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New Trends in Architecture of Azo Polymer Materials with Applications in Optical Field. 2. Solvatochromic and Photochromic Investigation

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In the large family of polymers, the azobenzene derivatives represent one fascinating materials class, along with stylbene and azomethinic derivatives. This interest is explained by combination of the properties of anisotropy with the photoinduced behaviors. The photoinduced birefringence, relief grating, the high optical nonlinearity resulted from the sin-anti isomerism, molecular reorientation, the exceptional stability to writing and erasing by laser radiation, are just the most important arguments for their usage of these polymeric architectures in the NLO field as: LCD, chemical sensing, devices for storage and transmission of information. This presentation covers the development and characterization a new series of materials from viewpoint of the modification of the polymer materials by the chemical transformation of the "common" polymer support an underlining: solvatochromic and photorefractivity properties.

Keywords Azo polymers; isomerism; molecular reorientation

Introduction

The starting point for the development of the technical strategies of real NLO polymers is the design synthesis and characterization of chromophores molecules which large molecular hyperpolarizability (β, γ). The generous experimental and theoretical materials regarding utilization of the organic materials (particularly polymers) into NLO application reveal specially the composition-properties relationship.

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Another more important and proper aspect will be making up, at the side of practical techniques for realization of the materials assembly, the synthesis and characterization of these materials.

The major problem for NLO polymer, beyond optimizing the individual responses of the constituent chromophores is to maximize the chromophore number density with achieving and preserving the properties of the microstructure. In this context various strategies achieves these end are developed. The macromolecular structures fulfilling the above restrictions may be obtained according to two alternative strategies [1]:

1. The chromophore fragment may be attached to a pre-formed macromolecular chain, through a polymer-analogous reaction.
2. A macromolecular arrangement with a foreseen architecture may be obtained through copolymerization of some monomers containing incorporated chromophore fragments.

The azobenzene materials are perhaps the more fascinating NLO materials. That is duet on one hand, because it is fairly well known and on the other hand because it has produced and continues to reveal completely unexpected phenomena, some of them still unexplained. In the literature a large attention is dedicated to these materials class for them potential application in the optical field [2–11]. In this context, the azoic polymers show a peculiar applicative interest. When the azobenzene group is incorporated into polymeric matrix, conformational modification plays a fundamental role in the recording and preserved process [12–17]. According to the Figure 1, when utilized light radiation at λ_1 or λ_2, wavelength, determine an intern conformational change of the azoic group. In this process are involved several distinct process: a decoupling for a double bond π electrons an turning around a simple bond N–N, following of the improvement a double bond in a new configuration.

These phenomenological microscopic suite (E(anti)-Z(sin) isomerization) involve a π-π^* and n-π electronic transitions [18]. This process is reversible when the photochromic moieties exist, as usually occurs, in two different forms, whose relative concentration depends on the wavelength of incident light. As absorption intensity such as lifetime of Z(sin) form, which is relative long, are determined by electrochemical character of the aromatic rings substituent. A very important factor for rate of photoisomerization is neighbourhood nature of photochromic moieties. Apparition and stability of optical phenomena's, as a photoisomerization consequence, are determined one side of the internal constitutive properties (free volume, nature and structure of polymeric matrix, etc.) and the other side by technical parameters work: temperature, solvent nature, etc.

Experimental Part

We have investigated the solvatochromic and photochromic properties of the modified copolymers of maleic anhydride (MA) [19–24] with different azoic

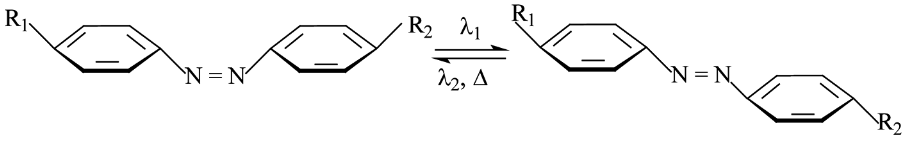

Figure 1. Photostimulate conversion of E(anti)-Z(sin) isomers in azocompounds structures.

