Photoconductivity of Poly(*N*-vinylcarbazole). VI.* Photocoductivity of Poly(β -*N*-carbazolylethyl vinyl ether)

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ABSTRACT: β -*N*-carbazolylethyl vinyl ether, a representative vinyl monomer with widely-spaced pendant carbazolyl groups connected to the skeletal chain, was synthesized and polymerized in 50–80% yields with a cationic initiator. The photoconductivity of the polymer (PCzEVE) was investigated together with that of an oligomer of *N*-vinylcarbazole (VCzOlig) and of poly(*N*-vinylcarbazole) (PVCz). The VCzOlig has almost the same photoconductive properties as observed for PVCz. In the case of PCzEVE, the photocurrent with positive or negative electrode illumination (i_{ph}^+ or i_{ph}^-) is ohmic and shows only a peak at 380 nm corresponding to the absorption edge. The magnitude of i_{ph}^+ is nearly equal to that of i_{ph}^- in every wavelength region even in a high applied fields. This behavior is quite different from that for PVCz. Moreover, the magnitude of the photocurrent of PCzEVE is much smaller than that of PVCz and of VCzOlig. The poor photoconductivity of PCzEVE was discussed in relation with the singlet exciton migration, and was attributed to the difficulty of carrier migration because of the weakness of the electronic interaction between neighboring carbazolyl groups. The indispensable conditions essential for more highly photoconductive polymers were given.

KEY WORDS Cationic Polymerization / β -*N*-Carbazolylethyl Vinyl Ether / Photoconductivity / Poly(*N*-vinylcarbazole) / *N*-Vinylcarbazole Oligomer / Poly(β -*N*-carbazolylethyl vinyl ether) /

In the previous papers,¹⁻³ the present authors have suggested that the large photoconductivity of poly(*N*-vinylcarbazole) (PVCz) can be attributed both to the high efficiency of carrier generation due to the field-assisted thermal dissociation of an exciplex formed between an excited carbazolyl (Cz) group and some electron-accepting impurity and to the ease of carrier migration due to the overlapping of π -electrons of neighboring Cz groups in one polymer chain. In other words, it seems to be due to the presence of a short-range electronic interaction between the neighboring Cz groups connected directly to the skeletal chain of the polymer. It is, therefore, very interesting to examine if vinyl polymers with widely-spaced Cz groups connected to the skeletal chains are less photoconductive than PVCz.

Poly(9- Δ^4 -pentenylcarbazole), one of such vinyl polymer, has been reported to be very photoconductive.⁴ However, this polymer is not suit-

able for detailed studies of photoconductivity, because of unavoidable contamination by the polymerization catalysts judging from both the conditions of polymerization and insolubility of the polymer.⁵

In the present paper, we have synthesized poly(β -*N*-carbazolylethyl vinyl ether) (PCzEVE), where pendant Cz groups are connected to the skeletal chain at a distance of about 4 Å by —O—CH₂—CH₂—bonds, and examined its photoconductivity in comparison with the photoconductivity of PVCz in order to obtain some information on relationship between the photoconductivity and the chemical structure of the polymer.

EXPERIMENTALS

Materials

Synthesis of β -N-Carbazolylethyl Vinyl Ether (CzEVE). The CzEVE was synthesized from

* Part V, ref 1.

β -*N*-carbazolyethanol by the method similar to that for 1-pyranylmethyl vinyl ether.⁶

β -*N*-carbazolyethanol was prepared from purified Cz⁷ according to the literature⁸ and purified first by column chromatography (silica gel, benzene) and then by recrystallization from a mixture of cyclohexane—benzene.

A mixture of β -*N*-carbazolyethanol (10 g), isobutyl vinyl ether (100 ml), and Hg(OCOCH₃)₂ (1.0 g) was refluxed for a day; then another 50 ml of isobutyl vinyl ether and 0.5 g of Hg(OCOCH₃)₂ were added and the reflux continued for one more day. The reaction mixture was then washed with water and the isobutyl vinyl ether was removed under reduced pressure. The CzEVE was isolated from the residue by column chromatography (silica gel, benzene) and then recrystallized twice from ligroin. Yield, 4.0 g (36%); mp 79.0—80.5°C. *Anal.* Found: C, 81.05; H, 6.27; N, 5.85%. Calcd. for C₁₆H₁₅NO: C, 80.98; H, 6.37; N, 5.90%. IR (KBr disk): δ_{CH} of vinyl-ether 960 and 830 cm⁻¹. NMR (CDCl₃): 1.95—2.1 τ (quartet, two ring protons); 2.5—3.0 τ multiplet, six ring protons; 3.6—3.8 τ (quartet, —O—CH=CH₂); 5.4—5.6 τ (triplet, —CH₂—CH₂—O—); 5.8—6.2 τ (multiplet, —CH₂—CH₂—O—CH=CH₂).

