Copolymeric Systems with Pendant Thioxanthone and α-Morpholinoacetophenone Moieties as Photosensitizing and Photoinitiating Agents for UV-Curable Pigmented Coatings

LUIGI ANGIOLINI, DANIELE CARETTI, ELENA CORELLI, and CARLO CARLINI*

Dipartimento di Chimica Industriale e dei Materiali, University of Bologna, Viale Risorgimento 4, 40136 Bologna, Italy

SYNOPSIS

The synthesis and structural characterization of copolymers of 1-[(2-acryloyloxy)ethoxycarbonyl]thioxanthone (ATX) with 1-[4-(2-acryloyloxyethylthio)phenyl]-2-methyl-2-morpholino-propan-1-one (AMMP), as well as ATX, AMMP and n-butyl acrylate (BA) terpolymers, is reported. These copolymeric systems have been checked in the photoinitiated polymerization in film matrix of the 1,6-hexanediol diacrylate (HDDA)–BA equimolar mixture under UV irradiation over 380 nm, i.e., under conditions simulating a TiO_2-pigmented acrylic coating formulation, and compared with the corresponding mixture of low-molecular-weight structural models 1-[(2-isobutyroyloxy)ethoxycarbonyl]thioxanthone (ITX) and 1-[4-(2-isobutyroyloxyethylthio)phenyl]-2-methyl-2-morpholino-propan-1-one (IMMP). The much higher photoinitiation activity shown by the copolymers is discussed in terms of close vicinity of thioxanthone and α-morpholinoacetophenone moieties along the backbone, which favors the excitation energy transfer from the former to the latter photosensitive group. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Polymeric systems bearing side-chain photoreactive moieties have recently gained a great deal of interest as photoinitiators for ultraviolet-curable coatings.[1,2] However, their use has been mainly claimed to improve the performances of ultraviolet (UV) clear coatings,[3] particularly in terms of low-odor and nonyellowing properties.[4,5] Indeed, the UV cure of pigmented coatings, particularly white lacquers based on TiO_2 (rutile), due to their strong absorption below 380 nm, fails with photoinitiators usually applied for clear coatings.

Very recently, polymers with pendant 2,6-dimethyl-benzoyldiphenylphosphinoxide moieties, having an appreciable UV absorption over 380 nm (similar to that reported[6,7] for the commercially (BASF) available low-molecular-weight analog "Lucirin TPO"), have been prepared and successfully applied[8] by us in the photocuring of TiO_2-pigmented coatings. However, as these polymeric systems exhibit poorer solubility in the acrylic formulations and lower photoinitiation activity than Lucirin TPO, they do not appear to be completely satisfactory for practical applications.

In order to circumvent the drawback of pigment absorption, the use of thioxanthone derivatives, which display[9] a strong absorption band around 380 nm with a tail over 420 nm, is also recommended, particularly in combination with tertiary amines.[10,11] However, the presence of amines causes yellowing, which generally increases upon further exposure of the coating to light, and is too high for applications in white lacquers.[12,13]

Another approach to this problem is based on the use of a photosensitizer absorbing over 380 nm, capable to efficiently transfer the excitation energy to a photoinitiator, thus promoting the free radical polymerization initiation and crosslinking of unsaturated monomers. The energy transfer may be, however, effective only when the triplet state energy level of the photosensitizer is higher than that of the photoinitiator. Thus, several differently substituted low-molecular-weight thioxanthone–acetophenone derivative systems have been investigated by time-resolved laser spectroscopy[14–19] and time-resolved

chemically induced dynamic nuclear polarization (CIDNP),[20-22] in order to find the most effective couple in terms of excitation energy transfer. Actually, the most favorable photosensitizer–photoinitiator combination is obtained when 1-alkyloxycarbonylthioxanthones or 2-isopropylthioxanthone is jointed to α-aminoacetophenones, and particularly to 1-[4-(methylthio)phenyl]-2-methyl-2-morpholino-propan-1-one (MMMP), giving rise to a remarkable synergistic effect in the UV curing of white pigmented lacquers and blue silk screen inks.[20-24] Indeed, the triplet state energy level of the above-mentioned thioxanthone derivatives (63 and 61.4 kcal mol^{-1}, respectively) is slightly higher than that of MMMP (61 kcal mol^{-1}). In this context, it appeared very interesting to prepare copolymers bearing side-chain 1-alkyloxycarbonylthioxanthone and 1-(4-alkylthiophenyl)-2-methyl-2-morpholino-propan-1-one moieties, as the forced close vicinity of the sensibilizing and photoinitiating species would not only favor the excitation energy transfer and hence increase the UV curing rate of TiO$_2$-pigmented coatings, but also improve their performances in terms of nonyellowing and low-odor properties, due to the macromolecular nature of the system.

Therefore, in the present article the synthesis and structural characterization of copolymers of 1-[(2-acryloyloxy)ethoxycarbonyl]thioxanthone (ATX) with 1-[4-(2-acryloyloxyethylthio)phenyl]-2-methyl-2-morpholino-propan-1-one (AMMP) [poly(ATX-co-AMMP)s] as well as terpolymers of ATX with AMMP and n-butyl acrylate (BA) [poly(ATX-co-AMMP-co-BA)s] is reported.

poly(ATX-co-AMMP) (x + y = 1)
poly(ATX-co-AMMP-co-BA) (x + y < 1)
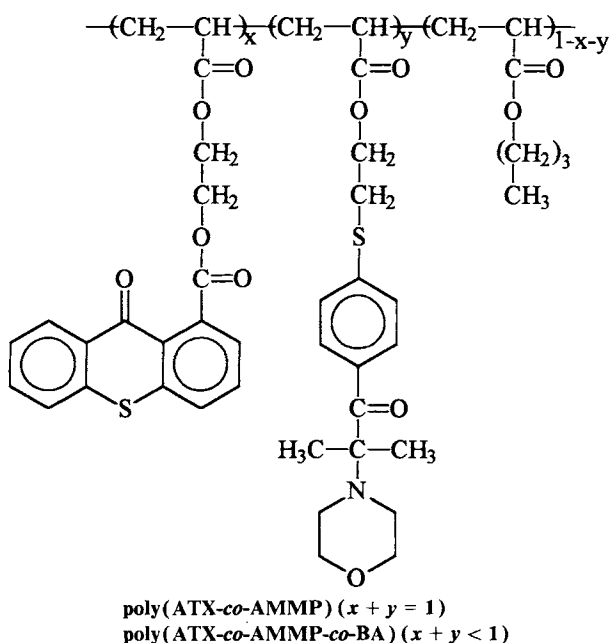
The above systems have been checked in the curing of HDDA–BA equimolar mixture, by UV irradiation at wavelengths over 380 nm in order to simulate the behavior of a TiO$_2$-pigmented acrylic coating, and the results compared with those obtained by using the corresponding mixtures of the homopolymers as well as of the low-molecular-weight structural models 1-[(2-isobutyroyloxy)ethoxycarbonyl] thioxanthone (ITX) and 1-[4-(2-isobutyroyloxyethylthio)phenyl]-2-methyl-2-morpholino-propan-1-one (IMMP), in order to evidence possible synergistic effects.

