Polymer Architectures Containing Azobenzene Type Molecules in Side-chains

Solvatochromic behaviour

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In this article, some advantages and disadvantages of the incorporation method of azobenzene moieties in several polymer matrices (polymethacrylate, poly(styrene-alt-maleimide), poly(oxazoline-co-methacrylate), poly(methacrylate-co-methacryloxypropyl trimethoxy-silane)) are highlighted. Their physical properties (molecular weights, glass transition temperatures, chromophore load, solubility, and solvatochromism) are discussed with regard to their macromolecular architecture. Solvent effect on the UV-Vis absorption spectra of azo-polymers was investigated using Reichardt’s E_T^N *solvent polarity scale and Kamlet-Taft multiparameter equation. Kamlet-Taft equation revealed that hydrogen bond acceptor properties and dipolarity/polarizability of the solvent have a significant contribution upon the solvatochromic behaviour of azopolymers.*

Keywords: azobenzene, side-chain polymers, solvatochromism, Kamlet-Taft equation

During the last decades, the azobenzene type molecules have been the topic of many research articles, ranging from fundamental studies to practical applications [1-4]. Azobenzene functionalized polymers have been widely investigated for surface relief gratings (SRG) [5, 6], optical storage data [7], holographic memories [8-10], and nonlinear optical properties [11-13]. All these applications rely on azobenzene’s unusual photo-responsive behaviour in contact with light, having the wavelength anywhere within the broad absorption band. The photo-responsive properties of an azo-polymer are based on the *trans*-to-*cis* and *cis*-to-*trans* photo-isomerizations of the incorporated azo-moiety, which leads to considerable changes in their molecular shape and dipole moments [14]. In order to exploit the photo-chemical behaviour of azobenzene, some incorporation strategies have been explored. One of the most attractive methods for incorporating azobenzene into functional materials is covalent attachment to polymers [15]. The versatility of these photoactive systems is that the azo groups can be selectively attached in the side-chain either by copolymerization [16] or by polymer analogous reactions [17, 18]. Both techniques are desirable because they each bring some advantages. The first method is preferred for its simplicity and control of sequence distribution; while the second one provides control over the choromophore load and molecular weights. Either way, the resulting materials benefit from the inherent stability, rigidity, and processability of polymers, in addition to the unusual photo-responsive behaviour of the azo moieties. Many different backbones have been used as scaffolds for azo moieties; but a thorough survey of the literature background on polymers containing azobenzene derivatives revealed that the most studied class is represented by polymethacrylates and derived copolymers [13, 19-23]. The attractions presented by these polymers are that they exhibit excellent film forming ability, solubility and good optical properties.

Azo dyes can be prepared with a wide range of donor and/or acceptor groups. In addition due to the planarity of the azo bridge versus the non-planarity of stilbenes or other systems, they will contribute to larger π electron transmission effects leading to higher optical activity of these materials in solutions [24]. Taking into account that solvent can significantly influence the chemical and physical properties of the solute, the investigation of solvent-solute interaction is very important. In the case of azobenzene dye such preliminary investigation can give an idea about the magnitude of their hyperpolarizability [25]. Solvatochromism is caused by the different solvation of the ground and first excited states of the light-absorbing molecule and thus it is a convenient tool to study the nature of solvent-solute interactions.

The aim of this study is to investigate the effect of the substitution pattern of the azobenzene moiety upon the solvatochromic behaviour of some of the azo-polymers. Solvent effects on the longest wavelength UV/Vis absorption band of the azo-polymers will be quantified using both Reichardt’s E_T^N [26]solvent polarity scale and the Kamlet-Taft multiparameter equation [27].

Also, an overview of different polymer architectures containing azobenzenes with various substitution patterns is presented. The polymers prepared by us (see Figure 1), exhibit distinct solubility, molar weights, glass transition temperatures & thermal stabilities and as well as different solvatochromic behavior. All these features relate to their macromolecular structure and azobenzene nature of each particular class; therefore, the advantages and disadvantages of each class of azo-polymers are being highlighted.

