Detection of Residual Acidic Groups in Several Poly(*N*-alkyl methacrylate)s Using Photophysical and Photochemical Probes

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ABSTRACT: This work describes three different methods for detecting acidic groups copolymerized in poly(methyl methacrylate), poly(ethyl methacrylate), and poly(n-butyl methacrylate) chains using molecular spectroscopy. The first was based on the shift of the tautomeric equilibrium of 4-dimethylaminoazobenzene by acidic groups that modify the absorption band in the UV/vis spectra. We also show that the acidic groups present in the polymer influenced the *anti-syn* photoisomerization reaction of this dye. Further, a mercury–dithizonate complex was completely bleached when sorbed in poly(n-alkyl methacrylate) matrices containing acidic groups. Finally, Nile Blue A was used as a spectrophotometric probe to quantify the amount of acidic groups in these polymers. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 830–838, 2004

Key words: poly(*n*-alkyl methacrylate)s; acidic groups; azodyes; Nile Blue A; mercury dithizonate

INTRODUCTION

Applications of poly(*n*-alkyl methacrylate)s are very extensive. The uses are varied and take advantage of their unique combinations of weather resistance, dimensional stability, heat resistance, formability, mechanical strength, easy processability, and high optical transparence. Because they are nontoxic, they are also used in the packaging and handling of food, in dentures and dental fillings, as medicinal dispensers, and for contact lenses. For example, safety applications take advantage of the strength and shatter resistance of poly(methyl methacrylate) (PMMA).[1]

Furthermore, PMMA has also been used as a host for dyes exhibiting nonlinear optical properties because of the facility of processing and good optical properties. Additionally, because PMMA contains a significant number of polar groups, several polar dyes are highly soluble in this polymer, allowing the preparation of homogeneous thin films having dye concentrations up to 30%.[2] Thus, there are also several types of nonlinear optical applications of dyed PMMA that include waveguides, optical modulators, optical memory storage, and materials for holography.[3]

The most important characteristics for application of dyes with nonlinear optical properties are the presence of a large permanent dipole moment, the facility of incorporation of the dye in the polymer matrices, and a high orientation capability in the host, producing a noncentrosymmetric distribution of the dipole moments.[4] Usually, three types of methods may be used for the incorporation of the guest in the polymer host: sorption of the guest in the host by casting, swelling, or vapor deposition; copolymerization during polymer preparation; and chemical modification of the preformed polymers.[5–7]

Once a suitable polymer–dye pair is chosen, the necessary conditions for good performance of the nonlinear optical material are its stability in the oriented form and the reproducibility of the response. These requirements for high-quality optical properties are achieved only with high purity, with homogeneous distributions of the dye in the host and when the dye–polymer interactions are of the same type and strength. Thus, one important property for application of poly(acrylate)s as high-performance materials is the high purity of the polymers. As a consequence, development of easy and sensitive methodologies to evaluate the purity of the polymer, the dye properties, and knowledge of the dye/polymer interactions are important tasks. Usually, dyes may be well and easily characterized by several chromatographic and spectrometric methods. Polymers, on the other hand, may be well characterized by spectrometric (FTIR, NMR), chromatographic (GPC), and thermal analysis meth-

ods. Among the spectrophotometric methods, Palit and Gosh[8] used the dye Rhodamine 6G as a spectrophotometric probe for quantitative analysis of acidic groups in polymers. Nevertheless, the sensitivity of these methods of polymer analysis is limited to impurities below 5%.[9]

The presence of copolymerized acidic groups in poly(alkyl methacrylate)s should be expected when a nonefficient esterification is carried out.[1] The occurrence of residual acidic groups depends on the efficiency of the polymerization processes and usually their concentration reaches a submicromolar level. Although the concentration of acidic groups is usually too low to be detected by current methods, they may produce important changes of some physical and chemical properties. Hence, it is relevant to establish simple methods for detecting copolymerized impurity groups because these impurities will affect material performance.

This work describes three simple spectrophotometric methods for detecting acidic impurities in poly(alkyl methacrylate)s: (1) photochromic properties of 4-dimethylaminoazobenzene (DAB) and the influence of protonation on its *anti-syn* photoisomerization reaction (Scheme 1)[10–15]; (2) photochromic properties of mercury (II) dithizonate $[Hg(DTz)_2]$ (Scheme 2)[14–19]; and (3) photochromic properties of Nile Blue A (NBA) (Scheme 3).[20–25] In addition, we present a quantitative spectrophotometric methodology to quantify the acidic groups in poly(n-alkyl methacrylate)s using the absorption spectra of Nile Blue A. Polystyrene is always used for comparison.

EXPERIMENTAL

Materials

4-Dimethylaminoazobenzene (DAB; Paragon Testing Laboratories) was purified by recrystallization with water from an ethanolic solution. Nile Blue A (NBA; Sigma, St. Louis, MO) was used as received. Mercury (II) dithizonate $[Hg(DTz)_2]$ was prepared as described elsewhere.[14–19] Spectrometric-grade solvents (dichloromethane, acetonitrile, heptane, and ethanol) (Aldrich, Milwaukee, WI) were used after drying and distillation. Benzene (gold label; Aldrich) was used as received. Analytical grade HCl (Aldrich) was used as received.