ITX   IMMP
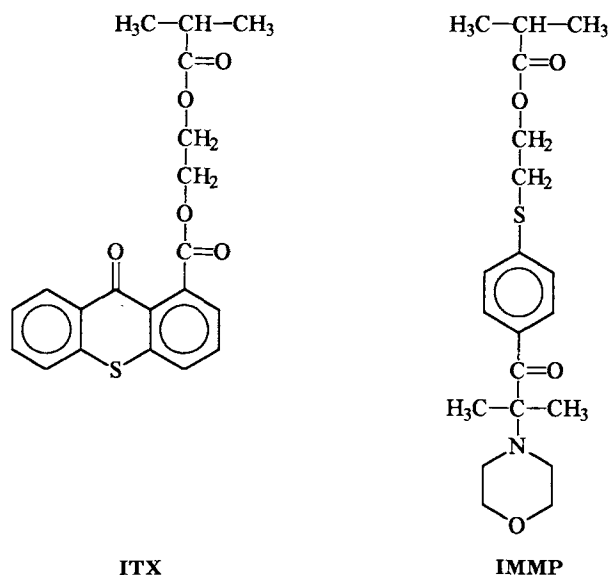
EXPERIMENTAL

Monomers

n-Butyl acrylate (Aldrich) was washed with aq. dil. NaOH and water, in that order, dried on CaCl$_2$, and finally distilled at reduced pressure under nitrogen atmosphere just before use (bp = 50°C/21 mbar). 1,6-Hexanediol diacrylate (HDDA) (Aldrich) was distilled under high vacuum just before use (bp = 94°C/0.02 mbar).

1-[(2-Acryloyloxy)ethoxycarbonyl]thioxanthone (ATX) was synthesized starting from 3-fluorophthalic acid (81 mmol) by reaction[25] with acetic anhydride (89 mmol) to give in 89% yield pure 3-fluoro-phthalic anhydride (FPAn) having mp = 159–160°C (lit.[26]: 163–164°C). FPAn (71 mmol) was then reacted[27] with mercaptobenzene (78 mmol) in anhydrous dimethylformamide (DMF) and in the presence of triethylamine (TEA) (78 mmol) to afford in 86% yield pure 3-phenylthio-phthalic anhydride (PTPAn), having mp = 147–148°C. PTPAn (54 mmol) was treated with a large excess of polyphosphoric acid (140 mmol), in the same conditions as

reported[28] for the analogous reaction of 3-phenyl-thio-phthalic acid, to give 90% yield pure thioxan-thone-1-carboxylic acid (TXC) (mp = 257–258°C). TXC (32 mmol) was refluxed[28] for 5 h in a large excess of thionyl chloride (45 mL) and the resulting solution evaporated under vacuum to dryness, to afford thioxanthone-1-carboxylic acid chloride (TXCC). TXCC was finally allowed to react in situ with freshly distilled 2-hydroxyethyl acrylate (64 mmol) under the same conditions as those reported[28] for the synthesis of the corresponding methacrylic derivative. ATX was isolated as described for the methacrylic compound[28] and crystallized from methanol to give in 42% yield the pure product (mp = 105–107°C).

^{1}H-NMR (CDCl$_3$): 8.5 (dd, 1H, aromatic proton in ortho position to the CO ester group), 7.7–7.4 (m, 6H, other aromatic protons), 6.4 and 5.8 (2dd, 2H, C$\underline{H}_2$=CHCO), 6.1 (dd, 1H, CH$_2$=C$\underline{H}$CO—), 4.7 (t, 2H, ArCOO—C$\underline{H}_2$—CH$_2$—), and 4.6 (t, 2H, ArCOO—CH$_2$—C$\underline{H}_2$—) ppm.

IR (KBr): 3080 (ν_{CH}, aromatic and vinyl group), 2980, 2948, and 2890 (ν_{CH}, aliphatic), 1723 ($\nu_{C=O}$, acrylic and aromatic ester), 1633 ($\nu_{C=O}$, aromatic ketone), 1594, 1581, 1569, 1449 ($\nu_{C=C}$, aromatic), 1417 (δ_{CH2}, vinyl group), 1274 (ν_{C-O}, aromatic ester), 1203 (ν_{C-O}, acrylic ester), 998 (δ_{CH}, vinyl group), and 812, 747, 718, 669 (δ_{CH}, aromatic) cm^{-1}.

1-[4-(2-Acryloyloxyethylthio)phenyl]-2-methyl-2-morpholino-propan-1-one (AMMP) was prepared starting from 1-(4-chlorophenyl)-2-methyl-propan-1-one (CMP), obtained[29] by Friedel-Crafts acylation of chlorobenzene with isobutyroyl chloride. The synthesis provides the chlorination[30] of CMP to give 2-chloro-1-(4-chlorophenyl)-2-methyl-propan-1-one, its transformation[30] by sodium methoxide into 2-(4-chlorophenyl)-3,3-dimethyl-2-methoxy-oxyrane (CDMO); the subsequent reaction of CDMO with morpholine affords 1-(4-chlorophenyl)-2-methyl-2-morpholino-propan-1-one, which is then allowed to react[30] with 2-mercaptoethanol to give 1-[4-(2-hydroxyethylthio)phenyl]-2-methyl-2-morpholino-propan-1-one (HMMP). Finally the reaction[31] of HMMP with acryloyl chloride affords AMMP, which is purified by column chromatography on silica gel (70–230 mesh) using chloroform as eluent (total yield with respect to CMP = 24%).

^{1}H-NMR (CDCl$_3$): 8.5 (d, 2H, aromatic protons in the ortho position to CO group), 7.3 (d, 2H, aromatic protons in the ortho position to S), 6.4 and 5.8 (2dd, 2H, C$\underline{H}_2$=CH—CO—), 6.1 (dd, 1H, CH$_2$=C$\underline{H}$—CO—), 4.4 (t, 2H, —CH$_2$—O—CO—), 3.7 (t, 4H, —CH$_2$—O— in the morpholino ring), 3.3 (t, 2H, —CH$_2$—S—), 2.5 (t, 4H, —CH$_2$—N—), and 1.3 (s, 6H, —CH$_3$) ppm.

IR (liquid film on KBr): 3120, 3082, 3050 (ν_{CH}, aromatic and vinyl group), 2960, 2893, 2853 (ν_{CH}, aliphatic), 1728 ($\nu_{C=O}$, ester group), 1673 ($\nu_{C=O}$, aromatic ketone), 1635, 1620 ($\nu_{C=C}$, acrylic group), 1586, 1552 ($\nu_{C=C}$, aromatic), 1408 (δ_{CH2}, vinyl group), 1385, 1374 (δ_{CH}, geminal methyl groups in isopropyl moiety), 981 (δ_{CH}, vinyl group), and 836 (δ_{CH}, disubstituted phenyl ring) cm^{-1}.

