Copolymeric Systems Bearing Side-Chain Thioxanthone and α-Aminoacetophenone Moieties as Photoinitiators for Ultraviolet-Curable Pigmented Coatings

LUIGI ANGIOLINI,[1] DANIELE CARETTI,[1] ELENA CORELLI,[1] CARLO CARLINI,[2] PIER ANGELO ROLLA[3]

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

[2] Dipartimento di Chimica e Chimica Industriale, University of Pisa, Via Risorgimento 35, 56126 Pisa, Italy

[3] INFM, Dipartimento di Fisica, University of Pisa, Piazza Torricelli 2, 56100 Pisa, Italy

Received 11 October 1996; accepted 21 November 1996

ABSTRACT: Copolymers of 1-(4-morpholinophenyl)-2-benzyl-2-[*N*-methyl-*N*-(3-methacryloyloxy propyl)]aminopropan-1-one and of 1-(4-morpholinophenyl)-2-benzyl-2-[*N*-methyl-*N*-(3-methacryloyloxypropyl)]aminobutan-1-one with 1-[(2-methacryloyloxy)ethoxycarbonyl]thioxanthone were prepared and structurally characterized. The above systems were also checked in the ultraviolet cure of an acrylic mixture upon irradiation over 380 nm, thus simulating the conditions of a TiO_2-pigmented formulation. The curing results were compared with those obtained in the presence of the mixtures of the corresponding homopolymers as well as of their low-molecular-weight models. The copolymeric systems display synergistic effects of activity with respect to the structural models but show lower photoinitiation efficiency against the homopolymers mixtures. These data are discussed and interpreted in terms of structural requirements and photochemical mechanistic aspects of the above systems. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 2247–2258, 1997

Key words: polymeric photoinitiators; ultraviolet curing; pigmented coatings

INTRODUCTION

Polymeric systems with side-chain photoinitiating moieties have recently gained a great deal of interest for their applications in the field of ultraviolet (UV)-curable coatings.[1–3] Their higher cost, as compared with the corresponding low-molecular-weight counterparts, may be justified only by their enhanced performances. Indeed, several advantages of their use were claimed due to the improvement of the coating characteristics in terms of nonyellowing and low-odor properties as well as of lower contaminants release.[4–6] Other practical aspects, such as solubility and compatibility improvement with formulation components and higher photoinitiation activity, usually expected due to the well-known polymer effect,[1–3] may also favor the development of the polymeric photoinitiators.

Moreover, synergistic effects on efficiency, peculiar of the macromolecular nature of the system, may be originated by the contemporary presence along the backbone of different photosensitive moieties. For example, polymeric systems bearing pendant thioxanthone and α-morpholinoacetophenone moieties, such as the copolymers of 1-

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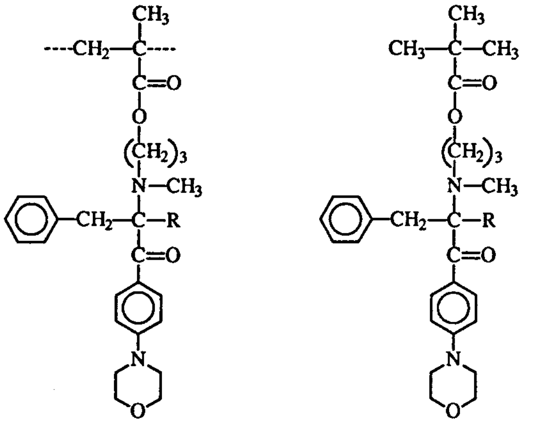
Correspondence to: C. Carlini.

[(2-acryloyloxy)ethoxycarbonyl]thioxanthone with 1-[4-(2-acryloyloxyethylthio)phenyl]-2-methyl-2-morpholinopropan-1-one [poly(ATX-*co*-AMMP)], were recently reported by us[7] to succeed in the UV cure of TiO_2-pigmented acrylic coatings, where photoinitiators applied for clear coatings usually fail.

Indeed, the above systems can efficiently work thanks to the presence of thioxanthone groups displaying an absorption maximum at around 380 nm with a tail over 410 nm, which behave as photosensitizers and may transfer their excitation energy to the α-morpholinoacetophenone moieties. These, in turn, may finally generate, by photocleavage, free radicals able to promote the polymerization and crosslinking reactions of the coating formulation. In such copolymer systems, the photosensitization process has been found to be very efficient[8] for the following two reasons:

1. the triplet state energy level (E_T) of thioxanthone moiety is higher than that of the α-morpholinoacetophenone moiety, and
2. both the photosensitive moieties are forced to be very close each other along the polymer chain.

Very recently, the polymeric analogues of the low-molecular-weight photoinitiators 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)propan-1-one (BDMP) and 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butan-1-one (BDMB),[9,10] i.e., the homopolymers of 1-(4-morpholinophenyl)-2-benzyl-2-[*N*-methyl-*N*-(3-methacryloyloxypropyl)]aminopropan-1-one (BMMP) and of 1-(4-morpholinophenyl)-2-benzyl-2-[*N*-methyl-*N*-(3-methacryloyloxypropyl)]aminobutan-1-one (BMMB) [poly(BMMP) and poly(BMMB), respectively] were prepared and successfully applied to the UV cure of a standard acrylic formulation, under irradiation conditions simulating a TiO_2-pigmented coating ($\lambda_{irr} > 380$ nm).[11] In particular, poly(BMMP) and poly(BMMB) were found to display equal or even higher photoinitiation activity as compared with the corresponding low-molecular-weight models 1-(4-morpholinophenyl)-2-benzyl-2-[*N*-methyl-*N*-(3-pivaloyloxypropyl)]aminopropan-1-one (BMPP) and 1-(4-morpholinophenyl)-2-benzyl-2-[*N*-methyl-*N*-(3-pivaloyloxypropyl)]aminobutan-1-one (BMPB).

