# Developing of Fluorescence Probes Based on Stilbazolium Salts for Monitoring Free Radical Polymerization Processes. II

**Agnieszka Bajorek,[1] Katarzyna Trzebiatowska,[1] Beata Jędrzejewska,[1] Marek Pietrzak,[1] Ryszard Gawinecki,[1] and Jerzy Pączkowski[1,2]**

The series of 1-methyl-4-(4-aminostyryl)pyridinium perchlorates was investigated as fluorescent probes for the monitoring of the free radical polymerization progress. The study on the changes in fluorescence intensity and spectroscopic shifts of studied compounds were carried out during thermally initiated polymerization of methyl methacrylate. The purpose of these studies was to find a relationship between the structure of fluorophore and the changes in their fluorescence shape and intensity observed during the monomer conversion into polymer. The probes under the study during the course of polymerization increase their fluorescence intensity at least one order of magnitude. Such increase qualified the tested probes as good fluorescence probes.

## INTRODUCTION

In the recent years dyes are widely used as photoinitiators of free radical polymerization and as fluorescence probes which are spectroscopic tools used in chemistry for monitoring specific properties of the medium in which they are incorporated. 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 polarity of medium or degree of cure by measuring the changes in their emission intensity or value of the emission maximum shift.

An important application of fluorescent probes in polymer chemistry is a monitoring of the polymerization process. Polymers belong to a group of compounds, in which one observes very often the difference between the local and macroscopic viscosities. The local viscosity combines the effect of solvent and interaction of polymer segments surrounding the relaxing fluorophore. The dif-

ference between local and macroscopic viscosity, which is measured by commonly used viscometric techniques, were illustrated by Nishijama and co-workers [1–3]. They compared the local viscosity measured by the depolarization of fluorescence to the melt viscosity of polyethylene. It was documented that the local viscosity changes linearly up to certain degree of polymerization and beyond that degree becomes independent of molecular weight.

Fluorescent probes, in polymer chemistry, can be used to observe the changes in properties of a polymerization mixture that occur during polymerization by measuring the changes in the fluorescence intensity and spectral characteristics of a small molecular probe incorporated in polymerizing formulation. Changes in fluorescence yield [4–9], the position of fluorescence maximum [10], changes in fluorescence polarization [2,3] and the efficiency of intramolecular [11,12] or intermolecular [13] excimer formation have been related to the local viscosity changes occurring during polymerization. More detailed discussion covering the various aspects of this problem the reader can find in review articles [14,15].

Essentially there are four different kinds of fluorescent probes: (1) excimer forming, (2) TICT probes, (3) charge transfer probes (D-$\pi$-A or D-$\sigma$-A) and

(4) specific, relatively new, fluorescent organic salts (D-$\pi$-A$^+$X$^-$ type) [16,17].

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 peak in pyrene vibronic emission spectrum. The intensity ratio of excimer emission to monomer emission in the pyrene spectrum also reflects the interaction among polymer chain and 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 fluorescence intensities ratio of monomeric and pyrene excimer emissions and degree of polymerization [13,18].

Molecules exhibiting the presence of TICT state consist of the dialkylamino group linked by a $\sigma$-bond with phenyl ring substituted in *para* position with strong electron-withdrawing group [19,20]. Dual fluorescence of these compounds is caused by presence of two different singlet excited states. Fluorescence originating from locally excited state results in the *b*-band observed in the blue area of the emission spectrum. The other one 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 aromatic ring, and has transferred an electron to it. 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 TICT state. Charge separation existing in the perpendicular form causes fluorescence occurring from this molecule to be dependent on solvent polarity and viscosity [21]. Molecules possessing TICT state were used for the testing of properties of the polymeric chain in diluted solution [22,23] as well as for the study of the kinetics of free radical polymerization [24].

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 a well defined orientation with respect to each other. The classical fluorescence probes possessing typical ICT (*e.g.* series of p-($N,N$-dialkylamino)benzylidene malononitriles) were described by Loutfy [4–6]. Very sensitive ICT probe were described by Verhoeven's research group. This group tested the properties of 1-phenyl-4-(4-cyano-1-naphtylmethylene)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 fluorescent polarity and viscosity probe [10,25]. This kind of probes can be applied for monitoring of polymerization kinetics.

The fourth group of probes are organic salts of D-$\pi$-A$^+$X$^-$ type. Structurally D-$\pi$-A$^+$X$^-$, called also the charge resonance probes, resemble charge transfer probes (D-$\pi$-A or D-$\sigma$-A). However their spectroscopic behavior is quite different. They display blue shift in their emission maximum during polymerization, but their fluorescence is only slightly dependent on changes in solvent polarity. That is why they are essentially nonsolvatochromic probes.

## Chart 1
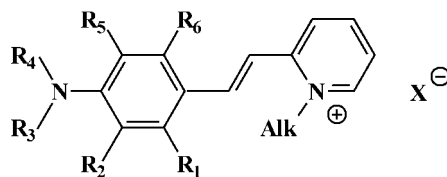


In literature there are two different explanations that describe mechanism of observed photophysical behavior of D-$\pi$-A$^+$X$^-$ salt. The first, proposed by Neckers *et al.* [16] assumes that the positive charge in the cation is localized on the pyridinium ion in the ground state, but it changes its location in the excited state (see Fig. 1). 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 this type of probes to monitor the rigidity of their environment is explained by the decreased mobility of the counterion which is not able to follow delocalization of the cation in rigid media (see Fig. 2) and this causes lesser stabilization of the excited molecule.

The second explanation of the specific photophysical properties of stilbazolium salts is given by Rettig *et al.* [26]. According to these authors the excited and ground-states energies can be presented as plotted in Fig. 3.

