Novel Polymeric Photoinitiators Bearing Side-Chain α-Aminoacetophenone Moieties for Ultraviolet-Curable Pigmented Coatings

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ABSTRACT: New polymeric photoinitiators with pendant α-aminoacetophenone moieties, such as the homopolymers of 1-(4-morpholinophenyl)-2-benzyl-2-[*N*-methyl-*N*-(3-methacryloyloxypropyl)]aminopropan-1-one and of 1-(4-morpholinophenyl)-2-benzyl-2-[*N*-methyl-*N*-(3-methacryloyloxypropyl)]aminobutan-1-one have been prepared and fully characterized. Their photoinitiation activity has been also checked in the ultraviolet cure of a standard acrylic mixture, under irradiation over 380 nm, thus simulating the absorption conditions of a TiO_2-pigmented coating formulation. The results have been compared with those found by using the corresponding low-molecular-weight structural models, purposely synthesized. The activity data obtained are discussed and related to the structural requirements of the above systems. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 2237–2246, 1997

Key words: polymeric photoinitiators; ultraviolet curing; pigmented coatings

INTRODUCTION

Polymeric photoinitiators with pendant photoreactive groups have received in the last decade an increased interest for their applications in the field of ultraviolet (UV)-curable coatings.[1–3] The main advantage of their use is claimed to be the improvement of performances when applied to the UV clear coatings, in terms of nonyellowing and low-odor properties.[4–6] However, in general, polymeric systems show a relevant increase of photoinitiation activity,[1–3] thus allowing one to save energy and increase productivity in the coating industrial processes.

It is also well established[7] that the UV cure of pigmented coatings, especially white lacquers based on rutile TiO_2, fails in the presence of photoinitiators usually applied for clear coatings, as they are completely obscured by the strong absorption of the pigment below 380 nm.

Very recently, we succeeded[8] in the UV curing of TiO_2-pigmented acrylic coatings by using polymeric systems having side-chain thioxanthone and α-aminoacetophenone moieties, such as the copolymers of 1-[(2-acryloyloxy)ethoxycarbonyl]-thioxanthone with 1-[4-(2-acryloyloxyethylthio)-phenyl]-2-methyl-2-morpholinopropan-1-one [poly(ATX-*co*-AMMP)]. Indeed, although AMMP

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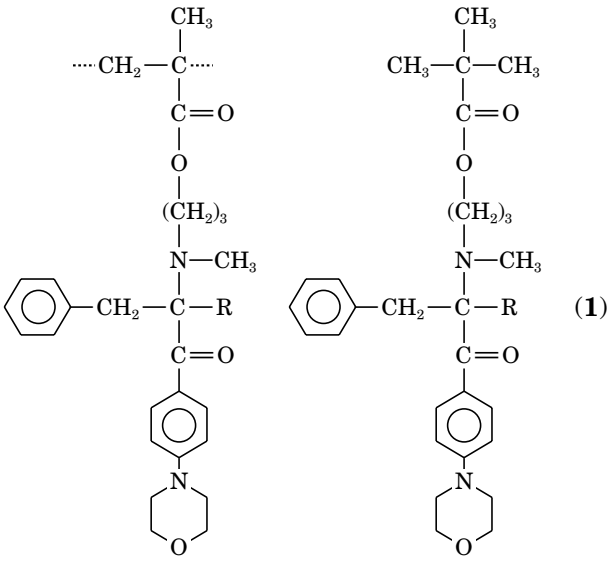
chromophore, absorbing at around 300 nm, cannot be directly excited in the presence of the pigment, thioxanthone group, owing to its absorption maximum at about 380 nm with a tail over 420 nm, behave as photosensitizer, transferring the excitation energy to the α-aminoacetophenone group, which can thus promote the free radical polymerization and crosslinking of the acrylic formulation. In the above system, the photosensitization process is very efficient[9] for two reasons as follows: the triplet state energy level of the thioxanthone moiety is higher than that of the α-aminoacetophenone moiety; and the two types of photosensitive moieties are forced to stay very close each other along the polymer chain.

Quite recently, low-molecular-weight photoinitiators, such as 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)propan-1-one (BDMP) and 2-benzyl-2-dimethylamino-1-(4-morpholino phenyl)-butan-1-one (BDMB) have been successfully applied to the photocuring of pigmented coatings, with the latter being more efficient than the former.[7] These compounds, although they display an absorption maximum at 322 nm, also show a tail over 380 nm, with the molar extinction coefficient (ϵ) in this spectral region being higher in BDMB as compared with BDMP. However, the main drawback of these photoinitiators is that they promote yellowing and fast aging of the coating film.[10] In this context, in order to overcome these problems, it appeared of interest to prepare polymeric systems bearing pendant photoreactive moieties similar to BDMP and BDMB. Therefore, the present article deals with the synthesis of novel polymeric photoinitiators such as the homopolymers poly(BMMP) and poly(BMMB), respectively, obtained from the corresponding monomers 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-methacryloyloxy propyl)]aminobutan-1-one (BMMB), purposely prepared (see, for instance, Scheme 1).

