

Polymeric Systems Bearing Side-Chain 2,6-Dimethylbenzoyldiphenylphosphinoyl Moieties for UV Curable Coatings: Synthesis and Photoinitiation Activity

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SYNOPSIS

Polymeric photoinitiators with pendant 2,6-dimethylbenzoyldiphenylphosphinoyl moieties were prepared by reacting the homopolymer of 4-acryloyloxy-2,6-dimethyl benzoic acid, and its copolymers with *n*-butyl acrylate with thionyl chloride followed by methoxydiphenylphosphine. These polymeric systems were characterized and their photoinitiation activity checked in the UV curing of a standard acrylic mixture, by irradiation both at 330 and over 380 nm, the latter conditions being applied to simulate a TiO₂-pigmented coating formulation. The results were compared with those obtained by using the low molecular weight analog 2,4,6-trimethylbenzoyldiphenylphosphinoyl and previously prepared polymeric systems based on the benzoyldiphenylphosphinoyl moiety. The stability to light and to hydrolytic conditions of the polymeric photoinitiators with respect to the model compound was also tested. The results obtained are discussed and related to the structural requirements of these systems. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

There has been recent increased interest in polymeric systems bearing side-chain photoreactive groups as photoinitiators for UV-curable coatings.^{1,2} In particular, the use of these systems has been claimed to improve UV clear coatings performances, in terms of nonyellowing and low-odor properties.³⁻⁵

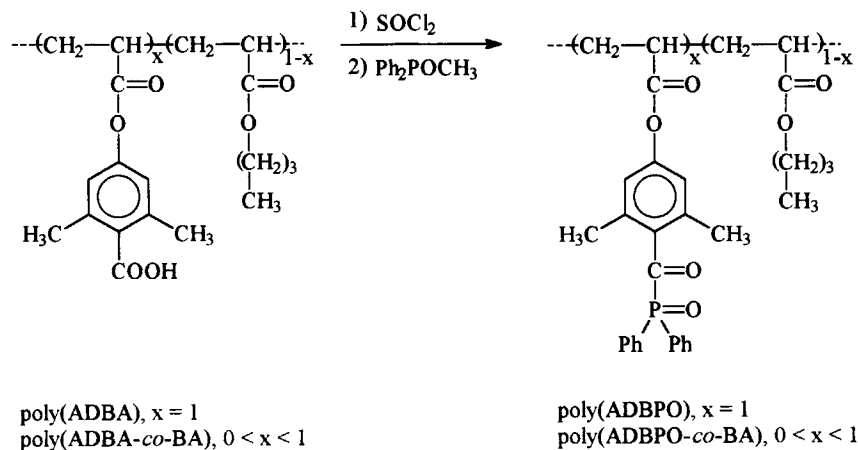
Low molecular weight photoinitiators based on the acylphosphinoyl moiety have been described quite recently.⁶ They are reported to give, under UV irradiation, a Norrish I-type fragmentation^{7,8} and are claimed, due to their absorption over 380 nm, to very efficiently cure TiO₂-pigmented coatings⁹ as well as thick-walled glass fiber-reinforced polyesters.¹⁰

In a previous article¹¹ we described the first example of polymeric systems containing side-chain aliphatic acyldiphenylphosphinoyl moieties. Indeed, the homopolymer of methacryloyldiphenylphosphinoyl [poly(MAPO)] and its copoly-

mers with methyl methacrylate [poly(MAPO-*co*-MMA)s], at different content of photosensitive groups, were found to display similar photoinitiation activity as the corresponding low molecular weight structural model. However, the above polymers appeared superior, because they displayed higher stability, both under light exposure and in hydrolytic conditions, and a significant shortening of the curing process induction period.

Taking into account what it is known about low molecular weight acyldiphenylphosphinoyls,^{12,13} polymeric systems bearing side-chain benzoyldiphenylphosphinoyl moieties were successively prepared,¹⁴ with the idea to improve their performances in terms of stability and photoinitiation activity. In particular, the homopolymer of 4-vinylbenzoic acid and its copolymers with MMA were functionalized to give the corresponding poly(4-vinyl benzoyldiphenylphosphinoyl) [poly(VBPO)] and poly(VBPO-*co*-MMA)s. Although these systems revealed a remarkable improvement of photoinitiation activity with respect to poly(MAPO) and poly(MAPO-*co*-MMA)s, in terms of both polymerization rate and induction period of the curing process, they however displayed lower stability compared

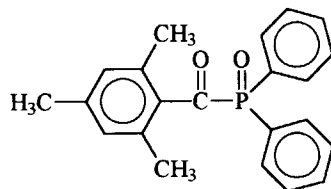
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Scheme 1

with the corresponding low molecular weight analog, and poor solubility in acrylic coating formulations.

On the other hand, a very high stability toward nucleophilic agents was observed¹³ for 2,4,6-trimethylbenzoyldiphenylphosphinoyl (TMBPO), commercially available under the trademark Lucirin TPO, with respect to other differently substituted low molecular weight aromatic acyldiphenylphosphinoyls.



TMBPO

Moreover, TMBPO, contrarily to 2-methylbenzoyldiphenylphosphinoyl, does not undergo any photoenolization reaction,¹⁵ thus markedly increasing the quantum yield of α -scission and hence the initiation efficiency of photoinitiated polymerization processes. This behavior has been attributed to the presence of the two methyl groups in the *ortho* position to the carbonyl chromophore, which are responsible for a molecular distortion, analogously to what occurs in the case of 2,4,6-trimethylphenylalkyl ketones.¹⁶ This hypothesis is further supported by UV spectroscopy data that shows a remarkable hypsochromic effect on the absorption band related to the $n \rightarrow \pi^*$ electronic transition of the carbonyl group on passing from 4-methylbenzoyldiphenylphosphinoyl to TMBPO.¹⁷ In this context, it was very interesting to design polymeric systems bearing side-chain benzoyldiphenylphosphinoyl moieties containing two methyl groups in the *ortho* position

to the carbonyl chromophore, with the aim of obtaining polymeric photoinitiators with improved performances with respect to the previously prepared systems. Thus, the present article deals with the synthesis of the homopolymer of 4-acryloyloxy-2,6-dimethylbenzoyldiphenylphosphinoyl [poly(ADBPO)] and its copolymers with *n*-butyl acrylate [poly(ADBPO-*co*-BA)s], obtained from the corresponding polymers derived from 4-acryloyloxy-2,6-dimethylbenzoic acid [poly(ADBA) and poly(ADBA-*co*-BA)s, respectively] by treatment with thionyl chloride followed by functionalization with methoxydiphenylphosphine, according to the Michaelis-Arbuzov reaction¹⁸ (Scheme 1).

