

Synthesis and photochromic properties of poly[*N*-vinyl-2-(phenylazo)-imidazole] derivatives in the near UV range*

M. KOSZYKOWSKA**, M. TOKAREK, S. KUCHARSKI

Wrocław University of Technology, Faculty of Chemistry,
Wybrzeże Wyspiańskiego 50-370 Wrocław, Poland

The following novel photochromic poly(*N*-vinylimidazole) polymers have been synthesized: poly[*N*-vinyl-2-(4-cyano-phenylazo)imidazole] (PV-4-CBAI), poly[*N*-vinyl-2-(3-cyano-phenylazo)imidazole] (PV-3-CBAI) and poly[*N*-vinyl-2-(4-methoxy-phenylazo)imidazole] (PV-4-MBAI). Quantum chemical calculations of monomeric chromophores were carried out to foresee their linear and nonlinear optical properties. The polymeric materials were characterized by UV-vis spectroscopy and ellipsometry to determine changes in their properties during illumination. It was found that the stable *trans* form of polymeric chromophores absorbed in the range of 360–380 nm (absorption band maximum) and underwent *trans-cis* isomerization on illumination with 395 nm light. The ellipsometric measurement showed a change of the refractive index of polymer films during illumination, which was in the range of 0.010 to 0.014, depending on chromophore type.

Key words: *photochromic polymers; 2-(phenylazo)imidazole; trans-cis photoisomerization; ellipsometry*

1. Introduction

The polymers containing azobenzene groups have been widely studied due to their potential applications in optical data storage, surface relief grating formation and as optoelectronics switches [1–3]. The photochromic azo compounds show reversible *trans-cis* isomerization upon irradiation with light. The reverse *cis-trans* process is realized thermally (thermal relaxation) or on illumination with light. During illumination, the chromophores show reversible changes in their molecular properties such as geometrical structures, electric permittivities, absorption and fluorescence spectra, and refractive indices. The changes in chemical and physical properties during irradiation have been widely employed in optics and optoelectronics [4–9].

*The paper presented at the 11th International Conference on Electrical and Related Properties of Organic Solids (ERPOS-11), July 13–17, 2008, Piechowice, Poland.

**Corresponding author, e-mail: maria.koszykowska@pwr.wroc.pl

The papers dealing with isomerization of azo compounds mainly referred to the compounds containing six-member aromatic rings on both sides of the diazo group and distinct electron donor functional group on one side of the molecule, and a strong electron acceptor group on its opposite side. Such chromophores, particularly those containing $-\text{NO}_2$ or $-\text{CN}$ acceptor groups, showed an absorption maximum at ca. 460–485 nm.

In this work, the main attention was focused on the synthesis of novel poly [*N*-vinyl-2-(phenylazo)imidazole] derivatives. Phenylazoimidazoles belong to analogues of azobenzene which have a heterocyclic ring instead of the phenyl group. The presence of the five-member heterocyclic ring has an effect on photochromic properties of the material, shifting the maximum of the absorption band to shorter wavelengths [8–13]. The main goal of this work was to obtain chromophoric polymers having the maximum of the absorption band in the near UV range. The presence of a five-member ring in the chromophore fragment was expected to be helpful in this context. The change in the properties of poly [*N*-vinyl-2-(benzoazo)imidazoles] on *trans*–*cis* photoisomerization were to be evaluated with the help of UV-vis spectroscopy and ellipsometry.

2. Materials and methods

Materials. *N*-vinylimidazole monomer (Aldrich) was distilled under vacuum before use. 2,2'-Azobisisobutyronitrile, AIBN, (Fluka) initiator was recrystallized twice from methanol. Benzene (POCH, Gliwice) as a solvent was dried over metallic sodium chips and distilled before use. 4-Aminobenzonitrile, 3-aminobenzonitrile, 4-methoxyaniline (Aldrich) were reagent grade quality and were used as received. Poly(*N*-vinylimidazole) was prepared by a reported procedure [14, 15]. The route of synthesis is shown in Fig. 1. Polymerization was carried out in benzene solution at 70 °C with AIBN as an initiator in nitrogen atmosphere. After 24 h of polymerization, the product was separated by filtration and dried. Yield: 87%. T_g : 171.7 °C. $^1\text{H NMR}$ (DMSO- d_6): 1.93 (s, 2H, $-\text{CH}_2-$), 2.46 (d, 1H, $-\text{CH}-$), 6.95 (m, 2H, in imidazole ring, $-\text{CH}=\text{CH}-$), 7.09 (m, 1H, in imidazole ring, $-\text{N}=\text{CH}-$).

