

Absorption spectra of poly-*N*-vinylcarbazole derivatives by experiment and simulation

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Abstract

Geometry molecular optimization and quantum chemical simulations of absorption spectra for newly synthesized poly-*N*-vinylcarbazole derivatives were performed using a semi-empirical approach. The studied polymers were modified by changing the positions of the carbazole group with respect to the polymer backbone. The absorption spectra were calculated for different numbers of PNVK monomers. A sufficient agreement between the calculated and experimentally measured spectra was observed. A change of the red shift absorption with respect to the blue shift was observed for cases when the number of monomers was higher than 4. The theoretical simulations indicate that this behavior is a consequence of the specific molecular structure of the considered molecules. The results demonstrate the potential of combined simulation and experimental studies in materials engineering and searching of new electroluminescent materials.

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1. Introduction

The derivatives of poly-*N*-vinylcarbazole (PNVK) are promising polymeric materials for electroluminescent devices, dynamic holography, light emitting diodes, displays etc. [1–3]. PNVK has good thermal stability and optical activity. The glass transition temperature (T_g) of this polymer is about 500 K, which is the highest among known vinyl polymers [4]. Based on this high T_g value PNVK may be good polymer matrix for the organic chromophores [5–7], including photoconductors [8]. A search of the appropriate substitution of the particular chromophore groups is the main strategy for the creation of modified PNVK with enhanced opto-

electronic features. However, the wide use of this polymer in industry is hampered by the lack of systematic studies regarding the origin of the electron absorption. Particularly, it is important to study the occurrence of a possible shift of the absorption edge versus the number of monomers for different chemical substitutions. To know this it is necessary to perform quantum chemical calculations of the HOMO and LUMO levels as well as of the corresponding dipole moments. These parameters are crucial for the estimation of the applicability of these materials and for recommendations for the technologists synthesizing the materials. The absorption spectra give important information concerning the quantum chemical states and may serve as a powerful tool for understanding the nature of the observed absorption and related luminescence. At the same time, these calculations may give an advice for directed changes of the absorption using appropriate substitution chemistry.

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In the present work, we modify the structure of PNVK by shifting the position of the carbazole group with respect to the polymer chain. Experimental spectra are compared to the theoretically calculated by the quantum chemical methods. The synthesis and notation of the investigated materials are presented in Section 2. In Section 3 the calculations are described in details. The Section 4 is devoted to discussion of the obtained results.

2. Polymer synthesis

Four monomers, ω -(9-carbazolyl)alkyl methacrylates, were prepared from 9-(ω -bromoalkyl)carbazoles and sodium salts of methacrylic acid by a method described in Ref. [9]. The starting compounds for the synthesis of the monomers (e.g., 9-(bromoalkyl)carbazoles) were obtained by the alkylation reaction of carbazole with an excess of α . The alkyl spacers in the monomers were designed to contain 2, 4, 5 and 6 methylene groups, respectively. In order to purify and separate the monomers from the starting materials (9-carbazolyl)alkyl methacrylates were recrystallized several times from ethanol, while others were subjected to column chromatography. The synthetic route for the preparation of the monomers is depicted in Fig. 1. Subsequently, ω -(9-carbazolyl)alkyl methacrylates were polymerized by using AIBN (1 mol%) as an initiator in toluene in ampoules at 333 K for 48 h. The polymers were precipitated from methanol and purified by repeated precipitated from THF solution into methanol. The molecular weights of all polymers were established in THF by gel

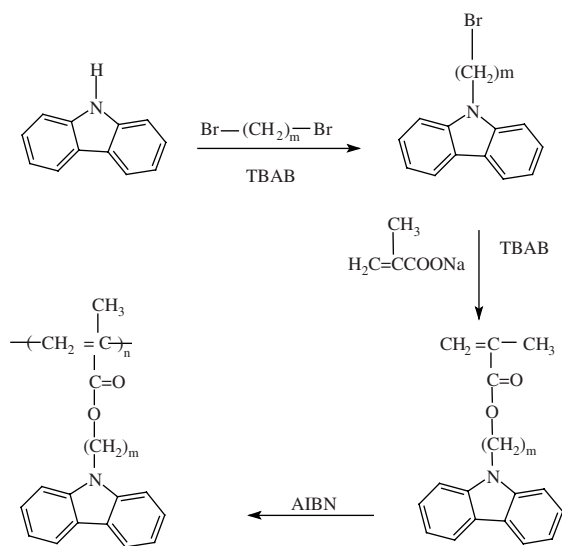


Fig. 1. General scheme of synthesis.

