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Sensitization of Photoconductivity. Poly-*N*-vinylcarbazole with the Copolymerized Dye Molecule

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

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

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The sensitization of the photoconductivity of PVCz by dyes was investigated by the measurement of the characteristics of the decay of the surface charge put on the polymer films. MG was selected as a dye and the following three systems were measured and the degree of the sensitization was compared; *i. e.*, PVCz-MG, copolymer of VCz and VMG and PVCz-PVMG systems. The sensitization was observed in the wavelength region from 300 to 1200 mμ. Sensitization in the visible region was larger than in the ultraviolet. The copolymer system was inferior to the PVCz-MG system, probably because of the large loss of the carriers by the recombination and trapping in the bulk. There was the optimum concentration of the dye content, probably because of the disturbing effect of the dye molecule for the migration of the carriers. To make sure this point, the inhomogeneous films with the dye only on the surface were investigated. The results were explained by the difference in the distiribution of the centers of carrier generation and those of recombination and trapping of the carriers in the bulk.

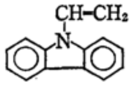
Poly-*N*-vinylcarbazole (PVCz) film is photoconductive and useful as an organic photoconductive material for electrophotography. However its sensitivity is small and limited only in the ultraviolet region. It is, therefore, necessary to improve the senstivity. There are two kinds of method which have been much studied. One is the formation of charge transfer complexes,[1-4] and the other is the addition of dyes.[2,3]

There are many reports about the sensitization with dyes, but there are none about the sensitization by the copolymerization with dye monomers. It has been reported that the absorption spectrum of polyvinylmalachitegreen (PVMG) shows a new peak at 590 mμ in methanol solution beside the absorption bands of the malacitegreen (MG).[5] This peak seems to be due to the associated MG structures caused by the large interaction between neighboring MG groups.[6] If we introduce MG dye molecules directly into the PVCz molecular chain by chemical bond, we may expect results different from the case where MG dye is simply mixed, because the interaction between carbazole groups and MG groups will be different in both cases.

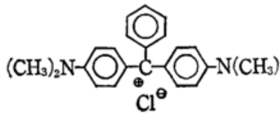
From this view point *N*-vinylcarbazole(CVz)-4''-vinylmalachitegreen(VMG) copolymer was synthesized, and the characteristics of the surface potential decay of its film were investigated and compared with that of the PVCz film mixed with MG (PVCz-MG system). The characteristics of the surface potential decay of the PVCz film mixed with PVMG (PVCz-PVMG), were investigated also.

Experimental

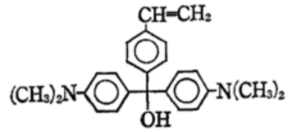
(a) Materials.



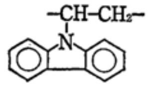
(VCz)



(MG)

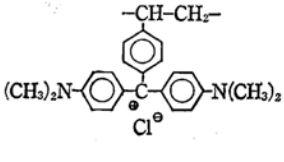


(VMG carbinol)



PVCz: -A-A-A-A-A-

(express as A)



VCz-VMG copolymer:
-A-A-A-B-A-

(express as B)

PVMG: -B-B-B-B-B-

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

1) S. Oka, T. Mori, S. Kusabayashi, A. Taniguchi, Y. Yamamoto, M. Ishiguro and H. Mikawa, *Electrophotography*, **5**, (No. 3), 77 (1964).

2) H. Högel, Japanese Pat. 261664.

3) Y. Hayashi, M. Kuroda and A. Inami, This Bulletin, **39**, 1660 (1966).

4) M. Lardon, E. L. Döller and J. W. Weigl, *Molecular Crystals*, **2**, 241 (1967).

5) D. Braun, *Makromol. Chem.*, **33**, 181 (1959).

6) To be published.

PVCz: Purified VCz was polymerized by azobisisobutylonitrile in benzene and the polymer obtained was used after being purified by repeated reprecipitation ($\overline{M}_v=110000$).

MG: Commercial MG was purified by the L. Lewis's method.[7]

PVMG: PVMG was prepared from VMG carbinol.[8]

VCz-VMG Copolymer: The copolymer was obtained from VCz and VMG carbinol.[6] The dye mentioned above was used as HCl salts. In changing the dye carbinols into HCl salts, all attention was payed in order to prevent the formation of their dications by excess HCl, chlorine content being confirmed by potentiometric analyses.

(b) Preparation of the Films for the Measurement. In the case of the PVCz-MG and PVCz-PVMG systems, the methanol solution of MG or PVMG was added to the benzene solution of PVCz with stirring (benzene : methanol=20 : 1 by volume), 0.2 m*l* of 5 wt% solution thus prepared was dropped on a copper plate (22 mm in diameter) and the solvent was evaporated slowly.

