

Polymeric Photoinitiators Bearing Side-Chain Acyldiphenylphosphin oxide Moieties for UV Surface Coatings

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SYNOPSIS

Polymeric photoinitiators bearing side-chain acyldiphenylphosphin oxide moieties have been prepared by reacting poly(methacryloyl chloride) and methacryloyl chloride/methyl methacrylate copolymers with methoxydiphenylphosphine. The activity of the above polymeric systems has been checked in the UV curing of both clear and pigmented coating formulations and compared with that of the low molecular weight analog pivaloyldiphenylphosphin oxide. The stability to light and to different hydrolytic conditions of the polymeric photoinitiators with respect to pivaloyldiphenylphosphin oxide has also been tested. The data concerning activity and stability are discussed in terms of structural features of the above systems. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Polymeric systems bearing side-chain photoreactive groups are gaining a great deal of interest for their application in the field of UV-curable surface coatings as nonyellowing and low-odor photoinitiators.¹⁻³ In addition, extensive research has established that most polymeric photoinitiators, based on benzophenone, benzophenone/tertiary amine, and benzoin methyl ether moieties, display higher activity in the UV curing of acrylic formulations for clear coatings than do the corresponding low molecular weight analogs.⁴⁻⁶ However, both low and high molecular weight systems, based on the above-mentioned photoreactive moieties, fail in the UV curing of pigmented surface coatings due to their absorption in the same spectral region as TiO₂, the most used component for these types of formulations. Recently, low molecular weight photoinitiators, based on the acylphosphin oxide moiety, have been prepared.⁷ They are claimed to work with a Norrish I type frag-

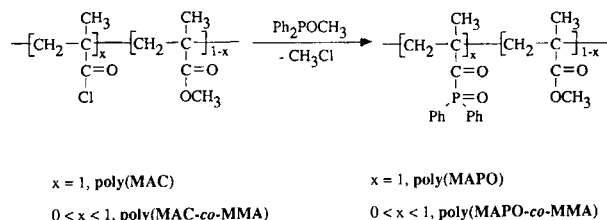
mentation mechanism^{8,9} and exhibit an absorption band centered at about 380 nm, with a tail extended over 400 nm.^{7,10} This absorption at relatively long wave lengths makes this class of photoinitiators particularly suitable for the UV curing of TiO₂-pigmented coatings¹¹ as well as of thick-walled glass fiber-reinforced polyesters.¹² In this context, it appeared very interesting to prepare polymeric systems containing side-chain acylphosphin oxide moieties and to check their activity, compared to low molecular weight analogs, in the photocross-linking of both clear and pigmented coating formulations. Therefore, this paper reports the synthesis of polymers of the above type obtained by allowing the homopolymer of methacryloyl chloride [poly(MAC)] and its copolymers with methyl methacrylate [poly(MAC-co-MMA)_s] to react with methoxydiphenylphosphine, according to the Michaelis-Arbuzov reaction¹⁸ (Scheme 1).

The possible existence of a "polymer effect" has been also investigated by comparing their activity with that of a low molecular weight structural model, such as pivaloyldiphenylphosphin oxide⁷ (PIVPO), in the photoinitiated polymerization of the 1,6-hexanediol-diacrylate (HDDA)/*n*-butyl acrylate (BA) equimolar mixture under nitrogen and of an epox-

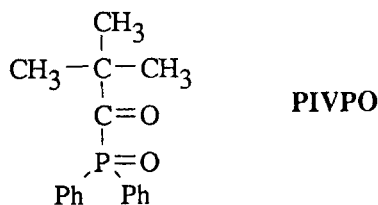
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acrylate formulation with a high content of TiO_2 , in air:



Scheme 1



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. BA and MMA (Fluka) were washed with 5% aq NaHCO_3 , dried over anhydrous Na_2SO_4 and then distilled under nitrogen just before use.

MAC (Fluka) was distilled under dry nitrogen (bp = 99°C/60 mmHg) just before use. Commercial (UCB) epoxyacrylate Ebecryl 600, trimethylolpropane triacrylate (TMPTA), tripropylenglycole diacrylate (TPGDA), and OTA-480, another trifunctional acrylic monomer, were used as received.

Methoxydiphenylphosphine was prepared as previously reported,⁷ 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. Commercial (Aldrich) diphenylphosphinic acid was used without any further purification. ^{31}P -NMR (CDCl_3): 30.0 ppm; UV (CHCl_3): $\epsilon_{\text{max}} = 785$ at 265 nm. Diphenylphosphinoyl (Aldrich) was used as received. ^{31}P -NMR (CDCl_3): 18.8 ppm; UV (CHCl_3): $\epsilon_{\text{max}} = 550$ at 259 nm. Diphenylphosphinic anhydride was prepared by reacting diphenylphosphinic chloride with the sodium salt of diphenylphosphinic acid, as previously reported.¹⁴ ^{31}P -NMR (CDCl_3): 25.6 ppm; UV (CHCl_3): $\epsilon_{\text{max}} = 1600$ at 265 nm. Tetraphenyldiphosphine dioxide was synthesized, according to the literature,¹⁵ by oxidation of

tetraphenyldiphosphine, which was, in turn, obtained by reacting diphenylphosphine with chlorodiphenylphosphine.¹⁵ ^{31}P -NMR (CDCl_3): 20.9 ppm; UV (CHCl_3): $\epsilon_{\text{max}} = 2840$ at 260 nm.

Low Molecular Weight Photoinitiator

Pivaloyldiphenylphosphinoyl (PIVPO) was synthesized from pivaloyl chloride (Aldrich) and methoxydiphenylphosphine as previously described.⁷ UV (CHCl_3): $\epsilon_{\text{max}} = 311$ at 360 nm.