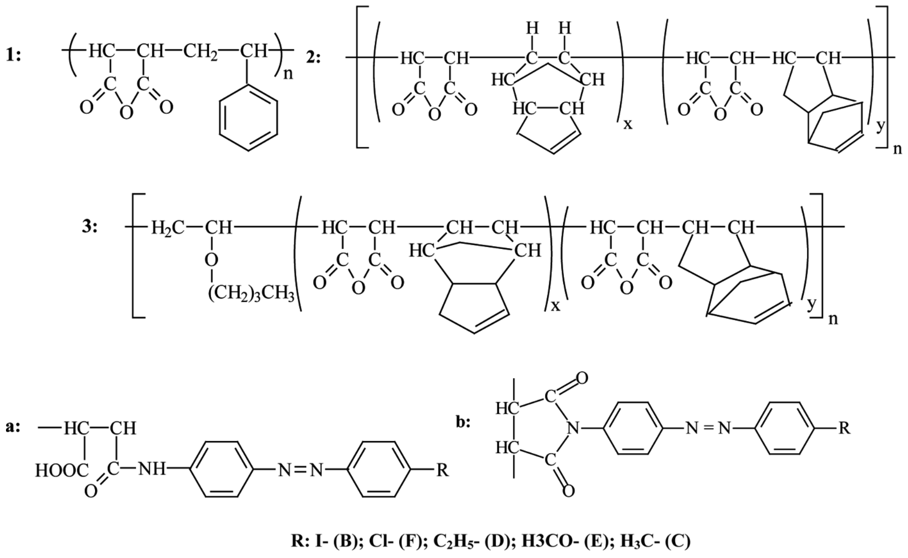

Figure 2. Chemical structures of the modified copolymers.

chromophores (Fig. 2). Synthesis and characterisation of the azobenzene derivates are described elsewhere [25].

For obtaining modified polymers with azocompound sequences, we used the synthetic method reported as Patels and co-workers procedure [26]. We obtained the ami and imide structures. The initial characteristics of the polymer substrate are MA-DCPD: $M_n \approx 2300$, $X_{MA} \approx 64.65\%$; $GP_n \approx 25$; BVE-MA-DCPD: $M_n \approx 30\,000$, $X_{MA} = 50\%$; $GP_n \approx 290$; and S-MA: $M_n \approx 95\,000$, $GP_n \approx 940$; $X_{MA} = 50\%$.

The studies were preformed using UV-Vis spectroscopic techniques on solution and thin films. For these purpose the JASCO UV-Vis-NIR spectrophotometer, model V 670, was used. Thin films were obtained by spin coating of solution on the carefully cleaned glass substrate (the spin coating machine was Laurell-model WS-400B-6NPP/LITE). The FT-IR spectra was recorded using a BRUKER EQUINOX 55 apparatus.

Results and Discussion

I. *Solvatochromic Investigations of Azo Polymer*

In the FT-IR spectra can be distinguished the structural differences between the amic and imide forms of the transformed copolymers and in the same time as the specific vibration band of the copolymer support (Fig. 3). Thus, all polymer supports presented the characteristic peaks of the MA (1851–1852 and 1776–1777 cm^{-1}, respectively). For the amic compounds, (see Fig. 3) we remark the peaks at 3600 cm^{-1} (OH from the carboxyl group) and the carbonyl peak at $\approx$1710 cm^{-1}. The amide groups (I; II) is situate around 1660–1600 cm^{-1}, 1598–1544 cm^{-1}, respectively.

The imide forms are characterize by diminution of the 3600 cm^{-1} peak in the same time with the shift of the carbonyl peak ($1710 \rightarrow 1700\,cm^{-1}$). As the same time is remarked diminution of the peak to the 1851 cm^{-1} and increasing for them to the

