CHEMISTRY
A EUROPEAN JOURNAL

FULL PAPER

DOI: 10.1002/chem.201300622

Squarylium-Triazine Dyad as a Highly Sensitive Photoradical Generator for Red Light

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Abstract: New dyads, based on squarylium dye and substituted-triazine, were synthesized that exhibit an intramolecular photodissociative electron-transfer reaction. The compounds were used as a red-light photoradical generator. The photochemical activity of the dyad was compared to the corresponding unlinked systems (S+T) by determining the rate constant of electron transfer. The efficiency of the radical generation from the dyad compared to the unlinked system was demonstrated by measuring the maximum rate of free radical polymerization of acrylates in film. An excellent relationship between the rate of electron transfer and the rate of polymerization was found, evidencing the interest of this new approach to efficiently produce radicals under red light.

Keywords: donor–acceptor systems · dyads · electron transfer · photochemistry · polymerization

Introduction

Generating radicals is considered as one of the most important route of synthesis in organic chemistry. Among the different ways used to produce efficiently different radicals, photochemistry appears as very popular, affording a good and clean control of the release process, with high yields and without thermal heating. Therefore, development of photoradical generators (PRG) is still a lively topic that finds attractive applications in many different fields such as cosmetics, medicals, microelectronics, optics, and photoresists. Indeed, modern applications use PRG in triggering bioactivity,[1] in drug[2] or fragrance[3] release, in the fields of microelectronics.[4] The term of phototrigger is often employed, specifying that the PRG is used to launch a given chemical process.[5] Organic synthesis can take advantage of such PRG by building photolabile protective groups that could be released under irradiation by light.[6,7] In photopolymerization, the term of photoinitiator underlines the role of the PRG to prompt the initiation of the polymerization through a chain reaction.[8]

Whatever the application cited, most of the PRG exhibit absorption spectra in the UV-blue region of the electromagnetic spectrum.[9] Although this generally occurs at high quantum yields, irradiation in this high energy region limits the use of PRG in medical or cosmetic application, as well as preventing the use of other chemical additives that should absorb in the same region, such as pigments or anti-UV additives in photopolymerization. However, this could also be a drawback when developing new applications with new irradiation sources such as laser diodes or light-emitting diodes (LED) that are found to be quite inexpensive when emitting in the green or red region.

Therefore, there is a need to design new PRG that can be irradiated in the green to red region of the electromagnetic spectrum. In this paper, we have developed a new approach in which a photodissociative electron transfer within a dyad based on a dye linked to a releasing group produces a radical. As a first target, squarylium dye was chosen as a highly absorbing dye in the red region.[10–12] Squarylium dyes have unique photophysical and photochemical features and have found many technological applications in non-linear optics,[13] electrochromic materials,[14] electroluminescent materials,[15] and photoconductive materials.[16] Recently, some squarylium dyes together with initiators have been used in photopolymerization for potential applications in holographic information recording.[17,18] Positive photoresists using squarylium dyes/trichloromethyltriazine combinations are also reported.[19] On the other side of the molecule, a trichloromethyltriazine derivative was selected as a photodissociative electron acceptor (Scheme 1).[20]

It is shown that after irradiation, electron transfer occurs between the dye and the triazine moiety, which leads to the dissociation of a C–Cl bond.[20] As a result, a C-centered radical is produced that could effectively initiate a polymerization reaction.[21–24] Therefore, we expect an efficient electron-transfer reaction between the squarylium and the triazine moieties followed by a fast C–Cl bond cleavage that would lead to the formation of radicals. Spectroscopic experiments were performed to support this contention and the efficiency of a photopolymerization reaction of an acrylate initiated by this dyad was compared to that obtained by a physical mixture of dye and triazine derivative. It is clearly

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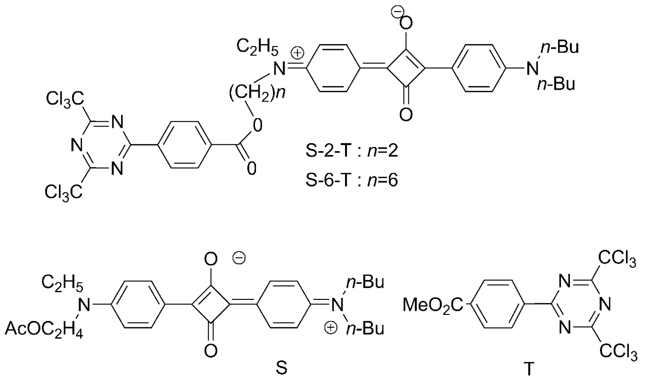

Scheme 1. Compounds used in this work.