Experimental part

Materials and methods

The colored monomers (Mx) used in copolymerizations were prepared in our laboratory after the recipes reported

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in reference [28]. The 4-(4-Hydroxy-3,5-dimethylphenylazo)benzoic acid (C_0); (4-[N'-(4-cianoethyloxy)phenylazo]-2,6-dimethylphenol, *M1S*; (4-[N'-(4-nitroethyloxy) phenylazo]-2,6-dimethylphenol, *M2S*; (4-[N'-(2-ciano-4-nitroethyloxy) phenylazo]-2,6-dimethylphenol, *M3S*; and (4-[N'-(2,4-dinitroethyloxy) phenylazo]-2,6-dimethylphenol, *M4S* were prepared as first reported in references [29]. Methylmethacrylate and methacryloxypropyl trimethoxysilane were distilled prior to use.

Polymer synthesis

The polymers used in our experiments are some poly(methacrylate)s bearing azo moieties, MMA-Mx illustrated in Fig.1a and MEMO-Mx in figure 1b, which were prepared by free radical copolymerization, starting from methyl methacrylate or 3-methacryloxypropyl trimethoxysilane with some original azo-monomers (Mx). The characterization of these monomers can be found in ref [28]. The other two classes of side-chain polymers, MASt-Mx shown in figure 1c and MMA-IPRO-C_0 in figure 1d, were synthesized by polymer analogous reaction, starting from preformed copolymers and tailored azo-dyes (C_0 and MxS).

Synthesis of MMA-Mx copolymers

The MMA-Mx copolymers were obtained by free radical copolymerization, starting from 1.47 mmole of methyl methacrylate (MMA) and 0.63 mmole of *Mx*, as previously described in reference [30]. To prepare the final solutions, 2,2'-azobis(2-methylpropionitrile) ($5 \cdot 10^{-3}$ mole/L) and 2 mL of dry dioxane were added. The resulting mixtures were well degassed and sealed off under argon cushion. The polymerizations were carried out at 80°C for 21 h. After cooling down, the solutions were precipitated in 40 mL of diethyl ether. The copolymers were purified from unreacted monomers by reprecipitation from acetone in diethyl ether. Yields: MMA-M1 41%; MMA-M2 38%; MMA-M3 40%; MMA-M4 36%; MMA-M5 24%.

Synthesis of MEMO-Mx copolymers

The MEMO-Mx copolymers were also obtained by free radical copolymerization, following the recipe from reference [31, 32]. In a similar run, 4.7 mmole of 3-methacryloxypropyl trimethoxy-silane (MEMO) were added to a well degassed solution of 1.56 mmole of Mx and 0.09 mmole of 2,2'-azobis(2-methylpropionitrile) in 6 mL of dried dichlorobenzene. The copolymerization was allowed to continue for 24 h at 80°C in a sealed ampoule. After that, the mixture was precipitated in 20 mL of petroleum ether. The precipitated copolymer was then dissolved in $CHCl_3$ and precipitated in petroleum ether to get rid of any unreacted monomers. The procedure was repeated four times for each synthesized substrate and dried at 50°C under vacuum. Yields: MEMO-M1 47%; MEMO-M2 37%; MEMO-M3 36%; MEMO-M4 25%; MEMO-M5 52%.

Synthesis of MASt-Mx copolymers

The functionalized copolymers MASt-Mx were obtained via *Mitsunobu* condensation reaction, as first reported in reference [29]. In a typical run, 20 mL of dried dimethylsulfoxide were added to 1.4 mmole of MxS azobenzenes, 1.4 mmole of triphenylfosfine, and 0.3 g of poly(styrene–*alt*–meleimide) copolymer (MASt, maleimide units: 0.746 mmole) in a round bottom flask. The solution was left under stirring for 15 min and then 1.4 mmole of diizopropylazodicarboxylate was slowly added. The alcohol (MxS) was used in excess to ensure a complete substitution of the succinimide units. The reaction was allowed to continue for 24 h at room temperature. Afterwards, the reaction mixture was precipitated in ethanol; the resulting coloured polymer was filtered and dried. The product was purified twice by reprecipitation from chloroform in ethanol and dried at 70°C for 48 h under vacuum. Yields: MASt-C1S 65%; MASt-C2S 53%; MASt-C3S 58 %; MASt-C4S 49%.