Polystyrene (PS; EDN, Brazil), poly(methyl methacrylate) (PMMA, Aldrich, cod. [9011-147]), poly(methyl methacrylate) (PMMA-p; Polysciences, Warrington, PA), poly(ethyl methacrylate) (PEMA; Aldrich, cod. [9003-42-3]), poly(n-butyl methacrylate) (PBMA; Aldrich, cod. [9003-63-8]) were used. These polymers were submitted to an extraction process in a Sohxlet for 8 h, using ethyl acetate as solvent. Spectrophotometric (FTIR [Perkin Elmer] and UV–vis absorption) measurements using purified and unpurified samples were compared.

Techniques

Preparation and characterization of the polymer films

Films of the above polymers containing DAB and $Hg(HDz)_2$ were prepared by casting from a solution containing 2.63×10^{-4} mol L^{-1} of the dyes in dichloromethane. To avoid aggregation of the dyes, the volume of the dye solution was adjusted for a well-defined amount of polymer and evaluated by the spectral profile, which has to be similar to the spectrum for the dye in a dichloromethane solution with concentration lower than 10^{-4} mol L^{-1}. Under these conditions the dye is present as a completely solvated molecule.[14,15] Dyes were incorporated in the polymer by casting a solution containing both dye and polymer on a petri dish, which was previously silanized to avoid adhesion of the material. Films were extracted from these dishes and dried under vacuum at 50°C for 24 h to ensure the complete removal of the solvent. The thickness of the films obtained after drying was approximately 30 μm. The thermal properties of the films were characterized by differential scanning calorimetry (DSC; model v2.2A 990, DuPont, Boston, MA) from 0 to 150°C, at a heating rate of 10°C/min, confirming that all of them were completely amorphous polymers.

Molecular weights and molecular weight distributions (polydispersities) were determined by gel permeation chromatography (GPC) using a Waters 510 chromatograph (Waters Chromatography Division/Millipore, Milford, MA) coupled to an IR 410 refractive index detector at 40°C. Polystyrene standards were used for all experiments. THF was used as eluent.

The concentration of the dye in the polymer host was determined by UV–vis absorption spectroscopy using a HP-8452 spectrophotometer (Hewlett–Packard, Palo Alto, CA) with a diode array detector. Other spectrophotometric properties, such as the photochemical isomerization reactions of DAB and the UV–vis absorption of the dyes in solution and in polymer matrices, were evaluated using the same instrument. Spectra of solutions were obtained in a quartz cuvette with an optical path of 10 mm.

Photoisomerization measurements

Irradiation was performed using a 100-W Hg arc lamp (Oriel Corp., Strotford, CT). Immediately after the exit of the lamp housing we set a water-cooled cell (Oriel) to reduce the infrared emission and the heating of the sample. A set of optical glass filters was employed to

| | T_g (°C)[a] | | | |
Polymer	Pure polymer	DAB-containing polymer	$\overline{M_n}$	Polydispersity
PS	103	104	71,462	2.5
PMMA	95	96	91,628	2.6
PEMA	64	67	74,952	2.1
PBMA	30	33	46,655	2.3

[a] T_g determined by DSC at a heating rate of 10°C/min.

ensure sample excitation with $\lambda_{irr} > 400$ nm. At the exit of this set of filters was connected to an electromechanical shutter, a collimator and a quartz fiber-optic mount (Oriel). Films and solutions were irradiated directly inside the spectrophotometer sample compartment using a glass fiber-optic cable (Oriel). A Peltier thermostatized sample holder was used in all experiments to control the temperature of the samples.

Preparation of solutions

Nile Blue A stock solutions in benzene were freshly prepared and obtained as benzophenoxazine anhydro-base by benzene extraction from alkali solution of NBA (10^{-5} mol L^{-1}) at pH 12. It is worth noting that all absorbance values were adjusted to values < 0.2 to meet the Beer's law condition. Under these conditions, we also prevented dye aggregation.

RESULTS AND DISCUSSION

Polymer properties

The DSC curves (not shown) show that these polymers are completely amorphous materials with virtually the same value for the glass-transition temperatures, irrespective of whether the material contains some dye. In Table I we show some physical properties for polymers containing DAB. Data for polymer with other dyes are equivalent, demonstrating that the intrinsic properties of the polymer host are not disturbed by the dyes, at least for the low concentrations as used here (10^{-4} mol L^{-1}).

Table I also shows the molecular weights for poly(n-alkyl methacrylate)s by GPC, following previously described protocols.[14] These data reveal relatively polydisperse polymer samples, all of them with the same range of molecular weight.

