Optical properties of some bismaleimide derivatives

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New bismaleimides containing azobenzene chromophores obtained by condensation reaction of maleic anhydride with azoaromatic diamines and their corresponding polytioetherimides were characterized by spectral and thermal methods. Thin films of polythioetherimides were corona poled and the orientational order parameter was determined. These polymers show good thermal stability with 10% weight loss temperature above 285 °C. Exposing to UV irradiation the bismaleimide derivatives based on Disperse Red 19 are photochemically stable while the bismaleimide derivatives based on 2,4-diamino-2', 4'-methyl azobenzene exhibited *trans-cis-trans* isomerization in DMF solutions. Kinetics of isomerisation reaction of azobenzene moieties was monitored by electronic absorption spectra.

(Received March 28, 2011; accepted June 9, 2011)

Keywords: Azobismaleimide, UV-Vis absorption spectra, Corona poling, Isomerization

1. Introduction

Azobenzene–containing polymers are promising materials due to their unique optical and mechanical properties which make them possible candidates for a large area of practical applications such as optical data storage, surface relief gratings, liquid crystalline displays, optical switching, nonlinear optical materials, etc [1-6]. Poled amorphous polymers incorporating azobenzene chromophores are among the most promising materials for second-order thin film nonlinear optical (NLO) applications [1, 7].

A great deal of research has been focused on polyimide-based materials for nonlinear optical applications due to their low dielectric constant, high glass transition temperatures (Tg), excellent poling stability of induced dipoles, high thermal stability. Recent studies on side-chain polyimides containing heterazo chromophores for second order nonlinear optics show some encouraging results [8-13]. All these side chain polyimides exhibit excellent properties, including high temperature alignment stability, good mechanical properties, low optical losses and compatibility with semiconductor processes. However, most of side chain polyimides are prepared via standard condensation reaction between diamines containing NLO chromophore and dianhydrides to obtain poly(amic acid) precursor polymers, followed by a thermal cyclization at high temperatures during poling process. Unfortunately, high poling field could not be applied to polyimide films because they release small molecules (such as water) in the imidization process [14]. To overcome these problems, high Tg chromophore-functionalized polyimides were synthesized by addition polymerization between NLO diamine monomers and bismaleimides [15, 16], NLO bismaleimide monomers with aromatic diamines [17, 18] or vinyl monomers [19, 20]. In this paper, we report the synthesis and characterization of new bismaleimide monomers containing azobenzene chromophores and their polyaddition polymers with bis-2-mercaptoethylether. These azo products were studied in term of their optical, thermal and NLO properties.

2. Experimental

Materials

Maleic anhydride, sodium azide, 4-aminobenzoic acid, 1,3-diaminobenzene, Disperse Red 19, dibutyltin laurate were purchased from Aldrich and used as received without further purification. All solvents used for spectral analysis were in spectrophotometric grade (Aldrich).

2,2'-({4-[4-[(E)-phenyldiazenyl] phenyl}imino) diethanol (DABDEA) was prepared according to a method described in literature [21]. 2,4-Diamino-4'-methylazobenzene (DA4MAB) and 2,4-diamino-2'-methylazobenzene (DA2MAB) were synthesized via the one-step diazonium coupling reaction of o- or p-toluidine with m-phenylenediamine [7]. 4-Maleimidophenyl isocyanate (MPI) was obtained to our reported procedure [22, 23].

Bismaleimide synthesis

Urethane bismaleimides BMI 1 and BMI 2 were prepared by addition reaction of DABDEA or Disperse Red 19 (0.1 mol) with MPI (0.2 mol) in dimethylformamide (DMF) in presence of dibutyltin laurate as catalyst, at 60 ^{o}C for 6 h. The reaction mixture was precipitated in water and the solid was separated by filtration. The crude product was purified by recrystallization from a 1,2-dichloroethane/ethanol mixture (1:2).

BMI 1 was precipitated with ethanol resulting brown stable crystals and the yield was about 78%, mp = 145-148 ^{o}C. Elemental analysis calcd for $C_{38}H_{30}N_8O_{10}$ (758.693):

C, 60.16; H, 3.99; N, 14.77. Found: C, 60.28; H, 4.03; N, 14.63%.

FT-IR (KBr, cm^{-1}): 3390, 3097, 2925, 1699, 1600, 1550, 1514, 1392, 1338, 1314, 1219, 1140, 1064, 820, 688.

