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Photosensitizer/photoinitiator interactions in copolymeric systems bearing side-chain thioxanthone and α-morpholino acetophenone moieties

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Laser irradiation at 355 nm of copolymers obtained from 1-[(2-acryloyloxy)ethoxycarbonyl]thioxanthone with 1-[4-(2-acryloyloxyethylthio)phenyl]-2-methyl-2-morpholino-propan-1-one in toluene or 1,6-hexanediol diacrylate/n-butyl acrylate (1:1) solution, clearly indicates that the rate constant of excitation transfer from side-chain thioxanthone to α-morpholinoketone moieties is two orders of magnitude higher than that observed for the corresponding low-molecular-weight structural models mixture, such as 1-[2-isobutyroyloxy)ethoxycarbonyl]thioxanthone and 1-[4-(2-isobutyroyloxyethylthio)phenyl]-2-methyl-2-morpholino-propan-1-one. Evaluation of the efficiency of the above photosensitization process confirms that it is much higher in the copolymer systems. Photophysical and photoinitiation polymerization data suggest that the sensitization process mainly occurs through an energy transfer rather than an electron transfer mechanism, favoured by the forced close vicinity of the two photosensitive moieties attached to the same macromolecule.

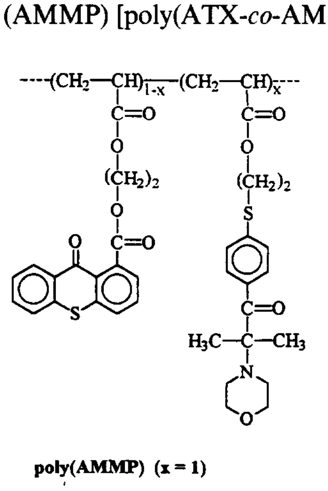
(Keywords: photosensitization; polymeric photoinitiators; thioxanthone/α-morpholino acetophenone systems)

INTRODUCTION

Polymers with pendent photosensitive moieties are attracting increasing interest as photoinitiators for u.v.-curable coatings[1,2]. The above systems have been mainly applied for improving the performances of u.v. clear coatings[3], particularly as far as low-odour and non-yellowing properties are concerned[4,5]. However, the majority of photoinitiators fail in the u.v. cure of pigmented coatings, particularly when their formulations are based on TiO_2 rutile, due to its strong absorption below 380 nm.

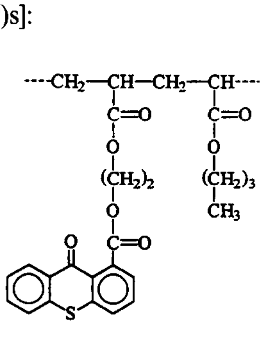
Quite recently, it was proposed to circumvent this problem by using systems comprising a photoinitiator and a photosensitizer, the latter component being able to absorb the u.v. radiation over 380 nm and efficiently transfer the excitation energy to the former. Thus, the formation of primary radicals deriving from the photoinitiator would be promoted even in the presence of a pigment. Indeed, a relevant synergistic effect was found to occur[6–10] in the u.v. cure of white pigmented lacquers and blue silk screen inks by combining a photosensitizer such as 1-alkyloxycarbonyl thioxanthones or 2-isopropyl-thioxanthone with an α-aminoacetophenone such as 1-[4-(methylthio)phenyl]-2-methyl-2-morpholino-propan-1-one (MMMP), the triplet-state energy of the above-mentioned thioxanthone derivatives being higher than that of MMMP[7,10].

Very recently[11] we proposed the use of copolymeric systems prepared from 1-[(2-acryloyloxy)ethoxycarbonyl]thioxanthone (ATX) and 1-[4-(2-acryloyloxyethylthio)phenyl]-2-methyl-2-morpholino-propan-1-one (AMMP) [poly(ATX-*co*-AMMP)s]:



poly(AMMP) (x = 1)

poly(ATX-*co*-AMMP)s (0 < x < 1)



poly(ATX-*co*-BA)