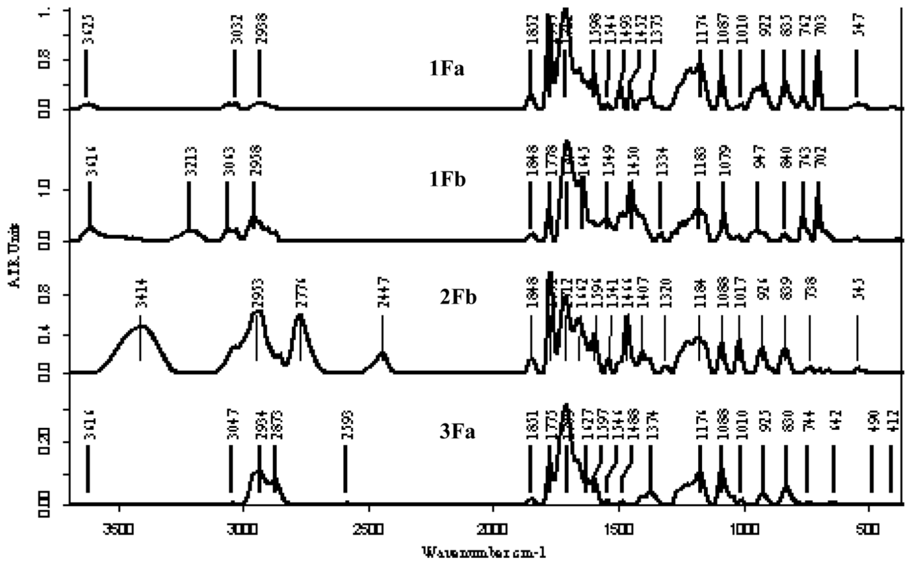

Figure 3. Exemplifiant FT-IR spectra.

$1776\,cm^{-1}$ and apparition of the amide III band situated around $1333\,cm^{-1}$. Unluckily, the absorption band characteristic to the substituent is not identifiable. The vibration of the skeleton ($500\,cm^{-1}$ ν_{Cl}, $600\,cm^{-1}$ ν_{CCl}, $1020–1275\,cm^{-1}$ ν_{C-O-C}) overlaps them.

Electronic absorbtion spectra of synthetized materials in diferents solvents showed an energie charge-transfer absorbtion in the UV-vis region. Thus, bathochromic shift is stimuled by the incresing of the solvent polarity, indifferent to the nature of the polymer support or substituant (see Table 1). For the same subtituant and support the bathochromic effect is high for the amic form ($\Delta\nu = -9002\,cm^{-1}$ for 2Fa rapported to $\Delta\nu = -8114\,cm^{-1}$ for 2Fb). That is perhaps duet to the sterical hidrance determined by the bonding modality of the chromogene sequence (Table 1 and Fig. 4).

How we can observed, the absorbtion energy of all materials decreases as the solvent polarity increase. Solvent stabilization of dipolar excited state accounts for bathocromic shift, all material being caracterized by negative solvatochromic effect. The low extinction coefficient of 2Fb (lesser at one magnitude order) account for distorsions in alkyl chain duet to the close of the imide cycle.

Figure 5 show the electronic transition energy plotted versus $E_T(30)$ solvent scale. The negative slope observed from all analysed materials, indicate how the solvent stabilize the ground and excited state. Therefore, specifically to the azoic derivates, the dominant is the $\pi \rightarrow \pi^*$ transition and the stabilization involves the intermolecular charge transfer (ICT). Similar to the other studies dedicated to the solvatochromic effect of the azocompound we can conclude than the $E_T(30)$ scale is considered suitable for the materials which not influence the each other the hydrogen bonding interaction and the solvent polarity. Since, the charge, electron, polarizability, steric hindrance, hydrophobicity and hydrophilicity of materials influence the electronic transition energy of a solute, assessment of solvent-solute interaction should be accompanied with that of polarity.