Table 1

Molecular weights of the methacrylate polymers used in this study

Polymer	M_n (g/mol)	M_w (g/mol)
Poly[2-(9-carbazolyl)ethyl methacrylate]	11,200	36,400
Poly[4-(9-carbazolyl)butyl methacrylate]	12,500	34,300
Poly[5-(9-carbazolyl)pentyl methacrylate]	12,900	28,500
Poly[6-(9-carbazolyl)hexyl methacrylate]	12,400	28,100

permeation chromatography (GPC) by using polystyrene as a standard to mass and number average molecular weights shown in Table 1.

3. Theoretical simulations

The probability P of transition from electronic ground j to excited k state is proportional to the density of radiation $\rho(\omega_{jk})$ and to induced Einstein coefficient B_{jk} :

$$P = B_{jk}\rho(\omega_{jk}) \quad (1)$$

The Einstein coefficient is expressed by equation:

$$B_{jk} = \frac{8\pi^3}{3h^2} |(\mu)_{jk}|^2 \quad (2)$$

where $(\mu)_{jk}$ is a transition dipole moment described by

$$(\mu)_{jk} = i\hbar \int \Psi_j^* \vec{\nabla}_r \Psi_k dV \quad (3)$$

where Ψ_j and Ψ_k are wave functions of j and k energy levels, respectively; $i\hbar \vec{\nabla}_r$ is a transition dipole momentum operator of molecule.

The intensity of absorption during the calculations was expressed by the formula:

$$I(\omega) \approx \omega \sum_{k=1}^n \frac{\sum_{i=x,y,z} |\langle \Psi_{j_i} | \vec{\nabla}_r | \Psi_{k_i} \rangle|^2}{(\omega - \omega_k)^2 + (\frac{\Gamma}{2})^2} \quad (4)$$

where n is number of excited states. Γ determines the Gaussian line shape widening and ω is the frequency of the incident electromagnetic radiation.

The geometry optimization and the calculations of electronic structure for separated molecules were performed by a semi-empirical quantum-chemical method with the PM3 approach [9]. In order to optimize the molecular geometry the GAMESS quantum chemical program was used [10]. The single state calculations have given a possibility to obtain the minimum of the total energy as well as the corresponding optimized molecular structure. As a criterion of self-consistent

Table 2
Optimized parameters of ethylocarbarol, B2, B4 and B6 molecules for selected atoms (for atom identification see Fig. 5)

	Ethylocabrazol	B2	B4	B6	PNVK 2 monomers	PNVK 3 monomers	PNVK 6 monomers
Bonds [Å]							
I _N –I _C	1.44	1.42	1.44	1.44	1.44	1.44	1.44
I _N –II _C							
I _C –IX _C	1.42	1.45	1.42	1.42	1.42	1.42	1.42
II _C –X _C							
I _N –IV _C					1.49 1.47	1.49 1.49	1.48 1.48
	1.48	1.43	1.48	1.45		1.47	1.48 1.49 1.47
VII _C –VI _O	–	1.23	1.21	1.21	–	–	–
Improper dihedral [°]							
II _C –I _N –III _C (IV _C)					146.79 145.14	148.94 141.59 145.39	147.93 149.68 149.21 142.34 144.95
	140.75	153.22	146.72	145.57			

iteration convergence, for the molecule geometry optimization and electronic structure calculation we have chosen the energy convergence of about 2×10^{-8} eV, which corresponds to the model error. The atomic position optimized by these methods are presented in the Table 2.

