

Synthesis and fluorescence of polyurethane cationomers *N*-modified with a stilbene chromophore

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Abstract

Preparation of a polyurethane cationomer with stilbene chromophore on urethane nitrogen atoms was performed by stepwise modification of a neutral polymer (PU-S1, stilbene units: 13.6 wt.%), followed by the quaternization with benzyl chloride (PUC-S1, 34.8 meq. ionic groups/100 g polymer). A linear polyesterurethane based on poly(ethylene adipate) diol (M_n : 2000), 4,4'-methylene-bis(phenyl isocyanate), 1,4-butanediol and *N*-methyl-diethanolamine (1:6:3:2 molar ratio) was used as precursor. The *trans*–*cis* photoisomerism and fluorescent emission of the stilbene in polycation was studied and compared with the non-ionomeric form and the urethane-stilbene derivative. Another cationomer with fluorophore introduced via quaternization of the same precursor with urethane-stilbene halide was also taken in study (PUC-S2, 39.7 meq. ionic groups/100 g polymer). All polymers absorb in the UV region (λ_A : 313–332 nm) and reemit the light as violet–blue fluorescence in the region 420–470 nm. The significant red shift of the emission band in both polymer solution and film was assigned to the formation of excimers between fluorophores.

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1. Introduction

In recent years there has been an increasing interest in the insertion of photoactive chromophores into polymeric backbone for modification of properties of polymers tailor-made for a large range of special applications. Among these, the *trans*-stilbene chromophore was widely used for developing of unique polymer properties such as liquid-crystalline behavior, non-linear optical response or electroluminescent effects [1–3]. Moreover, the incorporation of a stilbene probe in biopolymers has proved to be a useful tool to investigate the processes affecting the functionality and dynamics of biomembranes [4]. Given the broad spectrum of properties of the polyurethanes, some materials carrying stilbene groups were prepared and studied taking into account the development of new electroluminescent [5–7] or optical devices [8–13]. Though great attention has been focused on such polymers, there are no examples in the literature of ionic polyurethanes with stilbene fragment in the polymer chain. Ionic polyurethanes are recognized for their unique abilities to form aqueous dispersions and films at ambient

temperature which could be exploited for producing modern adhesives and special coating materials [14].

Our work is devoted to the systematic investigation of the effect of ionomeric structure on the properties of polyurethanes bearing chromophoric functionalities as seen quinone [15,16], azoaromatic [17–20], triazene [21], and has been recently directed towards insertion of stilbene groups in such polymers, whose photobehavior is governed by the contribution of structural factors and electrostatic interactions. In the preceding paper [22], polyetherurethane cationomers with a stilbene moiety attached to the ammonium quaternary structure of the polymer chains were prepared and studied with respect to the *trans*–*cis* photoisomerization and fluorescent emission of the fluorophore both in the polymer solution and film.

To understand the effects of ionic groups on the photoreactivity of stilbene related to its anchoring point, we diversified the structure of polycations to investigate the photoluminescence properties of some polymers functionalized with stilbene either by a stepwise substitution of urethane hydrogen atoms or a quaternization reaction of the same precursor. Previously, we synthesized cationomers with azoaromatic groups on urethane nitrogen atoms and some properties of these polymers were presented [18]. In this

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paper, we describe the synthesis, characterization and fluorescence of polyurethane cationomers with a stilbene chromophore introduced via *N*-modification or quaternizing of a neutral polyesterurethane with a particular structure, composed of long rigid segments and ammonium quaternary groups.

2. Experimental

2.1. Materials

Polyethylene adipate diol (PEAD, $M_n = 2000$) prepared according to the industrial method [23] was dried and degassed at 100–110 °C and 1–2 mmHg for 2 h before utilization. 4,4'-Diphenylmethanediisocyanate (Aldrich) was distilled under reduced pressure and *N*-methyl-diethanolamine (Aldrich) was used as received. Dimethylformamide (DMF) was dried over 5 Å molecular sieves.

2.2. Synthetic procedures

4-Chloromethylphenylcarbamoyloxymethyl-*para*-stilbene (S-Cl) was obtained by reacting 4-hydroxymethylstilbene with 4-chloromethylphenylisocyanate. $^1\text{H NMR}$ (DMSO, δ , ppm): 4.72 (s, 2H, CH_2Cl), 5.2 (s, 2H, CH_2OCONH), 7.2–7.68 (m, 13H, aromatic protons), 7.8–7.9 (d, 2H, $\text{CH}=\text{CH}$), 9.65 (s, 1H, NHCOO). For comparison, in the fluorescence study the ionic diol (S-D) was used with stilbene on the ammonium quaternary structure prepared as described elsewhere [22].