Table 1. Spectral and solvatochromic parameters

	Film	Dioxane ($\pi^* = 0.55$)**			THF ($\pi^* = 0.58$)			DMF ($\pi^* = 0.88$)				
Cod*	λ_{max} (nm)	λ_{max} (nm)	ε (l/mol cm)	$E_T(30)$*** (kcal/mol)	λ_{max} (nm)	ε (l/mol cm)	$E_T(30)$*** (kcal/mol)	λ_{max} (nm)	ε (l/mol cm)	$E_T(30)$*** (kcal/mol)	$\Delta\lambda_{max}$	$\Delta\nu_{max}$
1Fa (0.61)	300	374	$1.7 \cdot 10^5$	76.5	394	$1.3 \cdot 10^5$	72.6	419	$1.5 \cdot 10^6$	68.2	45 (119)	−2872 (−9467)
2Fa (0.59)	300	366	$6.4 \cdot 10^5$	78	390	$5.8 \cdot 10^4$	73	411	$4.5 \cdot 10^5$	69.6	45 (111)	−2991 (−9002)
2Fb (0.59)	300	356	$1.1 \cdot 10^5$	80.3	360	$4.1 \cdot 10^4$	79.4	397	$3.6 \cdot 10^4$	72	41 (97)	−2901 (−8144)
1Ca (0.59)	300	371	$7.5 \cdot 10^5$	77.1	382	$1.4 \cdot 10^6$	74.8	411	$1.2 \cdot 10^6$	69.6	40 (111)	−2623 (9002)
1Da (0.5)	300	366	$1.1 \cdot 10^6$	78	386	$1.2 \cdot 10^6$	74.1	406	$1.3 \cdot 10^6$	70.4	40 (106)	−2692 (−8703)

*in the bracelets is marked the substitution degree of the polymer support;
**values according [27];
***$E_T(30)(\text{kcal/mol}) = hc\upsilon_{max}N_A = 2.8591 \cdot 10^{-3}\nu_{max}(\text{cm}^{-1}) = 2859/\lambda_{max}(\text{nm})$ [28].

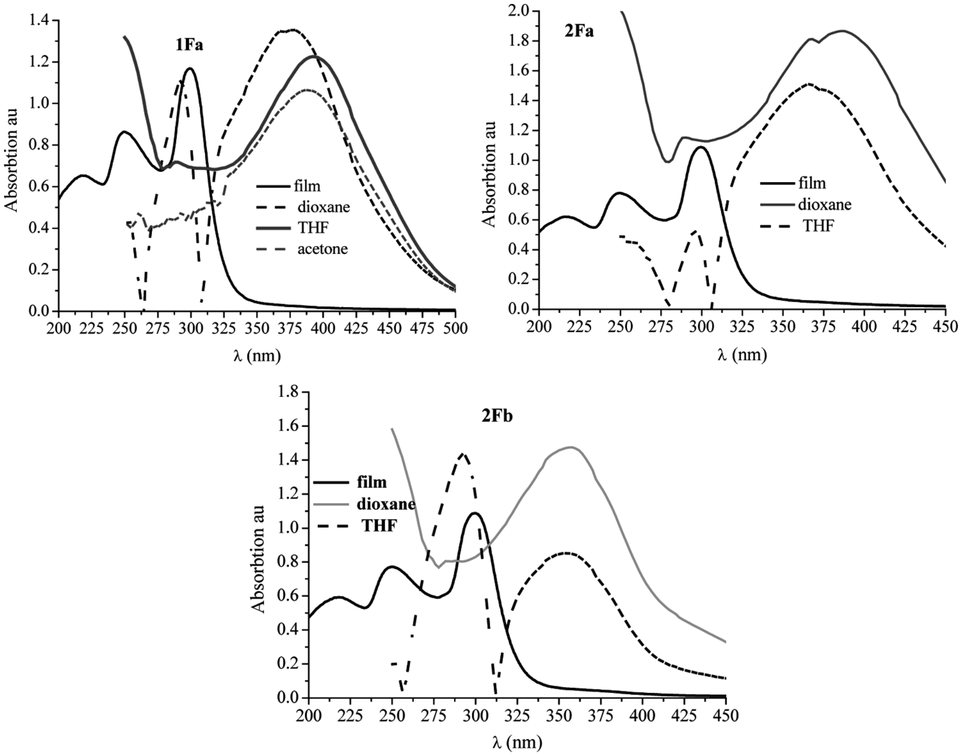

Figure 4. Exemplificative absorption UV-vis spectra for photochromic synthesized materials.