The electronic spectra were calculated by the configuration interaction (CI) method with the orbital criterion three occupied and three unoccupied orbitals, by assuming the excitation of single excited states [10]. The CI give additional levels below LUMO levels. The calculated parameters are presented in the Tables 3–6.

Table 3
Calculated properties of ethylocarbarol, B2, B4 and B6 molecules

		Ethylocabrazol	B2	B4	B6
Static dipole moment	μ_x [D]	0.32	1.84	1.30	0.78
	μ_y [D]	–1.02	–1.66	–1.36	–0.27
	μ_z [D]	–0.73	0.95	–1.77	–2.54
μ [D]		1.29	2.66	2.58	2.67
E_{HOMO} [eV]		–8.40	–8.20	–8.35	–8.38
E_{LUMO} [eV]		–0.29	–0.28	–0.28	–0.30
ΔE [eV]		8.11	7.29	8.07	8.30
First excited state [nm]		415.2	424.8	419.6	418.8
First excited state permissible for transition [nm]		327.6	339.9	330.0	329.5
		348.1 ^a			
E_{tot} [eV/at]		–3.84	–4.22	–4.02	–3.86

^a Experimental data.

Table 4
Partial charges of selected atoms of ethylcarbazol, B2, B4 and B6 molecules

Atom	Ethylcarbazol charge	B2	B4	B6
I _N	0.161	0.232	0.173	0.172
II _C , III _C	-0.095	-0.115	-0.095	-0.098
IV _C	-0.075	-0.145	-0.083	-0.084
VO	-	-0.262	-0.263	-0.271
VI _O	-	-0.384	-0.379	-0.377
VII _C	-	0.368	0.368	0.372
VIII _C	-	0.043	0.076	0.074

4. Results and discussion

The calculations performed have shown that all considered carbazole group are planar and the structure of two benzene rings is very stable. During the modification (substitution of different molecular groups) of the carbazole to obtain the **B2** sample only the geometry of pirole groups is slightly changed (see Table 2). Comparing the molecular geometry of **B2** to the **B4**, **B6** and ethylcarbazole groups, the C=C bonds in the pirole group become longer and the C–N bonds become shorter. The geometry of the carbazole group is not changed during simulations of the PNVK chain. The geometry of the carbazole group of **B2** is completely different compared with other **B** samples, ethylcarbazole and the PNVK polymer, respectively. The improper dihedral angle between the carbazole groups and the chain of polymer vary from 145–149 Å for ethylcarbazole, **B4**, **B6** and the PNVK polymer. The improper dihedral angle is higher for the **B2** sample compared

Table 6
Calculated properties of B4 molecule

	1 monomer	2 monomers	5 monomers
μ_x [D]	1.30	2.13	1.95
μ_y [D]	-1.36	-2.36	-2.20
μ_z [D]	-1.77	-1.21	-1.65
μ [D]	2.58	3.40	3.37
E_{HOMO} [eV]	-8.35	-8.32	-8.36
E_{LUMO} [eV]	-0.28	-0.30	-0.49
ΔE [eV]	8.07	8.02	7.87
First excited state [nm]	419.6	373.9	370.6
First excited state permissible for transition [nm]	330.0	295.4	293.7
E_{tot} [eV/at]	-4.02	-4.09	-4.13

with the other samples. The **B2** molecule is the most planar-like. During the building procedure the PNVK polymer changes its geometry. With increasing the number of monomers *N* the molecule become more linear (Fig. 2).

The geometry of the carbazole group changes the electronic properties of **B2** samples. The **B2** molecule has the lowest HOMO–LUMO splitting. The HOMO and LUMO energies are originated from the atomic orbital energies of the carbazole group and agreed well with experimental data. Comparing the absorption spectra for carbazole and ethylcarbazole obtained from experiments one can say that only the carbazole group