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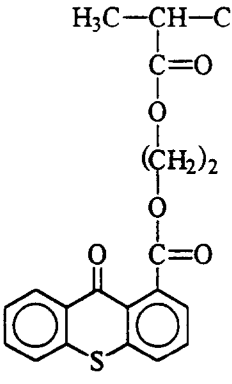
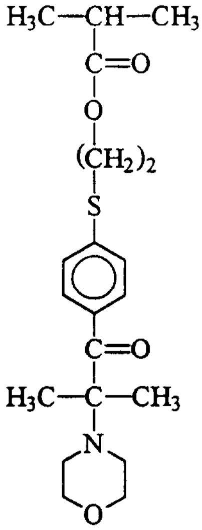
Indeed, the cure of 1,6-hexanediol diacrylate (HDDA)/n-butyl acrylate (BA) equimolar mixtures in the presence of poly(ATX-*co*-AMMP)s under u.v. irradiation over 380 nm (simulating the absorption conditions of a white pigmented coating) was found to be much more efficient than that observed in the presence of mixtures of the corresponding low-molecular-weight structural models 1-[(2-isobutyroyloxy)ethoxycarbonyl]-thioxanthone (IBTX) and 1-[4-(2-isobutyroyloxyethylthio)phenyl]-2-methyl-2-morpholino-propan-1-one (IMMP)



IBTX



IMMP

or of polymers derived from only one single photosensitive structural unit, such as the copolymer of ATX with BA and the homopolymer of AMMP [poly(ATX-*co*-BA)/poly(AMMP)]. The much higher photoinitiation activity of the copolymer systems was tentatively explained by assuming that the forced close vicinity of the two side-chain photosensitive groups dramatically increases the energy transfer efficiency from excited thioxanthone to ground-state α-morpholino acetophenone moieties[11].

However, as revealed by time-resolved laser spectroscopy[12–17] and chemically induced dynamic nuclear polarization (CIDNP)[6–8], in thioxanthone/α-morpholinoketone systems another type of excitation transfer may occur, depending on the relative triplet-state energy levels and polarity of the medium. This photophysical pathway, well known for amine/thioxanthone systems[18], involves an electron transfer from the α-aminoketone to the excited sensitizer, followed by a proton transfer with the formation of ketyl and α-aminoalkyl radicals, the latter being the effective initiating species.

Although the improvement of photoinitiation activity on decreasing the content of ATX co-units in poly(ATX-*co*-AMMP)s[11] seems to support that the energy transfer mechanism should be at least predominant, a photophysical investigation of the above systems would clarify this point.

The present paper, therefore, is devoted to the study, by time-resolved laser spectroscopy, of the excited state processes in poly(ATX-*co*-AMMP)s, in order to better define the type of interactions between thioxanthone and α-morpholino acetophenone moieties when attached to the same macromolecule.

EXPERIMENTAL

Materials

Poly(ATX-*co*-AMMP)s with $\bar{M}_n$ in the range 3200–3900 and $\bar{M}_w/\bar{M}_n = 1.8-2.1$, prepared by free radical initiation as previously described[11], have been employed. In particular, samples containing 11, 24, 35 and 45 mol% of ATX co-units have been studied.

Poly(AMMP) ($\bar{M}_n = 2700$, $\bar{M}_w/\bar{M}_n = 2.5$) and poly-(ATX-*co*-BA) (52 mol% of ATX co-units, $\bar{M}_n = 4800$ and $\bar{M}_w/\bar{M}_n = 2.3$), prepared by the same procedure[11], have been used.

1-[(2-Isobutyroyloxy)ethoxycarbonyl]thioxanthone (IBTX) and 1-[4-(2-isobutyroyloxyethylthio)phenyl]-2-methyl-2-morpholino-propan-1-one (IMMP), prepared as previously reported[11], have been tested as reference samples.

Methyl methacrylate (MMA), n-butyl acrylate (BA) and 1,6-hexanediol diacrylate (HDDA), commercially available from Aldrich, were purified as described elsewhere[19,20].

Photoinitiated polymerizations

The photoinitiated polymerization of HDDA/BA equimolar mixtures was carried out in film matrix under nitrogen, upon u.v. irradiation over 380 nm and in the presence of different photosensitizer/photoinitiator systems (concentration of thioxanthone moiety: 0.1 mol%), as previously reported in full detail[11]. The time evolution of the above experiments was followed by microwave dielectrometry at 9.5 GHz, as reported elsewhere[20]. The measurement apparatus and method have been fully described[21].

Photophysical measurements

Time-resolved laser spectroscopy measurements were performed on low- and high-molecular-weight photosensitive compounds in degassed toluene or HDDA/BA (1 : 1) solution by using a short light pulse (3 ns) delivered by a YAG/Nd laser at 355 nm. A full description of the above apparatus has been given previously[12,22].