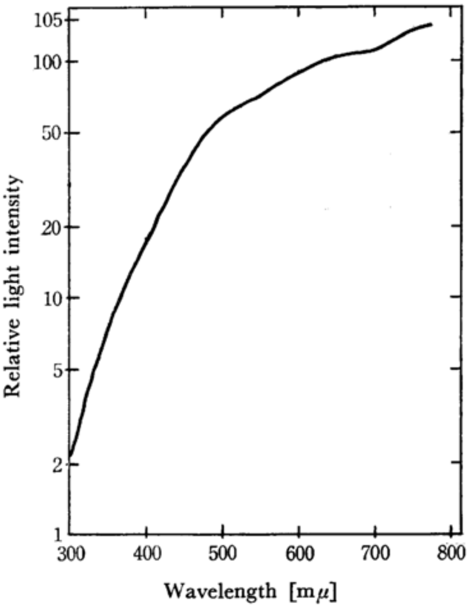


Fig. 1. Energy distribution of the light of xenon lamp measured by a thermopile using a monochrometer (slit width: 2 mm).

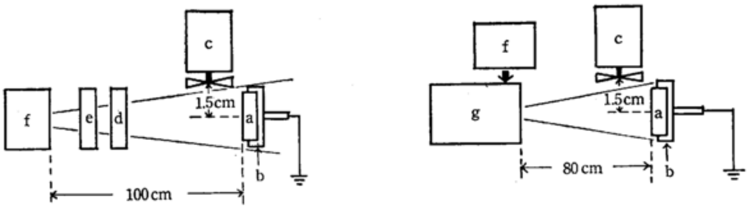
In the case of the VCz-VMG system, 5 wt% benzene solution of the copolymer was treated likewise. The films were used for the measurement, after being dried for more than 20 hr under 1 mmHg vacuum. These films were estimated to be 20 μ thick.

(c) Measurement of the Decay of Surface Potential. A 500 W xenon lamp was used for the light source. Its energy distribution is shown in Fig. 1. This is different from the usual energy distribution of the xenon lamp, for the relative light intensity is expressed by the number of photons and the slit width of the monochrometer is fixed at 2 mm in the whole wavelength region. Figure 2 is the schematic representation of the experimental arrangement. The films were charged positive or negative by corona discharge. The initial surface potential of the films as observed by our arrangement was about 100 V.

Results

(a) Absorption Spectra of the Films. The absorption spectra of PVCz, MG, PVMG, VCz-VMG copolymer and PVCz-MG mixture*2 (99.7 : 0.3 mol%) are shown in Fig. 3. The absorption spectrum of the film of PVCz-MG mixture is similar to that of the MG solution rather than to the MG solid film. In the film of PVCz-MG mixture, the splitting reported in MG solid[9] was not observed and only a slight red-shift of the first absorption peak was observed with somewhat broadening of the peak in comparison with that of the MG solution.

(b) Experimental Equation of the Surface Potential Decay. An example of the decay of surface potential is shown in Fig. 4(a). A linear relation was found between the logarithm of surface potential *V* and the root of time *t* as shown



Illumination with polychromic light

Illumination with monochromatic light

Fig. 2. Schematic arrangement of the measurement of the photo-decay of surface charge. a) Copper plate with photoconductive films charged positive or negative. b) Supporter for a copper plate. c) Probe of the rotating sector type fieldmeter. The signal is amplified and fed to a recoder. d) Toshiba's filter UV39 (390 mμ<), if necessary. e) Water filter (2 cm thick). f) 500 W xenon lamp. g) Monochrometer.

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[7] L. Lewis, T. Magel and D. Lipkin, *J. Am. Chem. Soc.*, **64**, 1774 (1942).

[8] G. Manecke and G. Kosmehl, *Chem. Ber.*, **93**, 1899 (1960).

*2 The concentration of dye is expressed in this paper by the amount of the dye structure unit to the carbazole unit.

[9] J. W. Weigl, *J. Chem. Phys.*, **24**, 364 (1956).