Table 5
Calculated properties of PNVK

	1 monomer (ethylcarbazol)	2 monomers	3 monomers	4 monomers	6 monomers	10 monomers
μ_x [D]	0.32	-0.32	-0.27	0.28	0.80	-0.99
μ_y [D]	-1.02	-1.12	0.22	0.48	1.08	0.64
μ_z [D]	-0.73	-0.36	-0.48	-1.34	-0.98	0.75
μ [D]	1.29	1.22	0.60	1.45	1.66	1.40
E_{HOMO} [eV]	-8.40	-8.39	-8.42	-8.35	-8.39	-8.15
E_{LUMO} [eV]	-0.29	-0.37	-0.37	-0.50	-0.51	-0.62
ΔE [eV]	8.11	8.02	8.05	7.85	7.88	7.53
First excited state [nm]	415.2	373.3	369.5	363.3	222.3	229.8
First excited state permissible for transition [nm]	327.6	296.4	296.3	292.3	222.0	229.8
	348.1 ^a					345.3 ^a
E_{tot} [eV/at]	-3.84	-3.95	-3.99	-4.01	-4.03	-4.06

^a Experimental data.

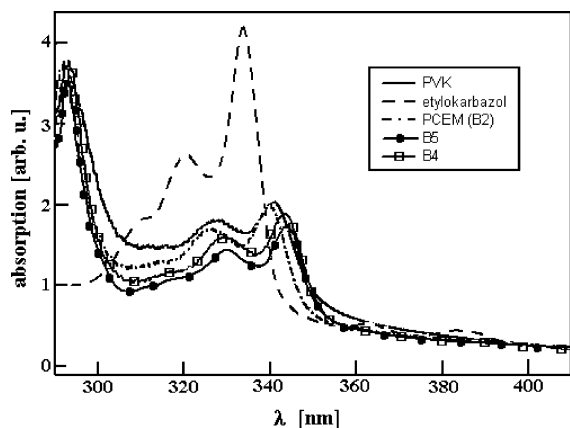


Fig. 2. Typical experimental absorption spectra of the different PNVK derivatives.

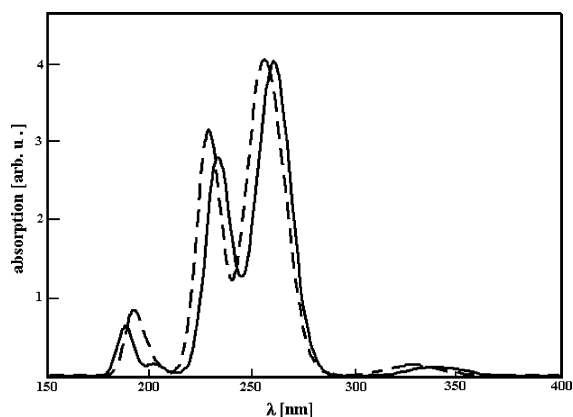


Fig. 3. Calculated spectra of the **B2** (—) and the **B4**, **B6**, ethylocarbazol (---).

has influence on the absorption. The shift of the absorption spectrum for the **B2** molecule may be related with the specific geometry of the pirole group (Fig. 3).

The values of the total energy minima were varied at around 4 eV/atom. The comparison with the Austin method (AM1) [10] gives the similar result. The value of the total energy per atom become saturated for $N = 10$ monomers of PNVK polymer (Table 5). The same result is obtained for **B4** polymer (see Table 4). The most stable is the **B2** monomer (Table 3).

From the Tables 3, 5 and 6 one can see that the energy distance between the first excited (CI) state and the LUMO level is varied within the 2–6 eV range. Thus, one can calculate that the first excited state will play a crucial role in the absorption spectra of the investigated molecules. The CI excited spectra and corresponding transitions dipole moments for the in vacuo molecules were calculated by a method described above and are

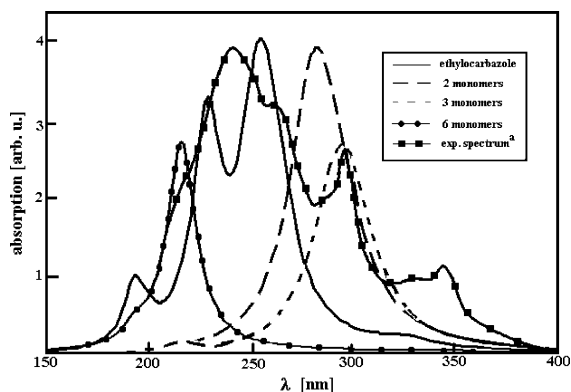


Fig. 4. Calculated spectra of the PNVK composed on different number of monomers and experimental spectrum of powder PNVK from cited work [12].