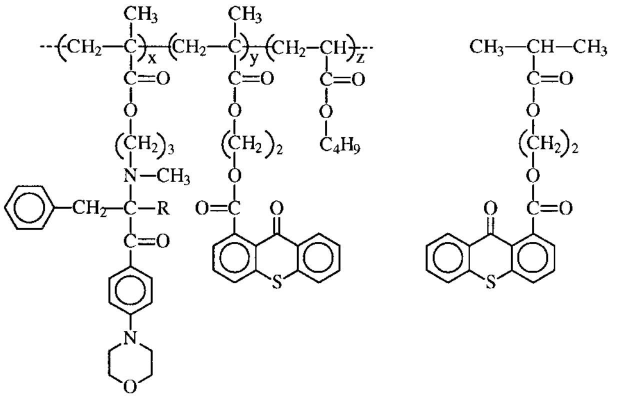


poly(BMMP) (R = Me) BMPP (R = Me)
poly(BMMB) (R = Et) BMPB (R = Et)

(1)

The superiority of poly(BMMB) and BMPB with respect to poly(BMMP) and BMPP was explained, taking into account that the former systems, in addition to an absorption maximum at around 325 nm, show also a tail over 380 nm with a higher molar extinction coefficient (ε) as compared with the latter systems.

In this context, taking into account that 1-methyloxycarbonylthioxanthone) (E_T = 63 kcal/mole) is able[10] to photosensitize BDMP and BDMB (E_T = 60 kcal/mole) by energy transfer, copolymers, containing in the same macromolecules, side-chain 1-alkoxycarbonyl-thioxanthone and α-aminoacetophenone moieties derived from BMMP and BMMB appeared very promising for improving the photoinitiation activity in the cure of pigmented coatings. Indeed, an increase of the photocure efficiency by the above copolymers is expected, not only through an energy transfer mechanism from excited thioxanthone groups to the adjacent ground state α-morpholinoacetophenone moieties, but also through a photoreduction process involving the thioxanthone moieties in the triplet state and the tertiary amino groups in β-position with respect to the ketone functions, more basic than the amino groups in the morpholino rings. In fact, it is well established[12,13] that, through a photochemical pathway involving both electron and proton transfer processes, thioxanthone ketyl and α-aminoalkyl radicals are formed, with these last species being responsible for the polymerization and cross-linking reactions of the acrylic formulation. Therefore, this article deals with the synthesis and the structural characterization of copolymers of BMMP and BMMB with 1-[(2-methacryloyloxy)ethoxycarbonyl]thioxanthone (MATX) [poly(BMMP-*co*-MATX) and poly(BMMB-*co*-MATX), respectively].



poly(**BMMP**-*co*-**MATX**) (z = 0, R = Me)

poly(**BMMB**-*co*-**MATX**) (z = 0, R = Et)

poly(**MATX**-*co*-**BA**) (x = 0)

poly(**MATX**) (x = z = 0)

(2)

IBTX

Moreover, in order to evidence possible synergistic effects on the photoinitiation activity due to the close vicinity of the two different photosensitive moieties along the macromolecule, the photocuring behavior of the above copolymers has been checked and compared with that of the corresponding mixtures of their low-molecular-weight structural models BMPP or BMPB with 2-isobutyroyloxyethyl-thioxanthone (IBTX), previously prepared,[7,11] as well as of poly(BMMP) and of poly(BMMB) with the copolymer of MATX with *n*-butyl acrylate (BA) [poly(MATX-*co*-BA)], this last was preferred to poly(MATX) due to a better solubility in the acrylic formulation.

Therefore, the above depicted low- and high-molecular-weight photoinitiators have been checked in the cure of 1,6-hexandiol diacrylate (HDDA)/BA equimolar mixtures under UV irradiation over 380 nm, thus simulating the conditions of a TiO_2-pigmented acrylic formulation.

EXPERIMENTAL

Monomers

n-Butyl acrylate (BA) (Aldrich) was washed with aq dil NaOH and water, in that order, dried on anhydrous $CaCl_2$ and finally distilled at reduced pressure under nitrogen atmosphere just before use (bp = 50°C/21 mbar). 1,6-Hexandiol diacrylate (HDDA) (Aldrich) was distilled under high vacuum just before use (bp = 94°C/0.02 mbar). 1-[(2-Methacryloyloxy)ethoxycarbonyl]thioxanthone (MATX) has been prepared as reported elsewhere,[14] but according to some procedure modifications as described for the acrylate analogue.[7] Characterizations for MATX are as follows. ^{1}H-NMR ($CDCl_3$): 8.5 (d, 1H, aromatic proton at C-8), 7.7–7.4 (m, 6H, all other aromatic protons), 6.2 and 5.6 (2d, 2H, $C\underline{H}_2{=}C(CH_3){-}$), 4.7 (t, 2H, $ArCOO{-}C\underline{H}_2{-}CH_2{-}$), 4.6 (t, 2H, $ArCOO{-}CH_2{-}C\underline{H}_2{-}$), 1.9 (s, 3H, CH_3) ppm. IR (KBr): 3066 (ν_{CH}, aromatic and vinylidenic), 2964 (ν_{CH}, aliphatic), 1723 ($\nu_{C=O}$, methacrylic and aromatic ester groups), 1631 ($\nu_{C=O}$, aromatic ketone and $\nu_{C=C}$, methacrylic group), 1594 ($\nu_{C=C}$, aromatic), 1274 (ν_{C-O}, aromatic ester), 744, 718, and 699 (δ_{CH}, aromatic) cm^{-1}. 1-(4-Morpholinophenyl)-2-benzyl-2-[N-methyl-N-(3-methacryloyloxypropyl)]aminopropan-1-one (BMMP) and 1-(4-morpholinophenyl)-2-benzyl-2-[*N*-methyl-*N*-(3-methacryloyloxypropyl)]aminobutan-1-one (BMMB) have been prepared as previously described.[11]