BA has been chosen as comonomer to increase the solubility properties of the polymeric photoinitiators. The activity of the above systems was tested in the UV curing of a 1,6-hexanediol diacrylate (HDDA)/BA equimolar mixture under irradiation at 330 and over 380 nm and compared with that of TMBPO as well as of the previously reported¹⁴ poly(VBPO-*co*-MMA)s.

EXPERIMENTAL

Monomers and Reagents

HDDA (Aldrich) was distilled under high vacuum (bp = 109–110°C/0.1 mmHg) just before use and stored under nitrogen in the freezer.

BA (Aldrich) was washed with 5% aq NaHCO₃, dried on anhydrous Na₂SO₄, and distilled under nitrogen just before use.

ADBA was synthesized starting from 4-bromo-3,5-dimethylphenol (BDP) (Aldrich). The synthetic route involves several reactions steps: the benzyla-

tion of BDP with benzyl bromide¹⁹ to give 80% yield 4-benzyloxy-2,6-dimethylbromobenzene (BDBB); the transformation of BDBB in the corresponding Grignard reagent and its successive reaction with dry ice¹⁹⁻²¹ to yield 45% 4-benzyloxy-2,6-dimethylbenzoic acid; the deprotection¹⁹ of the phenolic group by H₂ on Pd/C to yield 76% 4-hydroxy-2,6-dimethylbenzoic acid (HDB); and finally the acylation of HDB with acryloyl chloride to give ADBA. Only the last step, not reported elsewhere, is described in detail.

Triethyl amine (26 mmol) was added, under nitrogen, to HDB (12 mmol) dissolved in 30 mL of tetrahydrofuran (THF). During the addition a white solid was observed to precipitate. After dropping freshly distilled acryloyl chloride (13 mmol), at 0°C under stirring and in the presence of traces of 2,6-di-*tert*-butyl-4-methylphenol as polymerization inhibitor, the reaction mixture was allowed to stay at 0–10°C for 2 h and at 50°C for additional 2 h. The reaction was stopped by the addition of water followed by diluted aq HCl. The organic layer was separated and combined with the diethyl ether washings of the aqueous layer. After drying on Na₂SO₄, the solvent was removed at reduced pressure and the crude product crystallized from ligroin to give pure ADBA (mp = 105°C) in 71% yield. ¹H-NMR (CDCl₃): 6.8 (s, 2H, aromatic protons), 6.6 and 6.0 (2dd, 2H, —CH=CH₂), 6.3 (dd, 1H, —CH=CH₂), 2.4 (s, 6H, CH₃) ppm. IR (KBr): 3600–2500 (ν_{OH}, carboxylic group), 3000–2920 (ν_{CH}, aliphatic), 1738 (ν_{C=O}, ester group), 1688 (ν_{C=O}, carboxylic group), 1640 (ν_{C=C}, phenyl ring), 1407 (δ_{C=C}, acrylic group), 1296 (ν_{C-O}), 1200–1150 (ν_{Ph-O}), 975 and 804 (δ_{CH}, CH= and CH₂=, acrylic group), 848 (δ_{CH}, 1,4-disubstituted phenyl ring) cm⁻¹.

Methoxydiphenylphosphine was prepared as previously reported,⁶ starting from chlorodiphenylphosphine (Aldrich) and methanol in the presence of *N,N*-diethylaniline, distilled under high vacuum (bp = 114–115°C/0.1 mmHg), and stored under dry nitrogen.

Low Molecular Weight Photoinitiator

TMBPO was stored under dry nitrogen in the dark and used as received.

Polymeric Photoinitiators

Synthesis of Poly(ADBA) and Poly(ADBA-co-BA)s

The title compounds were prepared by free radical homo- and copolymerization in THF, using 2,2'-

azobisisobutyronitrile (AIBN) as initiator (2 wt %). The reactants were introduced in glass vials under dry nitrogen and submitted to several freeze-thaw cycles. After sealing under high vacuum, the vials were kept at 70°C for suitable periods of time; then the reaction mixture was poured into a large excess of petroleum ether, and the coagulated polymer redissolved in THF, precipitated again by petroleum ether, filtered, and finally dried at reduced pressure. All polymers were characterized by ¹H-NMR and FTIR analyses. In particular, the ¹H-NMR spectrum of poly(ADBA) [Fig. 1(d)] displays broad signals at 6.9–6.6 (aromatic protons), 2.5–2.4 (CH₃ groups on the phenyl ring), and 2.4–1.8 (aliphatic protons in the main chain) ppm. In the ¹H-NMR spectra of poly(ADBA-co-BA)s [Fig. 1(a–c)] additional signals at 4.2–3.9 (OCH₂) and 1.7–0.7 (CH₂ and CH₃ in the side chain) ppm, related to the BA co-units, are present.

Copolymers composition was determined by matching the integrated area of the resonances of the aromatic protons, related to the ADBA co-units, with that of the ester O—CH₂ groups of BA co-

