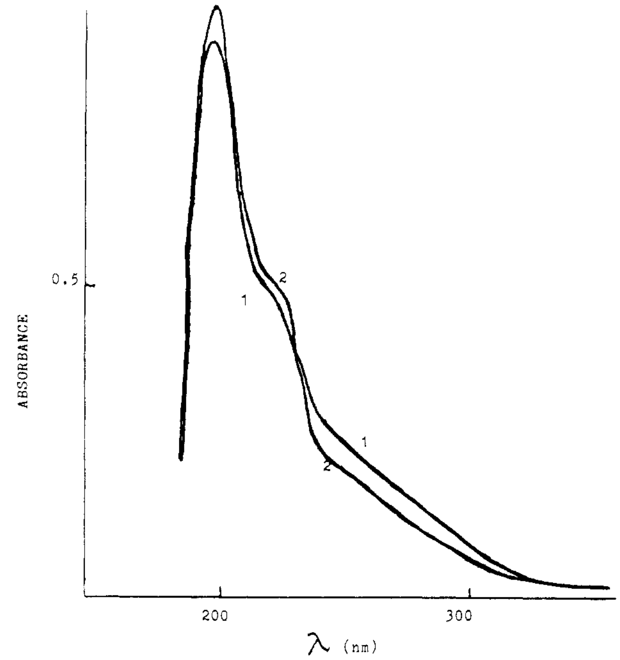


Figure 1. Change of absorbance for the film of **1a** with irradiation. Irradiation was carried out at the distance of 10 cm from a 75-W high-pressure mercury lamp under nitrogen atmosphere and the light below 310 nm was cut off with a filter: curve 1, before irradiation; curve 2, after 5-h irradiation. Film thickness, 0.01 mm.

comparatively low monomer concentration the vinyl double bond almost exclusively polymerized to afford vinyl polymers with pendant norbornadiene units. Two double bonds of the norbornadiene unit may hardly participate in the vinyl polymerization due to poor polymerizability for steric and electronic reasons. The bulky character of monomers as well as the chain-transfer reaction to the norbornadiene double bonds may explain the moderate conversions and low [η] values in Table I. The IR spectrum of each polymer indicated the absorptions attributable to the vinyl polymer backbone (CH_2, CH) at 2680 and 2940 cm^{-1} with loss of vinyl absorptions (990, 900 cm^{-1}). Characteristic absorptions of ester and/or amide remained; two norbornadiene double bonds were hardly identifiable due to very weak absorptions as well as their overlappings with other peaks.

Figure 1 indicates the UV absorption spectrum of a film made of a polymer of **1a** under nitrogen atmosphere, together with its change with irradiation by light above 310 nm, obtained by placing a filter in front of a high-pressure mercury lamp. Five hours of irradiation were necessary to obtain an appreciable change. Polymers involving at least one amide group, such as polymers **1c–j**, on the other hand, show a remarkable red shift of the absorption spectra as compared with polymers **1a,b** and much higher photosensitivity was obtained in both solution and film, as shown in Figures 2 and 3. Thus, the broad absorption at 320–350 nm almost disappeared with 20–50-min irradiation and new absorption peaks appeared at 250–260 nm. Moreover, an isosbestic point can be seen at around 280 nm, indicating that the change of the norbornadiene to the quadricyclane unit occurred with irradiation by light above 310 nm. No appreciable change of IR was recognized before and after irradiation under nitrogen atmosphere, since the norbornadiene double bonds were hardly identifiable, as mentioned above. The nitrogen atmosphere for both solution and film was necessary to obtain reproducible results. In the prescence of air (oxygen), spectral changes with irradiation were different from those under