Polyurethane precursor (PU-PR) was synthesized by a two-step condensation reaction, from polyethylene adipate diol (PEAD, M_n : 2000, 0.01 mol), 4,4'-diphenylmethane diisocyanate (MDI, 0.06 mol) and 1,4-butane diol (BD, 0.03 mol)/*N*-methyl-diethanolamine (NMDA, 0.02 mol). As previously reported [18] the stilbene groups were introduced by a modification of the above polyurethane with 4-chloromethylphenylcarbamoyloxymethyl-*para*-stilbene. The resulting polymer (PU-S1) treated with an excess of benzyl chloride to allow its quaternization (PUC-S1). Similarly, PU-PR was quaternized with stilbene derivative for preparing PUC-S2. Both polymers were precipitated in diethyl ether, collected by filtration and then dried under reduced pressure.

2.3. Equipment

Molecular weight distribution of the precursor (PU-PR) was measured by a PLEMD 950 apparatus equipped with two PL gel mixed columns at 120 °C (M_w : 48500). The concentration of ammonium quaternary groups was estimated from the content of ionic chlorine. Reduced viscosity of PU-PR (η_{red} : 0.56 dl g $^{-1}$) was measured to 25 ± 0.2 °C in a DMF solution (c : 0.4 g dl $^{-1}$) with an Ubbelohde viscometer having a 0A capillary. Thermal analysis was performed

with a Perkin-Elmer differential scanning calorimeter. The samples (15 ± 2 mg) were cooled to -130 °C and heated at a rate of 20 °C/min up to 230 °C. Irradiation was performed with a 500 W high-pressure mercury lamp at room temperature using an appropriate filter ($\lambda = 365$ nm). The samples were placed at 10 cm distance. The polymer film was prepared by casting of the polymer solution in DMF (c : 1%) onto quartz plates and then was allowed to dry at 50–55 °C under reduced pressure.

The fluorescence spectra were obtained at room temperature (without corrections) with an equipment containing a double monochromator with a diffraction network of the GDM-1000 type, a compensatory printer of the K-201 type and a selective amplifier, as presented earlier [22].

PU-S1, $^1\text{H NMR}$ (DMSO, δ , ppm): 1.67 (m) represents the resonances of the center methylene group of both adipic acid and tetramethylene glycol; 2.35 (s) protons the adipic acid CH_2 adjacent to the carbonyl group; 2.7 (m) CH_2 protons from NMDA; 3.9 (s) are CH_2 protons from MDI; 4.1–4.3 (d) CH_2 protons bound of ester or urethane group; 5.3 (d) CH_2 protons bound to urethanestilbene; 7.1 (d) aromatic protons *orto* to CH_2 and 7.4 (d) aromatic protons *orto* to urethane from MDI; 7.6–7.9 (m) unsaturated protons from stilbene; 9.5 (s) urethane protons.

3. Results and discussion

A segmented polyesterurethane (PU-PR) with a higher concentration of urethane structures was prepared as matrix for ionomer synthesis by addition reaction between polyester (PEAD, M_n : 2000) and MDI, followed by chain extending with 1,4-butane diol together with *N*-methyl-diethanolamine (1:6:3:2 molar ratio). Synthesis of stilbene polymer is based on ability of the polyurethanes to be chemically modified at amide nitrogen atoms [24]. Using a two-step procedure, the polyurethane above described was derivatized by partial deprotonation of nitrogen atoms from the urethane groups to form a sodate compound. Sodium-substituted polymer was then treated with 4-chloromethylphenylcarbamoyloxymethyl-*para*-stilbene (S-Cl), when stilbene side groups were attached on the polymer backbone. The desired proportion of chromophores inserted was controlled by the ratio between reagent quantity and the urethane nitrogen content, as shown in Table 1. To avoid chromophore–chromophore interactions that often accentuate photochemical complexity in polymers, the degree of substitution with stilbene fluorophore was limited to 13.6 wt.% (PU-S1). Classical preparation of cationomer involved a subsequent quaternization of tertiary nitrogen atoms from the stilbene functionalized polymer with benzyl chloride (PUC-S1: 34.8 meq. ionic groups/100 g polymer). Scheme 1 is a schematic representation for synthesis of polyurethane cationomers *N*-modified with stilbene groups.

The structures of the polymers were confirmed by spectral analysis including FTIR, UV-Vis and NMR techniques,