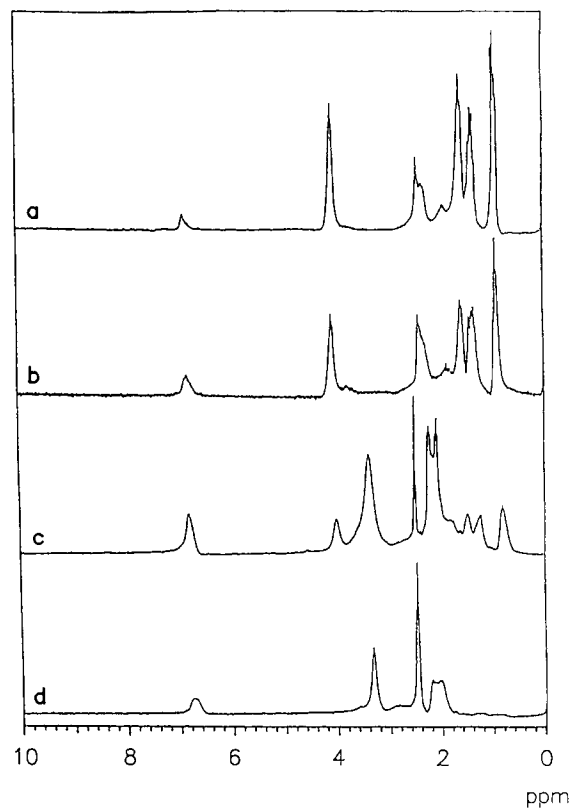


Figure 1 ¹H-NMR spectra of poly(ADBA-co-BA)s containing (a) 12, (b) 26, and (c) 44 mol % of ADBA co-units, respectively, and of (d) poly(ADBA). Spectra (c) and (d) were recorded in DMSO-*d*₆ solution.

Table I Synthesis and Characterization of Poly(ADBA) and Poly(ADBA-co-BA)s

Feed ADBA (mol %)	Duration (h)	Conversion ^a (%)	Polymeric Product	
			ADBA	Co-Units ^b (mol %)
10	118	57		12
13	142	70		16
20	22	34		23
30	142	80		26
60	136	72		44
100	142	95		100

In THF solution at 70°C, using AIBN as free radical initiator.

^a Calculated as (wt of polymer/wt of monomers) × 100.

^b Determined by ¹H-NMR analysis.

units. The most relevant properties of poly(ADBA) and poly(ADBA-co-BA)s are reported in Table I.

Synthesis of Poly(ADBPO) and Poly(ADBPO-co-BA)s

Poly(ADBA) and poly(ADBA-co-BA)s were dissolved in a large excess of thionyl chloride in the presence of few drops of dimethylformamide (DMF), and the mixture refluxed for several hours (usually 16–20 h) under dry nitrogen, until a complete conversion was obtained. The progress of the reaction was monitored by IR analysis following the progressive depletion of the band at 1700 cm⁻¹, related to the CO stretching vibration of the carboxylic group in ADBA co-units, and the contemporary appearance of a new band at 1790 cm⁻¹, typical of the corresponding vibration of the acyl chloride group in the functionalized polymeric product. Due to the

sensitivity to hydrolysis, the chlorinated polymers were not isolated, but directly submitted to the successive reaction, after distillation removal of the excess thionyl chloride. Thus, the polymeric compound was dissolved in anhydrous THF and allowed to react, under nitrogen and in the dark, with a large excess of methoxydiphenylphosphine (5 : 1 mol/mol with respect to the acylchloride moieties) at 60°C until a substantially complete disappearance of the IR band at 1790 cm⁻¹ (usually after 20–22 h) was observed in test samples drawn from the reaction mixture. The contemporary appearance of bands at 1671, 1438, and 1211 cm⁻¹, typical of the acyldiphenylphosphinoyl moiety, confirmed the occurrence of the functionalization reaction. After partial evaporation of the solvent under reduced pressure, the polymeric product was precipitated by addition of anhydrous *n*-pentane. The polymer was redissolved in THF and precipitated again by cyclohexane, washed, dried under vacuum, and finally stored under dry argon, in the dark. The obtained functionalized polymers were characterized in terms of composition by ¹H-NMR and UV spectroscopy as well as by elemental analysis of chlorine content (Table II).

Photoinitiation Activity Experiments

Two sets of experiments were carried out. Formulations of the HDDA/BA equimolar mixture, containing 0.5 mol % of low or high molecular weight photoinitiator in terms of acyldiphenylphosphinoyl moiety, were submitted to UV irradiation at 25°C as liquid films (200 μm) under nitrogen, at either 330 nm ($I_0 = 53 \text{ W/m}^2$) or over 380 nm. In the second set of experiments the light emitted by a 100-

Table II Synthesis and Characterization of Poly(ADBPO) and Poly(ADBPO-co-BA)s

Starting Polymer Sample	Functionalized Polymer ^a						
	ADBA Co-units (mol %)	ADBPO Co-units		BA Co-units (mol %)	ADBC ^b Co-units (mol %)	\bar{M}_n^c	\bar{M}_w/\bar{M}_n^c
	(mol %)	(mol %)	(mmol/g)	(mol %)	(mol %)		
Poly(ADBA-co-BA)	12	9.5	0.60	88	2.5	17,800	1.6
Poly(ADBA-co-BA)	16	13	0.78	84	3	25,100	1.5
Poly(ADBA-co-BA)	23	19	1.03	77	4	ND	ND
Poly(ADBA-co-BA)	26	21	1.10	74	5	11,100	1.9
Poly(ADBA-co-BA)	44	36	1.52	56	8	7,600	2.1
Poly(ADBA)	100	83	2.21	0	17	13,000	2.9

ND, no data.

^a The content of ADBPO and ADBC co-units (mol %) was determined by combining ¹H-NMR and elemental (chlorine) analyses.

^b Residual acylchloride co-units.

^c Determined by size exclusion chromatography (SEC).

W high pressure OSRAM HBO Hg lamp was filtered by a glass colored passband filter LG-400 (Corion Corporation) to collect on the sample only UV radiation over 380 nm. Even if these last experiments were performed with the same irradiation intensity, as checked by a photodiode, the absolute value of the light intensity was not determined. In both sets of experiments the time evolution of the curing process was followed by microwave dielectrometry at 9.5 GHz, in terms of ϵ'' (loss factor) measurements, as previously reported.^{22,23}

Physicochemical Measurements

¹H-NMR spectra were carried out at 200 MHz by a Varian FT-NMR Gemini 200 spectrometer on samples dissolved in CDCl₃, with tetramethylsilane (TMS) as internal standard. ³¹P-NMR spectra were performed at 30 MHz on a Varian FT-80A spectrometer on samples in CDCl₃ solution, by using H₃PO₄ 85% as external standard.

