

Fluorescence Properties of Some Triazene Polyacrylates for Possible Sensor Applications

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We report here a first study on the capacity of the triazene chromophore attached to a polymeric backbone to present fluorescence properties. The sensing ability of two triazene copolymers poly[1-(phenyl)-3-(2 acryloyloxyethyl)-3-methyl triazene-1-*co*-methyl methacrylate] (TCP-1) and poly[1-(paramethoxy-phenyl)-3-(2 acryloyloxyethyl)-3-methyl triazene-1-*co*-methyl methacrylate] (TCP-2) in dimethylformamide (DMF) has been investigated by fluorescence spectroscopy in tandem with a quenching experiments using a variety of metal ions (Fe^{3+} , Fe^{2+} , Cu^{2+} and Cu^+), which suggests that these triazene polymers could find practical applications for detection of metal ions. The emission spectra exhibited strong fluorescence emissions at 375 nm (TCP-1) and 410 nm (TCP-2) respectively, while the ability of Fe^{3+} , Fe^{2+} , Cu^{2+} and Cu^+ to quench the fluorescence of the triazene fluorophore has been explained on the basis of energy transfer processes involving the triazene excited state and the metal ion. The corresponding Stern-Volmer representations for all fluorescence emission spectra were also described.

KEY WORDS: Polyacrylates / Fluorescence / Quenching / Sensor /

Fluorescence spectroscopy and its applications in biochemical, medical, and chemical research have improved rapidly during the past decade.¹ The increased interest on fluorescence emission appears to be the consequence of numerous developments and the fast appearance of new fluorescence methods in explaining physical and life sciences research. Based on sensitivity, selectivity and non-destructive characteristics, fluorescence spectroscopy can evidence various photophysical properties like fluorescence intensity,¹ emission maximum,² anisotropy, excimer or exciplex formation,³ etc., whereas any variation caused by connecting or interacting with special external species (for instance, metal ions) could be used for sensing purposes.⁴ In fact, the fluorescent sensors can offer several distinct advantages in terms of sensitivity, selectivity, response time and local observation. In the case of selective fluorescence sensors for cation detection, the scientists made considerable efforts for the development of these kinds of systems.

As a general characteristic, fluorescence quenching refers to any process which undergoes emission intensity changes of a given molecule. Fluorescence response can be generated by a variety of mechanisms, including excited state reactions, energy transfer, complex formation, and collision quenching,^{5,6} while photoinduced electron transfer and electronic energy transfer are considered the two main deactivation pathway responsible for an efficient fluorescence inhibition.

Our group has specially focused on designing and fabricating a diversity of (co)polymers bearing different fluorophores such as pyrene,^{7,8} dansyl,⁹ stilbene^{10,11} or anthracene¹² characterized through high quantum yields and good extinction coefficients, making them attractive components of biological and chemical sensors.

Recently, the polymeric systems with light controlled surface topology have been intensively explored due to their unique properties that allow various applications as photo-responsive materials¹³ for medical purpose¹⁴ and optical data storage¹⁵ area. In this context, promising candidates to accomplish all targets are polymers with triazene moieties ($>N=N=N-$), whose biological activity was successfully tested in cancer therapy,¹⁴ and which have gained importance as useful tools in organic synthesis¹⁵ or in processes following the laser structuring compared to the UV-light.¹⁶⁻¹⁸

Taking in consideration the special properties of triazene compounds and our interest in developing photopolymers including triazene polyacrylates,^{19,20} here we report a first study on the ability of the triazene copolymers to present fluorescence properties. Also, significant arguments about physical and chemical aspects of triazene moieties will be presented, because these investigations can offer essential information in understanding the mechanism of fluorescence. Moreover, the interaction between triazene copolymers and some metal cations (Fe^{3+} , Fe^{2+} , Cu^{2+} and Cu^+) can cause the quenching of fluorescence intensity, property exploitable in the field of chemical sensors.

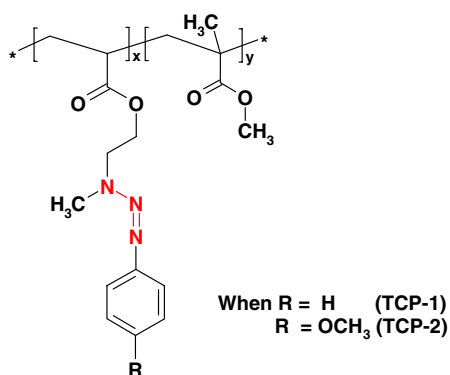
EXPERIMENTAL

Synthesis of Triazene Acrylic Copolymers

Detailed synthesis of triazene copolyacrylates are presented in our previously research papers.^{19,20} Generally, the preparation of triazene acrylic copolymers poly[1-(phenyl)-3-(2 acryloyloxyethyl)-3-methyl triazene-1-*co*-methyl methacrylate] (TCP-1) and poly[1-(para methoxy-phenyl)-3-(2 acryloyloxyethyl)-3-methyl triazene-1-*co*-methyl methacrylate]

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Scheme 1. General chemical structure of the triazene acrylic copolymers TCP-1 and TCP-2.