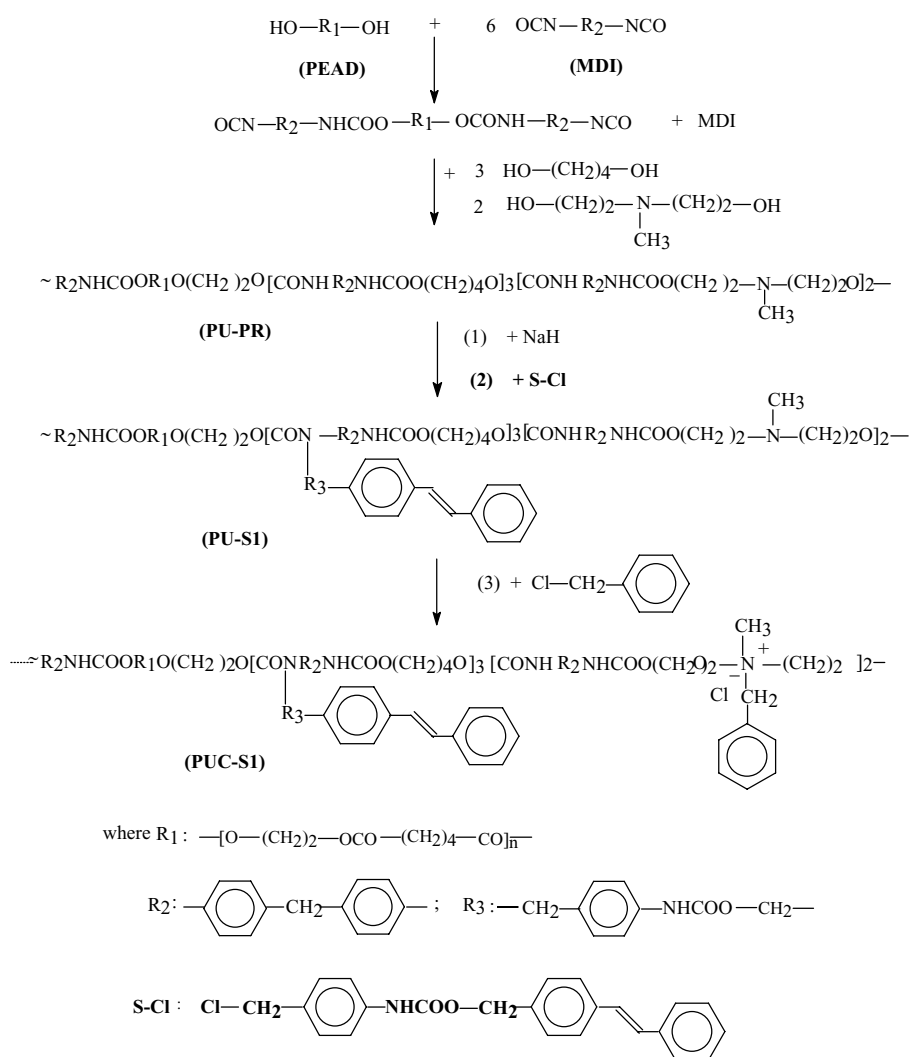
Table 1
Some characteristics of PU cationomers with stilbene pendant

Polymer		Elemental analysis			Ionic groups (meq./100 g polymer)	Stilbene content (%) ^a	T _g (°C)
		C (%)	H (%)	N (%)			
PU-PR	Calculated	62.90	7.84	4.89	–	–	–30
	Found	62.85	7.82	4.85			
PU-S1	Calculated	65.30	7.58	4.78	–	13.6	–
	Found	65.25	7.55	4.74			
PUC-S1	Calculated	65.35	7.48	4.57	34.8	12.5	–36
	Found	65.30	7.46	4.54			
PUC-S2	Calculated	64.98	7.62	4.80	39.7	13.5	–40
	Found	64.94	7.59	4.77			

^a Calculated.

and elemental analysis (Table 1). The degree of substitution of the –NH–COO– groups by stilbene fragment was obtained from NMR spectral data, for example (PU-S1), area of the signals of the protons of CH₂ group from MDI cen-

tered at 3.9 ppm and the CH₂ protons bound of urethanestilbene at 5.3 ppm, and the CH=CH protons of stilbene units from 7.8 ppm. On the other hand, the absence of chlorine in PU-S1 shows that the stilbene fragment is covalently linked



Scheme 1. Schematic representation for synthesis of polyurethane cationomers *N*-modified with stilbene groups.

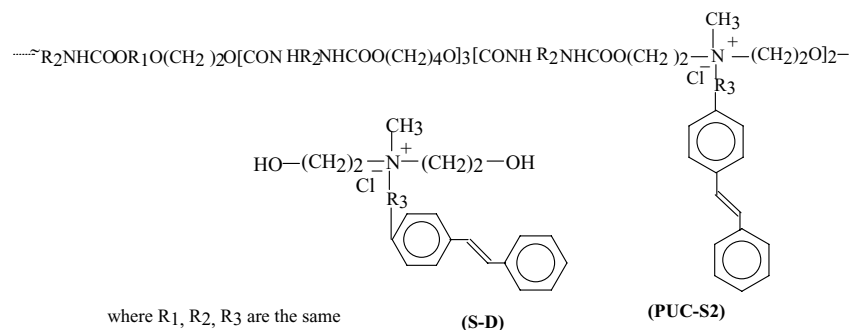


Fig. 1. Schematic representation of PUC-S2 and S-D.

to polyurethane arguing that the precursor was indeed modified by chromophoric groups. Upon quaternization of the aliphatic tertiary nitrogen atoms with benzyl chloride, the formation of quaternary ammonium structure with chlorine as anion (PUC-S1) was evident.