Polymeric Photoinitiators

Synthesis of Precursors Poly(MAC) and Poly(MAC-co-MMA)s

Poly(MAC) and poly(MAC-co-MMA)s of different compositions were prepared by free radical homo- and copolymerization in benzene, using 2,2'-azobisisobutyronitrile (AIBN) as initiator (1.0 wt%). The components were introduced in glass vials under dry nitrogen and degassed several times. After sealing under high vacuum, the vials were kept at 60°C for some hours, then the reaction mixture was poured under dry nitrogen in a large excess of anhydrous *n*-pentane. The coagulated polymers were filtered, washed with *n*-pentane, dried in vacuum, and stored under dry nitrogen. All the polymers were characterized by ^1H -NMR and FTIR analyses. In particular, the ^1H -NMR spectrum of poly(MAC) showed two main peaks between 1.0 and 1.6 ppm, related to CH_3 groups in triads of different tacticity, and broad multiplets from 1.8 to 2.6 ppm connected with the CH_2 moiety. On increasing the content of MMA co-units in poly(MAC-co-MMA)s, the above signals were progressively overlapped to the resonances of MMA α - CH_3 groups in the 0.8–1.2 ppm region (triads of different tacticity) and CH_2 groups between 1.3 and 2.1 ppm. Moreover, a signal at 3.6 ppm, due to the ester CH_3 groups of MMA co-units, was present in the copolymers. This peak was used to determine the composition of poly(MAC-co-MMA)s. The most relevant information about the synthesis of the above polymers is reported in Table I.

Synthesis of Poly(MAPO) and Poly(MAPO-co-MMA)s

Poly(MAC) and poly(MAC-co-MMA)s have been functionalized, according to Scheme 1, by allowing them to react with a 10% molar excess of methoxydiphenylphosphine in anhydrous toluene under dry nitrogen at 80°C and in the dark. The reaction was carried out by adding dropwise the methoxydiphe-

Table I Synthesis and Physical Properties of Poly(MAC) and Poly(MAC-co-MMA)s^a

Feed MAC (mol %)	Duration (h)	Conversion ^b (%)	Polymeric Products	
			MAC units ^c (mol %)	$[\eta]$ ^d (dL/g)
100.0	48	54.2	100.0	0.40
74.9	48	46.6	53.6	0.45
49.9	14	70.5	50.6	0.50
25.0	2	14.7	29.4	0.70
5.0	2	22.7	11.3	0.66

^a In benzene at 60°C using AIBN as free-radical initiator.

^b Calculated as (wt of polymer/wt of monomers) \times 100.

^c Determined by ¹H-NMR analysis.

^d In chloroform solution at 30°C.

nylphosphine to the toluene solution of the above polymers at 50°C under stirring. The reaction mixture was then kept at 80°C for 8 h. After cooling, the precipitation of a white product was observed. This was washed with anhydrous petroleum ether, dried in vacuum, and stored, as a white powdery product, in the dark under dry nitrogen. All the obtained functionalized polymers have been characterized in terms of composition by ¹H-NMR and UV spectroscopy as well as by elemental analysis based on P and Cl (Table II).

Photoinitiating Activity Experiments

When acrylic formulations for clear coatings were used (HDDA/BA equimolar mixtures containing 0.1 mol % in terms of acyldiphenylphosphinoyl moieties), the polymerization experiments were carried out under nitrogen on film matrix (200 μ m) by UV

irradiation at 330 nm ($I_0 = 53 \text{ W/m}^2$). The rather low amount of photoinitiator was the maximum allowed by the solubility of the polymeric systems in the acrylic formulation.

The time evolution of the polymerization and cross-linking reactions was followed by microwave dielectrometry at 9.5 GHz in terms of ϵ'' (loss factor), as previously reported.^{5,16} When UV curing was carried out on pigmented coatings, the following formulation was used:

Component	Wt %
Ebecryl 600	38.9
TiO ₂ (as 80% dispersion in TPGDA)	37.5
TMPTA	8.6
OTA-480	13.0
Photoinitiator (in terms of acyldiphenylphosphinoyl moiety)	2.0

Table II Synthesis and Physical Properties of Poly(MAPO) and Poly(MAPO-co-MMA)s^a

Starting Polymer	Functionalized Polymer				
	MAC Units (mol %)	Content of MAPO Units			MAC ^b Units (mol %)
Sample		¹ H-NMR (mol %)	Elem. Anal. ^b (mol %)	UV ^c (mmol/g)	
Poly(MAC)	100.0	68.7	82.6	1.78	17.4
Poly(MAC-co-MMA)	53.6	34.6	n.d.	1.53	n.d.
Poly(MAC-co-MMA)	50.6	41.9	45.5	1.97	5.1
Poly(MAC-co-MMA)	29.4	13.1	17.2	1.01	12.2
Poly(MAC-co-MMA)	11.3	6.0	6.0	0.20	5.3

^a In toluene at 80°C for 8 h.

^b On the basis of phosphorus and chlorine content, assuming that only MAPO, MAC, and MMA co-units are present.

^c Evaluated assuming that MAPO units in the polymers display the same molar extinction coefficient as does the low molecular weight analog PIVPO ($\epsilon_{360} = 311 \text{ Lmol}^{-1} \text{ cm}^{-1}$).

In a photocuring Giardina apparatus, a glass plate coated with the above formulation (25 μm) was passed, by a conveyor belt with a 8 m/min speed, under (29 cm distance) a medium pressure mercury lamp with a power of 80 W/cm (Hanovia 6512-A-431). The activity of the photoinitiator (curing rate capability) was checked either in terms of passes under the lamp required for obtaining a nontacky surface coating or in terms of surface hardness (Koenig pendulum hardness method, according to the German DIN standard 53157).