^{1}H NMR (DMSO-d_6, 400 Hz), δ (ppm): 3.90 (t, 4H, CH_2-N), 4.45(t, 4H, CH_2-O), 7.20 (S, 4H, CH=O), 7.30 (d, 2H, aromatic), 7.45 (d, 4H, aromatic), 7.65 (d, 2H, aromatic), 7.88 (d, 4H, aromatic), 8.16 (d, 2H, aromatic), 8.44 (d, 2H, aromatic), 8.65 (s, 2H, NH-).

Bismaleimides BMI 3 and BMI 4 were synthesized from DA2MAB or DA4MAB (1 mol) and maleic anhydride (2 mol) in dry acetone by a two-step method [23]. BMI 3 was obtained from DA2MAB and maleic anhydride as solid crystals by recrystallization from ethanol; yield 77%, mp=135-138 ^{o}C.

Elemental analysis calcd for $C_{21}H_{14}N_4O_4$ (386.360): C, 65.28; H, 3.65; N, 14.50;

Found : C, 65.42; H, 3.48; N, 14.83 %

FT-IR (KBr, cm^{-1}): 3090, 1719, 1590, 1510, 1443, 1368, 1148, 830, 767, 692

^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 2.69 (s, 3H, CH_3); 6.88 (d, 4H; CH = maleimide protons), 7.14-7.32 (m, 4H, aromatic), 7.65 (d, 2H, aromatic), 7.94 (s, 1H, aromatic)

BMI 4 was obtained as mustard solid crystals by recrystallization from 1,2-dichlorethane/ethanol; yield 83%, mp = 255-288 ^{o}C.

Elemental analysis calcd for $C_{21}H_{14}N_4O_4$ (386.360): C, 65.28; H, 3.65; N, 14.50;

Found: C, 64.96; H, 3.73; N, 14.78%

FT-IR (KBr, cm^{-1}): 3090, 1715, 1600, 1991, 1444, 1373, 1144, 830, 690.

^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 2.46 (s, 3H, CH_3), 6.88 (d, 4H, CH = maleimide protons), 7.26 (d, 2H, aromatic), 7.60-7.69 (d, 4H, aromatic), 7.98 (s, 1H, aromatic).

Polymer synthesis

A 50 ml three-necked flask equipped with magnetic stirrer, thermometer and condenser was charged with bis-2-mercaptoethylether (2.3 mmol, 0.3 ml), freshly distilled m-cresol (8 ml) and BMI 1 (2.3 mmol). Two drops of tributylamine were added and the reaction mixture was maintained at 70 ^{o}C for 10 h. The polymer was isolated by pouring the reaction mixture into 50 ml methanol acidified with glacial acetic acid. The precipitate was washed for several times with methanol and then extracted overnight with methanol using a Soxhlet extractor and dried in a vacuum oven at 60 ^{o}C for 14 h. The same procedure was used to prepare all other polymers.

Characterization

FT-IR absorption spectra were recorded on a Bruker Vertex 70 instrument equipped with a golden gate single reflection ATR accessory. ^{1}H NMR (400 MHz) spectra were taken using a Bruker Avance DRX spectrometer using DMSO-d_6 and $CDCl_3$ as solvents and tetramethylsilane as an internal standard.

Differential scanning calorimetry (DSC) measurements were done using a Mettler TA Instrument DSC 12E with a heating rate of 10 ^{o}/min, in nitrogen. Thermogravimetric analysis was performed under nitrogen flow (15 cm^3/min) at a heating rate of 10 ^{o}C/min from 25 to 750 ^{o}C with a Mettler Toledo model TGA/SDTA 851. Melting and softening points were determined with a Gallenkamp hot-block point apparatus.

Fluorescence spectra were carried out with a Perkin Elmer LS55 luminescence spectrometer. Excitation wavelength was set at 365 nm.

UV-Vis absorption spectra were measured by SPECORD 200 Analytik Jena spectrophotometer. Photoirradiation was carried out using a 500 W high pressure mercury arc lamp by incorporating suitable glass filters. All measurements were performed at room temperature. Reaction progress of photoisomerization on UV irradiation and thermal recovery isomerization in the dark was monitored by the change of electronic absorption spectra. The reverse *cis-trans* isomerization was also detected by irradiation with 436 nm visible light.

The polymer films were prepared on transparent glass substrate by casting from a DMF solution (5% polymer) and then were dried at 70 °C for 3 h.

