Copolymers of N-Vinylcarbazole with Monomers Containing Carboxylic Acid Groups or Carboxylic Anhydride Groups. II. Photoconductivity and Composition

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SYNOPSIS

Copolymers of N-vinylcarbazole containing olefinic monomers that possess carboxylic acid or anhydride functionality have been produced. The photoconductive properties of the copolymers were measured. Fluorimetry has been used to relate this photoconductivity to the copolymer composition. Photoconductivity was greatest in copolymers containing high percentages of vinylcarbazole. It is suggested that this is due to block copolymer formation, since the development of such blocks allows greater interchromophore overlap than would be possible with alternating copolymers, which exhibit low photoconductivity.

INTRODUCTION

The photoconductive behavior of poly(vinylcarbazole) (PVK) has been widely investigated in recent years, mainly because of its great utility in reprographic processes.[1,2]

PVK is known to depend on transient chromophore overlap for its photoconductivity, two neighboring carbazole pendants of equal energy overlapping during molecular vibrations to form an excited complex ("exciplex"), and electron–hole transfer taking place.[3,4] For this reason many copolymers of N-vinylcarbazole, (NVK) have low conductivity. In these copolymers the carbazole chromophores are separated by the comonomeric groups, which do not have the facility to photoconduct.

Chromophoric overlap, giving rise to photoconductivity, is seen in the fluorescence spectra of polymers such as PVK. This has been clearly demonstrated in the composition of copolymers of NVK with monomers such as fumaronitrile and maleic anhydride.[5,6]

EXPERIMENTAL

Reagents

N-Vinylcarbazole was supplied by Howson Algraphy Ltd. (Leeds). It was recrystallized from ligroin (60–80°C) and dried in vacuo at 35°C. The initiator, azobis(isobutyronitrile) (AIBN), was supplied by B.D.H. (Poole) and was recrystallized from methanol. The reaction solvent, tetrahydrofuran (THF) was distilled from lithium aluminum hydride.

Further, full details of the comonomers used, of the preparation of copolymers of NVK, and their compositional evaluations are given elsewhere.[7]

Fluorescence Measurements

The fluorescence spectra of the copolymers were measured on a Perkin-Elmer LS5 fluorimeter. Copolymer solutions were made up at a concentration of 30 mg/dm^3 in dry tetrahydrofuran. Spectra were measured at ambient temperature in the wavelength range from 190 to 500 nm in each case.

Photoconductivity Testing

The photoconductive behavior of the copolymers was tested as follows. In each instance, the copoly-
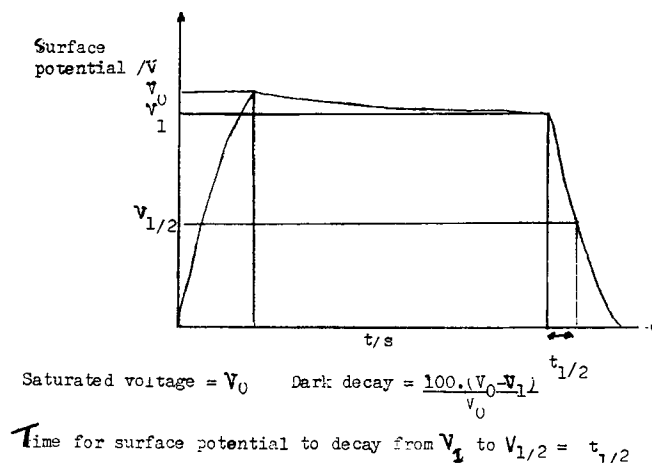

Figure 1 Saturated voltage, % dark decay and $t_{1/2}$ related to the charge analysis profile.

mer (1.00 g) was dissolved in 10 cm³ of a suitable solvent (methyl ethyl ketone, acetone, THF, etc.) together with the commercial cyanine, sensitizing dye, (1 cm³ of a ~ 1% w/w solution in methyl ethyl ketone) and 0.1 g of a film-forming agent, e.g., dodecylamine.

Each solution was filtered through a grade 4 sintered crucible. It was then spin coated at 70 rpm

onto an anodized aluminum sheet. When most of the solvent had evaporated (approximately 5 min), the plate was baked at 120°C for a further 5 min. It was then tested on a Princeton static charge analyzer.[8] Analyses were controlled and monitored by a Sirius computer.