The synthesis of poly [*N*-vinyl-2-(4-cyano-phenylazo)imidazole] (PV-4-CBAI) was carried out according to the route shown in Fig. 1 [16–18]. To the HCl solution (15 cm³, 1 M) of 4-aminobenzonitrile (1.30 g, 0.011 mol) under ice-cold conditions (0–5 °C) the aqueous solution of NaNO₂ (0.80 g, 0.012 mol) was added dropwise under stirring. This mixture was stirred at low temperature for a period of 1 h. Then diazotized solution was added in drops to a solution of poly(*N*-vinylimidazole) (1.30 g, 0.011 mol) in methanol (15 cm³) and aqueous solution of Na₂CO₃ (2.00 g in 15 cm³ water) at 0–5 °C. This solution was stirred for 2 h and then was kept at low temperature for several hours. The solution was basic in nature. Cold HCl (1 M) was added in drops to reach pH = 7. The precipitate was filtered off, washed and dried. Yield: 92%. T_g : 131.8 °C. $^1\text{H NMR}$ (DMSO- d_6): 1.85 (s, 2H, CH₂), 2.90 (s, 1H, CH), 6.83 (s, 2H,

CH in imidazole ring, $-\text{CH}=\text{CH}-$), 7.63 (d, 2H, $-\text{CH}-$, in benzene ring), 7.94 (d, 2H, $-\text{CH}-$, in benzene ring).

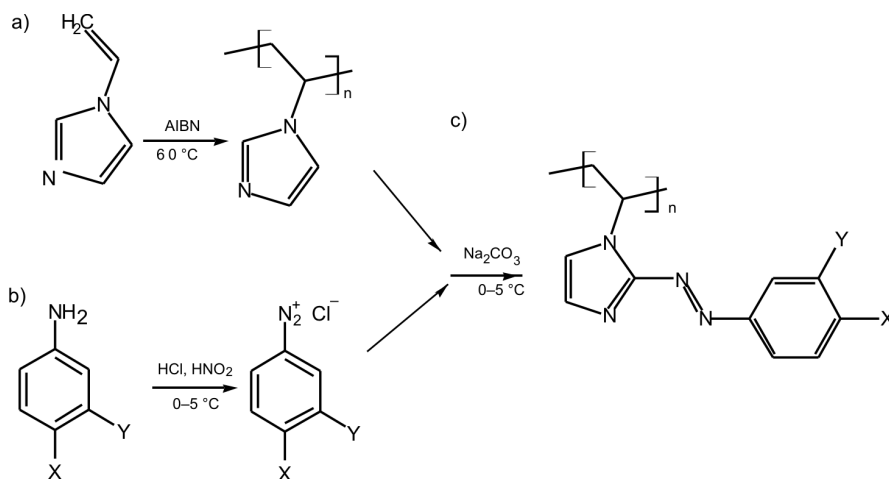


Fig. 1. Radical polymerization of *N*-vinylimidazole (a), diazo reaction of aniline derivatives (b), coupling a phenyldiazonium ion with poly(*N*-vinylimidazole) (c), PV-4-CBAI: X = CN, Y = H; PV-3-CBAI: X = H, Y = CN; PV-4-MBAI: X = OCH₃, Y = H

Poly[*N*-vinyl-2-(3-cyano-phenylazo)imidazole] (PV-3-CBAI) was prepared following an identical reaction procedure. Yield: 89%. T_g : 164.3 °C. ¹HNMR (DMSO-*d*₆): 1.85 (s, 2H, CH₂), 3.00 (s, 1H, CH), 6.84 (s, 2H, CH in imidazole ring, $-\text{CH}=\text{CH}-$), 7.68 (m, 1H, $-\text{CH}-$, in benzene ring), 7.80 (m, 2H, $-\text{CH}-$, in benzene ring), 7.94 (m, 1H, $-\text{CH}-$, in benzene ring).

