Polymers containing side-chain benzophenone chromophores: a new class of highly efficient polymerization photoinitiators*

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In the present paper the efficiency of side-chain benzophenone chromophores containing polymers has been tested in the u.v. photoinitiated polymerization of acrylic monomers. Poly(4-acryloxybenzophenone) (poly(ABP)) and copolymers of acryloxybenzophenone (ABP) with (−)-menthyl acrylate (MtA), methyl acrylate (MA) and 1-acryloxy-2-ethoxyethane (AEE) exhibit much higher efficiency than that observed for the low molecular weight model compound 4-(2-methylpropionyloxy)benzophenone (IBP). The experimental findings indicate that the efficiency of the copolymer as photoinitiator depends markedly on the nature of benzophenone non-containing co-units and on the sequence length of ABP monomeric units. When poly(ABP) is used as photoinitiator in combination with a tertiary amine such as *N,N*-dimethylaniline (DMA) or poly[4-(*N,N*-dimethylamino)styrene] (poly(DMAS)), its efficiency is higher than that observed for the corresponding IBP/DMA and IBP/poly(DMAS) systems. Only in the case of the substantially alternating copolymer of ABP with DMAS is the efficiency of the macromolecular photoinitiator lower with respect to that of the mixture of the monomeric analogues (IBP + DMA).

Keywords Photoinitiated polymerization of acrylic monomers; macromolecular photoinitiators; poly(4-hydroxybenzophenone acrylate); copolymers of 4-acryloxybenzophenone with methyl acrylate; (−)-menthyl acrylate; 1-acryloxy-2-ethoxyethane; 4-(*N,N*-dimethylamino)styrene

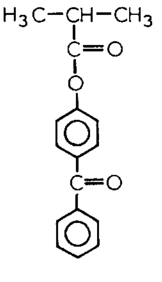
INTRODUCTION

A fundamental role in u.v.-curable formulations for non-polluting coatings is played by the photoinitiator which by irradiation gives rise to the formation of radical species able to initiate the polymerization and crosslinking of unsaturated monomers[1,2].

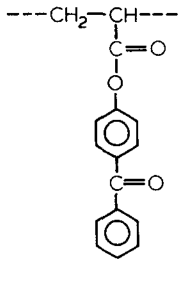
Low molecular weight benzophenone derivatives have been widely used as photoinitiators operating essentially with a hydrogen abstraction mechanism[1-4].

On the other hand, polymeric systems containing side-chain benzophenone moieties have been reported to induce, by u.v. irradiation, grafting[5-7] and crosslinking[8-11] reactions, due to termination reactions of semipinacolinic radicals with growing macroradicals[6] and coupling of macroradicals[12,13], respectively.

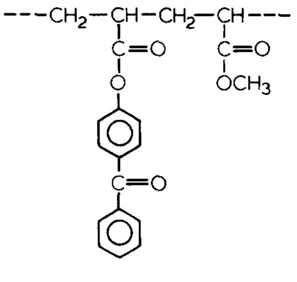
In this context macromolecular systems bearing side-chain benzophenone chromophores, such as the homopolymer of 4-acryloxybenzophenone (poly(ABP)) and its copolymers with (−)-menthyl acrylate (MtA) (poly(ABP-*co*-MtA)s), methyl acrylate (MA) (poly(ABP-*co*-MA)s), 1-acryloxy-2-ethoxyethane (AEE) (poly(ABP-*co*-AEE)s) and 4-(*N,N*-dimethylamino)styrene (DMAS) (poly(ABP-*co*-DMAS)s) have been used in the photoinitiated polymerization of acrylic monomers and their efficiency compared with that of the low molecular weight model compound 4-(2-methylpropionyloxy) benzophenone (IBP).



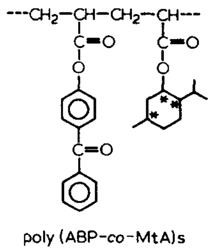
IBP



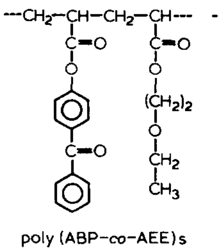
poly (ABP)



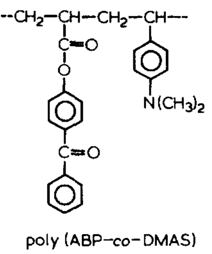
poly (ABP-*co*-MA)s



poly (ABP-*co*-MtA)s



poly (ABP-*co*-AEE)s



poly (ABP-*co*-DMAS)

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EXPERIMENTAL

Monomers

1,6-Hexanedioldiacrylate (*HDDA*). The commercial product SR-238 from 'Sartomer' was distilled under vacuum just before use.

2-Acryloxy-2′-propionyloxy-diethylether (*APDG*).

(i) *Synthesis of 2-hydroxy-2′-propionyloxy-diethylether* (*PDG*). 106 g (1 mol) of diethyleneglycol, 37 g (0.5 mol) of propanoic acid and 1.2 g (7.0 mmol) of *p*-toluenesulphonic acid were allowed to react in 250 ml of benzene. The reaction mixture was refluxed and the water collected by azeotropic distillation. After dilution with diethylether, the organic solution was treated with 5% aqueous $NaHCO_3$ and then with water saturated with NaCl. After drying over anhydrous Na_2SO_4, benzene and diethylether were removed in vacuum and a residue crude product, containing both PDG and 2,2′-dipropionyloxy-diethylether, was obtained. The latter was removed from PDG by adding an excess of water and extracting several times with n-pentane. The aqueous phase was saturated with NaCl and extracted with diethylether. After drying over anhydrous Na_2SO_4 the ethereal solution was distilled to give 40.5 g (0.25 mol) of pure PDG (b.p. = 133°C at 10 mmHg) as tested by g.l.c. analysis (50% yield with respect to propanoic acid).