Polymerization of CzEVE. Solvents and BF₃·OEt₂ were purified by ordinary methods. The monomer (0.2—0.5 g) and solvent (toluene, 5—12.5 ml) were placed in a polymerization tube which was filled with dried nitrogen after evacuating to *ca.* 0.1 mmHg. The tube was kept at a given temperature and catalyst solution (BF₃·OEt₂/toluene=1/50 in volume) was added while stirring vigorously with a magnetic stirrer. After a given polymerization time, the tube contents were poured into a large amount of methanol. The polymer filtered off was fractionated according to its benzene solubility. The benzene-soluble portion was reprecipitated from the benzene solution with methanol and dried *in vacuo*. The benzene-insoluble portion was washed with benzene and dried *in vacuo*.

Oligomer of N-Vinylcarbazole (VCzOlig). The VCzOlig was prepared by the method described previously⁹ and had a degree of polymerization ($\overline{\text{DP}}$) of 10.

Electrical Measurements

The sample of PCzEVE (No. 8 in Table I), which had the highest value of $\overline{\text{DP}}$ (33), was reprecipitated three times from the benzene solution with methanol and used for the electrical measurements. A thin film of PCzEVE could not be used for the electrical measurements, since it was easily cracked because of the relatively low value of $\overline{\text{DP}}$. A sandwich-type cell (0.8—1.1 cm² in area and 0.05—0.15 mm in thickness) of PCzEVE was therefore prepared by softening (at 140—150°C) and solidifying the powder of the polymer between two nesa-coated quartz plates. A sandwich-type cell of VCzOlig was also prepared by the same method (softening point: 175—185°C) and used as a standard for comparison of photoconductivity instead of a sandwich-type cell of a thin film of PVCz. The electrical measurements were carried out by a DC method with a Takedariken TR81 vibrating-reed electrometer in a high vacuum of 10⁻⁵ mmHg. A 500 W Xenon lamp was used as the light source, and it was monochromatized by a grating monochrometer.

RESULTS AND DISCUSSION

Polymerization of CzEVE

The cationic polymerization results of CzEVE are shown in Table I. The PCzEVE was obtained in fairly good yields at or above -40°C, although no polymer was obtained at -78°C. The benzene-insoluble portion was obtained above 0°C, the yield of which increased with increasing polymerization temperature and with increasing concentration of catalyst.

The benzene-insoluble portion was also insoluble in all solvents tried and its softening point was above 300°C. The benzene-soluble portion was soluble in some organic solvents such as tetrahydrofuran and ethylene chloride. Both softening point and molecular weight of the soluble portion were roughly dependent not only on yield of the insoluble portion but also on polymerization temperature. They were higher in the case of the polymerization conditions where the insoluble portion was obtained in higher yields. In the case of the other polymerization conditions, they were the higher for the polymer obtained at -25°C and became

Table I. Polymerization of CzEVE^a

No.	Cat. (BF ₃ OEt ₂) mol% to monomer	Temp, °C	Time, hr	Polymer yield, %		Properties of soluble portion		
				Soluble	Insoluble	SP/°C ^b	η_{sp}/C^c	Mol wt ^d
1	1	50	5	26	33	148—160		7000
2	3	20	5	30	30	140—150		
3	1	20	3	51	3	130—136		
4	0.5	20	12.5	55	trace	127—140		
5	1	0	12.5	60	trace	114—125		5000
6	1	0	3	66	0	120—126	0.02	
7	1	-15	15	70	0	118—125		
8	1	-25	9	78	0	137—148	0.04	7600
9	1	-40	3	74	0	117—124	0.02	
10	1	-78	3	0	0			

^a CzEVE, 0.5—0.2 g; monomer concentration, 0.2 M; solvent, toluene.^b SP, softening point. The SP of insoluble portion is above 300°C.^c 0.14 g/10 ml in benzene at 15°C.^d Measured by a vapor pressure osmometer.

lower with either increasing or decreasing polymerization temperature from -25°C. There was no significant difference in both the IR and the X-ray diffraction spectra between the soluble and the insoluble portions and the X-ray diffraction spectra showed both portions to be amorphous. It is not clear whether the difference in the solubility is due to the difference in molecular weight and/or to that in stereoregularity.