(TCP-2) (Scheme 1) was performed as a free-radical polymerization in dioxane using 0.2% AIBN as initiator. The reaction mixture was kept in sealed glass ampoules at 60 °C for 3 h and the resulting polymer were precipitated in methanol and dried for 48 h under reduced pressure.

TCP-1. M_w (determined by GPC): 193,400; $M_w/M_n = 1.9$. $^1\text{H NMR}$ (DMSO- d_6 , δ , ppm): 7.1–7.4 (aromatic protons), 3.69–4.3 ($\text{CH}_2\text{-CH}_2$), 3.58 ($-\text{COOCH}_3$), 3.29–3.37 (N-CH_3), 1.5–2.2, (CH-COOCH_3), 0.8–1.5 (CH_2 and CH_3 from acrylic backbone). Molar fraction of triazene monomer in copolymer (determined by NMR analysis): 0.24.

TCP-2. M_w (determined by GPC): 85,000; $M_w/M_n = 1.8$. $^1\text{H NMR}$ (DMSO- d_6 , δ , ppm): 7.30–6.9 (aromatic protons), 4.14–3.75 ($\text{CH}_2\text{-CH}_2$), 3.70 (O-CH_3), 3.54 ($-\text{COOCH}_3$), 3.17 (N-CH_3), 2.1–1.4 (CH-COO-), 1.35–0.74 (CH_2 and CH_3 from acrylic backbone). Molar fraction of triazene monomer in copolymer: 0.16.

Materials

All chemicals (Aldrich) were used as received without purifications. Only dimethylformamide (DMF) was dried over 5 Å molecular sieves.

Instruments

The structure of acrylic copolymers was verified by $^1\text{H NMR}$ and FT-IR spectroscopy using a Bruker 400 MHz spectrometer and a Bruker Vertex 70 spectrophotometer, respectively. For UV investigations, the samples were exposed to UV irradiation using a 500 W high-pressure mercury lamp without wavelength selection, at room temperature. The fluorescence spectra were recorded with an SLM 8000 spectrofluorimeter (Japan) and the quenching study was carried out using different transition metal ions.

RESULTS AND DISCUSSION

In our recent communications^{19,20} we have reported a series of novel polyacrylates with triazene units in the side chain tailored for microlithography²¹ and photoresist technique,²² owing to specific behavior of photocurable triazene chromophore capable to undergo a photochemical decomposition with

Table I. UV-vis spectral characteristics of triazene copolymers TCP-1 and TCP-2

Copolyacrylates	UV-vis absorption maxima (nm)	Rate constants (s^{-1})
TCP-1	286, 320 (DMF)	8×10^{-3}
TCP-2	290, 330 (DMF)	2.3×10^{-3}

release of molecular nitrogen. In order to connect the photochemical data with photophysical ones, the photodecomposition of the synthesized copolyacrylates (TCP-1 and TCP-2) was monitored by UV spectroscopy during irradiation performed with a high-pressure mercury lamp. For both copolymers, UV-vis spectra are similar and show strong absorption bands (Table I) attributed to $\pi\text{-}\pi^*$ transition of the triazene unit. Thus, upon their exposure to UV irradiation, the absorption maxima measurements confirm the progressive decomposition of the triazene chromophore and its exhaustive irradiation cause the disappearance of all the absorption bands, proving in this way an irreversible cleavage of triazene moieties attached to the polymeric backbone. Moreover, the kinetic evaluation of the process can be expressed by a first-order rate equation using the equation:

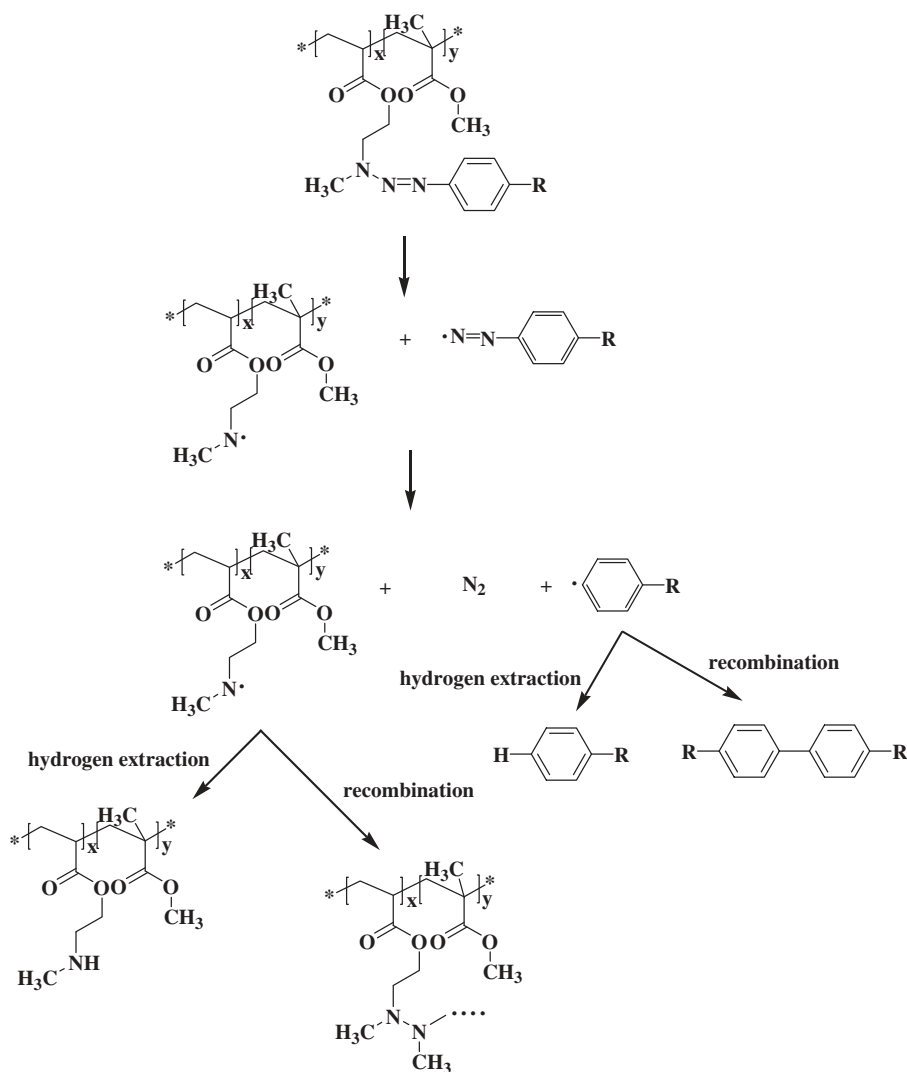
$$\ln \frac{A_0}{A_t} = kt$$

where A_0 and A_t are the values of the absorbance at times t_0 and t , respectively, and k is a rate constant. Accordingly, the k value calculated for the *phenyl*- and respectively, *methoxyphenyl* triazene copolyacrylates (TCP-1 and TCP-2) are presented in Table I, too.

Having established that the triazene chromophores can be photodecomposed in DMF, we next proposed a possible decomposition scheme for the synthesized triazene polyacrylates (Scheme 2). In the first step, we suppose a *trans-cis* photoisomerization of the $\text{N}=\text{N}$ bond with the formation of the *cis* isomer, thermodynamically instable. However, UV irradiation cleaves this link releasing a molecule of molecular nitrogen and generating others active macroradicals, including phenyl/methoxy-phenyl diazenyl ones. All these species appeared in system can be stabilized by hydrogen extraction or recombination, with the mention that there is a possibility that the latter one be capable to form fluorescent products.

Arguments in favor of the above mentioned assumption can be obtained by irradiation of the TCP-1 solution in DMF up to the disappearance of the absorption band of triazene unit in the corresponding UV-vis spectrum (Figure 1).

Indeed, after 10 min of irradiation with a high pressure mercury lamp, the absorption maxima located at 286 nm and 320 nm disappeared completely, sustaining thus the irreversible decomposition of the triazene units from copolymer. Under these circumstances, using an excitation wavelength of $\lambda_{\text{exc}} = 320$ nm and measuring the fluorescence emission, we see that the TCP-1 solution exhibited a broad emission band centered at 375 nm. Figure 2 illustrates the effect of UV-irradiation on the emission spectrum of TCP-1 solution that agrees almost perfectly with our prediction.



Scheme 2. A possible decomposition scheme for triazene based polyacrylates.

