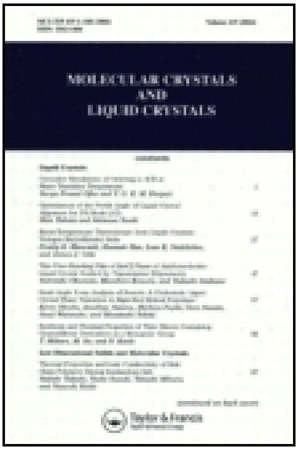

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Usability of Polymers Modified by Changing the Carbazole Group in the LEDs Devices

Jerzy Sanetra [a] , Stanisław Nizioł [b] & Jan Pielichowski [a]

[a] Krakow University of Technology, ul. Podchorazychl, 30 84, Kraków, Poland

[b] University of Mining and Metallurgy, Kraków, Poland

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Usability of Polymers Modified by Changing the Carbazole Group in the LEDs Devices

JERZY SANETRA[a], STANISŁAW NIZIOŁ[b] and JAN PIELICHOWSKI[a]

[a]*Krakow University of Technology, ul. Podchorazych1, 30 84 Kraków, Poland and*
[b]*University of Mining and Metallurgy, Kraków, Poland*

In order to find proper materials for making electroluminescent diodes electrooptics properties of polymers were investigated. Three polymer groups based on carbazole molecule were the subjects of the studies: PVK modified by substituting the acceptor group or donor group in the carbazole ring, poly-ω-(9-carbazolyl)alkyl methacrylates and copolimer ω-(9-carbazolyl)alkyl - methacrylates with 3-(2-metakryletoxy)carbonyl 7 diethylamincoumarin. Absorption and photoluminescent spectra of polymer in solution and films were measured. Electroluminescent diodes were obtained using the polymers mentioned above. Also, hole mobility was measured according to the distance between the carbazole group and the main chain.

Keywords: polymer; PVK; carbazole; photoluminescence; LED; electroluminescence

INTRODUCTION

Carbazole is a prototypical organic molecule that has shown a potential for technological applications. Polymers based on this molecule exhibits good electro- and photo-active properties on account of their high hole transporting mobility, strong absorption in the ultraviolet spectral region and blue light emission [1].

Poly(N-vinylcarbazole) (PVK) has been a research subject for number of years now. It displays a wide range of physical and chemical properties, which are interesting, as far as the basic research and applications are concerned. Furthermore it is stable and relatively easy to process.

In the xerographic industry the use of such polymers as photoconductive charge-transport layers has also been considered . Recently PVK has attracted attention in applications related to the organic light-emitting diode (LEDs) in which the emitting layer is formed by PVK itself or it is blended with other materials. Such systems have shown a remarkable increase in the luminescence efficiency as compared with those into which PVK was not incorporated [2].
However, thought a great deal has been published on the properties and behavior of PVK, there is only a limited number of papers on the synthesis and properties of other polymers in which the carbazolyl group is separated from the polymer backbone by two or more atoms [3].

The story of the light emission diodes made of polymer started in 1990 [4] with the report by a Cambridge group, which dealt with the light emission occurring when the voltage was applied to a thin film of the PPV polymer. Today, a lot scientific groups in the world perform polymer LED's studies. They use of great many methods to receive diodes emitting different colors with the better efficiencies and a longer lifetime. The progress made regarding the properties has required betterment of interdisciplinary approach in which chemists and physicist worked closely together. Research has been conducted so as to obtain new electroluminescent materials for the LED devices. It was discovered that such materials could be obtained in the number of methods, such as vacuum - sublimed low molecular weight compounds, conjugated polymers with chromophore in the main or in side chain as well as in a disperse form. The majority of these materials are hole transporting and therefore in most cases it is easier to inject holes than electrons. Requirements imposed on the materials, which show EL properties and which could be used in the LED structures are:

- they should be soluble and should have good film-forming properties (smooth films without pinholes and with thickness of 50 nm)
- they should have good thermomechanical stability
- they should be transparent in the visible region of the spectrum
- films should be amorphous
- they should not be degraded by the light