RESULTS AND DISCUSSION

Reactivity of the excited states

U.v. absorption spectra of the thioxanthone moiety in IBTX and poly(ATX-*co*-BA) show[11], between 310 and 410 nm, a broad structured band centred at 385 nm, related to the n → π^* electronic transition of the ketone group[8,23]. Laser excitation at 355 nm of the above samples, in degassed toluene solution, leads to the formation of long-lived triplet-state species with similar lifetime ($\tau^\circ_{\mathrm{IBTX}} = 1.6\,\mu$s and $\tau^\circ_{\mathrm{ATX}} = 2.0\,\mu$s), as evaluated from their transient decay (*Figure 1*). Indeed, τ° values have been determined by computer processing the initial part of the triplet relaxation signal which well fits a first-order decay. A deviation from this kinetic behaviour is observed (*Figure 1*) in the subsequent part of the transient curve, due to the presence of longer-lived absorbing species assignable to thioxanthone ketyl radicals, generated by intramolecular hydrogen abstraction,

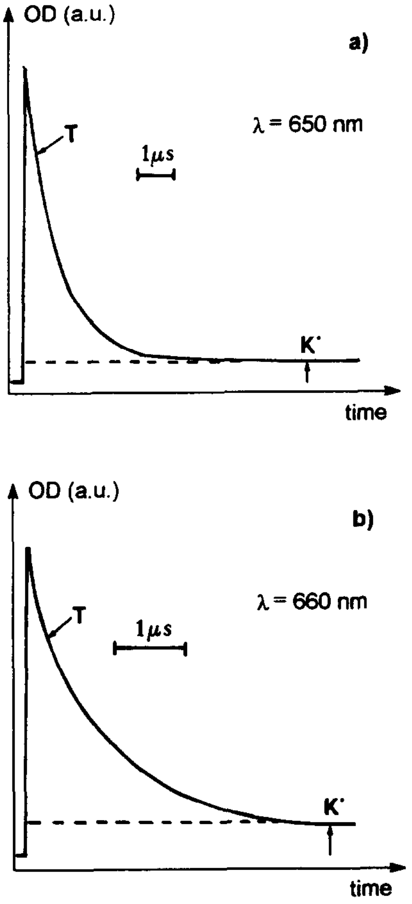


Figure 1 Transient decay of long-lived species in toluene solution after laser pulse irradiation of (a) IBTX and (b) poly(ATX-*co*-BA); T and K' represent triplet and ketyl radical, respectively

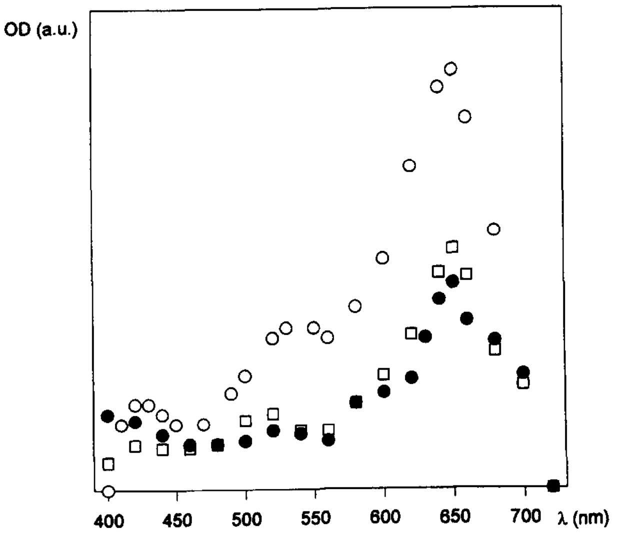


Figure 2 Absorption spectra of the triplet state in toluene solution of (○) IBTX, (□) poly(ATX-*co*-BA) and (●) poly(ATX-*co*-AMMP) with 35 mol% of ATX co-units