In order to investigate the effect of chromophore on fluorescent activity, we have also prepared one polycation (PUC-S2, Fig. 1) using the stilbene derivative as quaternizing agent for the starting precursor. From determination of the ionic chlorine content, the degree of quaternization of the polycations at 85 and 88%, respectively was estimated. By the concentration of ionic groups under 40 meq./100 g polymer, these polymers belong to the ionomer class. The elemental analysis data were in good agreement with values calculated from the structures of the polymers.

The basic structure of the ionomeric backbone was of the block copolymer type with long flexible segments including polyester component and hard segments comprising the quaternary ammonium structure besides urethane groups with or without stilbene pendants grouped together in large domains. The main difference between the above polymers and preceding polycations could be related to the polymer structure and the way of introduction of stilbene on the polyurethane chains in the former. Structural changes produced by functionalization of polymer were evidenced by FTIR and UV absorption spectroscopy. In the FTIR spectrum of PU-S1, the hydrogen-bonded NH stretching vibration appeared at around 3338 cm^{-1} , while the carbonyl stretching band occurred as a doublet with one component at 1725 cm^{-1} (ester carbonyl) and the other at 1700 cm^{-1} (hydrogen-bonded urethane component). Absorption bands due to CH_2 stretching at $2875\text{--}2958\text{ cm}^{-1}$ and at 1596 cm^{-1} (CH aromatic C-H) were observed and a small absorption band at 964 cm^{-1} was assigned to the *trans*-vinylidene group from the stilbene.

Since the properties of polyurethane ionomers are mainly due to the phase behavior of two different segments, DSC measurements of the polymer films were performed. Evidence for microphase separation of these polymers can be observed in the DSC thermograms (Table 1). According to DSC results, the stilbene cationomers showed glass transition temperature values between $-36\text{ }^\circ\text{C}$ (PUC-S1) and $-40\text{ }^\circ\text{C}$ (PUC-S2) attributed to the soft segment rich

phase, since an imperfect phase separation of the constituent flexible and hard segments in both polycations occurred. Compared to the ionic polymers, DSC result for the starting PU-S1 given in the same table, indicates an increase in the glass transition temperature to around $-30\text{ }^\circ\text{C}$ (PU-PR), reflecting a certain solubility of the hard segments into the soft segment phase. Furthermore, the T_g variation is obviously for polycations, owing to aggregation of ionic groups by coulombic interactions as primary driving force for an enhanced biphasic separation, as evidenced in other ionomers [25]. Additionally, in all polymers higher temperature melting endotherms were not observed and this result is in accordance with the literature data found in DSC thermograms. The stilbene polycations had decomposition temperatures in the range of $210\text{--}230\text{ }^\circ\text{C}$ by thermogravimetric analysis indicating a good thermal stability.

3.1. The *trans*–*cis* photoisomerization of the stilbene induced by UV irradiation

One of the attractive properties introduced by the presence of photoisomerizable chromophores is the geometrical structure change of stilbene from the *trans* configuration to *cis* form, useful to control the chain conformation in the polymer backbone. Even though it is well known that the isomerization to *cis* configuration causes loss of the fluorescence properties, no complete theory exists to explain how the photochemical and photophysical process is correlated to polymer properties. To examine the effect of hindered motions of the stilbene on its photobehaviour, sensitivity of the polymers was studied comparatively with that of stilbene derivative (S-Cl), by following the structural changes what appeared in the electronic absorption spectra during UV irradiation. Exhaustive irradiation with monochromatic light (λ : 365 nm) provides evidence that the *trans*–*cis* photoisomerization is induced in all cases, but it is accompanied by an irreversible photobleaching reaction. Fig. 2 (plot a) shows the UV spectra for the *trans* form of S-Cl exposed to UV light in DMF solution. Specifically, this structure absorbs within the range of absorption for stilbene, with maxima or shoulders at 286, 300, 314 and 328 nm. As seen from this figure, the intensity of $\pi\text{--}\pi^*$ electronic transition of the

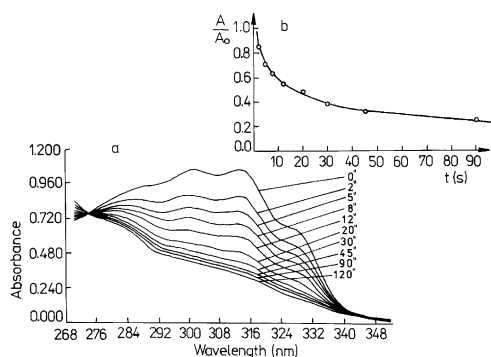


Fig. 2. Changes in the electronic absorption spectra of stilbene derivative (S-Cl) in DMF solution during UV irradiation (a); dependence of relative absorbance on the irradiation time for S-Cl solution (b).