According to this model, a simultaneous fluorescence can occur from $\mathbf{E}$, $\mathbf{A_2}$ and $\mathbf{A_3}$ and this explains the broad steady-state spectra measured. It should be noted that all deactivation processes start from planar conformation of
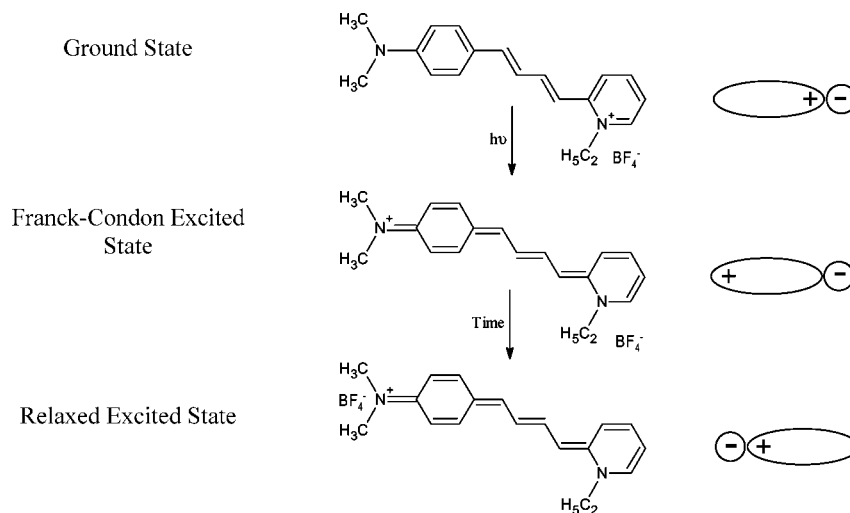
**Fig. 1.** Schematic representation of the ground state, the Franck Condon excited state, and the fully relaxed excited state proposed for D-$\pi$-A$^+$X$^-$ type of probes.

the excited molecule and are related to the rotation about its separate bonds. In particular:

1. The twist of the dialkylamino group leads to a TICT state ($A_1$), however its energy level is con-

siderably higher than for nontwisted conformation **E**, therefore it can not be easily thermally activated and to contribute in the emission spectra.

2. A twist of the double bond gives a state **P** with a relatively narrow $S_1$-$S_0$ gap. The deactivation
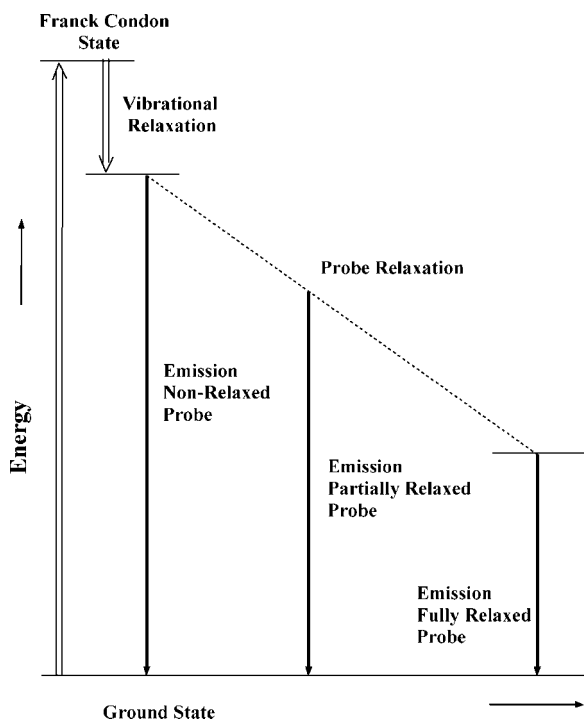


**Fig. 2.** Schematic representation of the probes emission as a function of the medium relaxation.
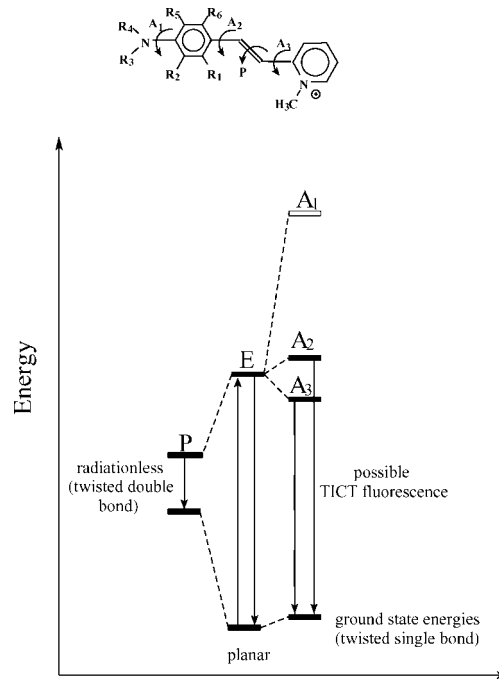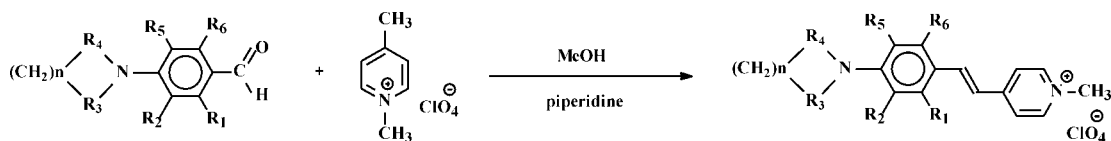


**Fig. 3.** Conceptual presentation of energy gaps between the ground states energy and the lowest excited states for tested probes. The index 1, 2 and 3 denote the states reached after the twist of a single bond, **P** corresponds to the state after the twist of double bond and **E** is the lowest excited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

, where: $R_1$, $R_6$: H; $CH_3$     $R_2$, $R_5$: H; $CH_3$; $-CH_2-$     $R_3$, $R_4$: H; $CH_3$; $C_2H_5$; $-CH_2-$
n: 0; 2; 3; 4

**Fig. 4.** General route for synthesis of styrylpyridinium perchlorates.

of this state should be radiationless in character because of a small energy gap to the ground state.

3. An emission from $A_2$ and $A_3$ states should be possible because their energies are similar to that of **E** state.

Since the energies of all emitting states are very similar, the fluorescence of D-$\pi$-$A^+X^-$ salt is observed as a one broadened band that shifts to the blue as the degree of polymerization is increasing. Stilbazolium salts were successfully applied as fluorescence probe for the monitoring of curing of epoxy resins [27] as well for the measuring the progress of photopolymerization of dimethacrylates [16].