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Results and Discussion

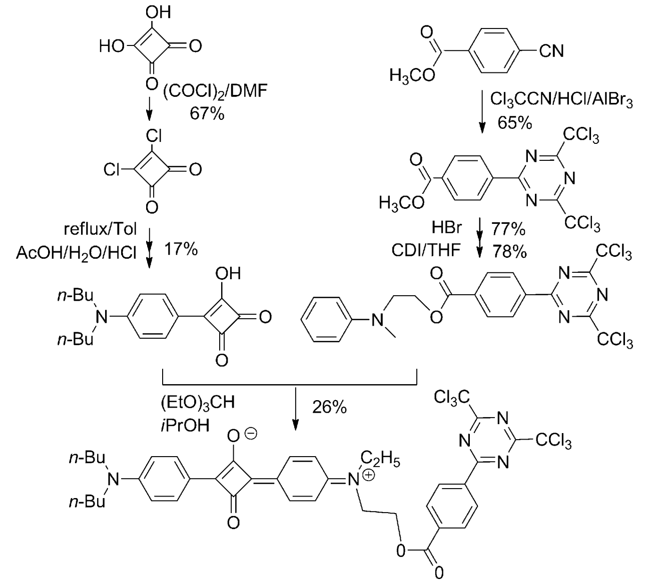
Excited state reactivity of the S-*n*-T dyad: Linked compounds S-2-T and S-6-T were synthesized by using a procedure adapted from the literature (Scheme 2).[25,26]

The photophysical properties of the dyads S-2-T, S-6-T and the parent dye S were measured in ethyl acetate. All compounds were found to have similar absorption and fluorescence features (Table 1), indicating that there is no appreciable ground-state interaction between the two groups in the dyads. Upon irradiation at 630 nm, the absorbance of S-2-T decreased rapidly, whereas no change was observed in the equimolar mixture of S and T (Figure 1).

When compared to the initial dye S, steady-state fluorescence show a decrease of the emission down to 55 and 7% for S-6-T and S-2-T, respectively (Table 1). This indicates that the intramolecular interaction in S-2-T is more effective than the physical mixture of S and T under irradiation.

Table 1. Absorption and fluorescence properties of the compounds studied in ethyl acetate.

Compound	Absorption λ_{max} [nm] (log ε)	Fluorescence λ_{max} [nm] (rel. int. [%])
S	633 (5.58)	645 (100)
S-2-T	633 (5.58)	645 (7)
S-6-T	636 (5.47)	648 (55)



Scheme 2. Synthesis of triazine-linked squarylium dye S-2-T; CDI = 1,1′-carbonyldiimidazole.

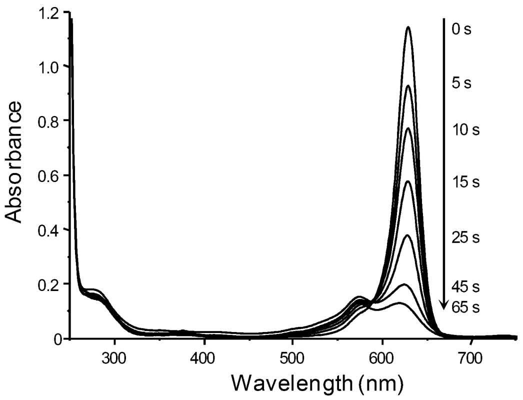


Figure 1. Photolysis of S-2-T in ethyl acetate followed under irradiation (630 nm, 0.1 mW cm^{-2}).

A clear evidence of intramolecular electron transfer in S-2-T was obtained with femtosecond pump-probe transient absorbance spectroscopy by irradiating ethyl acetate solution of S-2-T with 610 nm light pulses of 100 fs duration. The corresponding transient spectra are given in Figure 2 for pump-probe delays ranging from 2.2 ps to 2.6 ns. The positive band before 500 nm is ascribed to the transient absorbance of the emissive excited state of the chromophore in S-2-T.[27,28] The negative band with a maximum at 630 nm is assigned to the (S-2-T) bleaching and stimulated emissions of the (S-2-T) emissive excited state. All bands decay quite homothetically in the first hundred femtoseconds. Interestingly, for delays higher than 150–200 ps, a positive band grows around 650–700 nm. This positive band was observed in all solvents with the linked compound (S-2-T), but was