trans-stilbene from 314 nm decreased gradually with irradiation time attaining a photostationary state in about 120 s, when photoconversion of the *trans* isomer is about 67%. The obtained percent content according to

$$C_{\text{trans}} = \frac{A_i - A_t}{A_i} \times 100$$

where A_i and A_t , are the absorptions of the *trans* isomer before and after UV irradiation, is the result of the elementary process of *trans*–*cis* photoisomerization followed by side reactions. During the spectral measurements, the appearance of two isobestic points at 344 and 272 nm indicates that the *trans*–*cis* photoisomerization of the stilbene molecule is a major reaction. Unfortunately, the *cis* isomer peak positioned probably below 262 nm can not be observed owing to its ability to form 9,10-dihydrofenantrene [26] and the overlap of the solvent absorption. In addition, a photodimerization reaction with the formation of (2+2) cycloadduct is expected to occur via a singlet excimer, as suggested for the photo-behavior of *trans*-stilbene in organic solvents [27]. Similar considerations mentioned earlier limit the control of the latter structure which absorbs below 280 nm. In an attempt to prove the presence of *cis* isomer, a sensitizer close energetically to the stilbene excited triplet level, as Erythrosin B was added in the irradiated solution. The fact that the UV irradiation (λ : 546 nm) had a negligible effect on the stilbene photosensitivity confirms no return to its initial *trans* configuration, since *cis* isomer once formed prefers saturation of the double bond by photocyclization. Monitoring kinetics of phototransformation of the *trans*-stilbene for S-Cl in DMF solution, a two-steps process which occurred with different rates was observed. Plot of the dependence of relative absorbance versus irradiation time is linear to fairly high photoconversion representing about 80% from all transformed chromophore in only 20 s (Fig. 2, plot b).

The rate constants of the photoprocess were calculated using expression

$$k = \frac{2.3}{t} \log \frac{A_0}{A}$$

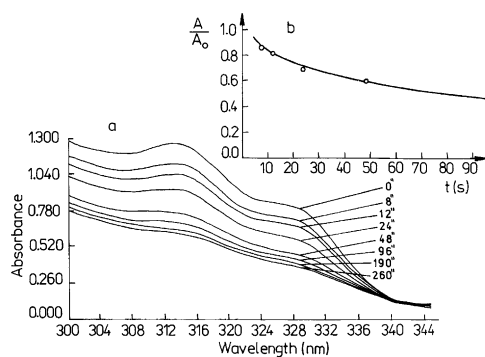


Fig. 3. Changes in UV-Vis absorption spectra of polyurethane (PU-S1) in DMF solution upon UV light exposure (a), and (b), dependence of relative absorbance with the irradiation times.

where A_0 and A are the absorbances of the stilbene in *trans* form, before and after irradiation for a time t . For the *trans*-stilbene molecule in DMF (S-Cl), a relative rate constant of $5.72 \times 10^{-2} \text{ s}^{-1}$ was found and this value was higher than that obtained for one stilbene ionic diol (S-D, Fig. 1) in methanolic solution [22].

For the stilbene polyurethane (PU-S1) in DMF solution the *trans*–*cis* photoisomerization of stilbene is induced inside the polymer backbone (Fig. 3, plot a) but it was relatively slow. This result can easily be appreciated if one considers the macroscopic consequences of the polymer properties determining the structure, the rigidity of hard segments, the extent of hydrogen bonds, the interaction between chromophore and the main chain or chromophore–chromophore and inter/intrapolymeric association. In this case, the photostationary state after about 9 min irradiation with 50% photoconversion of the *trans*-stilbene is reached. As shown in the figure, PU-S1 presents two characteristic absorption bands at 313 and 328 nm, with maximum at 313 nm. Experimentally, we found that the photoisomerization follows the same kinetics as in the case of S-Cl and the calculated rate constant was $1.28 \times 10^{-2} \text{ s}^{-1}$ (Fig. 3 plot b). Comparison of the absorption spectrum of a polymer solution with that of thin film reveals that the change in polymer state had a minor effect upon the positions of the absorption maxima in *trans* PU-S1 film, when the characteristic absorption bands were shifted towards red, namely at 315 and 332 nm with maximum at 315 nm (Fig. 4). Subsequent irradiation of the polymer film indicated that these absorption bands decreased monotonously in favor of the formation of *cis* isomer, photodimer or other product in which the stilbene double bond is saturated. Therefore, the transformation degree of *trans* isomer at equilibrium of about 44 % (after 13 min irradiation) was significantly affected by the restricted mobility of the chromophore located in the hard fragment of the polymer matrix. As result, the photoisomerization rate in PU-S1 film ($k = 5.6 \times 10^{-3} \text{ s}^{-1}$) is approximately two times lower than that reported before for solution (Fig. 4, plot b).