DAB absorption spectra

The UV–vis absorption spectra of DAB was studied in different media: in three nonprotic solvents with different polarities: dichloromethane, acetonitrile, and n-heptane; in two protic solvents: aqueous HCl solution and ethanol; in polystyrene (PS) and PMMA-p and in poly(n-alkyl methacrylate)s. Figure 1 shows a strong absorption band centered at 410 nm that shifts to longer wavelengths when the polarity of nonprotic solvent decreases. Other absorption bands were also observed at higher energies, with lower intensities.
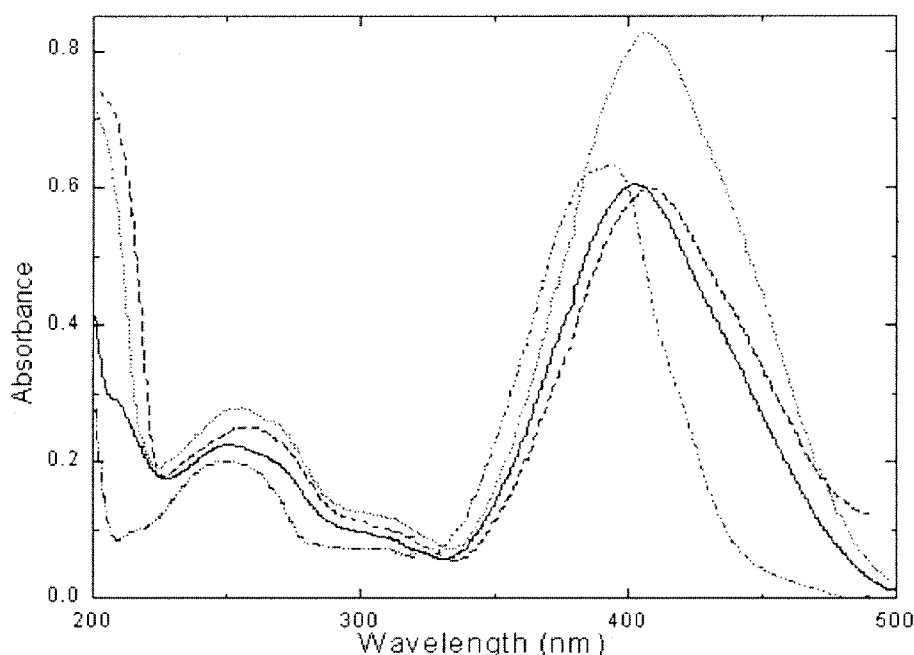

Figure 1 UV–vis absorption spectra of DAB in (2×10^{-5} mol L^{-1}) solutions of heptane (- · · -), acetonitrile (· · ·), dichloromethane (——), and ethanol (—).

TABLE II
Maximum of the Absorption Bands (nm) ($\pi_N \rightarrow \pi_N^*$) for DAB in Some Solvents
(2×10^{-5} mol L^{-1}) and Polymer Matrices

	Solvent				
	Dichlorometane	Acetonitrile	*n*-Heptane	Ethanol	HCl
λ (nm)	409	410	396	410	332

	Polymer							
	PS	PMMA	PMMA[a]	PMMA-p	PBMA	PBMA[a]	PEMA	PEMA[a]
λ (nm)	412	352	358	412	348	348	356	358

[a] Purified by Soxhlet extraction.

The wavelengths for the maximum absorption bands are depicted in Table II for DAB in these solvents. The absorption spectra of azobenzene and its derivatives were studied very extensively,[10–15] being composed of: a band covering the 385- to 440-nm range assigned to the $\pi_N \rightarrow \pi_N^*$ transition; a weak band centered at 450 nm assigned to the $n_a \rightarrow \pi_N^*$ transition that it is strongly overlapped with that assigned to the $\pi_N \rightarrow \pi_N^*$ transition, and, finally, a band at 250 nm attributed to the $\pi_\phi \rightarrow \pi_\phi^*$ transition.

Figure 2 shows the UV–vis spectrum of DAB in concentrated aqueous HCl solution and in polymers. The absorption band at 410 nm observed in nonprotic solvents are completely absent and a new band centered at 350 nm is observed. For comparison, in Figure 2 we also show the absorption spectra of DAB in the four poly(*n*-alkyl methacrylate) and PS hosts. The wavelength of the peak of the higher intensity visible absorption band is shown in Table II. It is worth noting that the spectra of DAB in PS and PMMA-p matrices are similar to those obtained in nonprotic solvents (Fig. 1), whereas the spectra for the other poly(alkyl methacrylate)s showed a blue-shifted band centered at 352 nm, similar to that in HCl. This unexpected similarity reveals that acidic groups are present in the polymer chain of some poly(alkyl methacrylate)s as acidic impurities copolymerized into the polymer chain because they could not be removed by physical methods (extraction by solvents).

