Development of fluorescence probes based on stilbazolium salts for monitoring free radical polymerization processes

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A series of 1-methyl-2-(4-aminostyryl)pyridinium perchlorates and iodides were investigated as fluorescent probes for the monitoring of the progress of free radical polymerization. The study on the changes in the fluorescence intensity and spectroscopic shifts of studied compounds were carried out during thermally initiated polymerization of methyl methacrylate and during photoinitiated polymerization of a 2-ethyl-2-(hydroxymethyl)propane-1,3-diol triacrylate (TMPTA)–1-methylpyrrolidin-2-one (MP) mixture. The purpose of these studies was to find a relationship between the changes in the shape and intensity of probe fluorescence and degree of monomer conversion into polymer. The polymer formation was estimated gravimetrically or by the measurement of the degree of monomer double bond disappearance using FTIR spectroscopy.

Introduction

Fluorescent probes are used in chemistry for monitoring specific properties of the medium in which they are incorporated.[1,2] It is possible because their fluorescence is sensitive to changes in temperature, polarity or rigidity of the environment. Therefore, one can use them to estimate the polarity of the medium or degree of cure in a polymer by measuring the changes in their emission intensity or value of the emission maximum shift. Essentially there are four different kinds of fluorescent probes: (1) excimer forming, (2) twisted intramolecular charge-transfer (TICT) probes, (3) charge-transfer probes and (4) fluorescent organic salts.

Pyrene is a typical excimer forming probe. The polarity of a pyrene microenvironment can be probed by measuring the intensity ratio of the first and third peaks in the pyrene vibronic emission spectrum. The intensity ratio of excimer emission to monomer emission in the pyrene spectrum also reflects the interaction between the polymer chain and the solvent molecule. The steady-state fluorescence technique used to study the polymerization rate showed that for a low degree of polymerization, one observes a linear correlation between the fluorescence intensity ratio of the monomeric and pyrene excimer emissions and the degree of polymerization.[3,4] Pyrene was also used to study the Trommsdorf effect,[4] cyclization dynamics of polymers[5] and to estimate the Hildebrand solubility parameter δ_H.[6] The advantage of pyrene as a fluorescent probe is the possibility of controlling the fluorescence intensity ratio of monomer to excimer emission by adjusting the concentration of pyrene.[3] The disadvantage of pyrene as a fluorescent probe is that in the case of viscous multiacrylates, high concentrations are required in order to see a well-defined excimer emission, which limits observation to only a very thin surface layer.

Molecules exhibiting the presence of a TICT state contain a dialkylamino group linked by a σ-bond to a phenyl ring substituted in the *para* position with a strong electron-withdrawing group.[7,8] Dual fluorescence of these compounds is caused by the presence of two different singlet excited states. Fluorescence originating from a locally excited state results in the *b*-band observed in the blue area of the emission spectrum. The other occurs from a new state formed through an excited-state isomerization reaction. This new state is a twisted intramolecular charge-transfer (TICT) state, in which the dialkylamino group is twisted 90° with respect to the plane of the aromatic ring, and has transferred an electron to it. Consequently, charge separation is complete between the acceptor and the donor, with the acceptor group containing a full negative charge and the donor group containing a full positive charge. Fluorescence occurring from the TICT state results in the so-called *a*-band which is red shifted in comparison to the *b*-band due to a lower energy of transition from the TICT state.[7,8] Charge separation existing in the perpendicular form causes fluorescence occurring from this molecule to be dependent on solvent polarity and viscosity.[9–11] Molecules possessing a TICT state were used for the testing of properties of the polymeric chain in diluted solution[12–15] as well as for the study of the kinetics of free radical polymerization.[16]

Intramolecular charge-transfer (ICT) probes are solvatochromic probes. These are molecules that incorporate an electron-donor group (D) and an electron-acceptor (A) group connected by a spacer which keeps D and A at a fixed distance (D–spacer–A, D–S–A) and at a well defined orientation with respect to each other. The classical fluorescence probes possessing typical ICT (*e.g.* the series of *p*-(*N*,*N*-dialkylamino)benzylidenemalononitriles) were described by Loutfy.[17–20] The properties of the ICT probe described by Verhoeven's research group are spectacular. This group tested the properties of 1-phenyl-4-(4-cyano-1-naphthylmethylene)piperidine ("Fluoroprobe"). It was found that this molecule emits charge-transfer-type fluorescence with the quantum yield exceeding 0.5 and displays the enormous solvatochromism of this fluorescence making this molecule attractive as a fluorescent polarity and viscosity probe.[21–25] Other well known ICT probes applied for monitoring of polymerization kinetics are 4-(dimethylamino)-4′-nitrostilbene,[26] 2-dimethylamino-7-nitrofluorone (fluorone = 3*H*-xanthen-3-one),[27] dansylamide,[28,29] carbazole derivatives and 9,9′-bianthryl,[30,31] stilbene and coumarin derivatives.[32,33]

The fourth group of probes are organic salts of the D–π–A^+X^- type. This includes substituted stilbazolium (stilbazole = styrylpyridine) salts which exhibit a very strong temperature effect above the polymer glass transition temperature of polymers interpretable as dependence on the surroundings. Although structurally D–π–A^+X^- type probes are similar to the charge transfer probes, their photophysical properties are different. They display a blue shift in their emission maxima during polymerization, but their fluorescence is only slightly dependent on changes in solvent polarity. That is why they are essentially nonsolvatochromic probes. The photophysics and spectroscopic behaviour of this class of compounds have been described by Fromherz's[34–36] and Rettig's[37] research groups. Stilbazolium salts were successfully applied as fluorescence probes for the monitoring of curing of epoxy resins[38] as well for measuring the progress of photopolymerization of dimethacrylates.[39]

In this report, we describe the relationship between the change in the emission spectra of a series of structurally different stilbazolium salts during thermally initiated polymerization of monomethacrylate and photopolymerization of polyol acrylates.

Experimental

Methyl methacrylate, 2-ethyl-2-(hydroxymethyl)propane-1,3-diol triacrylate (TMPTA), 1-methylpyrrolidin-2-one (MP), all spectroscopic grade solvents used for spectroscopic measurements and substrates for synthesis of tested probes were purchased from Aldrich.