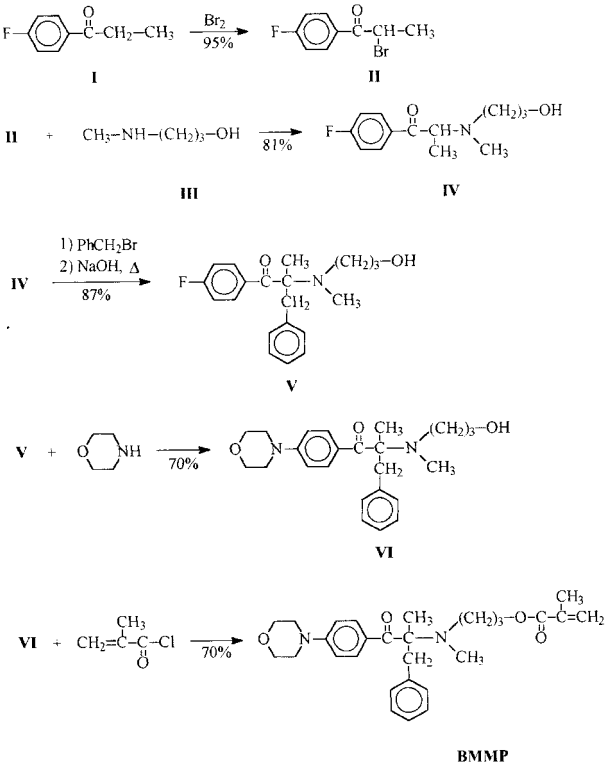
Finally, the synthesis of low-molecular-weight model compounds, such as 1-(4-morpholinophenyl)-2-benzyl-2-[*N*-methyl-*N*-(3-pivaloyloxypropyl)]aminopropan-1-one (BMPP) and 1-(4-morpholinophenyl)-2-benzyl-2-[*N*-methyl-*N*-(3-pivaloyloxypropyl)]aminobutan-1-one (BMPB), has been also carried out with the aim to compare their photoinitiation activity withthat of the corresponding polymeric systems and hence to evidence possible synergistic polymer effects.



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

(**1**)

Both low- and high-molecular-weight samples have been checked in the cure of 1,6-hexandiol



Scheme 1

diacrylate/*n*-butyl acrylate (HDDA/BA) equimolar mixture upon irradiation over 380 nm, thus simulating the conditions of a TiO_2-pigmented acrylic formulation; and the process has been kinetically followed in real time by microwave dielectrometry at 9.5 GHz, a new technique we have recently introduced,[11–14] which allows one to measure the induction period and the rate of the process, as well as the amount of residual monomers after the cure.

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-(4-Morpholinophenyl)-2-benzyl-2-[*N*-methyl-*N*-(3-methacryloyloxypropyl)]aminopropan-1-one (BMMP) has been prepared, according to the procedure depicted in Scheme 1, from 1-(4-fluorophenyl)propan-1-one (**I**) (Aldrich) (32 mmol) and bromine[15] to give in 95% yield pure 1-(4-fluorophenyl)-2-bromopropan-1-one (**II**). This was then reacted[16] with *N*-methyl-*N*-(3-hydroxypropyl)amine (**III**) (obtained, in turn, by formylation[17] of 3-hydroxypropylamine with ethyl formiate followed by successive reduction[17] with $LiAlH_4$) to afford in 81% yield pure 1-(4-fluorophenyl)-2-[*N*-methyl-*N*-(3-hydroxypropyl)]-aminopropan-1-one (**IV**). The amino ketone **IV** was then treated with benzyl bromide[7] to give the corresponding quaternary ammonium salt, which was allowed to transpose,[18] in conc aq NaOH, to crude 1-(4-fluorophenyl)-2-benzyl-2-[*N*-methyl-*N*-(3-hydroxypropyl)]aminopropan-1-one (**V**) (87% yield). **V** was successively reacted with morpholine[7] to afford in 70% yield pure 1-(4-morpholinophenyl)-2-benzyl-2-[*N*-methyl-*N*-(3-hydroxypropyl)]aminopropan-1-one (**VI**), which was finally esterified by methacryloyl chloride to give in 70% yield pure BMMP.

Further details on synthesis and spectroscopic data of the novel compounds prepared are reported below.

1-(4-Fluorophenyl)-2-[N-methyl-N-(3-hydroxypropyl)]aminopropan-1-one (IV)

To *N*-methyl-*N*-(3-hydroxypropyl)amine (**III**) (27.4 mmol), dissolved in 50 mL of anhydrous diethyl ether, 32 mmol of 1-(4-fluorophenyl)-2-bromopropan-1-one (**II**) in 10 mL of the same solvent were slowly dropped at 0°C. The reaction mixture, analyzed by thin layer chromatography (TLC) in $CHCl_3$, was allowed to stay at 0°C for 18 h and then warmed up to room temperature. After washing with 100 mL of water, the ethereal layer was dried on Na_2SO_4, and the solvent was removed under vacuum. The crude product was then purified by chromatography on SiO_2 (70–230 mesh) by using a $CHCl_3/CH_3OH$ (20 : 1) mixture as eluent. Upon evaporation of the solvent, 26 mmol of pure liquid **IV** were obtained. Other spectroscopic characterizations are as follows.

^{1}H-NMR ($CDCl_3$): 8.0 (m, 2H, aromatic protons), 7.1 (t, 2H, aromatic protons), 4.2 (q, 1H, —CH—), 3.6 (m, 2H, —C$\underline{H}_2$OH), 3.3 (bs, 1H, —OH), 2.7 (t, 2H, —N—CH_2—), 2.3 (s, 3H, —N—CH_3), 1.6 (m, 2H, —N—CH_2—C$\underline{H}_2$—), and 1.2 (d, 3H, —CH—$\underline{CH}_3$) ppm.