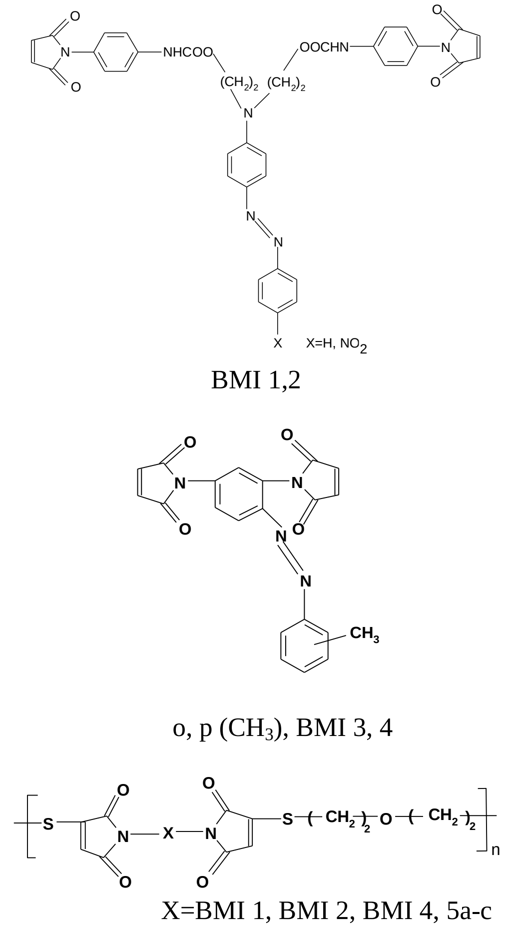
In order to induce NLO properties the polymer films were electrically poled in a corona-discharge set up. The poling process was carried out bellow glass transition temperature for 40 minutes. Then the films were cooled down to room temperature in the presence of the poling field and finally it was switched off. The poling conditions were as follows: poling voltage applied to a needle, perpendicular to the film 5 kV; distance between sample surface and the needle electrode about 1 cm.

3. Results and discussion

New bismaleimides bearing pendant azobenzene groups and corresponding polythioetherimides have been obtained according to Scheme 1. Chemical structures of the synthesized bismaleimides/polythioetherimides were confirmed by FTIR and ^{1}H NMR spectral techniques and elemental analysis.

The thermal behavior of bismaleimides and azopolymers 5a-c was investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). In Fig. 1, DSC profiles of bismaleimides taken on the heating process are indicated. For bismaleimides BMI 1-3 an endothermic peak between 120-150 ^{o}C was observed followed by an exothermic peak between 185-220 ^{o}C, while for BMI 4 the endothermic peak was located at higher temperatures (259 ^{o}C) and the exothermic peak at 269 ^{o}C (Table 1).

The glass transition temperature (Tg) values ranged between 67-100 ^{o}C for azopolymers 5a-c but polymer 5c exhibited the lowest value of Tg (Table 2). These relatively low values of T_g can be due to the presence of flexible urethane linkages and bulky side chromophores in the polymer chain.



BMI 1,2

o, p (CH_3), BMI 3, 4

X=BMI 1, BMI 2, BMI 4, 5a-c

Scheme 1. Chemical structure of bismaleimide derivatives.

The azo polythioetherimides have 10 % weight-loss temperatures above 280 ^{o}C, indicating good thermal stability that can be ascribed to maleimide units. High thermal stability is an advantage for their further applications. The TGA data showed that the initial decomposition temperatures (IDT) of polymers 5a-c were much higher than their corresponding Tg's, suggesting that high temperature poling is possible without a damage of the NLO chromophores.

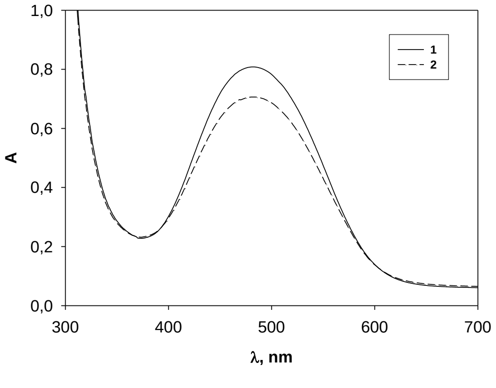


Fig. 1. Electronic absorption spectra of 5a film before (1) and after (2) poling.