Fluorescence measurements were recorded on a F-4500 (Hitachi) spectrofluorimeter using classical measurements for monitoring the degree of methyl methacrylate polymerization and the front-face mode for photoinitiated polymerization of TMPTA. Absorption spectra were recorded on a Varian Cary 3E spectrophotometer. IR spectra were recorded on a Brucker Vector 22 FT-IR spectrometer. The reduction potentials of the dyes were measured by cyclic voltammetry. An Electroanalytical Cypress System Model CS-1090 was used for the measurements, and an Ag/AgCl electrode served as the reference electrode. The supporting electrolyte was 0.5 M tetrabutylammonium perchlorate. Semiempirical calculations of the molecular geometries and the ground state dipole moment were performed using the Hyper-Chem v.4 AM1 method.

Thermally initiated polymerization of methyl methacrylate

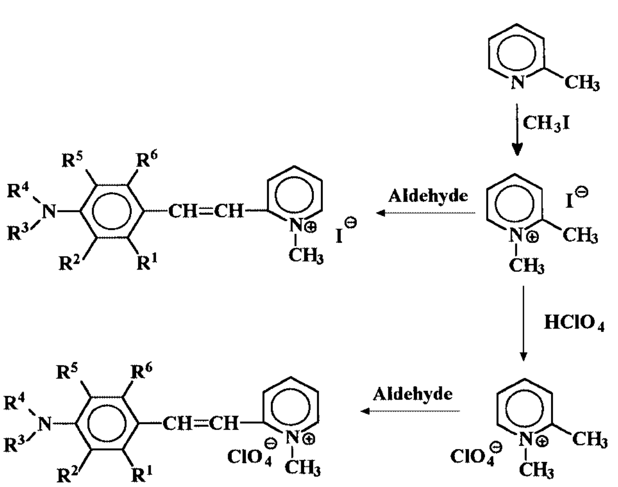
Methyl methacrylate solution, containing α,α′-azoisobutyronitrile (AIBN) as the free radical polymerization initiator (1%) and probe being tested at concentrations which gave the maximum intensity of absorption in the range of about 0.5, was placed in Pyrex test tubes. Polymerization was initiated at 55 °C. The samples were periodically (15 or 20 min) removed from the water bath and cooled with ice to a temperature of about 0 °C in order to stop the polymerization and were then warmed up to room temperature. The fluorescence of the solutions was measured after the subsequent time of polymerization and degrees of polymerization were estimated by a gravimetrical method after precipitation of the polymer in methanol.

Photoinitiated polymerization

Studies on the changes in probe fluorescence during polymerization initiated photochemically were carried out using a mixture of 2-ethyl-2-(hydroxymethyl)propane-1,3-diol triacrylate (TMPTA) and 1-methylpyrrolidin-2-one (MP) (9:1) and DAROCUR 1116 as initiator (2%), the concentration of the tested fluorescence probe was about 0.5%. A thin film of this mixture was prepared between two sheets of polyethylene film, separated by a ring of aluminium foil to prevent the outflow of the mixture. The film was irradiated using UV emission of a xenon lamp, type XBO 150W (OSRAM). The emission spectra and double bond conversion (measured by following the disappearance of the C=C stretch at 810 cm^{-1}) were measured after subsequent irradiations.

Synthesis

Tested probes were prepared by the sequence of reactions described in Scheme 1 starting from the appropriate *p*-aminobenzaldehyde and 1,2-dimethylpyridinium perchlorate or iodide.



Scheme 1

1-Methyl-2-(4-aminostyryl)pyridinium perchlorates and iodides were obtained by refluxing (1–2 h) the appropriate *p*-aminobenzaldehyde (0.01 mol) with 1,2-dimethylpyridinium perchlorate or iodide (0.01 mol), respectively, in methanol (20 mL) in the presence of piperidine (few drops). The precipitate formed after cooling down the reaction mixture was filtered and twice recrystalized from aqueous ethanol or methanol. The products were identified by elemental analysis and spectroscopically (^{1}H NMR and IR). The detailed procedures and physical data for tested salts are given elsewhere.[40] *p*-Aminobenzaldehydes used were prepared following the procedures given by Gawinecki *et al.*[41]

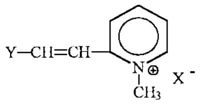
1,2-Dimethylpyridinium iodide was obtained in 95% yield by refluxing the mixture of freshly distilled α-picoline (50 mL, 47.2 g, 0.51 mol) and methyl iodide (31.6 mL, 72.1 g, 0.51 mol) in acetone (150 mL) for 1.5 h. The precipitated crystals were filtered off, dried under vacuum, and used directly in the next step. To transform iodide into perchlorate 70% perchloric acid (15 mL, 25 g, 0.147 mol) was added to the warm solution of 1,2-dimethylpyridinium iodide (40 g, 0.17 mol) in methanol (85 mL). The crystals of products precipitated after cooling down the reaction mixture were filtered off and dried under vacuum. The product was obtained in 85% yield. Other probes containing perchlorate ion were prepared by a similar procedure.

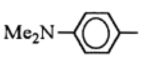
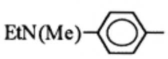
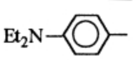
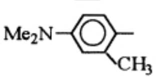
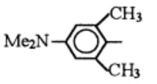
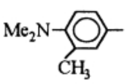
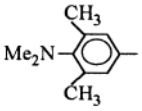
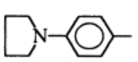
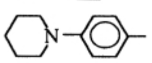
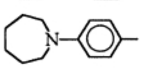
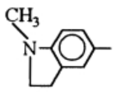
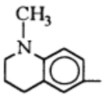
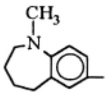
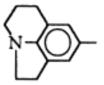
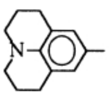
Results and discussion

The structures of the series of 1-methyl-2-(4-aminostyryl)-pyridinium salts tested are presented in Table 1. All the probes tested are soluble both in the monomers and in the solid polymers. There was no indication that during the course of polymerization molecular aggregates are formed or precipitation of the probes occurs. Fig. 1 shows illustrative electronic absorption spectra recorded in CH_2Cl_2 solution. The basic spectroscopic properties of the tested probes are also summarized in Table 1.