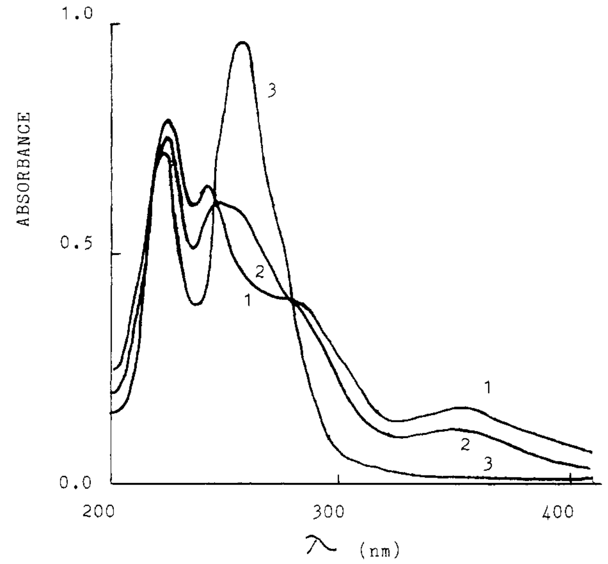


Figure 2. Change of absorbance for polymer of **1d** in THF solution under nitrogen: curve 1, before irradiation; curve 2, after 10-min irradiation; curve 3, after 50-min irradiation. Concentration, 3.0 × 10^{-5} mol dm^{-3}.

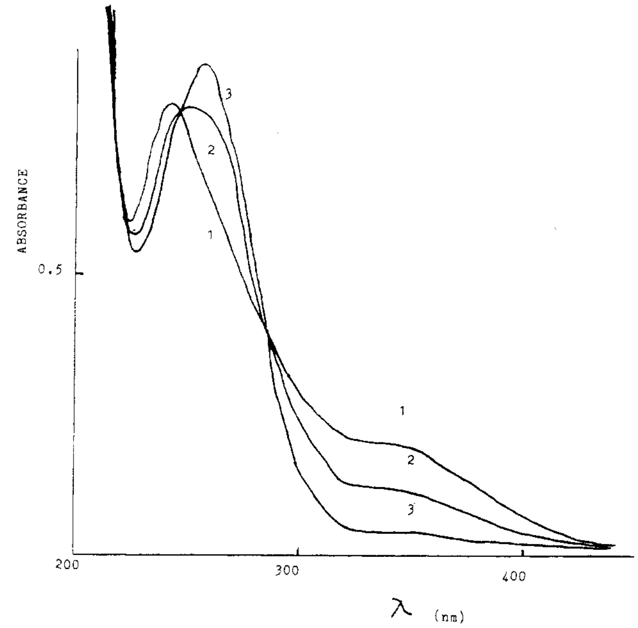


Figure 3. Change of absorbance for the polymer film of **1c** with irradiation under nitrogen: curve 1, before irradiation; curve 2, after 4-min irradiation; curve 3, after 20-min irradiation. Film thickness, 0.01 mm.

nitrogen and reversibility was destroyed, due to the destruction of the carboxylate and/or carboxamide groups as judged from the changes in IR.

Table II summarizes the rates of decrease of absorbances on the longer wavelength side of the isosbestic points, which remarkably depend upon R_1 and R_2. Thus, the rates of polymers of **1c,d,g,h** are greater than those for polymers of **1a,b,e,f,i,j**, indicating that polymers involving both amide and ester groups are converted more rapidly than those involving amide or ester group alone.

Moreover, it is interesting to note that, in the case of polymer films bearing amide groups, the absorption spectra, once changed with irradiation by light above 310 nm, recovered to the original state when the light of 250 nm was applied to the polymer films, as indicated in Figure 4 and Table III. This fact may indicate that the norbornadiene unit in polymer films is reversibly converted to the quadricyclane unit first with light above 310 nm and

Table II
Relative Change of Absorbance with Irradiation[a]

polym[b] of 1a–j	wavelength, nm	A/A_0[c] after irrad 5 min	10 min	state of[e] polym
1a	252	82.9	75.0	CH_2Cl_2 soln
	252	94.9[d]		film
1b	252	96.3	94.2	CH_2Cl_2 soln
	252	94.8*d*		film
1c	340	87.8	81.2	THF soln
	330	52.0	34.0	film
1d	340	84.2	74.5	THF soln
	330	63.5	49.8	film
1e	320	95.1	90.9	THF soln
	320	80.0	70.9	film
1f	320	91.8	85.4	THF soln
	320	80.3	68.3	film
1g	330	84.5	25.7	THF soln
	320	60.7	34.6	film
1h	330	78.3	29.2	THF soln
	330	65.0	42.6	film
1i	320	98.1	95.3	THF soln
	320	80.1	66.9	film
1j	320	95.7	94.1	THF soln
	320	78.0	61.4	film

[a] At the distance of 10 cm from a 75-W high-pressure mercury lamp, the light below 310 nm cut with a filter. [b] Polymer of Table I. [c] A_0, absorbance before irradiation; A, absorbance immediately after. [d] After 1-h irradiation. [e] Kept under nitrogen atmosphere. Concentration, 3.0×10^{-5} mol dm^{-3}; film thickness, 0.01 mm. Optical path length for solution, 1 cm.