Low-Molecular-Weight Models

1-[4-(2-Isobutyroyloxy)ethoxycarbonyl]thioxanthone (IBTX) was obtained as previously reported.[7] 1-(4-Morpholinophenyl)-2-benzyl-2-[*N*-methyl-*N*-(3-pivaloyloxypropyl)]aminopropan-1-one (BMPP) and 1-(4-morpholinophenyl)-2-benzyl-2-[*N*-methyl-*N*-(3-pivaloyloxypropyl)]-aminobutan-1-one (BMPB) were synthesized as previously described,[11] according to the same procedure reported for BMMP and BMMB, but replacing methacryloyl chloride with pivaloyl chloride in the last step.

Polymeric Photoinitiators

Poly(BMMP) and poly(BMMB) were prepared as previously reported.[11] Copolymers were obtained by free radical polymerization in tetrahydrofuran (THF) solution, using 2 wt % (with respect to the monomers) of 2,2′-azobisisobutyronitrile (AIBN) as thermal initiator. The monomers and AIBN were introduced in a glass vial under dry nitrogen and submitted to several freeze–thaw cycles. After sealing under high vacuum, the vials were

Table I Synthesis and Structural Characterization of Photosensitive Polymers Derived from α-Aminoacetophenone (AAP) Monomers and MATX

Feed			Polymeric Product		
AAP	mol %	Conversion[a] (%)	AAP co-units[b] (mol %)	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]
BMMP	100	41	100	18,500	1.3
BMMP	90	59	83	28,200	1.6
BMMP	80	65	75	22,100	1.5
BMMP	70	63	62	21,000	1.6
BMMB	100	43	100	15,700	2.1
BMMB	90	62	82	22,600	2.9
BMMB	80	57	77	16,500	2.6
BMMB	70	68	61	16,500	1.7

[a] Determined as (weight of polymer/weight of monomers) × 100.
[b] Evaluated by ^{1}H-NMR analysis.
[c] Determined by GPC analysis.

kept at 60°C for 150 h in the dark. Usually, the polymeric product was isolated by pouring the reaction mixture into a large excess of methanol. However, for poly(BMMB-*co*-MATX)s, due to their partial solubility in methanol, petroleum ether was used as precipitating agent. The coagulated polymer was redissolved in chloroform and again precipitated with methanol or petroleum ether, filtered, dried under vacuum, and finally stored in the refrigerator in the dark. All the polymer samples were characterized by ^{1}H-NMR, Fourier transform infrared (FTIR), and UV spectroscopy, as well as by gel permeation chromatography (GPC) measurements. The most relevant properties of the polymers are reported in Table I.

Photoinitiation Activity Experiments

All cure experiments were performed at 25°C, under nitrogen, on chloroform solutions of the HDDA/BA equimolar mixture [$CHCl_3$/(HDDA/BA) 2 : 1 (wt/wt)] containing 0.1 mol % of thioxanthone and different content of α-aminoacetophenone moieties, depending on copolymers composition. The reason why neat HDDA/BA (1 : 1) acrylic formulation was not used for dissolving the photoinitiators is due to the scarce solubility in that medium of the thioxanthone containing polymeric systems. UV irradiation was carried out with a high-pressure 100W OSRAM HBO Hg lamp in the presence of a glass-colored passband filter LG-400 (Corion Corporation) in order to cut completely light wavelengths below 380 nm and then to simulate the irradiation conditions of a TiO_2-pigmented coating formulation. The same irradiation intensity, as detected by a photodiode, was applied by properly defocusing the elliptical mirror that collects the light emitted by the lamp.[7,15] The time evolution of the curing processes was followed by microwave dielectrometry at 9.5 GHz, in terms of ε'' (loss factor), as described previously.[16–18]

Physicochemical Measurements

^{1}H-NMR spectra were carried out at 300 MHz on samples in $CDCl_3$ solution by using a Varian FT-NMR Gemini 300 spectrometer and tetramethylsilane (TMS) as an internal standard.

UV absorption spectra of the samples were recorded at 25°C in $CHCl_3$ solution on a Perkin-Elmer Lambda 17 spectrophotometer. The spectral region between 500 and 250 nm was investigated by using cell path lengths of 1 and 0.1 cm, respectively; molar extinction coefficient values (ε) are expressed in liters per mole per centimeter (L mol^{-1} cm^{-1}).

FTIR spectra were carried out on a Perkin-Elmer Model 1750 spectrophotometer equipped with a Perkin-Elmer Model 7700 data station. The samples were prepared either as KBr pellets or as liquid films between KBr discs.

Average molecular weights of the polymer samples were determined by a HPLC Waters Millipore 590 apparatus, equipped with an injector

Table II Synthesis and Structural Characterization of Poly(MATX) and Poly(MATX-*co*-BA)

Feed (mol %)		Conversion[a] (%)	Polymeric Product		
MATX	BA		MATX co-units[b] (mol %)	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]
100	0	70	100	45,500	2.3
50	50	80	51	39,900	2.0

[a] Determined as (weight of polymer/weight of monomers) × 100.
[b] Evaluated by ^{1}H-NMR analysis.
[c] Determined by GPC analysis.

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 and Characterization of the Photosensitive Polymers

Poly(BMMP-*co*-MATX)s and poly(BMMB-*co*-MATX)s with a content of MATX co-units lower than 40 mol % were prepared in order to obtain polymeric systems appreciably soluble in acrylic coating formulations, the poor solubility being the main drawback of thioxanthone derivatives.[7,19] Thus, MATX/BMMP and MATX/BMMB mixtures containing only 10–30 mol % of MATX were submitted to free radical copolymerization in THF solution at 60°C, in the presence of 2 wt % of AIBN as thermal initiator (Table I).