The analysis of the electronic absorption spectra clearly indicates the presence of absorption bands that correspond to the transition $S^0 \rightarrow CT$ which appears at the red-energy side of the absorption spectrum (see Fig. 1). A well separated CT absorption band is observed for almost all dyes tested. Inspection of the absorption spectra, presented in Fig. 1, shows that the position and intensity of the CT absorption band strongly depends on the molecular structure. This finding can be summarized as follows: (i) the planar conformation of molecules **XIV** and **XV** increases the probability of the radiative transitions in comparison to the other molecules, (ii) the coplanar conformation

Table 1 Structures and basic spectroscopic and photochemical properties of probes tested



No.	−Y	X^-	Abs. λ_{max}/nm[a]	Abs. $\Delta\lambda$/nm[b]	$E_{red} - E_{ox}$/mV	μ/D
I		ClO_4^-	498	−40	2264	8.4
II		ClO_4^-	506	−42	2142	9.7
III		ClO_4^-	513	−44	2156	10.8
IV		ClO_4^-	508	−45	2108	8
V		ClO_4^-	436	+34	2332	9.7
VI		ClO_4^-	459	−52	2066	10.9
VII		ClO_4^-	460	+66	2128	13.8
VIII		ClO_4^-	513	−43	2164	10.3
IX		ClO_4^-	486	−9	1844	12.3
X		ClO_4^-	514	−42	2222	13.6
XI		ClO_4^-	519	−53	2080	7.9
XII		ClO_4^-	523	−46	2150	8.9
XIII		ClO_4^-	468	−39	2140	11.3
XIV		ClO_4^-	548	−63	1864	9.7
XV		ClO_4^-	546	−49	1920	11.1

[a] In CH_2Cl_2. [b] Solvatochromic shift calculated as a difference of absorption λ_{max} measured in CH_2Cl_2 and DMF solutions. **Note:** Iodides were prepared for **I**, **III**, **VI** and **XII** chromophores and are referred to as **Ia**, **IIIa**, **VIa** and **XIIa** respectively.

decreases this probability which is demonstrated by a significant blue shift of the CT absorption band and a decrease of its molar absorption coefficient. It is worth specifying some interesting properties of **IX** and **XIII** probes. The position of the CT band suggests a strong decoupling effect between the dialkylamino group and the electron-accepting part of the molecule. This specific irregularity can be supported by the data obtained by Gawinecki *et al.* during their study on the resonance substituent constants of *para*-substituted benzaldoximes.[42] CT character of the long-wavelength absorption band is additionally reflected by the values of the ground state dipole moments.

As can be seen in Table 1, the dyes tested as probes were selected in a way that allowed changes in the structure of the rotating part of the molecules and changes in the electron-donating properties of the dialkylamino group, to force a pretwist or to prevent the rotation of the dialkylamino group. These can be achieved by the control of the freedom of all possible rotations around the bonds. Additionally the "sensitivity" of the probe may be changed by the size of the negative ion.

The term *solvatochromism* is used to describe the change in position of the electronic absorption band, accompanying a change in the polarity of the medium. Tested dyes show in most cases a moderate negative solvatochromism with the exception of **V** and **VII** which display distinct positive solvatochromism. The hypsochromic shift of the absorption λ_{max} as the solvent polarity increases is observed when the ground state is more dipolar than the excited state ($\mu_g > \mu_e$). This relation allows us

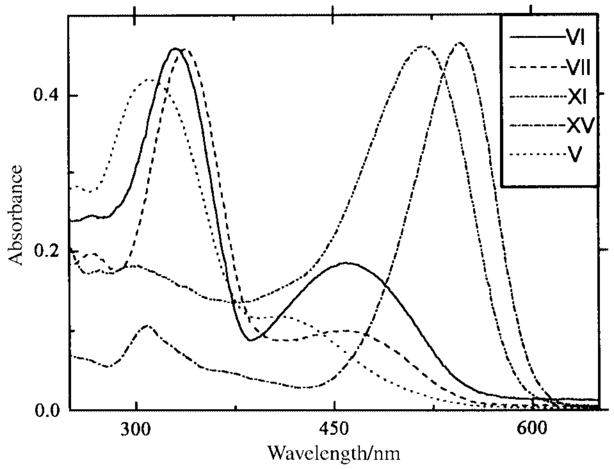


Fig. 1 Illustrative electronic absorption spectra of selected probes recorded in CH_2Cl_2 solution.

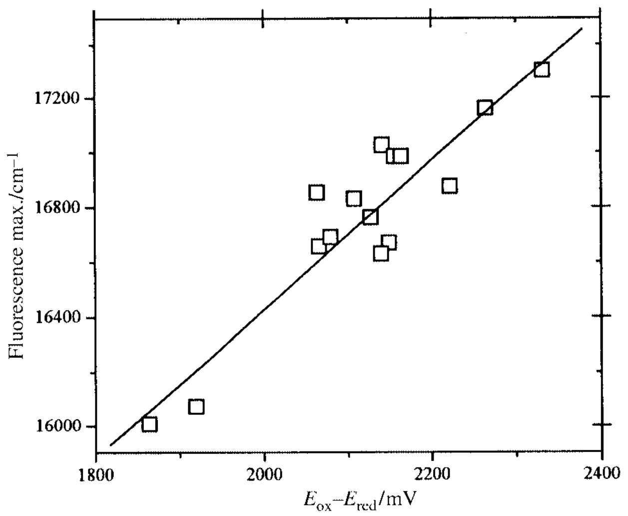


Fig. 2 Fluorescence frequency of compound tested *versus* $E_{ox}(D) - E_{red}(A)$.

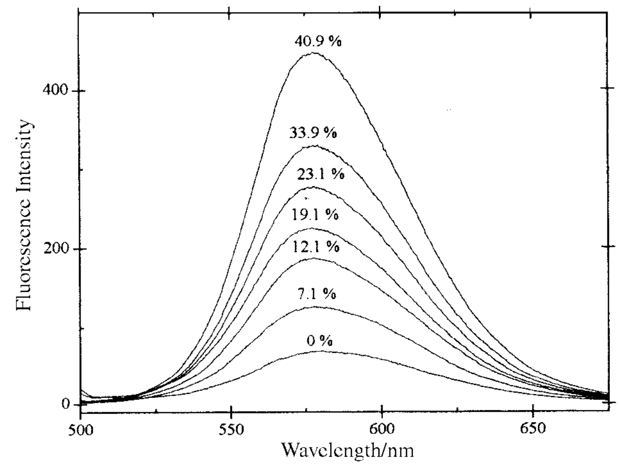


Fig. 3 Changes of the fluorescence spectra of **XV** during thermally initiated polymerization of methyl methacrylate for low degrees of polymerization.