^1H n.m.r. (CCl_4): $\delta = 4.35$–4.05 ppm (m; $-\underline{\mathrm{CH_2}}-\mathrm{O}-\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}-$), 3.85–3.25 ppm (m; $\underline{-\mathrm{OH}}$ and $\underline{-\mathrm{CH_2}}-\mathrm{O}-$), 2.6–2.15 ppm (q; H_3 5$-\underline{\mathrm{CH_2}}-\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}-$), 1.3–1.0 ppm (t; $\underline{\mathrm{H_3C}}-\mathrm{CH_2}-$).

Intensity ratios 2:7:2:3.

(ii) *Acrylation of 2-hydroxy-2′-propionyloxy-diethylether.* 27 g (0.3 mol) of acryloyl chloride were added dropwise under stirring to 40.5 g (0.25 mol) of PDG, 35.8 g (0.35 mol) of triethylamine and 0.3 g of 2,6-di(t-butyl)-4-methylphenol dissolved in 100 ml of anhydrous diethylether, maintaining a gentle reflux of the solvent. After 2 h the reaction mixture was hydrolysed by dilute aqueous HCl and extracted with diethylether. After drying over anhydrous Na_2SO_4 the ethereal solution was distilled to give 39 g (0.18 mol) in 72% yield of pure APDG (b.p. = 90°C at 0.3 mmHg), as tested by g.l.c. analysis.

^1H n.m.r. (CCl_4): $\delta = 6.6$–5.6 ppm (m; $\underline{\mathrm{CH_2}}=\underline{\mathrm{CH}}-\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}-\mathrm{O}-$), 4.4–4.05 ppm (m; $-\underline{\mathrm{CH_2}}-\mathrm{O}-\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}-$), 3.85–3.55 ppm (m; $-\underline{\mathrm{CH_2}}-\mathrm{O}-\underline{\mathrm{CH_2}}$), 2.5–2.1 ppm (q; $\mathrm{H_3C}-\mathrm{CH_2}-\mathrm{O}-$) and 1.4–1.0 ppm (t; $\mathrm{H_3C}-\underline{\mathrm{CH_2}}-$).

Intensity ratios 3:4:4:2:3.

n-Butyl acrylate (*BA*). The commercial product was treated with 5% $NaHCO_3$ aqueous solution, dried over anhydrous Na_2SO_4 and distilled just before use.

(−)*-Menthyl acrylate* (*MtA*). MtA having $[\alpha]_D^{25} = -89$ (neat) was prepared and purified as reported elsewhere[14].

Methyl acrylate (*MA*). The commercial product from 'Merck' was purified and distilled with the same procedure reported for BA.

1-Acryloxy-2-ethoxyethane (*AEE*). This was prepared starting from 1-hydroxy-2-ethoxyethane and acryloyl chloride in the presence of triethylamine[15]. After distillation under vacuum, pure AEE, as tested by g.l.c. analysis, was obtained in 70% yield (b.p. = 71°C at 17 mmHg).

^1H n.m.r. (CCl_4) : $\delta = 6.6$–5.6 ppm (m; $\mathrm{CH_2}\underline{=\mathrm{CH}-}$), 4.3 ppm (t; $-\mathrm{CH_2}\underline{-\mathrm{O}-\underset{\overset{\|}{\mathrm{O}-}}{\mathrm{C}}}$), 3.6 ppm (m; $-\mathrm{CH_2}-\mathrm{O}\underline{-\mathrm{CH_2}}\underline{-\mathrm{CH_3}}$) and 1.2 ppm (t; $-\mathrm{O}-\mathrm{CH_2}-\underline{\mathrm{CH_3}}$).

Intensity ratios 3:2:4:3.

4(N,N*-Dimethylamino)styrene* (*DMAS*). This was prepared from 4-(*N*,*N*-dimethylamino)benzaldehyde and methyl-magnesium bromide as previously reported[16].

Photoinitiators

4-(2-Methylpropionyloxy)benzophenone (*IBP*) *and 4-acryloxybenzophenone* (*ABP*). These have been prepared as previously reported[15].

Polymeric materials containing side-chain benzophenone chromophores. Homo- and copolymerizations of ABP with different acrylic derivatives have been performed in glass vials using 2,2′-azoisobutyronitrile (AIBN) and benzene as radical initiator and solvent, respectively. After introducing the reaction mixture the vial, degassed and sealed under high vacuum, was allowed to stand at 60°C for a suitable time and then the polymerization was stopped by pouring the polymeric solution into a large excess of methanol. The coagulated polymer was filtered, dissolved in chloroform and then precipitated in methanol. This procedure was repeated several times. After drying under vacuum at room temperature, the polymeric products were stored in a refrigerator. All the operations were performed as far as possible in the dark. Following the above procedure poly(ABP)[15], poly(ABP-*co*-MtA)s[15], poly(ABP-*co*-MA)s and poly(ABP-*co*-AEE)s were prepared. Data concerning the synthesis and the properties of the polymers are reported in *Table 1*.

Poly(*ABP*-co-*DMAS*)*s*. These were prepared according to the above procedure. However, the copolymers were recovered by pouring the reaction mixture into a large excess of n-pentane.

Photosensitizers

N,N*-Dimethylaniline.* The commercial product from 'Carlo Erba' has been distilled under vacuum over KOH pellets.

Poly(*DMAS*). This was prepared following the same procedure reported for poly(ABP-*co*-DMAS)s.

1-(2-Methylpropionyloxy)-2-ethoxyethane (*IEE*). This was prepared with the same procedure as reported for AEE in 72% yield (b.p. = 79–80°C at 20 mmHg).

^1H n.m.r. (CCl_4): $\delta = 4.2$ ppm (t; $-\mathrm{CH_2}\underline{-\mathrm{O}-\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}-}$), 3.5 ppm (m; $-\underline{\mathrm{CH_2}}-\mathrm{O}-\underline{\mathrm{CH_2}}-$), 2.5 ppm (m; $-\underline{\mathrm{CH}}(\mathrm{CH_3})_2$) and 1.2 ppm (m; $\underline{\mathrm{H_3C}}-\mathrm{CH_2}$ and $-\mathrm{CH}(\underline{\mathrm{CH_3}})_2$).