Charge-decay profiles were recorded as follows. Each plate was charged to about 600 V over 10 s in

Table I Photoconductive Behavior of Some Copolymers of N-Vinylcarbazole with Comonomers Containing Carboxylic Acids or Anhydrides

| Comonomer	Ratio Feed	(NVK–Comonomer) Actual	Solvent	$t_{1/2}$/s
Acrylic acid	1 : 1	0.92 : 1	Acetone	8.0
Acrylic acid	2 : 1	1.19 : 1	Acetone	6.2
Acrylic acid	4 : 1	1.27 : 1	Acetone	3.4
Acrylic acid	10.1	1.47 : 1	Acetone	1.2
Methacrylic acid	1 : 1	0.76 : 1	Tetrahydrofuran	9.6
Methacrylic acid	2 : 1	1.25 : 1	Tetrahydrofuran	3.4
Methacrylic acid	4.1	1.35 : 1	Tetrahydrofuran	2.1
Methacrylic acid	10.1	1.52 : 1	Tetrahydrofuran	1.4
Itaconic acid	1 : 1	1.15 : 1	Ethanol	9.6
Itaconic acid	2.1	1.56 : 1	Tetrahydrofuran	7.5
Itaconic acid	4.1	1.98 : 1	Tetrahydrofuran	7.0
Itaconic acid	10.1	3.10 : 1	Tetrahydrofuran	1.2
Maleic anhydride	1 : 1	1.05 : 1	Methylethylketone	9.6
Maleic anhydride	2 : 1	1.15 : 1	Methylethylketone	9.6
Maleic anhydride	4 : 1	1.44 : 1	Methylethylketone	7.8
Maleic anhydride	10 : 1	1.19 : 1	Methylethylketone	4.2
Citraconic anhydride	1 : 1	0.57 : 1	Methylethylketone	9.6
Citraconic anhydride	2 : 1	0.69 : 1	Methylethylketone	9.6
Citraconic anhydride	4 : 1	0.75 : 1	Methylethylketone	9.6
Citraconic anhydride	10 : 1	0.59 : 1	Methylethylketone	9.6
Fumaric acid	1 : 1	1.19 : 1	Methylethylketone	9.6
Fumaric acid	2 : 1	1.45 : 1	Methylethylketone	9.6
Fumaric acid	10 : 1	5.80 : 1	Tetrahydrofuran	2.8

volts
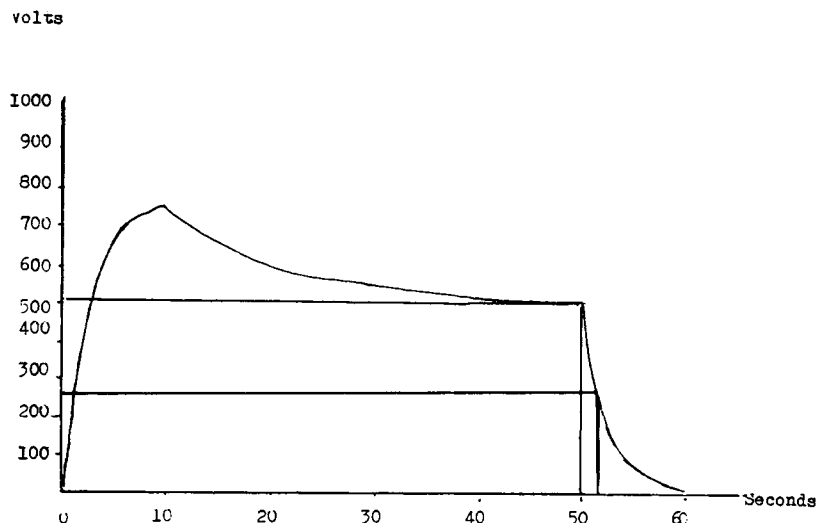
Figure 2 Charge decay profile for poly(NVK-co-acrylid acid) 1.47 : 1; $t_{1/2}$ = 1.2 s.

the dark by an electric corona. The charged plate was then left for 40 s to give a measure of charge leakage (dark decay). After this period, white light was shone on the plate, causing it to lose charge by photoconductivity.

Photoconductivity is measured in terms of the rate of decrease of the surface potential from the instant of irradiation of the plate with white light until the potential has reached half of its value at irradiation. The time taken for this decay, ($t_{1/2}$), is shown in Figure 1. Thus, a highly photoconductive sample will have a low $t_{1/2}$ (commercial materials have a value of 0.6–1.0 s). The maximum reading for this method is 9.6 s.