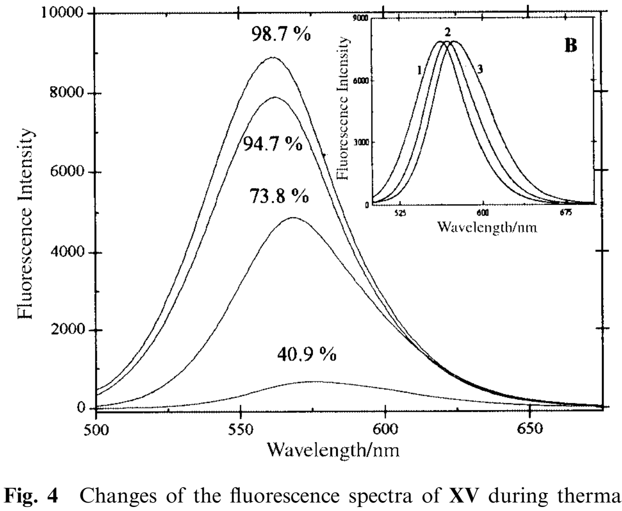


Fig. 4 Changes of the fluorescence spectra of **XV** during thermally initiated polymerization of methyl methacrylate for high degrees of polymerization. Inset: Normalized fluorescence emission curves illustrating a blue shift observed during thermally initiated polymerization recorded at high degree of monomer conversion; (1) 98.7%, (2) 94.7% and (3) 73.8% of monomer conversion.

to conclude that the dipole moments of the excited states reached directly after excitation are rather small.

Tested probes represent bichromophoric conjugated molecules that show large Stokes shifts (see Table 2). This indicates that the emitting state is not the Franck–Condon S_1 state reached in the absorption transition but a different one, the solvent relaxed state, from which the fluorescence originates. It cannot also be assumed that the excited state dipole moment remains unchanged during the transition from the Franck–Condon state to the emitting state. The nature of the emitting state in D–S–A molecules may change with the solvent (see Table 2) or can be changed with the dye structure that is forcing or precluding the excited state relaxation *via* selected channels (see Table 2 and ref. 43) or may be controlled by the viscosity of the medium.[38]

Not only the solvent, but also the nature of the electron donating part of the molecule has a strong influence on the CT fluorescence. Theoretically[44] the energy level of the molecule excited CT state, relative to its ground state can be expressed by eqn. (1), where $E_{ox}(D)$ and $E_{red}(A)$ are the one-electron

$$E_{CT} = E_{ox}(D) - E_{red}(A) + C \qquad (1)$$

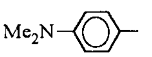
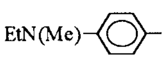
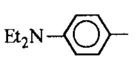
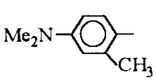
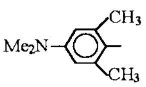
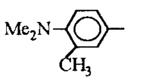
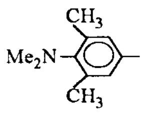
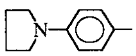
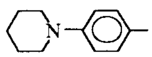
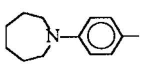
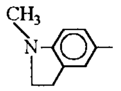
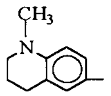
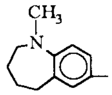
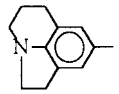
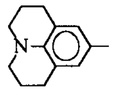
oxidation and reduction potentials of the donor and acceptor and C is a constant that depends on the degree of charge separation.

Verhoeven,[45] analyzing the properties of rod-shaped donor–acceptor systems, illustrated that the fluorescence frequency of intermolecular exciplexes and excimers as well as intramolecular donor–acceptor systems is linearly dependent on the value described by eqn. (1), namely on the value of $E_{ox}(D) - E_{red}(A)$. As is shown in Fig. 2 similar properties are observed for probes described in this paper. Fig. 2 clearly shows that the emissions observed for tested probes occur from the excited CT state.

An increase in the intensity of probe fluorescence is observed during methyl methacrylate polymerization when the degree of monomer conversion gradually increases. This effect is accompanied additionally by a blue shift in their emission maxima. Figs. 3 and 4 show the emission spectra of the **XV** probe recorded for different degrees of polymerization. Fig. 5 summarizes the changes in fluorescence intensity observed for the **VI** probe during thermally initiated polymerization of methyl methacrylate.

As one can see, emission of the probe changes gradually for low degrees of monomer conversion and undergoes a distinct blue shift and a strong increase in its intensity during conversion of the sample into a rigid polymer matrix. An increase in medium rigidity causes a reduction in the rates of all processes controlled by diffusion. In the literature there are two different explanations that describe the mechanism of the observed photophysical behavior of D–π–A salts. The first, proposed by Neckers *et al.*,[39] assumes that the positive charge in the cation is

Table 2 Spectroscopic properties of tested probes

No.	−Y	X	Fl. $\Delta\lambda$/ nm	$\Phi_{Fl} \times 10^3$ in THF	Stokes shift[a]/ cm^{-1}	Stokes shift[b]/ cm^{-1}	$\lambda_0 + \lambda_i$[c]/ kJ mol^{-1}	$-\Delta G_{CT}$[c]/ kJ mol^{-1}
I		ClO_4^-	16	4.71	3015	5140	18.03	204.7
II		ClO_4^-	13	5.78	2756	4885	16.48	219.9
III		ClO_4^-	9	7.16	2486	4600	14.87	218.3
IV		ClO_4^-	8	2.12	2907	4987	17.38	218.4
V		ClO_4^-	12	<1.0	6101	7770	36.49	237.9
VI		ClO_4^-	17	3.92	4895	8389	29.27	230.0
VII		ClO_4^-	5	2.72	4904	8237	29.33	230.9
VIII		ClO_4^-	13	5.01	2515	4665	15.05	218.2
IX		ClO_4^-	12	5.60	3713	4463	22.21	223.9
X		ClO_4^-	9	7.34	2563	4575	15.32	217.2
XI		ClO_4^-	14	1.61	2573	5146	15.38	213.9
XII		ClO_4^-	8	2.45	2564	4624	15.33	213.4
XIII		ClO_4^-	9	4.23	4839	7023	28.94	225.1
XIV		ClO_4^-	3	0.83	2248	4670	13.44	144.6
XV		ClO_4^-	9	1.66	2238	4248	13.38	205.7