IR (liquid film on KBr): 3359 (ν_{OH}), 3075 (ν_{CH}, aromatic), 2942, 2869 (ν_{CH}, aliphatic), 1683 (ν_{CO}), 1599, 1505 ($\nu_{C=C}$, aromatic), 1230 (ν_{CF}), and 851 (δ_{CH}, 1,4-disubstituted phenyl ring) cm^{-1}.

1-(4-Fluorophenyl)-2-benzyl-2-[N-methyl-N-(3-hydroxypropyl)]aminopropan-1-one (V)

To 26 mmol of **IV**, dissolved in 25 mL of acetonitrile, 31 mmol of benzyl bromide were added dropwise, under nitrogen atmosphere at 35°C. The reaction mixture, whose time evolution was checked by TLC in $CHCl_3/CH_3OH$ (20 : 1), was allowed to stay at 35°C for 12 h; the solvent was then removed in vacuum, and the residue was dissolved in 50 mL of water and additioned at 60°C with 52 mmol of 34% aq NaOH (w/v). The reaction mixture was allowed to stay at 60°C for 0.5 h, cooled at room temperature, and finally extracted with $CHCl_3$. The organic layer, dried on Na_2SO_4 gave, after evaporation of the solvent under vacuum, 23 mmol of crude **V**, which was not further purified but was directly used for the successive reaction.

^{1}H-NMR ($CDCl_3$): 8.4 (m, 2H, benzoyl ring aromatic protons), 7.1 (m, 5H, benzyl ring aromatic protons), 6.9 (m, 2H, benzoyl ring aromatic protons), 3.6 (t, 2H, —C$\underline{H}_2$OH), 3.5 and 3.1 (2d, 2H,

—C$\underline{H}_2$Ph), 2.7 (2m, 2H, —N—CH_2—), 2.3 (s, 3H, —N—CH_3), 1.7 (m, 2H, N—CH_2—C$\underline{H}_2$—), and 1.2 (s, 3H, C—CH_3) ppm.

IR (liquid film on KBr): 3343 (ν_{OH}), 3065, 3030 (ν_{CH}, aromatic), 2944, 2869 (ν_{CH}, aliphatic), 1679 (ν_{CO}), 1597, 1498 ($\nu_{C=C}$, aromatic), 1228 (ν_{CF}), 847 (δ_{CH}, 1,4-disubstituted phenyl ring), 761, and 703 (δ_{CH}, monosubstituted phenyl ring) cm^{-1}.

1-(4-Morpholinophenyl)-2-benzyl-2-[N-methyl-N-(3-hydroxypropyl)]aminopropan-1-one (VI)

To 23 mmol of **V**, under nitrogen atmosphere, 45 mmol of morpholine, 45 mmol of K_2CO_3, and 25 mL of dimethylsulfoxide were added. The reaction mixture was warmed up to 160°C for 14 h, its time evolution being followed by TLC in $CHCl_3$/CH_3OH (20 : 1), to give, after work up, 16 mmol of pure **VI**.

^{1}H-NMR ($CDCl_3$): 8.4 (d, 2H, aromatic protons in ortho position to carbonyl group), 7.1 (m, 3H, aromatic protons in metha and para positions to CH_2), 6.9 (m, 2H, aromatic protons in *ortho* position to CH_2), 6.8 (d, 2H, aromatic protons in *ortho* position to the morpholino group), 3.9 (m,4H, —CH_2—O—CH_2—), 3.6 (t, 2H, —C$\underline{H}_2$OH), 3.3 (m, 4H, —CH_2—N—CH_2—), 3.5 and 3.0 (2d, 2H, —C$\underline{H}_2$Ph), 2.7 and 2.4 (2m, 2H, CH_3—N—C$\underline{H}_2$—), 2.3 (s, 3H, —N—CH_3), 1.9 (bm, 1H, OH), 1.7 (m, 2H, CH_3—N—CH_2—C$\underline{H}_2$—), and 1.2 (s, 3H, C—CH_3) ppm.

IR (liquid film on KBr): 3413 (ν_{OH}), 3062, 3028 (ν_{CH}, aromatic), 2961, 2856 (ν_{CH}, aliphatic), 1658 (ν_{CO}), 1595, 1452 ($\nu_{C=C}$, aromatic), 832 (δ_{CH}, 1,4-disubstituted phenyl ring), 749, and 701 (δ_{CH}, monosubstituted phenyl ring) cm^{-1}.

1-(4-Morpholinophenyl)-2-benzyl-2-[N-methyl-N-(3-methacryloyloxypropyl)]aminopropan-1-one (BMMP)

To 13 mmol of **VI**, dissolved in 40 mL of anhydrous THF, 19 mmol of triethylamine were added under nitrogen atmosphere; then, 19 mmol of methacryloyl chloride in 10 mL of anhydrous THF were added dropwise at 0°C. The reaction mixture, whose time evolution was checked by TLC by using a $CHCl_3$/CH_3OH (20 : 1) mixture as eluent, was maintained at room temperature for 12 h. After removal of the solvent under vacuum, the reaction product was dissolved in the minimum amount of $CHCl_3$ and washed with water in order to remove the ammonium salt. The excess of methacryloyl chloride was successively eliminated by washing with 200 mL of aq NaOH. The organic layer, after treatment with anhydrous Na_2SO_4 and removal of the solvent under vacuum, gave 8.8 mmol of pure BMMP.