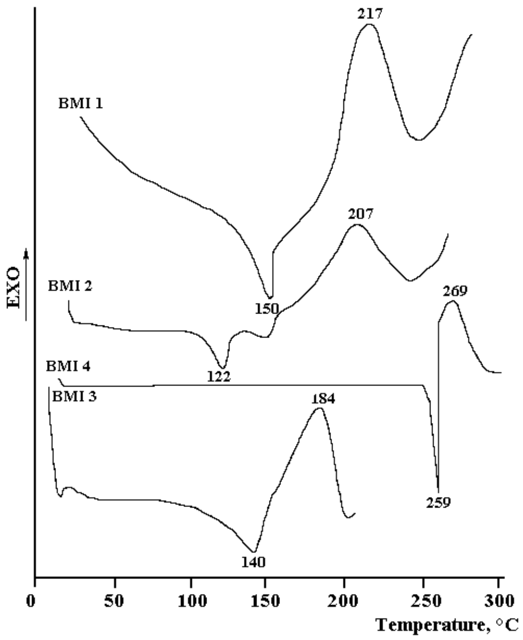


Fig. 2. DSC curves of azo bis-maleimides BMI 1-4.

Table 1. Thermal and optical properties of BMI 1-4.

BMI	X	λ_{max} (nm)	Melting point (°C)	T_{endo} [a] (°C)	T_{exo} [b] (°C)
BMI 1	H	494	145-148	150	217
BMI 2	NO_2	494	117-120	122	207
BMI 3	*o*-CH_3	342	135-138	140	184
BMI 4	*p*-CH_3	345.5	255-258	259	269

Table 2. Characteristics of azopolymers 5(a-c).

Poly-mer	η_{inh} [a] (dL/g)	λ_{max} (nm)	T_g (°C)	IDT[b] (°C)	T_{10} [c] (°C)	PDT_{max} [d] (°C)
5a	0.183	490	90	285	310	410
5b	0.172	488	100	283	308	405
5c	0.270	343	67	245	280	285

a) measured at 25 ^{0}C using DMF as solvent, the standard concentration is 0.5 g/dL;
b) initial decomposition temperature (onset) at which the sample started to lose weight;
c) temperature at which 10% weight loss occurred;
d) temperature at the maximum weight loss rate.

Fig. 2 shows the UV-Vis absorption spectra of polymer film 5a before and after corona poling. After the corona poling the dipole moments of azo chromophore moieties in the polymer were aligned along the poling field direction and an expected decrease in the absorbance at about 486 mm was observed. The orientational order parameter was estimated according to the relation Φ = 1 – A/A_0, where A and A_0 are the absorbances of the polymer film after and before corona poling. The absorption changes are directly related to the orientation of chromophores [27, 28]. Then, the estimated order parameter value Φ was equal to 0.26 for polymer 5a, showing a good chromophore alignment during poling process.

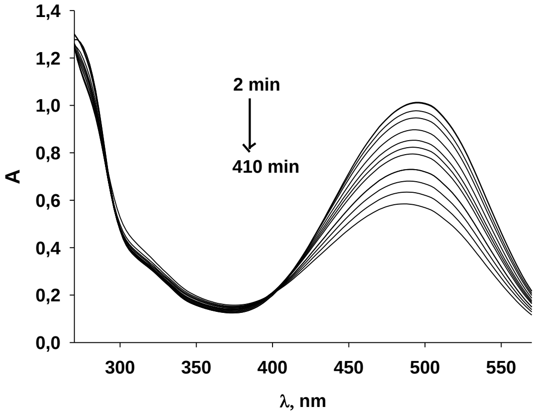


Fig. 3. Spectral change of BMI 1 in DMF solution on UV irradiation.

Acoording to Rau's classification [5, 29], BMI 1 and BMI 2 are pseudostilbene type azobenzene compounds, which means that the $\pi \to \pi^*$ transition is overlapping to the $n \to \pi^*$ one. These azoaromatic derivatives and their corresponding polymers (5a, 5b) have a strong and large structureless band located at 494 (BMI 1,2), 488 (5a) and 486 nm (5b) in DMF, respectively (Table 1).