UV absorption spectra of the photoinitiators were recorded at 25°C in CHCl₃ solution on a Kontron Instruments Model UVICON 860 spectrophotometer. The spectral region between 450 and 340 nm was investigated by using a cell path length of 1 cm and concentrations, in terms of acyldiphenylphosphinoyl moiety, in the 0.8–1.4 mmol/L range; ϵ values are expressed in L mol⁻¹ cm⁻¹.

FTIR spectra were performed on a Perkin-Elmer Model 1750 spectrophotometer equipped with a Perkin-Elmer Model 7700 data station. The samples were prepared as KBr pellets or as cast films on KBr discs.

Elemental analyses, carried out by Redox s.n.c. (Milan) on poly(ADBPO) and poly(ADBPO-*co*-BA)s resulted as follows:

ANAL: Found: poly(ADBPO): Cl, 1.60%; poly(ADBPO-*co*-BA) [88%]: Cl, 0.56%; poly(ADBPO-*co*-BA) [84%]: Cl, 0.63%; poly(ADBPO-*co*-BA) [77%]: Cl, 0.77%; poly(ADBPO-*co*-BA) [74%]: Cl, 0.92%; poly(ADBPO-*co*-BA) [56%]: Cl, 1.20%, where the percentage in brackets represents the content of BA co-units in the copolymers.

Average molecular weight of the polymeric photoinitiators was determined by a HPLC Waters Millipore 590 apparatus equipped with an injector Model U6K, a Waters 500-Å column, and UV-VIS Perkin-Elmer LC-95 detector working at 254 nm. CHCl₃ was used as eluent. The calibration curve was obtained by using several monodisperse polystyrene standards.

RESULTS AND DISCUSSION

Poly(ADBA) and Poly(ADBA-*co*-BA)s

The chemical characterization of the above polymeric products clearly confirms the expected structure as reported in Scheme 1. In fact, ¹H-NMR spectra (Fig. 1) do not evidence any signal in the 6.6–6.0 ppm region, related to the acrylic double bond originally present in both ADBA and BA comonomers. Moreover, in the IR spectra (Fig. 2) no bands between 1640 and 1620 cm⁻¹, as well as around 1407, 975, and 804 cm⁻¹, typical of the carbon-carbon double bonds in acrylic groups, are observed. It may be therefore concluded that homo- and copolymerizations occurred involving the acrylic function of both comonomers. In particular, IR spectra of the copolymerization products show a broad band at 3600–2500 (ν_{OH} , carboxylic group) cm⁻¹ as well as bands at 1760 ($\nu_{C=O}$, aromatic ester), 1700 ($\nu_{C=O}$,

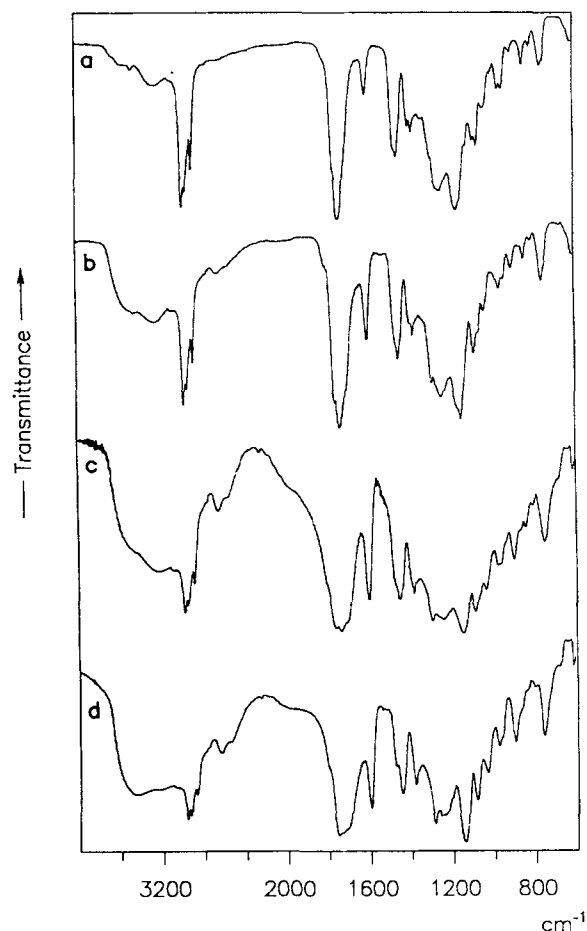


Figure 2 FTIR spectra of poly(ADBA-*co*-BA)s containing (a) 12, (b) 26, and (c) 44 mol % of ADBA co-units, respectively, and of (d) poly(ADBA).

carboxylic group), 1600 ($\nu_{C=C}$, phenyl ring) and 899 (δ_{CH} , 1,4-disubstituted phenyl ring) cm^{-1} , connected with the ADBA co-units as well as bands at 1733 ($\nu_{C=O}$, aliphatic ester) and 1244 (ν_{O-CH_2} , ester group) cm^{-1} , related to BA co-units, whose relative intensity changes on composition. Finally, taking into account that poly(ADBA) is not soluble in chloroform, the complete solubility in this solvent observed for the copolymerization products containing less than 30 mol % of ADBA co-units, confirms that they are really constituted by copolymer macromolecules.

As reported in Table I, the copolymers are enriched in co-units deriving from ADBA with respect to the corresponding feed, in the 10–20 mol % range of compositions, the reverse occurring for feeds with a content of ADBA higher than 30 mol %. Indeed, in the copolymerization diagram (Fig. 3) a well-defined azeotropic point is observed at 23 mol % content of ADBA in the feed. Although calculation of the comonomers reactivity ratios is not possible, due to the high conversions obtained in all the copolymerization experiments, the data indicate that both reactivity ratios are less than unity, thus suggesting a certain tendency of the co-units to give an alternating distribution along the polymer chains.²⁴ On the other hand, the need of having at our disposal a sufficient amount of material to be submitted to the successive functionalization step justified a high copolymerization conversion.