^{1}H-NMR ($CDCl_3$): 8.4 (d, 2H, aromatic protons in ortho position to carbonyl group), 7.1 and 6.9 (m, 5H, benzyl ring aromatic protons), 6.8 (d, 2H, aromatic protons in *ortho* position to the morpholino group), 6.0 and 5.5 (2s, 2H, =CH_2), 4.1 (t, 2H, CH_2—OCO—), 3.8 (m, 4H, —CH_2—O—CH_2—), 3.3 (m, 4H, —CH_2—N—CH_2—), 3.4 and 3.0 (2d, 2H, —C$\underline{H}_2$Ph), 2.7 and 2.4 (2m, 2H, CH_3—N—C$\underline{H}_2$—), 2.3 (s, 3H, —N—CH_3), 1.9 (s, 3H, =C—CH_3), 1.7 (m, 2H, —N—CH_2—C$\underline{H}_2$—), and 1.2 (s, 3H, C—CH_3) ppm.

IR (liquid film on KBr): 3020 (ν_{CH}, aromatic), 2961, 2856 (ν_{CH}, aliphatic), 1718 (ν_{CO}, ester group), 1662 (ν_{CO}, ketone group), 1637 ($\nu_{C=C}$, methacrylic group), 1596, 1496 ($\nu_{C=C}$, aromatic), 831 (δ_{CH}, 1,4-disubstituted phenyl ring), 744, and 703 (δ_{CH}, monosubstituted phenyl ring) cm^{-1}.

1-(4-Morpholinophenyl)-2-benzyl-2-[*N*-methyl-*N*-(3-methacryloyloxypropyl)]aminobutan-1-one (BMMB) was synthesized with the same procedure as reported in Scheme 1 for BMMP, starting from 1-(4-fluorophenyl)-2-bromobutan-1-one, obtained in turn by a Friedel–Crafts acylation of fluorobenzene with butyric acid chloride.[18] We report here only the spectroscopic features related to novel intermediate products.

1-(4-Fluorophenyl)-2-[N-methyl-N-(3-hydroxypropyl)]aminobutan-1-one

^{1}H-NMR ($CDCl_3$): 8.0 (m, 2H, aromatic protons), 7.1 (t, 2H, aromatic protons), 4.1 (dd, 1H, —CH—), 3.8, (bm, 1H, —OH), 3.7 (m, 2H, —C$\underline{H}_2$OH), 2.7 (dt, 2H, —N—CH_2—), 2.4 (s, 3H, —N—CH_3), 1.9 (m, 2H, —CH—C$\underline{H}_2$—), 1.7 (m, 2H, —N—CH_2—C$\underline{H}_2$—), and 0.9 (t, 3H, —CH_2—C$\underline{H}_3$) ppm.

IR (liquid film on KBr): 3397 (ν_{OH}), 3074 (ν_{CH}, aromatic), 2965, 2877 (ν_{CH}, aliphatic), 1681 (ν_{CO}), 1596, 1505 ($\nu_{C=C}$, aromatic), 1226 (ν_{CF}), and 845 (δ_{CH}, 1,4-disubstituted phenyl ring) cm^{-1}.

1-(4-Fluorophenyl)-2-benzyl-2-[N-methyl-N-(3-hydroxypropyl)]aminobutan-1-one

This product, differently from the corresponding intermediate employed in the synthesis of BMMP, due to the lower conversion to the ammonium salt precursor, was purified from the unreacted 1-(4-

fluorophenyl) - 2 - [*N* - methyl - *N* - (3 - hydroxypropyl)]aminobutan-1-one by chromatography on SiO_2 (70–230 mesh), by using a $CHCl_3/CH_3OH$ (20 : 1) mixture as eluent.

^{1}H-NMR ($CDCl_3$): 8.4 (m, 2H, benzoyl ring aromatic protons), 7.2 (m, 5H, benzyl ring aromatic protons), 6.9 (m, 2H, benzoyl ring aromatic protons), 3.5 (t, 2H, —C$\underline{H}_2$OH), 3.2 (2d, 2H, —C$\underline{H}_2$Ph), 2.8 and 2.5 (2m, 2H, —N—CH_2—), 2.3 (s, 3H, —N—CH_3), 1.9 (m, 2H, —C$\underline{H}_2$—CH_3), 1.7 (m, 2H, N—CH_2—C$\underline{H}_2$—), and 0.7 (t, 3H, —CH_2—C$\underline{H}_3$) ppm.

IR (liquid film on KBr): 3369 (ν_{OH}), 3066, 3030 (ν_{CH}, aromatic), 2942, 2878 (ν_{CH}, aliphatic), 1678 (ν_{CO}), 1597, 1499 ($\nu_{C=C}$, aromatic), 1229 (ν_{CF}), 848 (δ_{CH}, 1,4-disubstituted phenyl ring), 753, and 704 (δ_{CH}, monosubstituted phenyl ring) cm^{-1}.

1-(4-Morpholinophenyl)-2-benzyl-2-[N-methyl-N-(3-hydroxypropyl)]aminobutan-1-One

^{1}H-NMR ($CDCl_3$): 8.4 (d, 2H, benzoyl ring aromatic protons), 7.2 (m, 5H, benzyl ring aromatic protons), 6.8 (m, 2H, benzoyl ring aromatic protons), 3.9 (m, 4H, —CH_2—O—CH_2—), 3.5 (t, 2H, —C$\underline{H}_2$OH), 3.3 (m, 4H, —CH_2—N—CH_2—), 3.2 (2d, 2H, —C$\underline{H}_2$Ph), 2.7 and 2.5 (2m, 2H, CH_3—N—C$\underline{H}_2$—), 2.3 (s, 3H, —N—CH_3), 2.1 and 1.9 (2m, 2H, —C$\underline{H}_2$—CH_3), 1.7 (m, 2H, CH_3—N—CH_2—C$\underline{H}_2$—), and 0.7 (t, 3H, CH_2—C$\underline{H}_3$) ppm.