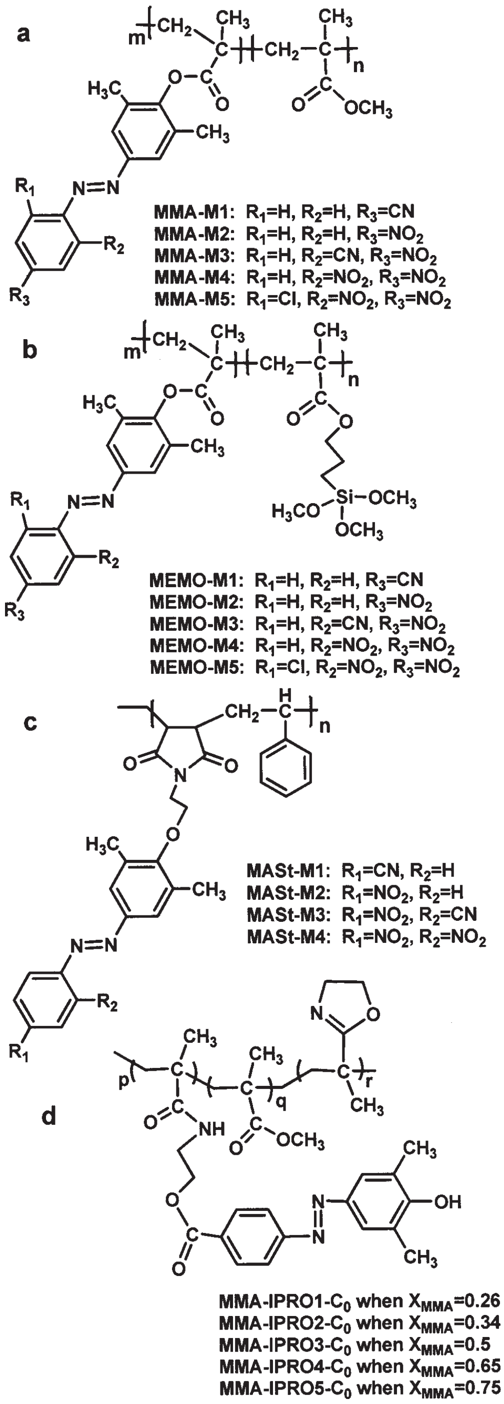

Fig. 1. Side-chain polymers containing different substituted-azobenzene chromophores: a) MMA-Mx and b) MEMO-Mx copolymers obtained by radical copolymerization; c) MASt-Mx and d) MMA-IPROx-C_0 copolymers obtained by polymer analogous reactions

Synthesis of MMA-IPROx-C_0 copolymers

The modified copolymers were obtained by oxazoline ring opening addition in the presence of 4-(4-Hydroxy-3,5-dimethylphenylazo)benzoic acid (C_0) as described before in reference [21]. In a typical run, 15 mL of dried dimethylformamide were added to 1.33 mmole of C_0 and 2.37 mmole of poly(oxazoline-co-methacrylate) (MMA-

Table 1
PHYSICAL PROPERTIES OF THE STUDIED AZO-POLYMERS

Copolymer Code	[a]w	T_g (°C)	[b]T_d (°C)	M_n (Da)	[c]λ_{max} (nm)
MMA-M1	0.46	161.3	277	6,684	337
MMA-M2	0.51	152.7	293	3,026	346
MMA-M3	0.51	148	271.5	3,030	361
MMA-M4	0.51	146	278.6	3,068	348
MMA-M5	0.47	168.1	268.2	33,300	-
MEMO-M1	0.43	-	327	3,201	337
MEMO-M2	0.43	-	312	3,413	345
MEMO-M3	0.46	-	284	4,797	361
MEMO-M4	0.43	-	275	4,988	348
MEMO-M5	0.45	-	263	3,125	-
MASt-M1	0.78	188	345	500,000	347
MASt-M2	0.79	184	338	500,000	358
MASt-M3	0.73	210	353.5	500,000	370
MASt-M4	0.71	208	317	500,000	363
MMA-IPRO1-C_0	0.91	188	261.4	26,300	
MMA-IPRO2-C_0	0.88	186.2	271.0	27,700	
MMA-IPRO3-C_0	0.79	175.6	276.4	28,900	376
MMA-IPRO4-C_0	0.67	168.9	286.8	29,600	
MMA-IPRO5-C_0	0.56	153.8	302.6	30,500	