Poly(ADBPO) and Poly(ADBPO-co-BA)s

$^1\text{H-NMR}$ spectra of poly(ADBPO) and poly(ADBPO-co-BA)s show (Fig. 4), in addition to the

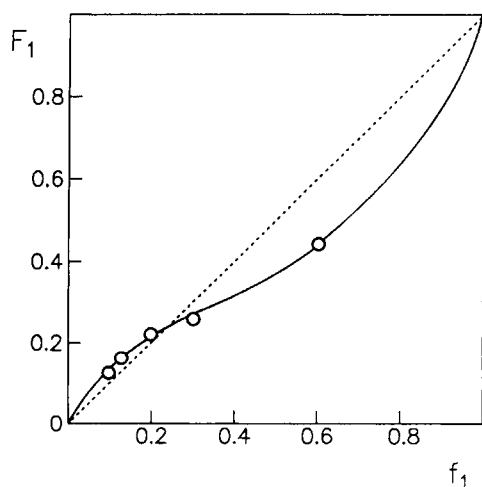


Figure 3 Copolymerization diagram for the ADBA/BA system; F_1 and f_1 represent the ADBA content (molar fraction) in the copolymerization product and in the feed, respectively.

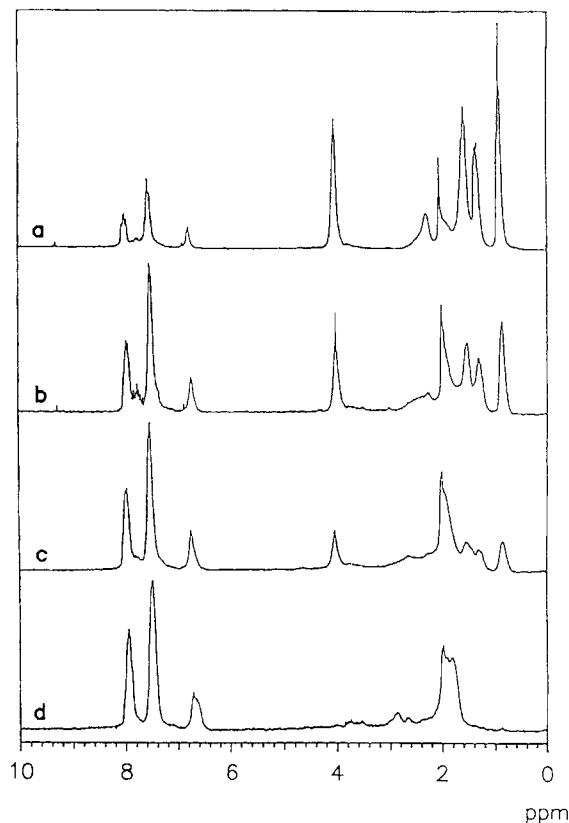


Figure 4 $^1\text{H-NMR}$ spectra of poly(ADBPO-co-BA)s containing (a) 9.5, (b) 21, and (c) 36 mol % of ADBPO co-units, respectively, and of (d) poly(ADBPO).

signals present in the corresponding polymeric precursors, two broad signals centered at about 8.0 and 7.5 ppm, related to the aromatic protons of the Ph_2PO group. The integrated area of these signals, compared with that of the signal at about 4.0 ppm, connected with the $\text{O}-\text{CH}_2$ group of BA co-units, was used for the determination of the composition of the functionalized copolymers. The calculation is based on the reasonable assumption that the content of BA co-units does not change after the reaction. The data (Table II) clearly indicate that the two-step functionalization reaction is not complete, as also confirmed by the elemental analysis of chlorine content (see Experimental), that suggests the presence of significant amounts of residual 4-acryloyloxy-2,6-dimethylbenzoylchloride (ADBC) co-units. The conversion of ADBA to ADBPO co-units was found to be, almost independently on composition of the sample, about 80%. Therefore poly(ADBPO) has to be considered as a copolymer consisting of ADBPO and ADBC co-units, whereas poly(ADBPO-co-BA)s as terpolymers, BA co-units being included. However, IR spectra (Fig. 5) do not evidence any band

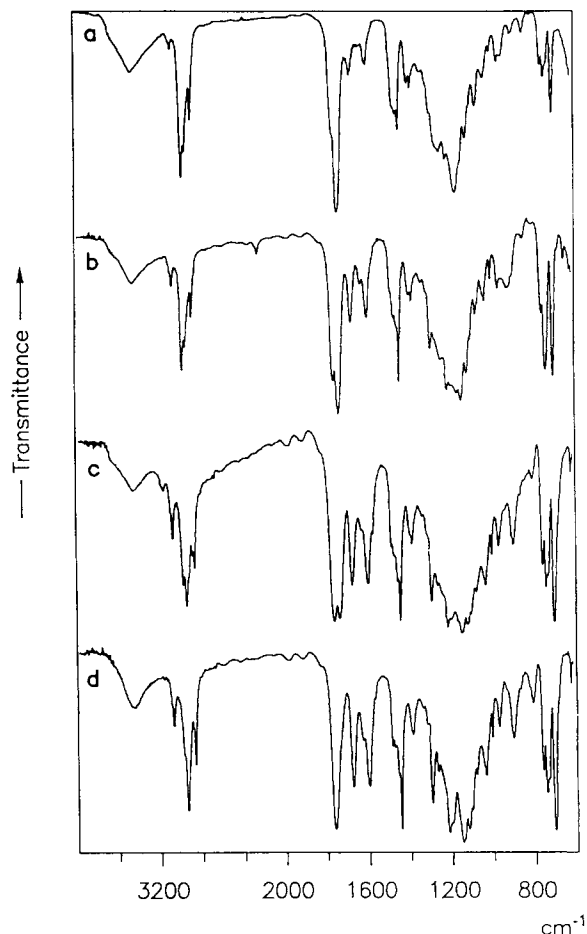


Figure 5 FTIR spectra of poly(ADBPO-co-BA)s containing (a) 9.5, (b) 21, and (c) 36 mol % of ADBPO co-units, respectively, and of (d) poly(ADBPO).

at 1790 cm^{-1} , connected with the residual ADPC co-units, as it is obscured by the much more intense band at 1760 cm^{-1} , due to the carbonyl stretching vibration of the phenyl ester group. The presence of bands at 1671 cm^{-1} ($\nu_{\text{C}=\text{O}}$, COPO group), 1438 cm^{-1} ($\nu_{\text{P}-\text{Ph}}$), 1211 cm^{-1} ($\nu_{\text{P}=\text{O}}$), 752 and 698 cm^{-1} (δ_{CH} , monosubstituted phenyl ring) cm^{-1} , related to the ADBPO co-units, and bands at 1733 cm^{-1} ($\nu_{\text{C}=\text{O}}$, aliphatic ester) and 1244 cm^{-1} ($\nu_{\text{O}-\text{CH}_2}$, butyl ester) cm^{-1} , related to the BA co-units, confirms the proposed structure.