Table III
Spectral Recovery of Polymer Film Irradiated by UV Light[a]

polym of 1a–j	wavelength, nm	absorbance[b] before 1st irrad, B	after irrad 1st, 1	2nd, 2	recovery, %, $2 - 1/B - 1$
1c	330	0.142	0.018	0.091	58.9
1d	330	0.400	0.086	0.234	47.1
1e	320	0.642	0.296	0.368	20.8
1f	320	0.404	0.164	0.204	44.2
1g	320	0.358	0.042	0.186	45.6
1h	320	0.152	0.032	0.117	70.1
1i	320	0.666	0.240	0.470	54.0
1j	320	0.259	0.080	0.209	72.1

[a] First irradiation, 3 h by the light above 310 nm; second irradiation, 40 min by the UV light of 250 nm, obtained through a grating monochrometer. [b] For film of 0.01 mm thickness.

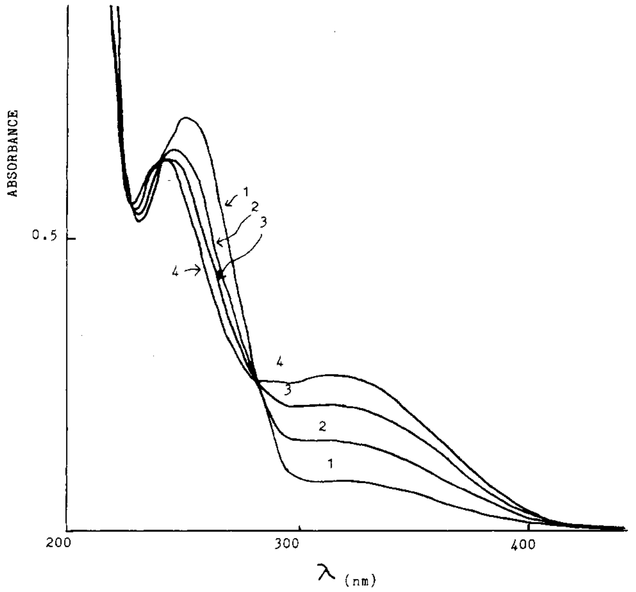
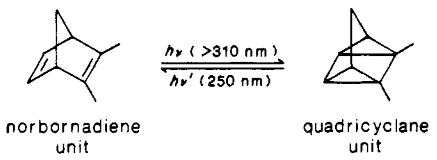


Figure 4. Change of absorbance for the polymer film of **1j** with first irradiation of the light above 310 nm and subsequent second irradiation of UV light of 250 nm under nitrogen: curve 1, 3-h first irradiation with light above 310 nm; curve 2, 10- min second irradiation with UV light of 250 nm for the film subjected to the first irradiation; curve 3, second irradiation time was prolonged to 40 min instead of 10 min in curve 2; curve 4, before first irradiation. Film thickness, 0.01 mm.

then with the light of 250 nm, as shown in the following scheme.



This scheme, particularly with the catalytic reverse reaction, is well known in low molecular weight compounds,[5] but in this case, the pendant portions of vinyl polymers are considered to follow this scheme, as in the previous study.[1] This reversible operation can be repeated at least several times.

As expected in [2 + 2] cycloaddition reactions, the two units are mutually interchangeable by changing the wavelength of irradiation. The reverse reaction, as is well-known,[1] also occurred when the irradiated (>310 nm) film was immersed in a solution of [*meso*-tetrakis(4-methyl-*N*-pyridyl)porphyrin]cobalt(II)-I_4 in H_2O-THF (5:1 v/v). However, this may be the first case that the reverse reaction took place without addition of photosensitizer.[6] In the case of polymers of **1c–j**, UV absorptions at 300–400 nm, when exposed to light above 310 nm, were replaced by those below 300 nm, which were susceptible to the light of 250 nm. On the other hand, in the cases of polymers of **1a,b** and polymers of the previous study,[1] the original UV absorptions were practically below 300 nm and not replaced by those susceptible to UV light of an appropriate wavelength.