Poly(BMMP) and poly(BMMB), synthesized as reported elsewhere,[11] as well as poly(MATX) and poly(MATX-*co*-BA) containing 51 mol % of MATX co-units, were also prepared (Tables I and II) in order to compare the photoinitiation activity of the copolymers with that of the corresponding homopolymers mixtures in the cure of the HDDA/BA formulation. Indeed, poly(MATX-*co*-BA) was used in the place of poly(MATX) for preparing the above mixtures, as the latter was found to be, as expected, substantially unsoluble in the acrylic formulation.

^{1}H-NMR analysis (Fig. 1) of the polymeric samples does not show any evidence of signals in the 6.0–5.5 ppm region, related to methacrylic protons, present in the corresponding monomers, thus suggesting that homo- and copolymerizations occurred as expected by a free radical chain addition mechanism involving the methacrylic functions.

Copolymers composition was determined by ^{1}H-NMR analysis. In particular, it was calculated from the spectra of poly(BMMP-*co*-MATX)s and

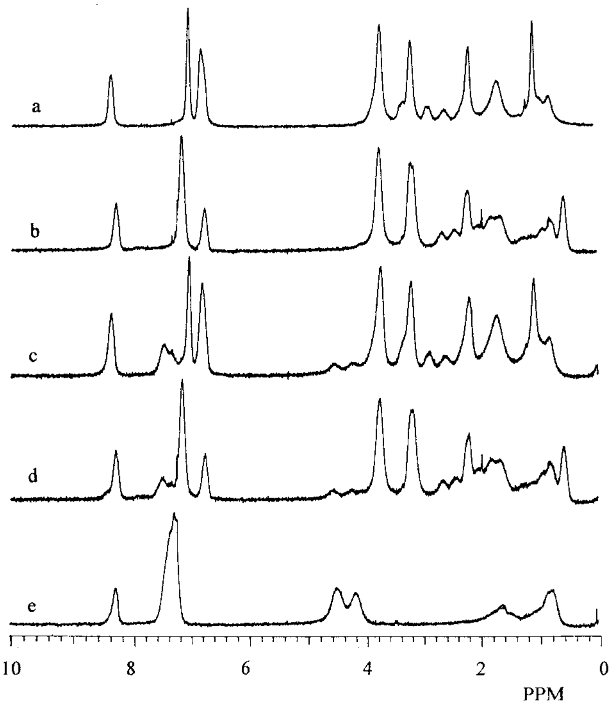


Figure 1 ^{1}H-NMR spectra in $CDCl_3$ solution of (a) poly(BMMP); (b) poly(BMMB); (c) and (d) poly(BMMP-*co*-MATX) and poly(BMMB-*co*-MATX) with 25 and 23 mol % of MATX co-units, respectively; and (e) poly(MATX).

poly(BMMB-*co*-MATX)s by comparing the area of the signal at 6.8 ppm, related to the two aromatic protons in *ortho* position to morpholino group in BMMP or BMMB co-units only, with that of the superimposed signals at 8.4 ppm belonging to the aromatic proton at C-8 of thioxanthone moiety in MATX co-units, as well as to the two aromatic protons in *ortho* position to ketone group of BMMP or BMMB co-units.

As far as poly(MATX-*co*-BA) is concerned, its composition was determined by comparing the area of the signal in the 3.9 ppm region, related to the ester methylene group in BA co-units, with that of the signal at 8.4 ppm, connected with the aromatic proton at C-8 of MATX co-units.

A qualitative evaluation of copolymers composition can be also obtained from IR spectra of poly(BMMP-*co*-MATX)s or poly(BMMB-*co*-MATX)s by comparing the relative intensity of the bands connected to the ketone carbonyl stretching in BMMP or BMMB co-units (around 1663 cm^{-1}) with that of MATX co-units (around 1645 cm^{-1}) (Fig. 2).

Although the conversions obtained in the copolymerization reactions were too high in order to determine the reactivity ratios of the comonomers, the values reported in Table I indicate that poly(BMMP-*co*-MATX)s and poly(BMMB-*co*-MATX)s display a higher content of MATX co-units with respect to the corresponding feeds, thus suggesting a higher reactivity of MATX as compared with BMMP and BMMB. Accordingly, the polymerization conversion was found to increase with an increase in the content of MATX in the feed, the highest and lowest values being observed (Table I) for poly(MATX) and the homopolymers of α-aminoacetophenone monomers, respectively. Moreover, BMMP and BMMB show a similar reactivity against MATX, as they give rise to copolymers with substantially equal composition starting from feeds containing the same content of MATX.