Low-Molecular-Weight Models

1-[4-(2-Isobutyroyloxy)ethoxycarbonyl]thioxanthone (ITX) was obtained in 17% yield starting from TXCC and 2-hydroxyethyl isobutyrate (HEI) with the same procedure above reported for the synthesis of ATX. HEI, in turn, was synthesized by dropping, at 0°C under dry nitrogen, isobutyroyl chloride (0.14 mol), dissolved in an equal volume of tetrahydrofuran (THF) to ethylene glycol (0.14 mol) in 200 mL of anhydrous THF and in the presence of TEA (0.14 mol). Then, the reaction mixture was maintained at room temperature for 2 h, filtered and the resulting THF solution evaporated under vacuum. The residual liquid was diluted with diethyl ether and washed with water. The ethereal layer, after drying on Na$_2$SO$_4$ and removal of the solvent, was distilled under reduced pressure to obtain in 18% yield pure HEI (bp = 101°C/19 mbar). Pure ITX (mp = 98–100°C) was obtained by crystallization from methanol.

^{1}H-NMR (CDCl$_3$): 8.5 (d, 1H, aromatic proton in the ortho position to the CO group), 7.7–7.3 (m, 6H, other aromatic protons), 4.7 (t, 2H, ArCOOC$\underline{H}_2$—CH$_2$—), 4.6 (t, 2H, ArCOO—CH$_2$—C$\underline{H}_2$—), 2.6 (hept, 1H, —C$\underline{H}$—), and 1.2 (d, 6H, —CH$_3$) ppm.

IR (KBr): 3083 (ν_{CH}, aromatic), 2969 (ν_{CH}, aliphatic), 1729 ($\nu_{C=O}$, aliphatic and aromatic ester groups), 1634 ($\nu_{C=O}$, aromatic ketone), 1593, 1583, 1472 ($\nu_{C=C}$, aromatic), 1386, 1375 (δ_{CH}, gem. methyl groups), 1262 (ν_{C-O}, aromatic ester), 1192 (ν_{C-O}, aliphatic ester), and 802, 746, 734, 668 (δ_{CH}, aromatic) cm^{-1}.

1-[4-(2-Isobutyroyloxyethylthio)phenyl]-2-methyl-2-morpholino-propan-1-one (IMMP) was prepared in 82% yield with the same procedure described for the synthesis of AMMP, starting from HMMP and isobutyroyl chloride.

^{1}H-NMR (CDCl$_3$): 8.5 (d, 2H, aromatic protons in the ortho position to the CO group), 7.3 (d, 2H, aromatic protons in the ortho position to S), 4.3 (t, 2H, —CH$_2$—OCO—), 3.7 (t, 4H, —CH$_2$—O— in the morpholine ring), 3.2 (t, 2H, —CH$_2$—S—), 2.6 (m, 5H, —CH$_2$—N—CH$_2$— and —CH—),

1.3 [s, 6H, —C(CH₃)₂—N—], and 1.1 [d, 6H, —CH(C$\underline{H}$₃)₂—] ppm.

IR (KBr): 3066 (ν_{CH}, aromatic), 2975, 2852 (ν_{CH}, aliphatic), 1738 ($\nu_{C=O}$, ester group), 1673 ($\nu_{C=O}$, aromatic ketone), 1586, 1551 ($\nu_{C=C}$, phenyl ring), 1387, 1362 (δ_{CH}, gem. methyl groups), 835 (δ_{CH}, 1,4-disubstituted phenyl ring) cm^{-1}.

Polymeric Photoinitiators

Homopolymers and copolymers were prepared by free radical polymerization in THF or benzene solution, using 2 wt % (with respect to the monomers) of 2,2′-azobisisobutyronitrile (AIBN) as thermal initiator. The monomers were introduced into glass vials under dry nitrogen and submitted to several freeze–thaw cycles. After sealing under high vacuum, the vials were kept at 70°C for 150–170 h in the dark. The polymeric product was isolated by pouring the reaction mixture into a large excess of petroleum ether. The coagulated polymer was redissolved in chloroform, precipitated again into petroleum ether, filtered, dried under vacuum, and finally stored in the refrigerator in the dark. All the polymer samples were characterized by ¹H-NMR and FT-IR analyses. The most relevant properties of the polymers are reported in Table I.

Photoinitiation Activity Experiments

HDDA–BA equimolar mixtures containing 0.1 mol % of photosensitizer, in terms of thioxanthone chromophores, and a higher content of morpholinoketone moieties were cured on film matrix (200 μm), at 25°C under nitrogen, by irradiation with a high-pressure 100-W OSRAM HBO Hg lamp equipped with a glass-colored passband filter LG-400 (Corion Corporation) in order to absorb completely the UV light below 380 nm. All the curing experiments were carried out at the same irradiation intensity, as detected by a photodiode, by properly defocusing the elliptical mirror that collects the light emitted by the lamp.[32] The time evolution of the curing process was followed by microwave dielectrometry at 9.5 GHz, in terms of ε'' (loss factor) as previously reported.[32,33]

Physicochemical Measurements

¹H-NMR spectra were performed at 200 MHz on samples in CDCl₃ solution by using a Varian FT-NMR Gemini 200 spectrometer and TMS as internal standard. UV absorption spectra of the polymeric samples were recorded at 25°C in CHCl₃ solution on a Kontron Instruments Model UVICON 860 spectrophotometer. The spectral region between 500 and 250 nm was investigated by using cell path

Table I Synthesis, by Free Radical Initiation,[a] and Structural Characterization of Photosensitive Homopolymers [poly(ATX) and poly(AMMP)] and Copolymers [poly(ATX-co-AMMP)s, poly(ATX-co-AMMP-co-BA)s and poly(ATX-co-BA)]

Feed (mol%)			Conv.[b] (%)	Polymeric Product[c]				
ATX	AMMP	BA		ATX Co-units (mol %)	AMMP Co-units (mol %)	BA Co-units (mol %)	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
100	0	0	95	100	0	0	11,400	2.5
0	100[d]	0	21	0	100	0	2,700	2.5
10	90	0	46	11	89	0	3,800	2.1
25	75	0	71	24	76	0	3,200	2.1
33	67	0	82	35	65	0	3,900	2.0
50	50	0	93	45	55	0	3,400	1.8
13	37	50	25	17	42	41	3,800	2.2
17	33	50	28	23	39	38	3,400	2.2
50	0	50	73	52	0	48	4,800	2.3

[a] In THF solution if not otherwise indicated; duration: 150–170 h.

[b] Calculated as (wt of polymer/wt of monomers) × 100.

[c] Composition was evaluated by ¹H-NMR anaysis; number-average molecular weights ($\bar{M}_n$) and their distribution ($\bar{M}_w/\bar{M}_n$) determined by SEC measurements.

[d] In benzene solution.

lengths of 1 and 0.1 cm; molar extinction coefficient values (ε) are expressed in liters per mole per centimeter (L mol^{-1} cm^{-1}).

FT-IR spectra were carried out on a Perkin-Elmer Model 1750 spectrophotometer equipped with a Perkin–Elmer Model 7700 data station. The samples were prepared as KBr pellets or as liquid films between KBr discs. Average molecular weights of the polymeric samples were determined by a HPLC Waters Millipore 590 apparatus equipped with an injector Model U6K, a Waters 500 Å gel column and a Perkin–Elmer UV-VIS detector Model LC-95, working at 254 nm. CHCl$_3$ was used as eluent. The calibration curve was obtained by using several monodisperse polystyrene standards.