One-layer LED structures, with PVK as the optic active layer, emit blue light. However, their quantum yield is too small. Much better EL properties can be received when the PVK layers are mixed with other polymers, e.g. with a multiblock coplymer CNMBC [5]. The spectra of these blends vary from green to blue as the weight ratio of the components is changed. The new peak appears in EL emission spectrum that is not present in either of two components in their pure form. The formation of an exciplex between them is suggested. By using chromophore dyes doped in PVK LED white light emission can be obtained [6]. It can also be expected that introducing a donor or acceptor group to the aromatic carbazole ring will cause the electron density change in the carbazole ring and, thereby, the change in the electron structure of the π electrons. It will lead to the modifications in the absorption and luminescent spectra. Moreover, it should also alter the mobility of the holes injected from the anode to the polymer layer.

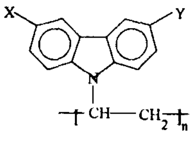
The hole conductivity of PVK is of a hoping type and it generally depends on the polymer's geometry, i.e. the degree of amorphism [7]. There is, however, no explicit description of the relations between the mobility and the electric field applied. The possibility of modifying the hole mobility is of enormous importance when it comes to creating host-guest layers for the LED structures in order to maintain the equilibrium between the number of the electrons and the holes in the optic active layer. Moving the carbazole ring away from the main chain through the alkyl group of different length should decrease the hole mobility. For PVK excimers are formed even in its solution. In the case of the moved away carbazole ring there appears a fluorescent spectrum, which is a distinctive feature of an individual molecule with a greater intensity than PVK. The paper will present the results of experiments on three different modified polymers based on the carbazole molecules which can be used in the optic active layers of the LED structures:

1. PVK modified by substituting the acceptor group (i.e. Cl) or donor group (i.e. $-O-CH_3$) in the position 3 or 3 and 6 of the carbazole ring (Fig. 1)
2. Poly-ω-(9-carbazolyl)alkyl methacrylates (Fig. 2a)
3. Copolimer ω-(9-carbazolyl)alkyl methacrylates and 3-(2-metakryletoxy)carbonyl 7 diethylamincoumarin (Fig. 2b)

EXPERIMENTS

Materials

Several derivatives of N-vinylcarbazole have been used in the synthesis of the new group of polymers showing electroluminescence property.



X=Y=H	PVK
X =Cl Y=H	P3ClVK
X = Y = Cl	P3,6ClVK
X =OCH Y=H	P3MVK
X = Y = OCH	P3,6MVK

FIGURE 1 Molecular structure of PVK, P3ClVK, P3,6ClVK, P3MVK and P3,6MVK.

The molecular weights of polymers were established in THF by gel permeation chromatography (Table 1) using polystyrene as a standard of mass and number average molecular weights.

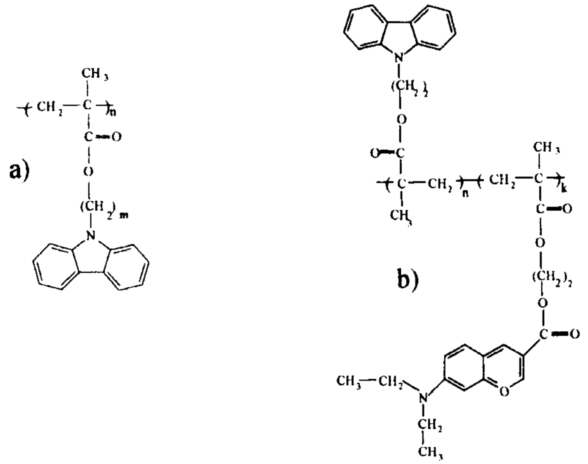


FIGURE 3 Molecular structure of polymers type poly[ω-(9-carbazolyl)alkyl methacrylates]. For m=2 - B2, m=4 - B4, m=5 - B5, m=6 - B6 (a); copolymer B2K1 (99% of mB2 and 1% of mK1) (b)

TABLE 1 Molecular weights of synthesized polymers

Polymer	Abbreviation	M_n	M_w
Poly(N-vinylcarbazole)	PVK	28 300	52 400
Poly(3-Cl-N-vinylcarbazole)	P3ClVK	23 200	48 700
Poly(3,6-diCl-N-vinylcarbazole)	P3,6ClVK	9 720	30 200
Poly(3-methoxy-N-vinylcarbazole)	P3MVK	5 600	11 200
Poly(3,6-dimethoxy-N-vinylcarbazole)	P3,6MVK	6 570	12 000

Four polymers, poly-ω-(9-carbazolyl)alkyl methacrylates, were obtained from D. Bogdal[8]. The alkyl spacers in the monomers were designed to contain 2, 4, 5 and 6 carbon atoms. The molecular weights were established as shown above (Table 2).