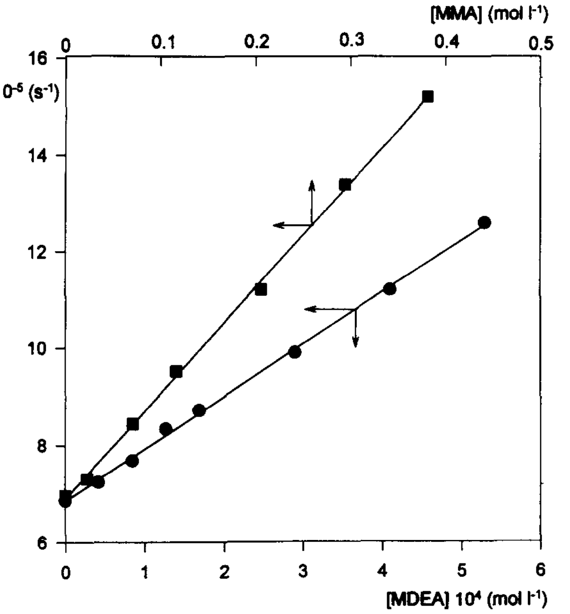


Figure 3 Stern–Volmer plot of the reciprocal value of triplet-state lifetime of IBTX as a function of the quencher concentration in toluene solution: (■) MMA and (●) MDEA

as previously found[24] for 1-(methoxycarbonyl)-thioxanthone in toluene solution. Analogous determinations on IBTX and poly(ATX-*co*-AMMP)s in HDDA/BA (1:1) solution give τ° values 0.58 and 0.90 μs, respectively, slightly lower than those obtained in toluene, due to the quenching by the acrylic nature of the medium. These data are in agreement with those previously observed for structurally similar low[7,24] and high[25] molecular weight thioxanthone derivatives. This indicates that the coiling of the macromolecular backbone around the thioxanthone moiety does not seem to appreciably affect its photophysical behaviour. It is worth noting that for both IBTX and poly(ATX-*co*-BA) systems the residual absorption of ketyl radical in the triplet transient decay is found also in HDDA/BA solution.

Triplet–triplet absorption spectra of poly(ATX-*co*-BA) and IBTX, in degassed toluene solution, show (*Figure 2*) the typical behaviour of thioxanthones in the same solvent[24] with a maximum at about 650 nm. An analogous spectrum is observed for poly(ATX-*co*-AMMP)s (*Figure 2*). Taking into account that the α-morpholinoketone moiety in the above copolymers, as well as in IMMP, exhibits[11] in the near u.v. a band centred at about 300 nm (the result of the overlapping of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electronic transitions of the alkylthiophenyl and ketone chromophores, respectively[15,16]) with a very weakly absorbing tail over 350 nm, the laser irradiation at 355 nm substantially causes only the excitation of the thioxanthone moiety.

Moreover, these long-lived triplet states are quenched, as represented for IBTX in *Figure 3*, by methyldiethanolamine (MDEA) and, although to a much lower extent (three orders of magnitude), also by methyl methacrylate (MMA). The values of the quenching rate constant (k_q) of excited poly(ATX-*co*-BA) and IBTX by MDEA and MMA in toluene solution, calculated by the usual Stern–Volmer plot, are reported in *Table 1* and appear very similar to that previously observed for 1-(methoxycarbonyl)thioxanthone[14].

The minor tendency of the triplet state to react with MMA is in agreement with the fact that thioxanthone/tertiary amine systems are used as photoinitiators for acrylic coatings.

In the presence of MDEA the quenching of the thioxanthone triplet state is accompanied by the formation of a long-lived species, absorbing between 400 and 450 nm, attributable to the ketyl radical[26].

Excitation transfer experiments in toluene solution

Excitation transfer from thioxanthone sensitizer to the α-morpholinoketone photoinitiator was followed by monitoring the decay of the T_1 triplet state (generated by direct excitation of thioxanthone moiety) as a function of the photoinitiator concentration. The rate constant k_{tr} for this bimolecular reaction

$$T_1(\text{thioxanthone}) + S_0(\alpha\text{-morpholinoketone}) \xrightarrow{k_{tr}} \text{excitation transfer}$$

can be calculated from the usual Stern–Volmer plot according to the following equation:

$$1/\tau = 1/\tau^{\circ} + k_{tr}[P]$$

where τ and τ° are the T_1 lifetimes in the presence and absence of photoinitiator (P), respectively. The k_{tr} values obtained from the interaction of IBTX and poly(ATX-*co*-BA) with IMMP and poly(AMMP) are reported in *Table 2*. As an example, the Stern–Volmer plots for IBTX against IMMP and poly(AMMP) concentration are shown in *Figure 4*.