Intensity ratios 2:4:1:9.

Photoinitiated polymerizations

The experiments were carried out on thin liquid films ($\simeq 10\,\mu m$) of equimolar mixtures of HDDA and APDG (in the presence of the photoinitiator—1 mol% of benzophenone chromophore) interposed between two flats of NaCl, substantially in the absence of air. With poly(ABP-*co*-AEE)s, equimolar mixtures of HDDA and BA were also used. The polymerization mixture was allowed to be irradiated for different times (seconds) at a distance of 20 cm from a medium-pressure 500 W u.v. linear (15 cm) lamp (Helios Italquartz model GN 500L). At the end of a pre-fixed irradiation time, the sample was directly submitted to i.r. analysis in order to detect the polymerization conversion. The dependence of such conversion on irradiation time has been evaluated on the basis of the progressive depletion of the acrylic double bonds by using the ratio between the optical densities of the i.r. bands at 1410 and 1450 cm^{-1} (baselines 1420–1390 and 1490–1420 cm^{-1}, respectively), connected with the scissor vibration of the terminal methylene of the acrylic groups and of paraffinic methylenes, respectively[17]. The band at 1450 cm^{-1} has been chosen as reference standard, its intensity being almost constant during the polymerization. However, the polymerization conversion was more accurately evaluated according to the Appendix.

Physicochemical measurements

I.r. spectra were recorded on a Perkin-Elmer model 283B spectrometer. 60 MHz ^1H n.m.r. spectra were carried out on a Varian T-60 spectrometer in CCl_4 solution, using TMS as internal standard. U.v. spectra in the range 400–240 nm were performed in $CHCl_3$ solution on a Varian DMS-80 spectrophotometer using a cell path length of 1 cm.

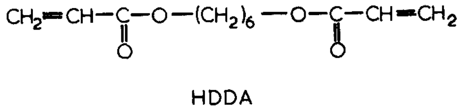
G.l.c. analyses were carried out on a Perkin-Elmer model 3920B instrument equipped with ionization flame detector using 2 m length SE-30 silicon columns.

Melting point determinations were carried out by using a hot-plate Kofler microscope with a heating rate of 3°C min^{-1}.

RESULTS AND DISCUSSION

*Photoinitiated polymerization in the presence of poly(ABP), poly(ABP-*co*-MtA)s and poly(ABP-*co*-MA)s*

The photoinitiated polymerizations were performed on equimolar mixtures of a mono(APDG) and bifunctional (HDDA) acrylic monomers which can be assumed as a simplified model of current industrial formulations of u.v.-curable coatings[18,19].



$$CH_2{=}CH{-}\underset{\underset{O}{\|}}{C}{-}O{-}(CH_2)_6{-}O{-}\underset{\underset{O}{\|}}{C}{-}CH{=}CH_2$$

HDDA

$$CH_2{=}CH{-}\underset{\underset{O}{\|}}{C}{-}O{-}(CH_2{-}CH_2{-}O)_2{-}\underset{\underset{O}{\|}}{C}{-}C_2H_5$$

APDG

First we have compared the efficiency of poly(ABP) with respect to IBP using the same concentration of benzophenone chromophore (1 mol% with respect to the total amount of polymerization mixture). As shown in *Figure 1*, where the percentage of residual acrylic double bonds ($100(1-C)$) is reported as a function of irradiation time, the efficiency of poly(ABP) is markedly higher than that observed for the low molecular weight model IBP, which needs a double irradiation time to reach the final value of conversion ($\simeq 95\%$).

These results could be interpreted assuming that energy migration, arising from interactions between neighbouring excited triplet-state and ground-state side-chain benzophene chromophores, enhances the efficiency of the macromolecular photoinitiator. This hypothesis has been proposed by Kamachi *et al.*[20] to explain the higher efficiency in hydrogen abstraction reaction from THF shown by poly(4-vinylbenzophenone) with respect to benzophenone and in the polymerization of methyl methacrylate initiated by the radicals thus formed. In fact, the energy migration should increase the effective collision distance between excited benzophenone chromophores and hydrogen donors, thus improving the initiation efficiency.

Accordingly measurements of relative phosphorescence yields of copolymers containing different amounts of side-chain benzophenone moieties in the presence of naphthalene as quencher have shown that the efficiency of energy transfer to naphthalene (evaluated as Hirayama critical transfer distance[21]) decreases with increasing mean distance between benzophenone chromophores in the copolymers[20,22]. In this context poly(ABP-*co*-MtA)s and poly(ABP-*co*-MA)s having different content of ABP units have been used as polymerization photoinitiators with the aim of verifying if the photoinitiators efficiency depends on the mean sequence length of ABP units. Therefore poly(ABP-*co*-MA)s containing ABP units in the range 10–80 mol% have been prepared by radical initiation at low conversion ($<17\%$) in order to obtain polymeric materials having homogeneous composition (*Table 1*). The reactivity ratios, obtained by least-squares evaluation of the Kelen–Tüdös parameters[24], were found to be $r_{ABP}=1.27$ and $r_{MA}=0.61$. Also poly(ABP-*co*-MtA)s containing 14–92.5 mol% of ABP units have been prepared as previously reported[15]. Values of reactivity ratios $r_{ABP}=1.32$ and $r_{MtA}=0.68$ were obtained analogously[15]. The molar fractions (%) of ABP and MA or MtA units ($X_{ABP(n)}$, $X_{MA(n)}$ and $X_{MtA(n)}$) inserted in sequence lengths of n units deriving from ABP, MA and MtA, respectively, have also been calculated[15,25]. Selected values of $X_{ABP(n)}$, $X_{MA(n)}$ and $X_{MtA(n)}$ are reported in *Table 2*, varying n in the range 1–5.

