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The Preparation of the Polyvinylmalachitegreen and Vinylcarbazole-Vinylmalachitegreen Copolymers and Their Absorption Spectra

Kenichi OKAMOTO, Yo HASEGAWA,*[1] Shigekazu KUSABAYASHI and Hiroshi MIKAWA

Department of Chemical Technology, Faculty of Engineering, Osaka University, Suita, Osaka

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It is well known that triphenylmethane dyes are photoconductive and that the photoconductivity of such polymers as poly-*N*-vinylcarbazole (PVCz) is sensitized by mixing the dyes. The present authors have previously reported on the sensitization of the photoconductivity in the PVCz film by copolymerized malachite green molecules.[1] This note will deal with the preparation of the polyvinylmalachitegreen (PVMG) and *N*-vinylcarbazole (VCz)-vinylmalachitegreen (VMG) copolymers and with their absorption spectra.

Preparation of PVMG. The VMG carbinol was prepared by the method reported by Manecke and Kosmehl[2] and was recrystallized three times from benzene-methanol under nitrogen stream. The VMG carbinol was polymerized by azobisisobutyronitrile (AIBN) in a vacuum-sealed tube at 80°C for 10 hr (Table 1). The resulting white PVMG carbinol was purified by repeated reprecipitation from the benzene solution by methanol. The molecular weight was 13000 (as ascertained by means of a vapor-pressure osmometer).

Found: C, 80.99; H, 7.35; N, 7.46%. Calcd for $(C_{25}H_{28}N_2)_n$: C, 80.61; H, 7.58; N, 7.56%.

The PVMG carbinol was transformed into the chloride (PVMG) as will be described below. An amount 1.7 times the calculated amount of a 0.3 N dry HCl-THF solution was stirred into the benzene solution of PVMG carbinol, and the resulting precipitate (PVMG) was reprecipitated three times from the methanol solution by Bz–THF (1 : 10 : 7 in vol. ratio). The potentiometric titration by a 0.01 N $AgNO_3$ aqueous solution showed that the PVMG thus obtained was monocationic (Cl^- ion content; Found: 9.26, Cacld for the monocation: 9.08%). It should be noticed that

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[*1] Present address: Research Laboratory, Wireless Division, Matsushita Electric Industrial Co. Ltd., Kadoma, Osaka.

1) K. Okamoto, Y. Hasegawa, S. Kusabayashi and H. Mikawa, This Bulletin, **41**, 2563 (1968).

2) G. Manecke and G. Kosmehl, *Chem. Ber.*, **93**, 1899 (1960); G. Manecke and G. Kosmehl, *Makromol. Chem.*, **80**, 22 (1964).

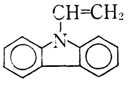
Table 1. Copolymerization of VCz with VMG carbinol[a)]

No.	Monomer mol% in feed		Conversion[b)] %	Fractionation %			VMG mol% in Fraction		
	VCz	VMG carb.		I	II	III	I	II	III
1	100	0	97.0		(100)			(0)	
2	99.9	0.1	92.0	0	100			0.073	
3	99.5	0.5	94.6	8.8	86.7	—	1.02	0.15	—
4	99.0	1.0	94.4	11.8	75.3	—	1.48	0.25	—
5	97.0	3.0	92.6	13.6	60.5	—	3.4	0.37	—
6	95.0	5.0	86.0	31.0	36.1	—	3.0	0.46	—
7	90.0	10.0	76.6	39.5	27.8	30.9	4.9	1.24	4.7
8	0	100	54.3	(100)			(100)		

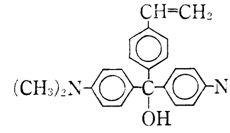
a) Solvent: benzene, initiator: AIBN, Monomer conc.: 0.5 mol/*l* (in No. 1—7) or 0.25 mol/*l* (in No. 8), AIBN conc.: 0.01 in molar ratio to monomer.

b) This is the yield after the reprecipitations three times.

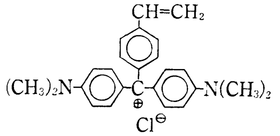
if a fairly large excess of a 0.3 N dry HCl–THF solution was added to the benzene solution of the PVMG carbinol, a fairly large proportion of the MG molecules were transformed into the dication.



VCz



VMG carbinol



VMG

Preparation of the VCz-VMG Copolymer. The copolymerization of VCz with the VMG carbinol was carried out by means of AIBN in a vacuum-sealed tube at 80°C for 10 hr. The resultant VCz–VMG carbinol copolymer was purified by the repeated reprecipitation from the benzene solution by methanol. The VCz–VMG carbinol copolymer was then transformed into the VCz–VMG carbinol copolymer was then transformed into the VCz–VMG (HCl salt) copolymer and fractionated as follows. The 0.3 N dry HCl–THF solution (1.5-times the estimated MG dye content) was stirred into the benzene solution of the VCz–VMG carbinol copolymer, after which the precipitate was separated by the use of a centrifuge (Fraction I). A large amount of methanol was added to the filtrate, and the resultant precipitate was filtered (Fraction II). The filtrate was evaporated to dryness under reduced pressure (Fraction III). The VMG content of the copolymer was determined colorimetrically by use of the absorption maxima (626 and 452 mμ) of VMG, shown in Fig. 1. The results are shown in Table 1. The homopolymer of VCz is not contained in Fraction I, for PVCz is soluble in Bz–THF. Fraction II does not contain PVMG because of its insolubility in Bz–THF. Furthermore, Fraction I shows the same absorption spectrum as Fraction II and does not have the absorption peak characteristic