RESULTS AND DISCUSSION

Synthesis of the Photosensitive Polymers

The preparation of poly(ATX-co-AMMP)s with a content of ATX co-units lower than 50 mol % was planned as it is known[34] that low-molecular-weight thioxanthone derivatives usually display a poor solubility in coating formulations. Another reason suggesting the use of copolymers containing a minor amount of ATX with respect to AMMP co-units is based on the consideration that the photosensitization mechanism, in principle, does not provide the consumption of thioxanthone moieties as they are regenerated after each single energy transfer step, only a catalytic amount of them being therefore required. However, a content of thioxanthone larger than 10 mol % was considered reasonable because other contemporary photochemical processes, such as electron transfer with tertiary amines,[35] due to the presence of morpholine moieties in AMMP co-units, and hydrogen abstraction from donor molecules, can cause the photoreduction of thioxanthone moieties, thus progressively reducing their amount in the copolymers during the UV cure of the formulation.

Therefore, ATX–AMMP mixtures containing 10–50 mol % of ATX were submitted to free radical copolymerization in THF solution at 70°C. Moreover, in order to improve the solubility of the polymers bearing side-chain thioxanthone and α-morpholinoacetophenone moieties, terpolymerization experiments were also carried out by using feeds containing 50 mol % of BA as the third component (Table I). Finally, homopolymers of AMMP and ATX [poly(AMMP) and poly(ATX), respectively]

were prepared in order to compare the photoinitiation activity of their mixtures with that of the corresponding copolymers in the UV curing of HDDA–BA formulations. A copolymer of ATX with BA [poly(ATX-co-BA)] was also prepared for replacing poly(ATX) in the mixtures with poly(AMMP), as poly(ATX) resulted practically insoluble in the acrylic formulation.

^{1}H-NMR analysis (Fig. 1) of the obtained polymeric samples does not show any evidence of signals, in the 6.4–5.8 ppm region, assignable to acrylic protons of ATX, AMMP, and BA monomers, thus clearly indicating that the homo- and copolymerizations occurred by a free radical chain addition mechanism involving the acrylic functions. Accordingly, in the IR spectra of the above polymers (Fig. 2) no bands appear in the 1417–1408 cm^{-1} region, connected with the CH$_2$ scissoring vibrations of the vinyl group in the acrylic functions and present in ATX and AMMP monomers (see Experimental).
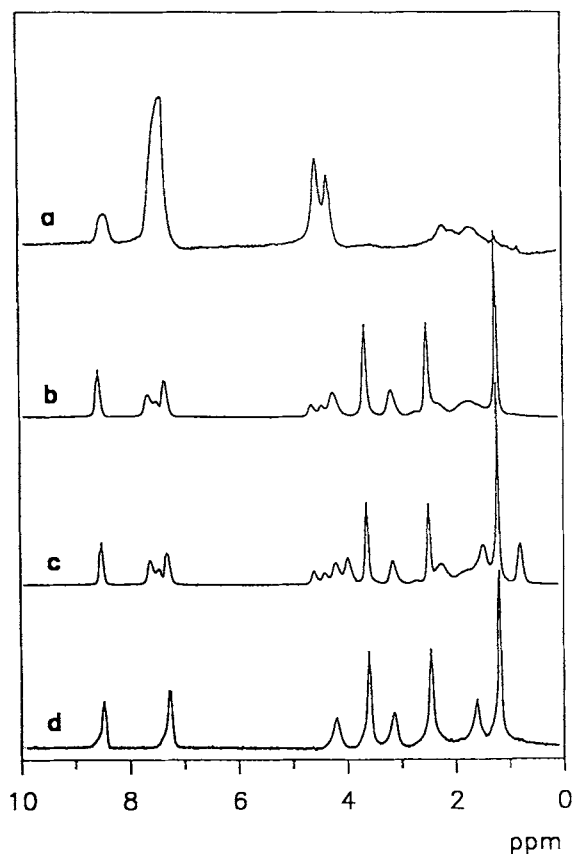

Figure 1 ^{1}H-NMR of (a) poly(ATX), (b) poly(ATX-co-AMMP) containing 24 mol % of ATX co-units, (c) poly(ATX-co-AMMP-co-BA) containing 17 and 42 mol % of ATX and AMMP co-units, respectively, (d) poly(AMMP).
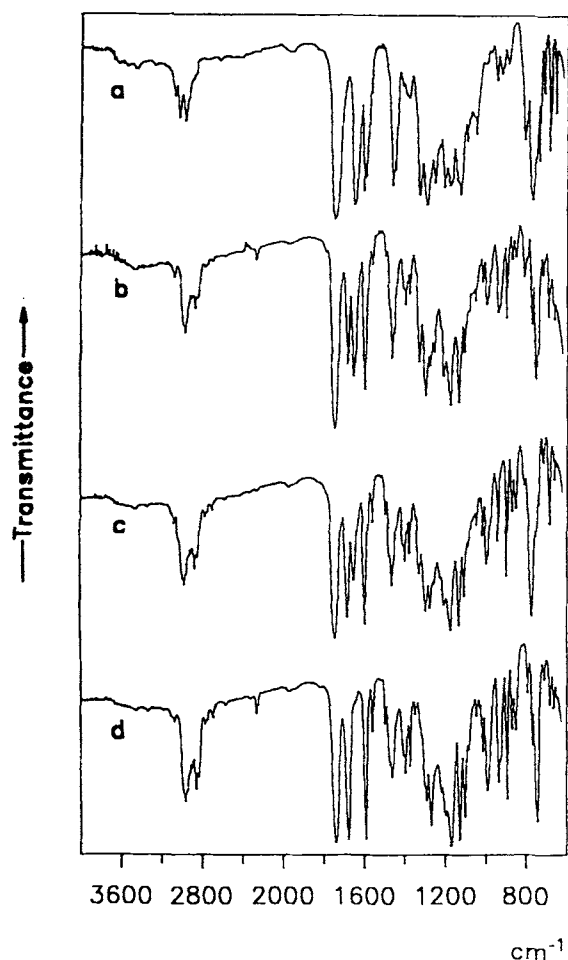
Figure 2 FT-IR spectra of (a) poly(ATX) and of poly(ATX-*co*-AMMP)s containing (b) 45 and (c) 24 mol % of ATX co-units, respectively, as well as of (d) poly(AMMP).