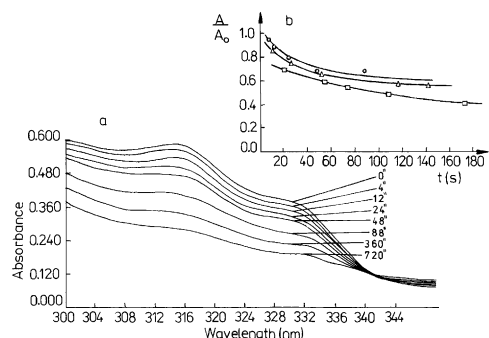


Fig. 4. Changes in UV-Vis spectra of PU-S1 in film during irradiation times (a); dependence of relative absorbance with the irradiation times (b) for PU-S1 (○), PUC-S1 (△) and PUC-S2 (□) films.

Referring to the (2 + 2) photocycloaddition, the most interesting property of the resulting product is the perturbation of the solubility of the polymeric films that occurs as a consequence of the crosslinking effect [28]. Invariably, the changes observed upon continued irradiation of the PU-S1 film with a mask are complex and irreversible, indicating perhaps a greater extent of the formation of (2 + 2) photodimer in the zone exposed to UV irradiation, which become insoluble.

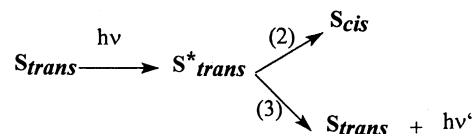
In comparison with its non-ionomeric form, the study of the corresponding ionomeric film (PUC-S1) suggested a more reduced sensitivity to UV irradiation in the latter (Fig. 4, plot b). The absorption maximum from 316 nm ascribed to the *trans* isomer decreased slowly as the exposure time increased ($k = 4.9 \times 10^{-3} \text{ s}^{-1}$) and after 16 min irradiation a phototransformation degree of the chromophore around 40% was determined. Photoresponse difference between the non-ionic and ionic-polymer may be attributed both to some overcrowding of the rigid and bulky chromophore fragments hindering their orientation as well as to the electrostatic interactions encountered in the ionomer systems.

However, it is interesting to compare the kinetic study on the above polymers with the photoisomerization of the stilbene attached on the quaternary ammonium groups into the underivatized polyurethane precursor. When PUC-S2 was irradiated in thin film (Fig. 4, plot b), the characteristic absorption bands centered at 315 and 333 nm mimic those of PUC-S1, but in this case photoconversion of the *trans* isomer upon irradiation was smaller. Under such conditions, the photoprocess evolution with a lower rate constant ($k = 2.8 \times 10^{-3} \text{ s}^{-1}$) occurred. Such low relative values measured for the studied polymers can, in principle, be related to a moderate photoactivity of the stilbene chromophore placed on the polyurethane backbone. This photobehavior, which is not unexpected, represents probably different conformations of the polymeric chains providing evidence for the role of the hydrogen bonds and specific ionic associates in the conformational rearrangements required of the stilbene molecule to photoisomerize to its *cis*-isomer. Therefore, the

set of results suggests that besides intermolecular interactions and aggregation which as a rule, decrease the efficiency of photochemical transformations, the polymer structure and the anchoring point of the stilbene chromophore control the photoisomerization mechanism and its kinetics.

3.2. Fluorescence of the stilbene group in solution and solid state

The absorption of one photon into *trans*-stilbene molecule has now created a singlet excited state which has three choices for returning to the ground state: (1) lose energy thermally, (2) undergo a photochemical reaction involving rotation of the stilbene molecule around the central ethylene bond or (3) lose energy in the form of a photon [29]. The electronically excited *cis*-stilbene (2) is non-fluorescent and the luminescence process (3) is called fluorescence, according to the scheme:



To investigate the photoinduced properties in our system, the fluorescence spectra for irradiated samples with UV light were compared to the corresponding absorption spectra. Fig. 5 depicts the absorption and emission spectra of S-Cl in solution and crystal, obtained at excitation with 303 or 365 nm. In both states, UV spectroscopy confirmed the absorbance peaks for S-Cl in the region $\lambda_A = 286\text{--}328 \text{ nm}$ (DMF) which emits a violet–blue fluorescence at $\lambda_F = 416 \text{ nm}$, whereas in the solid two maxima at $\lambda_F = 444$ and 470 nm were registered. This finding suggests formation of a excimer (excited dimer) of S-Cl, originating from the attractive interaction of an excited stilbene group with another stilbene group in the ground state. On the other hand, the vibronic structure of the fluorescence spectra is better resolved in the solid state but it is red shifted relative to that of dissolved derivative in DMF owing to the formation of aggregates between fluorophores. Moreover, exciting S-Cl in solution or in crystal with $\lambda_{\text{ex}}: 328 \text{ nm}$ a shift of excimer fluorescence was not recorded. This clearly indicates that