The PCzEVE prepared in the present study had a comparatively low molecular weight; the highest value of $\overline{DP}$ was 33. This value of $\overline{DP}$ for PCzEVE is, however, considerably higher than the values for poly(1-pyrenylmethyl vinyl ether) and poly(α -naphthylmethyl vinyl ether) (10 and 22, respectively).⁶

The considerably low softening points of the soluble portions of PCzEVE suggest the enhanced flexibility of the skeletal chain as compared with the case of VCzOlig (SP: 175—185°C, $\overline{DP}$ =10) and poly(1-pyrenylmethyl vinyl ether) (SP: 220—230°C, $\overline{DP}$ =10). This is clearly attributable to the long distance between a pendant Cz group and the skeletal chain. The long distance between a pendant Cz group and the skeletal chain is also estimated to cause a significant reduction in the interaction between neighboring Cz groups in one polymer chain, which is very strong in the case of PVCz and VCzOlig. This has been recently confirmed on the basis of the investigations on the UV, charge-transfer absorption

and NMR spectra of PVCz, VCzOlig, and PCzEVE.^{9,10}

Photoconductivity

The VCzOlig showed the two types of photo-response curves similar to those observed in a sandwich-type cell with a thin film of PVCz.³ One is the normal pattern, where the photocurrent rises monotonically to a steady-state value with light on and decays monotonically after light off. The other is the pattern, where the photocurrent reaches a peak value soon after light on and decreases slowly with time until it levels off to a steady-state value after 5—10 min. On the other hand, PCzEVE showed only the former type of the photoresponse curve. The results presented below were obtained for the steady-state values of the photocurrent.

The voltage dependence of the photocurrent is shown in Figure 1. The VCzOlig has the same voltage dependence on the photocurrent as observed for a thin film of PVCz;³ the superlinearity of the photocurrent on applied voltage is observed in the field higher than 8000 V/cm only for the photocurrent induced by illuminating the positive electrode with the light of the wavelength shorter than the absorption edge of the cell (380 nm for the present cell). On the other hand, the photocurrent of PCzEVE is proportional to the applied voltage in every wavelength region over the whole range of applied voltage (2000—45000 V/cm). It is noted that PCzEVE

Figure 1. Voltage dependence of the photocurrent of VCzOlig and of PCzEVE in a high vacuum at 25°C. 1–6, VCzOlig (0.10 mm thick); 7–8, PCzEVE (0.08 mm thick). 1, 420 nm, positive electrode illumination; 2, 360 nm, positive; 3, 310 nm, positive; 4, 420 nm, negative; 5, 360 nm, negative; 6, 310 nm, negative; 7, 360 nm, positive; 8, 400 nm, positive.

does not show the superlinearity of the photocurrent on applied voltage which has been regarded as one of the most important characters of the photoconductivity of PVCz.³

The photocurrent of PCzEVE is proportional to the 0.8–0.9-th power of the light intensity (10^{12} – 10^{14} photons/cm² s), while the photocurrent of VCzOlig is always proportional to the light intensity.

The spectral dependence of the photocurrent is shown in Figure 2. It was obtained by normalizing the observed photocurrent values to the values for the light intensity of 3×10^{13} photons/cm² s according to the light intensity dependence. The magnitude of the photocurrent of VCzOlig decreased gradually with repeated illumination with UV-light. This is the reason

for the difference in the magnitude of the photocurrent between either curves 1 and 2 or curves 3 and 4 in Figure 2. This may be due to the space charge effect and partly due to some decomposition of the sample with UV-light illumination.