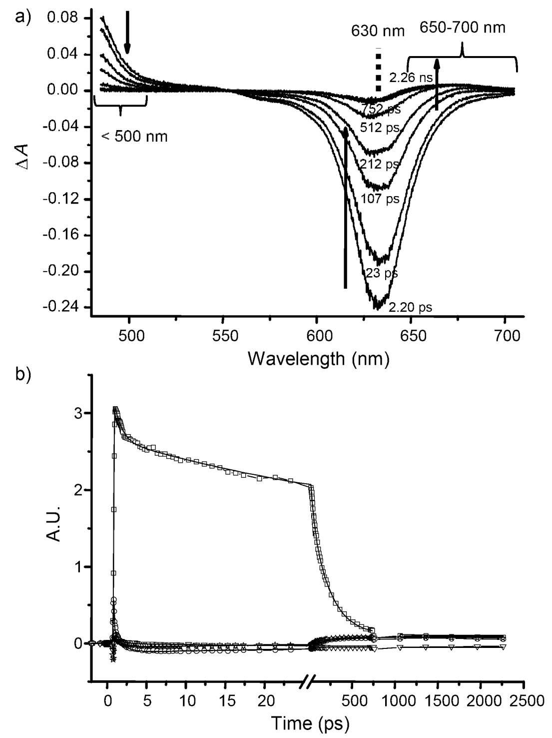
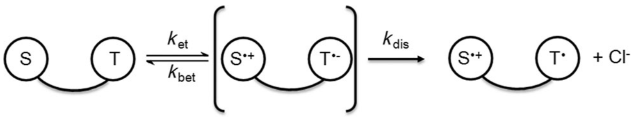


Figure 2. Femtosecond pump-probe transient spectroscopy of (S-2-T): a) in the ethyl acetate spectrum, and b) fourth first orthogonal kinetics obtained by singular value decomposition (SVD) analysis. Plain lines represent the best corresponding fit.

not present in experiments conducted with the unlinked chromophore squarylium S in ethyl acetate, acetonitrile, dichloromethane, and chloroform. Moreover the positive absorption band matches the radical cation $S^{\cdot+}$ of the chromophore S, which was generated by photoionization and pulse radiolysis as reported in the literature.[27–29] This indicates that the intramolecular electron transfer occurs from S to T and this process generates the cation radical $S^{\cdot+}$ in the S-2-T-linked molecule. It is worth noting also the photobleaching band around 630 nm indicating no ground state recovery in the time window of the apparatus.

The kinetic analysis of the spectro-temporal data was performed by singular value decomposition.[30–32] The best fit of the four first weighted orthogonal kinetics leads to three time constants and one step function. The two short kinetics (0.98 and 32.6 ps) are ascribed to the complex formation of the emissive state of the dye.[33,34] The longer one of 215 ps, corresponds to the lifetime of the emissive excited state in the linked compound, in agreement with the value obtained in ethyl acetate solution of S-2-T by using time-correlated single-photon counting (TCSPC). The step function is ascribed to the formation of transient species that do not recombine in the time window and is ascribed to the formation of the radical cation of the dye and the subsequent permanent bleaching.

According to these experiments, the general mechanism of reaction is given in Scheme 3. Under irradiation, the squarylium moiety S is excited into its first excited state, from which a photodissociative electron transfer occurs to the triazine moiety T. This leads to a fast C–Cl bond cleavage preventing back-electron-transfer and a carbon-centered radical is formed.



Scheme 3. Reaction mechanism of S-*n*-T.

The radicals produced during the photolysis of S-2-T or S-6-T can be used to photoinitiate the free-radical polymerization of acrylate. Therefore, it was tempting to test the photopolymerization efficiency of dyads compared to that of physical mixture of S in the presence of various concentration of T. Such experiments were performed in films at a concentration of 0.03 M for S-2-T, S-6-T and S. The dyads were compared to physical S+*n*T mixtures in which the concentration of added triazine in the matrix is increased from 0.03 to 0.21 M (S+T and S+7T, respectively; Table 2). The results are shown in Figure 3 and the relative rates of photopolymerization are collected in Table 2.