The spectral shifts observed for DAB can be explained by the tautomeric equilibrium of the aminoazobenzene derivatives that exhibit two basic centers: the β-nitrogen and the nitrogens of the amino groups (Scheme 1).[10–15] Dissolution of this molecule in an
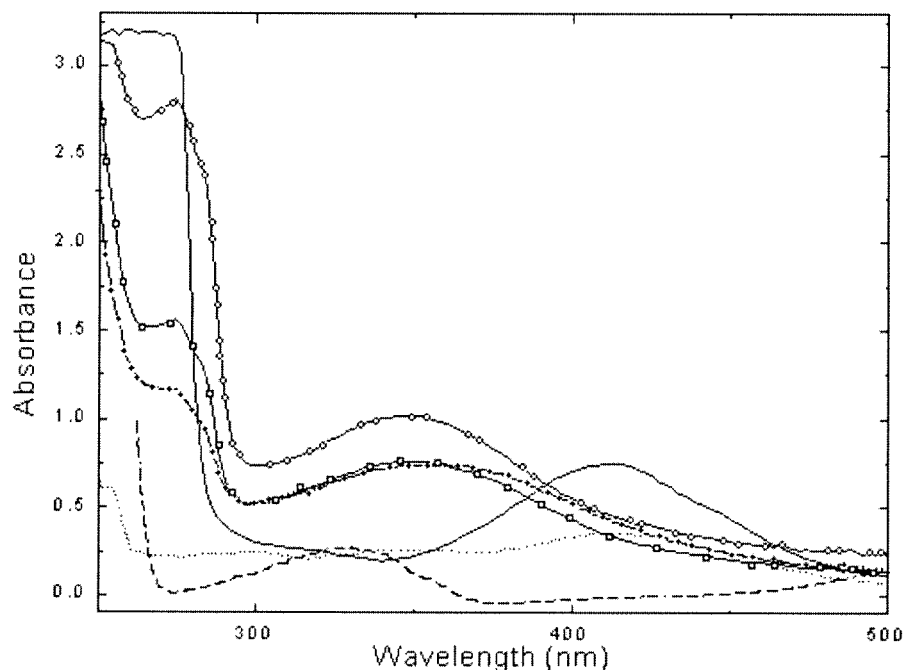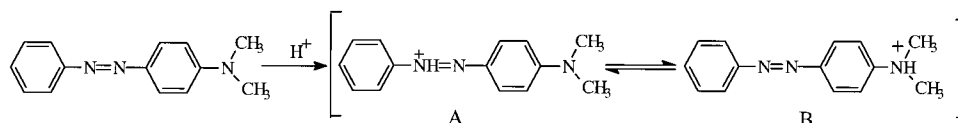

Figure 2 Absorption spectra of DAB in HCl (——), PMMA-p (· · ·), PMMA (–□–), PBMA (–○–), PEMA (–+–), and PS (——). Polymeric films containing 8.5×10^{-7} moles of DAB per polymer mass unit (g).

Scheme 1 Tautomeric equilibrium of DAB in acid medium.[10–15]

acidic solvent produces a tautomeric equilibrium between an amonium ion (A-form) with an absorption band centered at 320 nm and a protonated nitrogen of the azo-group (B-form) absorbing at longer wavelengths (500–550 nm). The band at 320 nm observed when DAB was dissolved in both poly(alkyl methacrylate)s and HCl demonstrates that the tautomeric equilibrium of the protonated form of DAB is shifted, forming the ammonium ion (A-form). In opposition, when it was dissolved in nonprotic solvents or in polymers, the equilibrium shifted to the neutral form of the dye. Therefore, through the analysis of spectral shifts we were able to detect the presence of acidic groups in both solvent and polymeric media.

Additional evidence for the presence of acidic groups in poly(alkyl methacrylate)s was obtained by the solvatochromic properties of Hg(DTz)$_2$. When this dye was dissolved in both PS and PMMA-p, the visible spectrum was composed of an absorption band centered at 490 nm (isomer A) that was shifted under irradiation to 610 nm (isomer B) (**Scheme 2**).[14–19] Nevertheless, this dye was completely bleached when it was incorporated in PMMA, PEMA, and PBMA samples, similar to that which was observed in an acidic solution. This reveals that Hg(DTz)$_2$ is chemically unstable under acidic conditions.

The role of acidity on *anti/syn* photoisomerization of DAB

Protonation should influence the kinetics of *anti-syn* photoisomerization of the azodyes because it changes the electronic density along the N=N bonding of the azo-linkage.[10–13] This influence was evaluated by the photochemical reaction of DAB in PS (nonprotonated form) and PMMA (protonated form) under irradiation with visible light ($\lambda > 400$ nm). The reaction was accompanied by absorption spectroscopy that in the case of DAB in PS, exhibited a decrease of the intensity at 410 nm (*anti*-form of nonprotonated species) and an increase at 330 nm (*syn*-form). In PMMA there is a decrease at 350 nm (*syn*-form of the protonated species) with an increase of the band at 270 nm (Fig. 3).

The photochemical kinetics of DAB dissolved in all polymers at three different temperatures (18, 28, and 58°C) were also studied by UV–vis absorption spectroscopy.