The spectral dependence of the photocurrent of VCzOlig are almost the same as observed for a thin film of PVCz,³ except that the photocurrent with negative electrode illumination (abbreviated to i_{ph}) in the UV region shows a spectral dependence corresponding more to the absorption spectrum and is relatively large in magnitude as compared with the photocurrent peak at the absorption edge (390 nm). That is, the following behavior characteristic of the photoconductivity of PVCz was observed even in the

Figure 2. Spectral dependence of the photocurrent of VCzOlig and of PCzEVE in a high vacuum at 28°C. 1—4, VCzOlig (0.11 mm thick), under 41000 V/cm; 5—6, PCzEVE (0.07 mm thick), under 45000 V/cm. The curves 1, 2, and 5 are for i_{ph}^+ and the curves 3, 4, and 6 are for i_{ph}^- . 7—8, transmittance of a cell of VCzOlig (7) and PCzEVE (8); 9, the absorption spectrum of a PCzEVE film 1 μ thick. (The spectra of a VCzOlig film is regarded to be almost same, in so far as we discuss the spectral dependence.)

case of the sandwich-type cell of VCzOlig used in the present study. (1) the photocurrent with positive electrode illumination (i_{ph}^+) is nearly equal to i_{ph}^- in magnitude in the low fields below 10000 V/cm, but is much larger than i_{ph}^- in the high fields as large as 45000 V/cm. (2) the spectral dependence of i_{ph}^+ corresponds to the absorption spectrum in the high fields.

The magnitude of the photocurrent of VCzOlig was not particularly small as compared with that of PVCz. The i_{ph}^+ was only 3—5 times smaller for VCzOlig than for PVCz under 41000 V/cm, while i_{ph}^- was almost the same for both of them. Epping has reported that the dark- and photo-conductivities of PVCz were independent on $\overline{DP}$ in the range of 500—5000.¹¹ It is noted that VCzOlig ($\overline{DP}$ =10) showed almost the same behavior characteristic as the photo-conductivity of PVCz ($\overline{DP}$ =600), regardless of the very small value of $\overline{DP}$, as mentioned above.

On the other hand, both the spectral depend-

ence and the magnitude of the photocurrent of PCzEVE are significantly different from those of VCzOlig mentioned above. In the case of PCzEVE, there is no difference between i_{ph}^+ and i_{ph}^- in both the spectral dependence and the magnitude. The photocurrent shows only a clear peak at the absorption edge (380 nm) and shows no clear peak in the UV region shorter than 350 nm, where the photocurrent is comparatively small in magnitude as compared with the peak at 380 nm. Furthermore, the magnitude of the photocurrent of PCzEVE is much smaller than that of VCzOlig in every wavelength region in both the low and high applied fields. In particular, the former is less than a hundredth of the latter in the 250—300 nm region under 45000 V/cm.

It is clear from the results mentioned above that the photoconductivity of PCzEVE is greatly inferior to that of both VCzOlig and PVCz. This is due neither to the relatively small value of $\overline{DP}$ nor to the preparation method of the sandwich-type cell, but is a characteristic of PCzEVE.

It has been already confirmed from the investigation on the UV and NMR spectra that both PVCz and VCzOlig have some electronic interaction between neighboring Cz groups in one polymer chain even in solution in the ground state but PCzEVE had no such interaction due to the large distance between adjacent Cz groups in the polymer chain.¹⁰ We have also examined recently host-sensitized energy transfer in films of PVCz and PCzEVE doped with dimethylterephthalate (DMTP) or perylene.¹² Even in the PCzEVE films doped with DMTP where the single-step energy transfer by the dipole—dipole resonance is impossible, the host fluorescence is quenched significantly, as is shown, for example, in Figure 3. This indicates that a singlet exciton can migrate over many Cz rings in a PCzEVE film. The application of the random hopping model of exciton migration to the process of host-sensitized energy transfer gave the following results for the singlet exciton migration.¹² (1) the concentration of excimer-forming site of PCzEVE (3×10^{-4} mol/mol Cz unit) is a tenth of that of PVCz. (2) the number of jumps of a singlet exciton during the

Figure 3. Fluorescence spectra of PCzEVE films doped with DMTP, at 20°C, 335 nm excitation. DMTP concentration: (1) 0; (2) 4.44×10^{-4} ; (3) 8.88×10^{-4} ; (4) 1.18×10^{-2} mol/mol Cz unit.

lifetime in the absence of excimer-forming sites, which is an imaginary number of jumps and is denoted by n hereafter, is 3×10^4 for PCzEVE and $2-8 \times 10^5$ for PVCz, respectively. (3) the number of jumps of a singlet exciton during the lifetime in the presence of excimer-forming site, which is an actual number of jumps and is denoted by n' hereafter, is 4000 for PCzEVE and 700 for PVCz, respectively.