It is recognized from Table III that the rate of the reverse reaction was affected by the chemical structure of the amine and/or alcohol moieties in this case too, although the light of 250 nm was obtained by passing the light from a 75-W high-pressure mercury lamp through a monochromator and was very weak in intensity. The rate is the highest for the polymer of **1j**, whereas it is the lowest for the polymer of **1e** even though it has the same amine moieties as those of polymer **1j**, except that the substituents are both located in the para position. This relationship is not necessarily consistent with that in Table II. The reason for this is unknown at present, although both electronic and steric factors might affect the rate of change in absorption spectrum.

Experimental Section

Infrared (IR), ^1H NMR, mass, and elemental analyses were conducted by using a Hitachi 215 spectrophotometer, a JNM-PMX60 spectrometer, a Hitachi M-80B spectrometer, and a Perkin-Elmer 240 instrument, respectively. Absorption spectra were measured on a Hitachi 200-10 spectrophotometer.

2-[[(*p*-Vinylbenzyl)oxy]carbonyl]-3-(methoxycarbonyl)-norbornadiene (1a). A 10% tetramethylammonium hydroxide solution in methanol was added to 2,3-norbornadienedicarboxylic acid (**2**; 1.80 g, 10 mmol), synthesized from cyclopentadiene and 1,2-acetylenedicarboxylic acid,[2] so as to afford a solution of pH 7. After the removal of the solvent on a rotary evaporator, the residue was dissolved in DMF, followed by addition of CH_3I (**3a**; 1.56 g, 10 mmol) and 24 h of stirring at 20 °C. The reaction mixture was again made to pH 7 with a methanolic solution (10%) of Me_4NOH, solvent was removed on the rotary evaporator, and the residue was dissolved in DMF, followed by addition of *p*-vinylbenzyl chloride (Seibi Chemicals, Ltd.; 2.29 g, 15 mmol) and 48 h of stirring at 20 °C. The reaction mixture was poured into ice water. Ether extraction was done and the extract was washed several times with water, dried over anhydrous Na_2SO_4, concentrated on the rotary evaporator, and purified by column (SiO_2) chromatography to afford a fluid in 34% yield. TLC provided single spot. Anal. Calcd for $C_{19}H_{18}O_4$: C, 73.55; H, 5.81. Found: C, 73.26; H, 5.81. IR ($CHCl_3$) 1710, 1630, 990, 910 cm^{-1}; NMR ($CDCl_3$) δ 1.9–2.3 (m, 2 H, CH_3), 3.6 (s, 3 H, OCH_3), 3.9 (m, 2 H, CH), 5.2 (s, 2 H, OCH_2), 5.3 (d, 1 H, CH_2=), 5.7 (d, 1 H, CH_2=), 6.7 (q, 1 H, CH=), 6.9 (m, CH=CH), 7.4 (s, 4 H, Ar H); mass spectrum, *m/e* 311 (M^+).

2-[[(*p*-Vinylbenzyl)oxy]carbonyl]-3-[[(*p*-methylbenzyl)oxy]carbonyl]norbornadiene (1b). Essentially the same procedure as that for **1a** was applied to *p*-methylbenzyl bromide (**3b**; 2.04 g, 11 mmol) instead of **3a** to afford a viscous fluid in 33% yield. Single spot by TLC. Anal. Calcd for $C_{26}H_{24}O_4$: C, 77.98; H, 6.04. Found: C, 77.90; H, 6.03. IR ($CHCl_3$) 1710, 1620, 990, 910 cm^{-1}; NMR ($CDCl_3$) δ 1.9–2.3 (m, 2 H, CH_2), 2.3 (s, 3 H, OCH_3), 3.9 (m, 2 H, CH), 5.1 (s, 4 H, OCH_2), 5.2 (d, 1 H, CH_2=), 5.7 (d, 1 H, CH_2=), 6.7 (q, 1 H, CH=), 6.9 (m, 2 H, CH=CH), 7.2 (s, 4 H, Ar H), 7.3 (m, 4 H, Ar H); mass spectrum, *m/e* 401 (M^+).