[a] Measured in CH_2Cl_2. [b] Measured in DMF. [c] Calculated for CH_2Cl_2 solution.

localized on the pyridinium ion in the ground state, but it changes its location in the excited state. Based on the calculation of the HOMO and the LUMO, one can conclude that in the excited state the positive charge is transferred from the pyridinium ion to the (dimethylamino)phenyl group. It is also assumed that the positive charge is primarily stabilized by the counterion. The lack of solvatochromism was explained by observing that the ground state and the fully relaxed excited state are roughly equivalent. Therefore the polarity of the solvent does not influence the emission wavelength of the probe. The ability of these types of probes to monitor the rigidity of their environment is explained by the decreased mobility of the counterion which is not able to follow the cation in rigid media and that causes lesser stabilization of the excited molecule.

The second, more convincing, explanation of specific photophysical properties of stilbazolium salts is given by Rettig *et al.*[37] These authors applied the global analysis technique to construct the spectral profile of several emitting states. A global fit of the emission data, obtained from time-resolved fluorescence spectroscopy, showed that a three-exponential model was necessary in order to obtain an acceptable fit. The well-known model of twisted intramolecular charge-transfer states (TICT)[7,8,46,47] can be a good basis for the description of multiple fluorescence of tested molecules. According to Rettig[37] the excited and ground-state energies can be presented as plotted in Fig. 6.

Fig. 6 shows that simultaneous fluorescence can occur from **E**, $\mathbf{A_2}$ and $\mathbf{A_3}$ and this explains the broad steady-state spectra measured. The twist of the dialkylamino group leads to a TICT state ($\mathbf{A_1}$), however its energy level is considerably higher than for nontwisted conformation **E**, therefore it cannot be easily thermally activated and thus cannot contribute to the emission spectra. A twist of the double bond gives a state **P** with a relatively narrow S_1–S_0 gap. The deactivation of this state should be radiationless in character because of a small energy gap to the ground state. An emission from $\mathbf{A_2}$ and $\mathbf{A_3}$ states should be

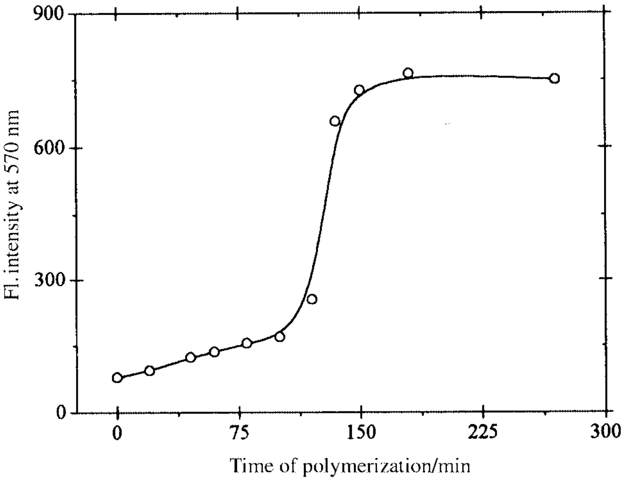


Fig. 5 Changes of fluorescence intensity (measured at $\lambda = 570$ nm) observed for the **VI** probe during thermally initiated polymerization of methyl methacrylate.

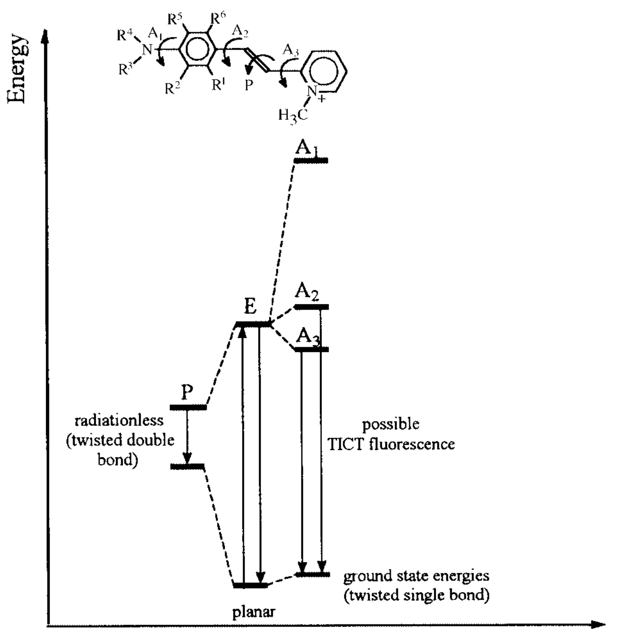


Fig. 6 Conceptual presentation of energy gaps between the ground state energy and the lowest excited states for tested probes. The indices 1, 2 and 3 denote the states reached after the twist of a single bond, **P** corresponds to the state after the twist of double bond and **E** is the lowest excited state for the planar conformation.

possible because their energies are similar to that of the **E** state. Accepting the mechanism of multiple fluorescence of the tested probes proposed by Rettig, it is easy to explain their specific properties observed in Fig. 5.

Changes in probe emission intensities, measured at a wavelength specific for each probe, were also recongnized as values characterizing probe response to an increase in the degree of polymerization. The relationship between these changes and changes in the degree of monomer conversion into polymer is linear for low degrees of polymerization. At higher degrees of conversion a sudden increase of fluorescence intensity occurs which is caused by the effect connected with conversion of polymer solution into the rigid polymer matrix (Fig. 7).

The increase of the fluorescence intensity during polymerization is easy to interpret in terms of high sensitivity to the viscosity of the *trans–cis* isomerization process of the imine double bond. The increase of viscosity reduces the efficiency of the isomerization about the C=N bond. This, in turn, decreases the efficiency of the formation of radiationless state **P** and, as a result, causes more effective emission from **E**, A_2 and A_3 states.