In this report, we describe the relationship between the change in the emission spectra of a series of structurally different stilbazolium salts, namely 1-methyl-4-(4-aminostyryl)pyridinium perchlorate, and degree of monomer convertion during thermally initiated polymerization of monomethacrylate. For better understanding in detail their photochemical and photophysical properties, the characterization of a large number of new hemicyanine probes in solvents of different polarity were studied. Thus, the spectroscopic, and electrochemical measurements of different dyes possessing different electron-donor part were performed to achieve better understanding of their sensing properties.

## Chart 2
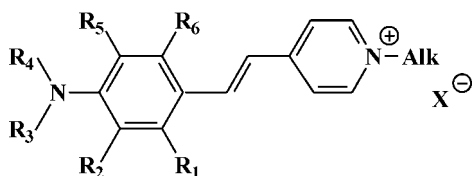


## EXPERIMENTAL

Methyl methacrylate and all spectroscopic grade solvents used for spectroscopic measurements were pur-

chased from Aldrich. Methyl metacrylate, before use, was purified using conventional methodology.

Absorption spectra were recorded on a Varian Cary 3E spectrophotometer. Fluorescence measurements were recorded on a F-4500 (Hitachi) spectrofluorimeter using classical measurements for monitoring the degree of methyl methacrylate polymerization. The reduction potentials of the dyes were measured by cyclic voltammetry. An Electroanalytical Cypress System Model CS-1090 was used for the measurements. A platinum 1 mm disk electrode was used as the working electrode, a Pt wire constituted the counter electrode, and Ag-AgCl electrode served as a reference electrode. The supporting electrolyte was 0.1 M tetra-$n$-butylammonium perchlorate in dry acetonitryle.

Semiempirical calculations of the molecular geometries and the ground state dipole moments were performed using the HF/6-31G and MP2/6-31G* methods with application of Gaussiam 98, Revision A. & programme [28].

Tested probes were prepared by the reaction schematically described in Fig. 4 starting from the appropriate $p$-aminobenzaldehyde and 1,4-dimethylpyridinium perchlorate.

The synthesis methodology of tested 1-methyl-4-(4-aminostyryl)pyridinium perchlorates was previously reported [29].
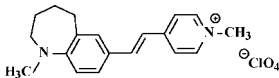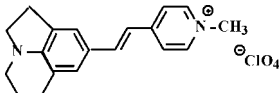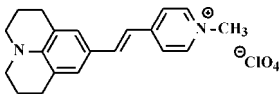
## Monitoring the Degree of Free Radical Polymerization

Deoxygenated methyl methacrylate solution, containing $\alpha,\alpha'$-azobisisobutyronitrile (AIBN) as free radical polymerization initiator (1%) and tested probe at concentration giving the maximum intensity of the absorption in the range of about 0.4, was placed in pyrex test tubes. Polymerization was initiated at 50°C. The samples were periodically (20 or 30 min) removed from the water bath and cooled with ice to temperature of about 0°C in order to stop the polymerization and than were warmed up to room temperature. The fluorescence of the solutions was measured after subsequent time of polymerization and degrees of

**Table I.** Structures, Absorption ($\lambda_{max}^{Ab}$) Maxima Wavelength, Molar Absorption Coefficient, Dipole Moments of the Ground State and Differences ($\Delta E$) Between Oxidation and Reduction Potentials of Tested Probes

| No | Structure | $\lambda_{max}^{Ab}$ [nm][a] | $\lambda_{max}^{Ab}$ [nm][b] ($\varepsilon_{max}$) [$M^{-1}cm^{-1}$] | $\lambda_{max}^{Ab}$ [nm][c] | $\Delta\lambda^{Ab}$ [nm][d] | $\Delta E$ [mV][e] | $\mu_g$[D] |
|---|---|---|---|---|---|---|---|
| 2a | | 459 | 454 (40800) | 466 | −5 | 2062 | 7.60 |
| 2b | | 465 | 468 (42700) | 497 | 3 | 2150 | 9.06 |
| 2c | | 473 | 471 (42600) | 523 | −2 | 1986 | 10.35 |
| 2d | | 476 | 476 (46200) | 530 | 0 | 1960 | 11.86 |
| 2e | | 481 | 482 (50600) | 536 | 1 | 2096 | 14.83 |
| 2f | | 479 | 477 (30900) | 534 | −2 | 1890 | 10.51 |
| 2g | | 475 | 473 (38300) | 532 | −2 | 2096 | 12.19 |
| 2h | | 421 | 416 (25900) | 474 | −5 | 1828 | 14.65 |
| 2i | | 406 | 408 (18300) | 472 | 2 | 1850 | 16.53 |
| 2j | | 483 | 481 (45800) | 573 | −2 | 2072 | 12.69 |
| 2k | | 466 | 461 (34300) | 524 | −5 | 1830 | 14.67 |
| 2l | | 486 | 484 (46300) | 537 | −2 | 1705 | 16.23 |
| 2m | | 479 | 475 (30000) | 543 | −4 | 1780 | 12.39 |
| 2n | | 483 | 487 (3500) | 514 | −9 | 1784 | 10.93 |
| 2o | | 493 | 489 (42200) | 546 | −4 | 1994 | 11.84 |

**Table I.** (*Continued*)

| No | Structure | $\lambda_{max}^{Ab}$ [nm]$^a$ | $\lambda_{max}^{Ab}$ [nm]$^b$ ($\varepsilon_{max}$) [M$^{-1}$cm$^{-1}$] | $\lambda_{max}^{Ab}$ [nm]$^c$ | $\Delta\lambda^{Ab}$ [nm]$^d$ | $\Delta E$ [mV]$^e$ | $\mu_g$[D] |
|---|---|---|---|---|---|---|---|
| **2p** | | 440 | 439 (28900) | 517 | −1 | 2072 | 16.15 |
| **2q** | | 512 | 496 (28200) | 571 | −16 | 1880 | 13.13 |
| **2r** | | 496 | 508 (35600) | 572 | 12 | 1798 | 13.02 |

$^a$In THF ($\varepsilon = 7.58$).

$^b$In DMF ($\varepsilon = 36.71$).

$^c$In CH$_2$Cl$_2$ ($\varepsilon = 8.93$).

$^d$Solvatochromic shift calculated as a difference of absorption $\lambda_{max}$ measured in DMF and THF solutions; $e - \Delta E = E_{ox} - E_{red}$.

polymerization were estimated by gravimetrical method after precipitation of the polymer in ethanol.