given in the Tables 3, 5 and 6. From these tables, one can see that no simple rule (correlation) can be observed between ground states, transition dipole moments and the structure of the molecule. This result indicates non-linear exchange-correlation effects contributing to the total Hamiltonian.

In Fig. 4 theoretically simulated absorption spectra are presented for PNVK with different number of monomers N simulated by the method described above. The molecular geometry of the carbazole group inside every monomer is very stable and it does not show any influence on the shift of the absorption edge. For $N = 10$ the absorption spectrum looks like that for the $N = 6$, i.e. one may observe a saturation. This is in a good agreement to the results obtained in Ref. [11–13]. The absorption maximum is red-shifted for $N = 2$ and 3 and for $N > 4$ monomers it is blue-shifted. This is an additional consequence of the geometry of the polymer chain. Several discrepancies between the calculated and

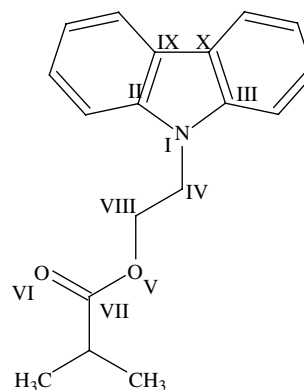


Fig. 5. Identification of selected atoms for ethylocarbazol, **B2**, **B4**, **B6** molecules.

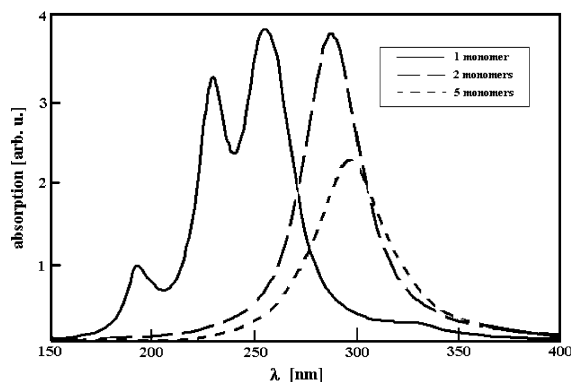


Fig. 6. Calculated spectra of the different numbers of **B4** monomers.

experimental spectra reflect a contribution of the intermolecular interaction. The experimental spectrum of the PNVK powder has an absorption threshold at about 360 nm, absorption peaks at about 345, 330, 295 and 260 nm respectively and a shoulder at 220 nm. This experimental spectrum can be constructed from the theoretically evaluated spectra for different numbers of monomers. In Fig. 6 the theoretical spectra are presented, obtained for different N in the **B4** monomers. The increase of N favors a red shift for the first UV-absorption maximum. This is a qualitative agreement with the observed experimental data.

5. Conclusions

Theoretical molecular geometry optimization and quantum chemical calculations for PNVK with different N (degree of polymerization) have shown that the molecular geometry of the carbazole group inside every monomer is very stable and it does not cause any shift of the absorption edge. For the number of monomers N higher than 6 both theoretical simulated as well as the experimental absorption measurements have shown a saturation. The absorption maximum is red-shifted for the $N = 2$ and 3 and for $N > 4$ it is blue-shifted. This is a

additional consequence of the specific molecular geometry of the polymer chain. PM3 and AM1 semi-empirical methods demonstrate a good agreement. Simultaneously there is no simple rule (correlation) observed between ground state dipole moments, transition dipole moments and the structure of the molecule. Comparing the absorption spectra for carbazole and ethylcarbazole obtained from the experiment one can see that only the carbazole group influence the absorption. The shift of the absorption spectrum for the **B2** molecule may be related with the specific geometry of the pirole group.

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