[a]w- represents the weight fraction of corresponding azobenzene (Mx) in copolymers calculated from elemental analysis; [b]Temperature represents 10% weight loss in TGA measurements at heating rate of 5 °C/min; [c]recorded in N,N-dimethylformamide

IPROx-C_0, where the IPRO molar fraction ranged from 0.25 to 0.74) in a round bottom flask. The solutions were heated at 160 °C and left under stirring for 10 h. The polymers were separated from the reaction mixture by precipitation in diethyl ether. The products were purified twice by reprecipitation from THF in diethyl ether and dried at 60°C for 48 h under vacuum. Yields: MMA-IPRO1-C_0 65%; MMA-IPRO2-C_0 69%; MMA-IPRO3-C_0 71%; MMA-IPRO4-C_0 81%; MMA-IPRO5-C_0 83%.

Characterization

The elemental analysis was carried out by employing a Costech ECS 4010 CHNS analyzer. The number average molecular weights (*Mn*) of the copolymers was evaluated by SEC with Agilent 1200 Series Refractive Index Detector, (G1310A)-ISO HPLC Pump; using dimethylformamide as eluent (flow rate 1 mL/min), against polystyrene standards. The thermal analysis (simultaneous TGA-DSC) was performed on a NETZSCH STA 449C Jupiter system. UV–Vis absorption spectra were acquired at 25 °C on a Varian Cary 100 Bio UV–Vis spectrophotometer. Spectroscopic quality solvents were used throughout the study to prepare the dye solutions (having concentrations $4 \cdot 10^{-5}$ mol/L). The absorption spectra of freshly prepared dye solutions were recorded between 200 nm and 600 nm. The E_T^N solvent polarity parameters given by Reichardt's review [26] were used. For the Kamlet-Taft solvent parameters (i.e. α, β, π^*) the most often used values were considered [25].

Results and discussions

Physical properties

First, we will focus our discussions on distinct physical properties exhibited by our side-chain polymers. Table 1 summarizes some physical properties of each class of polymers presented in the Experimental section. The azo-polymers we synthesized differ from one another either by the nature of the backbone, molecular weight, or by their azo side-chain moiety. The solubility of a polymer is generally influenced by both chemical composition and molecular weights. Therefore, MMA-Mx and MEMO-Mx obtained by copolymerization showed excellent solubility in a wide range of solvents ($CHCl_3$, CH_2Cl_2, dichlorobenzene, dioxane, tetrahydrofuran, acetone, dimethylformamide (DMF), and dimethylsulfoxide (DMSO)), while MASt-Mx and MMA-IPROx-C_0 copolymers exhibited good solubility in DMF, DMSO and chloroform. The poor solubility of the later polymers is linked to the high molecular weights of the starting copolymers which were conserved after the chemical modification.

All copolymers exhibited high glass transition temperatures, due to the impaired segmental motion of polymer chains induced by the bulky azo-moieties. The highest T_gs were found for MASt-Mx copolymers, closely followed by MMA-IPRO-C_0 copolymers (depending on the chromophore load) and last MMA-Mxs. The MEMO-Mx copolymers did not exhibited clear glass transition temperatures, due to the high content of silane moieties, which are known to considerably lower the T_gs.

The maximum chromophore load was attained by polymer-analogous reaction on the last ones, i.e. the MMA-IPROx-C_0 copolymers. The lower chromophore weight fractions found for MMA-Mx and MEMO-Mx copolymers, as displayed in table 1, are due to both poor reactivity of bulky azo-monomers and their tendency to chain–transfer. The polymer analogous reaction is a more efficient path for attaining desired chromophore loads (MMA-IPROx-C_0s) or copolymer distributions (MASt-Mxs). This can be adjusted either from the analogous-reaction conditions or from the fairly good control upon the units in copolymers (substrates) provided by the radical copolymerization. However, the radical copolymerization was preferred too, due to the fact it yields polymers that exhibit excellent solubility in a great variety of organic solvents. This is a necessary feature, because most of the physical characterization of the polymers is done in solution, for example: UV-Vis spectroscopy.