TABLE 2 Molecular weights of synthesized methacrylate polymers.

Polymer	Abbreviation	M_n	M_w
Poly[2-(9-carbazolyl)ethyl methacrylate]	B2	11 200	36 400
Poly[4-(9-carbazolyl)butyl methacrylate]	B4	12 500	34 300
Poly[5-(9-carbazolyl)pentyl methacrylate]	B5	12 900	28 500
Poly[6-(9-carbazolyl)hexyl methacrylate]	B6	12400	28 100

Copolymer was obtained by linking 2-(9-carbazolyl)ethyl methacrylate (MB2) with 3-(2-metakryletoxy)carbonyl 7 diethylamincumarine (MK1) [9]

Optical research

Spectrum research was carried out using spectrometer ORIEL MULTISPEC II. Light beams were brought to and from the sample through fiber optics. A xenon lamp was used as the source of light. A beam of monochromatic light, obtained using monochromator CARL ZEISS JENA, λ=340 was employed. The research on the photoluminescent spectrum was conducted not only for the polymers in the solutions of the tetrahydrofurane (THF) solvent but also for the polymers in form of films obtained using the spin-coating method on quartz. In order to enable comparisons between the fluorescence of the polymer solutions the spectral measurings in the THF solution were conducted in the quartz cuvette with the concentration selected so that the solutions would give the absorbance equal to 1. Taking into account the application possibilities of the explored polymers in the LED structures, structural experiments were conducted on the polymer films using the X-ray diffraction method. Their objective was to define the level of the amorphism of the layers.

LED preparation

Samples, except the polycarbazole, were prepared for the examination in a dry-box in an argon environment. The films were made from the THF 5mg/ml solution of the polymers by means of the spin-coating method. Polycarbazole was obtained directly on the ITO substrate from the solution. Metalic layers for the LED structures (ITO/polymer/Ca/Al) were prepared in the HVLS (PFEIFFER VACUUM) in the vacuum of $6*10^{-6}$ mbar.

RESULTS

PVK modified by the donor and acceptor groups.

Substituting an acceptor atom or a donor group in the position 3 or 3 and 6 shifts the absorption spectrum slightly towards the longer waves comparing to PVK and ethyl-carbazole spectra (see Fig. 3).

A profound change is observed in the case of the photoluminescence. Namely, substituting atoms of chlorine decreases the efficiency of the photoluminescence according to the number of chlorine atoms. When two of them are substituted the effect of heavy atom is visible, which causes the appearance of the triplet transition. Substituting the donor group - OCH_3 (metoxy) in the position 3 and/or 6 a greater shift of the absorption spectrum towards the longer waves (comparing to the chlorine atoms) is observed.

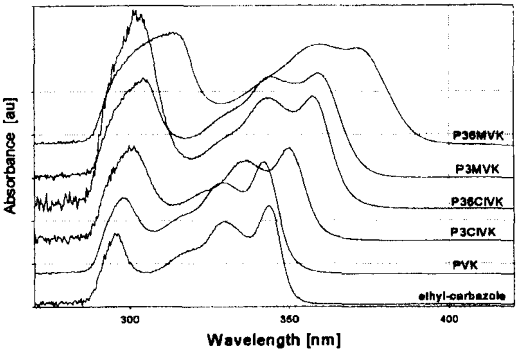


FIGURE 3 Absorption spectrum of the ethyl-carbazole, PVK, P3ClVK, P3,6ClVK, P3MVK and P3,6MVK.

