



ISOMERIZATION CHARACTERISTICS OF SOME AZOBISMALEIMIDES

Nicusor FIFERE,^a Anton AIRINEI,^{a,*} Mihaela HOMOCIANU,^a Constantin GAINA,^a Viorica GAINA^a
and Bogdan C. SIMIONESCU^{a,b}

^a"Petru Poni" Institute of Macromolecular Chemistry, Roumanian Academy, Aleea Grigore Ghica Voda, 41A,
700487, Iași, Roumania

^b"Gheorghe Asachi" Technical University, Department of Natural and Synthetic Polymers, 700050, Iași, Roumania

Received October 6, 2011

Photochromic behavior of some azobismaleimide derivatives was studied in solution. The photochromic characteristics depend on the substitution pattern on azobenzene moiety. The reversible photoisomerization of azo chromophore was evidenced by electronic absorption spectra following the evolution of absorption band of trans isomer. The back cis-trans relaxation took place in the presence of visible light (436 nm). Trans-cis photoisomerization was investigated kinetically. A distinct deviation from a first-order kinetics was observed in azopolythioetherimide. The kinetics of cis-trans recovery were fitted by a first-order relation in azobismaleimides.

INTRODUCTION

Azobenzene compounds are considered unique photoactive systems due to their efficient and widely reversible trans-cis photoisomerization with low degradation even after many switching cycles. Upon UV irradiation the azobenzene molecule isomerizes from a stable thermodynamically trans state having rod-like shape to a metastable cis state which has a bent form. Cis-trans back isomerization can occur either thermally or by visible light irradiation.¹⁻³ The isomerization process is linked to a variety of changes in the shape, size and moment of the molecule. Thus, the distance between the para-positions is dramatic reduced in parent azobenzene from 0.90 nm (trans isomer) to 0.55 nm in cis-isomer. This modification in the molecular dimensions is among the largest possible for a reversible reaction.^{4,5} Both photochemical and thermal isomerization kinetics are determined by the type of substituents on the azobenzene compounds.

UV-vis absorption spectroscopy is an appropriate method to study the azobenzene derivatives as during isomerization process the rearrangement of the

molecular orbital energy levels induces a change in electronic absorption spectrum. Azobenzene molecule in the ground state trans configuration exhibits a high intensity $\pi \rightarrow \pi^*$ absorption in the UV region ($\lambda_{\max} = 320$ nm). The absorption of the high-energy photon induces the molecular transition into the metastable cis configuration associated to the transition $n \rightarrow \pi^*$, which assigned to a less intense absorption band at longer wavelengths (around 440 nm).^{4,6,7} During isomerization process, the relative intensity of the two absorption bands changes and thus one can monitor the development of the reaction.

The photoisomerization of azobenzene chromophores is the basis for many functional organic materials with potential applications in photonics, data storage, optical switching, holography, nonlinear optics.⁸⁻¹¹ When azobenzene moiety is incorporated in a polymer matrix, the isomerization can determine the reorientation of chromophores or photoinduced motions of the polymer materials.^{12,13}

Despite a large number of papers devoted to bismaleimide derivatives and their properties, there is

* Corresponding author: airineia@icmpp.ro

a lack of information about their photosensitive properties. In the present work the photochromic features of some azobismaleimide derivatives were investigated in solvents with different polarities. The photoisomerization kinetics and visible light recovery of azochromophores in bismaleimides were also analyzed. Furthermore the photoisomerization behavior of azobenzene moieties in azopolythioetherimide was explored for comparison.