Poly[*N*-vinyl-2-(4-methoxy-phenylazo)imidazole] (PV-4-MBAI) was prepared following an identical reaction procedure. Yield: 76%. T_g : 120.0 °C. ¹HNMR (DMSO-*d*₆): 2.49 (s, 2H, $-\text{CH}_2-$), 3.67 (q, 1H, CH), 3.74 (s, 3H, $-\text{OCH}_3$), 6.88 (d, 2H, $-\text{CH}-$, in benzene ring), 6.95 (s, 2H, CH in imidazole ring, $-\text{CH}=\text{CH}-$), 7.33 (s, 2H, $-\text{CH}-$, in benzene ring).

Methods. Quantum chemical calculations were carried out at the Wrocław Supercomputer Centre using the Gaussian03 program [19] by the *ab initio* method at the RHF/3-21g level of theory. The UV-vis spectra were calculated with ZINDO method using optimized molecular coordinates from the RHF calculation. Glass transition temperatures (T_g) of polymers were measured by the differential scanning calorimetry (DSC) with a Mettler Toledo device. The rate of heating was 10 °C/min. UV-vis spectra were recorded with a Diode Array Hewlett Packard Spectrophotometer 8452A. Measurements were carried out using polymer films deposited on glass substrates before and during illumination with a diode light of 395 nm.

Ellipsometry measurements were carried out with an EL X-02C Ellipsometer, DRE-Ellipsometerbau GmbH (Germany), to characterize thin polymer film deposited on glass substrates before and during illumination with a diode light of 395 nm.

3. Results and discussion

3.1. Quantum-chemical calculations

Quantum chemical calculations were carried out with the Gaussian03 program by *ab initio* method at RHF/3-21g level of theory to foresee linear and nonlinear optical properties of the chromophores [20,21]. The calculations were performed for monomeric [*N*-ethyl-2-(phenylazo)imidazole] derivatives. Using vinyl derivatives for these purposes would be inadequate due to a possible electron conjugation of the vinyl group with the rest of the dye molecule. In polymers, the vinyl group disappears, giving a sequence of saturated (polyvinyl) chain units. As the *cis* form of the azo dye molecule is unstable and re-isomerises to the *trans* form in ambient conditions, it is impossible to determine experimentally its spectral and other physicochemical properties. Optimization of the geometry of the molecule makes it possible to characterize the difference of potential energy between the *trans* and *cis* isomers (ΔE), volume of the molecule (V) and the dipole moment (μ). Calculated values are presented in Table 1. The difference in shape of chromophoric molecule fragments between *trans* and *cis* isomer is shown in Fig. 2, based on the example of the PV-4-MBAI polymer. The molecules of the chromophores in question are rather short and on isomerization the change in the molecular shape is evidenced by small differences in the dipole moment. The potential energy difference between the *trans* and *cis* form, being in the range of ca. 51–60 kJ/mol, is low compared with that calculated for analogous azo chromophores containing two phenyl groups on both sides of the diazo group, if the same basis set is used [22].

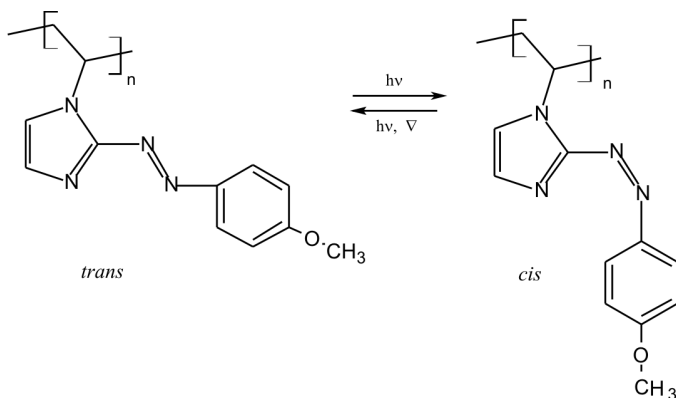


Fig. 2. Molecular shapes of *trans* and *cis* forms of the chromophore fragment of PV-4-MBAI polymer

The simulated UV-vis spectrum for monomer corresponding to PV-4-MBAI is shown in Fig. 3. The results of simulation of UV-vis spectra are presented in Table 2.