Figure 4 shows the luminescent spectra created in the solutions. They were prepared in such a way that their absorptions are comparable. The figure clearly indicates that donor subsititutes in PVK lower the photoluminescence while acceptor substitutes almost eliminate it. Similar photoluminescent spectra were obtained for the films.

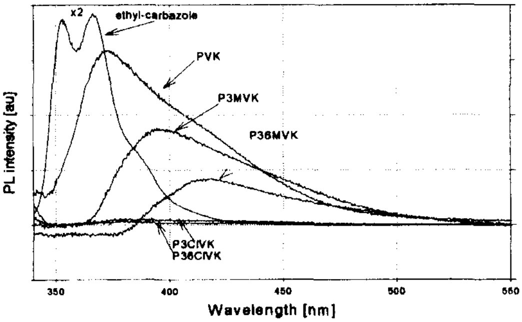


FIGURE 4 Phototoluminescence ethyl-carbazole, PVK, P3ClVK, P3,6ClVK, P3MVK and P3,6MVK.

Poly-ω-(9-carbazolyl)alkyl methacrylates

Four prepared polymers were the subject of investigation that was carried out in order to compare the photoluminescence properties of the methacrylates with PVK. The absorption spectra in the THF solutions are presented in the Fig. 5.

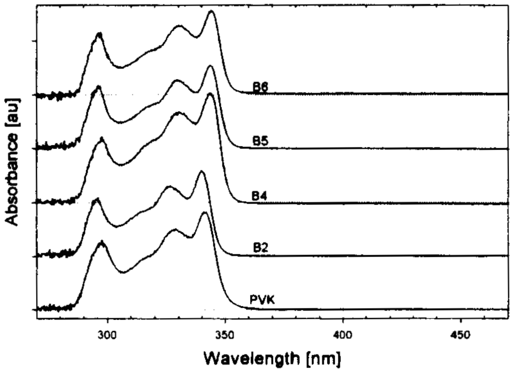


FIGURE 5 Absorption spectra for PVK, B2, B4, B5 i B6

After shifting the carbozolyl group away from the main chain absorption spectra change only slightly. The longer the alkyl chain the more the absorption spectrum of the polymer look like the spectrum obtained for the ethylocarbazole. In case of the fluorescent spectra (Fig. 6) exciton transitions of the S_1 - S_0 type with a clear vibration structure are visible.

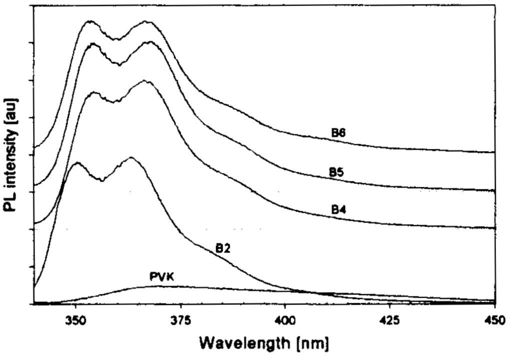


FIGURE 6 Phototoluminescence of, PVK, B2, B4, B5 and B6

Such a structure is not visible in case of PVK, what is indicated by the creation of the excimers [5]. For all examined polymers a clear increase in the intensity of the fluorescent spectrum, according to PVK, is seen and it is on about the same level as the photoluminescence of the ethylcarbazole.

Solid state photoluminescence spectra were measured for polymer films that were a few micrometers in thickness. They were slightly shifted towards the longer waves in comparison with the solutions. Vibration maximums, which can be ascribed to the exciton transitions, are also observed. However, in the solid state excimer transitions are not seen, unlike in PVK, for which only eximer transitions are observed.

Copolymer B2K1

Absorption spectra of the B2 solution, B2K1 copolymer and MK1 monomer are presented in the Fig. 7. As it is shown, the absorption spectrum of B2K1 copolymer is a sum of the absorption of B2 polymer and MK1 monomer. A similar absorption spectrum is observed for the examined film samples with a small shift towards the long waves (2 - 3 nm). The results of the photoluminescence experiments are presented in the figures 8 and 9.