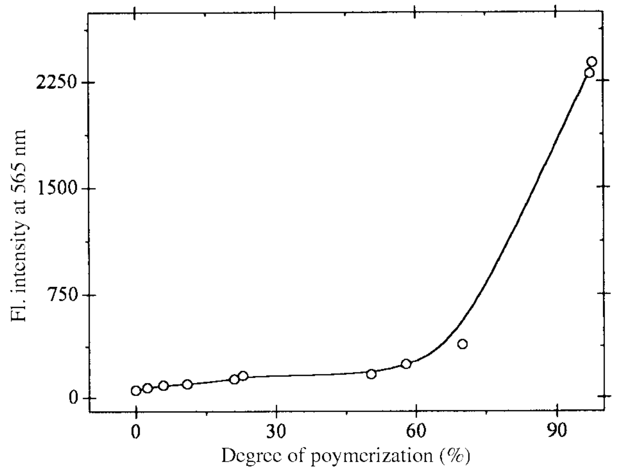


Fig. 7 Relationship between the probe emission intensity (recorded at $\lambda = 565$ nm, probe **VII**) and the degree of monomer conversion into polymer during methyl methacrylate polymerization.

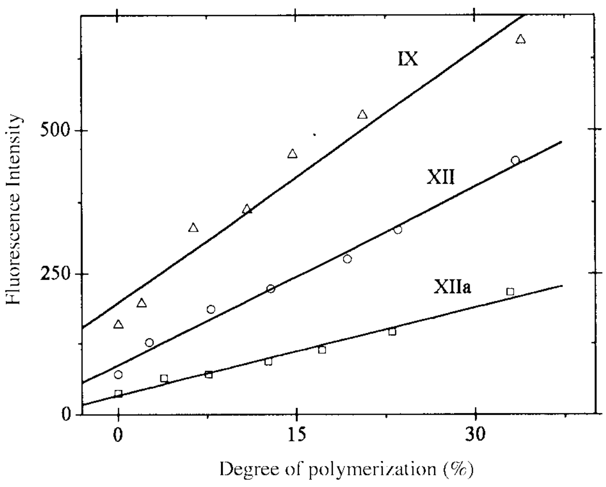


Fig. 8 Linear relationships between the fluorescence intensity and the degree of polymerization for selected probes illustrating their sensitivity. Type of molecule marked in the figure.

This effect can be rationalized in terms of the activation energy needed for isomerization of aromatic imines, which is of the order of 20 kcal mol^{-1} or less.[48–51]

Since the value of the probe response to changes in the degree of polymerization depends on a number of factors and differs for the probes of different structure, it was interesting to compare this response in a factor called the "probe sensitivity parameter". We define this as a value of the slope of a linear relationship obtained for the dependence of the probe emission intensity at a chosen wavelength on the degree of monomer conversion into polymer. Due to the low precision in selecting the fluorescence analyzing wavelength, this value is also an approximate characteristic of probe response. Fig. 8 presents the examples of such relationships used for calculation of the "probe sensitivity parameter".

Table 3 contains the values of "probe sensitivity parameters" for the studied pyridinium salts as well as the values of blue shifts in their emission maxima observed during methyl methacrylate polymerization. For comparison the values of the ratio of fluorescence intensity for the fully polymerized environment to the intensity at the same wavelength in the monomer are also summarized in Table 3.

As can be seen, values of the probe sensitivity parameter oscillate from 1.4 for **IV** to 14.7 for **IX**. Taking the dimethylamino substituted probe **I** as a standard (sensitivity parameter 7.4), it can also be seen that an increase in the size of the dialkylamino group causes an increase of the probe relative

Table 3 Sensitivity parameters, blue shifts in emission maxima and ratios of fluorescence intensity in the solid polymer and intensity in the monomer for pyridinium salts studied

Probe No.	Sensitivity (%$^{-1}$)	$\Delta\lambda_{max}$/nm	$I_{100\%}$/$I_{0\%}$	Probe No.	Sensitivity (%$^{-1}$)	$\Delta\lambda_{max}$/nm	$I_{100\%}$/$I_{0\%}$
I	7.4	32.8	50.2	**XI**	2.9	20.2	51.3
II	3.5	31.4	19.0	**XII**	13.1	24.4	153.4
III	9.5	26.6	31.4	**XIII**	8.3	32.4	11.6
IV	1.4	26.6	18.1	**XIV**	4.0	10.4	416.0
V	2.2	1.4	30.6	**XV**	10.6	18.4	88.6
VI	2.1	39.0	9.8	**Ia**	3.0	37.2	8.3
VII	4.1	37.6	48.4	**IIIa**	5.8	30.6	2.7
VIII	9.0	29.4	40.6	**VIa**	1.9	73.8	6.3
IX	14.7	29.8	16.4	**VIIIa**	6.3	32.6	12.7
X	10.2	30.4	8.0	**XIIa**	5.2	27.2	38.3

sensitivity. Thus, replacement of two methyl groups by ethyl groups (compare compounds **I** and **III**) increases the sensitivity from 7.4 to 9.5. This can also be seen for the "cyclic" amino substituents. Thus, increasing of the length of alkane bridges from five (**VIII**) to six (**IX**) and to seven (**X**) carbon atoms, increases the probe sensitivity by a factor of about 1.2–2 (9.0, 14.7 and 10.2 respectively). Dependence of the probe sensitivity on the size of the dialkylamino substituent probably results from the fact that the twisting of the olefinic double bond gives the **P** state. Deactivation of this state should occur mainly by radiationless processes because the energy gap between the **P** and the ground states is very small (see Fig. 6). For the probes possessing a bulky dialkylamino group, the efficiency of this nonradiative deactivation should decrease as the viscosity of the medium increases because of the larger reaction volume for this movement as opposed to the single-bond twisting pathway, giving emitting states $\mathbf{E}_2$ and $\mathbf{E}_3$. Substituents in the *ortho* position with respect to the dialkylamino group (**VI** and **VII**) as well as to the –CH=CH– group (**IV** and **V**), form a pretwisted molecule even in the ground state. This is reflected in the electronic absorption spectra where a blue shift is observed because of steric interactions, which decouple the dimethylanilino group from the electron-accepting part of the molecule. A pretwist distinctly decreases probe sensitivity (by about two times in the case of a pretwist with respect to the dialkylamino group and four times in case of the twist around the bond with the –CH=CH– group). The quantitative explanation of these specific probe responses may come from the estimation of a reorganization energy λ_o related to the solvent and solute motions and reorganization energy λ_i corresponding to the changes in the solute bond lengths and angles accompanying the excited-state electron transfer.[52–54] The following approximate expressions for the maxima of CT absorption and emission spectra can describe the dependence of both reorganization energies, as well as the value of ΔG_{CT}. Thus, the sum of the