The kinetics curve is represented by a function derived for reversible photochemical reactions[26,27]:

$$I(\delta) = \left(1 + \frac{D_\infty}{2} + \frac{D^2}{12}\right)\ln|\delta| - \left(\frac{1}{2} + \frac{D_\infty}{6}\right)\delta + \frac{\delta^2}{24} \quad (1)$$

where $I(\delta) = At + cte$; $A = -I_0\phi_t\varepsilon_t/y_\infty$; D_∞ and D are the absorbance values for the photostationary state and for time t, respectively; $\delta = D_\infty - D$; I_0 is the intensity of radiation; ϕ_t is the quantum efficiency; ε_t is the molar absorptivity; and y_∞ is the fraction of the *syn*-isomer in the photostationary state. This equation is a good approximation for reversible photochemical reactions as they occur in the present case.[26,27]

On the basis of the absorbance of the *trans* isomer at 410 and 350 nm for DAB in PS and poly(alkyl methacrylate)s, respectively, we determined D at time t and D_∞ as the absorbance value at the photostationary state and, using these values, $I(\delta)$ was evaluated. The curve profiles, $I(\delta)$ versus time, for the photoisomerization reactions may be fitted by a monoexponential function when these dyes were dissolved in solvents.
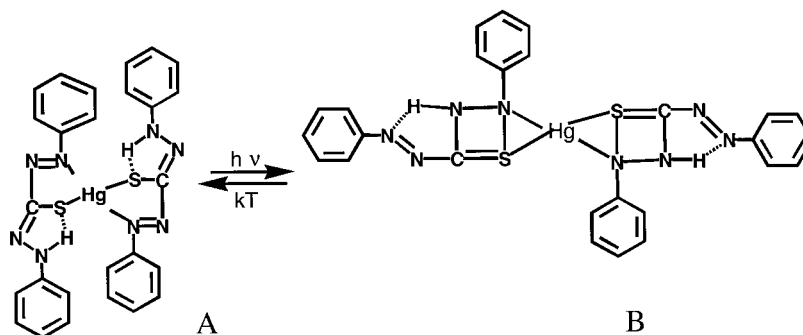
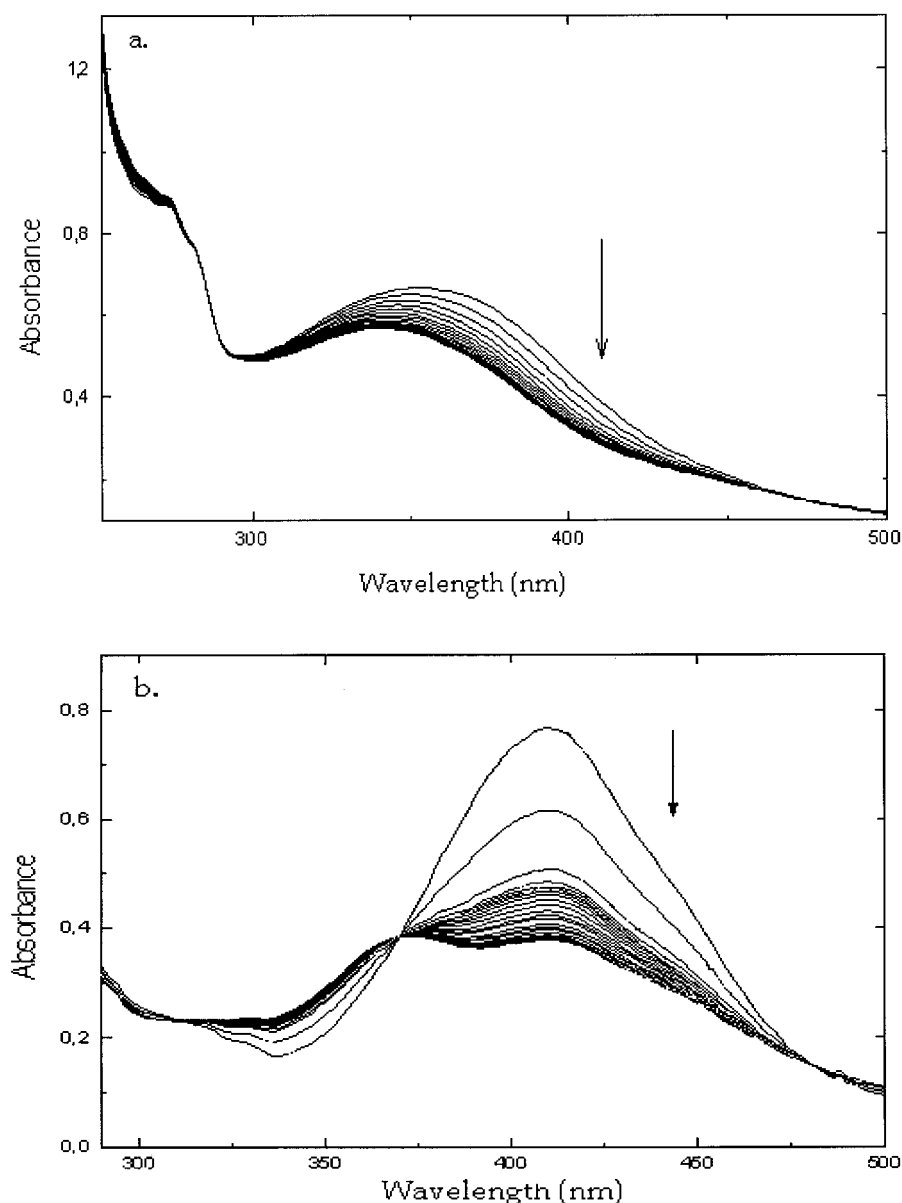**Scheme 2** Structural forms of the Hg(DTz)$_2$ isomers.[16–19]