IR (liquid film on KBr): 3457 (ν_{OH}), 3061, 3027 (ν_{CH}, aromatic), 2963, 2857 (ν_{CH}, aliphatic), 1657 (ν_{CO}), 1595, 1496 ($\nu_{C=C}$, aromatic), 830 (δ_{CH}, 1,4-disubstituted phenyl ring), 756, and 705 (δ_{CH}, monosubstituted phenyl ring) cm^{-1}.

1-(4-Morpholinophenyl)-2-benzyl-2-[N-methyl-N-(3-methacryloyloxypropyl)]aminobutan-1-one (BMMB)

^{1}H-NMR ($CDCl_3$): 8.4 (d, 2H, benzoyl ring aromatic protons), 7.2 (m, 5H, benzyl ring aromatic protons), 6.8 (d, 2H, aromatic protons), 6.0 and 5.5 (2d, 2H, =CH_2), 4.0 (t, 2H, CH_2—OCO—), 3.8 (m, 4H, —CH_2—O—CH_2—), 3.3 (m, 4H, —CH_2—N—CH_2—), 3.2 (s, 2H, —C$\underline{H}_2$Ph), 2.8 and 2.5 (2m, 2H, CH_3—N—C$\underline{H}_2$—), 2.3 (s, 3H, —N—CH_3), 2.0 (2m, 2H, —C$\underline{H}_2$—CH_3), 1.9 (s, 3H, =C—CH_3), 1.8 (m, 2H, CH_3—N—CH_2—C$\underline{H}_2$—), and 0.7 (t, 3H, —CH_2—C$\underline{H}_3$) ppm.

IR (liquid film on KBr): 3020 (ν_{CH}, aromatic), 2964, 2855 (ν_{CH}, aliphatic), 1718 (ν_{CO}, ester group), 1657 (ν_{CO}, ketone group), 1637 ($\nu_{C=C}$, methacrylic group), 1596, 1496 ($\nu_{C=C}$, aromatic), 816 (δ_{CH}, 1,4-disubstituted phenyl ring), 757 and 705 (δ_{CH}, monosubstituted phenyl ring) cm^{-1}.

Low-Molecular-Weight Models

1-(4-Morpholinophenyl)-2-benzyl-2-[*N*-methyl-*N* - (3 - pivaloyloxypropyl)]aminopropan - 1 - one (BMPP) was synthesized with the same procedure followed for BMMP (Scheme 1), just replacing methacryloyl chloride by pivaloyl chloride. Other spectroscopic characterizations are as follows.

^{1}H-NMR ($CDCl_3$): 8.4 (d, 2H, benzoyl ring aromatic protons), 7.1–6.9 (m, 5H, benzyl ring aromatic protons), 6.8 (d, 2H, aromatic protons), 4.1 (m, 2H, CH_2—OCO—), 3.8 (m, 4H, —CH_2—O—CH_2—), 3.3 (m, 4H, —CH_2— N—CH_2—), 3.4 and 3.0 (2d, 2H, —C$\underline{H}_2$Ph), 2.7 (2m, 2H, CH_3—N—C$\underline{H}_2$—), 2.3 (s, 3H, —N—CH_3), 1.8 (m, 2H, CH_3—N—CH_2—C$\underline{H}_2$—), 1.2 (s, 3H, —N—C—CH_3), and 1.1 [s, 9H, C(CH_3)$_3$] ppm.

IR (liquid film on KBr): 3062, 3028 (ν_{CH}, aromatic), 2968, 2856 (ν_{CH}, aliphatic), 1725 (ν_{CO}, ester group), 1662 (ν_{CO}, ketone group), 1595, 1496 ($\nu_{C=C}$, aromatic), 831 (δ_{CH}, 1,4-disubstituted phenyl ring), 757, and 703 (δ_{CH}, monosubstituted phenyl ring) cm^{-1}.

1-(4-Morpholinophenyl)-2-benzyl-2-[*N*-methyl-*N*-(3-pivaloyloxypropyl)]aminobutan-1-one (BMPB) was synthesized with the same procedure followed for BMMB, just replacing methacryloyl chloride by pivaloyl chloride. Other spectroscopic characterizations are as follows.

^{1}H-NMR ($CDCl_3$): 8.4 (d, 2H, benzoyl ring aromatic protons), 7.2 (m, 5H, benzyl ring aromatic protons), 6.8 (d, 2H, benzoyl ring aromatic protons), 4.0 (m, 2H, CH_2—OCO—), 3.8 (m, 4H, —CH_2—O—CH_2—), 3.3 (m, 4H, —CH_2—N—CH_2—), 3.2 (s, 2H, —C$\underline{H}_2$Ph), 2.8 and 2.5 (2m, 2H, CH_3—N—C$\underline{H}_2$—), 2.3 (s, 3H, —N—CH_3), 2.1 and 1.9 (2m, 2H, —NCC$\underline{H}_2$—CH_3), 1.7 (m, 2H, CH_3—N—CH_2—C$\underline{H}_2$—), 1.1 [s, 9H, C(CH_3)$_3$], and 0.7 (t, 3H, —N—C—CH_2—C$\underline{H}_3$) ppm.