RESULTS AND DISCUSSION

The photochromic behavior of bismaleimides ABM1 and ABM2 (Fig. 1) was investigated in different solvents (Table 1). The representative spectral changes during irradiation at 365 nm of azobismaleimide ABM2 in tetrahydrofuran (THF) are depicted in Fig. 2. The electronic absorption spectra of ABM2 exhibited a high intensity absorption band at 344 nm and a weak band located at 448 nm, which were attributed to the $\pi - \pi^*$ electronic transition of trans isomers and the $n - \pi^*$ transition of cis isomers, respectively.^{4,14,15} On irradiation with UV light, azobismaleimide ABM2 undergoes trans-cis photoisomerization process. The intensity of absorption band at 344 nm decreases gradually with increasing irradiation duration, while concomitantly the absorption band at 448 nm becomes more pronounced. After 200 s,

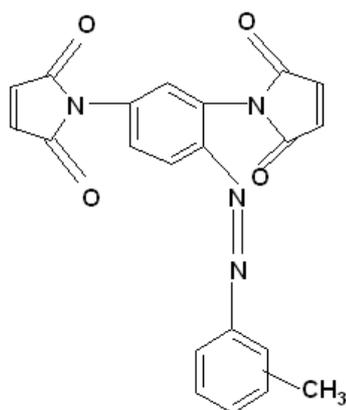
the photostationary state was reached consisting of 82% cis-isomer. The fraction of the photogenerated cis-isomers at the photostationary state can be determined from the following equation:

$$Y_{\infty} = [1 - (A_{\infty} / A_t)] / [(1 - (\epsilon_{\text{cis}} / \epsilon_{\text{trans}}))]$$

where ϵ_c , ϵ_t denote the molar absorptivities of the cis- and trans-isomers at a measured wavelength λ , A_t and A_{∞} are the absorbances of the sample before irradiation and at the photostationary state, respectively. Since the cis isomers could not be detected in a pure form due to their instability in solution, the value of ϵ_{cis} can be evaluated from the electronic spectra of photostationary trans-cis mixtures. The unknown spectrum of cis isomer can be calculated from two absorption spectra in the photostationary state obtained by irradiation with different wavelengths (334 and 365 nm) according to Fischer method.¹⁶ The method utilizes the following relation in the photostationary state:

$$[\text{cis}]/[\text{trans}] = \epsilon_t \phi_{\text{tc}} / \epsilon_c \phi_{\text{ct}}$$

where ϕ_{tc} and ϕ_{ct} are the quantum yields of trans-cis and cis-trans isomerization, respectively. The absorption spectrum of cis-isomer of ABM2 calculated for the first time by Fischer method in dimethylformamide (DMF) solution is presented in Fig. 3 beside the trans isomer spectrum.



ABM1: o - CH₃
ABM2: p - CH₃

Fig. 1 – Structure of azobismaleimides.

Table 1

Photokinetic analysis of the photoisomerization of azobismaleimide derivatives

Sample	Solvent	λ_{max} (nm)	P	$k_{\text{t-c}} \times 10^2$ (s)	$k_{\text{c-t}} \times 10^2$ (s)	$t_{1/2}^{\text{a}}$ (s)
ABM2	THF	344.0	0.18	1.81	2.27	33
	Toluene	345.0	0.17	1.99	2.55	30
	DMF	345.5	0.16	1.44	2.06	28
ABM1	DCM	344.0	0.39	0.98	1.17	118
	DMF	342.0	0.34	1.01	1.60	120
PATEI	DMF	343.0	0.35	1.52	2.47	68

^{a)} time taken for initial absorbance to be reduced by half during photoisomerization