## RESULTS AND DISCUSSION

### Solvatochromism of the Hemicyanine (Aminostyryl Pyridinium) Dyes

*Absorption Spectroscopy*

Hemicyanines are the class of dyes whose chemical structure is characterized by two nitrogen atoms (one of which is positively charged), which are separated by a conjugated bridge formed by a carbon framework. The structures of the series of 1-methyl-4-(4-aminostyryl)pyridinium salts tested and their basic spectroscopic properties are summarized in Table I.

UV-vis electronic absorption spectra of the dyes under the study display broad absorption bands in the range of 400–510 nm in both THF and DMF, and 460–570 nm in CH$_2$Cl$_2$ corresponding to the n $\rightarrow$ $\pi^*$ transition attributed to an intramolecular charge transfer (S$^0$ $\rightarrow$ CT) involving the electron lone pair of the amino nitrogen and the cationic pyridinium nitrogen terminal. Figure 5 shows illustrative electronic absorption spectra recorded in MeOH solution.

The analysis of the electronic absorption spectra clearly indicates a presence of two main bands, whose maxima are located in the 230–280 nm and $\lambda > 300$ nm regions. The shortest wavelength bands are attributed to the $\pi \rightarrow \pi^*$ transitions whereas the long-wavelength bands,

generally characterized by higher molar absorption coefficient, are attributed to CT transitions. The presence of an additional band at near 370 nm in the spectrum of compound **2n** is noteworthy (**2n**: $\lambda_{max} = 377$ nm; $\log\varepsilon = 4.15$ in MeOH). The previous Gawinecki's *et al.* work [29] documented the presence of a well-separated CT absorption band, observed for almost all dyes tested. Inspection of the illustrative absorption spectra, presented in Fig. 5, and the parameters of the UV-vis spectra of tested dyes collected in Table I allows to conclude that the position and intensity of CT absorption band depends on the molecular structure.
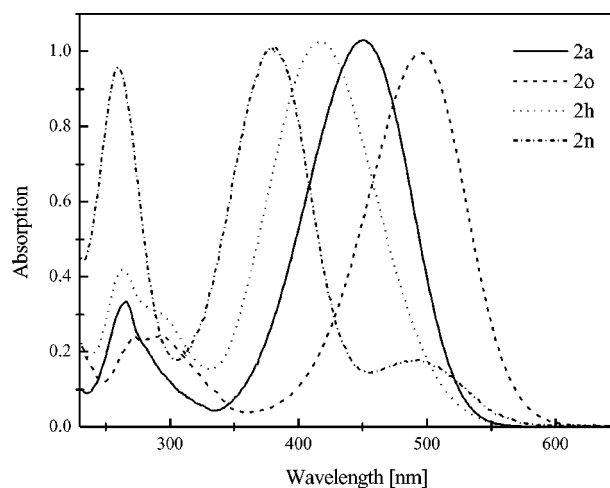


**Fig. 5.** Illustrative electronic absorption spectra of selected probes (marked in the figure) recorded in MeOH solution at 293 K. The applied dyes possess various donor group.

**Table II.** Absorption ($\lambda_{max}^{Ab}$) and Emission ($\lambda_{max}^{F}$) Maxima Wavelength of Tested Probes in Solvents of Various Polarities ($\Delta f = (\varepsilon - 1)/(2\varepsilon + 1) - (n^2 - 1)/(2n^2 + 1)$), at Room Temperature

| Solvent | $\Delta f$ | 2a | | 2f | | 2h | | 2n | | 2o | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $\lambda_{max}^{Ab}$(nm) | $\lambda_{max}^{F}$(nm) | $\lambda_{max}^{Ab}$(nm) | $\lambda_{max}^{F}$(nm) | $\lambda_{max}^{Ab}$(nm) | $\lambda_{max}^{F}$(nm) | $\lambda_{max}^{Ab}$(nm) | $\lambda_{max}^{F}$(nm) | $\lambda_{max}^{Ab}$(nm) | $\lambda_{max}^{F}$(nm) |
| DMSO | 0.263 | 455 | 594.0 | 477 | 623.0 | 420 | 639.4 | 487 | 547.6 | 489 | 639.2 |
| MeCN | 0.305 | 434 | 575.2 | 477 | 622.0 | 414 | 640.0 | 474 | 537.8 | 490 | 634.0 |
| DMF | 0.274 | 454 | 590.4 | 477 | 626.6 | 416 | 640.6 | 487 | 545.2 | 489 | 637.6 |
| AcMe | 0.284 | 447 | 581.4 | 478 | 616.2 | 419 | 638.8 | 484 | 547.0 | 493 | 631.8 |
| CH$_2$Cl$_2$ | 0.217 | 466 | 556.6 | 534 | 610.4 | 474 | 625.0 | 518 | 538.0 | 546 | 622.8 |
| THF | 0.210 | 459 | 578.4 | 479 | 607.0 | 421 | 615.8 | 483 | 565.2 | 493 | 616.6 |
| AcOEt | 0.200 | 438 | 566.0 | 470 | 596.4 | 410 | 607.2 | 462 | 578.6 | 479 | 610.4 |

This finding can be summarized as follows: (i) The planar conformation of molecules (**2q** and **2r**) increases the probability of the radiative transitions in comparison to the other molecules, (ii) the coplanar conformation decreases this probability which is demonstrated by a significant blue shift of CT absorption band and a decrease of its molar absorption coefficient (**2h** and **2i**). CT character of the long-wavelength absorption band is additionally reflected by the values of the ground state dipole moments.

Because of the strong charge transfer character of the tested dyes, the absorption spectra should be affected by the polarity of the solvent. For illustration of this phenomena, the absorption spectral data for five different dyes under the study in various solvents are collected in Table II.

The data presented in Table I and II indicate that there is a small blue shift in the absorption maxima when the solvent polarity increases. Such a negative solvatochromism is observed when the ground state is more polar than the excited state ($\mu_g > \mu_e$), and this, in turn, allows to conclude that the dipole moments of the excited states reached directly after excitation are rather small. Only in dichloromethane an opposite effect is observed for all probes. This red shift is likely caused by stabilization of the excited state by solvents whose highly polarizable electrons rearrange rapidly enough to influence the absorption spectra [16]. In general, tested dyes show a small negative solvatochromism in most cases.