Solvatochromic behaviour

Azobenzenes with polarized conjugated đ-electron systems have an ionic conjugation. Such structures are ionic in both their ground and their excited states, and thus the electronic transition causes only small polarity changes. These small polarity changes are expected to cause only small solvatochromic shifts with increasing solvent polarity. Although the use of a wide range of solvents was attempted (polar and non-polar, protic and aprotic, hydrogen bond donating and hydrogen bond accepting), the poor solubility of the azopolymers in non-polar and alcohols caused some limitations. The MASt-copolymers were excluded from the study due to their solubility limitations, while the MEMO-Mx were considered to be very similar with MMA-Mx copolymers.

Absorption spectra can show how the electronic properties can be modified by varying the donor and/or the acceptor strength (table 2). All azobenzene polymers (dissolved in N,N'-dimethylformamide) exhibited absorption maxima around 270 nm and between 336-380 nm (table 1), which were related to the π-π* transitions of the aromatic rings and to a π-π* first single electron transition of the azo double bond, depending on the substitution pattern and on the nature of the substituents. The weak band at 450 nm can be attributed to the n-π* transition of azobenzene.

For the same polymeric matrix the influence of the strength of the acceptor group is demonstrated by comparison of the absorption maxima of MMA-M1 (λ_{max} = 337 nm), MMA-M2 (λ_{max} = 346 nm), MMA-M3 (λ_{max} = 361 nm) and MMA-M4 (λ_{max} = 348 nm). The small absorption maxima difference between MMA-M2 and MMA-M4 can be explained by the fact that 4-nitro compound has a planar structure while 2',4'-nitro substituted is non-planar due to steric constraints between the o-nitro group and the lone electron pair of the azo group. This arrangement causes the group to rotate out of plane. The rotation takes place between the carbon atom of the aromatic ring and the nitrogen atom of the NO_2 group. The rotation about the double bond requires more energy than the rotation about a single bond. The first excited state in which this bond has considerable double bond character is destabilized relative to its ground state where the bond is closer to a single bond which results in the reduction in the bathochromic effect. The introduction of cyano substituent the 2'-position results in a large bathochromic shift as compared to MMA-M2 and MMA-M4. The nitrile substituent mainly raises the electronic conjugation of the system rather than interacting with the azo bond. The same bathochromic shift is preserved when using polystyrene-maleimide matrix and suggested an increase of molecular hiperpolarizability, according to theoretical NLO studies.

The influence of the matrix on the absorption maxima was also investigated. The maleimide type enhanced the delocalization of conjugated system of dye (higher polarizability) and therefore the absorption maximum was shifted with 10 nm for all azo dye polymers.

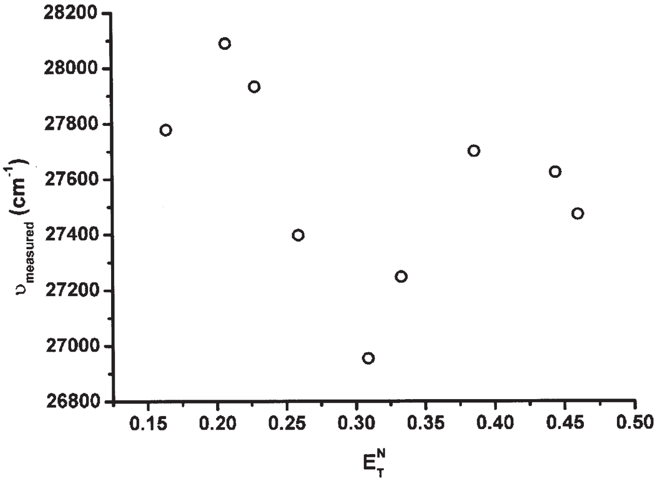

Fig. 2. $\nu_{measured}$ for MMA-M3 copolymer as a function of the Reichardt E^N_T solvent polarity parameter

The observed hypsochromic shift of MMA-Mx and MMA-IPRO3-C_0 copolymers was analyzed using both Reichardt's E_T^N solvent polarity scale and the Kamlet-Taft multiparameter equation. Figure 2 shows a typical plot of the position of absorption maximum of MMA-M3 as a function of Reichardt's solvent parameter. No linear correlation could be obtained. The poor correlation can have two possible explanations: a) solute-to-solvent interactions (hydrogen bonds) or b) such polarity scales, based on spectral data of a single indicator dye, can be applied only if the solute-solvent interactions of the examined dye are similar to those of the reference indicator dye.