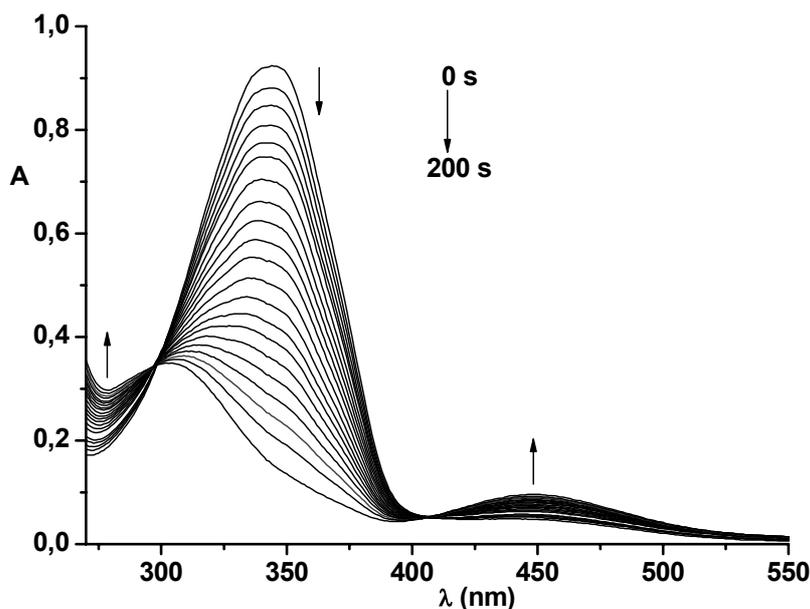


Fig. 2 – Variation of electronic absorption spectra of ABM2 during UV irradiation in THF solution.

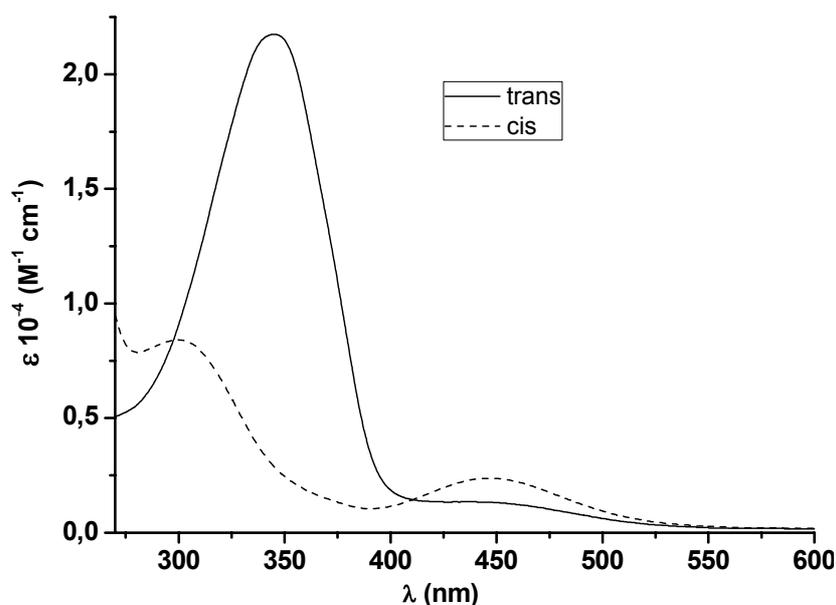


Fig. 3 – Electronic absorption spectra of trans and cis isomers of ABM2.

After obtaining the photostationary state the solution was irradiated with 436 nm visible light in order to induce the cis-trans back isomerization. The absorption band at 344 nm increased rapidly up to 90% of the starting value in about 200 s. The complete reversible process of the photochemical interconversion between trans and cis isomers of azochromophores for bismaleimides ABM2 and ABM1 in DMF solution was displayed in Fig. 4. The procedure was repeated by alternating UV and visible light irradiation and the photobehavior was

reproducible under these experimental conditions. The presence of isosbestic points at 298 and 405 nm in the UV/VIS absorption spectra (Fig. 2) suggests that the trans-cis photoisomerization occurs without any undesired side reactions. In order to obtain more information relating to the photochemical behavior of ABM2 in solutions, the absorbance difference (AD) diagram analysis was formulated to reveal the presence of side reactions other than the photoisomerization.