The cure efficiency of the photoinitiators was also evaluated in terms of solvent resistance of the coating after the same irradiation exposure, measured as the number of double rubs by a methyl ethyl ketone (MEK)-soaked cotton-wool required to remove the film from the support.

Technical Tests for Pigmented Coatings

Yellowness and whiteness indexes were checked, by using a BYK Chemie ASTM D-1925 colorimeter, on 25 μm -thick coatings after curing by three passes under the mercury lamp at 3 m/min speed.

Physicochemical Measurements

$^1\text{H-NMR}$ spectra were performed at 200 MHz on samples in CDCl_3 solution using a Varian FT-NMR Gemini 200 spectrometer. TMS was used as internal standard. $^{31}\text{P-NMR}$ spectra were recorded at 30 MHz by a Varian FT-80A spectrometer on samples dissolved in CDCl_3 and by using H_3PO_4 85% as external standard.

UV absorption spectra of the photoinitiators were recorded at 25°C in chloroform solution on a Kontron Instruments model UVICON 860 spectrophotometer. The spectral region between 400 and 300 nm was investigated by using a cell path length of 1 cm and concentrations of 0.1–0.8 mmol/L of acyl-diphenylphosphinoxide moieties; ϵ values are expressed as $\text{Lmol}^{-1} \text{cm}^{-1}$.

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 as KBr pellets. Intrinsic viscosity measurements on poly(MAC) and poly(MAC-co-MMA)s samples were performed in chloroform solution at 30°C, by using an Ubbelohde dilution viscometer. P and Cl elemental analyses, carried out by Redox s.n.c. (Milan) on poly(MAPO) and poly(MAPO-co-MMA)s resulted as follows:

ANAL: Found: Poly(MAPO): P, 9.54%; Cl, 2.30%.

Poly(MAPO-co-MMA) [49.4%]: P, 7.93%; Cl, 0.79%. Poly(MAPO-co-MMA) [70.6%]: P, 4.08%; Cl, 4.51%. Poly(MAPO-co-MMA) [88.7%]: P, 1.66%; Cl, 2.35%, where the percentage in square brackets represents the content of MMA units in the copolymers.

RESULTS AND DISCUSSION

Poly(MAC) and Poly(MAC-co-MMA)s

From the data reported in Table I, it can be noted that the copolymers are enriched in MAC units when the content in MAC of the corresponding feeds is lower than 50 mol %, the reverse occurring for compositions of the feed higher than 50 mol %. Even if, due to the relatively high conversion values obtained in all the copolymerization experiments, it was not possible to evaluate accurately the reactivity ratios of the two comonomers, the results clearly indicate that both reactivity ratios are lower than unity, thus suggesting a certain tendency to an alternating distribution of the two co-units in the copolymers macromolecules.¹⁷ The above picture fits quite well with the data previously obtained¹⁸ for the free radical copolymerization, under similar conditions, of MAC with MMA, whose reactivity ratios are reported to be 0.20 and 0.45, respectively. Furthermore, the values of intrinsic viscosity (Table I) indicate that the average molecular weight of the macromolecules increases on increasing the content of MMA co-units, thus suggesting that the free radicals derived from MAC in the growing chains have more tendency to give transfer and/or termination reactions as compared with the corresponding MMA derived radicals.

FTIR spectra (Fig. 1) confirm the expected structure of the copolymers. Indeed, bands at 1790 ($\nu_{\text{C=O}}$), 961, and 851 cm^{-1} ($\nu_{\text{C-Cl}}$), typical of the acyl chloride moiety in MAC units, as well as bands at 1732 ($\nu_{\text{C=O}}$) and 1266 cm^{-1} ($\nu_{\text{O-CH}_3}$), characteristic of the methyl ester group in MMA co-units, are present, the relative intensity of which changes on composition of the copolymer samples.

Poly(MAPO) and Poly(MAPO-co-MMA)s

The $^1\text{H-NMR}$ spectra of all the functionalized polymers show, in the 7.1–8.2 ppm region, signals due to the aromatic protons, in addition to those connected with the aliphatic protons present also in the polymeric precursors (see Experimental). Therefore, assuming that the content of MMA co-units