As reported in *Table 2*, the rate constant of excitation transfer from the thioxanthone to the α-morpholinoketone moiety decreases progressively upon going from the system consisting of two low-molecular-weight interacting components (IBTX/IMMP) to that constituted by two polymeric derivatives each of them consisting of monomeric units derived from only one photosensitive moiety [(poly(ATX-*co*-BA)/poly(AMMP)]. The above results can be explained by taking into account that when one thioxanthone or α-morpholinoketone moiety is attached to a macromolecule or when both photosensitive groups are bound to different polymer chains, the macromolecular coiling may generate a shielding around the side-chain photosensitive groups, thus reducing their interacting capability. It cannot, however, be excluded that the microheterogeneity of the distribution of the partners may play a certain role.

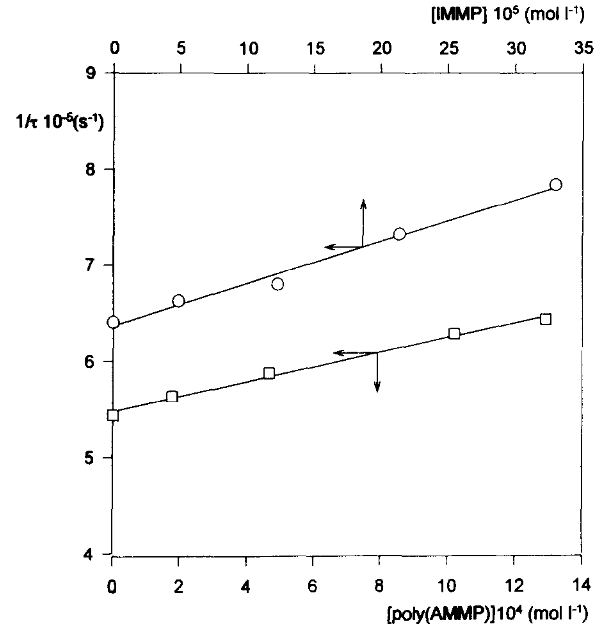


Figure 4 Stern–Volmer plots of the reciprocal value of triplet-state lifetime of IBTX as a function of α-morpholinoketone concentration in toluene solution: (○) IMMP and (□) poly(AMMP)

The formation of long-lived absorbing species, assignable to thioxanthone ketyl radicals, is observed to a low extent also in this case, during the excitation transfer experiments. However, considering that the amount of the above species does not seem to depend on the concentration of α-morpholinoketone moieties and that they are present to a similar extent also in the absence of photoinitiator, as mentioned above, it may be concluded that ketyl radicals are mainly generated by intramolecular hydrogen abstraction even in the presence of α-morpholino acetophenone moieties.

Sensitization experiments on poly(ATX-*co*-AMMP)s were performed at a fixed thioxanthone (1.5×10^{-4} M) and various α-morpholinoketone concentrations by using copolymer samples having different composition. Indeed, laser excitation at 355 nm of

Table 1 Quenching rate constants (k_q) in toluene between low- and high-molecular-weight thioxanthone moieties and MDEA or MMA

Thioxanthone derivative	Quencher	$k_q \times 10^{-6}$ ($l\,mol^{-1}\,s^{-1}$)
IBTX	MDEA	1100
	MMA	2.0
Poly(ATX-*co*-BA)	MDEA	1300
	MMA	1.6

Table 2 Rate constant (k_{tr}) of excitation transfer between low- and high-molecular-weight thioxanthones and α-morpholinoketones, in toluene or HDDA/BA (1 : 1) solution

Thioxanthone derivative	Medium	α-Morpholinoketone derivative	$k_{tr} \times 10^{-6}$ ($l\,mol^{-1}\,s^{-1}$)
IBTX	toluene	IMMP	430
	HDDA/BA	IMMP	120
	toluene	poly(AMMP)	74
	HDDA/BA	poly(AMMP)	200
Poly(ATX-*co*-BA)	toluene	IMMP	130
	toluene	poly(AMMP)	37
	HDDA/BA	poly(AMMP)	55
Poly(ATX-*co*-AMMP)	toluene	AMMP co-units	23 000
	HDDA/BA	AMMP co-units	20 000