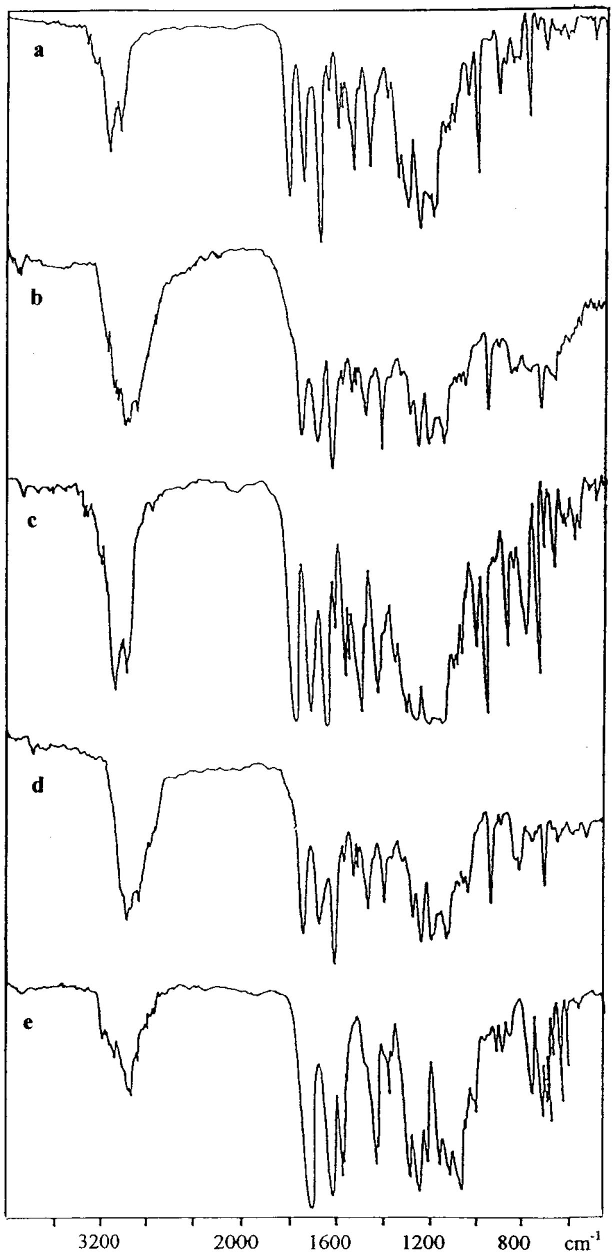


Figure 2 IR spectra of (a) poly(BMMP); (b) poly(BMMB); (c) and (d) poly(BMMP-*co*-MATX) and poly(BMMB-*co*-MATX) with 25 and 23 mol % of MATX co-units, respectively; and (e) poly(MATX).

As reported in Table I, the average-number molecular weight ($\bar{M}_n$) values of poly(BMMP-*co*-MATX)s and poly(BMMB-*co*-MATX)s are intermediate to those found for poly(MATX) and poly(BMMP) or poly(BMMB), thus suggesting that the α-aminoacetophenone containing monomers, due to the presence of tertiary amino groups, behave as chain transfer agents,[20] analogously to what previously observed in copolymers of benzoin methyl ether and *N,N*-dialkylamino acrylates.[21] Therefore, the lowering of conversion on increasing the content of α-aminoacetophenone containing monomer in the feed may be also addressed, in addition to the previously mentioned higher reactivity of MATX, to a degradative chain transfer reaction by BMMP and BMMB affording α-aminoalkyl radicals having a lower reinitiation

Table III UV Spectra in Chloroform Solution of Low- and High-Molecular-Weight Compounds Containing Thioxanthone (TX) and the α-Aminoacetophenone (AAP) Moieties

	TX			AAP		
Sample	(mol %)	λ_{max}[a]	ε_{max}[b]	(mol %)	λ_{max}[a]	ε_{max}[b]
Poly(MATX)	100	387	5950	0	—	—
Poly(MATX-*co*-BA)	51	387	6850	0	—	—
IBTX	100	385	7900	0	—	—
Poly(BMMP-*co*-MATX)	38	386	6950	62	325	23000
Poly(BMMP-*co*-MATX)	25	386	7200	75	325	23100
Poly(BMMP-*co*-MATX)	17	386	6350	83	325	22800
Poly(BMMP)	0	—	—	100	325	22700
BMPP	0	—	—	100	324	23600
Poly(BMMB-*co*-MATX)	39	386	6600	61	324	23900
Poly(BMMB-*co*-MATX)	23	386	7000	77	323	23400
Poly(BMMB-*co*-MATX)	18	386	6850	82	323	23800
Poly(BMMB)	0	—	—	100	324	23400
BMPB	0	—	—	100	323	24200

[a] Expressed in nm.
[b] Expressed in L mol^{-1} cm^{-1}.

capability,[20] the overall polymerization rate being thus depressed.

Finally, the narrower distribution of molecular weights of poly(BMMP-*co*-MATX)s with respect to poly(BMMB-*co*-MATX)s, as indicated by the $\bar{M}_w/\bar{M}_n$ values (Table I), may be caused by the presence of a larger amount of oligomers in the latter systems, as a consequence of polymer precipitation with petroleum ether instead of methanol (see the Experimental section). Accordingly, poly(BMMB-*co*-MATX)s also exhibit lower $\bar{M}_n$ values with respect to poly(BMMP-*co*-MATX)s having similar composition (Table I).

It is well known[10,22] that the thioxanthone chromophore displays in the near-UV region two absorption bands centered at about 260 and 380 nm, connected with the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electronic transition of the aromatic system and the ketone group, respectively. The latter transition, however, seems to have a partial $\pi \rightarrow \pi^*$ character, as evidenced by both a small hypsochromic shift of the absorption maximum[19,23,24] and the blue shift of phosphorescence maximum emission,[25] on increasing the polarity of the solvent. Indeed, poly(MATX) and poly(MATX-*co*-BA) show both the above absorption bands. In particular, the structured band related to the $n \rightarrow \pi^*$ electronic transition, usually involved in photoinitiation and photosensitization processes, exhibits in poly(MATX) a maximum at 387 nm and a tail extending over 410 nm with an ε_{387} value significantly lower than that observed[11] for the model compound IBTX (Table III).