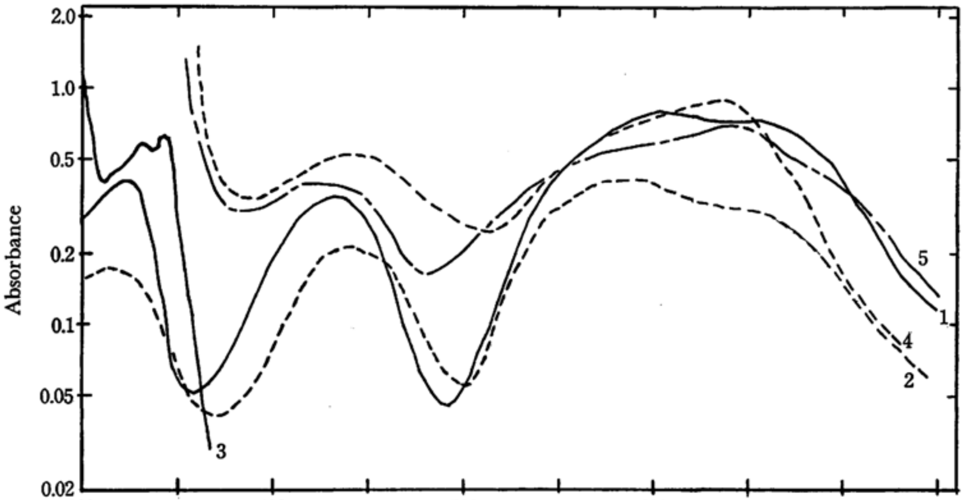

Fig. 3. The absorption spectra of solid films.
1 MG, 2 PVMG, 3 PVCz, 4 VCz-VMG copolymer (0.15 mol%),
5 PVCz-MG (0.3 mol%)

in Fig. 4(b). The results can be described as $V=V_0\exp(-\alpha t^{1/2})$, which equation had been used for ZnO by Inoue[10] and for several organic materials by us.[1,11] We shall use the value of α as the decay constant in the present paper.

(c) Effect of the Dye Content on Dark Decay Constant α_d. As shown in Fig. 5, α_d increases a little with the dye content (especially in the VCz-VMG copolymer system). The sign

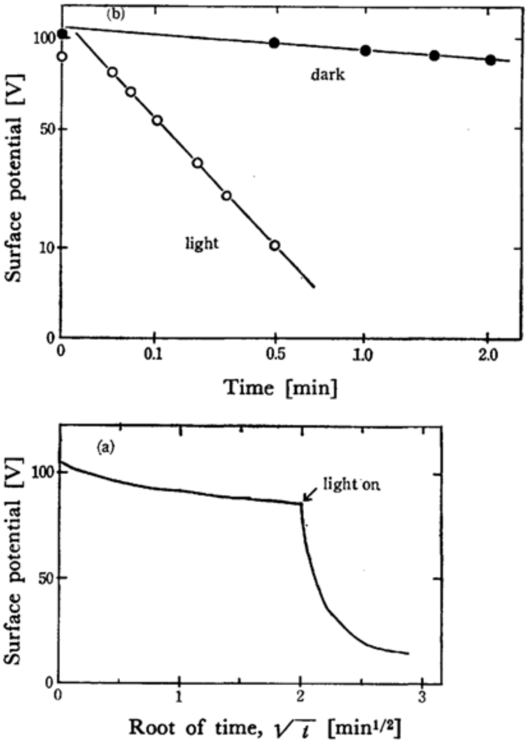

Fig. 4. Decay curves of surface potential.

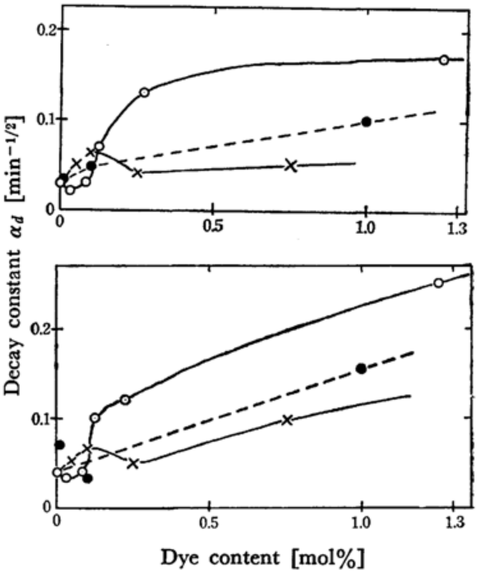

Fig. 5. Dark decay constant *versus* dye content.
—○— VCz-VMG copolymer
--●-- PVCz-MG
—×— PVCz-PVMG

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[10] E. Inoue, H. Kokado, T. Yamaguchi, S. Nagashima and K. Takahashi, *Electrophotography*, **1**, (No. 2), 27 (1959).

[11] S. Oka, T. Mori, S. Kusabayashi, A. Taniguchi, Y. Yamamoto, M. Ishiguro and H. Mikawa, *ibid.*, **5**, (No. 2), 52 (1963).

of the charge put on the film causes no difference in the α_d value.