The above data indicate that the distribution of co-units in the two copolymer systems is practically the same for analogous compositions.

As shown in *Figure 1* for the photoinitiated polymerization of the equimolar mixture HDDA/APDG, the efficiency of poly(ABP-*co*-MA)s, containing 80–33.4 mol% of ABP units, is, within the limits of experimental error, practically the same as or slightly lower than that of poly(ABP). On the contrary, when poly(ABP-*co*-MA) with 10.2 mol% of ABP units is used, a large decrease of efficiency is observed, even if this is still appreciably higher than that of the low molecular weight model IBP.

A different behaviour is observed in the case of

Table 1 Homo- and copolymerization of 4-acryloxybenzophenone (ABP) with (–)-menthyl acrylate (MtA), methyl acrylate (MA) and 1-acryloxy-2-ethoxyethane (AEE)[a]

Feed				Copolymer characterization		
Comonomer (M_1)	ABP (mol%)	Duration (h)	Conversion[b] (%)	ABP units[c] (mol%)	$\bar{l}^{d}_{\mathrm{ABP}}$	$\bar{l}^{d}_{\mathrm{ABP}}$
–	100.0	144.0	43.5	100.0	–	–
MtA	89.8	2.5	10.5	92.5	1.08	12.62
	75.5	2.0	7.3	80.0	1.22	5.07
	50.6	2.0	5.5	57.6	1.66	2.35
	25.1	1.5	3.2	32.5	3.03	1.44
	10.1	1.5	16.8	13.9	7.05	1.15
MA	74.8	2.5	4.1	80.0	1.21	4.77
	49.7	2.0	4.0	54.3	1.62	2.26
	24.9	1.5	7.7	33.4	2.84	1.42
	7.0	1.5	14.8	10.2	9.10	1.10
AEE	74.9	2.0	4.9	74.0	n.d.	n.d.
	50.0	1.5	2.9	55.0	n.d.	n.d.

[a] 3 g of comonomer mixture; 25 ml of benzene; $T = 60°C$; radical initiator, AIBN (1% w/w)

[b] Calculated as (weight of polymer/weight of starting comonomers) x 100

[c] Evaluated by ^1H n.m.r. analysis

[d] $\bar{l}_1 = \frac{[M_1]}{[ABP]} r_1 + 1 \quad \bar{l}_{ABP} = \frac{[ABP]}{[M_1]} r_{ABP} + 1$

where $[M_1]$ and [ABP] are molar concentrations of M_1 and ABP in the feed, respectively[23]

Table 2 Molar fraction (%) of ABP, MA and MtA units in sequence lengths *n* ($X_{ABP(n)}$, $X_{MA(n)}$ and $X_{MtA(n)}$) for poly(ABP-*co*-MA)s and poly(ABP-*co*-MtA)s

Copolymer		$X_{ABP(n)}$						$X_{M_1(n)}$[a]					
Type	ABP units (mol%)	*n* = 1	2	3	4	5	>5	*n* = 1	2	3	4	5	>5
Poly(ABP-*co*-MA)s	80.0	4.4	7.0	8.2	8.7	8.6	63.1	68.8	23.5	6.0	1.4	0.3	0.0
	54.3	19.7	21.9	18.3	13.6	9.4	17.1	38.2	29.2	16.7	8.5	4.0	3.4
	33.4	49.5	29.3	13.0	5.1	1.9	1.2	12.4	16.1	15.6	13.5	10.9	31.5
	10.2	83.3	14.5	2.0	0.2	0.0	0.0	1.2	2.0	2.9	3.4	3.8	86.7
Poly(ABP-*co*-MtA)	92.5	0.6	1.1	1.6	2.0	2.2	92.5	86.2	12.3	1.3	0.1	0.01	0.09
	80.0	3.9	6.2	7.5	8.0	8.1	66.3	67.1	24.2	6.6	1.6	0.3	0.2
	57.6	18.0	20.8	17.9	13.7	9.8	19.8	36.1	28.8	17.2	9.2	4.6	4.1
	32.5	48.0	29.5	13.5	5.5	2.1	1.4	10.9	14.6	14.7	13.1	11.0	35.7
	13.9	75.8	19.6	3.8	0.6	0.1	0.1	2.0	3.5	4.4	5.1	5.4	79.6

[a] $X_{m_1(n)} = X_{MA(n)}$ or $X_{MtA(n)}$

poly(ABP-*co*-MtA)s (*Figure 2*).

Indeed, all the copolymers containing 32.5–92.5 mol% of ABP units exhibit a higher efficiency than that observed for poly(ABP), particularly in the case of samples containing 32.5 and 57.6 mol% of ABP units. Unfortunately, poly(ABP-*co*-MtA) with 13.9 mol% of ABP units could not be used owing to its insolubility in the comonomer mixture. If the efficiency of the macromolecular photoinitiator depended essentially on energy migration, it should decrease monotonically[20,22] with decreasing content of ABP units. The results obtained in the case of poly(ABP-*co*-MA)s, combined with the distribution of co-unit sequences reported in *Table 2*, seem to indicate that if energy migration is still important it should occur mainly through relatively short sequences of ABP units. Accordingly only when the molar fraction (%) of isolated ABP units is very high (> 80%), as in poly(ABP-*co*-MA) with 10.2 mol% of ABP units, does the efficiency markedly decrease with respect to poly(ABP). On the other hand, the higher efficiency with respect to poly(ABP) shown by poly(ABP-*co*-MtA)s, in which the distribution of co-unit sequences is practically the same as for poly(ABP-*co*-MA)s having the same composition, clearly indicates that, at least in this system, the mean distance between ABP units is not the main factor affecting the efficiency. Therefore it may be concluded that the chemical nature and bulkiness of comonomer units inserted in the macromolecule in order to distance ABP co-units markedly influence the efficiency, modifying the photoreactivity of benzophenone moieties[26] either indirectly (changing the conformational rigidity of the macromolecule[27]) or directly (acting as hydrogen donor).