$$hc\nu_{abs} = -\Delta G_{CT} + \lambda_o + \lambda_i \qquad (2)$$

$$hc\nu_{fl} = -\Delta G_{CT} - \lambda_o - \lambda_i \qquad (3)$$

frequency of the CT absorption and fluorescence maxima is connected with ΔG_{CT} (eqn. (3)) and their difference is connected with the sum of the reorganization energies.

$$-\Delta G_{CT} = 1/2\ (hc\nu_{abs} + hc\nu_{fl}) \qquad (4)$$

$$\lambda_o + \lambda_i = 1/2\ (hc\nu_{abs} - hc\nu_{fl}) \qquad (5)$$

The data calculated from the electronic absorption and emission spectra, characterizing $-\Delta G_{CT}$ and $\lambda_o + \lambda_i$ values are also summarized in Table 2. Comparison of the data presented in Tables 2 and 3 shows that the lowest "sensitivity parameter" is mostly observed for molecules possessing the highest value for the reorganization energy (**IV**, **V**, **VI**). Elimination of the free rotation of the dialkylamino group by the bridging causes an increase in probe sensitivity in the case of **XII**, **XII** and **XV** and a decrease in the case of **XI**, and **XIV**. Summarizing, it is difficult to qualify unequivocally the influence of the elimination of free rotation of the dialkylamino group around the bridge to the benzene ring on the probe sensitivity. Replacement of the perchlorate anion in **I**, **III**, **VI**, **VIII** and **XII**, and by iodide anion in **Ia**, **IIIa**, **VIa**, **VIIIa** and **XIIa** decreases the probe sensitivity by about two times. This observation supports the mechanism proposed by Neckers' group, *i.e.* that a decrease in anion size causes a change in excited state stabilization efficiency because of a change in anion mobility.[39] Another explanation of the counterion size influence is the possibility of an effect on the relationship between the solvation effect and the CT fluorescence maxima. An increase in counterion size increases the effective radius of the Onsager[55] cavity, a_o, and this according to Lippert[56] and Mataga[57] can change the energy of an emitting state according to expression (6), where ν_{fl}^{CT} and ν_{fl}^{vac} are the

$$\nu_{fl}^{CT} \cong \nu_{fl}^{vac} - \frac{2\vec{\mu}_e(\vec{\mu}_e - \vec{\mu}_g)}{a_o^3}\left[\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2(2n^2 + 1)}\right] \cong \nu_{fl}^{CT} \cong \nu_{fl}^{vac} - 2\vec{\mu}_e(\vec{\mu}_e - \vec{\mu}_g)\Delta f'/a_o^3 \qquad (6)$$

spectral positions of the solvent equilibrated CT fluorescence maxima and the value extrapolated to the gas-phase, respectively and ε and n have conventional meanings. A decrease of the Onsager cavity radius increases the $2\vec{\mu}_e(\vec{\mu}_e - \vec{\mu}_g)\Delta f'/a_o^3$ value and this causes a blue shift of the fluorescence maxima. One can find this type of relationship by analyzing the data summarized in Table 3. As can be seen in Table 3, the exchange of perchlorate anion with iodine, causes a more pronounced blue shift to be observed for the fluorescence maxima during the transition from liquid monomer to rigid polymeric matrix (compare **I** and **Ia**, **III** and **IIIa**, **VI** and **VIa**, **VIII** and **VIIIa**). This finding suggests that dynamic medium reorganization of molecules possessing counterions of variable size occurs with different rates and this might be reflected by a decrease of probe sensitivity.

Values of the blue shifts in emission maxima during polymerization are rather small and are generally within the range of 20 to 40 nanometres. The value of this shift generally has no connection with the structure of the molecule. It is obvious that for all molecules tested, the energy differences between the states obtained from the Franck–Condon excited states and the states reached after rotations (see Fig. 6) depend strongly on the probe structure. An increase of the medium viscosity decreases the efficiency of the formation of a radiationless state **P** as well as emissive states $\mathbf{A}_2$ and $\mathbf{A}_3$. This can cause variation of the fluorescence photochromic effect. However, a better explanation of this effect is possible following the recognition of a relationship between the structure of a molecule and its photophysics. No relationship between the structure of the molecule and the ratio of the probe's emission intensity in the polymer

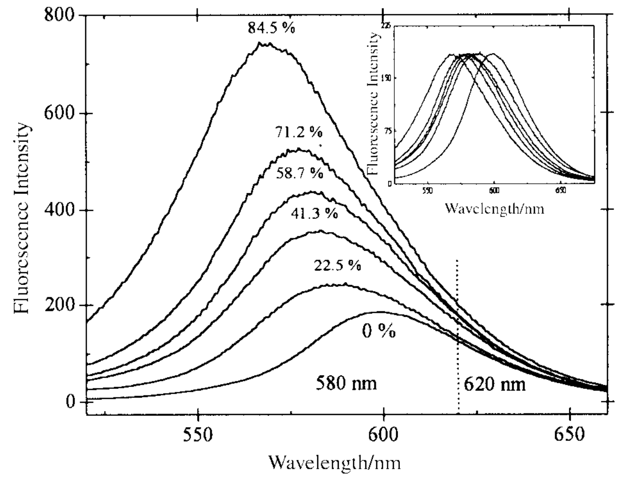


Fig. 9 Emission spectra of pyridinium salt **XIII** for different degrees of photoinitiation of TMPTA–MP (9 : 1) mixture. The degree of polymerization was calculated using FTIR spectroscopy. Inset: Normalized fluorescence spectra of the probe illustrating a blue shift of fluorescence λ_{max} during polymerization of TMPTA–MP (9 : 1) mixture.