The presence of diphenylphosphinoyl in some polymeric samples, as impurity, is also evidenced by $^1\text{H-NMR}$ spectra [Fig. 4(a,b)], where a low-intensity doublet, centered at 8.1 ppm and assigned^{25,26} to the P—H proton ($J = 482\text{ Hz}$), is present. Accordingly, in some copolymer samples, particularly in poly(ADBPO-co-BA) containing 21 mol % of ADBPO co-units, IR spectra show a weak band at 2240 cm^{-1} [Fig. 5(b)], assignable to the stretching vibration of the P—H bond.^{27,28}

$^{31}\text{P-NMR}$ spectra on dark-adapted CDCl_3 solutions of the polymeric samples show a sharp signal at about 10.9 ppm, attributable to the 2,6-dimethylbenzoyldiphenylphosphinoyl group (an analogous signal is observed at 13.1 ppm for TMBPO) and two weak signals at 18.6 and 27.8 ppm, assignable to impurities of diphenylphosphinoyl and diphenylphosphinic acid, respectively.¹¹

Average number molecular weights (\overline{M}_n) were evaluated only for poly(ADBPO) and poly(ADBPO-co-BA)s (Table II), because the polymeric precursors containing more than 30 mol % of ADPC co-units were insoluble in CHCl_3 used as eluent in SEC measurements. The collected data indicate that no clear trend of \overline{M}_n against copolymers composition exists. However, lower molecular weights are in general obtained in the functionalized samples deriving from polymeric precursors prepared from feeds having higher content of ADPC. This may indicate that ADPC is more prone to give transfer and/or termination reactions with respect to BA, in accordance with the increase of polydispersity ($\overline{M}_w/\overline{M}_n$) on increasing the content of ADBPO co-units (Table II).

UV spectra of poly(ADBPO) and poly(ADBPO-co-BA)s in the overall range of compositions (Fig. 6) show in the 450–340 nm region a structured absorption band with a maximum centered at 379 nm, assignable to the $n \rightarrow \pi^*$ electronic transition of the carbonyl group in the acyldiphenylphosphinoyl moiety. A similar spectrum is observed (Fig. 6) for TMBPO, which displays the absorption maximum at the same wavelength with a molar extinction coef-

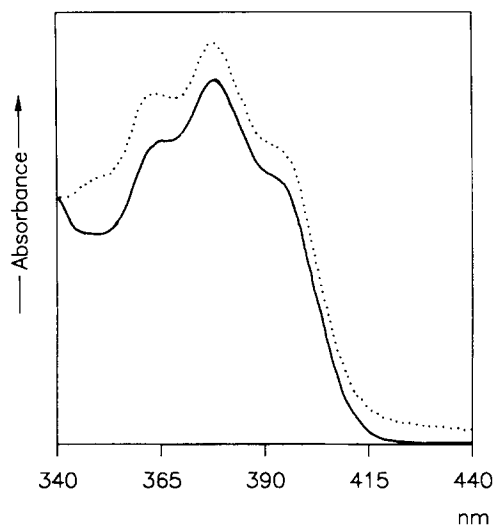


Figure 6 UV spectra in chloroform solution of (—) TMBPO and (· · ·) poly(ADBPO-co-BA) containing 19 mol % of ADBPO co-units.

ficient (ϵ) of $560 \text{ L mol}^{-1} \text{ cm}^{-1}$, according to the literature.²⁹ The above results indicate that the polymer backbone does not produce any further distortion on the side-chain acyldiphenylphosphin oxide moieties, in addition to that generated by the presence of the two methyl groups in *ortho* position to the photoreactive chromophore.

On the basis of compositions determined by ¹H-NMR and chlorine analyses, the $n \rightarrow \pi^*$ absorption band of the functionalized polymeric systems shows a remarkable hypochromic effect on increasing the content of ADBPO co-units, ϵ values varying from 600 to $495 \text{ L mol}^{-1} \text{ cm}^{-1}$ (Table III). The above data therefore seem to suggest^{30,31} that, contrary to information previously reported in analogous polymers bearing side-chain acyldiphenylphosphin oxide moieties,^{11,14} significant dipole-dipole interactions between photoreactive chromophores occur along the polymer chain. Similar results have also been observed in copolymers having side-chain aromatic chromophores.^{32,33}

Stability of Polymeric Photoinitiators

It is well established³⁴⁻³⁷ that low molecular weight acyldiphenylphosphin oxides are rather unstable, particularly in solution, when exposed to daylight and/or to hydrolytic conditions, giving rise to degradation products as a consequence of homolytic and heterolytic reactions involving free radicals and ionic species. In the case of aliphatic acyldiphenylphosphin oxides, we have reported¹¹ that the anchoring of the photoreactive moiety to a polymer backbone produced a significant improvement of stability. The better performances of the polymeric systems, in terms of photostability, were attributed¹¹ to a "cage effect" of the polymer coiling on the free radicals generated by the photofragmentation of the CO-PO bond. Analogously, the lower sensitivity to hydro-

lysis was explained assuming that the polymer chain, due to its steric hindrance, exerts a protective action on the side-chain acyldiphenylphosphin oxide groups. However, when benzoacyldiphenylphosphin oxide moieties were attached to the polymer backbone, a reduction of both light and hydrolytic stability was observed.¹⁴ This was attributed to the presence in the polymeric systems of residual carboxylic groups, which behave as promoters of degradation.

Taking into account the absence in poly(ADBPO) and poly(ADBPO-*co*-BA)s of residual carboxylic groups, the stability of poly(ADBPO-*co*-BA) containing 19 mol % photoreactive moieties was tested and compared with that of TMBPO. The samples, in freshly prepared chloroform solution under dry argon, were submitted to the same cyclic exposure of daylight and dark. The analogous solutions were also kept in the dark and used as reference samples. The dark-adapted solutions of both samples are stable even after 1 month; the light-exposed ones show a depletion of their absorption maximum at 379 nm, which is significantly faster in the case of TMBPO (Fig. 7). These data therefore confirm that, when no appreciable amount of residual acidic groups are present along the backbone, the polymer coiling increases the photostability of the acyldiphenylphosphin oxide moiety.