The effect of the polychromatic UV irradiation on the intensity of the absorption band around 494 nm in DMF solution of bismaleimide BMI 1 has been observed following the changes in the UV-Vis absorption spectra during UV irradiation (Fig. 3). The intensity of the absorption band at 494 decreased progressively with the irradiation duration, a blue shift of 8 nm being observed after 400 min and a transformation degree of 0.44. In the first stages of the photoreaction an isosbestic point was present at 405 nm when photoisomerization of azo chromophores is the only photochemical change in system. After 50 min of irradiation the isosbestic point did not maintained and a photobleaching process starts in solution occurring very slowly as the reaction goes on. These changes in the electronic absorption spectra of BMI 2 and polymers 5a, 5b take place with a much lower rate, the transformation degrees of chromophores being 0.27, 0.18 and 0.20, respectively after 200 min of UV irradiation. As seen the rate of photobleaching process is lower for polymer 5a, evidencing thus the photochemical stability of this polymer. The electronic absorption spectra of the azobismaleimides BMI 1, BMI 2 and polymers 5a, 5b did not modify by standing in dark for 48 h, the photoprocess being irreversible in these conditions.

The photoprocess evolution can be described by the relation $\ln A_0/A_t = kt$, where A_0 and A_t are the absorbances at the time 0 and t, k is rate constant. The rate constants are practically equal for the two bismaleimides: 2.65×10^{-5} s^{-1} (BMI 1) and 2.82×10^{-5} s^{-1} (BMI 2), respectively (Fig. 4). It was found that the photoprocess did not follow a first order kinetics for polymers 5a and 5b as if there is initially an acceleration of the photoprocess after which the kinetics becomes linear but with smaller rate constant (1.95×10^{-5} s^{-1}) (Fig. 4).

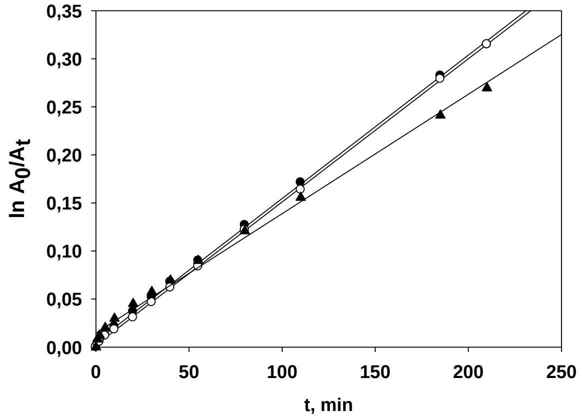


Fig. 4. Plots of ln A_0/A_t versus irradiation duration for BMI 1 (•), BMI 2 (o) and polymer 5b (▲).

Spectral modifications observed for azobismaleimide BMI 3 in DMF solution when it was exposed to 365 nm light irradiation are depicted in Fig. 5. Upon UV irradiation the absorption band around 342 nm decreased significantly in intensity, while the band around 445 nm increased slightly. The absorption bands at about 342 and 445 nm can be assigned to $\pi \to \pi^*$ and $n \to \pi^*$ transitions, respectively [29]. The continuously decreased absorption band in intensity around 342 nm shows that the isomerization of azobenzene chromophore from *trans*-to *cis*-state occurs in solution until the photostationary equilibrium was attained after 300 s. The degree of photoisomerization was only 0.60 due to presence of methyl group in ortho-position of the aromatic ring.

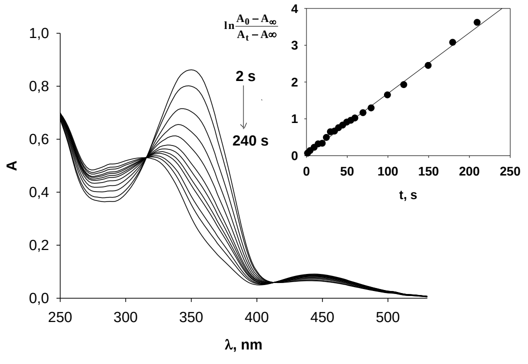


Fig. 5. Absorption spectral changes of BMI 3 in DMF under irradiation at 365 nm which were recorded for different irradiation times. Inset: the kinetic curve of the photoisomerization process.

The photoisomerization process of BMI 3 in DMF (Fig. 5) solution obeys first-order kinetics according to the relation:

$$\ln\frac{A_0 - A_\infty}{A_t - A\infty} = kt \tag{1}$$

where $A_{0,}$ A_t and A_∞ are the absorbances at 342 nm at time 0, time t and the photostationary state, respectively and k is the rate constant. The slope of the plot $\ln[(A_0 - A_\infty)/(A_t - A_\infty)]$ against time gives the first-order constant for *trans-cis* isomerization. The rate constant for BMI 3 in DMF solution was 1.29×10^{-2} s^{-1}.