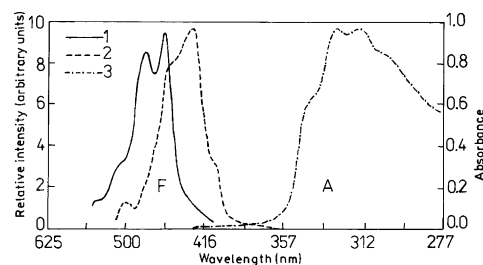


Fig. 5. Absorption spectrum of stilbene derivative (S-Cl) in DMF (1) and its fluorescence spectra in DMF (2) or solid (3), excitation at 303, 328 and 365 nm.

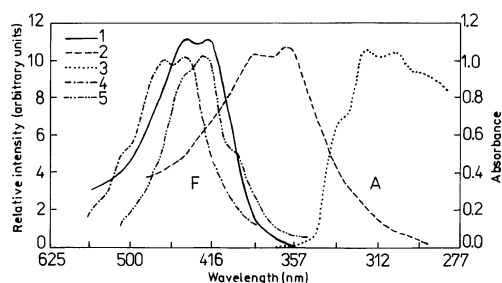


Fig. 6. Absorption spectrum of stilbene ionic derivative (S–D) in DMF (3) and its fluorescence spectra in solution, excitation at 344 nm (1), 334 nm (2), 365 nm (5) and solid state (4), excitation at 334, 344 and 365 nm.

in the stilbene derivative a hydrophobic aggregation takes place. When stilbene probe enters a structure of different polarity such as an ionic diol with one-sided chromophore placed on the ammonium quaternary structure (S–D, Fig. 1), no significant difference was observed between two stilbene compounds, although the local environments were different. Exciting the latter at 344 or 365 nm the broader wavelength band that had an emission peak at 416 nm (DMF) and 433 nm (solid) does not shift with the excitation wavelength. Therefore, it seems that there is no important difference in stilbene binding on the non-ionic or ionic derivative. If the fluorescence emission spectrum for S–D in DMF resulted by sample excitation at λ_{ex} : 334 nm, the appearance of only “monomeric” fluorescence at 357 nm with one shoulder at 379 nm was observed (Fig. 6). Exciting directly at 344 nm for ionic crystal an aggregate fluorescence at 415 and 440 nm was revealed. This photoselection of the monomer fluorescence may be result of structural reorganization of the ionic associates into polar solvent which facilitates the dissociation process to form isolated salt groups. The fact that in solid state the emission maximum of stilbene remains unmodified with the excitation wavelength region of the fluorescence spectrum provided evidence for the presence of more stable aggregates.

Quite surprisingly, we have found that the non-ionic polymer (PU-S1) presents a similar fluorescence with that of stilbene ionic in DMF solution (Fig. 7). Thus, PU-S1

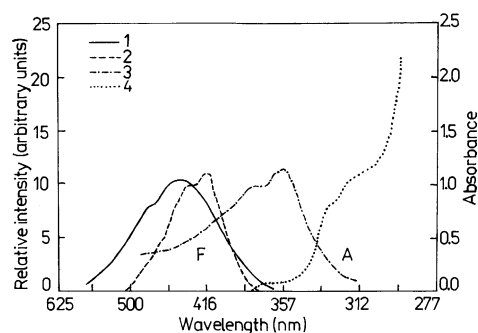


Fig. 7. Absorption spectrum of stilbene polyurethane (PU-S1) in DMF (4) and its fluorescence spectra in film, excitation at 328 and 365 nm (1) and in DMF solution, excitation at 365 nm (2) or 328 nm (3).

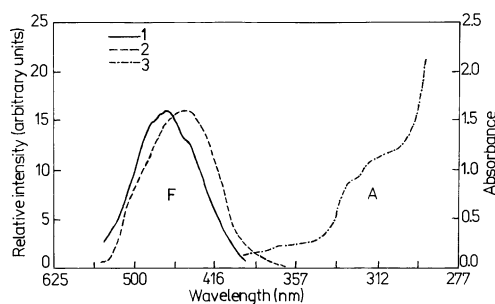


Fig. 8. Absorption spectrum of polycation (PUC-S2) in DMF (3) and the fluorescence spectra in film, excitation at 334, 365 nm (1), and in solution, excitation at 334 and 365 nm (2).