*Fluorescence Spectroscopy*

The nature of emitting state in D-$\pi$-A$^+$X$^-$ molecules may vary with the solvent (see Table II and III), can also be dependent on the dye structure that is forcing or precluding the excited state relaxation *via* selected channels (see Table III and [30]) or may be controlled by the viscosity of the medium. The emission spectra of the probes tested in solvents of different polarity show only one band

whose maxima are located in the range of 578–650 nm. The characteristic features of fluorescence for the tested dyes are summarized in Table III.

As the data collected in Table III show, the 1-methyl-4-(4-aminostyryl)pyridinium perchlorates tested, display a moderate batochromic shift in fluorescence spectra when the solvent polarity increases. This indicates that an emitting state is not the Franck-Condon S$_1$ state reached in the absorption transition but different, the solvent relaxed state, from which the fluorescence originates. It cannot be also assumed that the excited state dipole moment remains unchanged during transition from Franck-Condon state to the emitting state. These conclusions are supported by the finding that the static fluorescence spectra of tested dyes exhibit a larger Stokes shift for the solvent of higher polarity (see Table III). This behaviour is the well known manifestation of the charge transfer character of the solvent relaxed emissive state.

Not only the solvent, but also the nature of the electron donor part of molecule has a strong influence on the CT fluorescence. Theoretically [31], the energy level of the molecule excited CT state, relative to its ground state can be expressed by Eq. (1).

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

where: $E_{ox}(D)$ and $E_{red}(A)$ are the one-electron oxidation and reduction potentials of donor and acceptor and C is a constant that depends on the degree of charge separation.

Verhoeven *et al.* [32], analyzing the properties of rod-shaped donor-acceptor systems, illustrated that fluorescence frequency of intermolecular exciplexes and excimers as well as intramolecular donor-acceptor systems is a linearly dependent on the value described by Eq. (1), namely on the value of $E_{ox}(D) - E_{red}(A)$. As it is shown in Fig. 6 similar properties are observed for probes described in this paper. This observation permits to conclude that the emissions observed for tested probes occur from the excited CT state.

**Table III.** Emission ($\lambda_{max}^{F}$) Maxima Wavelength, Fluorescence Quantum Yields and Stokes Shift of Tested Probes in Different Solvents at 293 K

| No | $\lambda_{max}^{Fl}(nm)^a$ | $\lambda_{max}^{Fl}(nm)^b$ | $\lambda_{max}^{Fl}(nm)^c$ | Fl.$\Delta\lambda(nm)^d$ | $\Phi_{fl} \times 10^2$ in THF | Stokes shift $(cm^{-1})^a$ | Stokes shift $(cm^{-1})^b$ |
|---|---|---|---|---|---|---|---|
| **2a** | 590.4 | 578.4 | 556.6 | 12.0 | 2.94 | 5100 | 4500 |
| **2b** | 606.8 | 585.6 | 584.6 | 21.2 | 0.63 | 4900 | 4400 |
| **2c** | 610.4 | 603.8 | 607.6 | 6.6 | 1.92 | 4800 | 4600 |
| **2d** | 620.6 | 606.0 | 610.0 | 14.6 | 1.83 | 4900 | 4500 |
| **2e** | 622.4 | 601.6 | 613.6 | 20.8 | 2.75 | 4700 | 4200 |
| **2f** | 626.6 | 607.0 | 610.4 | 19.6 | 0.72 | 5000 | 4400 |
| **2g** | 601.6 | 592.8 | — | 8.8 | 0.15 | 4500 | 4200 |
| **2h** | 640.6 | 615.8 | 625.0 | 24.8 | 1.55 | 8400 | 7500 |
| **2i** | 631.8 | 609.2 | 612.8 | 22.6 | 1.38 | 8700 | 8200 |
| **2j** | 624.0 | 604.4 | 614.0 | 19.6 | 1.71 | 4800 | 4200 |
| **2k** | 628.0 | 610.8 | 619.8 | 17.2 | 2.34 | 5800 | 5100 |
| **2l** | 624.2 | 618.6 | 616.6 | 5.6 | 1.75 | 4600 | 4400 |
| **2m** | 641.2 | 615.2 | 618.0 | 26 | 0.41 | 5500 | 4600 |
| **2n** | 545.2 | 565.2 | 538.0 | 24.4 | 0.39 | 2200 | 3000 |
| **2o** | 637.6 | 616.6 | 622.8 | 42.8 | 1.15 | 4800 | 4100 |
| **2p** | 643.6 | 621.2 | 626.6 | 22.4 | 1.56 | 7200 | 6600 |
| **2q** | 646.4 | 625.2 | — | 21.2 | 0.66 | 4700 | 3500 |
| **2r** | 643.8 | 629.0 | 636.0 | 14.8 | 0.32 | 4200 | 4300 |

$^a$In DMF ($\varepsilon = 36.71$).
$^b$In THF ($\varepsilon = 7.58$).
$^c$In CH$_2$Cl$_2$($\varepsilon = 8.93$).
$^d$Solvatochromic shift calculated as a difference of emission $\lambda_{max}$ measured in DMF and THF solutions.