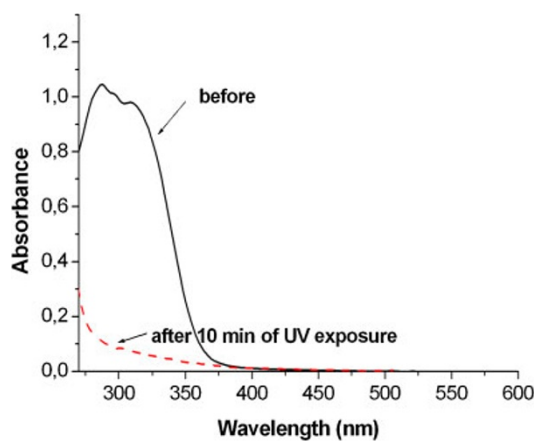


Figure 1. UV-vis absorption spectra for TCP-1 in DMF solution before and after 10 min of UV irradiation.

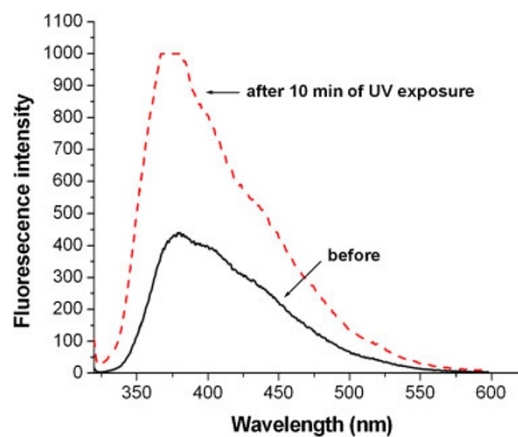


Figure 2. The fluorescence excitation spectra of TCP-1 in DMF before and after 10 min of UV irradiation ($\lambda_{exc} = 320$ nm).

On the other hand, an increase in the fluorescence intensity of about 3 times after 10 min irradiation of the polymer solution suggested us that the products formed through a recombination of diazenyl radicals emits fluorescence with a high quantum yield. From this experiment, it was clearly established that the triazene moiety ($>N-N=N-$) is responsible of emission maximum, and that, furthermore, the main photodecomposition products may lead to fluorescence structures with quantum yields significantly higher than of the starting polymer solution.

In a further demonstration of this behavior, we experimentally measured photoresponse in the TCP-1 film exposed under identical conditions (not evidenced here). Consequently, it was found that the effect of irradiation on the fluorescence maximum was reflected in a bathochromic shift with about 25 nm, which indicates the formation of aggregates in the polymeric film. Given these observations, we can conclude that the triazene polyacrylates are the first pattern of such polymers which exhibit emissive properties either in solution or film state, and hence they could play an important role in other applications. Additionally, the effect of varying irradiation time sustained that the irreversible decomposition of the triazene units is always accompanied of photocrosslinking of the polymeric film, as resulted from the solubility data of the irradiated area (developed in CHCl_3), which in turn decrease with increasing irradiation time (up to 2 h).

In order to obtain more information about microenvironment of the triazene fluorophore, we report here the influence of different metal ions (Fe^{3+} , Fe^{2+} , Cu^{2+} and Cu^+) on the emission intensity of TCP-1 and TCP-2 triazene copolyacrylates in DMF solution. To our best knowledge, this is a first example of fluorescent chemosensor for detecting various metal ions of environmental and biological interest using triazene polymers, as soon as their fluorescence is quenched completely or red/blue-shifted by the addition of metal ions, depending on the kind of metal ion. Keeping this in mind and in continuation of our studies on triazene polymers we measured the emission spectra of TCP-1 in DMF, excited by 320 nm. The changes in the fluorescence decay behavior of TCP-1 on the addition of the FeSO_4 (Fe^{2+} ions) are displayed in Figure 3.

It can be seen that with the addition of Fe^{2+} ions, the fluorescence intensity from 375 nm is found to disappear gradually, so that at a certain concentration of 1.6×10^{-4} M FeSO_4 the fluorescence decay is about 38%. Also, it is important to be noted that the minimum quencher concentration detected in the system is 0.16×10^{-4} M.

In a similar manner, the emission intensity of TCP-2 copolymer decreased at the beginning when the concentration of the quencher was 0.1×10^{-4} M (Figure 4), whereas a degree of quenching of 36% was determined for a concentration of 1.6×10^{-4} M FeSO_4 . The observed quenching efficiencies of the Fe^{2+} ions are found to be quite similar for both system, with a small improvement of about 2% for TCP-1 (38%) compared to TCP-2 (36%) at the same quencher concentration (1.6×10^{-4} M).