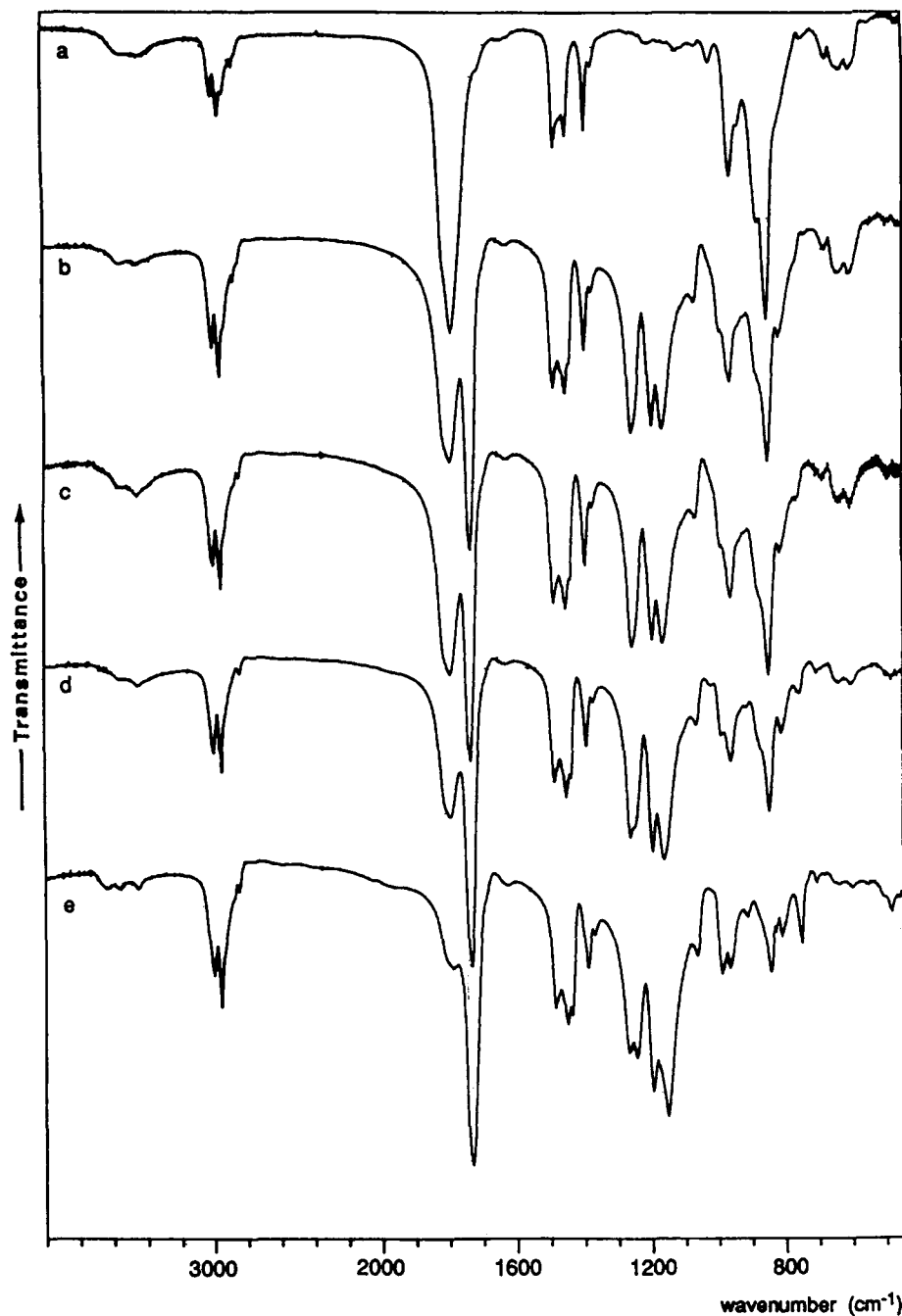


Figure 1 FTIR spectra of (a) poly(MAC) and of poly(MAC-co-MMA)s containing (b) 53.6, (c) 50.6, (d) 29.4, and (e) 11.3 mol % of MAC co-units, respectively.

remain unchanged after the functionalization reaction, it is possible to evaluate the composition of the reacted polymers in terms of MAPO co-units, provided that low molecular weight phosphorous-containing aromatic products are not present as impurities, due to hydrolytic and photolytic reactions

involving the side-chain acyldiphenylphosphinoyl moieties. It is worth noting that, even if this last hypothesis holds, $^1\text{H-NMR}$ data clearly indicate (Table II) an incomplete functionalization of poly(MAC) and poly(MAC-co-MMA)s substrates with appreciable amounts of unreacted MAC co-