Tests concerning hydrolysis stability have also been performed on the same samples. Both poly(ADBPO-*co*-BA) with 19 mol % photoreactive groups and TMBPO are stable in dark-adapted CHCl₃ solutions containing 20% by volume of either methanol or hydrochloric acid saturated methanol, even after long periods of time (1 month). The very high stability to hydrolysis of these polymeric photoinitiators, never observed in analogous polymeric systems previously prepared, has to be attributed to the presence of the two methyl groups in *ortho* position to carbonyl, thus protecting it from the attack

Table III UV Absorption Features of Chloroform Solutions of Poly(ADBPO), Poly(ADBPO-*co*-BA)s, and TMBPO in 450-340 nm Spectral Region

Sample	Acyldiphenylphosphin oxide ^a Moiety (mol %)	ϵ_{379} ($\text{L mol}^{-1} \text{ cm}^{-1}$)
Poly(ADBPO)	83	495
Poly(ADBPO- <i>co</i> -BA)	36	550
Poly(ADBPO- <i>co</i> -BA)	21	570
Poly(ADBPO- <i>co</i> -BA)	19	575
Poly(ADBPO- <i>co</i> -BA)	13	590
Poly(ADBPO- <i>co</i> -BA)	9.5	600
TMBPO	100	560

^a Calculated by combined ¹H-NMR and elemental (chlorine) analyses.

As reported in Table IV, poly(ADBPO-co-BA)s exhibit slightly lower $(R_c)_{\max}$ values, in the UV curing of the clear coating HDDA/BA mixture at 330 nm, compared with TMBPO, but shorter t_o values, thus displaying a substantially similar overall photoinitiation activity, as revealed by the $t_{1/2}$ values. A clear example is also given in Figure 8. A direct comparison between poly(ADBPO-co-BA)s and poly(VBPO-co-MMA)s, in terms of $(R_c)_{\max}$ values, cannot be made, due to the different concentration of the photoreactive moieties in the two cases (0.5 and 0.1 mol %, respectively). However, applying the well-known kinetic equation for photoinitiated free radical polymerizations^{38,39}:

$$R_p = 2.303 k_p/k_t^{1/2}(\Phi_i I_o \epsilon cl)^{1/2} [M]. \quad (1)$$

$(R_c)_{\max}$ values for poly(ADBPO-co-BA)s at 0.1 mol % concentration can be calculated from the corresponding data at 0.5 mol % concentration (Table V), provided that all the other parameters may be considered constant. Indeed, this assumption is reasonably valid as the photoinitiator concentration is in both cases sufficiently low. As reported in Table V, poly(ADBPO-co-BA)s and poly(VBPO-co-MMA)s display a substantially similar photoinitiating activity. These results clearly indicate that the introduction on the phenyl ring of two methyl groups in the *ortho* position to the CO—PO group does not appreciably improve the photoinitiation efficiency of the system but only increases their stability to light and hydrolysis, which is a very important aspect from a technological point of view.

Moreover, the kinetic data on the UV curing of the clear coating HDDA/BA formulation by poly(ADBPO-co-BA)s, as compared with those obtained for polymeric photoinitiators bearing side-

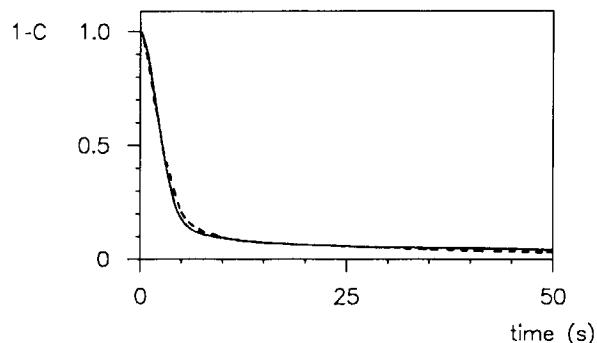


Figure 8 Fraction of residual monomers (1-C) vs. time in the UV curing of HDDA/BA equimolar mixture upon irradiation at 330 nm, in the presence of (—) TMBPO and (---) poly(ADBPO-co-BA) containing 1.52 mmol/g of ADBPO co-units.

chain benzoin methyl ether moieties under the same conditions¹ (in terms of light irradiation and concentration of photoreactive groups), clearly indicates that the former systems are superior. These results, taking also into consideration that acyldiphenylphosphinoxides, together with the bleaching of their absorption upon irradiation, do not form colored products upon prolonged exposure to daylight,¹⁷ suggest that these novel polymeric photoinitiators are especially versatile for applications where yellowing is the major concern.

It is well established^{40,41} that TiO₂, particularly in the rutile form, completely absorbs UV light below 380 nm. Poly(ADBPO-co-BA)s, having an absorption maximum at around 380 nm and tailing to about 420 nm, can be therefore usefully applied for curing TiO₂-pigmented acrylic coatings. Indeed, the above polymeric systems have been checked as photoinitiators in the UV curing of the HDDA/BA equimolar mixture upon irradiation at wavelengths longer than

Table IV Kinetic Data of UV-Initiated Polymerization of Clear Coating HDDA/BA (1 : 1) Formulation in Film Matrix, by Poly(ADBPO-co-BA)s and TMBPO, Upon Irradiation at 330 nm Under Nitrogen

Photoinitiator	Photoreactive Moiety (mmol/g)	t_o^a (s)	$t_{1/2}^b$ (s)	$(R_c)_{\max}^c$ (s ⁻¹)
TMBPO	2.87	0.6	2.7	26.6
Poly(ADBPO-co-BA)	0.60	0.4	2.9	21.9
Poly(ADBPO-co-BA)	0.78	0.4	2.7	24.0
Poly(ADBPO-co-BA)	1.03	0.4	3.4	17.1
Poly(ADBPO-co-BA)	1.10	0.5	3.0	20.9
Poly(ADBPO-co-BA)	1.52	0.4	2.6	24.0

Concentration of the photoinitiator: 0.5 mol % of acyldiphenylphosphin oxide moieties.