(d) Effect of the Dye Content on the Light Decay Constant $\alpha_{1,v}$ and $\alpha_{1,t}$. $\alpha_{1,v}$ is defined as the decay constant observed under the illumination with visible light covering from 390 to 1200 mμ and $\alpha_{1,t}$ as that under illumination with the total light from the ultraviolet to 1200 mμ. Preliminary experiment with the PVCz-MG system showed that $\alpha_{1,v}$ reached a maximum at the MG concentration of about 0.1 mol% and decreased considerably at higher concentrations. Decay constants were, therefore, measured with the films containing about 0.1 mol% of the dye.

Figure 6 shows the relation between $\alpha_{1,v}$ or $\alpha_{1,t}$ and the dye content. In every system, the light decay constants have maximum values at the dye content of 0.1 mol% and these values are in the following order; *i. e.*, PVCz-MG system > VCz-VMG copolymer system ≫ PVCz-PVMG system. The value of $\alpha_{1,t}$ is much larger as a film is charged positive than as it is charged negative. These values denoted respectively as $\alpha^{+}_{1,t}$ and $\alpha^{-}_{1,t}$. There is no large difference in $\alpha_{1,v}$ between a film charged positive ($\alpha^{+}_{1,v}$) and a one charged negative ($\alpha^{-}_{1,v}$). However in PVCz-MG system and PVCz-PVMG copolymer system $\alpha^{-}_{1,v}$ is a little larger than $\alpha^{+}_{1,v}$, and in VCz-VMG copolymer system $\alpha^{+}_{1,v}$ is a little larger than $\alpha^{-}_{1,v}$.

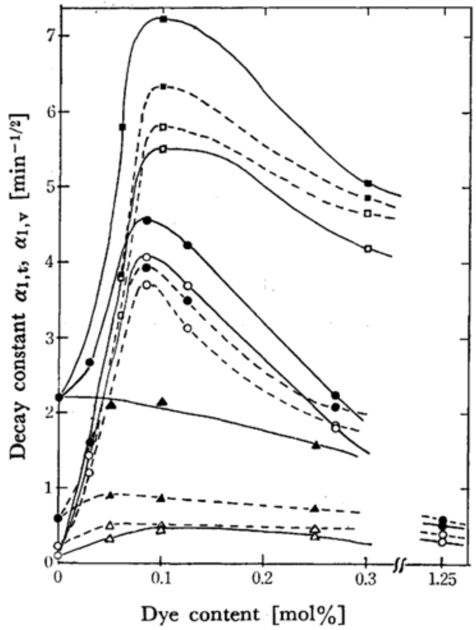

Fig. 6. Decay constant *versus* dye content.

$\alpha_{1,t}$	$\alpha_{1,v}$	Systems
—■—	—□—	PVCz-MG
—●—	—○—	VCz-VMG copolymer
—▲—	—△—	PVCz-PVMG

Solid lines show α values when charged positive and dotted lines show α values when charged negative.

The value, $\alpha_{1,UV}$, which is defined as $\alpha_{1,t}-\alpha_{1,v}$, is a measure of the effect of the UV light under the illumination with the total light. Figure 7 shows the effect of the dye content on $\alpha_{1,UV}$. The $\alpha^{-}_{1,UV}$ value ($\alpha_{1,UV}$ for the films charged negative) decreases

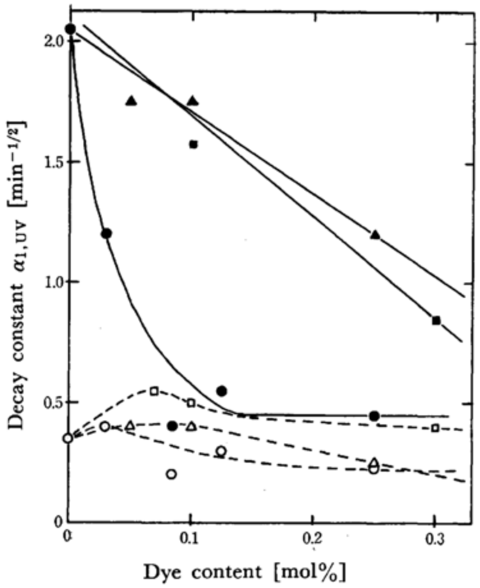

Fig. 7. Decay constant *versus* dye content.

—○— VCz-VMG copolymer
—□— PVCz-MG
—△— PVCz-PVMG

Solid lines show α value when charged positive and dotted lines show α values charged negative.