2-[(*p*-Vinylphenyl)carbamoyl]-3-(methoxycarbonyl)norbornadiene (1c). To a solution of **2** (0.90 g, 5.0 mmol) and *p*-vinylaniline (0.65 g, 5.5 mmol), prepared by the alkaline dehydration of *p*-(2-hydroxyethyl)aniline,[3] in dry acetone (17 mL) was added dropwise a solution of *N,N*-dicyclohexylcarbodiimide (DCC; 1.03 g, 5.0 mmol) in dry acetone (5 mL) with stirring, followed by stirring at 20 °C overnight. The reaction mixture was filtered and the filtrate was concentrated on a rotary evaporator and dissolved in a mixture of methanol (0.19 g, 6.0 mmol) and dichloromethane (30 mL). DCC (1.03 g) in dichloromethane (5 mL) was then added dropwise with stirring and stirring was continued at 20 °C overnight. The reaction mixture was filtered again and the filtrate was concentrated on the rotary evaporator. A few drops of acetic acid were added to the residue and the mixture was let stand for a while. The mixture was then poured into iced aqueous sodium hydroxide solution, followed by ether extraction. The extract was washed several times with water, dried over anhydrous Na_2SO_4, and concentrated on the evaporator. Purification by column chromatography afforded a viscous fluid in 42% yield. Single spot by TLC. Anal. Calcd for $C_{18}H_{17}NO_3$: C, 73.20; H, 5.80; N, 4.74. Found: C, 73.22 H, 5.87; N, 4.71. IR ($CHCl_3$) 3250, 1685, 1650, 990, 900 cm^{-1}; NMR ($CDCl_3$) δ 2.0–2.3 (m, 2 H, CH_2), 3.9 (s, 3 H, OCH_3), 4.2 (m, 1 H, CH), 4.5 (m, 1 H, CH), 5.2 (d, 1 H, CH_2=), 5.7 (d, 1 H, CH_2=), 6.7 (q, 1 H, CH=), 7.0 (m, 2 H, CH=CH), 7.3–7.9 (m, 4 H, Ar H); mass spectrum *m/e* 295 (M^+).

2-[(*p*-Vinylphenyl)carbamoyl]-3-[[(*p*-methylbenzyl)oxy]carbonyl]norbornadiene (1d). Essentially the same procedure as that for **1c** was employed except for the use of *p*-methylbenzyl alcohol (0.73 g, 6.0 mmol) instead of methanol to afford a viscous fluid in 21% yield. Single spot by TLC. Anal. Calcd for $C_{25}H_{23}NO_3$: C, 77.90; H, 6.01; N, 3.63. Found: C, 77.64; H, 6.01; N, 3.56. IR ($CHCl_3$) 3250, 1690, 1650, 990, 900 cm^{-1}; NMR ($CDCl_3$) δ 1.9–2.3 (m, 2 H, CH_2), 2.4 (s, 3 H, CH_3), 4.2 (m, 1 H, CH), 4.4 (m, 1 H, CH), 5.2 (d, 1 H, CH_2=), 5.3 (s, 2 H, OCH_2), 5.7 (d, 1 H, CH_2=), 6.7 (q, 1 H, CH=), 7.0 (m, 2 H, CH=CH), 7.3–7.8 (m, 8 H, Ar H); mass spectrum, *m/e* 385 (M^+).

2-[(*p*-Vinylphenyl)carbamoyl]-3-[(*p*-methylphenyl)carbamoyl]norbornadiene (1e). Essentially the same procedure as that for **1c** was followed except for the use of *p*-toluidine (0.64 g, 6.0 mmol) instead of methanol to afford a viscous fluid in 64% yield. Single spot by TLC. Anal. Calcd for $C_{24}H_{22}N_2O_2$: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.89; H, 5.94; N, 7.69. IR ($CHCl_3$) 3450, 1660, 990, 900 cm^{-1}; NMR ($CDCl_3$) δ 1.9–2.2 (m, 2 H, CH_2), 2.3 (s, 3 H, CH_3), 4.2 (m, 2 H, CH), 5.2 (d, 1 H, CH_2=), 5.7 (d, 1 H, CH_2=), 6.7 (q, 1 H, CH=), 7.0 (m, 2 H, CH=CH), 7.1–7.8 (m, 8 H, Ar H); mass spectrum, *m/e* 370 (M^+).