The calculated maxima of absorption bands for *trans* forms of monomers are located in the near UV range (373–380 nm). Analogous absorption bands corresponding

to the *cis* form are shifted towards shorter wavelengths, and consequently, the intensities of the bands, expressed by the oscillator strengths, are lower for the *cis* forms. The most significant difference between the *trans* and *cis* form can be observed in methoxyphenyl derivatives that varied in the maximum absorption wavelength as well as in the oscillator strength.

Table 1. The calculated properties of monomeric chromophores [19]

Monomer corresponding to	ΔE^a [kJ/mol]	Volume of molecule ^b V [cm ³ /mol]		Dipole moment $\mu/10^{-30}$ [C·m]	
		<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>
PV-4-MBAI	52.138	190.72	186.75	9.56	11.05
PV-3-CBAI	51.481	183.66	169.87	27.87	25.21
PV-4-CBAI	60.274	159.23	148.28	20.46	25.50

^aDifference of potential energies *cis* and *trans* isomers.

^bCalculated by Gaussian using the Monte Carlo method.

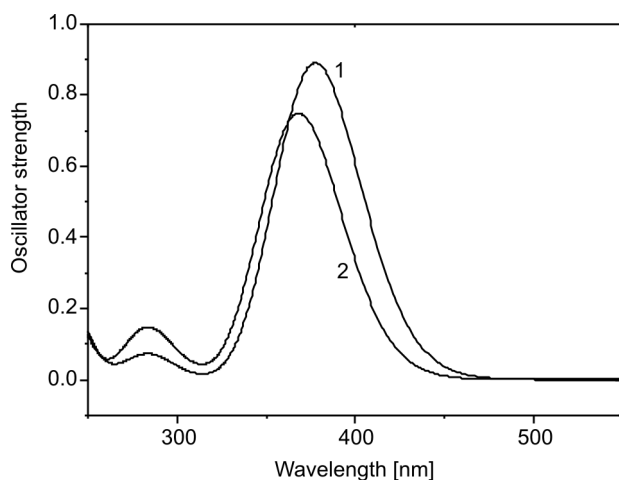


Fig. 3. UV-vis spectrum of the monomer corresponding to PV-4-MBAI (*N*-ethyl-2-(4-methoxy-phenylazo)imidazole): 1 – *trans* form, 2 – *cis* form

Table 2. Spectral properties of monomeric chromophores calculated with ZINDO method of Gaussian program [19]

Monomer corresponding to	Maximum of absorption band [nm]		Oscillator strength	
	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>
PV-4-MBAI	377	368	0.8896	0.7481
PV-3-CBAI	373	359	0.8034	0.6890
PV-4-CBAI	380	329	0.8963	0.4864

The calculations of linear and nonlinear optical properties were carried out for isolated molecules which had been optimized before by Gaussian. The calculated values of polarizability and hyperpolarizability for monomeric species are presented in Table 3. In the *trans* form, the polarizability was slightly higher than in the *cis* form and, as polarizability is correlated with molecular volume, the same tendency was observed in the case of the latter parameter (Table 2).

Table 3. Polarizability and first hyperpolarizability of monomeric chromophores

Monomer corresponding to	Polarizability α $\alpha^{\circ}/10^{-30}$ [m ³]		Hyperpolarizability β $\beta^{\circ}/10^{-40}$ [m ⁴ /V]	
	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>
PV-4-MBAI	22.29	21.85	2.52	32.97
PV-3-CBAI	21.79	21.47	42.21	20.74
PV-4-CBAI	22.35	20.05	54.91	24.04

There was an observed difference in the first hyperpolarizability (β) data between *trans* and *cis* isomers, although the absolute values of β for long *trans* forms and short *cis* forms are rather small. The chromophore corresponding to the PV-4-MBAI polymer, contrary to the other two chromophores, contains a relatively weak electron acceptor (methoxy group). This is manifested in the higher value of the dipole moment and the first hyperpolarizability of its *cis* form, in comparison with the *trans* form. And this is analogous fact to that observed in the case of unsubstituted azobenzene. The dyes with stronger cyano acceptor group behave, one may say normally, showing higher values of dipole moment and first hyperpolarizability value in the case of *trans* forms. The difference in the first hyperpolarizability value of the border structures is distinct for all three chromophores. This fact could eventually be utilized at the macromolecular scale, by forcing a change in the value of β during illumination of the polymers with UV light, however the second order nonlinear susceptibility of the materials is expected to be rather moderate.