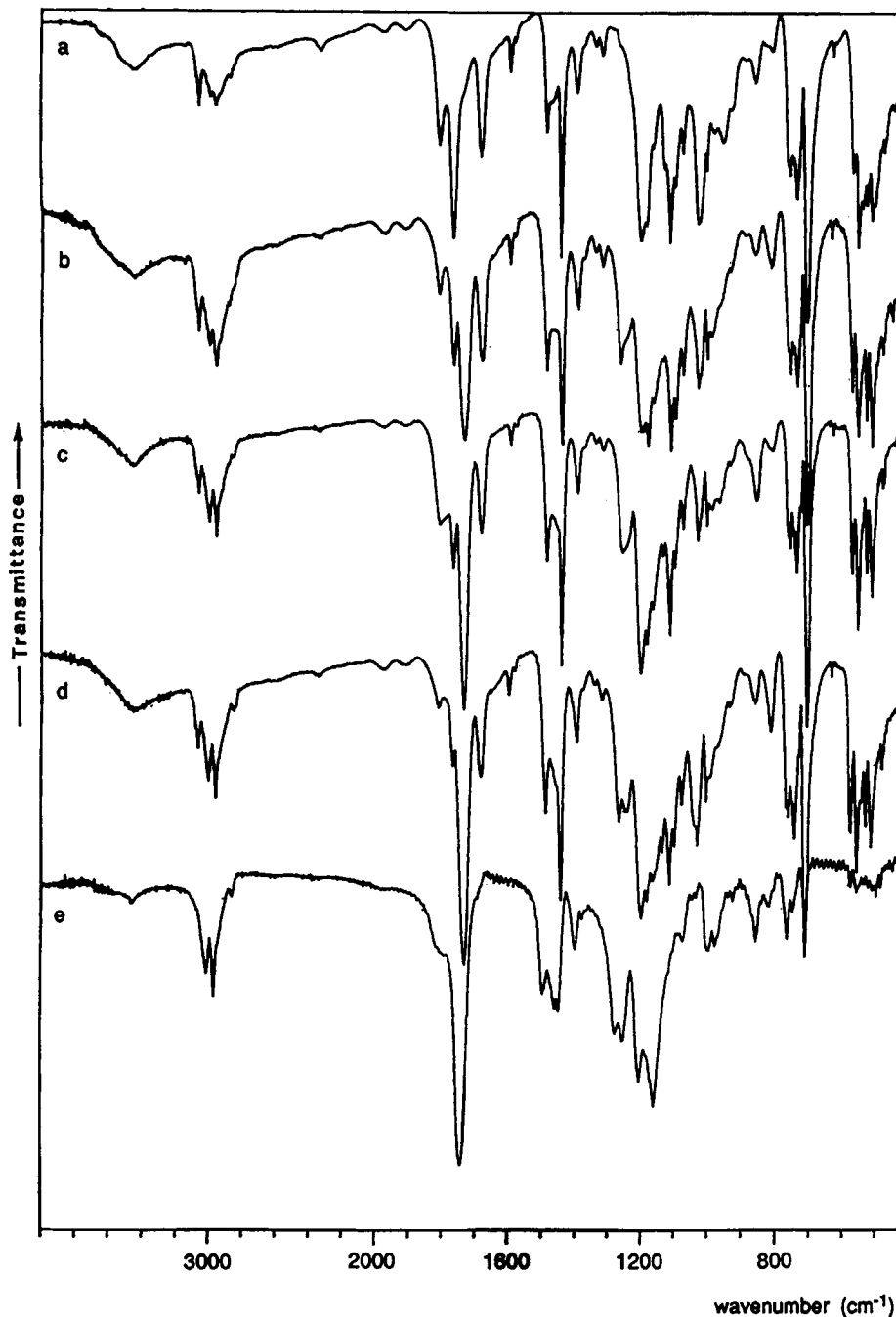


Figure 2 FTIR spectra of (a) poly(MAPO) and of poly(MAPO-co-MMA)s containing (b) 1.97, (c) 1.53, (d) 1.01, and (e) 0.20 mmol/g of MAPO co-units, respectively.

units present in the resulting polymers. A confirmation to these findings comes from their elemental analyses, which indicate the presence of significant amounts of chlorine, due to the residual MAC co-units. However, the composition determined by elemental (P and Cl) analysis, assuming that only MAPO, MAC, and MMA co-units are present in the

reacted polymeric samples, does not always result in good agreement with the corresponding values obtained by $^1\text{H-NMR}$ analysis (Table II). IR spectra (Fig. 2) of the reacted polymers are also in accordance with the proposed picture. In fact, new bands, as compared with the polymeric precursors, appear at 1677 ($\nu_{\text{C=O}}$), 1436 ($\nu_{\text{P-Ph}}$), 1170–1178 ($\nu_{\text{P=O}}$), 737,

and 695 cm^{-1} ($\delta_{\text{C-H}}$, aromatic), connected to MAPO co-units. Moreover, two bands assignable to $\nu_{\text{C=O}}$ of residual MAC co-units are present at 1803 and 1760 cm^{-1} against only one broad band at 1790 cm^{-1} found in the corresponding polymeric precursors. The splitting of this band can be explained as due to the presence of isolated unreacted MAC co-units in the functionalized polymers. Accordingly, the IR spectrum of pivaloylchloride, where a single acylchloride moiety per molecule is present, shows two distinct bands at 1828 and 1778 cm^{-1} , which disappear after the Arbuzov reaction to give PIVPO (Fig. 3). In conclusion, on the basis of the spectroscopic characterizations and elemental analyses, poly(MAPO) and poly(MAPO-*co*-MMA)s have to be actually considered as copolymers and terpolymers, respectively, constituted by variable amounts of MAPO, MAC, and MMA co-units.

In addition, in $^1\text{H-NMR}$ spectra of poly(MAPO) and of some samples of poly(MAPO-*co*-MMA)s, particularly when the content of MAPO co-units is quite high, a weak doublet centered at 8.1 ppm typical of the P—H proton ($J_{\text{PH}} = 482\text{ Hz}$) of diphenylphosphinoyl^{19,20} is present. Accordingly, IR spectra also show a weak band at 2322 cm^{-1} , attributable to the stretching vibrations of the

P—H bond.²¹ On the basis of this evidence, therefore, we cannot exclude that some other low molecular weight compounds, containing phosphorus bound to aromatic rings, are present as impurities in the functionalized polymers. Indeed, $^{31}\text{P-NMR}$ spectra of dark-adapted freshly prepared CDCl_3 solutions of poly(MAPO) and poly(MAPO-*co*-MMA)s show, in addition to the signals at 8.5 , 10.2 , and 12.1 ppm , belonging to the acyldiphenylphosphinoyl moiety²² of MAPO co-units in different structural environments, a signal at 18.8 ppm , assigned, against an authentic sample, to diphenylphosphinoyl. As other weak signals at 25.6 and 30.5 ppm were also present, a quantitative evaluation from $^{31}\text{P-NMR}$ spectra of the content of MAPO co-units was scarcely reliable.

Taking into account that the photoinitiating activity of poly(MAPO) and poly(MAPO-*co*-MMA)s has to be compared with that of PIVPO at the same concentration of acyldiphenylphosphinoyl moieties in the coating formulations, the accurate determination of the content of MAPO co-units in the above polymeric systems was essential. Thus, a quantitative analysis by UV spectroscopy appeared more reliable, assuming that the band connected with the $n-\pi^*$ electronic transition of the acyl-