2-[(*p*-Vinylphenyl)carbamoyl]-3-[(*m*-methylphenyl)carbamoyl]norbornadiene (1f). Essentially the same procedure as that for **1c** was followed except for the use of *m*-toluidine (0.64 g, 6.0 mmol) instead of methanol to afford a viscous fluid in 64% yield. Single spot by TLC. Anal. Calcd for $C_{24}H_{22}N_2O_2$: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.73; H, 6.09; N, 7.54. IR ($CHCl_3$) 3430, 1650, 990, 900 cm^{-1}; NMR ($CDCl_3$) δ 1.69–2.3 (m, 2 H, CH_2), 2.4 (s, 3 H, CH_3), 4.2 (m, 2 H, CH), 5.2 (d, 1 H, CH_2=), 5.7 (d, 1 H, CH_2=), 6.7 (q, 1 H, CH=), 7.0 (m, 2 H, CH=CH), 7.1–7.8 (m, 8 H, Ar H); mass spectrum, *m/e* 370 (M^+).

2-[(*m*-Vinylphenyl)carbamoyl]-3-(methoxycarbonyl)norbornadiene (1g). Essentially the same procedure as that for **1c** was followed except for the use of *m*-vinylaniline (0.65 g, 5.5 mmol), synthesized starting with *m*-aminoacetophenone via its $NaBH_4$-reduction product, *m*-(1-hydroxyethyl)aniline,[4] instead of *p*-vinylaniline to afford a viscous fluid in 38% yield. Single spot by TLC. Anal. Calcd for $C_{18}H_{17}NO_3$: C, 73.20; H, 5.80; N, 4.74. Found: C, 73.04; H, 5.78; N, 4.93. IR ($CHCl_3$) 3260, 1680, 1645, 980, 900 cm^{-1}; NMR ($CDCl_3$) δ 1.9–2.3 (m, 2 H, CH_2), 3.9 (s, 3 H, OCH_3), 4.1 (m, 1 H, CH), 4.4 (m, 1 H, CH), 5.3 (d, 1 H, CH_2=), 5.8 (d, 1 H, CH_2=), 6.7 (q, 1 H, CH=), 7.0 (m, 2 H, CH=CH), 7.2–7.8 (m, 4 H, Ar H), 7.9 (s, 1 H, NH); mass spectrum, *m/e* 295 (M^+).

2-[(*m*-Vinylphenyl)carbamoyl]-3-[[(*p*-methylbenzyl)oxy]carbonyl]norbornadiene (1h). Essentially the same procedure as that for **1c** was followed except for the use of *m*-vinylaniline (065 g, 5.5 mmol) and *p*-methylbenzyl alcohol (0.73 g, 6.0 mmol) instead of *p*-vinylaniline and methanol, respectively, to afford a viscous fluid in 22% yield. Single spot by TLC. Anal. Calcd for $C_{25}H_{23}NO_3$: C, 77.90; H, 6.01; N, 3.63. Found: C, 77.88; H, 6.01; N, 3.74. IR ($CHCl_3$) 3250, 1680, 980, 900 cm^{-1}; NMR ($CDCl_3$) δ 1.9–2.3 (m, 2 H, CH_2), 2.4 (s, 3 H, CH_3), 4.1 (m, 1 H, CH), 4.4 (m, 1 H, CH), 5.3 (d, 1 H, CH_2=), 5.3 (s, 2 H, OCH_3), 5.8 (d, 1 H, CH_2=), 6.7 (q, 1 H, CH=), 7.0 (m, 2 H, CH=CH), 7.1–7.7 (m, 8 H, Ar H), 7.9 (s, 1 H, NH); mass spectrum, *m/e* 385 (M^+).

2-[(*m*-Vinylphenyl)carbamoyl]-3-[(*p*-methylphenyl)carbamoyl]norbornadiene (1i). Essentially the same procedure as that for **1c** was followed except for the use of *m*-vinylaniline (0.65 g, 5.5 mmol) and *p*-toluidine (0.64 g, 6.0 mmol) instead of *p*-vinylaniline and methanol, respectively, to afford a viscous fluid in 73% yield. Single spot by TLC. Anal. Calcd for $C_{24}H_{22}N_2O_2$: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.88; H, 5.98; N, 7.55. IR ($CHCl_3$) 3430, 3230, 1655, 980, 900 cm^{-1}; NMR ($CDCl_3$) δ 1.9–2.3 (m, 2 H, CH_2), 2.3 (s, 3 H, CH_3), 4.2 (m, 2 H, CH), 5.2 (d, 1 H, CH_2=), 5.7 (d, 1 H, CH_2=), 6.7 (q, 1 H, CH=), 7.0 (m, 2 H, CH=CH), 7.0–7.8 (m, 8 H, Ar H); mass spectrum, *m/e* 370 (M^+).