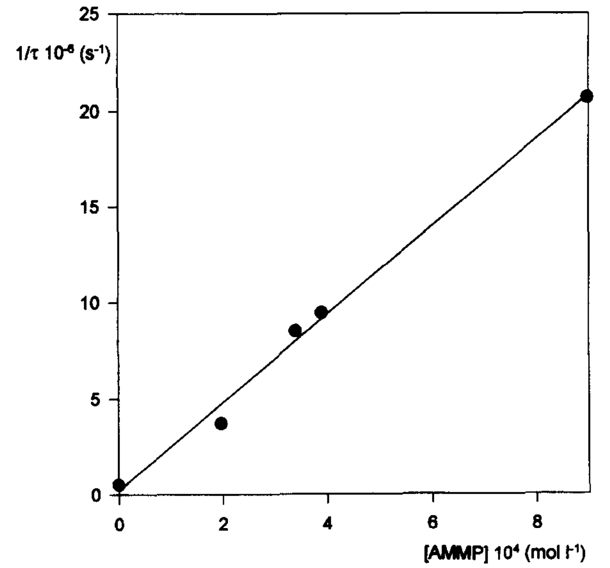


Figure 5 Stern–Volmer plot of the reciprocal value of triplet-state lifetime of thioxanthone moiety in poly(ATX-*co*-AMMP)s as a function of AMMP co-units concentration in toluene solution

poly(ATX-*co*-AMMP)s generates a thioxanthone triplet state whose lifetime is strongly influenced by copolymer composition, τ_{ATX} decreasing on increasing the content of AMMP co-units. Therefore, k_{tr} was calculated by using the usual Stern–Volmer plot (*Figure 5*). Long-lived absorbing species, attributable to thioxanthone ketyl radicals, are observed to a low extent also for these copolymers. However, the amount of the above species decreases on increasing the content of AMMP co-units in the copolymers, i.e. decreasing the lifetime of the thioxanthone triplet state. These results support the hypothesis that the quenching of thioxanthone triplet state by α-morpholinoketone moieties in the copolymers is mainly due to excitation energy transfer, the electron transfer playing a minor role, if any.

As reported in *Table 2*, the value of k_{tr} for poly(ATX-*co*-AMMP)s is two or three orders of magnitude higher than those observed for IBTX/IMMP and poly(ATX-*co*-BA)/poly(AMMP) systems, respectively.

Excitation transfer experiments in HDDA/BA (1 : 1) solution

When excitation transfer experiments are carried out in the equimolar HDDA/BA medium, the IBTX/IMMP system shows a decreased value of k_{tr} with respect to that observed in toluene solution, the reverse occurring for the IBTX/poly(AMMP) and poly(ATX-*co*-BA)/poly(AMMP) systems (*Table 2*). Whereas the first result is in agreement with that previously observed for low-molecular-weight thioxanthone/α-morpholinoketone systems of similar structure upon passing from toluene to HDDA[24], it is more difficult to explain the latter results. A tentative explanation, based on the hypothesis that the macromolecules of poly(AMMP) are more expanded in HDDA/BA than in toluene, thus favouring diffusive effects and hence providing an increased interaction with IBTX and poly(ATX-*co*-BA) excited thioxanthone moieties, may be suggested.

Poly(ATX-*co*-AMMP)s in HDDA/BA solution show a k_{tr} slightly lower than in toluene (*Table 2*) and again two and three orders of magnitude higher than those observed for IBTX/IMMP and poly(ATX-*co*-BA)/poly(AMMP) systems, respectively, in the same medium.

In accordance with the above hypothesis, the lower k_{tr} value of poly(ATX-*co*-AMMP)s in HDDA/BA than in toluene solution may be attributed to the presence of more expanded copolymer coil in the former medium, thus increasing the relative distance between side-chain photosensitive moieties and hence slightly reducing their interaction capability.

The efficiency of the sensitization process (ϕ_{tr}) can be evaluated[7] by the following equation:

$$\phi_{tr} = \frac{k_{tr}[P]}{1/\tau^\circ + k_{tr}[P]}$$

where τ° is the triplet lifetime of thioxanthone in the absence of α-morpholinoketone moieties and [P] is the molar concentration of the α-morpholinoketone (photoinitiator) moieties. In order to evaluate ϕ_{tr} for poly(ATX-*co*-AMMP)s, the τ° value (0.90 μs) of poly(ATX-*co*-BA) has been used. At the 5×10^{-4} M concentration of the photoinitiator, expressed in AMMP co-units (the average value used for excitation experiments), $\phi_{tr} = 0.90$ is calculated for poly(ATX-*co*-AMMP)s. Much lower values for IBTX/IMMP and poly(ATX-*co*-BA)/poly(AMMP) systems are found at the same P concentration (*Table 3*).