Table 2. Relative rate of polymerization R_p for the different systems studied.[a]

Combination	[T] [M]	R_p (rel.)	Fluorescence lifetime [ns]	k_{et} [$10^9 s^{-1}$]
S	0	0	2.90	–
S+T	0.03	1.0	2.84	0.01
S+3T	0.09	3.5	2.54	0.05
S+5T	0.15	6.2	2.37	0.08
S+7T	0.21	7.3	2.18	0.11
S-2-T	0	16.3	2.17	0.11
S-6-T	0	4.9	2.63	0.03

[a] [S]=[S-2-T]=[S-6-T]=0.03 M.

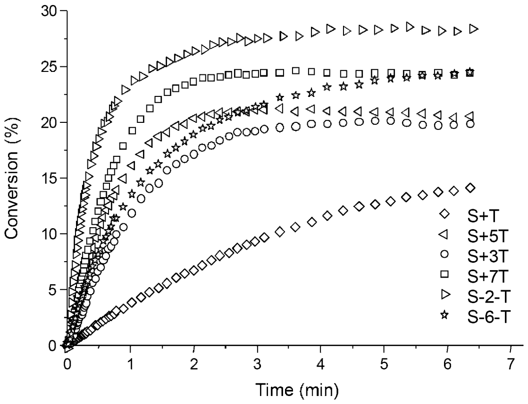


Figure 3. Real-time photopolymerization experiments.

As can be seen, the photopolymerization reaction is much more efficient for both S-2-T and S-6-T systems compared with the S+T system. The S-2-T system even outperforms the efficiency of the physical mixture S+7T in which the triazine is in large excess (0.21 M). This effect clearly demonstrates that the efficiency of radical generation is related to the intramolecular electron-transfer process.

To get more insight into this reaction, the electron-transfer rates were calculated from time-resolved fluorescence decays in films of the dyad S-2-T, S-6-T and the unlinked systems S+T to S+7T.

As it was seen that no ground state interaction occurs in the dyads, the fluorescence lifetime τ_0 of the dye alone (S) was taken as a reference for measuring the intrinsic rate of electron transfer occurring in the dyads. The rates were calculated according to Equation (1):

$$k_{\mathrm{et}} = {}^{1}\!/_{\tau} - {}^{1}\!/_{\tau_0} \tag{1}$$

in which τ the fluorescence lifetime of the dyad or, in the case of physical mixture, the fluorescence lifetime of S in the presence of T. The results collected in Table 2 show that S-2-T exhibits a higher rate constant of electron transfer than S-6-T, and is quite similar to the physical mixture S+7T. These results are in line with the close proximity between S and T in S-2-T (which is almost the same in S+7T) than in S-6-T.

It is worth noting that the rates of polymerization exhibit the same trend, that is, they increase with increasing rates of electron transfer in physical mixtures S+*n*T and in the dyads S-2-T and S-6-T. However, the rate of polymerization is larger in S-2-T compared with the unlinked S+7T system, even if they have the same rate of electron transfer.

Assuming a monomolecular termination reaction for the polymerization process, the maximum rate of polymerization R_p is given by Equation (2):[35,36]

$$R_p = k_p\left(\frac{\phi_i\, I_{\mathrm{abs}}}{k_t}\right)[\mathrm{M}] \tag{2}$$

in which k_p and k_t are the rate constants of propagation and termination, respectively, I_{abs} is the absorbed light intensity and [M] is the concentration of the monomer. ϕ_i stands for the initiation quantum yield, which is related to Equation (3):

$$\phi_i = \tau \times k_{\mathrm{et}} \times \phi_{\mathrm{rad}} \tag{3}$$

in which ϕ_{rad} is the yield of radical formation. Then, Equation (2) turns into Equation (4):

$$R_p = K \times \tau \times k_{\mathrm{et}} \times \phi_{\mathrm{rad}} \tag{4}$$

in which K is a constant that depends on experimental conditions. Figure 4 shows the plot of the relative polymerization rate as a function of $k_{\mathrm{et}} \times \tau$ for linked and unlinked systems. A linear relationship is outlined between the two parameters.