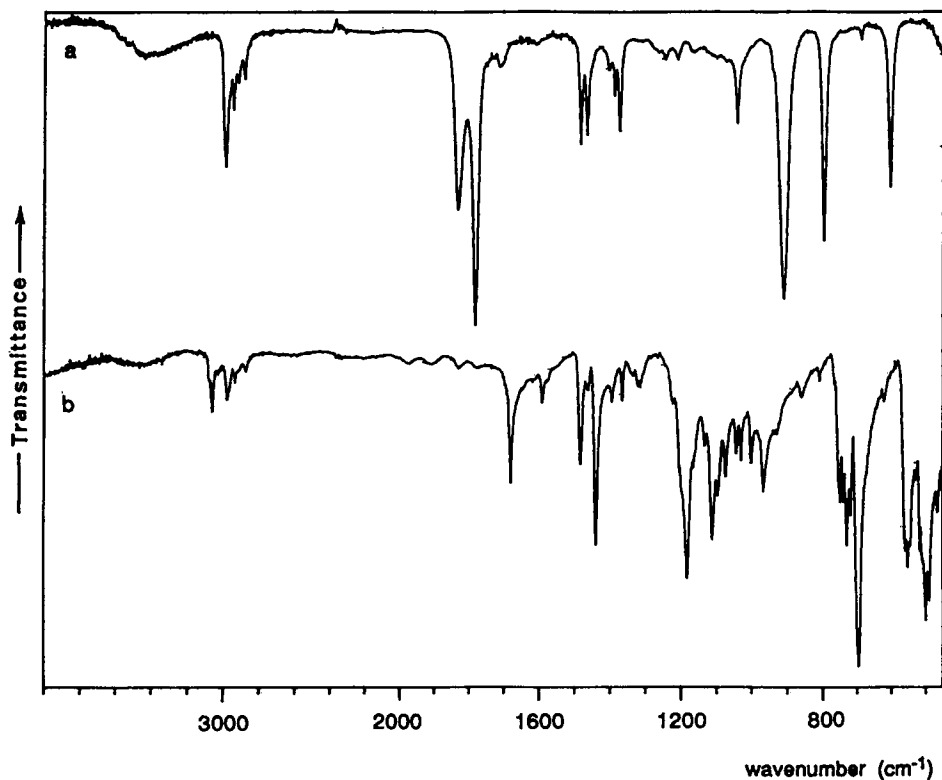


Figure 3 FTIR spectra of (a) pivaloylchloride and (b) PIVPO.

phosphinoyl chromophore in the MAPO units exhibits at its absorption maximum (360 nm) the same molar extinction coefficient (ϵ) as does PIVPO. Whereas this hypothesis is valid for isolated MAPO units, electronic interactions between neighboring acyldiphenylphosphinoyl chromophores could cause a progressive hypochromic effect^{23,24} with increasing content of MAPO units, analogous to that reported for copolymers containing aromatic chromophores.^{25,26} However, this behavior is usually also associated with a slight hypsochromic effect.²⁵⁻²⁷ As poly(MAPO) and poly(MAPO-*co*-MMA)s show identical UV spectra, independent of composition, with a structured absorption band having the maximum centered at 360 nm, analogous to what was observed for PIVPO (Fig. 4), it may be concluded that no appreciable interactions occur between side-chain acyldiphenylphosphinoyl moieties in the polymeric systems. The content of MAPO *co*-units in the polymers, as determined by UV spectroscopy, is reported in Table II.

Stability of Polymeric Photoinitiators

Low molecular weight acyldiphenylphosphinoyls are known^{22,28-33} to give, particularly in solution,

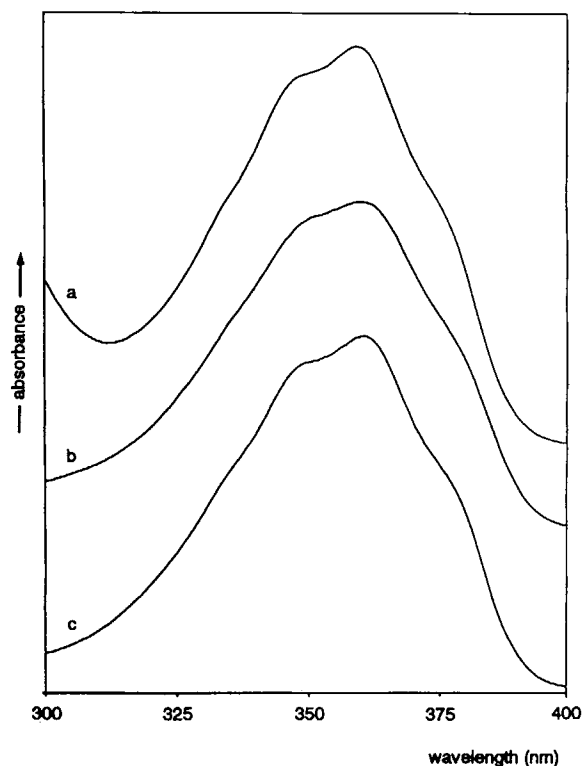


Figure 4 UV spectra in chloroform solution of (a) PIVPO, (b) poly(MAPO), and (c) poly(MAPO-*co*-MMA) containing 1.01 mmol/g of MAPO *co*-units.

degradation products by a combined action of light, heating, air, and humidity, involving both heterolytic and homolytic reactions as well as free radical and ionic species. Therefore, the stability of poly(MAPO) and poly(MAPO-*co*-MMA)s, compared with PIVPO, has been investigated by ¹H-NMR, ³¹P-NMR, and UV spectroscopy on samples maintained for variable times in different conditions of light and atmosphere, in order to gain better insight into the main impurities present in the functionalized polymers.

As far as light stability is concerned, chloroform solutions of poly(MAPO-*co*-MMA) containing 70.6 mol % of MMA *co*-units and PIVPO, under an argon atmosphere, were submitted to the same cyclic exposure of daylight and dark for a prolonged period of time and compared with the corresponding dark-adapted solutions. Whereas these latter samples did not show any appreciable variation of the absorbance of acyldiphenylphosphinoyl moiety at 360 nm after 1 month in the dark, the former samples displayed, as shown in Figure 5, a more pronounced depletion under light exposure in the case of PIVPO, as compared with poly(MAPO-*co*-MMA). These results clearly indicate that, whereas both polymeric and low molecular weight photoinitiators are stable in the chloroform solution in the dark, PIVPO is appreciably less stable when exposed to daylight. The better light stability of the polymeric systems can be tentatively explained by invoking a "cage effect" by the polymer backbone on the free radicals produced by photofragmentation of the CO—PO bond.