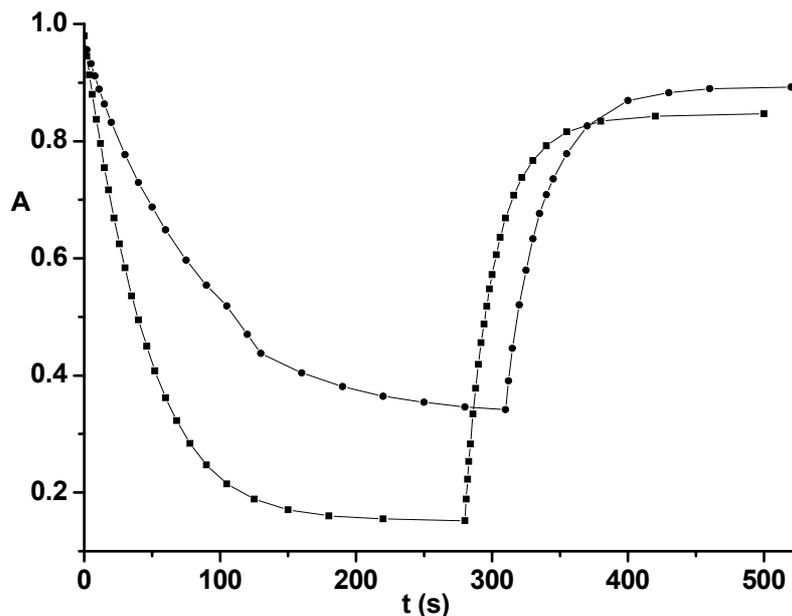


Fig. 4 – Reversibility of photoisomerization for azobismaleimide ABM2 (■) and ABM1 (●).

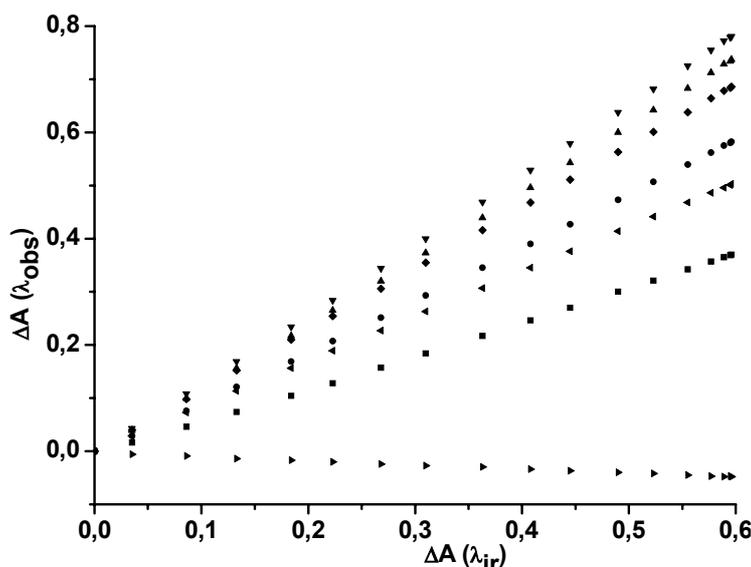


Fig. 5 – Absorbance difference diagram for the photoisomerization process of ABM2. The absorbance at 365 nm is plotted against those at 320 (■), 330 (●), 340 (▲), 350 (▼), 360 (◆), 370 (◀), 447 (▶) nm.

AD diagrams are based on the dependence of absorbance changes at a reference wavelength (ΔA_{λ_1}) as against those of absorbances at the other wavelengths,¹⁷ according to the relation:

$$\Delta A^{\text{ir/obs}}(t) = (\epsilon_t^{\text{obs}} - \epsilon_c^{\text{obs}}) / (\epsilon_t^{\text{ir}} - \epsilon_c^{\text{ir}}) \Delta A^{\text{ir}}(t) \quad (1)$$

In Fig. 5 the absorbance difference at 365 nm (λ_{ir}) was plotted against the absorbances at 320, 330, 340, 350, 360, 370 and 447 nm (λ_{obs}) for ABM2 in DMF solution during photoisomerization process. The AD diagram was characterized by a straight line fascicle, without no crossing and

passing by zero (Fig. 5). The linear plots of absorbance differences showed that only trans-cis isomerization and no other photochemical reactions occurred upon irradiation with 365 nm light. The slope of each straight line from Fig. 5 is given by the ratio $(\epsilon_t^{\text{obs}} - \epsilon_c^{\text{obs}}) / (\epsilon_t^{\text{ir}} - \epsilon_c^{\text{ir}})$ for λ_{obs} . The negative slope from $\lambda_{\text{obs}} = 447$ nm denotes the antagonist evolution of isomer cis, suggesting that the cis-isomer development occurs exclusively through the transformation of trans isomer in system.