These results confirm the fact that there is a direct relationship between R_p and the primary photochemical process, the photodissociative electron transfer. Interestingly, both dyads outperform the physical mixtures: two regression lines with different coefficients are obtained, separating linked and unlinked systems in two groups. Thus, linear regression coefficient of the linked systems is higher than that of the physical mixtures. This could be ascribed to the yield of radical generation (ϕ_{rad}) after electron transfer, which may differ for linked and unlinked systems in the matrix. Indeed ϕ_{rad} could be related to the rate of dissociation of triazine k_{dis} and the rate of back-electron-transfer k_{bet} (Scheme 3) according to the following Equation (5):

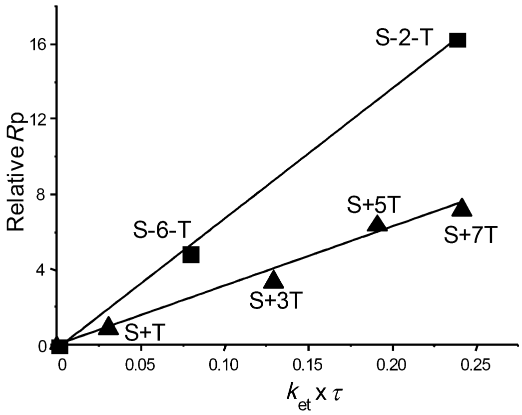


Figure 4. Plot of the maximum rate of polymerization versus the electron-transfer rate for S-2-T, S-6-T, and S+*n*T.

$$\phi_{\mathrm{rad}} = \frac{k_{\mathrm{dis}}}{k_{\mathrm{dis}} + k_{\mathrm{bet}}} \tag{5}$$

One can assume that the rate constant of C−Cl bond cleavage is the same for all the systems. Consequently, the differences in ϕ_{rad} can be ascribed to variation of k_{bet}. The k_{bet} depends on the energetics of the reaction as well as the distance between the reactants. Obviously, the latter factor clearly differs for linked and unlinked systems, and as a consequence, a higher quantum yields should be the consequence of a lower k_{bet} in the dyads compared with the physical mixtures.

Conclusion

In this paper new dyads were synthesized, based on squaryllium dye and triazine derivatives, which absorb strongly the light in the red region. It was shown that excitation of the dyad leads to an intramolecular photodissociative electron transfer and then to the formation of radicals. Rate constants for electron transfer were measured within the dyad and compared with that obtained for a physical mixture of the dye and substituted-triazine in solid film, showing that the photo-process occurs much more efficiently in former case. To exemplify this effect, photopolymerization experiments were performed, exhibiting higher rates of polymerization when the dyads are used. The outstanding performance of the dyad compared with the physical mixture of reactants places this compound as a very efficient dissociative photoinitiator for free radical photopolymerization or as phototrigger. This concept of visible light absorbing dye linked to a dissociative electron acceptor open new opportunities for the development of photoradical generators absorbing in the green–red region of the electromagnetic spectrum.

Experimental Section

Triazine-linked squarylium dyes S-*n*-T: Synthesis of linked compound S-2-T and S-6-T was performed according to the general procedure[11,25,26] shown in Scheme 2.

Synthesis of S-2-T: A mixture of [2-(*N*-ethylanilino)ethyl] 4-[4,6-bis-(trichloromethyl)-1,3,5-triazin-2-yl]benzoate (2.00 g, 3.42 mmol) and 3-hydroxy-4[4-(*N*,*N*-dibutylanilino)]cyclobut-3-ene-1,2-dione (1.03 g, 3.13 mmol) in dry 2-propanol/triethylorthoformate (20 mL, 5:1, v/v) was heated at reflux for 5 h under nitrogen, under green light because of the red sensibility of the product. The reaction was then stopped by addition of a mixture of cyclohexane/ethyl acetate (60 mL, 5:1, v/v). The solvent was evaporated, and the residue was purified by using column chromatography (cyclohexane/ethyl acetate = 1:1, v/v as eluent), to afford the product as a green solid (0.703 g, 0.81 mmol, 26 %). ^{1}H NMR ($CDCl_3$): δ = 0.99 (t, J = 7.2 Hz, 6H), 1.20–1.48 (m, 8H), 3.44 (t, J = 7.5 Hz, 4H), 3.63 (q, J = 6.9 Hz, 2H), 3.90 (t, J = 5.7 Hz, 2H), 4.61 (t, J = 5.7 Hz, 2H), 6.72 (d, J = 9.0 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 8.16 (d, J = 7.5 Hz, 2H), 8.37 (d, J = 8.7 Hz, 4H), 8.75 ppm (d, J = 7.5 Hz, 2H); HRMS: *m/z* calcd for $C_{40}H_{40}N_5O_4Cl_6$: 866.1181 $[M+H^+]$; found: 866.1164.