### Probing of Thermally Initiated Polymerization of Methyl Methacrylare

All the probes under the study are well 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.
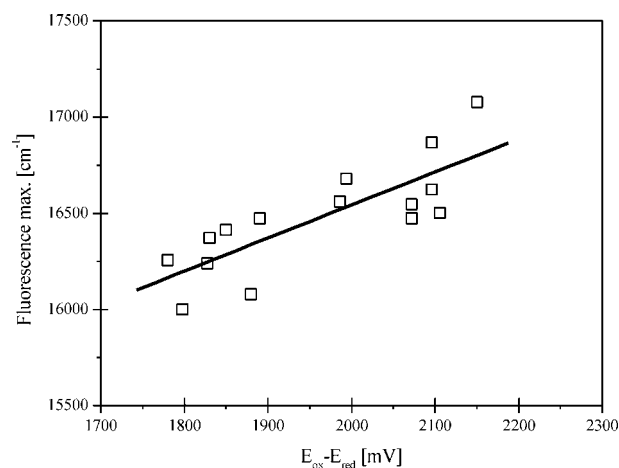
An increase in intensity of probes fluorescence are observed during methyl methacrylate polymerization when degree of monomer conversion is gradually increasing. This effect is accompanied additionally by a blue shift in their emission maxima. Figures 7 and 8 show the emission spectra of **2d** probe recorded for different degrees of polymerization.
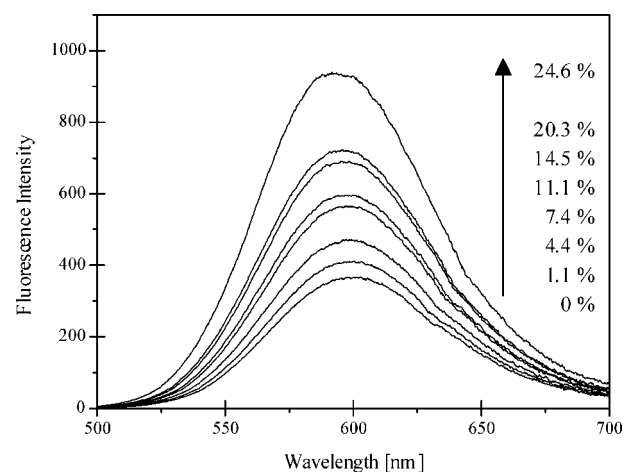


**Fig. 6.** Fluorescence frequency of compound tested versus $E_{ox}(D)-E_{red}(A)$.



**Fig. 7.** Changes in the fluorescence spectra of **2d** during thermally initiated polymerization of methyl methacrylate recorded for conversion below the transition point of the sample into a rigid polymer matrix.
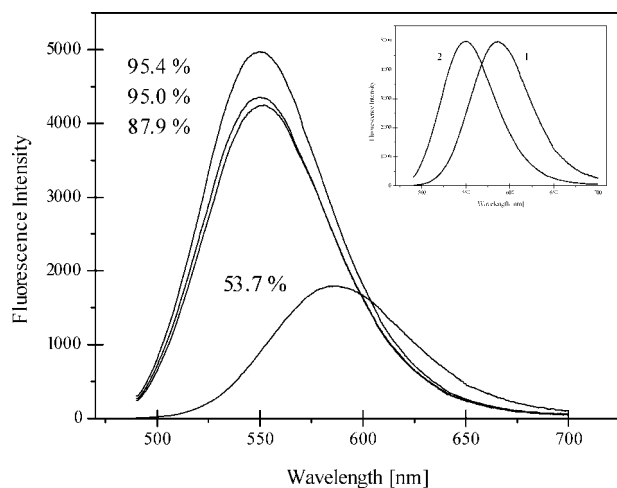
**Fig. 8.** Changes in the fluorescence spectra of **2d** during thermally initiated polymerization of methyl methacrylate recorded above the point of transition of the sample into a rigid polymer matrix. Inset: Normalized emission curves illustrating a blue shift observed during thermally initiated polymerization recorded at high degree of monomer conversion: (1) 53.7%, and (2) 95.4% of degree of polymerization.

As one can see, there is no significant increase in the intensity of fluorescence probe during methyl methacrylate (MM) polymerization for low degrees of monomer conversion (the emission of the probe changes gradually), whereas there is a distinct blue shift and a strong increase in its fluorescence intensity during conversion of the sample into a rigid polymer matrix. An increase in medium rigidity causes essential reduction in rates of all processes controlled by diffusion. The observed effect can be explained either by a limited mobility of the counterion which is not able to follow the cation in rigid media and that causes lesser stabilization of the excited molecule [16] or by more restricted $E$, $A_2$ and $A_3$ emitting states formation (see Fig. 3 and [26,27]).

Figure 9 summarizes the changes in fluorescence intensity observed for the **2f** probe during thermally initiated polymerization of methyl methacrylate.

According to Fig. 9 the "S" shape of the curve on polymerization time is observed. This is a common behaviour and is observed in the polymerization that shows a distinct transition from fluid to a rigid glass. In order to quantify the results presented in Fig. 9, we assumed that the probe emission intensity increases as polymerization propagates. In other words, as monomer consumption increases due to the polymerization, probe molecules are starting to be trapped in the rigid polymethyl methacrylate (PMM) environment, and as a results emission intensity increases. Below the time needed for the onset of the gel effect, since the probe molecules are relatively free, they can easily relax to the ground state. This causes a low flu-
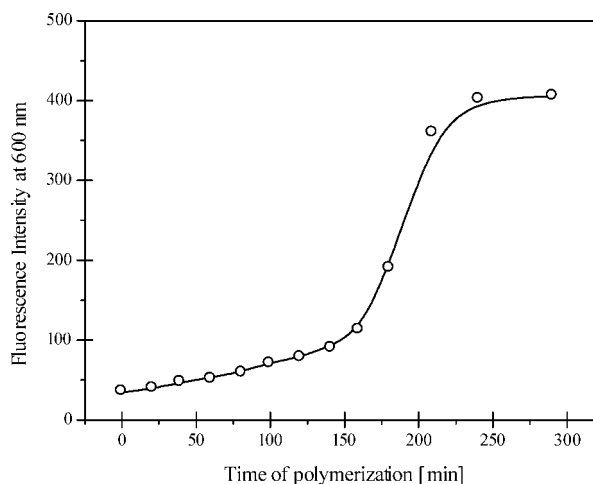


**Fig. 9.** Changes in fluorescence intensity (measured at $\lambda = 600$ nm) for **2f** probe during thermally initiated polymerization of methyl methacrylate in the presence of AIBN (1%).

orescence intensity of the probe. However, above the time needed for the onset of the gel effect, since the reaction mixture is highly viscous and the relaxation processes become less effective, emission intensity can rise to a high values. In general, the specific behavior of the probes in the transition area of fluid monomer to a rigid polymer is explained by the dramatic increase in viscosity and this, in turn, rapidly decreases the efficiency of nonradiative deactivation of the emitting state.