2-[(*m*-Vinylphenyl)carbamoyl]-3-[(*m*-methylphenyl)carbamoyl]norbornadiene (1j). Essentially the same procedure as that for **1c** was followed except for the use of *m*-vinylaniline (0.65 g, 5.5 mmol) and *m*-toluidine (0.64 g, 6.0 mmol) instead of *p*-vinylaniline and methanol, respectively, to afford a viscous fluid in 78% yield. Single spot by TLC. Anal. Calcd for $C_{24}H_{22}N_2O_2$: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.64; H, 6.03; N, 7.50. IR ($CHCl_3$) 3430, 3240, 1650, 980 cm^{-1}; NMR ($CDCl_3$) δ 1.9–2.3 (m, 2 H, CH_2), 2.3 (s, 3 H, CH_3), 4.2 (m, 2 H, CH), 5.2 (d, 1 H, CH_2=), 5.7 (d, 1 H, CH_2=), 6.7 (q, 1 H, CH=), 7.0 (m, 2 H, CH=CH), 7.1–7.8 (m, 8 H, Ar H); mass spectrum *m/e* 370 (M^+).

Polymerizations of Monomers 1a–j. In a typical example, a solution of monomer **1a** (0.4 g) and AIBN (0.02 g) in THF (2 mL) was put into a glass ampule, which was evacuated, filled with nitrogen, and sealed in a conventional manner. Polymerization was carried out at 50 °C for 72 h. The content of the ampule was then precipitated into ether, followed by drying. Table I summarizes the obtained results. Data of elemental analyses for the polymerization products were all satisfactory. IR spectra indicated the absorptions attributable to the vinyl polymer backbone at 2860 and 2940 cm^{-1}, together with characteristics absorptions of the pendant portions.

Measurements of Absorption Spectra. Polymers of 1a–j were dissolved in either dichloromethane or THF to afford solutions of known concentrations. Absorption spectra were taken as they were or for the films of 0.01 mm thickness, obtained by spreading the solutions over quartz plates and evaporating off the solvents, under nitrogen atmosphere.

Irradiation of Ultraviolet (UV) Light. Irradiation was carried out at the distance of 10 cm from a 75-W high-pressure mercury lamp (Toshiba SHL100UV-2) under nitrogen atmosphere. The light above the wavelength of 310 nm was obtained by setting a filter (Toshiba UV-31) in front of the lamp. The light of wavelength 250 nm was obtained by passing the light from the lamp through a grating monochrometer (Jasco GT-10S).

Tables II and III and Figures 1–4 summarize the results obtained by applying light to polymers either in solution (concentration, 3.0×10^{-5} mol dm^{-3}) or film (thickness, 0.01 mm) state. The solution optical path length was 1 cm.

Registry No. **1a**, 113008-87-0; **1a** (homopolymer), 113008-88-1; **1b**, 113008-89-2; **1b** (homopolymer), 113008-90-5; **1c**, 113008-91-6; **1c** (homopolymer), 113008-92-7; **1d**, 113008-93-8; **1d** (homopolymer), 113008-94-9; **1e**, 113008-95-0; **1e** (homopolymer), 113008-96-1; **1f**, 113008-97-2; **1f** (homopolymer), 113008-98-3; **1g**, 113008-99-4; **1g** (homopolymer), 113009-00-0; **1h**, 113009-01-1; **1h** (homopolymer), 113009-02-2; **1i**, 113009-03-3; **1i** (homopolymer), 113009-04-4; **1j**, 113009-05-5; **1j** (homopolymer), 113009-06-6; **2**, 72602-64-3; **3a**, 74-88-4; **3b**, 1520-21-4; 3-$H_2C{=}CHC_6H_4NH_2$, 15411-43-5; 4-$H_2C{=}CHC_6H_4CH_2Cl$, 1592-20-7; CH_3OH, 67-56-1; 4-$H_3CC_6H_4CH_2OH$, 589-18-4; 4-$H_3CC_6H_4NH_2$, 106-49-0; 3-$H_3CC_6H_4NH_2$, 108-44-1.