*Photoinitiated polymerization in the presence of poly(ABP-*co*-AEE)s*

With the aim of clarifying the influence of chemical structure of acrylic monomeric co-units on the efficiency

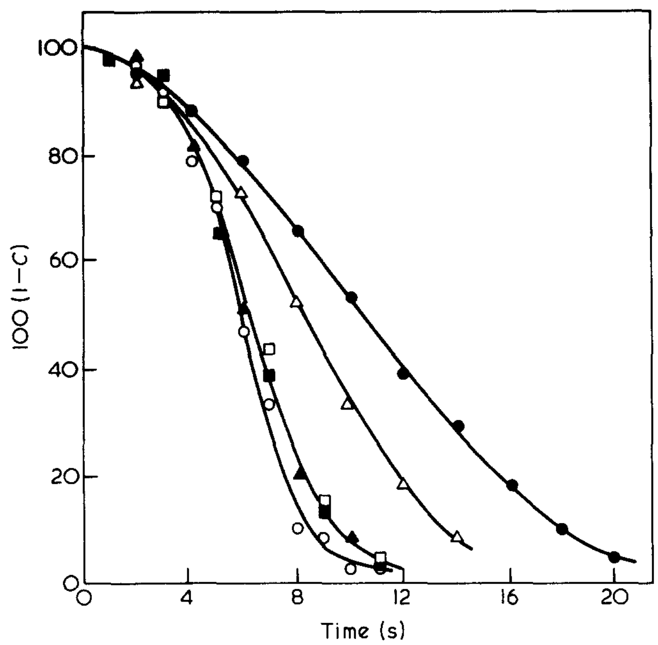


Figure 1 **Percentage of residual acrylic groups [100(1–C)] for the HDDA/APDG equimolar mixture in the presence of 1 mol% of benzophenone moieties photoinitiator, as a function of u.v. irradiation time: ●, IBP; △, poly(ABP-*co*-MA) with 10.2 mol% of ABP units; ■, poly(ABP-*co*-MA) with 33.4 mol% of ABP units; ▲, poly(ABP-*co*-MA) with 54.3 mol% of ABP units; □, poly(ABP-*co*-MA) with 80.0 mol% of ABP units; ○, poly(ABP)**

of benzophenone moieties in the macromolecular photoinitiator, u.v.-initiated polymerization of the HDDA/APDG equimolar mixture has been performed in the presence of poly(ABP-*co*-AEE)s (concentration of ABP units 1 mol%). The choice of AEE as comonomer was due to the well known reactivity of ethers in the hydrogen abstraction reaction by aromatic carbonyl compounds^{1,28}.

As shown in *Figure 3* poly(ABP-*co*-AEE) containing 55.0 mol% of ABP units exhibits efficiency higher than poly(ABP) and intermediate between poly(ABP-*co*-MA) and poly(ABP-*co*-MtA) having similar composition. The presence in the polymerization mixture of an acrylic ether derivative (APDG) in large excess with respect to the amount of AEE units present in the polymeric photoinitiator could in principle depress the difference of efficiency between poly(ABP-*co*-AEE) and poly(ABP). Therefore the polymerization of equimolar mixtures of HDDA with BA using poly(ABP-*co*-AEE)s containing 55.0 and 74.0 mol% of ABP units was performed under the same conditions. The results have been compared with those obtained for the same mixture using poly(ABP) alone or in combination with the corresponding amount of 1-(2-methylpropionyloxy)-2-ethoxyethane (IEE), a low molecular weight model of AEE units.

On the basis of the results reported in *Figures 1* and *4* the efficiency of poly(ABP) decreases by replacing APDG with BA in the polymerization mixture, thus confirming that the acrylic ether derivative, as expected, is involved in the initiation reaction as hydrogen donor to benzophenone moieties. Accordingly the efficiency

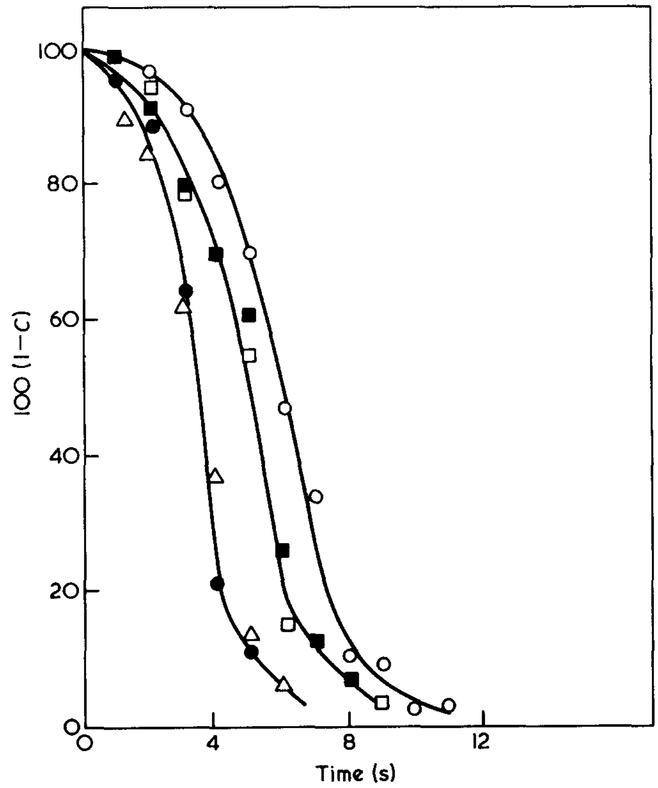


Figure 2 Percentage of residual acrylic groups [100(1–C)] for the HDDA/APDG equimolar mixture in the presence of 1 mol% of benzophenone moieties photoinitiator, as a function of u.v. irradiation time: ●, poly(ABP-*co*-MtA) with 32.5 mol% of ABP units; △, poly(ABP-*co*-MtA) with 57.6 mol% of ABP units; ■, poly(ABP-*co*-MtA) with 80.0 mol% units; □, poly(ABP-*co*-MtA) with 92.5 mol% of ABP units; ○, poly(ABP)