This hypochromic effect, well known in polymeric systems bearing side-chain aromatic chromophores,[26–28] may be attributed to dipole–dipole electrostatic interactions[29,30] between the pendant thioxanthone moieties along the polymer chain. Accordingly, poly(MATX-*co*-BA) exhibits an intermediate ε value (Table III). An analogous behavior was also observed[7] for the corresponding acrylic thioxanthone homopolymer and the copolymer with BA. The ε values obtained for poly(BMMP-*co*-MATX)s and poly(BMMB-*co*-MATX)s substantially confirm this picture (Table III). The above copolymers also display a strong absorption band centered at about 325 nm, related to the $\pi \rightarrow \pi^*$ electronic transition of the aromatic chromophore in the α-aminoacetophenone moieties, analogously to what was observed for poly(BMMP) and poly(BMMB),[11] for their low-molecular-weight models BMPP and BMPB,[11] as well as for the photoinitiators BDMP and BDMB, reported previously.[9,10] Indeed, the electron withdrawing character of the morpholino group in the para position to the benzoyl group causes a bathochromic shift of the $\pi \rightarrow \pi^*$ transition from 250 to over 320 nm, thus completely

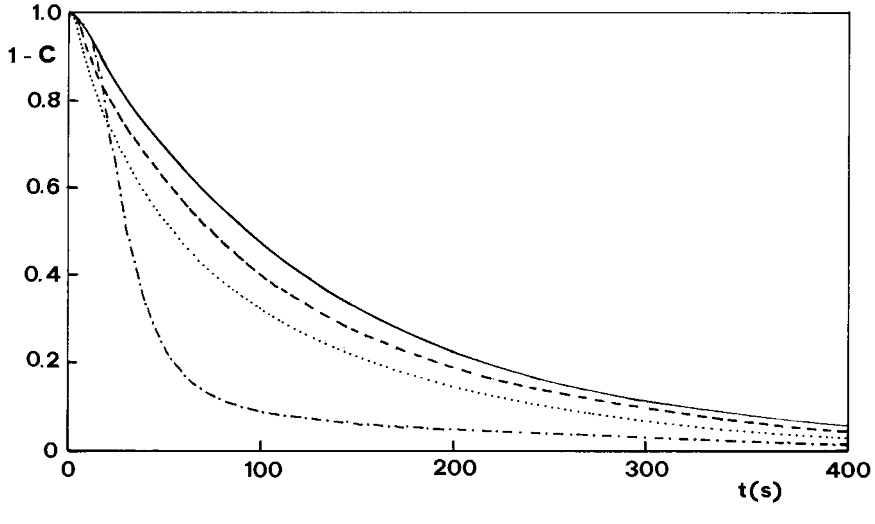


Figure 3 Fraction of residual monomers (1-C) versus time in the UV cure of HDDA/BA (1 : 1) in chloroform solution upon irradiation over 380 nm, in the presence of (------) poly(BMMP-*co*-MATX) with 25 mol % of MATX co-units, (——) BMPP/IBTX 75/25 mol/mol, (· · · · · ·) poly(BMMP)/poly(MATX-*co*-BA) 75/25 mol/mol, and (– · – · – · –) poly(BMMP); concentration of thioxanthone and α-aminoacetophenone moieties in the acrylic formulation = 0.1 and 0.3 mol %, respectively.

obscuring the much less intense $n \rightarrow \pi^*$ transition of the ketone group, located in this spectral region.

It is worth noting that in the copolymer samples, in agreement with what was observed for poly(BMMP) and poly(BMMB),[11] the α-aminoa-

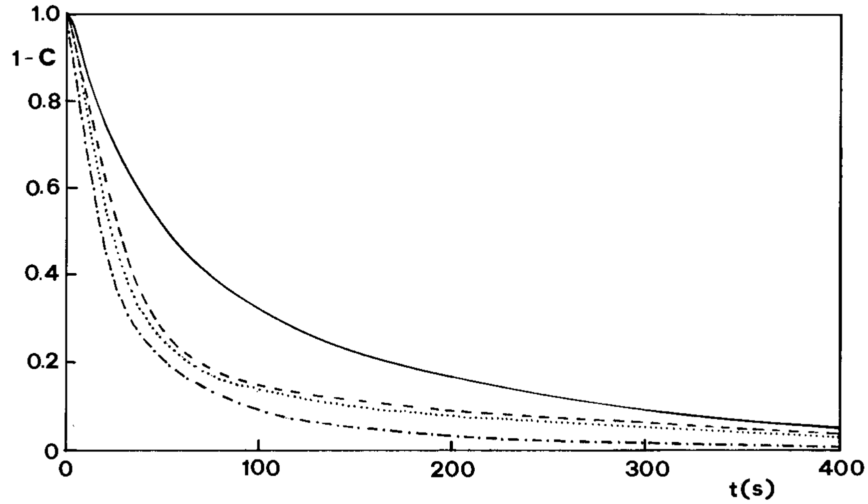


Figure 4 Fraction of residual monomers (1-C) versus time in the UV cure of HDDA/BA (1 : 1) in chloroform solution upon irradiation over 380 nm, in the presence of (------) poly(BMMB-*co*-MATX) with 23 mol % of MATX co-units, (——) BMPB/IBTX 77/23 mol/mol, (· · · · · ·) poly(BMMP)/poly(MATX-*co*-BA) 77/23 mol/mol, and (– · – · – · –) poly(BMMP); concentration of thioxanthone and α-aminoacetophenone moieties in the acrylic formulation = 0.1 and 0.33 mol %, respectively.

cetophenone containing co-units display an absorption tail extending over 380 nm, which is covered by the much higher absorption of the thioxanthone moieties in MATX co-units.