Moreover, IR bands at about 1735, typical of the ester group present in all co-units, as well as at 1672 and 1640 cm^{-1}, characteristic of the ketone moieties in ATX and AMMP co-units, respectively, whose relative intensity changes on composition, are observed, thus confirming the expected structure. Copolymer composition was determined by ^{1}H-NMR analysis. In particular, the relative content of the two co-units in poly(ATX-*co*-AMMP)s was evaluated by comparing the integrated signals located in the 4–3 ppm region, assigned to the methylene groups bound to oxygen in the morpholine ring and to sulfur atom in AMMP co-units, with the resonances at 9–7 ppm of the aromatic protons related to both ATX and AMMP co-units. In the case of poly(ATX-*co*-AMMP-*co*-BA)s the comparison of the areas of the signals in the 3.8–3.0 ppm region,

due to only AMMP co-units, with those at 9–7 ppm, connected with the aromatic protons of ATX and AMMP co-units, and at 5–0 ppm, related to the aliphatic protons belonging to all the three co-units, allows one to determine the copolymers composition. In ATX–AMMP copolymerization experiments the conversion results (Table I) too high (> 45%) to allow one to correctly evaluate the comonomers reactivity ratios. However, taking into account that the composition of poly(ATX-*co*-AMMP)s, independently from the conversion degree, is very close to that of the corresponding feed, it may be concluded that the above copolymers display a substantially random distribution of the two photosensitive units. In the case of ATX–AMMP–BA copolymerizations it is possible to see that BA is less reactive than the other two comonomers, the resulting terpolymers being enriched in ATX and AMMP co-units. Moreover, the presence of BA in the feed appreciably reduces the copolymerization conversion, thus confirming its minor reactivity. The copolymerization conversion for the ATX–AMMP system decreases on increasing the content of AMMP in the feed (Table I). The examination of the average molecular weight of the polymeric products clearly indicates that poly(ATX) and poly(AMMP) display the highest and the lowest values, respectively, whereas copolymers and terpolymers show an intermediate behavior (Table I). A possible explanation of the above phenomenon can be based on the consideration that in the AMMP comonomer a tertiary amine group is present that may behave as a chain transfer agent,[36] thus reducing the average molecular weight of the macromolecules. In addition, taking into account that the reinitiation process by the generated alkylamino radicals is usually[36] slower than the chain propagation process, the overall polymerization rate is lowered and hence the conversion to polymer. Indeed, analogous results were obtained in the copolymerization of benzoin methyl ether acrylic derivatives and *N,N*-dialkylamino acrylates.[37]

It is well established that the thioxanthone chromophore displays in the near UV two distinct absorption bands centered at about 260 and over 380 nm, related to the $\pi \to \pi^*$ and $n \to \pi^*$ electronic transitions of the aromatic system and ketone group, respectively.[10,22] However, this last transition seems to contain a partial $\pi \to \pi^*$ character, as suggested by the occurrence of a small hypsochromic shift on increasing the solvent polarity.[34,38,39] As a triplet, $n \to \pi^*$ transition is generally insensitive to changes in solvent polarity, the observed blue shift of the phosphorescence emission maximum confirms the

Table II UV Absorption Spectra in Chloroform Solution of Photosensitive Polymers Based on Thioxanthone and α-Morpholinoacetophenone Moieties as Well as of the Corresponding Low-Molecular-Weight Structural Models

Sample	Thioxanthone Moiety			α-Morpholinoacetophenone Moiety		
	mol %[a]	λ^{b} (nm)	ε^{b} (L mol^{-1} cm^{-1})	mol %[a]	λ^{b} (nm)	ε^{b} (L mol^{-1} cm^{-1})
Poly(ATX)	100	386	5,300	—	—	—
Poly(ATX-co-BA)	52	385	6,600	—	—	—
ITX	100	385	7,100	—	—	—
Poly(ATX-co-AMMP)	11	386	6,400	89	302	14,300
Poly(ATX-co-AMMP)	24	386	6,900	76	302	14,600
Poly(ATX-co-AMMP)	35	386	6,900	65	303	14,300
Poly(ATX-co-AMMP)	45	386	6,500	55	303	14,700
Poly(ATX-co-AMMP-co-BA)	17	386	6,100	42	302	15,000
Poly(ATX-co-AMMP-co-BA)	23	386	6,900	39	302	14,900
Poly(AMMP)	—	—	—	100	301	14,500
IMMP	—	—	—	100	303	15,400

[a] Determined by ^{1}H-NMR analysis.
[b] Value corresponding to the absorption maximum.

involvement of π character of the lowest triplet excited state, which indeed is enhanced in polar solvents.[40] The low-molecular-weight structural model ITX shows, as expected, both the absorption bands in the cited spectral regions. In particular, the structured band connected with the $n \rightarrow \pi^{*}$ electronic transition, usually involved in photosensitization and photoinitiation processes, exhibits a maximum at 385 nm with a molar extinction coefficient (ε) of 7100 L mol^{-1} cm^{-1} and a tail extending over 410 nm (Table II, Fig. 3). A similar absorption spectrum is shown by poly(ATX), the $n \rightarrow \pi^{*}$ transition of which displays, however, a significant hypochromic effect, its ε_{max} value being 5300 L mol^{-1} cm^{-1} (Table II, Fig. 3). This behavior can be attributed to dipole–dipole electronic interactions of side-chain thioxanthone chromophores along the polymer backbone[41,42] and has been previously observed in several polymeric systems bearing side-chain aromatic chromophores.[43–45] Accordingly, poly(ATX-co-BA) exhibits (Table II) an intermediate ε value, due to the insertion of BA co-units, which distantiate the thioxanthone chromophores along the polymer chain. The ε values obtained for poly(ATX-co-AMMP)s and poly(ATX-co-AMMP-co-BA)s substantially confirm this picture (Table II).

Considering now the α-morpholinoacetophenone moiety, it has to be pointed out that the presence of a thioalkyl substituent in the para position of the phenyl ring markedly modifies the absorption characteristics of this chromophore with respect to the

unsubstituted benzoyl group. In fact, the presence of the thioalkyl group implies the shift of the $\pi \rightarrow \pi^{*}$ electronic transition from 250 to slightly over 300 nm, thus completely obscuring the much less intense $n \rightarrow \pi^{*}$ transition of the ketone moiety.[17,18] Indeed, IMMP displays in the near UV only an absorption band with a maximum at 303 nm (Table II, Fig. 4), analogously to what was observed for MMMP.[17,20] A similar UV spectrum is given by poly(AMMP), although an appreciable hypochro-
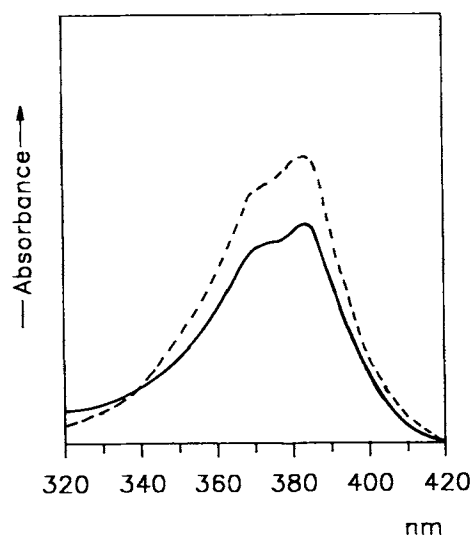

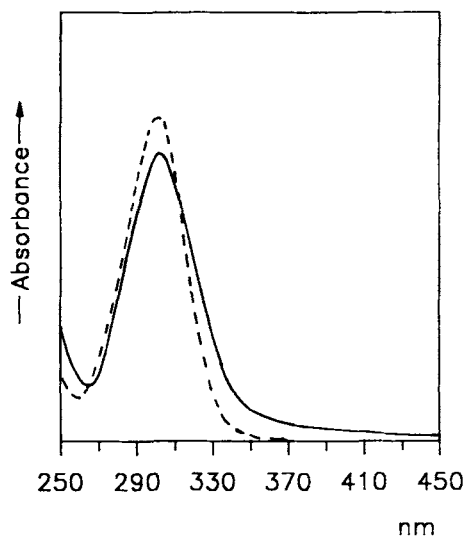**Figure 3** UV spectra in chloroform solution of (——) poly(ATX) and (-----) ITX.