RESULTS

Various types of copolymer were synthesized over a range of monomer feeds. The actual copolymer compositions were calculated using nonaqueous titration of the acidic moieties and data derived from ultraviolet absorption studies for pendant carbazole, as detailed in an earlier work.[7] Relevant data, along with a measure of the photoconductive behavior, as shown by the $t_{1/2}$, are presented in Table I.

In Table I different solvents are given for different copolymers. This was to ensure total copolymer solution. In was noticed that different solvents were required for this, even for copolymers containing
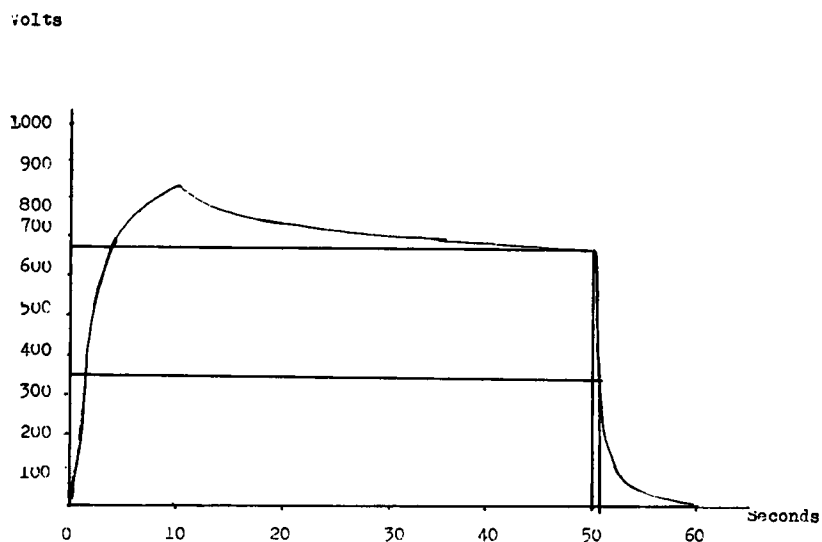
volts

Figure 3 Charge decay profile for poly(N-vinylcarbazole): $t_{1/2}$ = 0.4 s.

identical monomer pairs. Therefore, different morphologies may be associated with the different copolymer samples of the same original makeup.

Figures 2 and 3 show examples of charge-decay profiles, for the NVK–acrylic acid system and, as a comparison, for poly(NVK). They also indicate the value of $t_{1/2}$, giving a measure of the photoconductivity of the samples.

The variations of $t_{1/2}$ with copolymer composition are given in Figure 4 for a number of the NVK copolymer systems. For each series of copolymers, the plot shows a linear dependence of $t_{1/2}$ (and therefore photoconductivity) on percentage carbazole composition. The steeper the slope of the plot, the smaller the increase in NVK monomer feed needed

to give increased photoconductivity. In this respect the steepest slope is that of the poly(NVK-co-acrylic acid) series. Thus, for this system, sufficient alkali solubility may be endowed while maintaining a reasonable level of photoconductivity.[7]

For this reason the spectral properties of the poly(NVK-co-acrylic acid) system were further investigated by fluorimetry.