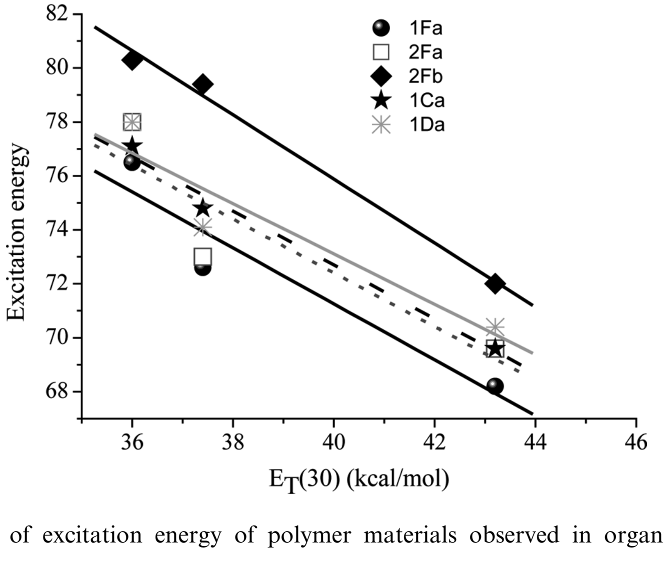

Figure 5. Plot of excitation energy of polymer materials observed in organic solvent vs. $E_T(30)$.

II. *Photochromic Properties Investigations of Azo Polymer*

Kinetic analysis is developed based to the reversible photoisomerization of azobenzene. All experiments and measurements were realized at room temperature. We are determined the isomerization rate constant, k(T_{isom}), by performing UV measurements, as a function of time. In the similar manner assigned to the literature [29], applying Eq. (1); the amount of E(anti) photochrome group is assumed to be linearly related to absorbance at λ_{max}(t) since during the whole process the absorbance was less than 1.

$$k(T_{isom})t = \ln\left(\frac{A_{E(anti)} - A_{Z(sin)}}{A_{E(anti)} - A_t}\right) \tag{1}$$

where: $A_{E(anti)}$ is the absorbance after storage in the dark before irradiation with UV light; $A_{Z(sin)}$ is the absorbance measured after irradiation; A_t is the absorbance at time t after irradiation.

The absorbance value was evaluated at λ_{max} (t). The half-time, $t_{1/2}$, of the Z(sin) form were derived from:

$$A_{t1/2} = A_{Z(sin)} + \left(A_{E(anti)} - A_{Z(sin)}\right) \tag{2}$$

$$t_{1/2} = \frac{\ln 2}{k(T_{isom})} \tag{3}$$

The Eq. (2) is assumed to the first order process. Because k(T_{isom}) is not constant during the thermal back isomerization process, the value $t_{1/2}$ was determined from Eq. (3).

The thermal back-isomerization process from cis Z(sin) to trans E(anti) for polymer is shown in Figure 6. The UV-Vis spectra, recorded for all polymer materials,

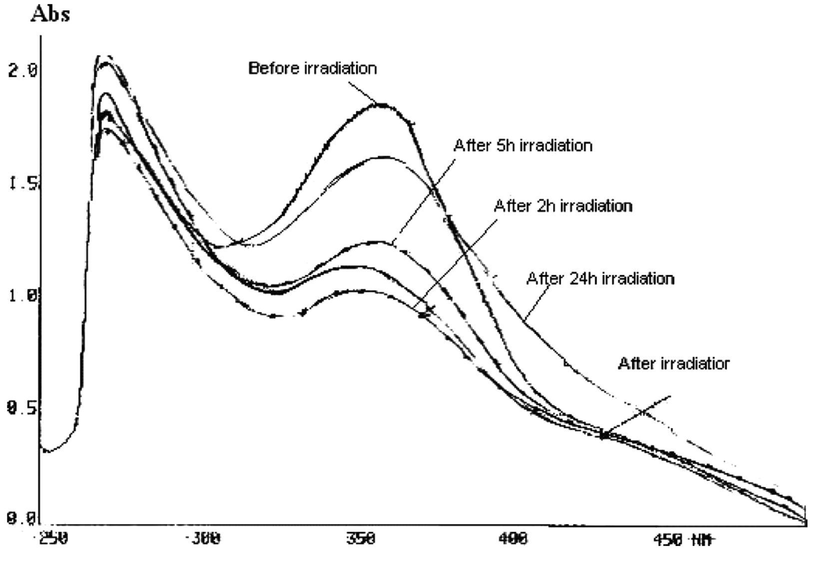

Figure 6. Exemplification of the Z(cis)-E(trans) isomerization of polymers 3Fa.