Figure 4 UV spectra in chloroform solution of (———)
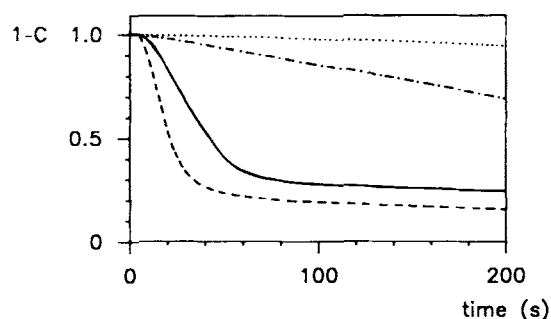poly(AMMP) and (-----) IMMP.

Figure 5 Residual monomers concentration $(1 - C)$ vs.
time in the UV curing, in film matrix and under nitrogen,
of the HDDA-BA equimolar mixture, upon irradiation
over 380 nm in the presence of (· · · · · · · ·) poly(ATX-
co-BA)-poly(AMMP) with a 35/65 ATX-AMMP molar
ratio; (-·-·-·-·) ITX-IMMP with a 35/65 molar ratio,
as well as of poly(ATX-co-AMMP)s with (———) 35 and
(-----) 11 mol % of ATX co-units, respectively.

mism is present (Table II, Fig. 4). Moreover, a tail
expending over 450 nm is observed in the UV spec-
trum of this polymeric sample (Fig. 4). This tail is
not, however, present in IMMP and in all copolymer
samples, its absorption substantially vanishing over
380 nm. In poly(ATX-co-AMMP)s and poly(ATX-
co-AMMP-co-BA)s ε values of the $n \rightarrow \pi^*$ absorp-
tion band usually lie between those of poly(AMMP)
and IMMP and substantially increase on decreasing

the content of AMMP co-units (Table II), thus sug-
gesting that dipole–dipole interactions between α-
morpholinoacetophenone moieties also occur to an
extent that depends on the distance of the inter-
acting chromophores.

Photoinitiating Activity

The time evolution of the UV curing of the HDDA–
BA equimolar mixture, in the presence of equal

Table III UV Curing of the HDDA–BA Equimolar Mixture, in Film Matrix and under Nitrogen, in the
Presence of High- and Low-Molecular-Weight Thioxanthone (TX) and α-Morpholinoacetophenone (MK)
Systems, by Irradiation over 380 nm

	Photoinitiating System[a]				
Type	TX (mol %)	MK (mol %)	t_0[b] (s)	$t_{1/2}$[c] (s)	(R_c)max[d] (s^{-1})
Poly(ATX-co-AMMP)	35	65	10	41	1.8
Poly(ATX-co-BA)[e]–poly(AMMP)	35	65	87	[f]	0.04
ITX–IMMP	35	65	17	[f]	0.2
Poly(ATX-co-AMMP)	11	89	6	22	3.4
Poly(ATX-co-AMMP)	24	76	13	36	2.4
Poly(ATX-co-AMMP)	45	55	10	56	1.4
Poly(ATX-co-AMMP-co-BA)[g]	23	39	13	51	1.5
Poly(ATX-co-AMMP-co-BA)[h]	17	42	10	41	1.8

[a] Induction period.
[b] Thioxanthone moiety concentration: 0.1 mol %.
[c] Time required for reaching 50% conversion of HDDA-BA mixture.
[d] Maximum polymerization rate, expressed as percentage of conversion over time.
[e] Poly(ATX-co-BA) was used in the place of poly(ATX), this last being insoluble in the HDDA–BA mixture.
[f] Not determined, as a conversion lower than 50% was obtained at the end of the curing experiments (200 s).
[g] In this sample the MK–TX molar ratio was similar to that of poly(ATX-co-AMMP) with 35 mol % of ATX co-units.
[h] In this sample the MK–TX molar ratio was similar to that of poly(ATX-co-AMMP) with 24 mol % of ATX co-units.
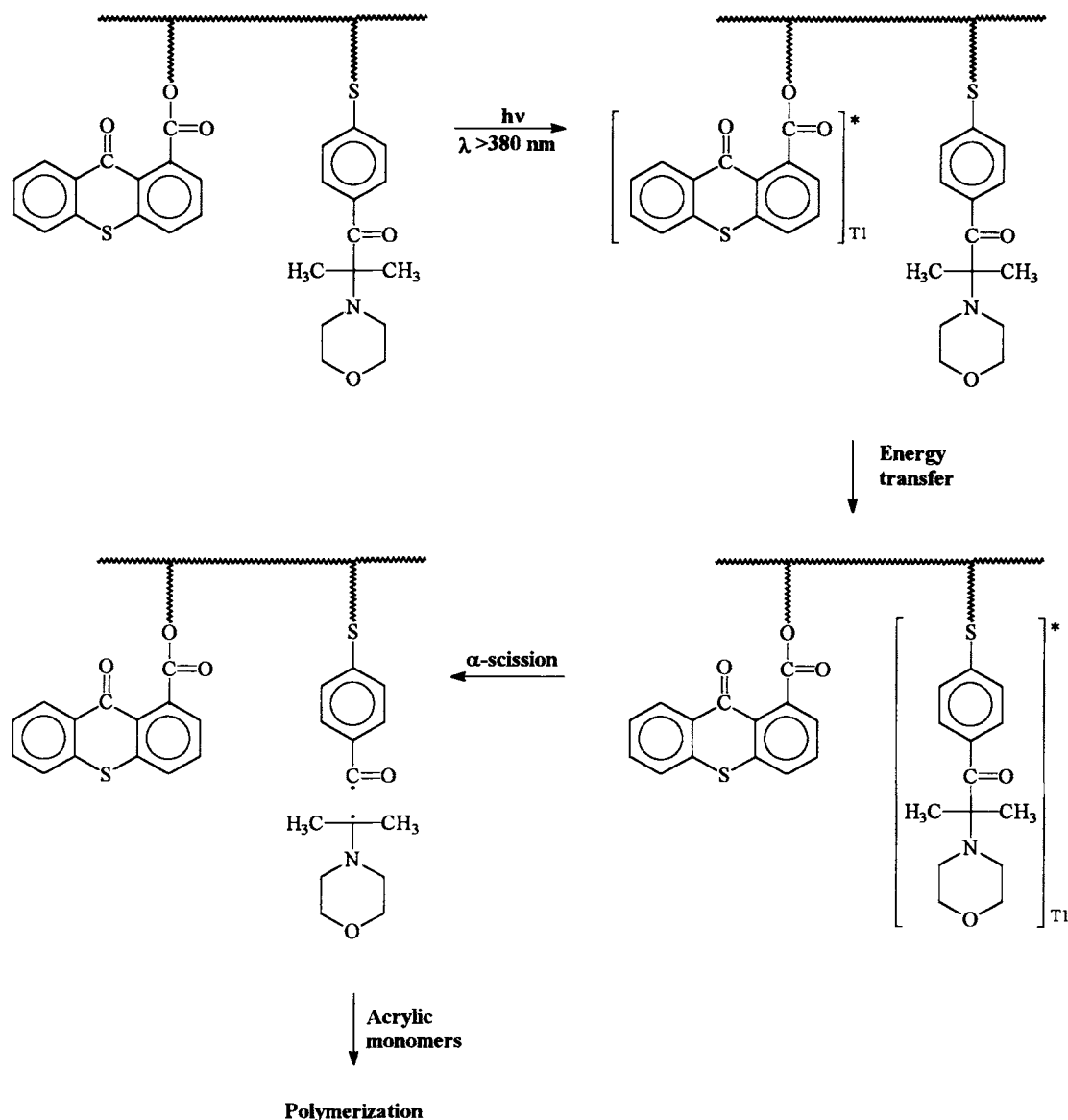
Scheme 1