A range of poly(NVK-co-acrylic acid) samples was produced from mixtures of the two monomers in feeds whose molar ratios varied from 1 : 1 to 10 : 1 (NVK–acrylic acid). These feeds, on copolymerization, gave constitutions for the resultant copolymers from 0.92 : 1 to 3.41 : 1, respectively. The fluorescence spectra of the copolymers are given in
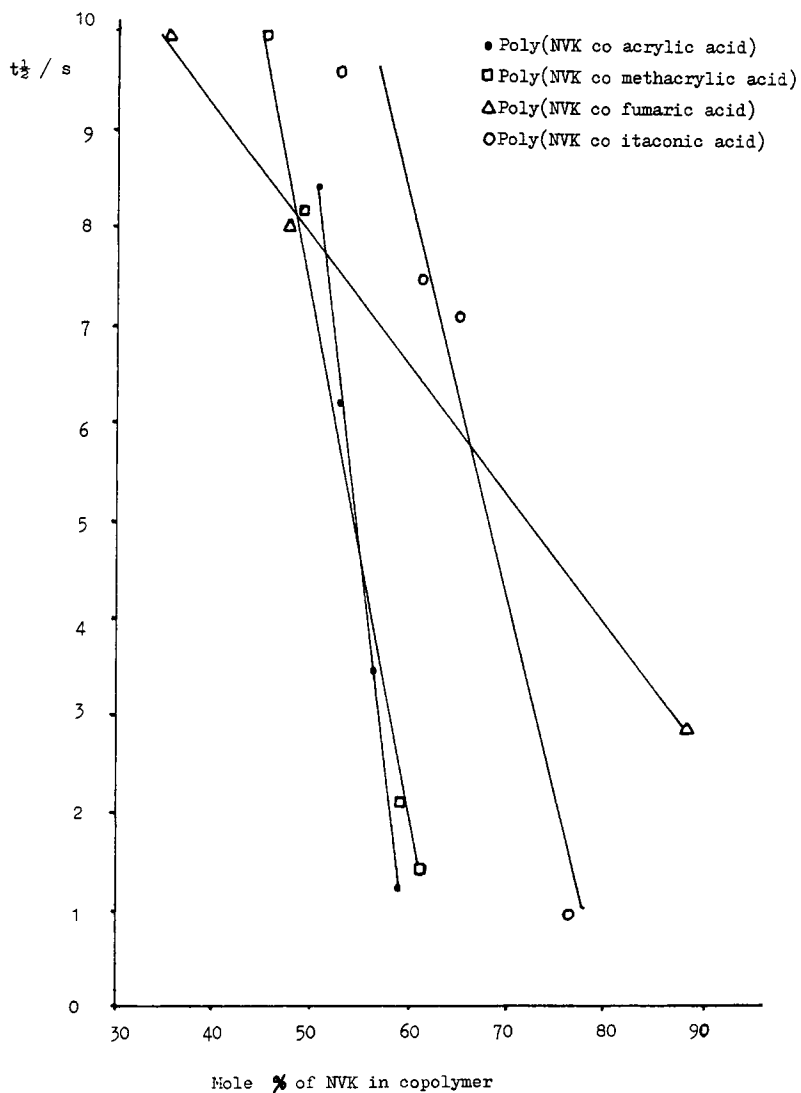

Figure 4   Variation in $t_{1/2}$ of several copolymers with their mol % N-vinylcarbazole.
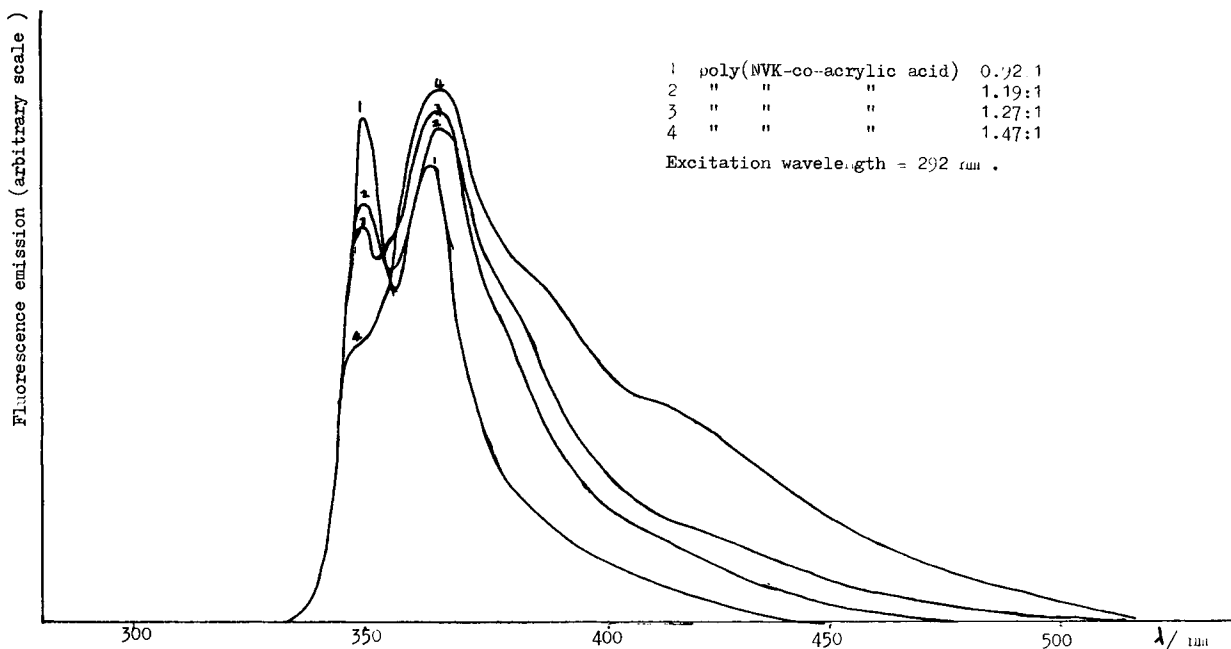
Figure 5 Emission spectra of copolymers of NVK with acrylic acid.