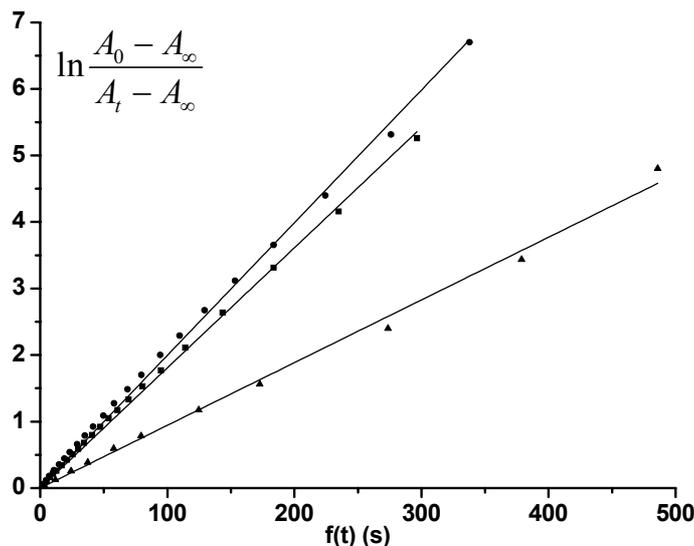


Fig. 6 – Trans-cis photoisomerization kinetics of ABM2 in THF (◆); ABM2 in toluene (●); ABM1 in DCM (▲).

The photoisomerization process of azobenzene moieties in ABM2 follows a first-order reaction according to the kinetic equation:¹⁸⁻²¹

$$\ln [(A_0 - A_\infty)/(A_t - A_\infty)] = k f(t) \quad (2)$$

where A_0 , A_t , A_∞ are the initial absorbance, absorbance at time t and absorbance at the photostationary state, k is the photoisomerization rate constant. The photokinetic factor is defined as:^{18,22}

$$F(t) = (1 - 10^{-A'}) / A' \text{ and } f(t) = \int F(t) dt$$

where A' is the absorbance at irradiation wavelength. The relative content, P , of cis-isomer (Table 1) can be estimated from $(A_0 - A_\infty)/A_0$,²³ where A_0 and A_∞ are the absorbances at 344 nm before and after UV irradiation.

The photoisomerization kinetic curve for azobismaleimide ABM2 in THF is plotted in Fig. 6. The results confirmed a first order plot for the trans-cis photoisomerization of azobenzene

chromophores in ABM2. Estimated from Fig. 6, the photoisomerization rate constant was $1,81 \times 10^{-2} \text{ s}^{-1}$. The trans-cis isomerization rate constants in different solvents for ABM2 are of the same order of magnitude (Table 1). Also, the extent of the trans-cis photoconversion was almost the same for all solvents for ABM2 and a decreased conversion efficiency was observed for ABM1 and PATEI.

The first order trans-cis photoisomerization kinetics for azobismaleimide ABM1 is shown in Fig. 6. The photoisomerization rate constant was much lower than that of ABM2 (Table 1) and also the half-life time ($t_{1/2}$) was about three times higher when compared with the corresponding ABM2 azobismaleimide, giving a relatively high stability of the cis-isomer for ABM1. The reason was considered due to sterically hindering effect of the methyl groups in ortho-position leading to conversion of 60% in cis isomers in dichloromethane (DCM) solution.

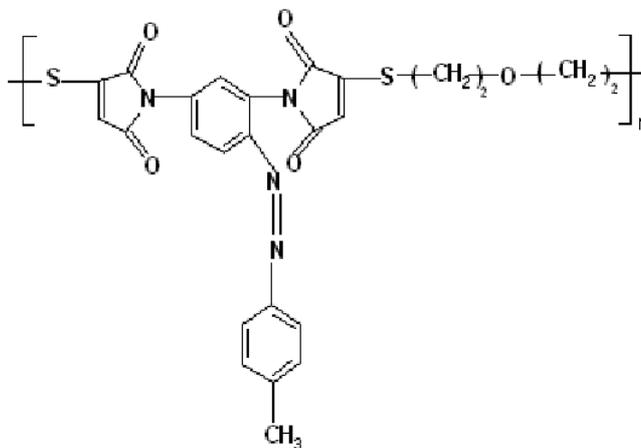


Fig. 7 – Chemical structure of azo polymer.