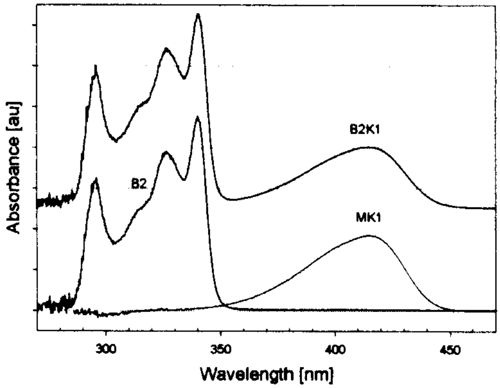


FIGURE 7 Absorption spectrum of B2, MK1 and B2K1.

For the solutions as well as for the films a profound influence of monomer MK1 is indicated in spite of its low content in the copolymer (1 % of the weight). In the solution photoluminescence of the copolymer creates emission spectrum consisting of the B2 polymer and MK1 monomer emissions. In the solid state only light emission from MK1 monomer for λ=465 nm can be observed.

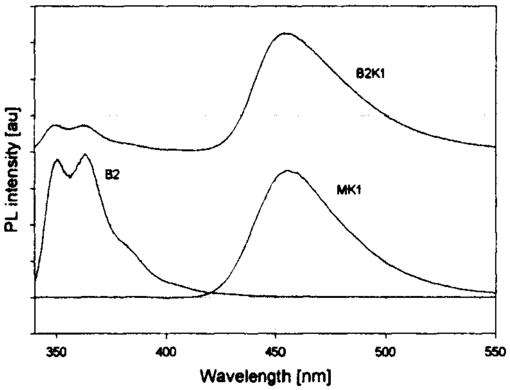


FIGURE 8 Photoluminescence of B2, MK1 and copolymer B2K1 in solution.

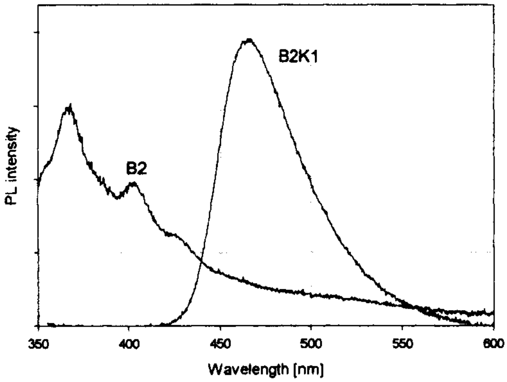


FIGURE 9 Photoluminescence of B2 and copolymer B2K1 in films.

Electroluminescence

For all polymers one-layer LED structures (ITO/polymer/Ca/Al.) were created. The results for same of them are presented in Fig. 10. Shifting the carbazole group away form the main chain moves the emission towards shorter waves, even in UV. Comparing the results of photoluminescence and electroluminescence examinations it can be stated that in case of B2 polymer both excimer and exciton transitions are observed. The spectrum of the diode made of B2K1 copolymer is dominated by the MK1 monomer.

Measurements of the dependence of I(U), EL(U), and EL(I) (Fig. 11) were done. The received results are characteristic for the LED structures [10].

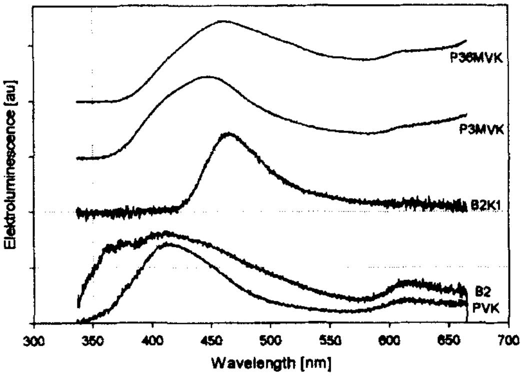


FIGURE 10 Elektroluminescence spectra of polymers

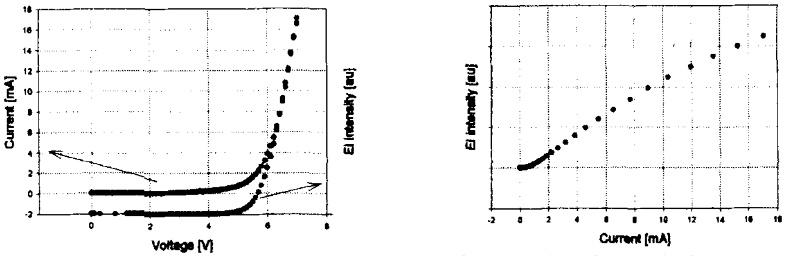


FIGURE 11 *I-V*, *EL-V*, and *EL-I* for ITO/P36MVK/Ca/Al LED device.