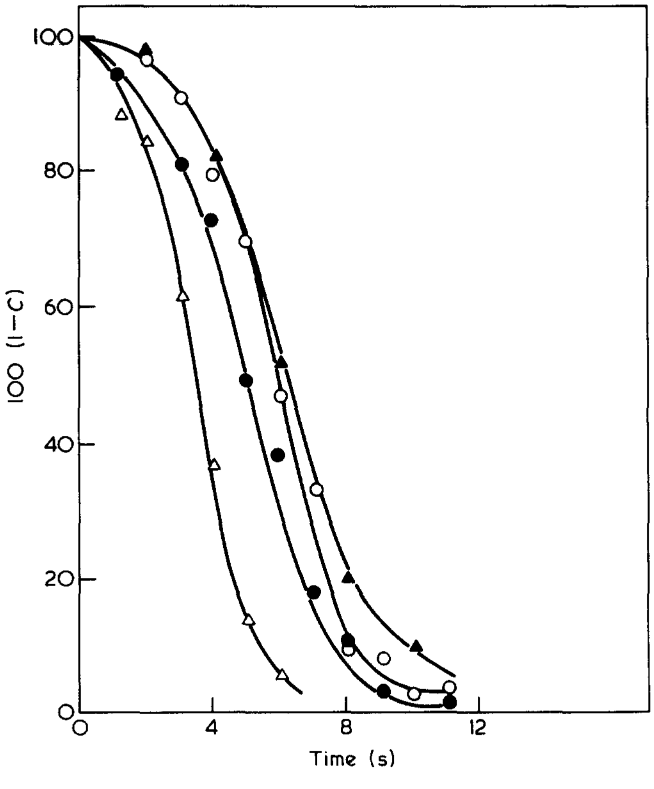


Figure 3 Percentage of residual acrylic groups [100(1 – C)] for the HDDA/APDG equimolar mixture in the presence of 1 mol% of benzophenone moieties photoinitiator, as a function of u.v. irradiation time: ▲, poly(ABP-*co*-MA) with 54.3 mol% of ABP units; ●, poly(ABP-*co*-AEE) with 55.0 mol% of ABP units; △, poly(ABP-*co*-MtA) with 57.6 mol% of ABP units; ○, poly(ABP)

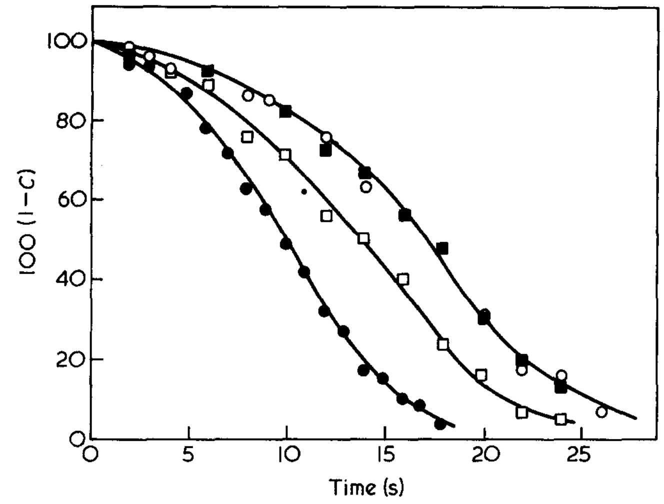


Figure 4 Percentage of residual acrylic groups [100(1 − *C*)] for HDDA/BA equimolar mixture in the presence of 1 mol% of benzophenone moieties photoinitiator, as a function of u.v. irradiation time: ●, poly(ABP-*co*-AEE) with 55.0 mol% of ABP units; □, poly(ABP-*co*-AEE) with 74.0 mol% of ABP units; ■, poly(ABP) + IEE (the same molar amount as AEE in poly(ABP-*co*-AEE) with 55.0 mol% of ABP units); ○, poly(ABP)

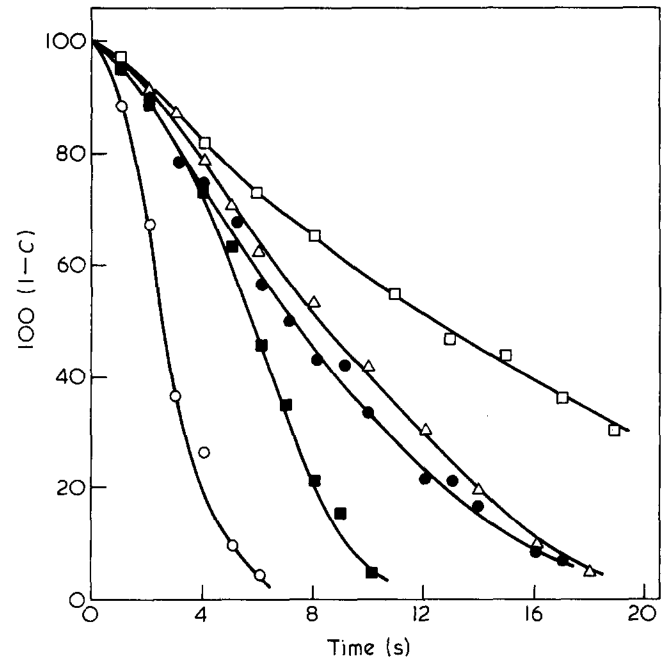


Figure 5 Percentage of residual acrylic groups [100(1 − *C*)] for the HDDA/APDG equimolar mixture in the presence of 1 mol% of benzophenone moieties photoinitiator and 1.5 mol% of tertiary amine sensitizer, as a function of u.v. irradiation time: □, poly(ABP-*co*-DMAS) with 43.2 mol% of ABP units; △, IBP/poly(DMAS); ●, IBP/DMA; ■, poly(ABP)/poly(DMAS); ○, poly(ABP)/DMA