The stability of poly(MAPO-*co*-MMA), containing 70.6 mol % of MMA *co*-units, and of PIVPO, has been also checked in the presence of heterolytic reagents such as methanol, methanol-water, and methanol saturated with gaseous hydrochloric acid. All these experiments were carried out on dark-adapted chloroform solutions of the above samples by adding about 10% by volume of the heterolytic reagent and following the time evolution of the acyldiphenylphosphinoyl moiety content by UV spectroscopy. Both samples were stable when treated with methanol or methanol-water for prolonged periods of time in the dark. By contrast, PIVPO showed an appreciable decrease of the content of acyldiphenylphosphinoyl moiety when treated with HCl saturated methanol as compared with poly(MAPO-*co*-MMA), which was stable under the same conditions (Fig. 6).

A better insight to the possible degradation products present as impurities formed during the synthesis and/or the subsequent handling of the pho-

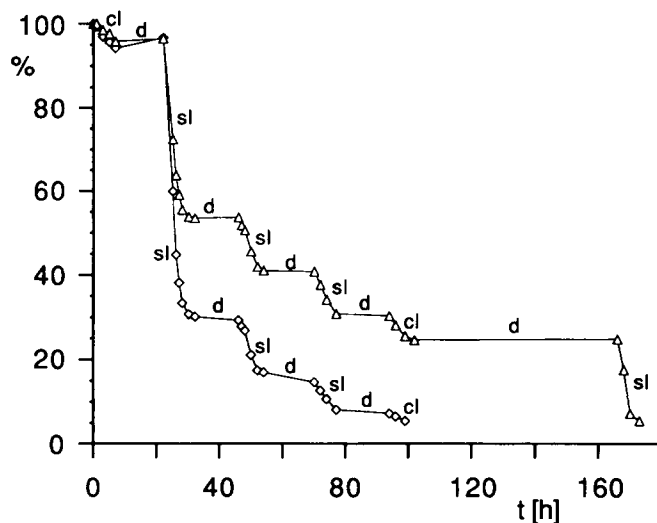


Figure 5 Residual acyldiphenylphosphinoxide moieties (%) as a function of light exposure time for chloroform solutions of (Δ) poly(MAPO-co-MMA) containing 1.01 mmol/g of MAPO co-units and (\diamond) PIVPO (d = dark, cl = cloudy daylight, sl = sunny daylight).

toinitiators based on the acyldiphenylphosphinoxide moiety was obtained by ^1H - and ^{31}P -NMR spectrometry. The ^1H -NMR spectrum of PIVPO changes with exposure of the chloroform solution to the daylight at room temperature for prolonged time. A progressive depletion of the singlet at 1.35 ppm, due to the protons of the *tert*-butyl group, is accompanied by the concurrent appearance of a new singlet at 1.25 ppm, assigned to the protons of the same group of pivalic acid.³⁴ In addition, the appearance of the doublet at 8.1 ppm and the increase of its

relative intensity indicate also the progressive formation of diphenylphosphinoxide. Further, the pattern of the aromatic proton signals becomes increasingly complex and the area of the aliphatic protons progressively decreases compared with that of the aromatic protons. This last evidence suggests the production of volatile aliphatic compounds. The ^{31}P -NMR spectrum of PIVPO in CDCl_3 solution, originally constituted by a singlet at 15.9 ppm, related to the acyldiphenylphosphinoxide moiety, also showed the appearance of the peak at 18.8 ppm of

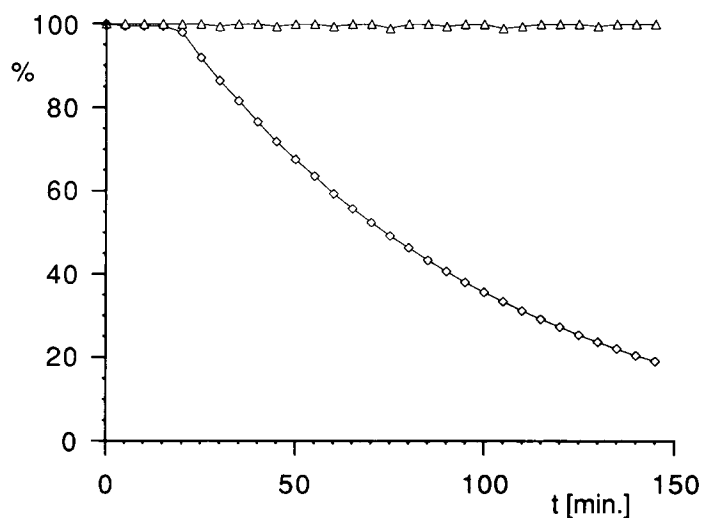
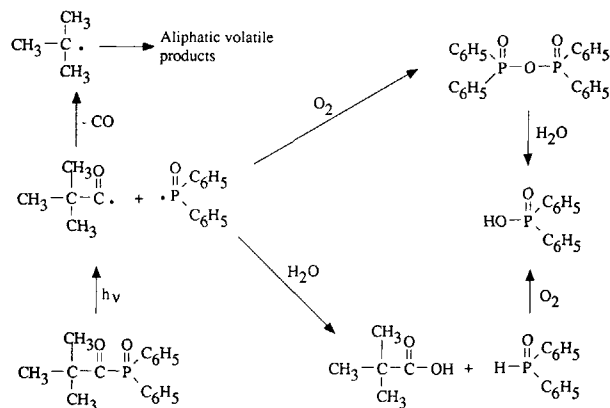


Figure 6 Residual acylphosphinoxide moieties (%) for chloroform solutions of (\diamond) PIVPO and of (Δ) poly(MAPO-co-MMA) containing 1.01 mmol/g of MAPO co-units as a function of HCl-methanol treatment time.