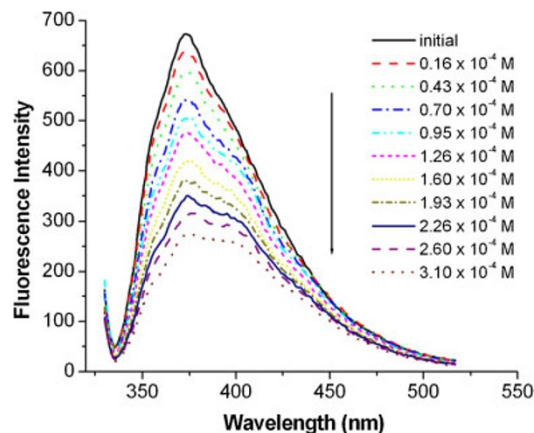


Figure 3. Emission spectra changes recorded for TCP-1 in DMF after addition of Fe^{2+} metal ions.

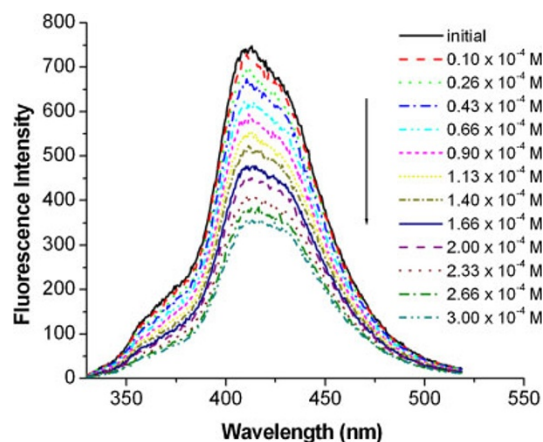


Figure 4. Effect of FeSO_4 quencher on the fluorescence intensity of 1-(*para* methoxy-phenyl)-3-(2 acryloyloxyethyl)-3-methyl triazene-1-*co*-methyl methacrylate (TCP-2) in DMF.

In parallel, for FeCl_3 used as quencher the same course of action was observed, so that at a concentration of 1.0×10^{-4} M FeCl_3 the emission decay is about 40%. Moreover, the changes in the fluorescence decay behavior of TCP-2 on the addition of the FeCl_3 (Fe^{3+} ions) determined a higher degree of quenching (48%) for the concentration of 1.0×10^{-4} M FeCl_3 . Here the fluorescence maximum corresponding to TCP-2 copolymer decreased for the first time, when the concentration of the quencher was 0.2×10^{-4} M, also (as we will see later).

When metal quenchers, like Cu^{2+} and Cu^+ were added to triazene copolyacrylates solution, very sensitive fluorescence quenching occurred even at very low concentrations of ions. Furthermore, Cu^{2+} can be considered an excellent quencher for the triazene chromophore because it is a good electron scavenger as a consequence of its electronic structure (d^9),^{23,24} inducing accessible low energy levels to excited states of the molecules.

For example, if $(\text{CH}_3\text{COO})_2\text{Cu}$ was added to the TCP-1 and TCP-2 solutions, the strong emission bands around 375 nm and 410 nm respectively, moved bathochromically towards a longer

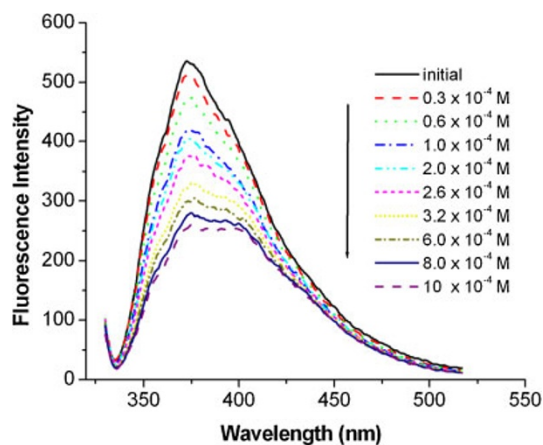


Figure 5. Changes in the fluorescence spectra of TCP-1 solution in DMF by the addition of $(\text{CH}_3\text{COO})_2\text{Cu}$.

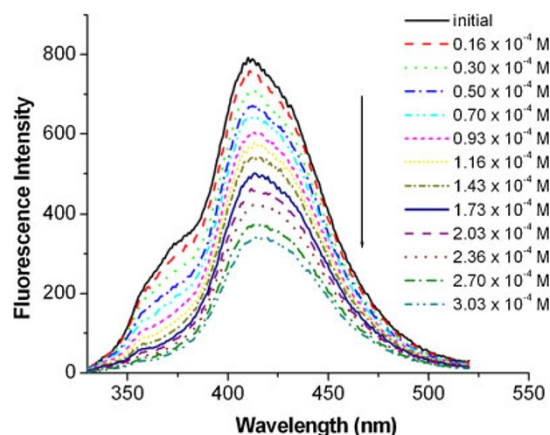


Figure 7. Emission spectra changes recorded upon addition of CuBr_2 to TCP-2 solution in DMF ($\lambda_{\text{exc}} = 320 \text{ nm}$).