Synthesis of S-6-T: S-6-T was synthesized by following the above procedure using [6-(*N*-ethylanilino)hexyl] 4-[4,6-bis(trichloromethyl)-1,3,5-triazin-2-yl]benzoate as a starting material. Yield: 25 %; ^{1}H NMR ($CDCl_3$): δ = 0.99 (t, J = 7.3 Hz, 6H), 1.31–1.90 (m, 19H), 3.43 (t, J = 7.7 Hz, 6H), 3.52 (q, J = 7.1 Hz, 2H), 4.39 (t, 6.9 Hz, 2H), 6.69 (d, J = 2.7 Hz, 2H), 6.73 (d, J = 2.7 Hz, 2H), 8.24 (d, J = 8.7 Hz, 2H), 8.34 (d, J = 0.7 Hz, 2H), 8.37 (d, J = 0.7 Hz, 2H), 8.77 ppm (d, J = 8.7 Hz, 2H); HRMS: *m/z* calcd for $C_{44}H_{48}Cl_6N_5O_4$: 922.1808 $[M+H^+]$; found: 922.1807.

Methods: Absorbance spectra of solutions were recorded on a Cary 4000 UV-Visible Spectrophotometer (Varian) and absorbance spectra of films were recorded on Agilent 8453E spectroscopy system (Agilent Technologies). HRMS were performed on Agilent Technologies Mass Spectrometer Detector 6510 (MSD; Q-TOF, LC/Mass) in positive Electro Spray Ionization (ESI) source mode. Monomer polymerization was monitored by RT-FTIR spectroscopy using a Vertex 70 FTIR spectrometer (Bruker Optik).[37]

A FluoroMax-4 (Horiba, Jobin–Yvon) spectrofluorometer coupled with a TCSPC accessory was used to measure steady-state fluorescence spectra and fluorescence decays. A 607 nm NanoLEDs (duration 1.7 ns) was used as pulsed excitation source leading to a time resolution, after deconvolution, of around 200 ps.

Femtosecond time-resolved transient absorption experiments were performed by using Excipro pump-probe apparatus (CDP corp). Femtosecond laser excitation wavelength was adjusted to 610 nm by mean of collinear 800 nm pumped CDP2017 (CDP corp) optical parametric amplifier. The 100 fs laser pulses (800 nm) were provided by a Spectra-Physics Tsunami Ti:Sa oscillator coupled to a Spitfire pro Spectra-physics regenerative amplifier. The resulting pump-probe cross-correlation of the setup was found to be about 200 fs.

UV-grade acetonitrile was purchased from Fluka and UV-grade ethyl acetate, dichloromethane, chloroform were purchased from Aldrich. Another solvents and chemicals were of reagent grade quality and used without further purification. Pentaerythritol tetraacrylate (PETTA, SR295) was supplied by Sartomer and used as received.

Films for the measurement of photophysical behavior and photopolymerization were typically prepared in the following manner. The photoinitiator (a squarylium dye/triazine combination or a triazine-linked squarylium dye), a polyfunctional acrylate monomer (pentaerythritol tetraacrylate) and a polymeric binder (polymethyl methacrylate M_W = 35 000 g mol^{-1}) were dissolved in a 16:1:1 (w/w/w) mixture of solvent (methyl ethyl ketone/1-methoxy-2-propanol/THF), and the solution was cast on a glass or on a polypropylene film by using a 24 μm RKprint K Hand Coater. The solvent was evaporated by heating at 90 °C for 2 min. The thickness of the film thus prepared was about 4 μm. Films were overcoated by a polyvinyl alcohol film (M_W = 2000 g mol^{-1}) to prevent diffusion of atmospheric oxygen.

The photosensitivity of the dyad were measured by Real-Time FTIR and performed by using a 635 nm laser diode as an irradiation source with the irradiance intensity at the surface of the sample adjusted to 10 mW cm^{-2}. The kinetics of the polymerization were measured by following the disappearance of the acrylic double bond at 1410 cm^{-1}. The degree of acrylate double bond conversion (C) was calculated from the decrease of the area of the IR absorption peak between 1402 and 1418 cm^{-1} of the sample after exposure using the following Equation (6):

$$\mathrm{C}\,(\%) = (A_0 - A_t)/A_0 \times 100 \qquad (6)$$

in which A_0 represent the initial peak area before irradiation and A_t represent the peak area of the acrylic double bond at time, t.[38]

Acknowledgements

The Cercle Gutenberg, Strasbourg is fully acknowledged for the Chaire d'Excellence provided to K.K.

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Received: February 18, 2013
Revised: June 3, 2013