difference between poly(ABP-*co*-AEE) with 55.0 mol% of ABP units and poly(ABP) increases when APDG is replaced by BA (see *Figures 3* and *4*). Moreover, the addition to the HDDA/BA equimolar mixture of the same amount of IEE as that present in poly(ABP-*co*-AEE) with 55.0 mol% of ABP units does not appreciably change the efficiency of poly(ABP), thus indicating that the interactions between ethereal groups and benzophenone moieties are more relevant when these functions are both attached to the same macromolecule. Finally the importance of the role played by the above interactions is confirmed by the efficiency of poly(ABP-*co*-AEE) with 74.0 mol% of ABP units which is intermiediate between those observed for poly(ABP) and poly(ABP-*co*-AEE) with 55.0 mol% of ABP units (*Figure 4*).

Photoinitiated polymerization in the presence of poly(ABP-co-DMAS)

The previous experiments have shown that it is possible to modify the efficiency of benzophenone moieties containing macromolecular photoinitiators by using suitable structural co-units acting as hydrogen donors. Benzophenone/tertiary amine systems are known$^{7,29-31}$ to be very active in the u.v.-initiated polymerization of unsaturated monomers due to a mechanism involving hydrogen abstraction by the excited triplet-state benzophenone from the amine after formation of their exciplex$^{2,4,31-33}$. The photoinitiated polymerization of the HDDA/APDG equimolar mixture has then been performed in the presence of low and high molecular weight benzophenone/tertiary amine derivatives. In all the experiments, concentrations of 1 mol% of benzophenone moieties and molar ratio of amine to benzophenone equal to 1.5 were used^{34}.

As shown in *Figure 5* the poly(ABP)/dimethylalinine(DMA) system exhibits much higher efficiency than the corresponding low molecular weight IBP/DMA system. These results, compared with those obtained in the same conditions using poly(ABP) and IBP in absence of DMA (*Figure 1*), clearly show that the use the use of the amine improves the efficiency of both systems. The IBP/poly(4-(*N*,*N*-dimethylamino)styrene) (poly(DMAS)) system shows a very low decrease of efficiency with respect to the IBP/DMA system. This should indicate that exciplex formation is not markedly affected by steric hindrance at least when one of the two interacting moieties is attached to a macromolecular chain. As a positive 'polymer effect' is observed only in side-chain benzophenone-containing polymers, the above results indicate that the interactions between side-chain chromophores are relevant only when such moieties can exist in the excited state, thus confirming the importance of energy migration. When the poly(ABP)/poly(DMAS) system is used, its efficiency is observed to be lower than that of the poly(ABP)/DMA system (*Figure 5*). Such a result suggests that, when benzophenone and amine moieties are attached to different macromolecules, exciplex formation is more difficult owing to steric hindrance connected with the reduced conformational mobility of the polymeric chains. Nevertheless, the poly(ABP)/poly(DMAS) system is still more efficient than IBP/DMA and IBP/poly(DMAS) systems (*Figure 5*), confirming that long sequences of benzophenone-containing units are necessary to show a positive 'polymer effect'. Finally, the efficiency of poly(ABP-*co*-DMAS) with 43.2 mol% of ABP units is by far the lowest with respect to all the previous benzophenone/amine systems.

Copolymerization experiments of ABP with DMAS indicate (*Table 3*) that poly(ABP-*co*-DMAS)s having similar composition (40–46 mol% of ABP units) have been obtained starting from comonomer mixtures having large difference of composition (25–75 mol% of ABP). These results suggest that ABP units in the resulting copolymers are substantially isolated, both co-units having a large tendency to an alternating distribution. This structural

Table 3 Homo- and copolymerization of 4-(*N*,*N*-dimethylamino)-styrene (DMAS) with 4-acryloxybenzophenone (ABP)[a]

Feed ABP (mol%)	Duration (h)	Conversion[b] (%)	Copolymer characterization: ABP units[c] (mol%)
0.0	120.0	12.0	0.0
75.0	2.0	3.5	46.0
33.3	144.0	49.5	40.0
25.0	2.5	17.1	43.2

[a] 2 g of comonomer mixture; 20 ml of benzene; $T = 60°C$; radical initiator, AIBN (1% w/w)

[b] Calculated as (weight of polymer/weight of starting comonomers) x 100

[c] Evaluated by ^1H n.m.r. analysis

situation can in principle explain the lower efficiency of poly(ABP-*co*-DMAS) with respect to poly(ABP)/DMA due to the suppression in the first system of energy migration, but cannot justify the lower efficiency also with respect to the IBP/DMA system. Therefore it can be concluded that, when both benzophenone and amine moieties are attached to the same macromolecule, only the amine groups in a favourable steric and geometrical disposition are able to interact with the excited benzophenone moieties to give exciplex species, the resulting number of these precursors of polymerization-initiating species being reduced with respect to the IBP/DMA system.

However, a rapid recombination between amine and semipinacol primary radicals[31,35], due to the forced close vicinity of the two species, could also explain the lower efficiency of the substantially alternating poly(ABP-*co*-DMAS) with respect to the IBP/DMA system because of the reduced quantum yield of polymerization initiation.

CONCLUSIONS

Macromolecular photoinitiators containing long sequences of side-chain benzophenone units exhibit higher efficiency with respect to low molecular weight model compounds according to energy migration along the chain, arising from interactions between neighbouring excited triplet and ground-state benzophenone chromophores.

However, the results obtained with copolymers of 4-acryloxybenzophenone with methyl acrylate, (−)-menthyl acrylate and 1-acryloxy-2-ethoxyethane with different compositions show that the efficiency of the polymeric photoinitiator also depends markedly on the nature of the comonomer. Indeed, this last can release hydrogen atoms to the excited triplet state of benzophenone moieties and influence the photoreactivity of this last chromophore by modifying the conformational rigidity of the macromolecules. It therefore seems possible to design very active macromolecular photoinitiators based on copolymers of benzophenone-containing monomers with suitable comonomers.