excited at λ_{ex} : 328 nm exhibited emission properties at 359 nm (DMF) and 450 nm (film) assigned to the monomer and excimer fluorescence, respectively. Exciting at red edge (λ_{ex} : 365 nm) the fluorescence spectrum of PU-S1 showed only the excimer form at λ_{F} : 420 nm (DMF) or 450 nm (film). This can suggest a compact conformation of the polymer chains in which local concentrations of stilbene molecules favor excimer formation. In fact, the excimer formation in polymer solution is a diffusion controlled process and the intrapolymeric association is expected to predominate. In contrast, the formation of excimers or dimers in the thin films is probably affected mainly by the topochemical alignment of the stilbene molecules and implicitly interpolymeric interactions should be preponderant. Upon polymer quaternization (PUC-S1), the excimer fluorescence peaks which arise at 422 nm (DMF) and 451 nm (film) are not dependent of the photoexcitation wavelength (λ_{ex} : 334 and 365 nm. On the basis of the observed excimer emission in PUC-S2 (λ_{F} : 445 nm/DMF; 466 nm/film) most importantly, is that the anchoring of stilbene onto the ammonium quaternary structure caused a red shift of the excimer (Fig. 8). This is again explained in terms of modification of the polymer conformation due to specific interactions generated by the physical crosslinking between polymer chains with effect on increasing of stability of the aggregates. The validity of the fluorescence data are conveniently sustained by the values of excited state energy. As seen from the data listed in Table 2, the value of excited state energy for monomer fluorescence measured at 328 nm (PU-S1) and 334 nm (S–D) was higher as compared with that of the excimer fluorescence. In good agreement with these results we find different values of the Stokes shift (Δ_{ν}), as parameter which indicates the differences in properties and structure between the ground state and the first excited state (S_1) of the stilbene chromophore.

The Stokes shift values [30] determined by relation $\Delta_{\nu} = 1/\lambda_{\text{A}} - 1/\lambda_{\text{F}} \times 10^7 \text{ (cm}^{-1}\text{)}$ were indeed higher for excimer than those in the case of monomer fluorescence (Table 2). This is an indication in the energy losses during the transition into excited state. On the other hand, the energy of the excited state E_{S_1} of the monomer and polymers is comparable only in solution. Such evidence lends support to

Table 2
Physical and fluorescence data for the stilbene derivative and PU cationomers in DMF solution and solid state

Sample	State	λ_A (nm)	λ_{ex} (nm)	λ_F (nm)	ϕ_F^a	E_{st} (kJ mol ⁻¹) ^b	$\Delta\nu$ (cm ⁻¹) ^c
S-CI	DMF	286, 300, 314, 328	303, 328, 365	416	0.20	305	7809
	Solid		328, 365	444, 470	0.22	287	9325
S-D	DMF	303, 308, 324	334	357, 379	0.22	371	4992
			344	416, 440	0.17	346	8965
			365	416	0.16		8965
	Solid	–	334, 344, 365	433, 449	0.18	304	9909
PU-S1	DMF	313, 328	328	359, 384	0.14	360	4093
	Film	315, 332	365	420, 438	0.12	330	8139
PUC-S1	DMF	313, 329	328, 365	422			8252
	Film	315, 333	334, 365	451	0.06	320	9524
PUC-S2	DMF	316, 328	334, 365	445	0.11	300	9174
	Film	316, 328, 334	334, 365	466	0.12	314	10186

^a Quantum fluorescent yield.

^b Excited site energy.

^c Stokes shift.

the assumption that in DMF there is the same equilibrium conformation of the excited species. To clarify the ability of the stilbene unit to emit the absorbed light energy, we calculated the quantum fluorescent yield (ϕ_F) using Parker method [31] and anthracene as standard. From the results found in our derivative and the corresponding polymers it can observe that important steric effects are responsible for the increasing of the quantum fluorescent yield (ϕ_F), in comparison with that of pure stilbene (ϕ_F : 0.05 at 25 °C) [27]. With one exception (PU-S1), the ϕ_F values in solution were similar to those obtained for the solid state suggesting thus relative importance of the interaction between the excited state and polar solvent in the non-radiative process. More fluorescence studies of these unique systems are planned, including hydrophilic backbones with other luminophores which will provide further information on the microscopic dynamics and conformations of polymers.

4. Conclusions

Polyesterurethane cationomers of ammonium type with stilbene incorporated on urethane hydrogen atoms or on ionic functionality were synthesized and their properties were presented. The new polymers exhibit good film-forming ability and a typical elastomeric behavior for ionic polyurethanes. A more accentuated sensitivity of polymers in solution than in film state was evidenced when the samples were exposed to UV irradiation. In particular, because of the presence of aggregates in the polymers, the *trans-cis* photoisomerization of the stilbene derivative was accompanied by (2+2) cyclobutane photoadduct formation.

In the fluorescence study it was found that the synthesized polymers showed different properties in solution and film state. Especially, aggregation produces strong effects on the

photophysics of the stilbene chromophores. Thus, a red shift of the emission band in film state occurs and formation of excimers in both state was observed. Only monomer fluorescence of *trans*-stilbene was observed at excitation of the non-ionic polyurethane solution at 328 nm.

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