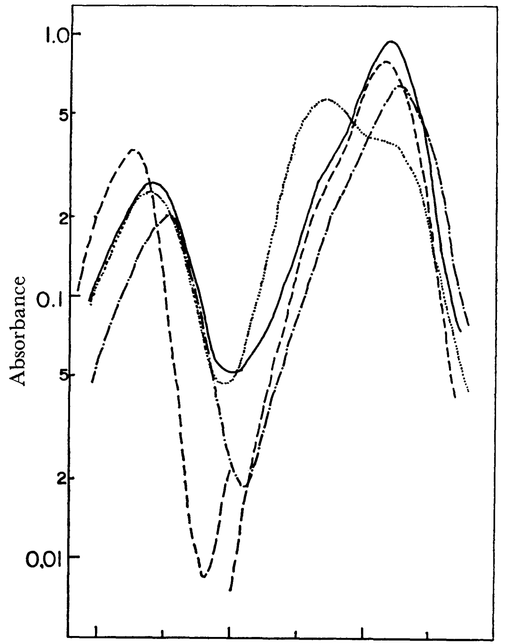


Fig. 1. Visible absorption spectra of MG dye derivatives in solution.
— — MG, 8.9×10^{-6} ($\lambda>500$ mμ) or 2.0×10^{-5} ($\lambda<500$ mμ) mol/*l* in 0.02 N HCl methanol.
—·— VMG, 9.0×10^{-6} mol/*l* in 0.01 N HCl THF-methanol (97 : 3 in volume ratio).
—— VCz-VMG copolymer (No. 4, Fraction II), 1.6×10^{-5} mol/*l* in 0.01 N HCl-THF-methanol (97 : 3 in volume ratio).
······ PVMG, 2.6×10^{-5} mol/*l* in 0.01 N HCl methanol.

TABLE 2. VISIBLE ABSORPTION MAXIMA λ_{max} AND APPARENT EXTINCTION COEFFICIENT ε_{app} OF MG DYE DERIVATIVES[a]

Dye	First				Second	
	λ_{max}	ε_{app}	λ_{max}	ε_{app}	λ_{max}	ε_{app}
MG[b]	617.5	9.83			426	1.81
VMG[c]	626	7.3			452	2.2
PVMG[b]	620	1.5	570	2.1	440	0.94
VCz-VMG copolymer[c]	620	5.6			440	1.6

a) λ_{max} [mμ], ε_{app} [$\times 10^4$ cm·*l*/mol]

b) in 1×10^{-2} N HCl-methanol solution

c) in 1×10^{-2} N HCl-THF-methanol solution (97 : 3 in volume ratio)

of PVMG at about 570 mμ. Fraction I, therefore, seems to consist of only the VCz–VMG copolymer. Fraction II will consist of the copolymer and PVCz (especially in the case of a low MG dye content). The molecular weight of the copolymer (Fraction II) is about 20000 (as determined by the use of the vapor pressure osmometer), a little lower than that of PVCz polymerized under the same conditions.

Absorption Spectra of the MG-dye Derivatives. Figure 1 shows the absorption spectra of PVMG, VMG, and the VCz–VMG copolymer in solution. The absorption maxima of these dye salts are listed in Table 2. The replacement of the 4-hydrogen of MG by the vinyl group or the main chain unit, >CH–CH_2–, causes the red shift of the visible absorption peaks.

It has been reported that MG has a small shoulder band at about 570 mμ in addition to its main peaks (426 and 618 mμ) and that this shoulder becomes larger with the increase in the concentration.[3] Furthermore, Manabe *et al.*, have reported that the maximum extinction coefficient, ε_{max}, of the main peaks decrease with the increase in the dye concentration.[4] These phenomena, which have also been observed in the spectra of such other cationic dyes as crystalviolet, have been attributed to the formation of the aggregate of the dye molecules, as is well known.[3-5] A similar shoulder band was observed at about 570 mμ in the absorption spectra of VMG, the VCz–VMG copolymer and PVMG ;[*2] it is also probably due to the formation of the aggregate. It should be noted that, in PVMG, the band attributed to the aggregation is larger than the main band and is not affected by either the temperature (0—50°C) or the concentration (0.5—50×10^{-5} mol/*l*). This suggests that the pendant MG group in the polymer chain aggregates much more easily than MG and VMG, and that most of the pendant dye molecules of PVMG exist in the aggregated form, even in a dilute solution.

It is well known that the aggregative cationic dyes show new peaks attributable to the aggregation, the so called methachromatic band, with the depression in the main band when they are adsorped on the anionic polymers and/or agar.[3] In PVMG the distance between adjacent MG molecules is short, because each MG molecule is linked to a paraffinic polymer chain by a short covalent bond. The aggregation ability of the MG molecule will be enhanced by the short intermolecular distance in PVMG. No information on the aggregation state has been obtained for either MG or PVMG, however.

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3) L. Michaelis and S. Granick, *J. Amer. Chem. Soc.*, **67**, 1212 (1945).

4) O. Manabe, K. Nanjo, S. Matsubara, M. Nakagaki and H. Hiyama, *Kagaku to Kogyo* (Osaka), **35**, 12 (1961).

5) M. Koizumi and N. Mataga, *Yuki Gosei Kagaku Kyokai Shi*, **14**, 181 (1956).

[*2] It has been reported that the PVMG prepared from poly-*p*-lithiumstyrol has two peaks (590 and 630 mμ) at wave lengths longer than 500 mμ (D. Braun, *Makromol. Chem.*, **33**, 181 (1959).