IR (liquid film on KBr): 3062, 3028 (ν_{CH}, aromatic), 2971, 2858 (ν_{CH}, aliphatic), 1727 (ν_{CO}, ester group), 1661 (ν_{CO}, ketone group), 1596, 1496 ($\nu_{C=C}$, aromatic), 828 (δ_{CH}, 1,4-disubstituted phenyl ring), 772, and 704 (δ_{CH}, monosubstituted phenyl ring) cm^{-1}.

Polymeric Photoinitiators

Homopolymers and copolymers were prepared by free radical polymerization in tetrahydrofuran

Table I Synthesis and Structural Characterization of Homopolymers from BMMP and BMMB

		Polymeric Product	
Monomer	Conversion[a](%)	$\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[b]
BMMP	41	18,500	1.3
BMMB	43	15,700	2.1

Polymerization conditions: 60°C in THF. Duration: 150 h.
[a] Determined as (weight of polymer/weight of monomer) × 100.
[b] Evaluated by GPC analysis.

(THF) solution, using 2 wt % (with respect to the monomers) of 2,2′-azobisisobutyronitrile (AIBN) as a 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 kept at 60°C for 150 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 and again precipitated with petroleum ether, filtered, dried under vacuum, and finally stored in the refrigerator in the dark. 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

HDDA/BA equimolar mixtures containing 0.3 mol % of α-aminoacetophenone moieties were cured on film matrix (300 μm) at 25°C under nitrogen, by irradiation with a high-pressure 100W OSRAM HBO Hg lamp. Cure experiments were performed by using the above lamp in the presence of a glass-colored passband filter LG-400 (Corion Corporation) in order to absorb completely the UV light below 380 nm. The time evolution of the curing process was followed by microwave dielectrometry at 9.5 GHz, in terms of ε'' (loss factor), by using the cavity perturbation method.[19,20]

Physicochemical Measurements

^{1}H-NMR spectra were carried out at 200 MHz on samples in $CDCl_3$ solution by using a Varian FT-NMR Gemini 200 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 450–330 and 330–250 nm spectral regions were investigated by using 0.1 and 1 cm cell path lengths, 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 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) and poly(BMMB) were obtained by free radical initiation, in the presence of AIBN, in quite low yields (<50%) (Table I). This may be addressed to chain transfer reactions involving the tertiary amino groups of the monomers.[21] Indeed, the α-alkylamino radicals thus generated usually have a lower reinitiation rate constant as compared with the propagation process,[21] thus implying a lowering of the overall polymerization rate and hence of the conversion to polymer. This is also confirmed by the rather low average molecular weight obtained for both polymers (Table I). Analogous results were found in the homopolymerization of acrylates containing α-morpholinoacetophenone or *N*,*N*-dialkylamino moieties.[8,22]

^{1}H-NMR and IR analysis of the polymers confirm the expected structures. Indeed, ^{1}H-NMR spectra (Fig. 1) do not show the signals in the 6.0–5.5 ppm region given by the methylene protons of the methacrylic group present in the corresponding monomers, thus clearly indicating that the polymerization reaction has involved the

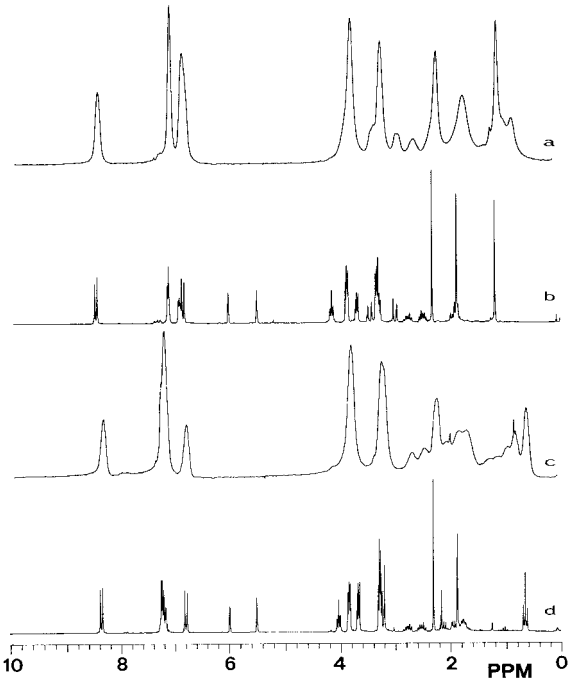


Figure 1 ^{1}H-NMR spectra in $CDCl_3$ solution of (a) poly(BMMP), (b) BMMP, (c) poly(BMMB), and (d) BMMB.

above unsaturated functions. Accordingly, in the IR spectra of the polymers (Fig. 2), the band at 1637 cm^{-1}, related to the stretching vibration of the carbon–carbon double bond of the methacrylic group disappears. Moreover, the IR band connected with the stretching vibration of the carbonyl group in the ester moiety is located in the polymers at the same frequency (1727–1725 cm^{-1}) as in the structural models, but at higher frequencies with respect to the corresponding monomers (1718 cm^{-1}). Similar results were previously observed in acrylic and methacrylic polymers bearing side-chain azoaromatic photochromic moieties.[23,24]

The UV spectra in chloroform solution of poly(BMMP) and poly(BMMB) show an intense absorption band ($\varepsilon > 22{,}000$) centered at about 325 nm (Table II), similarly to the low-molecular-weight photoinitiators BDMP and BDMB mentioned in the introduction. This absorption pattern was attributed[7,25] to the electron withdrawing character of the morpholino ring in para position to the benzoyl group, which causes a shift of the $\pi \rightarrow \pi^*$ electronic transition absorption towards lower frequencies (from 250 to 325 nm), thus completely obscuring the much less intense $n \rightarrow \pi^*$ transition of the ketone moiety. Analogous spectra are obtained for the corresponding low-molecular-weight structural models BMPP and BMPB (Table II).