Figure 3 Absorption bands of DAB dissolved in PMMA (a) and PS (b) under irradiation with $\lambda_{exc} > 400$ nm.

However, a biexponential function is required when the dyes are dissolved in polymer matrices below the glass-transition temperature (Figs. 4 and 5).[5,31–33] This type of kinetic description was previously reported for several polymer matrices and it has been explained by a distribution of free volumes in the solid medium.[31–33] The experimental data were fitted by biexponential functions and the corresponding rate constants resulted in one slower and one faster process, as shown in Table III.

Comparison between the k_1 and k_2 rate constants for the photoisomerization of DAB showed that, at the same temperature, they are higher in PS than for poly(n-alkyl methacrylate)s. Furthermore, both increased with tem-

perature and with the size of the side n-alkyl group of the poly(alkyl methacrylate)s. They were also higher for polymers with larger side groups (PBMA), compared with smaller side groups (PMMA), as shown in Figure 5, in agreement with the free-volume theory.[14,15,30,31] These results also demonstrate that the DAB photoisomerization rates depend on specific dye–polymer interactions, given that the protonated form is responsible for the reaction in the methacrylic polymers and depends on the free volume available for the dye in polymer matrices.

In addition, the relative contribution of the larger rate constant is increased at higher temperatures. Above the polymer glass transition, the curve profile can be fitted by a monoexponential function. This is
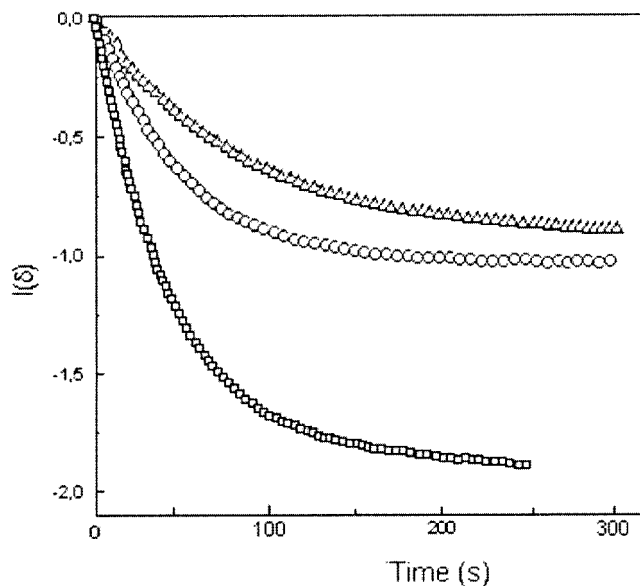
Figure 4 Kinetic behavior $I(\delta)$ of the photochemical reaction of DAB dissolved in PS, at 18 ($\triangle$), 28 ($\bigcirc$), and 58°C ($\square$).

the case of PBMA whose glass-transition temperature is 30°C, above which the matrix behaves as a viscous solvent.[14,15]

TABLE III
Rate Constants for DAB Sorbed in PS, PMMA, PEMA, and PMBA at 18, 28, and 58°C

Rate constant (s^{-1})	Temperature (°C)		
	18	28	58
		PS	
k_1	8.4×10^{-3}	1.4×10^{-2}	1.7×10^{-2}
k_2	7.0×10^{-4}	8.6×10^{-4}	1.8×10^{-3}
		PMMA	
k_1	3.0×10^{-3}	3.9×10^{-3}	8.1×10^{-3}
k_2	1.1×10^{-4}	2.8×10^{-4}	4.8×10^{-4}
		PEMA	
k_1	3.0×10^{-3}	4.2×10^{-3}	1.0×10^{-2}
k_2	2.5×10^{-4}	4.6×10^{-4}	6.6×10^{-4}
		PBMA	
k_1	2.9×10^{-3}	1.8×10^{-2}	2.6×10^{-2}
k_2	4.0×10^{-4}	1.4×10^{-3}	—[a]