The photoisomerization of azochromophores in polythioetherimide, PATEI, (Fig. 7) under UV irradiation also evidenced the transformation to the cis-isomer by the significant intensity decrease of the $\pi - \pi^*$ band at about 343 nm and at the same time, an increase in intensity of the absorption band located at 443 nm. The change in the absorption spectra of azopolymer was depicted in Fig. 8. The absorbance

$$(A_0 - A_\infty)/(A_t - A_\infty) = \alpha \exp(-k_f t) + (1 - \alpha) \exp(-k_s t) \quad (3)$$

in which the isomerization reaction proceeded faster in the beginning of photoreaction and then it was followed by a slower process.²⁴⁻²⁷ In equation (3) k_f and k_s represent the rate constants for the fast and slow photoreactions and α is the fraction of fast photoisomerization related to whole conversion. Thus, two different trans-cis photoisomerization processes occur in system. On the other hand, the absorbance difference diagram for azopolymer exhibits some deviations from a straight line, the plots having some intersection points (Fig. 9). This behavior implies that the photoisomerization process in polymer solution does not occur by a first-order mechanism. However, the small observed spreading of the isosbestic point from visible region confirm the deviation in the AD diagram and also it can be assumed an occurrence of a further photochemical reaction during UV irradiation of azopolymer.

The trans-cis photoisomerization kinetics of azobenzene chromophores in PATEI depends on the concentration of chromophore groups. For diluted concentrations of chromophore groups in azo polymer (10^{-6} M), the photoisomerization kinetics

variation corresponds to a conversion degree of 65% for the photostationary state due probably to the steric hindrance determined of the polymer chains. The photoisomerization process for azopolymer shows a deviation from first-order kinetics (Fig. 10). In this case the trans-cis photoisomerization kinetics in azopolymer could be fitted to a biexponential equation:

obey a first-order equation similarly to the free azo chromophore (ABM2, 10^{-5} M) (Fig. 10). The two photoisomerization rate constants are practically identical ($2.11 \times 10^{-2} \text{ s}^{-1}$). The similar photochemical behavior of the two azo chromophore species with different concentrations shows that the local environment for these chromophores is the same and the concentration of polymer chains in the proximity of azo chromophores in diluted solution is rather low so that the steric hindrances can be neglected. For the polymer solution having the same concentration in chromophore groups as ABM2 solution (10^{-5} M) the photoisomerization kinetics deviate from a straight line (Fig. 10) and the kinetics will be described by an biexponential function (eq. (3)). From Fig. 10 it is evident that for lower photoirradiation times, the three curves practically have the same way and then the photoreaction deviates from a first-order kinetics suggesting a combination of fast and slow processes for PATEI isomerization as compared to free chromophore ABM2.

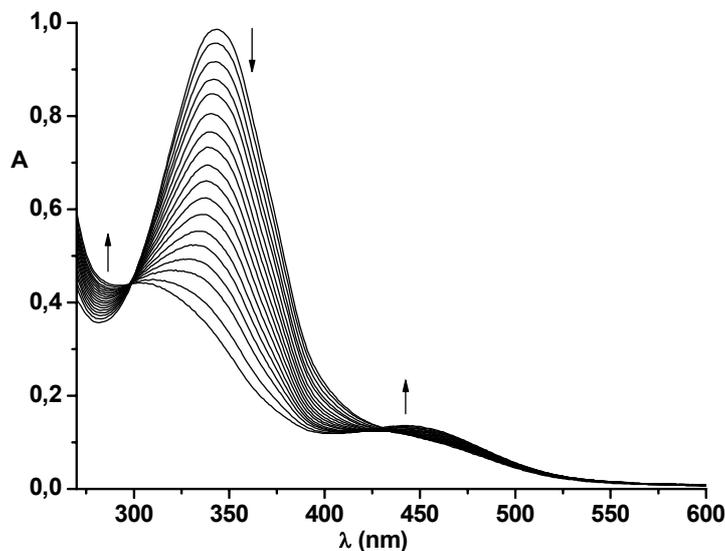


Fig. 8 – Absorption spectral changes of azopolymer PATEI on irradiation at 365 nm.