Photoinitiation Activity

The activity of poly(BMMP-*co*-MATX)s and poly(BMMB-*co*-MATX)s has been tested in the UV cure of the HDDA/BA equimolar mixture in chloroform solution, as they resulted only partially soluble in the neat acrylic formulation. Moreover, UV irradiation over 380 nm was applied in order to simulate the cure conditions of a TiO_2-pigmented coating formulation. The concentration of all copolymer samples in the above formulation was equal to 0.1 mol %, in terms of thioxanthone moieties. It is significant to mention that although this last parameter was maintained fixed, the concentration of α-aminoacetophenone moieties in the coating formulation (C_{AAP}) varied, depending on the copolymer composition (Table IV); as a consequence, the absorption over 380 nm changed also. However, taking into account that in this region the molar extinction coefficient (ε) of thioxanthone chromophores is almost 7.000 against 150–500 L mol^{-1} cm^{-1} of the α-aminoacetophenone moiety (depending on BMMP or BMMB co-units present),[11] all the copolymers should be characterized by a very similar absorption behavior over 380 nm at the fixed concentration of thioxanthone moieties. Nevertheless, each copolymer sample was compared with the corresponding low-molecular-weight models' mixture having the same composition, in order to evidence possible synergistic effects on activity due to both the close vicinity of the two photosensitive moieties along the backbone and the macromolecular nature of the system.

As reported in Table IV and Figure 3, poly(BMMP-*co*-MATX)s display (runs 1, 4, and 8) a higher photocure activity with respect to the corresponding BMMP/IBTX mixtures (runs 2, 5, and 9), as revealed by their polymerization rate values halfway through the cure process $(R_c)_{1/2}$, regardless of the relative amount of thioxanthone and α-aminoacetophenone moieties in the systems. An even larger improvement of activity was

Table IV UV Cure of the HDDA/BA Equimolar Mixture in Chloroform Solution, in the Presence of Poly(BMMP-*co*-MATX)s and the Corresponding Mixtures of Their Structural Models As Well As Homopolymers, by Irradiation over 380 nm at 25°C, Under Nitrogen

	Photoinitiator			
Run	Type	TX (mol %)	C_{AAP}[a] (mol %)	$(R_c)_{1/2}$[b] (s^{-1})
1	Poly(BMMP-*co*-MATX)	38	0.16	0.5
2	BMPP/IBTX	38	0.16	0.2
3	Poly(BMMP)	0	0.16	1.0
4	Poly(BMMP-*co*-MATX)	25	0.3	0.4
5	BMPP/IBTX	25	0.3	0.3
6	Poly(BMMP)/poly(MATX-*co*-BA)	25	0.3	0.5
7	Poly(BMMP)	0	0.3	2.0
8	Poly(BMMP-*co*-MATX)	17	0.5	0.8
9	BMPP/IBTX	17	0.5	0.2
10	Poly(BMMB-*co*-MATX)	39	0.15	1.1
11	BMPB/IBTX	39	0.15	0.3
12	Poly(BMMB-*co*-MATX)	23	0.33	1.5
13	BMPB/IBTX	23	0.33	0.6
14	Poly(BMMB)/poly(MATX-*co*-BA)	23	0.33	1.8
15	Poly(BMMB)	0	0.33	2.5
16	Poly(BMMB-*co*-MATX)	18	0.45	1.8
17	BMPB/IBTX	18	0.45	0.7

Concentration of thioxanthone moiety (when present) in the acrylic formulation: 0.1 mol %.

[a] Concentration of α-aminoacetophenone moieties in the acrylic formulation, expressed in mol %.

[b] Polymerization rate, calculated halfway through the cure process, and expressed as percentage of conversion over time.

found (Table IV and Fig. 4) for poly(BMMB-*co*-MATX)s (runs 10, 12, and 16) against BMMB/IBTX mixtures (runs 11, 13, and 17).

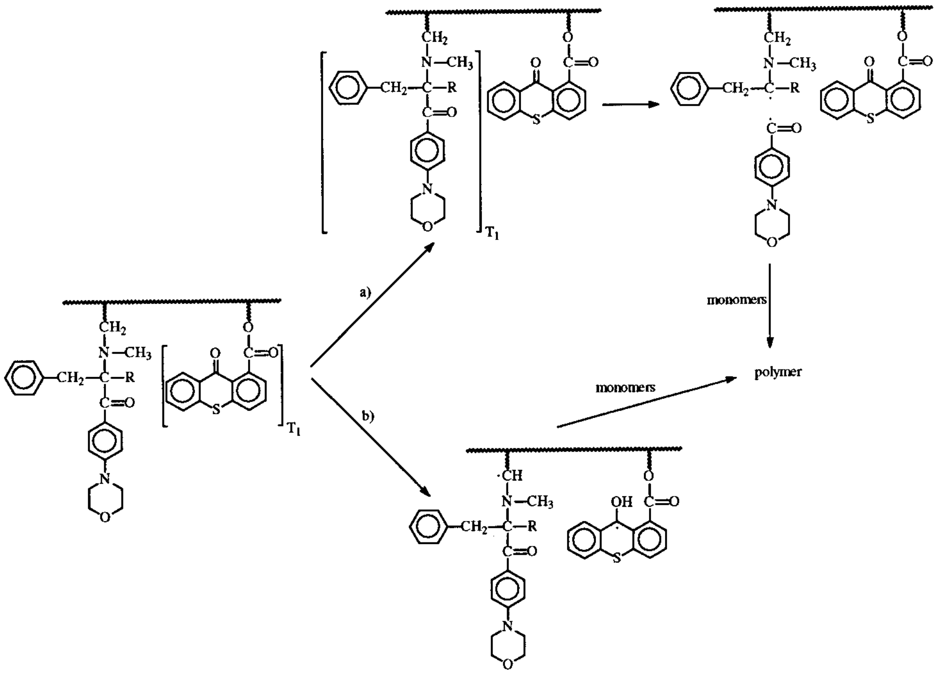
The comparison of poly(BMMP-*co*-MATX)s with poly(BMMB-*co*-MATX)s at similar compositions (Table IV, runs 1 vs. 10, 4 vs. 12, and 8 versus 16) clearly indicates that the latter system displays higher activity. The same result was observed[11] for poly(BMMB) against poly(BMMP) in the UV cure of neat HDDA/BA by UV irradiation over 380 nm. The higher activity of the copolymer systems with respect to the corresponding models mixtures may be explained by the fact that the excited thioxanthone chromophores (with the majority of light being absorbed by these species in the ground state), when anchored to the same macromolecule in close vicinity to α-aminoacetophenone moieties, gives rise to a more efficient process of excitation transfer. Indeed, the probability that excited thioxanthone chromophores may interact with ground state α-aminoacetophenone moieties increases with an increase in the local concentration of both the photosensitive species; this occurs when they are anchored to the same macromolecule. However, these results do not give any indication about the photochemical pathway involved in the excitation transfer. In other words, it cannot be established whether the above process occurs by either (a) energy transfer or (b) electron and proton transfers (photoreduction of thioxanthone moiety by the tertiary amino group in the α-aminoacetophenone moiety), as represented in Scheme 1. Nevertheless, the lower photoinitiation activity displayed by poly(BMMP-*co*-MATX)s and poly(BMMB-*co*-MATX)s with respect to poly(BMMP)/poly(MATX-*co*-BA) and to poly(BMMB)/poly(MATX-*co*-BA), the corresponding polymeric mixtures containing the same amount of each photosensitive species in distinct macromolecules (Table IV, runs 4 vs. 6 and 12 vs. 14; Figs. 3 and 4), seems to suggest that the photochemical pathway (b), described in Scheme 1, plays a main role. Indeed, in the case of the copolymer systems, the close vicinity of thioxanthone and α-aminoacetophenone moieties along the backbone, according to pathway (b), causes the formation in a cage of polymer-bound thioxanthone ketyl and α-aminoalkyl primary radicals, their recombination being favored with respect to the situation in which the two radical species belong to different macromolecules. However, the improvement of photoinitiation activity of poly(BMMP)/poly(MATX-*co*-BA) and poly(BMMB)/poly(MATX-*co*-BA) mixtures with respect to the corresponding copolymeric systems appears quite surprising, as one would expect a reduced interaction between thioxanthone and α-aminoacetophenone moieties belonging to different macromolecules due to the lower mobility resulting from the polymeric nature of the two reactants. A tentative explanation could be based on the assumption that a close vicinity of the two photosensitive moieties, caused by charge transfer complexes even in the ground state, equally occurs. In this situation, electron transfer and subsequent hydrogen abstraction, giving rise to thioxanthone ketyl and α-aminoalkyl primary radicals, would be favored with respect to the energy transfer mechanism; and the probability of coupling reactions between the two above radical species would be lowered, as they would more readily escape from the cage, belonging to different macromolecules.