Figure 5. For comparison the fluorescence spectra of poly(NVK) and N-ethylcarbazole (NEC) are shown in Figure 6.

Chapiro has reported alternating features in copolycrylic acid system regardless of feed.[9,10] Shirota and Pearson both made similar observations for the poly(NVK-co-maleic anhydride) system.[11,12] However, as mentioned earlier, we have found that the poly-(NVK-co-acrylic acid) samples showed increasing photoconductivity with increase in their mole percentage of NVK. This could not happen with alternating copolymers as increased photocon-
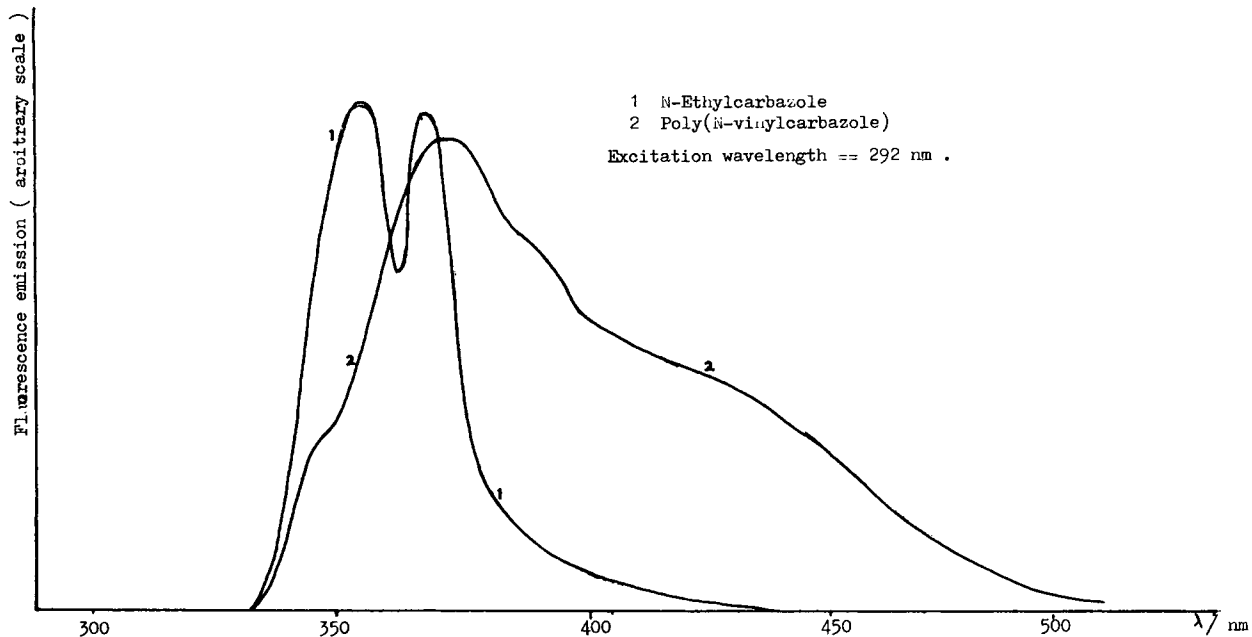

Figure 6 Emission spectra of N-ethylcarbazole and poly(N-vinylcarbazole).

ductivity indicates a greater continuity of carbazole units, more akin to a block copolymer situation. Figure 5 also shows that the fluorescence spectra differ with feed, indicating a change in the composition of the copolymers, becoming more like the homopolymer, poly(NVK), at higher NVK feeds.