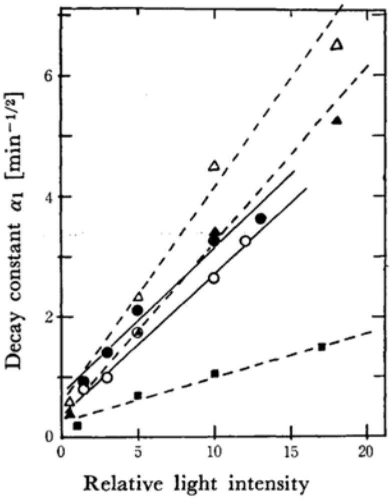

Fig. 8. Decay constant *versus* light intensity.

	Charged	λ	System
—○—	(−)	625 mμ	VCz-VMG copolymer
—●—	(+)	625 mμ	VCz-VMG copolymer
--△--	(−)	625 mμ	PVCz-MG
--▲--	(+)	625 mμ	PVCz-MG
--■--	(+)	435 mμ	PVCz-MG

with the increasing dye content after having reached a maximum, but $\alpha^{+}_{1,\mathrm{UV}}$ decreases uniformly with the increasing dye content. It must be noted that in VCz-VMG copolymer system the amount of decrease is much larger than in the other systems.

(e) Spectral Response of the Decay Constant. The linear relation between the decay constant under the illumination with a monochromatic light, $\alpha_{1,\mathrm{m}}$ and the relative light intensity is shown in Fig. 8. Figure 9 shows the spectral response of the decay constant normalized for the relative light intensity shown in Fig. 1, photon number of 365 mμ light being defined as a unity. In every system the sensitization by the dyes is positive at every wavelength measured and its degree is in the following order; *i. e.*, PVCz-MG system > VCz-VMG copolymer system ≫ PVCz-PVMG system. This order is the same with one