3.2. Characteristics of photochromic polymer films

The polymers were deposited on glass substrates in the form of thin transparent films by the spin coating technique. The solutions of poly[*N*-vinyl-2-(phenylazo)-imidazole] derivatives were prepared in 2-methoxyethanol in the presence of polyvinylpyrrolidone. The concentration of the photochromic poly(*N*-vinylimidazole) derivatives in solution was ca. 3 wt. %. Poly(*N*-vinylimidazole) derivatives and polyvinylpyrrolidone were used in the ratio of two to three.

The measurements of UV-vis spectra were carried out using thin films of polymers on glass plates. The polymers containing chromophoric fragments showed an absorption peak with the maximum in the range of ca. 362–376 nm, depending on

the polymer type. The changes in UV-vis spectra occurred during illumination with light. The materials showed a reversible *trans*–*cis*–*trans* photoisomerization of the chromophoric fragments; the route from *cis* to *trans* took place as a thermal relaxation, however, by using a light source emitting at the wavelength absorbed by the *cis* isomer would considerably accelerate this process. The UV-vis spectra were recorded before and after illumination with a diode light of 395 nm and the spectral parameters are presented in Table 4. Among the polymers tested, the cyano derivatives showed a certain resistance to isomerization and required longer illumination time to observe distinct changes in the spectra. The PV-4-MBAI whose UV-vis spectrum is shown in Figure 4, occurred to be the best material to show a reverse run of *trans*–*cis*–*trans* transformations, and its spectra before and after illumination with a 395 nm diode showed maximum difference in absorption intensity, although nearly no shift towards shorter wavelengths was observed.

Table 4. Spectral properties of polymeric chromophores

Polymer	Before illumination		After illumination		Time of illumination [s]
	Maximum of absorption band [nm]	Absorbance [a.u.]	Maximum of absorption band [nm]	Absorbance [a.u.]	
PV-4-MBAI	376	0.9263	370	0.6697	30
PV-3-CBAI	362	0.5576	360	0.5045	75
PV-4-CBAI	376	0.8411	372	0.7747	120

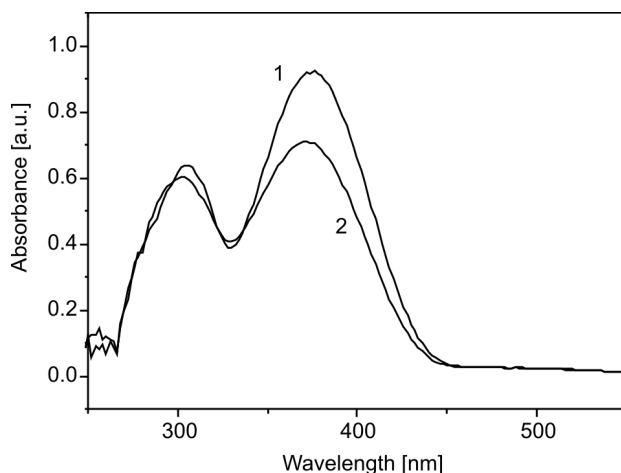


Fig. 4. The UV-vis spectrum of PV-4-MBAI: 1 – before illumination, 2 – after illumination

Comparison of data in Table 2 and 4 leads to the conclusion that the wavelengths of maximum absorption bands calculated for monomeric chromophores are close to those determined for respective polymers.

Ellipsometry is an optical method which makes it possible to determine the reversible changes in the refractive index of a given material after repeated illumination cycles with absorbed light [23]. This technique was used to investigate changes in ellipsometric parameters of the polymer films deposited on glass plates.