In addition to an hypochromic effect exhibited by poly(BMMP) and poly(BMMB) at the absorption maximum with respect to the corresponding models, indicative of the presence of dipole–dipole interactions between side-chain α-aminoacetophenone moieties along the backbone,[26,27] both polymers and models display a significant absorption tail extending over 380 nm, in agreement to what previously observed for BDMP and BDMB.[7,25] Similarly, a higher molar extinction coefficient in this region is displayed by poly(BMMB) with respect to poly(BMMP) (Fig. 3), as well as by BMPB with respect to BMPP (Table II).

Photoinitiation Activity

The photoinitiation activity of poly(BMMP) and poly(BMMB) has been checked in the UV-initiated bulk polymerization of the HDDA/BA equimolar mixture containing 0.3 mol % of α-aminoacetophenone moiety and compared with that of the corresponding structural models BMPP and BMPB. All measurements were carried out under irradiation over 380 nm, thus simulating the ab-

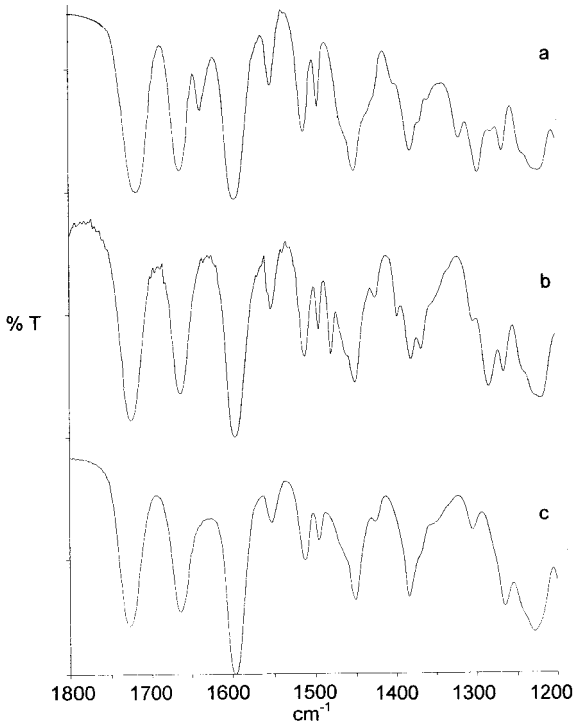


Figure 2 IR spectra in the 1800–1200 cm^{-1} range of (a) BMMP, (b) BMPP, and (c) poly(BMMP).

Table II UV Absorption Spectra in Chloroform Solution of Polymers and Models Containing the α-Aminoacetophenone Moiety

Sample	λ_{max} (nm)	ε_{max} (L mol^{-1} cm^{-1})	ε_{380} (L mol^{-1} cm^{-1})
Poly(BMMP)	325	22,700	180
BMPP	324	23,600	150
Poly(BMMB)	324	23,400	470
BMPB	323	24,200	390

sorption conditions of a TiO_2-pigmented coating formulation.

Poly(BMMP) displays (Fig. 4) a remarkably higher photoinitiation activity against the model BMPP, as revealed by the polymerization rate values calculated at the half-time of the curing process $(R_c)_{1/2}$ (Table III). Moreover, as reported in Figure 4, poly(BMMB) is more efficient, as compared with poly(BMMP), and equally active with respect to its model compound BMPB. Finally, poly(BMMP) and BMPP show a much higher induction period than poly(BMMB) and BMPB (Table III).

The significant increase of curing speed by poly (BMMB) and BMPB with respect to poly (BMMP) and BMPP can be attributed to the higher light absorption over 380 nm of the former systems, owing to the presence of an ethyl group against a methyl group in α-position to the ketone moiety, similarly to what previously observed[7] for BDMB and BDMP. This finding also implies both the shortening of the induction period in the curing process of the acrylic formulation and the improvement of productivity if applied to industrial coating lines. Indeed, the larger the photon absorption is, the faster the generation of primary radicals and their reaction with oxygen (in traces) responsible for the polymerization inhibition are. At present, it is not clear why poly(BMMB), despite its larger absorption over 380 nm, does not give rise to any improvement of the curing efficiency with respect to the corresponding low-molecular-weight model BMPB.

A tentative explanation of these results may be based on the following considerations. It is well established[7] that the main fragmentation pathway of these systems occurs by photocleavage at

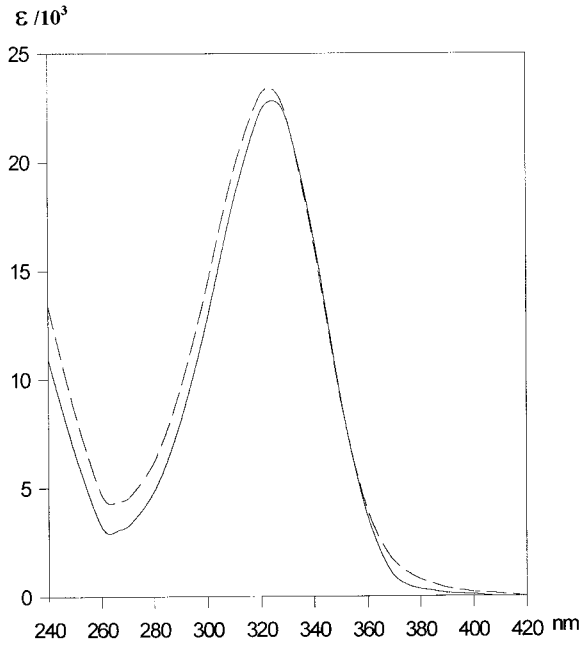


Figure 3 UV spectra in chloroform solution of (——) poly(BMMP) and (-----) poly(BMMB).