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Merocyanine–Spiropyran Photochemical Transformation in Polymers, Probing Effects of Random Matrices

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ABSTRACT: Isomerization kinetics of the merocyanine–spiropyran transformation in several poly(alkyl acrylates) are detected by time-resolved absorption spectroscopy. The decay of the colored merocyanine exhibits significant deviations from first-order patterns. The energy of activation can be separated into a stabilization energy for the isomer and an activation inherent to the amorphous matrix by observing the decoloration patterns for the corresponding photoisomerization. These observations can be explained by matrix effects in the isomerization modeled by statistics and fluctuations of matrix-site energies. Quantification of matrix effects is based on the concept of transport theories in random media applied to reflect the dynamics of potential energies. The gradual decrease of dispersion of reaction rates with rising temperature is correlated to the time a chromophore remembers its initial matrix cage, thereby extending the kinetic model to the range above the glass transition.

Introduction

The glassy state of matter gives rise to a wide variety of properties absent in counterpart states of higher regularity, e.g., crystalline systems. In most cases the characteristic phenomena of vitreous configurations can be explained on the basis of a statistical spread of microscopic contributions like site energies, intersite coupling, and relaxation times together with the notion that glasses are outside of thermodynamic equilibrium. The experimental elucidation of the glassy state covers practically all forms of spectroscopy as documented by Wong and Angell.[1] Apart from directly detecting the dynamics and structure of glasses, there are different methods of probing an amorphous matrix via guest sites as done, for instance, by hole-burning spectroscopy[2] and possibly with any observable guest property which is sensitive to its matrix cage. A well-known example for such indirect probing in a liquid matrix is the solvent shift of an absorbing dopant.

The effect of a rigid matrix on a (nondiffusive) reaction which is microscopically of first order is often the introduction of deviations from exponential kinetics observed for hole-burning,[3] proton-transfer reactions,[4] dielectric relaxation,[5] and photochromic isomerization.[6–10] Formally, any deviation from first-order kinetics can be modeled by an appropriate dispersion of rate constants to match experimental data.

Photochromic isomerization reactions as a probe for matrices combine the ease of detection via absorption spectroscopy with a high sensitivity of the kinetics to the configuration of its matrix cage. Transformation kinetics of azo compounds and spiropyrans in solution and polymer matrices are well investigated.[6–11] Following first order in solution,[8] they are notorious in exhibiting dispersive reaction patterns in rigid matrices[6–10] in the sense that the rate of isomerization decreases significantly during the course of the reaction. The extent of dispersion is found to decrease as the temperature is raised within a range far below the glass transition temperature T_g.[6] The sensitivity of decoloration kinetics to the extent of irradiation, driving the coloration reaction, has also been reported.[7] Practically all results concerning photochromic labels in polymer matrices argue for the kinetics reflecting the statistics of the matrix[8] and the amount of free volume,[10] also supported by azo labels shown to indicate physical aging of amorphous polymers.[12]

Extending previous work,[6] matrix effects on the decoloration kinetics of spiropyran are investigated in various poly(alkyl acrylates) thereby covering a temperature range from 75 K below to 95 K above T_g. The basis for rationalizing decay kinetics is the model of a Gaussian spread of energy barriers accounting for the statistics of individual reaction cages within the amorphous polymer. This interpretation reduces a decay pattern to its mean reaction rate and the dispersion of energy barriers which allows extracting an activation energy albeit observing nonexponential decoloration. To overcome the inconsistency of a simple Arrhenius law with thermal data, a model is advanced which describes the increase of motional freedom as the temperature is raised, predicting the matrix inherent energy barrier to follow a $1/T$ law.[13] Although such a temperature dependence cannot uniquely be established by experimental data covering a narrow temperature interval, the model allows disentangling the energy of activation into a part representing a stabilization energy of the merocyanine isomer (78 kJ/mol) and a part imposed by the steric hindrance of the matrix (16 kJ/mol), in analogy to the notions of Kryszewski et al.[8] This notion is strongly supported by a decrease of the activation energy

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