Judging from the facts that there is no significant difference in the electron-donating character between PCzEVE and PVCz,⁹ and that the value of n' for PCzEVE is six times as large as the value for PVCz because of the low concentration of excimer-forming sites in PCzEVE, the efficiency of the extrinsic carrier generation via a singlet exciton is thought to be somewhat higher for PCzEVE than for PVCz. The reason for the poor photoconductivity of PCzEVE, therefore, seems to be in the process of carrier migration rather than in carrier generation. The difficulty of carrier migration in PCzEVE is also inferred from that the value of n for PCzEVE (which is a measure of the ease of singlet exciton migration without any trapping site) is much smaller than the value for PVCz and is of the same order as for poly(vinyl toluene) ($n=9 \times 10^3$).¹³ This is clearly due to the weakness

of the electronic interaction between neighboring Cz groups because of the large distance between them in PCzEVE, where pendant Cz groups are widely spaced on the skeletal chain.

The discussion mentioned above leads to the following indispensable conditions for more highly photoconductive polymers; (1) the pendant π -electron groups should be connected directly to the skeletal chain of the polymer, and (2) the electronic interaction between neighboring pendant π -electron groups should be strong enough to be clearly detected by electronic and NMR spectra even in solution. Poly(1-vinylnaphthalene) and poly(acenaphthylene) have been reported to be very poorly photoconductive.¹⁴ This is understandable because these polymers satisfy only the former of the above-mentioned conditions and not the latter.^{10,15}

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REFERENCES

1. Part V of this series; K. Okamoto, S. Kusabayashi, and H. Mikawa, *Bull. Chem. Soc. Japan*, **46**, 2613 (1973).
2. K. Okamoto, K. Kato, K. Murao, S. Kusabayashi, and H. Mikawa, *ibid.*, **46**, 2883 (1973).
3. K. Okamoto, S. Kusabayashi, and H. Mikawa, *ibid.*, **46**, 2324 (1973).
4. W. A. Hewett and A. H. Sporer, *Chem. Abstr.*, **68**, 79037C (1968).
5. J. Heller, D. J. Lyman, and W. A. Hewett, *Makromol. Chem.*, **73**, 48 (1964).
6. S. Yoshimoto, K. Okamoto, H. Hirata, S. Kusabayashi, and H. Mikawa, *Bull. Chem. Soc. Japan*, **46**, 358 (1973).
7. K. Kihara, Y. Ishii, Y. Suzuki, and T. Takeuchi, *Kogyokagaku Zasshi*, **73**, 2630 (1970).
8. H. Otsuki, I. Okano, and T. Takeda, *ibid.*, **49**, 169 (1946).
9. K. Okamoto, M. Ozeki, A. Itaya, S. Kusabayashi, and H. Mikawa, *Bull. Chem. Soc. Japan*, **48**, 1362 (1975).
10. K. Okamoto, A. Itaya, and S. Kusabayashi, *Chem. Lett.*, **1974**, 1167.
11. R. H. Epping, "Curr. Probl. Electrophotography, Eur. Colloq.," 3rd 1971, p 215 (*Chem.*

- Abstr.*, **80**, 11475C).
12. K. Okamoto, A. Yano, S. Kusabayashi, and H. Mikawa, *Bull. Chem. Soc. Japan*, **47**, 749 (1974). A. Itaya, K. Okamoto, and S. Kusabayashi, 23rd Symposium on Macromolecules, Oct. 1974 (Tokyo), Preprint II-827, to be published elsewhere.
 13. R. C. Powell, *J. Chem. Phys.*, **55**, 1871 (1971).
 14. K. Morimoto, Y. Murakami, M. Ikeda, *National Technical Reports*, **15**, 125 (1969).
 15. J. Heller and D. Miller, *J. Polym. Sci., A-1*, **5**, 2323 (1967).