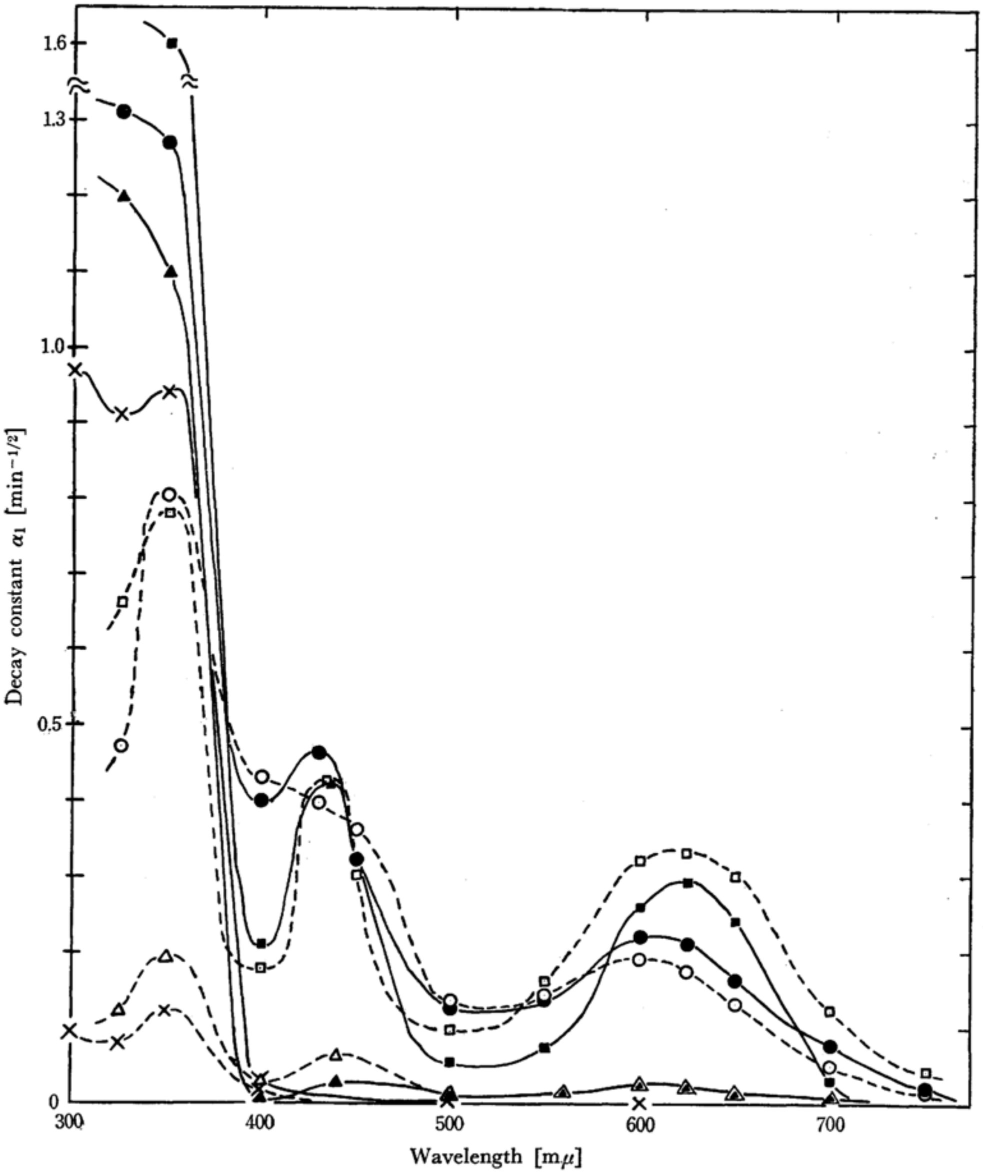

Fig. 9. Spectral response of decay constants normalized for the light intensity at 365 mμ.

Charged		System
Positive	Negative	
—×—	--×--	PVCz
—●—	--○--	VCz-VMG copolymer (0.085 mol%)
—■—	--□--	PVCz-MG (0.1 mol%)
—▲—	--△--	PVCz-PVMG (0.1 mol%)

for $\alpha_{1,v}$ mentioned above.

The spectral response of $\alpha_{1,m}$ is in agreement with the absorption spectra of the films, although in VCz-VMG copolymer system the considerable sensitization is found even in the weakly absorbed region (400 mμ) in comparison with PVCz-MG system. There is no difference in $\alpha_{1,m}$ between the films charged positive and negative in the visible light region. In the ultraviolet region, however, $\alpha_{1,m}$ of the former is considerably larger than the latter. The degree of sensitization in the ultraviolet region is about one and a half-fold when charged positive and about seven-fold when charged negative.

Discussion

(a) The Effect of HCl Addition on the Decay Constant. MG reacts with excess HCl to give its dication and the photoconductivity of this dication has been reported to be smaller than that of MG.[12] In preparing HCl salts of MG, PVMG and VCz-VMG copolymer, therefore, strictly controlled amount of HCl was used in order to avoid any formation of the dication structure.

The effect of HCl on the decay constants when added to PVCz and PVCz-MG (0.1 mol%) systems is shown in Fig. 10. By the addition of HCl the PVCz-MG system was desensitized, probably because of the formation of the dication structure. The PVCz system was, however, sensitized especially in the case of the positively charged film illuminated with total light.

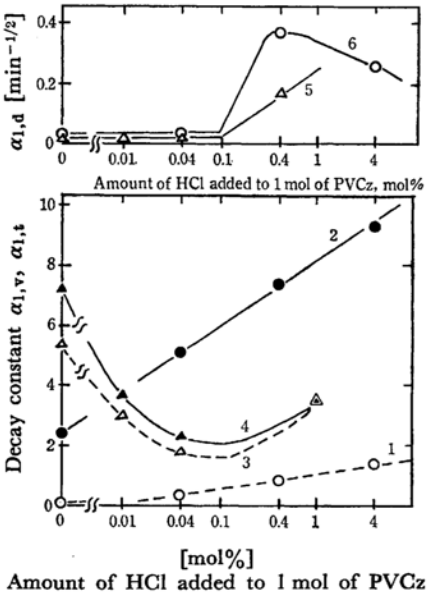

Fig. 10. Effect of HCl on decay constant (when charged positive).

1 $\alpha_{1,v}$ of PVCz, 2 $\alpha_{1,t}$ of PVCz,
3 $\alpha_{1,v}$ of PVCz-MG (0.1 mol%),
4 $\alpha_{1,t}$ of PVCz-MG (0.1 mol%),
5 α_d of PVCz,
6 α_d of PVCz-MG (0.1 mol%)

α_d of both films increased with the increasing amount of HCl. Thus HCl gives a large effect on the decay constants.

As one and a half-fold excess of HCl was used to get the HCl salt of the copolymer, the dication structure might be formed and this dication structure might have made the light decay constant of the copolymer smaller than that of PVCz-MG film. In order to confirm this point the effect of the amount of HCl on α was investigated which was added to obtain the HCl salt of the copolymer. As the amount of HCl (up to two fold excess) had no effect on α, the HCl salt of the copolymer used in this experiment seems not to contain the dication structure and the α_1 value of the copolymer seems to be small in itself.

(b) A Simple Model Explaining the Surface Potential Decay Constant under Light Illumination. The surface potential of the amorphous selenium charged positive by the corona discharge has been investigated as a function of the illumination time and explained by a model based on trapping and recombination of carriers.[13] The experimental results in this paper can also be explained by assuming an appropriate location of generation, trapping and recombination of carriers.