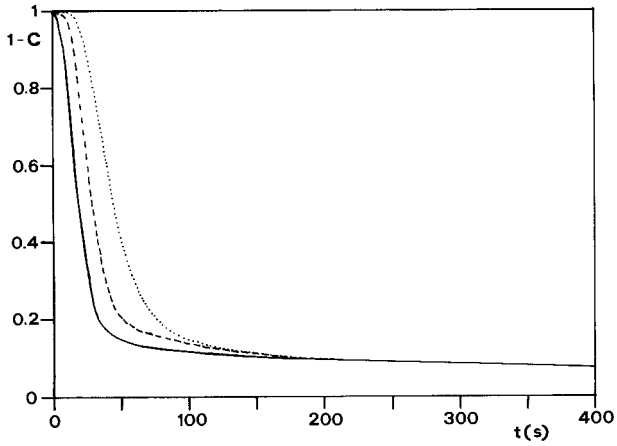


Figure 4 Fraction of residual monomers (1-C) versus time in the UV curing of HDDA/BA equimolar mixture upon irradiation over 380 nm, in the presence of 0.3 mol % of α-aminoacetophenone moieties: (——) poly(BMMB) and BMPB; (· · · · · ·) BMPP and (------) poly(BMMP).

Table III UV-initiated Polymerization in Film Matrix of HDDA/BA (1 : 1) Mixtures Under Nitrogen, Promoted by High- and Low-Molecular-Weight α-Aminoacetophenon Photoinitiators

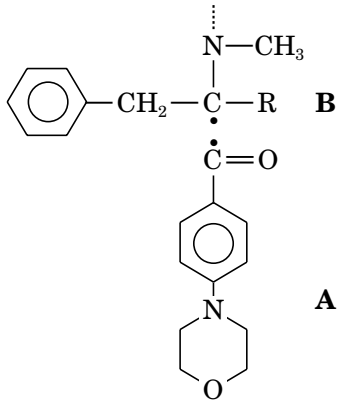
Photoinitiator	$(R_c)_{1/2}$[a] (s^{-1})	t_0[b] (s)
Poly(BMMP)	3.3	12
BMPP	2.0	19
Poly(BMMB)	3.7	5
BMPB	3.7	5

Photoinitiator concentration: 0.3 mol % of α-aminoacetophenone moiety; $\lambda_{irr} > 380$ nm.

[a] Polymerization rate calculated at the half-time of the curing process.

[b] Induction period of the curing process.

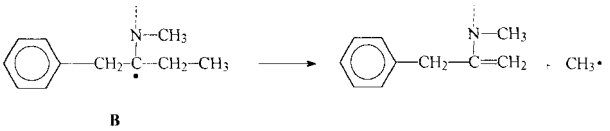
the α-position with respect to the ketone group, giving benzoyl (A) and alkyl (B) primary radicals.



(**2**)

In the case of the polymeric photoinitiators, polymer-bound B radicals are protected from coupling reactions by the macromolecular coiling, thus increasing the initiation efficiency as compared with low-molecular-weight B radicals deriving from the corresponding models.[28] The same activity exhibited by BMPB against poly(BMMB) seems therefore to suggest that when *R* is equal to *Et*, the steric hindrance of the ethyl group prevents B radicals recombination, with a similar effect to that given by a polymer backbone. It cannot be excluded, however, that B radicals further evolve to the generation of very active methyl radical species, thus vanishing any difference between low- and high-molecular-weight photoinitiators (Scheme 2).

Nevertheless, poly(BMMB)—particularly when applied to the cure of thick, white pigmented films (>100 μm), which require long exposure times—



Scheme 2

has to be preferred to BMPB, as the former, due to its polymeric nature, is expected to strongly reduce yellowing and aging phenomena.

CONCLUSIONS

On the basis of the reported data, the following concluding remarks can be drawn.

1. Novel polymeric systems bearing side-chain α-aminoacetophenone moieties have been prepared and fully characterized.
2. The above polymers display high photoinitiation activity in the UV cure of acrylic formulations under irradiation conditions which simulate the presence of TiO_2 rutile as white pigment. The activity of the polymeric photoinitiators is higher or equal as compared with that of the corresponding low-molecular-weight models.
3. The synthesized photoinitiators are expected to give, against the commercially available low-molecular-weight counterparts, significative advantages connected with their macromolecular nature, such as elimination or strong reduction of aging and yellowing processes of the coating film, owing to the decreased migration onto the film surface by residual photoreactive species; decrease of toxic and bad smelling emissions, as a large part of the photolysis products, remain anchored to the polymer matrix, and the unreacted photosensitive moieties are not volatile; and improvement of the ultimate properties of the coating film, in terms of adhesion and mechanical features, thanks to the participation by the polymeric photoinitiator to grafting and cross-linking processes with the coating formulation components.

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