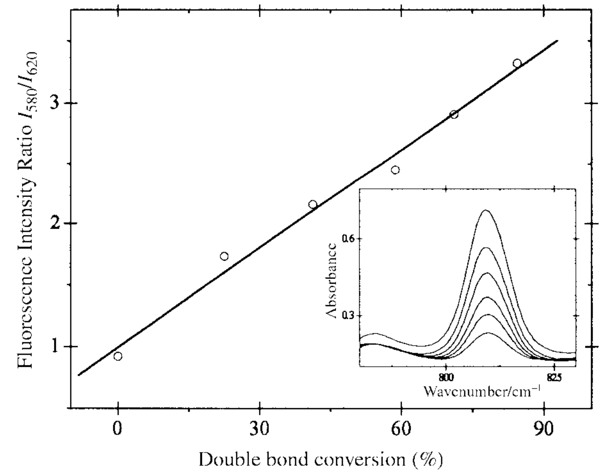


Fig. 10 Ratio of emission intensity at two selected wavelengths for **XIII** probe *versus* degree of double bond conversion during photoinitiated polymerization of TMPTA–MP (9 : 1) mixture. Inset: Changes of the absorption of –C=C– stretching frequency for TMPTA recorded at 810 cm^{-1}.

matrix to its intensity in the fluid monomer was found. Taking into account specific properties of the **V** probe, it is easy to see that the lowest blue shift is observed for **XIV** and **XV**. This suggests that the emissive state for these molecules is energetically very close to the Franck–Condon state obtained directly after excitation (see Fig. 6) or that the emission occurs mainly from the **E** state. This is easy to explain considering that the efficiency of the nonradiative deactivation should decrease as the viscosity of the medium increases because of the larger reaction volume needed for the movement giving nonemitting state **P** or emissive states $\mathbf{E}_2$ and $\mathbf{E}_3$. The greatest value of this ratio was found for **XIV** (416). However, it is necessary to emphasise that during the course of the polymerization, not only the local mobility, but also changes in polarity of the medium will affect the emission. Namely, the value of the blue shift will be dependent on those polarity changes, which might be illustrated by a decrease of the relative permittivity of methyl methacrylate ($\varepsilon = 6.32$) during the transformation of the liquid monomer into the solid polymer ($\varepsilon = 2.60$–3.60).[58] According to eqn. (6), this will cause the changes in the fluorescence maxima position. It is, however, worth emphasising that the probes tested are essentially nonsolvatochromic probes (see Table 2), therefore the contribution of the polarity to changes in the emission maxima is rather small.

Table 4 Probes relative value of sensitivity for studied pyridinium salts obtained for photoinitiated polymerization of multifunctional methacrylate. Relative sensitivity calculated at wavelengths tabulated

Probe	Relative sensitivity	Wave-lengths/ nm	Probe	Relative sensitivity	Wave-lengths/ nm
I	7.1	550/580	**XI**	5.5	555/585
II	9.7	550/590	**XII**	5.1	550/590
III	7.1	560/590	**XIII**	10.1	570/600
IV	4.3	550/580	**XIV**	1.3	575/590
V	1.0	540/580	**XV**	24.8	560/630
VI	9.1	550/580	**Ia**	5.3	550/580
VII	4.1	550/580	**IIIa**	6.0	550/590
VIII	7.5	560/590	**VIa**	4.2	560/590
IX	6.6	555/585	**VIIIa**	6.5	555/585
X	7.9	560/590	**XIIa**	7.7	560/590

An increase in the intensity of the probe fluorescence was observed during the photochemically initiated polymerization of a TMPTA–MP mixture with the gradual increase of the degree of monomer double bond conversion. This effect was accompanied by a blue shift in their emission maxima. Fig. 9 shows the illustrative emission spectra of pyridinium salt **XIII** for different degrees of polymerization.

As can be seen, fluorescence of the probe changes gradually with the gradual disappearance of the monomer double bond for all of the measurement range. No sudden increase caused by the rigid gel origination was observed (as is seen in the case of methyl methacrylate polymerization). However, the increase in the probe's emission intensity *versus* the monomer double bond conversion was not a well-defined linear function in all cases. Therefore, the ratio of emission intensities at two selected wavelengths (located at two sides of the emission maximum) was assumed to be a value characterizing the response of the probe. The relationship between this ratio and the degree of vinyl monomer double bond conversion is a linear function with a high correlation coefficient for all studied pyridinium salts.

Since the slope of the linear relationship shown in Fig. 10 depends significantly on the wavelengths at which emission intensities are measured, the meaning of the "probe sensitivity factor" in this case is not very precise. Nevertheless, the values of the relative sensitivity of the probes tested are collected in Table 4 (sensitivity of the weakest probe was assumed to be 1.0). The values of selected wavelengths with the best correlation coefficients for a linear relationship between the ratio of emission intensities and degree of double bond conversion are also available in Table 4. An increase in the distance between these wavelengths and their shift to longer wavelength would appear to cause an increase in the probe sensitivity factor, so a knowledge of analyzing wavelengths is needed in order to evaluate the probe quality.

As can be seen, the probe **V** is evidently of the lowest quality (the same was found in the case of methyl methacrylate polymerization). Relative sensitivities of the other probes are within the range of 4.1 to 10.1. The only exceptions are **XV** (24.8) and **XIV** (1.3), but in these cases "non-typical" values of sensitivities are perhaps caused by "non-typical" distance separating wavelengths used for the calculation of these values.

Conclusions

Studied pyridinium salts are good spectroscopic probes for monitoring the degree of cure in a polymer in their environment. The only exception is compound **V**. The relationship between the changes in their emission and the degree of polymerization for photochemically initiated polymerization, is a well-defined linear function for the whole range of monomer conversion. In the case of methyl methacrylate polymerization this relationship is linear only below the gel point and shows a sharp increase in the region of rigid gel origination. Sensitivity of pyridinium salts as probes increases with an increase in dialkylamino substituent size and decreases in the presence of substituents which twist the molecule in the ground state. This sensitivity also depends on the type of anion in the salt. The studied pyridinium salts are nonsolvatocromic (changes in polarity in their environment have no meaningful influence on their emission).

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