[a] The polymer is above the glass-transition temperature and the kinetic behavior is monoexponential.
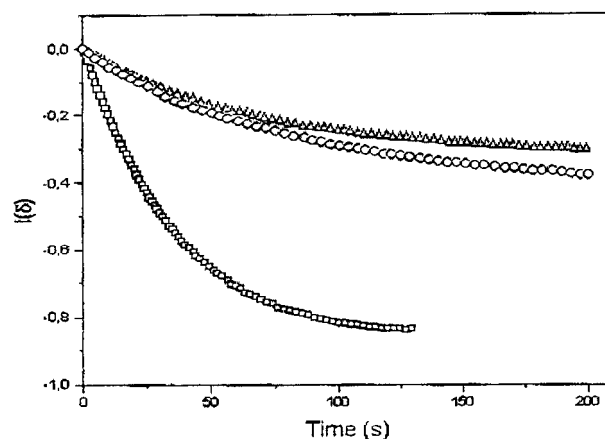

Figure 5 Kinetic behavior of the photochemical reaction of DAB dissolved in: PMMA ($\triangle$), PEMA ($\bigcirc$), and PBMA ($\square$) at 28°C.

Quantification of the acidic groups

As previously demonstrated, some samples of the poly(*n*-alkyl methacrylate)s present copolymerized acidic groups, which are able to protonate basic dyes.[35] This protonation produces solvatochromic shifts of the electronic absorption attributed to changes of the energy of the electronic states. We showed, that in the case of azo-dyes, it influences the tautomeric equilibrium, modifying the spectral absorption band and the values of the photoisomerization rate constants.

Nile Blue A is a well-known benzophenoxazine dye, widely used in proton transfer reactions[20] and as a biological stain.[21–24] These applications are based on its photochromic properties that depend on the equilibrium change between its conjugated forms in the pH range from 9.0 to 10.4 (Scheme 3).[25] The visible absorption spectrum of NBA in aqueous alkaline solution (0.1 mol L^{-1} NaOH) exhibits a band centered at λ_{max} = 520 nm (neutral benzophenoxazine form),[20] whereas in acetic acid or water it is centered at λ_{max} = 634 nm (protonated benzo[*a*]phenoxazonium salt form).[20]

When a very dilute benzene solution of NBA (10^{-5} mol L^{-1}) was prepared, the spectrum showed an absorption band, centered at 494 nm, attributed to the

A   B
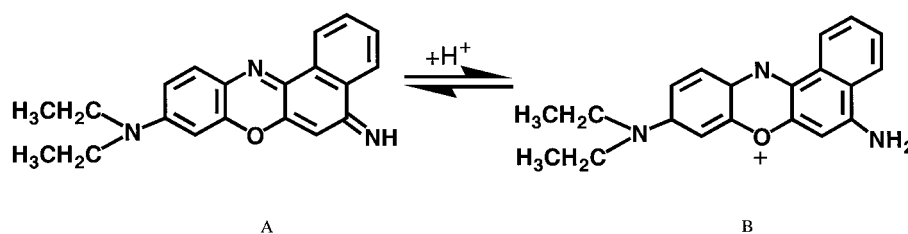
Scheme 3 NBA conjugated forms: benzo[*a*]phenoxazine (A) (λ_{max} = 494 nm) and benzo[*a*]phenazoxonium salt (B) (λ_{max} = 610 nm).[20]
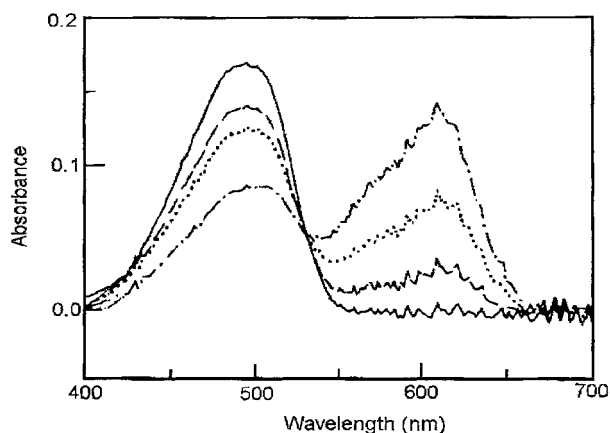
Figure 6 Absorption spectra of NBA in benzene solutions (10^{-5} mol L^{-1}) containing PMMA: 0 (—), 3 mg (——), 7.5 mg ($\cdots$), and 15.0 mg (- · - · -) per 3 mL of solution.

benzophenoxazine (neutral) form. Compared with the alkaline medium this band was blue-shifted from 520 (neutral form) to 494 nm, resulting from the stabilization of the NBA electronic ground state, probably attributed to a π–π interaction between the dye and the benzene molecules.