underline the presence of the isosbestic points at 403–427 and 269–272 nm, which are characteristic for the existence of two distinct absorbing species in equilibrium with each other. The results for kinetic analysis are reported in the Table 2 and Figure 7.

As indicated in Figure 7, $k(T_{isom})t$ versus t relation is not linear, as would be expected for first-order kinetics. This nonlinearity seem be duet to the difference of the environment of azobenzene groups. The rate of the thermal isomerization is enhancing by steric factors such as limited free volume in the polymer matrix or movements of chain segments. The slope of $k(T_{isom})t$ versus t can be regarded as a summation of individual *k* values for each sequence. The isomerization processes was strongly affects by conformational modification at macromolecular chain. The most relevant interpretations are the comparison result at half times of Z(sin) state ($t_{1/2}$), presented in the Table 2.

The first ascertainment points out as the stability of Z(sin) isomer can be enlargement by the modification of the intrinsically structure of polymer (amic-imide) (St–MA → MA–DCPD → BVE–MA–DCPD).

For same structural polymeric support (see Table 2; structure St–MA, all copolymers with index 1), $t_{1/2}$ increasing whit decreasing electronegative character of the substituent. Therewith, the $t_{1/2}$ value for the same structure of copolymer, increase, at modification of bonding chromogen electrical nature of the photochrome neighbourhood. This aspect is augmented by the steric hindrances which appear to the imide bond formation whence stiffness the polymer photochrome bond.

The relatively short half-times for Z(sin) isomer was obtained for amic forms of St–MA copolymer, modified with Cl (101 min) or I (97 min) to boot MA – DCPD copolymer (amic form) (172 min). The modification of $t_{1/2}$ to the change of substituent of the azoic sequence is duet to the different activation energies for the π–π and ν–π^* transitions. These differences are the result of the electronegative of the azobenzene group's substituent.

Table 2. Resulted data for the investigated polymers

Code	Substituent	X*	λ (t) nm	$t_{1/2}$ (min)
1Ca	CH_3	0.59	407	3322
1Fa	Cl	0.61	416	101
1Fb		0.61	382	5950
2Fb		0.59	360	1214
3Fa		0.49	409	6189
3Fb		0.59	366	1130
1Ba	I	0.64	379	97
1Bb		0.58	383	1181
2Ba		0.40	379	172
3Ba		0.61	379	933
3Bb		0.40	379	237
1Ea	CH_3O	0.66	379	2077
1Da	C_2H_5	0.50	399	5713
1Db		0.45	349	2923

**fraction of photochromic sequences bonded from the total anhydride sequences.*
This is evaluate on the UV-vis specific absorption, and verified by elemental analysis.