In the benzophenone/tertiary amine systems the most active photoinitiators are again those based on poly(ABP), where energy migration can occur, the lower efficiency of poly(ABP)/poly(DMAS) system with respect to the poly(ABP)/DMA system being attributable to lower mobility and higher steric hindrance of the two polymers.

The substantially alternating poly(ABP-*co*-DMAS) displays the lowest efficiency, even lower than that of the corresponding systems containing the low molecular weight benzophenone derivative (IBP), in spite of the close vicinity between side-chain benzophenone and amine moieties. The suppression of energy migration alone cannot justify these results. Recombination reactions between primary radicals as well as the reduced number of amine groups in a favourable steric and geometrical disposition to give exciplex precursors of polymerization-initiating species with excited benzophenone moieties must be taken into account.

APPENDIX

The absorbance of an i.r. band is expressed by the Lambert–Beer equation:

$$A = \varepsilon c l \qquad (1)$$

where: c = molar concentration of the group involved with the i.r. vibration band, ε = molar extinction coefficient connected with the i.r. band, and l = optical path length.

If we assume that A_a and A_{CH_2} are the absorbances of the i.r. bands at 1410 and 1450 cm^{-1} connected with acrylic and paraffinic methylene groups, respectively, we can write:

$$A_a = \varepsilon_a c_a l \qquad (2)$$

$$A_{CH_2} = \varepsilon_{CH_2} c_{CH_2} l \qquad (3)$$

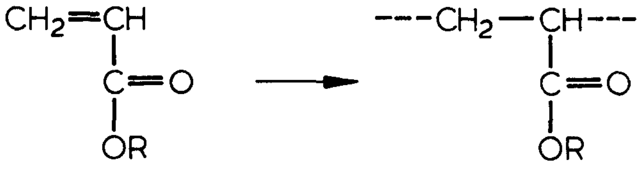
and then:

$$A_a = \varepsilon_a l \frac{N_a}{V N_A} \qquad (4)$$

$$A_{CH_2} = \varepsilon_{CH_2} l \frac{N_{CH_2}}{V N_A} \qquad (5)$$

where V, N_a, N_{CH_2} and N_A are the volume, the number of acrylic and paraffinic methylene groups in the volume V and the Avogadro number, respectively.

Considering that each acrylic group involved in the polymerization reaction gives rise to the formation of a paraffinic methylene group according to the reaction:



$$CH_2{=}CH{-}C({=}O){-}OR \longrightarrow {-}{-}{-}CH_2{-}CH({-}C({=}O){-}OR){-}{-}{-}$$

the ratio between the absorbances of acrylic and paraffinic methylene groups at the irradiation time t can be expressed as follows:

$$\frac{A_a^t}{A_{CH_2}^t} = \frac{\varepsilon_a}{\varepsilon_{CH_2}} \frac{N_a^0 - N_a^t}{N_{CH_2}^0 + N_a^t} \qquad (6)$$

where N_a^0 is the number of acrylic groups in the volume V at irradiation time $t=0$, N_a^t the number of acrylic groups in the volume V reacted at irradiation time t and $N_{CH_2}^0$ the number of paraffinic methylene groups in the volume V at irradiation time $t=0$, respectively. On the basis of the chemical structure and the relative amount of the two acrylic monomers used for the preparation of the mixture to be polymerized, the ratio

$$N_a^0/N_{CH_2}^0=\alpha$$

is known for the reaction mixture. For instance, $\alpha=0.267$ and 0.333 can be evaluated for the equimolar HDDA/APDG and HDDA/BA mixtures, respectively.

If

$$\frac{A_a^t}{A_{CH_2}^t}=B^t \qquad \text{and} \qquad \frac{\varepsilon_a}{\varepsilon_{CH_2}}=K$$

equation (6) can be transformed into:

$$B^t=\frac{K(\alpha N_{CH_2}^0-n_a^t}{N_{CH_2}^0+N_a^t} \tag{7}$$

Equation (7), by adding to and subtracting from the numerator the quantity $N_{CH_2}^0$, can be written as follows:

$$B^t=\frac{K(\alpha+1)N_{CH_2}^0}{N_{CH_2}^0+N_a^t}-K \tag{8}$$

From equation (8) N_a^t can be evaluated as follows:

$$N_a^t=\frac{N_{CH_2}^0[K(\alpha+1)-(B^t+K)]}{B^t+K}=\frac{\alpha K-B^t}{B^t+K}N_{CH_2}^0 \tag{9}$$

On the other hand the conversion C in the polymerization reaction can be expressed as follows:

$$C=\frac{N_a^t}{N_a^0}=\frac{N_a^t}{\alpha N_{CH_2}^0} \tag{10}$$

By combining equations (9) and (10) we obtain:

$$C=\frac{\alpha K-B^t}{\alpha B^t+\alpha K} \tag{11}$$

Considering that at the irradiation time $t=0$, $C=0$ and $B^t=B^0$, it follows that:

$$\alpha K=B^0 \tag{12}$$

and then:

$$C=\frac{B^0-B^t}{B^0+\alpha B^t} \tag{13}$$

where B^0 and B^t can be evaluated from transmittance i.r. spectra of the polymerization mixture at irradiation times 0 and t, respectively, as follows:

$$B^0=\frac{[\log(I_a^0/I_a)]_0}{[\log(I_{CH_2}^0/I_{CH_2})]_0}$$

and

$$B^t=\frac{[\log(I_a^0/I_a)]_t}{[\log(I_{CH_2}^0/I_{CH_2})]_t}$$

In *Figures 1–5* the percentage of residual acrylic groups in the polymerization mixture, expressed as $100(1-C)$, has been reported as a function of irradiation time.

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