In an attempt to visualize the effect of the acidic groups in the polymer on the NBA spectrum, we prepared benzene solutions containing, simultaneously, this dye (10^{-5} mol L^{-1}) and amounts of PMMA (from 0 to 15 mg in 3 mL of solution) (Fig. 6). Benzene is a nonprotic solvent and is quite convenient because it is a good solvent for the methacrylic polymers. The increase of PMMA concentration decreases the relative intensity of the band centered at 494 nm, with a corresponding increase of the intensity at 610 nm, explained by the shift of the equilibrium involving the benzophenoxazole and the benzo[a]phenazoxonium forms of the dye.[20] There was no observable absorbance in the 610-nm region for the NBA/PS/ benzene solution (a nonprotic polymer). It is worthy noting that both spectra were blue-shifted compared to aqueous solutions, showing a stabilization of the electronic ground state. The isosbestic point observed at 530 nm indicated that only two forms of the dye

were involved in the protonation–deprotonation equilibrium with the solubilized polymer samples. Similar behavior was observed for PEMA and PBMA (spectra are not shown).

To quantify the concentration of the protonated NBA form in the polymer samples, we assumed the applicability of Beer's law for NBA in benzene solutions containing the polymer samples and we used the molar absorptivity coefficient value as $\varepsilon = 38{,}000$ L mol^{-1} cm^{-1} at $\lambda_{max} = 634$ nm, determined for benzo[a]phenazoxonium in aqueous solution.[20] Therefore, for our calculations we assumed that the molar absorptivity in benzene was the same as that in water and that the effect of the solvent (water or benzene) was only producing a blue shift of the absorption spectra, from $\lambda_{max} = 634$ nm to $\lambda_{max} = 610$ nm.

Furthermore, assuming that the formation of the benzo[a]phenazoxonium species follows a 1 : 1 stoichiometric protonation reaction from the acidic group of the polymer/benzene solution, the concentration of the dye in the benzene solution was determined using the absortivity coefficient ($\varepsilon = 38{,}000$ L mol^{-1} cm^{-1}) and the experimental absorbance.

Based on the amount of polymer added to the benzene solution (3 mg/3 mL) and using the molecular weights of the polymers shown in Table I, we calculated the molar concentration of each polymer [$c_P = \left(m/\bar{M}_n V \right)$] (Table IV). Absorbances (A) were measured at 610 nm and, using $\varepsilon = 38{,}000$ L mol^{-1} cm^{-1}, we determined the molar concentration of acidic groups in the polymer chains ($c_{COOH} = A/\varepsilon$). Given that every polymer chain contains an average number of monomer units n_M, we used this value to estimate the average molar concentration of monomer units for every polymer added to the benzene solution as $c_M = c_P x n_M$, where n_M is the ratio between the average molecular weight ($\bar{M}_n$) and the molecular weight of the monomer unit M_m. The ratio ($I_{COOH} = c_{COOH}/c_M$) between the molar concentration of the acidic groups c_{COOH} and the molar concentration of the monomer units c_M defines the average number of the acidic groups present in the polymer chain. Table IV depicts the data for samples for which we determined, ap-

TABLE IV
Data Obtained from Absorption Spectra of NBA/Polymer/Benzene Solutions

Polymer	A	c_{COOH}[a] (10^{-7} mol L^{-1})	c_P[b] (10^{-5} mol L^{-1})	c_M[c] (10^{-5} mol L^{-1})	$I_{AU} \times 10^4$
PS	0.006	1.6	1.4	145.6	1.1
PMMA	0.034	8.9	1.1	111.1	8.0
PEMA	0.028	7.4	1.3	149.5	4.9
PBMA	0.082	22	2.1	300.3	7.3

[a] $c_{COOH} = A/\varepsilon$ ($\varepsilon_{610} = 38{,}000$ L mol^{-1} cm^{-1} [16]).
[b] $c_P = (m/\bar{M}_n V)$.
[c] $c_M = c_P \times n_M$; $n_M = \bar{M}_n/\bar{M}_m$; $I_{COOH} = c_{COOH}/c_M$.

proximately, one acidic group for 800 methacrylic groups, for PMMA and PBMA and one acidic group to 500 monomer units for the PEMA samples.

CONCLUSIONS

This work presents some spectrophotometric methods to detect and quantify the amount of acidic groups copolymerized in poly(*n*-alkyl methacrylate) samples. Evidence for the presence of these groups was previously obtained in luminescence studies of flavones that presented an unusual fluorescence emission typical of protonated molecules.[35] This contamination by acidic groups was further confirmed by the bleaching of mercury dithizone dissolved in the polymer matrices and by the solvatochromic effect on the electronic absorption spectrum of DAB. In the present work the concentration of the randomly copolymerized acidic groups was quantified by the solvatochromic properties of Nile Blue A, which exhibits very well separated absorption bands for the neutral and protonated forms of the dye.

We also showed that the presence of acidic groups in the polymer chain influenced the photochemical isomerization of DAB in poly(alkyl methacrylate)s. The kinetic description of the photochemical reaction was successfully analyzed by a biphasic model. This result was interpreted considering that the dye in the polymer matrix below the glass-transition temperature is distributed in microenvironments with different free volumes and two rate constants were necessary to describe the photochemical reaction. Above the glass transition, the polymer matrix should be considered as a viscous medium and only one rate constant described the kinetic curves. Similar results were obtained for several other dye/polymer systems.[5,14,15,31–34]

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