Changes in probes emission intensities, measured at wavelength specific for each probe, were also assumed as values characterizing probes response to an increase in degree of polymerization. The illustrative experimental results are shown in Fig. 10. The relationship between
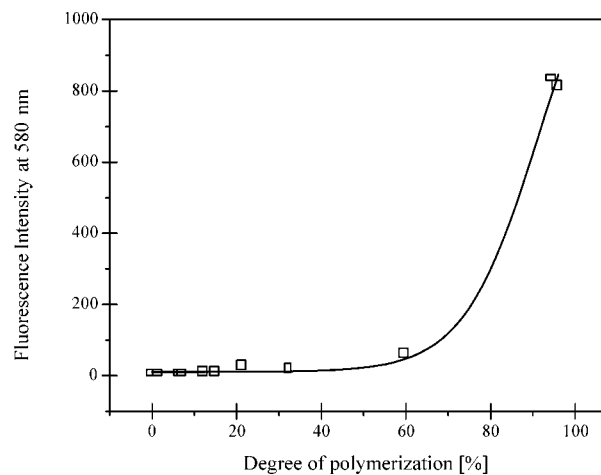


**Fig. 10.** Relationship between the probe emission intensity (probe **2g**, recorded at $\lambda = 580$ nm) versus degree of monomer conversion into polymer during polymerization of methyl methacrylate at 50°C.
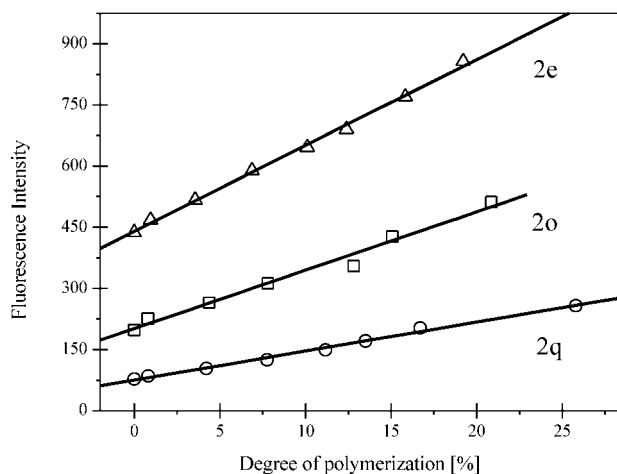
**Fig. 11.** Linear relationships between the fluorescence intensity and degree of polymerization for selected probes illustrating their sensitivity. Type of molecule marked in the figure.

changes in probe emission and changes in degree of monomer conversion into polymer is linear for low degrees of polymerization. At higher degrees of monomer conversion a sudden increase of the fluorescence intensity occurs which is caused by the effect connected with conversion of polymer solution into the rigid polymer matrix (Fig. 10).

In principle, the probe intensity emission can be used to characterize the kinetics of polymerization but only when the linear relationship between the increase of fluorescence intensity and the amount of obtained polymer is observed. The results in Fig. 11 show this type of relationship observed at low degrees of MM polymerization for the selected probes.

Since the value of the probe response to changes in 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 "probe sensitivity parameter." We define this as a value of the slope of a linear relationship obtained for the dependence between the probe emission intensity at chosen wavelength and a degree of monomer conversion into polymer. Figure 11 presents the examples of such relationships used for calculation of the "probe sensitivity parameter." The measured values of parameters characterizing the probes responses for all probes under the study are collected in Table IV.

On the basis of the data listed in Table IV, it appears that the values of probe sensitivity parameter oscillate from 0.48 for **2g** to 24.9 for **2k**. Assuming the probe **2a** as a standard (sensitivity parameter 4.64), it can also be seen that exchange of hydrogen atoms on an alkyl group causes an increase of the probe relative sensitivity (up

to the value 22.67). This can also be seen for the "cyclic" amino substituents. Substituents in the *ortho* position with respect to dialkylamino group as well as to —CH=CH— form a pretwisted molecule even in the ground state and this causes decrease in probe sensitivity in comparison to probes **2j**, **2k** and **2l**. It is worth noting that, as can be seen in Table IV, during the course of polymerization the probe fluorescence intensity increases at least one order of magnitude (with exeption of **2a** and **2b**). Such increase qualifies the probes under study as good fluorescence probes. In particular it is notewarthy mentionig that for **2g** probe the incrase of fluorescence intensity is more than two ordes of magnitude.

Dependence of the probe sensitivity on the size and preorientation of dialkylamino substituent results probably 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 ground states is very small (see Fig. 3). For the probes possessing bulky dialkylamino group, the efficiency of this nonradiative deactivations should decrease as 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 $A_2$ and $A_3$. Substituents in the *ortho* position with respect to dialkylamino group (**2h** and **2i**), 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 probes sensitivity.

The quantitative explanation of these specific probe response may come from the estimation of a reorganization energy $\lambda_o$ related to the solvent and solute motions and reorganization energy $\lambda_i$ corresponding to the changes in the solute bond lengths and angles accompanying the excited-state electron transfer [33–35]. The following approximate expressions for the maxima of CT absorption and emission spectra can describe the dependence of both organization energies, as well as the value of $\Delta G_{CT}$.

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

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

Thus, the sum of the frequency of CT absorption and fluorescence maxima is connected with $\Delta G_{CT}$ (Eq. (3)) and their difference with the sum of the reorganization energies respectively.