Consequently we decided to use Kamlet Taft multiparameter equation (a linear solvation energy relationship; equation 1) which associates each kind of solute-solvent interaction with a separate parameter:

$$\nu_{max} = \nu_0 + s \cdot \pi^* + a \cdot \alpha + b \cdot \beta + d \cdot \delta \qquad (1)$$

ν_{max} is the position of the UV-Vis absorption band in the given solvent, ν_0 is the position of the UV-Vis absorption band in a reference system (such as a non-polar medium, e.g. cyclohexane), π^* quantifies solvent dipolarity/polarisability, α quantifies the Lewis acidity (HBD) of the solvent and β quantifies the Lewis basicity (HBA). Additionally, a correction factor β, ascribed to polarisability, is sometimes necessary for aromatic and/or chlorinated solvents. The factors a, b, and s are solvent-independent correlation coefficients (i.e. constants characteristic for the solute). Their magnitudes and signs indicate the relative contribution of the respective solvent-solute interaction to

Table 2
THE POSITION OF THE LONGEST WAVELENGTH ABSORPTION MAXIMUM OF AZOPOLYMERS IN DIFFERENT SOLVENTS AND THE EMPIRICAL KAMLET-TAFT AND E_T^N PARAMETERS

Solvent	$\upsilon_{max\ experimental}$ (cm^{-1})					E_T^N	Kamlet-Taft solvent parameter		
	MMA-M1	MMA-M2	MMA-M3	MMA-M4	MMA-IPRO3-C_0		π^*	α	β
Dioxan	29762	28986	27778	28736	27174	0.164	0.55	0	0.37
Ethyl acetate	29762	28736	27397	28329	26954	0.228	0.55	0	0.45
Cloroform	29806	28902	27701	28736	27473	0.259	0.53	0.2	0.1
N,N'-Dimethylformamide	29674	29155	28090	28902	26596	0.386	0.88	0	0.69
Tetrahydrofuran	29762	28736	27473	28409	26667	0.207	0.58	0	0.55
Acetonitril	29762	28818	27624	28653	26882	0.46	0.75	0.19	0.4
Dimethylsulfoxide	29674	29070	27933	28818	26525	0.444	1	0	0.76
Benzonitrile	29674	28571	27248	28329	27624	0.333	0.9	0	0.37
Dichloromethane	29718	28409	26954	28011	28011	0.309	0.82	0.13	0.1

Table 3
SOLVATOCHROMIC BEHAVIOUR OF THE INVESTIGATED AZOPOLYMERS USING KAMLET-TAFT MULTIPARAMETER EQUATION

Code	Kamlet-Taft equation	R^2	F
MMA-M1	$\upsilon_{max} = 29882-246\cdot\pi^{*}+260\cdot\alpha+35\cdot\beta$	0.967	80
MMA-M2	$\upsilon_{max} = 29324-1209\cdot\pi^{*}-214\cdot\alpha+927\cdot\beta$	0.996	667
MMA-M3	$\upsilon_{max} = 28213-1677\cdot\pi^{*}-307\cdot\alpha+1435\cdot\beta$	0.989	244
MMA-M4	$\upsilon_{max} = 28946-1172\cdot\pi^{*}-625\cdot\alpha+1165\cdot\beta$	0.998	1591
MMA-IPRO3-C_0	$\upsilon_{max} = 27646+1220\cdot\pi^{*}-2489\cdot\alpha-3065\cdot\beta$	0.999	2434

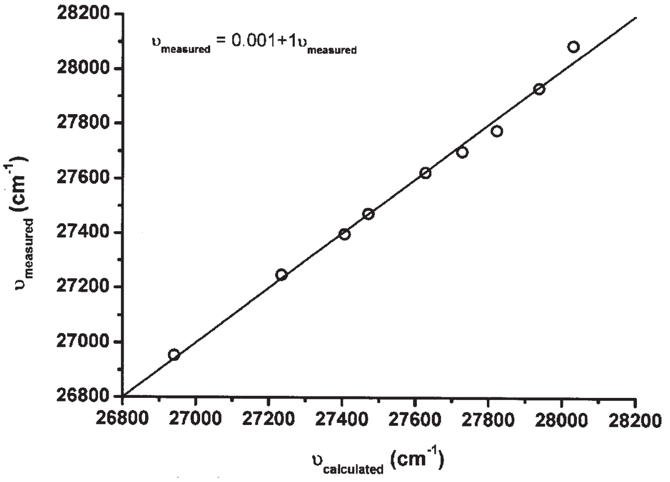

Fig. 3. $\nu_{measured}$ vs. $\nu_{calculated}$ plots for MMA-M3 copolymer. The calculated values were obtained using the theoretical Kamlet-Taft equations displayed in table 3