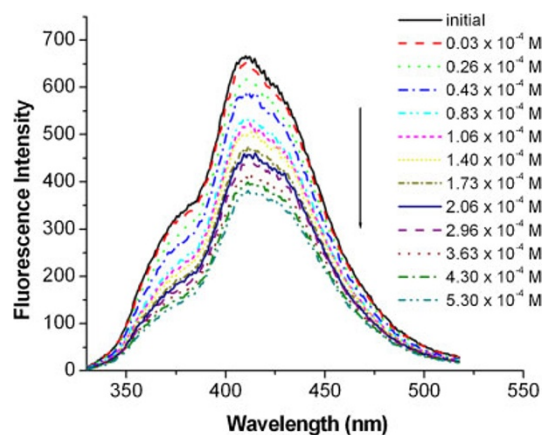


Figure 6. The fluorescence spectra of TCP-2 solution in DMF in the presence of $(\text{CH}_3\text{COO})_2\text{Cu}$.

wavelength ($\sim 2 \text{ nm}$) with a gradual decrease in fluorescence intensity (Figures 5 and 6). In addition, in the case of phenyl triazene copolymer (TCP-1) a small emission band grew around 400 nm .

Comparing all the spectroscopic data collected at the same quencher concentration ($2.0 \times 10^{-4} \text{ M}$), it can be observed that the fluorescence quenching of FeSO_4 (46% for TCP-1 and 40% for TCP-2) is considerably more efficient than that resulted in the case of using $(\text{CH}_3\text{COO})_2\text{Cu}$ (24% for TCP-1 and 30% for TCP-2). Such photoresponse in the above systems could be assigned to major energy transfer efficiency between the excited-states of the triazene fluorophore and transition metal ions.

The influence of CuBr_2 on the emission spectra of the triazene moiety was also investigated. For TCP-1 solution (not observed here), the shape and position of the fluorescence maximum remained the same, until the detection limit of Cu^{2+} became $0.03 \times 10^{-4} \text{ M}$. From this moment, the characteristic peak decreased obviously, when the concentration of metal ions increased.

As compared with TCP-1 polymer fluorescence spectra, for TCP-2 solution in DMF a quenching improvement was registered. The changes in emission spectra for TCP-2 by addition of Cu^{2+} can be seen in Figure 7. Here, a concentration of $2.03 \times 10^{-4} \text{ M}$ CuBr_2 causes a 42% quenching of fluorescence intensity as soon as a similar concentration for TCP-1 was generating a degree of quenching of 32.5%.

For a comparison purpose, the same experiment was also conducted for the low molecular monomer (1-(phenyl)-3-(2 acryloyloxyethyl)-3-methyl triazene-1). In this case, it was found that the fluorescence efficiency of CuBr_2 at the same molar concentration is lower (10%) than that found in the above polymeric system, where there is most probably stronger interaction with the former than the latter one does. We, therefore, conclude that the polymer structure is a noticeable advantage in the fluorescence quenching phenomenon caused mainly by structural factor often named as “fluorescence structural self-quenching effect.”²⁵

We also examined the effect of the Cu^+ ions on the fluorescence decay behaviour of both polymeric systems, when metal ion addition is associated with a gradual decrease in the fluorescence intensity. The changes in the fluorescence decay of TCP-1 on the addition of CuCl are illustrated in Figure 8. Thus, addition of metal ions in the polymer solution systematically decreased the degree of quenching, when for a concentration of $1.6 \times 10^{-4} \text{ M}$ CuCl , its value was 36%.

As can be seen from Figure 9, CuCl causes a large quenching of the triazene chromophore from TCP-2. In this case, when metal quencher CuCl was added to TCP-2 solution, very sensitive fluorescence quenching occurred even at very low concentration ($0.1 \times 10^{-4} \text{ M}$). Correspondingly, the triazene emission was quenched by CuCl , when the concentration of quencher was $2.3 \times 10^{-4} \text{ M}$ CuCl , the degree of quenching being only 11%.

Comparing the quenching efficiencies of the Cu^{2+} and Cu^+ ions at the same concentration ($2.1 \times 10^{-4} \text{ M}$) it was found a slight improvement for Cu^{2+} ions (32.5% for TCP-1; 41% for TCP-2) than for Cu^+ ions (15% for TCP-1 and respectively, 11% for TCP-2).