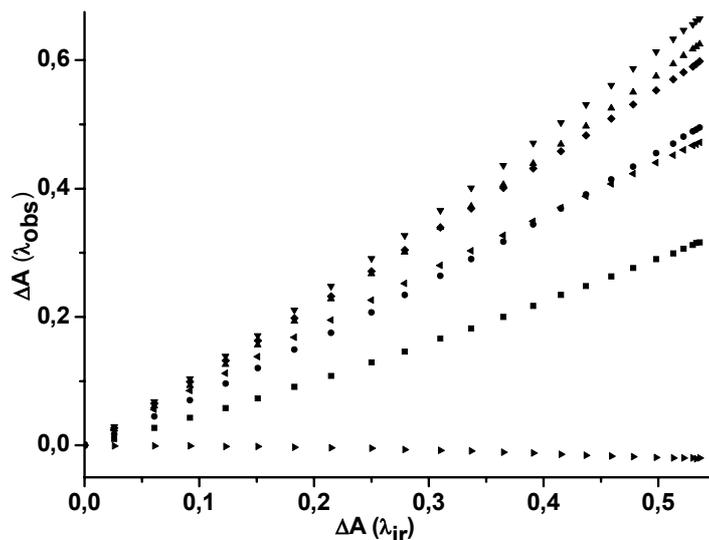


Fig. 9. Absorbance difference diagram for 365 nm irradiation of azopolymer PATEI in DMF solution. The absorbance at 365 nm is plotted against 320 (■), 330 (●), 340 (▲), 350 (▼), 360 (◆), 370 (◄), 447 (►) nm.

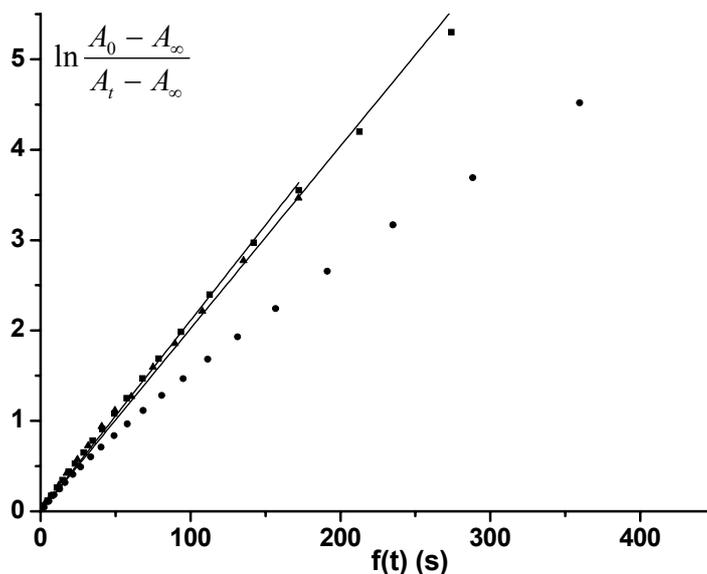


Fig. 10. Photoisomerization kinetics according eq. (2) for: free chromophore (ABM2) (10^{-4} M) (■); PATEI (concentration of chromophore groups of 10^{-6} M) (▲); PATEI (concentration of chromophore groups of 10^{-5} M) (●).