The light interacting with the sample undergoes a polarization change to elliptically polarized light. The change in the polarization is measured as a ratio of the complex Fresnel reflection coefficients, R_p and R_s , for p- and s-polarized light, respectively. The fundamental equation of ellipsometry is:

$$\rho = e^{i\Delta} \tan \Psi = \frac{R_p}{R_s} \quad (1)$$

where Ψ denotes the intensity ratio and Δ is the phase difference of the reflected p- and s-polarized light. From these measured values, it is possible to calculate the film thickness and complex dielectric function expressed by the complex refractive index:

$$n = n_r + ik, \quad i^2 = -1 \quad (2)$$

The measurements were carried out during illumination with a diode light of the wavelength of 395 nm and the change in the ellipsometric parameter Ψ was measured, dependent on the illumination time (first stage) and relaxation time (second stage) resulting in a change of refractive index, as shown for PV-4-MBAI in Fig. 5. The change in the real part of the refractive index n_r , measured for polymer thin films deposited on glass substrates was 0.011, 0.012 and 0.014 for PV-3-CBAI, PV-4-CBAI and PV-4-MBAI, respectively.

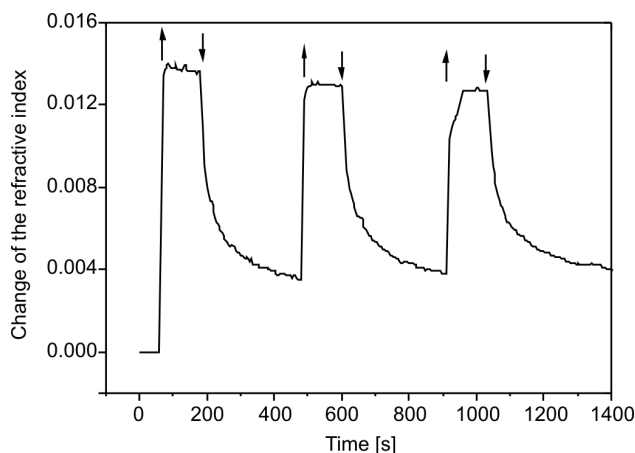


Fig. 5. Changes of the refractive index of PV-4-MBAI on illumination and thermal relaxation determined by the ellipsometry method: arrow up – light on, arrow down – light off

The periodic change in the refractive index on illumination and thermal relaxation is reversible, however the thermal relaxation needs a longer time for the sample to

recover its previous state. During illumination not only relatively fast photochemical isomerization takes place but also changes in the macroscopic properties of the material are observed being much slower. Thus, to recover the primary value of the refractive index, the time expressed in hours would be necessary. As the illuminating diode emitted unpolarized light, no formation of surface relief grating was expected.

4. Conclusions

Novel photochromic polymers, specifically poly[*N*-vinyl-2-(phenylazo)imidazole] derivatives, were obtained. The polymers showed a maximum absorption peak in the near UV range. The photoisomerization and thermal relaxation of poly(*N*-vinylimidazole) containing chromophores, as examined by ellipsometry, showed reversible changes in refractive indices in the range of 0.010 to 0.014, during illumination. The reverse *cis*–*trans* transformation run due to thermal relaxation and it was slower as compared with the previous step induced by light action. These photo-induced transformations resulted in a change in physicochemical properties of the materials in question, and could be interesting for practical applications in reversible optical data storage in the near UV range.

Acknowledgements

This work was supported by Grant No. NN507 3269 33 of the Polish Ministry of Science and Higher Education.