(i) In the case of the illumination with strongly absorbed light, the light creates electrons and holes near the illuminated surface. A part of them disappears by recombination and the rest moves in the electric field causing the surface potential decay. The carriers trapped in the bulk contribute also to the surface potential decay according to their positions.

All investigated systems when illuminated with only UV light and the PVCz system when illuminated with total light belong to the case (i). The values of $\alpha_{1,m}$ in the UV region and of $\alpha_{1,t}$ in the PVCz system are much larger when charged positive. This suggests that the hole carrier is more mobile than the electron carrier in these systems. PVCz film has been reported to be p-type.[1,3]

(ii) In the case of the illumination with weakly absorbed light, the light is absorbed uniformly in the bulk creating electron and hole carriers and the carriers move to the oppositely charged surfaces, a part of them being lost by trapping and recombination. As the situation is nearly equal both for positive and negative polarity, $\alpha^{+}_{1,v}$ and $\alpha^{-}_{1,v}$ are almost equal. The PVCz-MG, VCz-VMG copolymer and PVCz-PVMG systems containing less than 0.3 mol% of dye structures belong to the case (ii) when illuminated with visible light. As

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[12] R. C. Nelson, *J. Chem. Phys.*, **19**, 798 (1951).

[13] H. Tung Li and P. J. Regensberger, *J. Appl. Phys.*, **34**, 1730 (1963).

expected, $\alpha^{+}_{1,V} \approx \alpha^{-}_{1,V}$ in these systems.

(iii) In the case of the simultaneous illumination with strongly and weakly absorbed light, the phenomena (i) and (ii) take place simultaneously. The PVCz-MG, VCz-VMG copolymer and PVCz-PVMG systems containing less than 0.3 mol% of dye structural unit belong to the case (iii)when illuminated with total light.

The results of Fig. 7 suggest as follows. The $\alpha_{1,UV}$ value may be thought to be the measure of the surface potential decay by the carriers which are created near the illuminated surface and move through the bulk to the oppositely charged surface. If no dye is contained, the loss of the carriers in the bulk may be small.

If dyes are contained, however, the carriers are generated also in the bulk by the light absorbed by dyes. The dyes may act as the trapping centers for the carriers and a part of the carriers generated near the surface by UV light will be lost by the recombination and by the trapping in the bulk. For this reason $\alpha_{1,UV}$ seems to decrease with the increasing amount of dyes. As the decrease of $\alpha^{+}_{1,UV}$ is larger than that of $\alpha^{-}_{1,UV}$, the hole carriers will be lost much more than the electron carriers while passing through the bulk containing the dye. It should be noted that this loss of carriers in the VCz-VMG copolymer system may apparently be much larger than that in the other systems.

(c) Comparison of the Surface Potential Decay Constants of Homogeneous Films with That of the Inhomogeneous Films. Probably because of the two reasons there will be the most effective concentration of dyes for the sensitization of PVCz. One is a change in the state of the aggregation of the dye structures causing the change in the efficiency of carrier generation[14,15] and another is the disturbance of the carrier migration through the bulk. The following experiment was done to confirm the latter effect.

Inhomogeneous films (about 24 μ thick) were made from PVCz film (about 20 μ thick) by coating the surface with 0.04 m*l* of the 5 wt% benzene solution of PVCz-MG or VCz-VMG copolymer. These inhomogeneous films consist of the surface layer (about 4 μ thick) containing dyes and the base film of PVCz (about 20 μ thick). Decay constants of the inhomogeneous films thus prepared were compared with those of the homogeneous films (about 24 μ thick). In the case of the inhomogeneous films the decay curves deviated considerably from $V = V_0 \exp(-\alpha t^{1/2})$. The experimental results were, however, expressed by this equation, and the parameter α thus obtained was compared with the α values of the homogeneous films. The results are shown in Table 1. The following four important differences were evident.

(i) $\alpha^{+}_{1,V} > \alpha^{-}_{1,V}$ In homogeneous films $\alpha^{+}_{1,V}$ is nearly equal to $\alpha^{-}_{1,V}$, on the other hand, in inhomogeneous films $\alpha^{+}_{1,V}$ is much larger than $\alpha^{-}_{1,V}$. As the surface potential decay in inhomogeneous films belongs to the case of (b-i) mentioned above, this result is explainable.