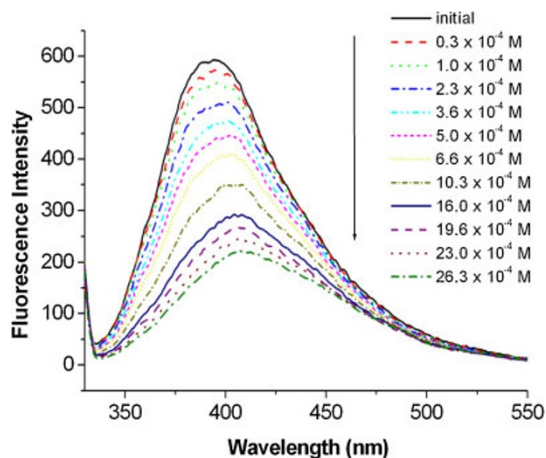


Figure 8. Fluorescence emission spectra of the TCP-1 solution in DMF as a function of CuCl concentration.

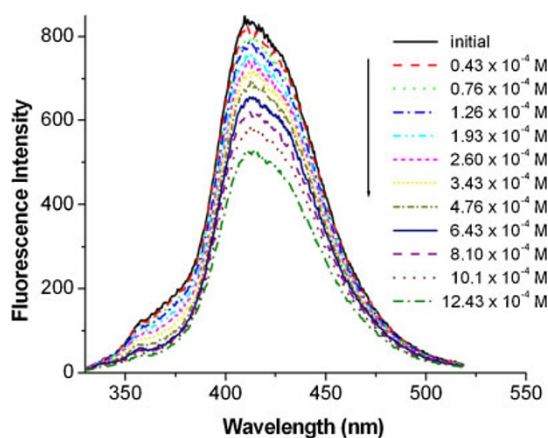


Figure 9. Emission spectra changes evidenced upon addition of CuCl to TCP-2 solution in DMF ($\lambda_{exc} = 320$ nm).

Interestingly, however, the fluorescence maxima of both triazene copolyacrylates in the presence of quenchers are slightly red-shifted with respect to the initial maxima in DMF. The bathochromic shift (by *cca* 10 nm) of the fluorescence maximum observed with an increase in the concentration of quencher is suggestive for the formation of aggregates, generally acknowledged as new ground-state species. Usually, their formation is coming with a red shift or/and generation of a new low-energy peak in the emission spectra, presumably due to a lowering in quantum efficiency of photoluminescence.²⁶ Another probable explanation may arise from dynamics of the interactions among metal ion and triazene group to promote to metal-bound triazene polymeric complexes.

To conclude and to prove once again that triazene chromophore is responsible for fluorescence maxima of the triazene copolymers, CuBr₂ was used to analyze its quenching effect on the solution of TCP-1 after its exposure with UV irradiation for 10 min. Even if a faster fluorescence quenching was previously observed for CuBr₂ (Figure 7) on the irradiated TCP-1 solution, the quenching process in this case was completely inefficient.

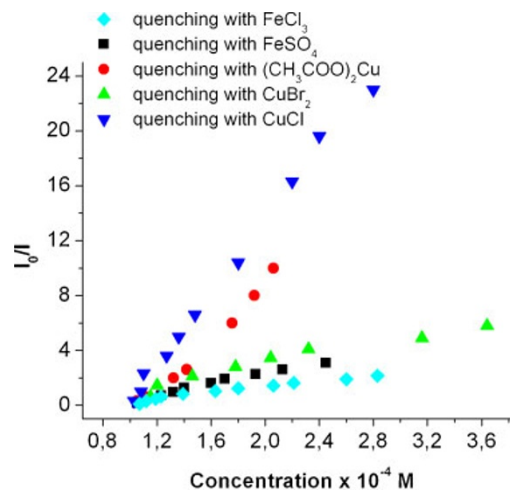


Figure 10. Stern-Volmer plots of TCP-1 copolymer as a function of different quencher concentrations.

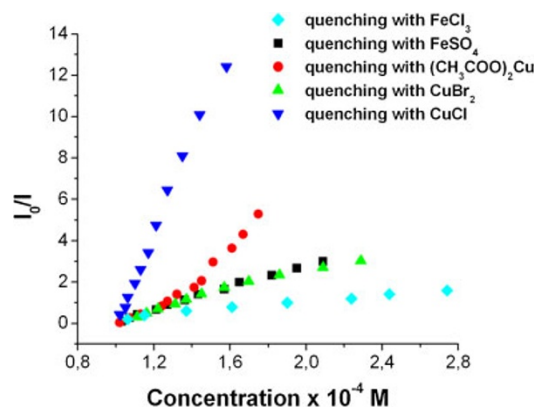


Figure 11. Stern-Volmer plots of TCP-2 copolyacrylate as a function of different quencher concentrations.