References

- [1] BOUAS-LAURENT H., DÜRR H., *Pure Appl. Chem.*, 73 (2001), 639.
- [2] NATANSOHN A., ROCHON P., *Chem. Rev.*, 102 (2002), 4139.
- [3] MATEE V., MARKOVSKY P., NIKOLOVA L., TODOROV T., *J. Phys. Chem.*, 96 (1992), 3055.
- [4] TAMAI N., MIYASAKA H., *Chem. Rev.*, 100 (2000), 1875.
- [5] WANG Y., ZHAN J., SI J., YE P., FU X., QIU L., SHEN Y., *J. Chem. Phys.*, 103 (1995), 5357.
- [6] RANGELO-ROJO R., YAMADA S., MATSUDA H., YANKELEVICH D., *Appl. Phys. Lett.*, 72 (1998), 1021.
- [7] CHIMURA K., *Chem. Rev.*, 100 (2000), 1847.
- [8] OTSUKI J., SUWA K., NARYTAKI K., SINHA C., YOSHIKAWA I., ARAKI K., *J. Phys. Chem. A.*, 109 (2005), 8064.
- [9] OTSUKI J., SUWA K., SARKER K.K., SINHA C., *J. Phys. Chem. A.*, 111 (2007), 1403.
- [10] ENDO M., NAKAYAMA K., KAIDA Y., MAJIMA T., *Tetrahedron Lett.*, 44 (2003), 6903.
- [11] FUKUDA N., KIM J.Y., USHIJIMA H., TAMADA K., *Jpn. J. Appl. Phys.*, 45 (2006), 460.
- [12] SCHULZ-EKLOFF G., WÖHRLE D., VAN DUFFEL B., SCHOONHEYDT R.A., *Microporous Mesoporous Mater.*, 51 (2002), 91.
- [13] KATSONIS N., LUBOMSKA M., POLLARD M.M., FERGINGA B.L., RUDOLF P., *Prog. Surf. Sci.*, 82 (2007), 407.
- [14] OZYALCIN M., KUCUKYAVUZ Z., *Synth. Met.*, 87 (1997), 123.
- [15] PEKEL N., SAHINER N., GUVEN O., RZAEV Z.M.O., *Eur. Polym. J.*, 37 (2001), 2443.
- [16] RAY U.S., MOSTAFA G., LU T.H., SINHA C., *Cryst. Eng.*, 5 (2002), 95.

- [17] SENAPOTI S., SARKER K.K., MONDA T.K.L., SINHA C., *Transition Met. Chem.*, 31 (2006), 293.
- [18] PAL S., DAS D., CHATTOPADHYAY P., SINHA C., PANNEERSELVAM K., LU T.H., *Polyhedron*, 19 (2000), 1263.
- [19] FRISCH M. J., TRUCKS G. W., SCHLEGEL H.B., SCUSERIA G.E., ROBB M.A., CHEESEMAN J.R., MONTGOMERY JR., J. A., VREVEN T., KUDIN K.N., BURANT J.C., MILLAM J.M., IYENGAR S.S., TOMASI J., BARONE V., MENNUCCI B., COSSI M., SCALMANI G., REGA N., PETERSSON G.A., NAKATSUJI H., HADA M., EHARA M., TOYOTA K., FUKUDA R., HASEGAWA J., ISHIDA M., NAKAJIMA T., HONDA Y., KITAO O., NAKAI H., KLENE M., LI X., KNOX J.E., HRATCHIAN H.P., CROSS J.B., BAKKEN V., ADAMO C., JARAMILLO J., GOMPERS R., STRATMANN R.E., YAZYEV O., AUSTIN A.J., CAMMI R., POMELLI C., OCHTERSKI J.W., AYALA P.Y., MOROKUMA K., VOTH G.A., SALVADOR P., DANNENBERG J.J., ZAKRZEWSKI V.G., DAPPRICH S., DANIELS A.D., STRAIN M.C., FARKAS O., MALICK D.K., RABUCK A.D., RAGHAVACHARI K., FORESMAN J.B., ORTIZ J.V., CUI Q., BABOUL A.G., CLIFFORD S., CIOŚLOWSKI J., STEFANOV B.B., LIU G., LIASHENKO A., PISKORZ P., KOMAROMI I., MARTIN R.L., FOX D.J., KEITH T., AL-LAHAM M.A., PENG C.Y., NANAYAKKARA A., CHALLACOMBE M., GILL P.M.W., JOHNSON B., CHEN W., WONG M.W., GONZALEZ C., POPLE J. A., Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford CT, 2004.
- [20] HAKEN H., WOLF H.C., *Molecular Physics and Elements of Quantum Chemistry*, Springer Verlag, Berlin, 1995.
- [21] FORESMAN J.B., FRISCH A., *Exploring Chemistry with Electronic Structure Methods*, 2nd Ed., Gaussian, Inc. Pittsburg, PA, 1996.
- [22] HEHRE W.J., *Computational Chemistry in Quantum Chemistry and Spectroscopy*, T. Engel, P. Reid (Eds.), Prentice Hall, San Francisco, 2006.
- [23] AZZAM R.M.A., BASHARA N.M., *Ellipsometry and Polarized Light*, North-Holland, New York, 1997.

Received September 2008

Revised 8 April 2009