^a Induction period of the curing process.

^b Time required for reaching 50% conversion of the HDDA/BA mixture.

^c Maximum polymerization rate, expressed as percentage of conversion over time.

Table V Photoinitiation Activity of Poly(ADBPO-co-BA)s and Poly(VBPO-co-MMA) in the UV Curing of Clear Coating HDDA/BA (1 : 1) Formulation in Film Matrix, upon Irradiation at 330 nm Under Nitrogen

Photoinitiator	Acyldiphenylphosphin oxide Moiety (mmol/g)	$(R_c)_{\max}$ (s^{-1})
Poly(VBPO-co-MMA)	2.07	9.4 ^a
Poly(VBPO-co-MMA)	1.83	11.0 ^a
Poly(VBPO-co-MMA)	1.17	9.2 ^a
Poly(VBPO-co-MMA)	0.70	9.4 ^a
Poly(ADBPO-co-BA)	1.52	10.7 ^b
Poly(ADBPO-co-BA)	1.10	9.3 ^b
Poly(ADBPO-co-BA)	1.03	7.6 ^b
Poly(ADBPO-co-BA)	0.78	10.7 ^b
Poly(ADBPO-co-BA)	0.60	9.8 ^b

^a Experimental values for 0.1 mol % concentration of acyldiphenylphosphin oxide moiety in the HDDA/BA mixture.¹⁴

^b Calculated values by eq. (1) at $c = 0.1$ mol % of acyldiphenylphosphin oxide moiety, on the basis of the data reported in Table IV at $c = 0.5$ mol %.

380 nm, with the aim to simulate the conditions for curing a pigmented coating. As reported in Table VI, all the copolymers are active in the UV curing of the HDDA/BA mixture under light absorption conditions analogous to those for TiO₂-pigmented coatings. The data indicate however that the polymeric systems display a lower photoinitiation efficiency with respect to TMBPO, as revealed by the $t_{1/2}$ values. Moreover, as reported in Figure 9, a significant amount of residual acrylic double bonds is still present even after prolonged times of irradiation (100 s), independent of whether low or high molecular weight photoinitiators are used. This phenomenon may be attributed to the quite low concentration of the photoinitiator with respect to that usually applied¹⁷ (about four times) for the curing of pigmented white coatings.

CONCLUSIONS

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

- The synthesis of polymeric systems having side-chain 2,6-dimethylbenzoyldiphenylphosphin oxide moieties was achieved by a two-step functionalization reaction of polymeric precursors obtained by homopolymerization of 4-acryloyloxy-2,6-dimethylbenzoic acid and its copolymerization with *n*-butyl acrylate.
- The characterization of poly(ADBPO) and poly(ADBPO-co-BA)s showed that the functionalization reaction is not complete, 4-acryloyloxy-2,6-dimethylbenzoylchloride co-units still being present in the final products. However,

Table VI Kinetic Data of UV-Initiated Polymerization of HDDA/BA (1 : 1) Formulation in Film Matrix, by Poly(ADBPO-co-BA)s and TMBPO, upon Irradiation over 380 nm, Under Nitrogen

Photoinitiator	Acyldiphenylphosphin oxide Moiety (mmol/g)	t_o^a (s)	$t_{1/2}^b$ (s)	$(R_c)_{\max}^c$ (s^{-1})
TMBPO	2.87	4.0	10.4	8.3
Poly(ADBPO-co-BA)	0.78	1.1	10.6	6.5
Poly(ADBPO-co-BA)	1.03	4.8	14.6	5.5
Poly(ADBPO-co-BA)	1.10	6.1	15.2	5.7
Poly(ADBPO-co-BA)	1.52	2.7	12.4	5.8

Concentration of photoinitiator: 0.5 mol % of acyldiphenylphosphin oxide moieties in the HDDA/BA mixture.

^a Induction period of the photoinitiated polymerization process.

^b Time required for reaching 50% conversion of the HDDA/BA mixture.

^c Maximum polymerization rate, expressed as percentage of conversion over time.

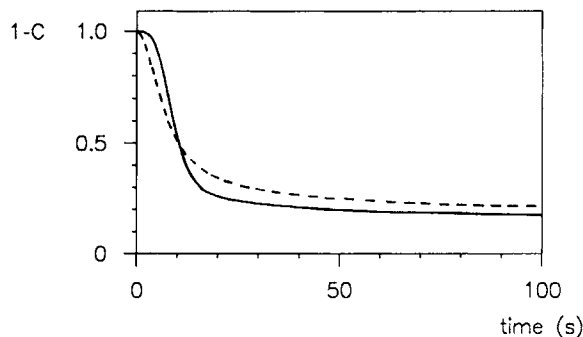


Figure 9 Fraction of residual monomers (1-C) vs. time in the UV curing of HDDA/BA equimolar mixture upon irradiation over 380 nm, in the presence of (—) TMBPO and (---) poly(ADBPO-co-BA) containing 0.78 mmol/g of ADBPO co-units.

phosphorus-containing low molecular weight impurities, such as diphenylphosphin oxide and diphenylphosphinic acid, are present to a much lower extent than that found in previously prepared polymeric systems based on acyldiphenylphosphin oxide moieties.

- The stability to daylight of this novel polymeric system is appreciably higher than that found for TMBPO, which is reported to be the most stable commercial member of this class of photoinitiators. Moreover, it displays an excellent stability to hydrolytic conditions, similar to that observed for TMBPO. The photoinitiation activity of poly(ADBPO-co-BA)s in UV curing of clear coating acrylic formulations is very high and of the same order of magnitude as that found for TMBPO, whereas the kinetic data on the UV curing, in conditions simulating a TiO₂-pigmented acrylic coating, seem to suggest that TMBPO is still superior. However, the higher stability to daylight of the polymeric system and its fivefold improved solubility in the acrylic formulation, as compared with the previously prepared analogous polymers, make poly(ADBPO-co-BA)s very attractive for practical applications in the field of surface protecting coatings.

This work was financially supported by Progetto Finalizzato di Chimica Fine II (CNR, Rome).

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Received April 12, 1994

Accepted December 22, 1994