amounts, in terms of thioxanthone moieties, of high- and low-molecular-weight photoinitiators, has been monitored by microwave dielectrometry (see Experimental). This technique allows one to determine the induction period (t_0), the half-time of the curing process $(t_{1/2})$ as well as the maximum of curing rate $[(R_c)_{max}]$. All curing experiments have been carried out in film matrix and under nitrogen, by employing the same irradiation intensity and a passband filter that completely absorbs the light below 380 nm, thus simulating the conditions of a TiO_2-pigmented acrylic coating formulation. Under this irradiation situation, the α-morpholinoacetophenone moieties cannot be directly excited by light and thioxanthone

chromophores are the only species absorbing in this spectral region. The photoinitiation activity of poly(ATX-co-AMMP) containing 35 mol % of ATX co-units has been compared with that obtained in the presence of the corresponding mixture of poly(ATX-co-BA) and poly(AMMP) as well as of the low-molecular-weight structural models ITX and IMMP. As reported in Table III, the copolymer sample displays a much higher photoinitiating activity, its $(R_c)_{max}$ value being 1 and 2 orders of magnitude larger than that found for the ITX–IMMP and poly(ATX-co-BA)–poly(AMMP) systems, respectively. Indeed, as shown in Figure 5, the curing process is very slow when the ITX–IMMP mixture

is used (after 200 s of irradiation the conversion of the HDDA–BA mixture was only 30%) and practically absent in the case of poly(ATX-co-BA)–poly(AMMP) system. The much higher cure efficiency of poly(ATX-co-AMMP) may be related to the fact that the photosensitizing and photoinitiating moieties are forced to be close to each other along the macromolecule, thus favoring the intramolecular excitation energy transfer from the thioxanthone triplet state to the ground state α-morpholino-acetophenone chromophore, as represented in Scheme 1.

In the case of the ITX–IMMP mixture, the photosensitizer and the photoinitiator are homogeneously distributed in the formulation and their average distance is much longer than in the copolymer system, thus strongly reducing the efficiency of the energy transfer. This picture is confirmed by the lowest photoinitiation activity of the poly(ATX-co-BA)–poly(AMMP) system. In fact, in this case photosensitizing and photoinitiating species belong to different macromolecules and the probability that an interaction between the two moieties occurs may be even lower than in the case of the ITX–IMMP system, thus causing a dropping of the efficiency of the excitation energy transfer.

Moreover, this result clearly indicates that in the poly(ATX-co-BA)–poly(AMMP) system the excited thioxanthone moieties appear also unable to give intramolecular hydrogen abstraction for generating free radical initiating species, contrary to what was previously observed for benzophenone-containing polymers.[33,46,47] The photoinitiation activity of poly(ATX-co-AMMP-co-BA)s is lower, as based on $t_{1/2}$ and $(R_c)_{max}$ values (Table III), than that of the corresponding poly(ATX-co-AMMP)s having similar ATX–AMMP molar ratio [compare poly(ATX-co-AMMP-co-BA)s with 17 and 23 mol % of ATX co-units with poly(ATX-co-AMMP)s having 24 and 35 mol % of ATX co-units, respectively], in agreement with the above proposed energy transfer mechanism. In fact, the insertion of BA co-units along the backbone increases the average distance between ATX and AMMP co-units in the macromolecules, thus reducing the photosensitization efficiency, although their molar ratio remains substantially unchanged with respect to the corresponding poly(ATX-co-AMMP) samples.

A detailed examination of the behavior of the different samples of poly(ATX-co-AMMP)s clearly indicates (Table III) that the photoinitiation activity increases on decreasing the content of ATX co-units in the copolymer, reaching the maximum value in the case of poly(ATX-co-AMMP) with 11 mol % of

ATX co-units (Fig. 5). These data are in agreement with the proposed photosensitization mechanism that provides the regeneration of ground-state thioxanthone moieties after each single energy transfer step to the adjacent α-morpholinoaceto-phenone chromophores, which give rise to free radical initiating species after α-scission. Indeed, in the copolymer samples with a low amount of ATX co-units, the presence of more than one α-morpholi-noacetophenone group in the close vicinity of each thioxanthone moiety makes possible its involvement in multiple photosensitization steps with the neighboring AMMP co-units, thus improving the overall photoinitiation activity.

As far as the induction period values (t_0) of the UV curing experiments are concerned, it is worth noting that a reduction of t_0 is in general accompanied by an increase of AMMP co-units content in the copolymer systems (Table III). This behavior, although t_0 values may be affected by unequal traces of oxygen dissolved in the HDDA–BA formulation during the preparation of the sample submitted to UV irradiation, seems to suggest that the tertiary amine functions of the morpholine groups behave also as oxygen scavengers, probably through a chain mechanism involving α-alkylamino- and peroxy-radicals, as previously proposed in copolymeric photoinitiating systems bearing side-chain benzoin methyl ether and tertiary amine moieties.[37]

It cannot be, however, excluded that exciplexes formation between adjacent excited thioxanthone and ground state α-morpholinoacetophenone moieties may occur. In this case, the subsequent electron and proton transfers would give rise to the generation of ketyl and α-aminoalkyl radicals, these last being the active initiating species in the UV cure of the acrylic formulation. However, this activation mechanism should play a minor role, in accordance to what was found[21] for the corresponding low-molecular-weight 1-methoxycarbonyl-thioxanthone–MMMP system in a HDDA–epoxyacrylate (1 : 1) medium, very similar to our HDDA–BA equimolar mixture, in terms of viscosity and polarity properties.

Photophysical studies by time-resolved laser spectroscopy are in progress in order to better clarify this point.

CONCLUSIONS

1. Copolymers and terpolymers containing side-chain 1-alkoxycarbonyl thioxanthone and α-

morpholinoacetophenone moieties have been prepared and fully characterized.

2. The above-mentioned polymeric systems, upon irradiation conditions simulating a TiO_2-pigmented coating, result much more active than the corresponding low-molecular-weight structural models mixtures as well as the homopolymers combinations in the UV cure of acrylic formulations.

3. All the kinetic data of UV cure experiments suggest that the main contribution to the photoinitiation activity of the copolymeric systems derives from a very efficient sensitization mechanism, which involves the excitation energy transfer from the thioxanthone triplet state to the ground state adjacent α-morpholinoacetophenone moieties.