When the irradiated sample BMI 3 after reached the photostationary state was exposed to blue light (436 nm), the absorption band at 342 nm gradually recovered to the starting value due to backward *cis-trans* isomerization of azobenzene chromophore. In this case the back-conversion kinetics from *cis* to *trans* form is linear on the all irradiation duration with a rate constant of 3.38×10^{-2} s^{-1}, higher to that of BMI 3 during photoisomerization. Also, the isosbestic points at 297 and 415 nm indicate that the azobenzene chromophore isomerization was the only process in solution.

Thermal *cis-trans* isomerization of the irradiated sample BMI 3 was studied at 45 °C in dichloromethane solution (Fig. 6). The intensity of the absorption band at 344 nm was slowly restored to the initial value before UV irradiation at about 400 min, confirming the thermal reversibility of the photoisomeization reaction. Kinetic data of the *cis-trans* thermal recovery of azobenzene chromophore were fitted satisfactorily to equation: $\ln[(A_\infty - A_o)/(A_\infty - A_t)] = k_1 t$, where A_∞, A_o and A_t are the absorbances at 344 nm of the $\pi \rightarrow \pi^*$ transition at time infinite, time zero and time t, respectively, and k_1 is the *cis-trans* rate constant. The first-order *cis-trans* thermal isomerization was indicated in Fig. 6 (inset) and *cis-trans* rate constant for BMI 3 was 3.62×10^{-3} s^{-1}.

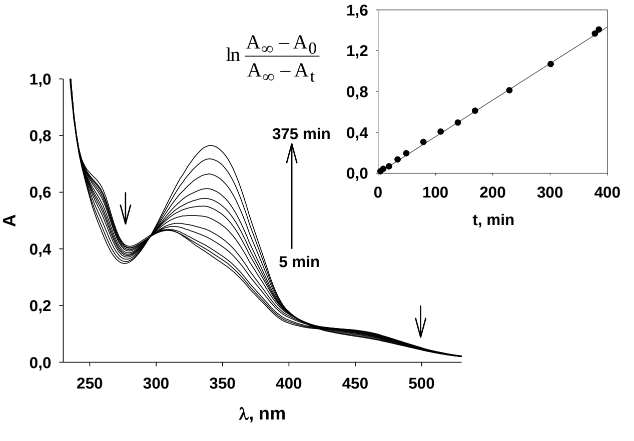


Fig. 6. Thermal back relaxation of BMI 3 at 45 °C in solution. Inset: first-order cis-trans isomerization kinetics

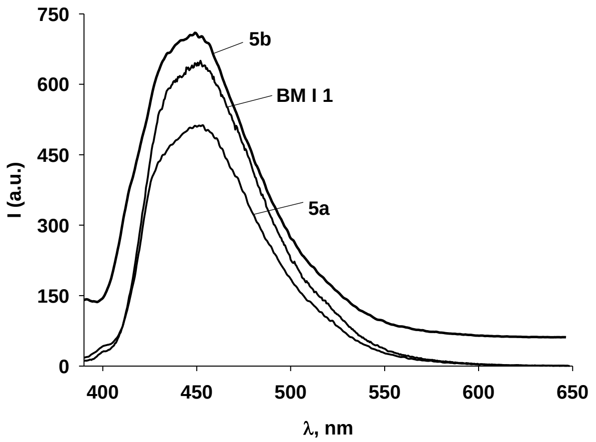


Fig. 7. Emission spectra of BMI 1 and polymers 5a, 5b in DMF solution

Dimethylformamide solutions of 5a, 5b and BMI 1 displayed a strong emission band around 450 nm (Fig. 7). The polymers 5a and 5b have the highest fluorescence emission intensity compared to azobismaleimide BMI 1, while polymer 5c and bismaleimide BMI 4 have no emission band. The higher intensity of fluorescence in polymers can be attributed to charge transfer interaction between electron-accepting maleimide moiety and electron-donating chromophore [30, 31].

4. Conclusions

Bismaleimides bearing pendant azobenzene groups have been synthesized and characterized by thermal and spectral methods. These compounds exhibit high termal stability that can be ascribed to maleimide units. Thin films of one resulting polymer showing a good chromophore alignment after corona poling process at high temperature. Comparative study of the photochemical behaviour of azobismaleimide and corresponding polymer was realized. The photoizomerization process in solution shows a pure first order kinetics for all studied samples.

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