Starting from these considerations it is important to examine the mechanism of the quenching process. That's way the emission spectra were analyzed carefully using Stern-Volmer equation:

$$I_0/I = 1 + K_{SV}[Q]$$

where I_0 and I are the fluorescence intensities in the absence and in the presence of the metal ions, respectively, K_{SV} is the Stern-Volmer constant and $[Q]$ is the concentration of the quencher. The kinetic scheme gives linear curves obtained for a plot I_0/I versus $[Q]$ for both systems. A representative Stern-Volmer plot for TCP-1 copolymer is shown in Figure 10.

Furthermore, Figure 11 displays that the Stern-Volmer plot for all quenchers (FeCl₃, FeSO₄, (CH₃COO)₂Cu, CuBr₂, CuCl) utilized in the case of TCP-2 triazene copolyacrylate, where linear portions of the plot of I_0/I versus $[Q]$ is also indicated. Apparent Stern-Volmer constants decrease in the order: Fe³⁺ > Fe²⁺ > Cu²⁺ > Cu⁺ and these results directly reflect the relative sensitivity of the method for the above metal ions. The quenching is pronounced in the case of Fe²⁺ and Cu²⁺

(CuBr₂ and (CH₃COO)₂Cu) and the minimum quenching is observed for Cu⁺.

All the observed quenching efficiencies of the metal ions were found to be relatively similar to those reported with other fluorophores.^{27,28}

The ability of transition metal cations (Fe³⁺, Fe²⁺, Cu²⁺ and Cu⁺) to quench the fluorescence of triazene polymers (TCP-1 and TCP-2) has been explained on the basis of energy transfer processes. Energy transfer quenching can occur when the energy of the triazene chromophore excited state is larger than the excited-state energy of the quencher and furthermore, the electronic motions of the two species are coupled, involving π -stacking formation.¹² The efficiency of energy transfer, however, would be a function of the overlap and efficiency of this π -stacking process. Generally, energy transfer can take place by two most important transfer mechanisms: electron-exchange (Dexter's electron exchange mechanism) and dipole-dipole interaction (Förster's mechanism). In the electron-exchange mechanism, the donor and the acceptor approach so close to each other that the electron exchange happens very quickly. So, the donor is returning to the ground state and the acceptor is being raised to the excited state. Energy transfer by dipole-dipole mechanism operates by Coulombic resonance interactions, in which the oscillating electron of the excited state donor are coupled to those of the acceptor by an induced dipole interaction.^{12,29}

In the light of these considerations, the *d* levels of low-energy of transition metal ions play an important role in the quenching of the triazene fluorescence *via* the energy transfer, too. For example, a faster fluorescence quenching can be observed for Fe³⁺ (*d*⁵), which can be attributed to a major efficiency of energy transfer between the triazene excited-state and metal ion and to the stability of the half-filled shell of *d*⁵-metal ion also. Moreover, Cu²⁺ is well known as an excellent quencher because it is good electron "hunter" on account of its electronic structure (*d*⁹), and can easily introduces accessible low energy levels, which are capable of quenching the fluorescent excited states of the molecules.⁵

Stern Volmer plots for all quenchers (FeCl₃, FeSO₄, (CH₃COO)₂Cu, CuBr₂, CuCl) present data that are nearly collinear, indicating the involvement of only one quenching mechanism (energy transfer of Dexter type) and pointing a pure dynamic nature of this process. All these observation clearly suggests that the quenching influence of the transition metal ions need to be given special consideration for designing efficient triazene fluorosensors.

CONCLUSIONS

This work shows that the triazene copolyacrylates present emissive properties at excitation with 320 nm, both in DMF solution and polymeric films, in the latter a bathochromic shift (25 nm) of the fluorescence maxima indicating the formation of aggregates. The results obtained during UV irradiation and excitation of the triazene groups in DMF solution sustain that that products appeared in the system by a recombination of

phenyl/methoxy-phenyl diazenyl radicals emit fluorescence with a high quantum yield. It was demonstrated that the quenching of triazene fluorescence by metal ions (Fe³⁺ > Fe²⁺ > Cu²⁺ > Cu⁺) occurred according to Stern Volmer plots, and the quenching mechanism for triazene copolymers can be represented through a energy transfer process of Dexter type. The photophysical investigations revealed that such photopolymers could function as fluorescent chemosensors for some metal ions.

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