The cis-trans photoisomerization of azobismaleimide derivatives in different solvents were also investigated under irradiation with 436 nm light. Fig. 11 shows absorption spectral change of ABM2 in toluene solution observed upon the blue light irradiation. As illustrated in Fig. 11, the absorption band of trans-azobenzene at 345 nm was rapidly restored to the starting value, while the intensity of cis-isomer was slightly decreased. The kinetics of cis-trans photoisomerization reaction were fitted satisfactorily to the equation (4):

$$\ln [(A_{\infty} - A_0)/(A_{\infty} - A_t)] = k_1 t \quad (4)$$

where A_{∞} , A_0 and A_t are the absorbances at 345 nm at time infinite, time zero and time t , respectively. The cis-trans rate constant, k_1 , of ABM2 was $2.55 \times 10^{-2} \text{ s}^{-1}$. The kinetics of cis-trans isomerization under visible light irradiation was almost independent of the solvent, the rate constant values varying in a enough narrow range (Table 1) for the two azobismaleimides. However, the photoinduced cis-trans isomerization kinetics of azobenzene chromophores in PATEI was described by a biexponential equation (3).

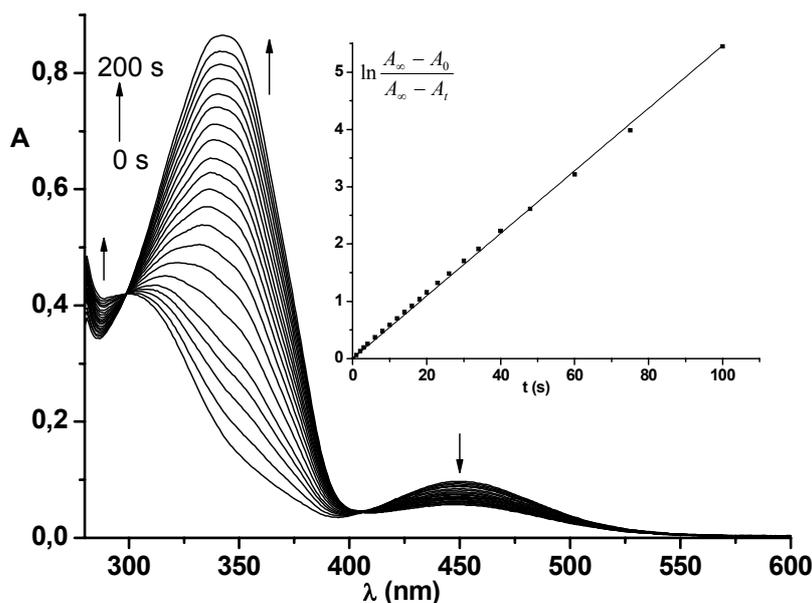


Fig. 11 – Absorption spectral change of ABM2 in toluene solution induced by 436 nm light irradiation. Inset: cis-trans isomerization kinetics.

EXPERIMENTAL

Electronic absorption spectra were performed using a Shimadzu UV 3600 spectrophotometer. Quartz cells of 10 mm spectral path were utilized for measurements. Photoirradiations was carried out with a 350 W medium-pressure mercury lamp at room temperature. The appropriate irradiation wavelengths were selected with glass filters. The isomerization was monitored by UV-Vis absorption spectroscopy.

Azobismaleimides were obtained by the condensation reaction of azoaromatic diamines (2,4-diamino-2'-methylazobenzene or 2,4-diamino-4'-methylazobenzene) with maleic anhydride in acetone by a two-step procedure.²⁸⁻³⁰ Polyazothioetherimide (PATEI) was prepared by reaction of azobismaleimide and bis-2-mercaptoethylether.^{29,30} Solvents used for the study were of spectrophotometric grade and obtained from Aldrich.

CONCLUSIONS

It has been determined for first time the electronic absorption spectrum of cis isomer of azobismaleimide ABM2. The photoisomerization and visible light back-isomerization behavior of azobismaleimides and azopolythioetherimide in solution were investigated and the results revealed that UV-induced photochromism occur in solution. The photoisomerization kinetics was described by a first-order equation for azobismaleimides but for azopolymer fast and slow processes have been found. It has achieved that the solvent nature practically doesn't influence the photoisomerization rates in solution.

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