The much higher value of ϕ_{tr} observed for poly(ATX-*co*-AMMP)s has therefore to be related to the forced close vicinity of thioxanthone and α-morpholinoketone moieties, when attached to the same macromolecule, this situation strongly favouring the excitation transfer. Indeed, this very efficient process was invoked[11] to explain the very high photoinitiation activity of poly(ATX-*co*-AMMP)s in the u.v. cure of the HDDA/BA equimolar mixture, under irradiation over 380 nm, as compared with that observed for IBTX/IMMP and poly(ATX-*co*-BA)/poly(AMMP) systems at the same overall concentration of thioxanthone and α-morpholinoketone moieties (*Table 3*).

It is worth noting that laser excitation at 355 nm of poly(ATX-*co*-AMMP)s generates a low amount of long-lived absorbing species assignable to thioxanthone ketyl radicals, also in HDDA/BA medium. Moreover, the concentration of the above species does not increase with the content of AMMP co-units in the copolymers. These results suggest that the sensitization process for poly(ATX-*co*-AMMP)s mainly occurs through an energy transfer mechanism also in this medium. A further support to the energy transfer photosensitization mechanism derives from the HDDA/BA u.v. cure data

Table 3 Rate constant (k_{tr}) and efficiency (ϕ_{tr}) of excitation transfer in HDDA/BA (1 : 1) and photoinitiation activity [$(R_c)_{max}$] in the same medium for thioxanthone (TX)/α-morpholinoketone (MK) systems

TX/MK system	$k_{tr} \times 10^{-6}$ ($l\,mol^{-1}\,s^{-1}$)	ϕ_{tr}	$(R_c)_{max}$[a] (s^{-1})
Poly(ATX-*co*-BA)/poly(AMMP)	55	0.02	0.04
IBTX/IMMP	120	0.03	0.2
Poly(ATX-*co*-AMMP)	20000	0.90	1.8

[a] Maximum polymerization rate, expressed as % of conversion per second; concentration of TX in HDDA/BA: 0.1 mol%; MK/TX molar ratio: 1.9. Irradiation time at $\lambda > 380$ nm; 200 s

in the presence of poly(ATX-*co*-AMMP)s, where an improved photoinitiation activity is observed on increasing the content of AMMP co-units at constant concentration of thioxanthone moieties[11]. As the proposed mechanism provides the regeneration of ground-state thioxanthone moieties after each single energy transfer step to the adjacent α-morpholinoketone groups, the presence of more than one photoinitiator moiety in the close vicinity of each thioxanthone group makes possible its involvement in multiple photosensitization steps in the copolymers having a larger content of AMMP co-units, thus improving the overall photoinitiation activity.

CONCLUSIONS

The above reported photophysical studies by laser spectroscopy on low- and high-molecular-weight thioxanthone/α-morpholinoketone systems allows the following concluding remarks to be made.

- Laser excitation at 355 nm in toluene and HDDA/BA solution of poly(ATX-*co*-AMMP)s shows that the excitation transfer between side-chain thioxanthone and α-morpholinoketone moieties is much higher than that observed for the corresponding low-molecular-weight structural model mixtures or for polymeric systems where the two photosensitive groups are attached to distinct polymeric chains. Accordingly, a much higher efficiency of the excitation transfer is found for poly(ATX-*co*-AMMP)s than for IBTX/IMMP and poly(ATX-*co*-BA)/poly(AMMP) systems.
- The low amount of thioxanthone ketyl radicals observed for poly(ATX-*co*-AMMP)s under laser excitation, substantially independent of the copolymer composition, suggests that the photosensitization process is mainly due to energy transfer rather than an electron transfer mechanism, although the latter cannot be completely excluded.
- The improvement of photoinitiation activity in the u.v. cure of HDDA/BA equimolar mixtures, given by poly(ATX-*co*-AMMP)s on decreasing the content of ATX co-units, and the higher triplet state energy level of low-molecular-weight 1-alkoxycarbonyl thioxanthones with respect to alkylthio-α-morpholino acetophenones, having the same structure as ATX and AMMP co-units, support the above conclusion.
- Finally, the presence in the same macromolecule of side-chain thioxanthone and α-morpholino acetophenone moieties, favouring excitation transfer due to the close vicinity of the two photosensitive groups, makes these copolymer systems very promising candidates for practical application to the u.v. cure of pigmented acrylic coatings based on TiO_2 rutile.