DISCUSSION

As previously mentioned, photoconductivity in poly(N-vinylcarbazole) arises from chromophore overlap and subsequent hole transfer. It is suggested that this is only possible with copolymers of NVK if:

1. The intervening comonomeric units are small enough to allow chromophore overlap.
2. Long chains of homopolymeric PVK occur within the copolymer.
3. There is a large amount of interchain-chromophore, overlap-hole transfer as reported by Klopffer.[13]

Of these possibilities, the second is the most likely, since block copolymers of NVK have been synthesized.[14,15] Additionally, possibility 2 is suggested by copolymerization mechanism studies. Initiation pathways have been investigated for the poly(NVK-co-acrylic acid) system involving charge-transfer species, which may give rise to a cationic vinylcarbazole initiator and, thus, to blocks of PVK.

Taking possibility 2 as the most likely option, it is logical that the photoconductivity of the NVK-acrylic acid copolymers would vary linearly with the NVK–acrylic acid ratio. Chapiro reported a weak molecular complex between NVK and acrylic acid leading to alternating copolymers.[9,10] If this is correct, the photoconductivity of the copolymers would be constant throughout the monomer feed range.

The only alternating character to be seen arose with the use of equimolar monomer feeds. For copolymers derived from these feeds, the photoconductivity was low. These copolymers also show that photoconductivity is diminished by interspersing the carbazole units with small molecules such as acrylic acid, thus implying that the interchromophoric dis-
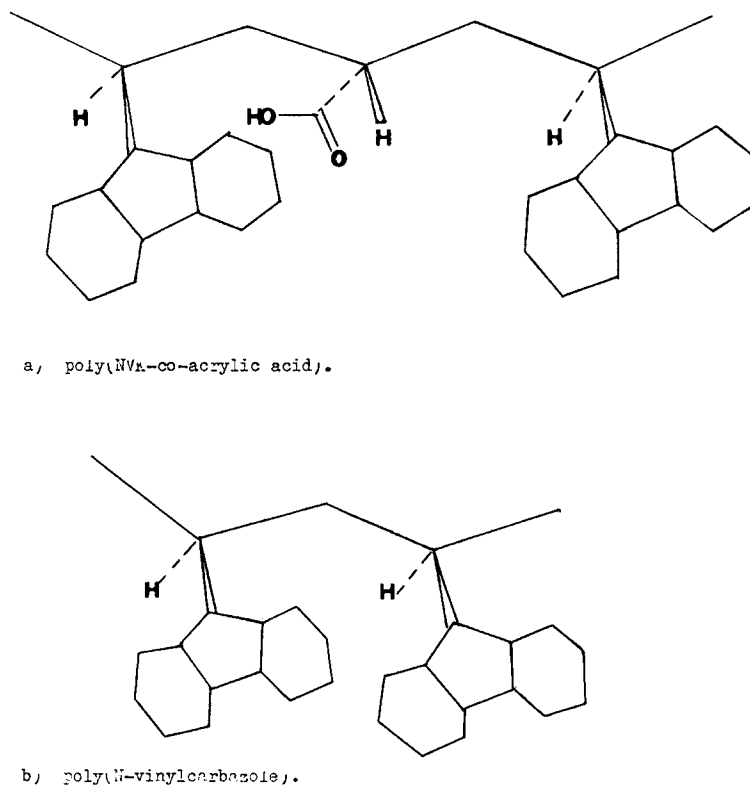

a) poly(NVK-co-acrylic acid).

b) poly(N-vinylcarbazole).

Figure 7 Separation of carbazole units by acrylic acid in poly(NVK-co-acrylic acid).

tance is too high for efficient overlap and hole transfer. The difference in interchromophoric distance in PVK and poly(NVK-co-acrylic acid) is shown schematically in Figure 7.

From a comparison of the fluorescence spectra of the poly(NVK-co-acrylic acid) samples with those of *N*-ethylcarbazole (NEC) and poly(*N*-vinylcarbazole) (PVK), Figures 5 and 6, respectively, it may be seen that there is a gradual change from NEC-like character for the alternating, equimolar feed copolymers to PVK character for the higher NVK feed copolymers. This appears as a growing shoulder in the spectra at around 420 nm, and the disappearance of the peak at 350 nm.

The shoulder at 420 nm occurs because of the existence of the so-called Sandwich excimer.[16-18] With lower concentrations of carbazole chromophores, as in the equimolar feed copolymers, these sandwich excimers will be reduced or may even be absent. The occurrence of such excimers will be more probable in copolymers of higher carbazole content.

The sandwich excimer is a feature of the photochemistry of PVK. It causes a loss of photoconductivity since it traps the charge carrier (hole) responsible for the phenomenon.

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