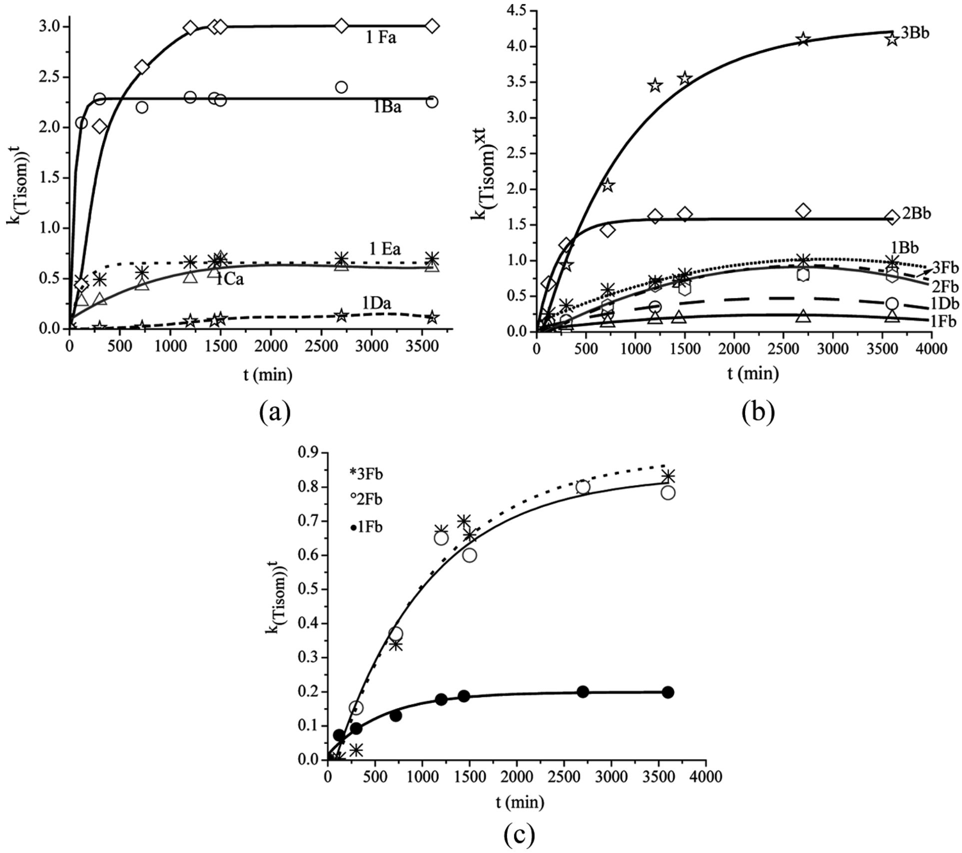

Figure 7. Dependence k(T_{isom})t vs. time for amorphous copolymers; (a) amic form of MA-S; (b) imide form of MA-S; (c) imide form for different support and the same with azoic-dye.

The large increase of $t_{1/2}$ values at the structural – conformational modifications of the copolymer (S–MA/MA–DCPD/BVE–MA–DCPD) are exclusive duet to the physical property's of the support. Including in the polymer structure of the DCPD unit stiffness the base chain and by consequence, induce, to the photochrome group, a hindering the free rotation around the basic chain.

Therefore, the free volume necessary to the E(anti) → Z(sin) → E(anti) isomerization is diminishing. Therefore, $t_{1/2}$ grows in the case in which first transition sequence (E(anti) → Z(sin)) is possible. Probably as introduction of spacer between the chromophore group and polymeric chain reduce the inconveniences. This aspect is underlined for acrylic copolymers [29]. Apparently not all azobenzene derivate side groups in the polymer matrix are available for photoisomerization, which is probably mainly due to steric hindrance.

Conclusions

The solvatochromic investigations reveal:

A high bathochromic effect for the amic form duet to the sterical hidrance consequence of the bonding modality of the chromogene sequence. The low extinction coefficient of 2Fb is duet to the distorsions in alkyl chain consequence of the closing of the imide cycle.

The solvent stabilization involves the intermolecular charge transfer (ICT).

Since, the charge, electron, polarizability, steric hindrance, hydrophobicity and hydrophilicity of materials influence the electronic transition energy of a solute, assessment of solvent-solute interaction should be accompanied with that of polarity.

The preliminary studies at photochromic investigation of modified polymers with azobenzene developed in this work distinguished:

The influence nature of chromophore – polymeric chain's bond: $t_{1/2}$ of Z (sin)-isomer is very important with that rigidity (amic → imide). To the same at level of chain, the determinate factor for stability of Z (sin)-isomer seem to be the nature of the substituent to the azoic group.

The type of polymeric chain have a decisive influence about the stability of Z (sin)-isomer. The high values $t_{1/2}$ are obtained in the case of chains with free useful reduced volume, due steric hindrances, consequences of reducing the possibility of rotation around at basic chain.

Thus of materials can be used like systems of photoinduced stabilization alignment nematic liquid crystals [30].

Acknowledgments

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