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

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

**Table IV.** Sensitivity Parameters, Blue Shifts in Emission Maxima, and Ratios of Fluorescence Intensity in the Solid Polymer and Intensity in the Monomer for Styrylpyridinium Dyes Tested
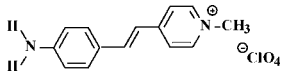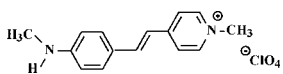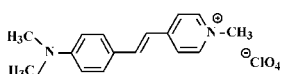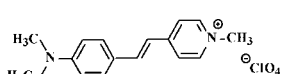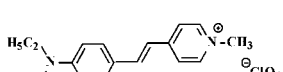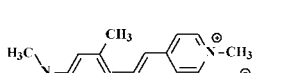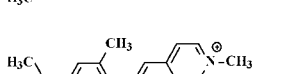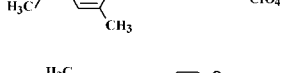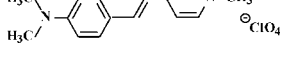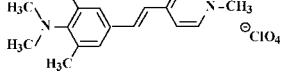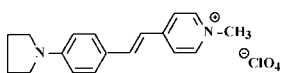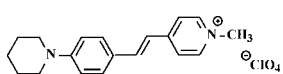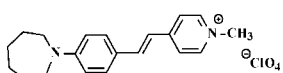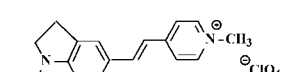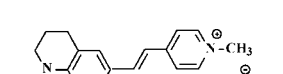
| No | Structure | Sensitivity ($\%^{-1}$) | $\Delta\lambda_{max}^{Fl}$ (nm) | $I_{100\%}/I_{0\%}$ |
|---|---|---|---|---|
| 2a | | 14.64 | 37.4 | 6.3 |
| 2b | | 10.84 | 44.6 | 8.1 |
| 2c | | 15.01 | 33.0 | 10.1 |
| 2d | | 20.49 | 53.6 | 13.6 |
| 2e | | 22.67 | 48.0 | 10.5 |
| 2f | | 2.46 | 41.4 | 23.3 |
| 2g | | 0.48 | 28.2 | 206.0 |
| 2h | | 9.96 | 69.4 | 21.0 |
| 2i | | 9.82 | 48.0 | 33.3 |
| 2j | | 19.77 | 44.6 | 13.6 |
| 2k | | 24.92 | 48.2 | 10.3 |
| 2l | | 17.92 | 45.2 | 10.7 |
| 2m | | 8.51 | 53.0 | 34.0 |
| 2o | | 18.77 | 46.8 | 21.6 |
| 2p | | 16.75 | 62.0 | 12.4 |

**Table IV.** (*Continued*)

| No | Structure | Sensitivity (%$^{-1}$) | $\Delta\lambda_{max}^{Fl}$ (nm) | $I_{100\%}/I_{0\%}$ |
|---|---|---|---|---|
| **2q** | | 6.92 | 44.2 | 43.7 |
| **2r** | | 3.55 | 44.2 | 59.1 |

The data calculated from the electronic absorption and emission spectra, characterizing $-\Delta G_{CT}$ and $\lambda_o + \lambda_i$ values are summarized in Table V.

Comparison of the data presented in Tables IV and V show that there is no correlation between the "sensitivity parameter" and the value of the reorganization energy.

Values of the blue shifts in emission maxima during polymerization are rather small and are comprised in most cases within the range from 30 to 40 nm. The value of this shift, generally has no connection with the structure of the molecule. An increase of the medium viscosity decreases efficiency of the formation of a radiationless state **P** as well as emissive states **A$_2$** and **A$_3$**. This can cause variation of the fluorescence photochromic effect. The value of fluorescence intensity ratio in the solid polymer and intensity in the monomer oscillates from 6 up to 106. The greatest "probe's sensitivity" was found for **2k**, the lowest for **2g**. It is noteworthy that for **2g** probe display the lowest batochromic shift of fluorescence spectra and the highest ratio of fluorescence intensity in the solid polymer and intensity in the monomer.

## CONCLUSIONS

In the context of the potential and practical applications of the hemicyanine dyes, we have synthesized a new series of styrylpyridinium salts and studied their spectroscopic properties. These novel dyes show unique solvatochromic behaviour. The absorption spectra are less sensitive to the solvent polarity while the fluorescence spectra are more solvatochromic yielding a large Stokes shift. The red-shift of fluorescence maxima, as the solvent polarity is increasing, demonstrate the formation of an intramolecular charge transfer state.

Studied styrylpyridinium salts can be used as spectroscopic probes for monitoring the degree of cure of their environment. The relationship between changes in their emission intensity and degree of thermally initiated polymerization of methyl methacrylate is linear below the gel point only and shows a sharp increase in the region of a rigid gel origination. Sensitivity of styrylpyridinium salts as probes increases with increase in dialkylamino substituent size and decreases for molecules with presence of substituents twisting in the ground state.

**Table V.** Spectroscopic Properties of Tested Probes (Sum of the Reorganization Energies ($\lambda_o + \lambda_i$) and ($\Delta G_{CT}$))

| No. | $\lambda_o + \lambda_i$ (kJ/mol)$^a$ | $\lambda_o + \lambda_i$ (kJ/mol)$^b$ | $\Delta G_{CT}$ (kJ/mol)$^a$ | $\Delta G_{CT}$ (kJ/mol)$^b$ | No. | $\lambda_o + \lambda_i$ (kJ/mol)$^a$ | $\lambda_o + \lambda_i$ (kJ/mol)$^b$ | $\Delta G_{CT}$ (kJ/mol)$^a$ | $\Delta G_{CT}$ (kJ/mol)$^b$ |
|---|---|---|---|---|---|---|---|---|---|
| **2a** | 30.45 | 26.89 | 233.0 | 233.6 | **2j** | 28.49 | 24.87 | 220.1 | 222.7 |
| **2b** | 29.24 | 26.48 | 226.3 | 230.7 | **2k** | 34.48 | 30.42 | 224.9 | 226.2 |
| **2c** | 28.98 | 27.38 | 224.9 | 225.4 | **2l** | 27.74 | 26.37 | 219.3 | 219.7 |
| **2d** | 29.28 | 26.95 | 222.0 | 224.3 | **2m** | 32.61 | 27.64 | 219.1 | 222.0 |
| **2e** | 28.00 | 24.92 | 220.1 | 223.7 | **2n** | 31.76 | 57.12 | 220.6 | 253.5 |
| **2f** | 29.90 | 26.32 | 220.8 | 223.3 | **2o** | 29.20 | 21.56 | 215.4 | 221.0 |
| **2g** | 27.01 | 25.01 | 225.8 | 226.7 | **2p** | 43.30 | 39.64 | 229.1 | 232.1 |
| **2h** | 50.40 | 44.93 | 237.1 | 239.1 | **2q** | 28.04 | 21.15 | 213.0 | 212.4 |
| **2i** | 51.91 | 49.12 | 241.2 | 245.4 | **2r** | 24.86 | 25.49 | 210.6 | 215.6 |

$^a$In DMF ($\varepsilon = 36.71$).
$^b$In THF ($\varepsilon = 7.58$).

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