Measuring hole's mobility

It was conducted on PVK, B2, B4, B5, B6 polymers and B2K1 copolymer. To do so ITO/polymer/Au was created as a hole device. Mobility was evaluated basing on the model SCLC (Space Charge Limited Current) defined by the equation[11]:

$$I = 9\varepsilon_0\varepsilon_r\mu S V^2 (2L)^{-3}$$

where: I - the current; V - the voltage applied; $\varepsilon_0\varepsilon$ - the permittivity of the polymer; S - the area; L - the thickness of the device; μ - the mobility

The results are presented in the table 3.

TAB. 3 Hole mobility of polymers

Polymer	Mobility 10^{-8} cm/(V*s)
PVK	50
B2	27
B4	9.2
B5	5.8
B6	4.3
B2K1	1.5

X-Ray results

The measurements of crystalinity of PVK and its derivatives were investigated by the X-ray diffraction method. In the diffraction patterms only diffuse scattering is observed for derivatives, see Fig 12.

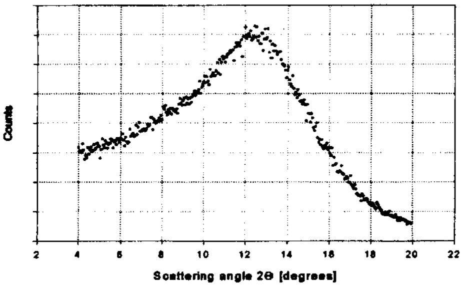


FIGURE 12 X-ray diffraction pattern for B2 polymer

For pure PVK the additional broad peak at $2\theta = 8^\circ$ (λ_{Cu} =0.154014 nm) and the amorphous hallo appears. It can be said that the short range ordering of the chain polymer exist and also, that it agrees with the results obtained elsewhere[12, 13]. Griffiths [14] pointed out that the degree of crystallinity in PVK strong depends on the molecular weight and it decreases together with the molecular weights decrease. Below M_n = 46 000 the crystalinity is not observed, and it increases sharply in the range of the molecular weight between 46 000 and 157 000. In our case, molecular weights of PVK and its derivatives are smaller than M_n = 46 000. On the other hand, it seems that shifting away the carbazolyl group from the main chain make it difficult to crystallize the polymers.

DISCUSSION

The samples used have relatively small molecular weight what ensures better possibilities of creating amorphous layers.

Shortness of the chain causes the decrease in the mobility of the holes which is beneficial, as well. Moreover, such decrease was obtained by shifting the corbazolyl group away from the main chain. It also creates light emission that comes from the exciton excitation what is shown in the Fig.10 dealing with the electroluminesce of the B2.

Introducing MK1 monomer in the copolymer generates a situation where the photoemission of the carbazolyl group in B2K1 greatly decreases while the MK1monomer emits huge light. On the other hand, it is only MK1 monomer that creates electroluminescence.

On the grounds of the Fig. 4 presenting PVK, P3ClVK, P3,6ClVK, P3MVK and P3,6MVK it can be stated that substituting an acceptor group in the carbazole lowers greatly the intensity of the light, especially in comparison with the case when a donor group is being substituted. The donor group not only shifts the exicimer spectrum of the photo- and electroluminescence towards the longer waves but also creates light emission around 600 nm if the excitation is generated by the electric field.

To sum up it can be said that polymers based on the carbazole group could be used as a layer transporting holes and as a polymer matrix in a structure of a host-guest type.

Furthermore, modification of polymers based on carbazole offers many possibilities of regulating the hole mobility, which is extremely important when it comes to creating multilayer EL diodes.

Acknowledgments

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