(ii) $\alpha^{h+}_{1,UV} < \alpha^{ih+}_{1,UV}$ There is no difference in $\alpha^{-}_{1,UV}$ between homogeneous and inhomogeneous films, but $\alpha^{+}_{1,UV}$ of the latter ($\alpha^{ih+}_{1,UV}$) is much larger than $\alpha^{+}_{1,UV}$ of the former ($\alpha^{h+}_{1,UV}$). As in inhomogeneous films the base PVCz film does not contain the dye and carriers are not created in the bulk, the carriers created near the illuminated surface will not be lost much by the recombination and trapping in the bulk. $\alpha^{ih+}_{1,UV}$ may be, therefore, larger than $\alpha^{h+}_{1,UV}$.

On the other hand in negative polarity, both for inhomogeneous and homogeneous films the values of $\alpha^{ih-}_{1,UV}$ and $\alpha^{h-}_{1,UV}$ are nearly equal to each other, probably because the loss of electrons by the existence of the dyes in the bulk, as stated above, is much smaller than that of holes, and

TABLE 1. COMPARISON OF α VALUES OF HOMOGENEOUS FILMS WITH THOSE OF INHOMOGENEOUS FILMS

Systems	Dye content	$\alpha^{+}_{1,V}$	$\alpha^{-}_{1,V}$	$\alpha^{+}_{1,t}$	$\alpha^{-}_{1,t}$	$\alpha^{+}_{1,UV}$	$\alpha^{-}_{1,UV}$
PVCz-MG	mol%			min$^{-1/2}$			
homogeneous	0.1	3.7	4.3	4.2	4.7	0.5	0.4
	0.3	1.8	1.9	2.2	2.2	0.4	0.4
inhomogeneous	0.1	6.6	4.3	9.2	4.9	2.6	0.6
	0.3	5.6	4.8	7.0	5.4	1.4	0.6
VCz-VMG copolymer							
homogeneous	0.087	3.7	3.2	4.2	3.3	0.5	0.1
	0.127	3.8	3.8	3.8	3.9	0	0.1
	0.27	2.6	2.1	2.7	2.3	0.1	0.2
inhomogeneous	0.087	3.5	1.5	5.0	1.6	1.5	0.1
	0.127	3.1	1.4	4.8	1.3	1.7	0
	0.27	3.7	1.3	4.5	1.4	0.8	0.1

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14) R. C. Nelson, *J. Opt. Soc. Am.*, **1958**, 948 .

15) R. C. Nelson, *J. Phys. Chem.*, **71**, 2517 (1967).

consequently, for electrons, the influence of the difference of the bulk constituents in homogeneous and inhomogeneous films may effectively be very small.

(iii) In homogeneous films $\alpha^{h+}{}_{1,v}$ decreases much with the increasing dye concentrations both in PVCz-MG films and in VCz-VMG copolymer films. In inhomogeneous films, however, $\alpha^{ih+}{}_{1,v}$ changes little with increasing dye concentrations. $\alpha^{ih+}{}_{1,v}$ is therefore much larger than $\alpha^{h+}{}_{1,v}$.

In carrier generation, the homogeneous films must be superior to the inhomogeneous films, as the increase of the total carrier is expected with the increasing volume where the dye molecules exist. The fact that in positive polarity $\alpha^{ih+}{}_{1,v}$ is larger than $\alpha^{h+}{}_{1,v}$ must, therefore, be understood by assuming the dual effect of the dye molecules, the generation of carriers and the disturbance for carrier migration. The latter effect must be predominant in this case.

In the case of the VCz-VMG copolymer system $\alpha^{-}{}_{1,v}$ of the homogeneous films is larger than that of the inhomogeneous films, probably because the carrier generation effect may be superior to the disturbance effect. In the case of the PVCz-MG system, however, the former is smaller than the latter, probably because the carrier generation effect may be inferior to the disturbance effect.

These results, (ii) and (iii), support that the hole carrier is lost much more than the electron carrier while passing through the bulk by the existing dye molecules and the loss is especially much in the VCz-VMG copolymer films.

(iv) α_d of inhomogeneous films is considerably smaller than that of homogeneous films in both VCz-VMG copolymer and PVCz-MG systems.

(d) The Degree of Sensitization. The degree of sensitization is in the following order; *i. e.*, PVCz-MG system > VCz-VMG copolymer system ≫ PVCz-PVMG system.

From this result it will be supposed that the efficiency of the carrier generation of PVMG is inferior to that of MG and the copolymer. The dyes in the aggregated states have been reported to have poor efficiency of sensitization, which fact has been explained on the electron transfer mechanism.[14,15)]

If so, the small degree of sensitization of PVMG as observed in the present investigations will be due to easy aggregation of the dye structures in the polymer chain.

In sensitizing PVCz the copolymer is inferior to the PVCz-MG system because of the loss of mobile carriers by the recombination and trapping in the bulk.