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REFERENCES

1 Carlini, C. and Angiolini, L. 'Radiation Curing in Polymer Science and Technology' (Eds J. P. Fouassier and J. F. Rabek), Elsevier Science Publ. Ltd, London and New York, 1993, Vol. II, p. 283

2 Davidson, R. S. *J. Photochem. Photobiol. A: Chem.* 1993, **69**, 263

3 Fabrizio, L. F., Lin, S. O. S. and Jacobine, A. F. *US Pat. 4 536 265*, Loctite Co., 1985

4 Hüsler, R., Kirchmayr, R., Rutsch, W. and Rembold, M. W. *Eur. Pat. Appl. 0 304 886*, Ciba-Geigy AG, 1989

5 Li Bassi, G., Nicora, C., Cadonà, L. and Carlini, C. *Eur. Pat. Appl. 0 161 463*, Fratelli Lamberti S.p.A. and Consiglio Nazionale delle Ricerche, 1985

6 Dietliker, K., Rembold, M. W., Rist, G., Rutsch, W. and Sitek, F. in 'Radcure Europe '87', Proc. 3rd Conference Assoc. Finishing Processes, SME, Deaborn, MI, 1987, pp. 3–37

7 Rist, G., Borer, A., Dietliker, K., Desobry, V., Fouassier, J. P. and Ruhlmann, D. *Macromolecules* 1992, **25**, 4182

8 Dietliker, K. 'Radiation Curing in Polymer Science and Technology' (Eds J. P. Fouassier and J. F. Rabek), Elsevier Science Publ. Ltd, London and New York, 1993, Vol. II, p. 155

9 Rutsch, W., Berner, G. and Kirchmayr, R. in 'Radcure '84', Proc. Conference Assoc. Finishing Processes, SME, Deaborn, MI, 1984, pp. 5–49

10 Desobry, V., Dietliker, K., Hüsler, R., Rutsch, W. and Löliger, H. *Polym. Paint J. Suppl.* 1988, **125**, 96

11 Angiolini, L., Caretti, D., Corelli, E. and Carlini, C. *J. Appl. Polym. Sci.* 1995, **55**, 1477

12 Fouassier, J. P., Lougnot, D. J., Paverne, A. and Wieder, F. *Chem. Phys. Lett.* 1987, **135**, 30

13 Fouassier, J. P. and Burr, D. *Eur. Polym. J.* 1991, **27**, 657

14 Fouassier, J. P. and Ruhlmann, D. *J. Photochem. Photobiol. A: Chem.* 1991, **61**, 47

15 Ruhlmann, D., Wieder, F. and Fouassier, J. P. *Eur. Polym. J.* 1992, **28**, 591

16 Ruhlmann, D., Fouassier, J. P. and Wieder, F. *Eur. Polym. J.* 1992, **28**, 1577

17 Ruhlmann, D. and Fouassier, J. P. *Eur. Polym. J.* 1993, **29**, 27

18 Lamola, A. A. and Roth, H. D. *J. Am. Chem. Soc.* 1974, **96**, 6270

19 Fouassier, J. P. and Lougnot, D. J. *J. Appl. Polym. Sci.* 1986, **32**, 6209

20 Angiolini, L. and Carlini, C. *Chim. Ind. (Milan)* 1990, **72**, 124

21 Carlini, C., Rolla, P. A. and Tombari, E. *J. Appl. Polym. Sci.* 1990, **41**, 805

22 Lougnot, D. J., Turck, C. and Fouassier, J. P. *Macromolecules* 1989, **22**, 108

23 Davis, M. J., Doherty, J., Godfrey, A. A., Green, P. N., Young, J. R. A. and Parrish, M. A. *J. Oil Colour Chem. Assoc.* 1978, **61**, 256

24 Fouassier, J. P. and Ruhlmann, D. *Eur. Polym. J.* 1993, **29**, 505

25 Coqueret, X. and Pouliquer, L. *Macromol. Symp.* 1994, **87**, 17

26 Yates, S. F. and Schuster, G. B. *J. Org. Chem.* 1984, **49**, 3349