4. These photosensitizer–photoinitiator polymeric systems appear very promising as future candidates to overcome the drawbacks inherent to the UV cure of white pigmented coating formulations.

REFERENCES

1. C. Carlini and L. Angiolini, in *Radiation Curing in Polymer Science and Technology*, J. P. Fouassier and J. F. Rabek, Eds., Elsevier Science, London, 1993, Vol. II, p. 283.
2. R. S. Davidson, *J. Photochem. Photobiol. A: Chem.*, **69**, 263 (1993).
3. L. F. Fabrizio, S. O. S. Lin, and A. F. Jacobine, U.S. Pat. 4,536,265 (1985) (to Loctite Co.).
4. R. Hüsler, R. Kirchmayr, W. Rutsch, and M. Rembold, Eur. Pat. Appl., 0,304,886 (1989) (to Ciba-Geigy AG).
5. G. Li Bassi, C. Nicora, L. Cadonà, and C. Carlini, Eur. Pat. Appl. 0,161,463 (1985) (to Fratelli Lamberti S.p.A. and Consiglio Nazionale delle Ricerche).
6. T. Sumiyoshi, W. Schnabel, A. Henne, and P. Lechtken, *Polymer*, **26**, 141 (1985).
7. P. Lechtken, I. Buethe, and A. Hesse, Ger. Pat. 2,830,927 (1980) (to BASF AG).
8. L. Angiolini, D. Caretti, and C. Carlini, *J. Appl. Polym. Sci.*, to appear.
9. K. Meier and H. Zweifel, *J. Photochem.*, **35**, 353 (1986).
10. M. J. Davis, J. Doherty, A. A. Godfrey, P. N. Green, J. R. A. Young, and M. A. Parrish, *J. Oil Colour Chem. Assoc.*, **61**, 256 (1978).
11. L. R. Gatechair and D. Wostratzky, *J. Radiat. Curing*, **10**(3), 4 (1983).
12. M. Jacobi, A. Henne, and A. Böttcher, *Polym. Paint Colour J.*, **175**, 636 (1985).
13. M. Jacobi, A. Henne, and A. Böttcher, *Adhäsion*, **4**, 6 (1986).
14. J. P. Fouassier, D. J. Lougnot, A. Paverne, and F. Wieder, *Chem. Phys. Lett.*, **135**, 30 (1987).
15. J. P. Fouassier and D. Burr, *Eur. Polym. J.*, **27**, 657 (1991).
16. J. P. Fouassier and D. Ruhlmann, *J. Photochem. Photobiol. A: Chem.*, **61**, 47 (1991).
17. D. Ruhlmann, F. Wieder, and J. P. Fouassier, *Eur. Polym. J.*, **28**, 591 (1992).
18. D. Ruhlmann, J. P. Fouassier, and F. Wieder, *Eur. Polym. J.*, **28**, 1577 (1992).
19. D. Ruhlmann and J. P. Fouassier, *Eur. Polym. J.*, **29**, 27 (1993).
20. K. Dietliker, M. W. Rembold, G. Rist, W. Rutsch, and F. Sitek, in *Radcure Europe '87*, Proceedings of 3rd Conference Association of Finishing Processes, SME, Deaborn, MI, 1987, p. 3–37.
21. G. Rist, A. Borer, K. Dietliker, V. Desobry, J. P. Fouassier, and D. Ruhlmann, *Macromolecules*, **25**, 4182 (1992).
22. K. Dietliker, in *Radiation Curing in Polymer Science and Technology, Photoinitiating Systems*, J. P. Fouassier and J. F. Rabek, Eds., Elsevier Science, London, 1993, Vol. II, p. 155.
23. W. Rutsch, G. Berner, and R. Kirchmayr, in *Radcure '84*, Proceedings of Conference of Association of Finishing Processes, SME, Deaborn, MI, 1984, p. 5–49.
24. V. Desobry, K. Dietliker, R. Hüsler, W. Rutsch, and H. Löliger, *Polym. Paint J., Suppl.* **125**, 96 (1988).
25. F. J. Williams and P. E. Donahue, *J. Org. Chem.*, **42**, 3414 (1977).
26. M. Passudetti, M. Prato, U. Quintily, and G. Scorrano, *J. Fluorine Chem.*, **50**, 251 (1990).
27. F. J. Williams and P. E. Donahue, *J. Org. Chem.*, **43**, 255 (1978).
28. V. Kvita, H. Zweifel, M. Roth, and L. Felder, Can. Pat. 1,180,486 (1985) (to Ciba-Geigy AG).
29. B. R. Dohner and W. H. Saunders, Jr, *J. Am. Chem. Soc.*, **108**, 245 (1986).
30. G. Berner, R. Hüsler, and R. Kirchmayr, Eur. Pat. Appl. 0,088,050 (1983) (to Ciba-Geigy).
31. L. Angiolini, D. Caretti, and C. Carlini, *J. Polym. Sci., Part A: Polym. Chem.*, **32**, 1159 (1994).
32. C. Carlini, P. A. Rolla, and E. Tombari, *J. Appl. Polym. Sci.*, **41**, 805 (1990).
33. C. Carlini, L. Toniolo, P. A. Rolla, F. Barigelletti, P. Bortolus, and L. Flamigni, *New Polym. Mat.*, **1**, 63 (1987).
34. F. Catalina, C. Peinado, R. Sastre, J. L. Mateo, and N. S. Allen, *J. Photochem. Photobiol. A: Chem.*, **47**, 365 (1989).
35. G. L. Gloss and J. Miller, *J. Am. Chem. Soc.*, **103**, 3586 (1981).

36. C. E. Hoyle, M. Keel, and K. J. Kim, *Polymer,* **29,** 18 (1988).
37. L. Angiolini, D. Caretti, C. Carlini, and N. Lelli, *Polym. Adv. Technol.,* **4,** 375 (1993).
38. N. S. Allen, D. Mallon, I. Sideridou, A. Green, A. Timms, and F. Catalina, *Eur. Polym. J.,* **28,** 647 (1992).
39. N. S. Allen, D. Mallon, A. Timms, A. W. Green, and F. Catalina, *Polymer,* **34,** 2401 (1993).
40. C. Peinado, F. Catalina, T. Corrales, R. Sastre, F. Amat-Guerri, and N. S. Allen, *Eur. Polym. J.,* **28,** 1315 (1992).
41. I. Tinoco, Jr., *J. Am. Chem. Soc.,* **82,** 4785 (1960).
42. K. Okamoto, A. Itaya, and S. Kusabayashi, *Chem. Lett.,* 1167 (1974).
43. E. Chiellini, R. Solaro, G. Galli, and A. Ledwith, *Macromolecules,* **13,** 1654 (1980).
44. R. N. Majumdar and C. Carlini, *Makromol. Chem.,* **181,** 201 (1980).
45. C. Carlini and F. Gurzoni, *Polymer,* **24,** 101 (1983).
46. C. Carlini, *Brit. Polym. J.,* **18,** 236 (1986).
47. C. Carlini, F. Ciardelli, F. Donati, and F. Gurzoni, *Polymer,* **24,** 599 (1983).