the electronic transition energy. When analyzing the solvatochromic data by Kamlet-Taft multiparameter equation, the F-ratio (related to the analysis of variance ANOVA) was used to determine: (i) the solvatochromism of which dye is described by this multiparameter equation, and (ii) terms of the equation that are statistically significant in fitting. This approach was described in the literature [33]. If F increases, when a new variable (i.e. π^*, α, or β) is introduced, the term is retained; conversely, if F decreases the term is rejected.

The excellent fit of the experimental data ($\nu_{measured}$) and the absorption maxima calculated with the theoretical equation ($\nu_{calculated}$) (fig. 3) prove that Kamlet-Taft model predicts very well the position of maximum absorption in solvents of different polarities, and different hydrogen bond donating or hydrogen bond accepting properties.

The negative sign of s (table 3) reflects the positive solvatochromism (bathochromic shift) of MMA-M_x copolymers corresponding to a more dipolar excited state and less dipolar groud state [34]. On the contrary MMA-IPRO3-C_0 copolymer exhibited negative solvatochromism (hypsochromic) behaviour. The larger the magnitude of s the more solvatochromic is the solute.

The Kamlet-Taft equation emphasizes that MMA-M1 copolymer is not affected by HBA or HBD properties of the solvents. Also lower value obtained for s, suggest that the dye is charged both in the ground and excited states and therefore will not be affected by the solvent dipolarity/polarizability. In the case of MMA-M2 copolymer we can observe that is equally sensitive to the dipolarity/polarizability and the HBA properties of the solvent. The same behaviour is preserved also in the case of MMA-M3 copolymer. This copolymer exhibited the highest value for s, due to the cyano group in the 2'-position, which makes the copolymer more sensitive to the HBA abilities of the solvent. For MMA-M4 we can notice that the HBD properties of the solvent start to have a more pronounced effect. However, the HBD and HBA abilities of the solvents have opposite effects on the position of the copolymer maximum (the positive sign of b indicating a hypsochromic shift which is never noticed experimentally).

According to multiparameter equation the MMA-IPRO3-C_0 is more sensitive to HBA and HBD abilities of the solvent than to dipolarity/polarizabilty of the solvents. These results are chemically reasonable taking into account that the insertion of a hydroxyl group in the structure of a dye enhances the hydrogen bond ability of the respective dye (i.e. such dyes will react stronger with HBA solvents). The above results prove the usefulness of solvatochromic data obtained in pure solvents to reveal the nature and extent of solvent-solute interactions.

Conclusions

This research provides specific synthetic strategies resulting in the desired macromolecular architecture and the related material properties. Each particular system exhibited different physical properties depending on the nature of the azobenzene moiety, their molecular weights and chromophore loads. Therefore, if a high thermal stability is required, then the best choice would be the MASt-Mx copolymers, while the MMA-IPROx substrates are suitable for attaining high chromophore loads. The best solubility behaviour was exhibited by the MMA-Mx and MEMO-Mx copolymers obtained by free radical copolymerization.

The solvent effects on the UV-Vis absorption spectra of azo-polymers were investigated. Solvent-solute interactions determine the shift of π-π* adsorption bands. The effect of the nature of substituent and substitution pattern of azopolymers on the maximum wavelength has been put into evidence. The absorption maximum in N,N'-dimethylformamide was influenced by the polymer matrix in which the azobenzene moiety is incorporated. The solvatochromic behaviour was analyzed using both Reichardt's E_N^T solvent polarity scale and the Kamlet-Taft multiparameter equation. Poor results were obtained when using Reichardt's solvent polarity scale. Correlations with high degree of confidence ($R^2 > 0.96$ in all cases) for Kamlet-Taft equation were obtained. They revealed that all azo-polymers, except MMA-M1, are sensitive to dipolarity/polarizability and HBA properties of the solvent. MMA-IPRO-C_0 polymer was influenced stronger by the HBA and HBD abilities of the solvent due to the 4'-hydroxil group.

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