The main role played by the electron transfer with respect to energy transfer mechanism is confirmed also by the fact that poly(BMMB) and poly(BMMP) show the highest photoinitiation activity when compared with poly(BMMP-*co*-MATX)s and poly(BMMB-*co*-MATX)s, as well as with their corresponding mixtures with poly(MATX-*co*-BA) at the same concentration of α-aminoacetophenone moieties in the acrylic formulation (Table IV, runs 3 vs.1, 7 vs. 4 and 6, and 15 vs. 12 and 14). In fact, despite the lower photon absorption by poly(BMMB) and poly(BMMP) with respect to the case in which thioxanthone moieties are present, α-aminoacetophenone groups are directly excited by light to afford, by photocleavage, with very high efficiency, two primary radicals both active as polymerization initiating species. On the contrary, it is well established[12,13,31,32] that thioxanthone ketyl radicals behave as terminating agents in the systems containing both thioxanthone and α-aminoacetophenone moieties when the photoreduction pathway (b) takes place (Scheme 1), with α-aminoalkyl primary radicals being capable only to initiate the polymerization process.

CONCLUSIONS

On the basis of the obtained results, the following concluding remarks can be drawn.

1. Novel copolymeric systems bearing side-chain thioxanthone and α-aminoacetophe-



Scheme 1

none moieties, such as poly(BMMP-*co*-MATX)s and poly(BMMB-*co*-MATX)s, have been prepared and fully characterized.

2. The above copolymers show synergistic effects of activity in the photocure of pigmented coating formulations as compared with the corresponding mixtures of their structural models, due to a more efficient excitation transfer process connected with the close vicinity of the two interacting photosensitive moieties.
3. The photoinitiation activity of poly(BMMP-*co*-MATX)s and poly(BMMB-*co*-MATX)s is lower, however, than that found for poly(BMMP) and poly(BMMB) at the same concentration of α-aminoacetophenone moieties in the coating formulation, despite the lower absorption over 380 nm of these last groups with respect to the thioxanthone chromophores. This behavior can be addressed to a different photochemical mechanism working in the two systems. Indeed, poly(BMMP) and poly(BMMB), by photocleavage, give rise to two initiating radical species per each absorbed photon; whereas in poly(BMMP-*co*-MATX)s and poly(BMMB-*co*-MATX)s, the main photoreduction process affords only one initiating α-aminoalkyl radical, with the thioxanthone ketyl radical formed being active only in termination reactions.
4. The higher photoinitiation activity displayed by poly(BMMP)/poly(MATX-*co*-BA) and poly(BMMB)/poly(MATX-*co*-BA) mixtures with respect to poly(BMMP-*co*-MATX)s and poly(BMMB-*co*-MATX)s, despite the two photosensitive moieties belong to different macromolecules, may be explained by two different reasons: the formation of charge-transfer ground-state complexes between thioxanthone and α-aminoacetophenone moieties, which equally allow the occurrence of their close vicinity; and the reduced possibility of coupling reactions involving the thioxanthone ketyl and α-aminoalkyl radicals generated by electron transfer and successive hydrogen abstraction.

The financial support from C.N.R. to the research project "Materiali polimerici per applicazioni elettroottiche ed elettroniche" through the Consorzio Interuniversitario Nazionale per la Chimica dei Materiali (I.N.C.M.) is gratefully acknowledged.

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