Scheme 2

diphenylphosphinoxide, the intensity of which afterward decreased in favor of another signal at 30.0 ppm, assigned to diphenylphosphinic acid by comparison with an authentic sample. In addition, a weak signal at 25.6 ppm, corresponding to diphenylphosphinic anhydride, was also observed. No signal connected with the presence of tetraphenyldiphosphine dioxide was observed at 21.0 ppm, as found for a prepared sample. Therefore, on the basis of the above results, it may be concluded that the degradation of PIVPO in solution is promoted by light, humidity, and air playing roles, as proposed in Scheme 2.

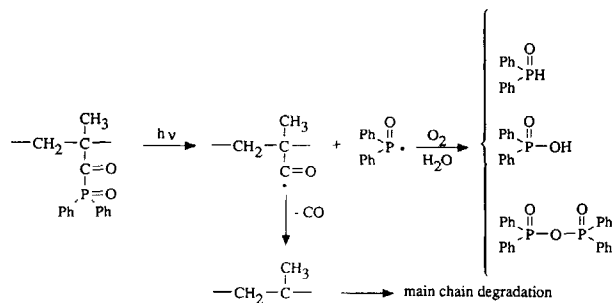
Poly(MAPO) and poly(MAPO-*co*-MMA)s in chloroform solution behave similarly under light exposure although at a reduced photodegradation rate. In contrast to PIVPO, in the polymeric systems, no volatile aliphatic low molecular weight products should be formed from the homolytic fragmentation of the CO—PO bond in MAPO *co*-units, as the acyl group is directly attached to the aliphatic polymer backbone. Also taking into account the absence of cross-linking (no precipitation of polymeric products), this situation should eventually give rise to main-chain degradation (Scheme 3).

The above results support the validity of UV spectroscopy as a tool for the quantitative evaluation of MAPO units in the polymeric photoinitiators, as the presence even in a small amount of low molecular weight phosphorus-containing aromatic byproducts does not allow a reliable analysis by NMR spectrometry. The absence of absorption bands due to the phosphorus-containing compounds (see Experimental) in the spectral region connected with the acyldiphenylphosphinoxide moiety (360 nm) further confirms the validity of the UV analysis.

Photoinitiating Activity of Poly(MAPO) and Poly(MAPO-*co*-MMA)s

The time dependence of the HDDA/BA photoinitiated polymerization and cross-linking reactions was followed by microwave dielectrometry (see Experimental), which allowed determination of the induction period (t_0), the half-time of the polymerization process ($t_{1/2}$), and the maximum polymerization rate (R_c)_{max}. Figures 7 and 8 show, as examples, plots of the residual monomer-to-polymer conversion and of R_c vs. irradiation time, respectively. The results for all the investigated samples are given in Table III. The (R_c)_{max} data indicate that activity of the polymeric photoinitiators is independent of the content of MAPO *co*-units, without any specific trend indicative of cooperative interactions between vicinal photosensitive moieties. Moreover, the presence in the macromolecules of variable amounts of unreacted, potentially photolabile MAC *co*-units does not seem to affect the activity of the photoinitiators, thus suggesting a negligible contribution of the acyl chloride moieties to the overall activity. It may be therefore concluded that the polymeric samples show, on average, a similar activity to the low molecular weight structural model PIVPO. This compound, however, exhibits a longer $t_{1/2}$ value than do poly(MAPO) and poly(MAPO-*co*-MMA)s. This is due to the induction period (t_0) of the polymerization process, which appears appreciably shorter in the presence of polymeric photoinitiators than with PIVPO (Table III). The results therefore indicate that poly(MAPO) and poly(MAPO-*co*-MMA)s are less sensitive to the presence in the formulation of traces of oxygen, which is known³⁵ to be usually responsible for this effect.

UV-curing experiments were also carried out on the TiO₂-pigmented coating formulation based on the Ebecryl 600 epoxyacrylate (Table IV). The



Scheme 3

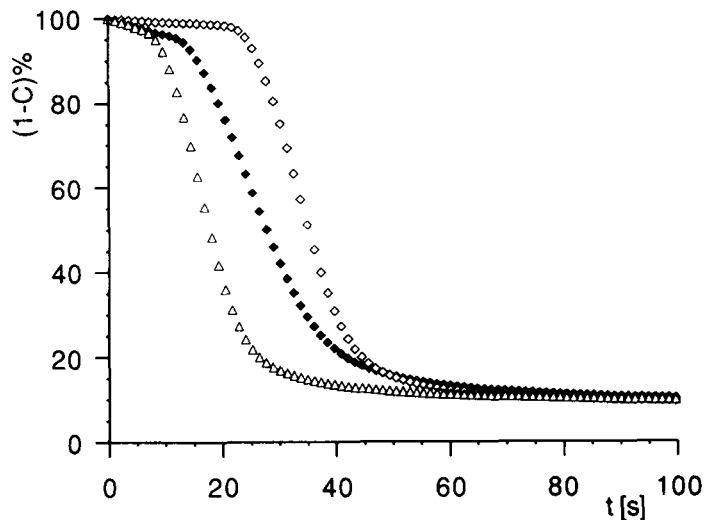


Figure 7 Percentage of residual monomers concentration ($1 - C$)% as a function of irradiation time in the photoinitiated HDDA/BA polymerization by (Δ) poly(MAPO-co-MMA) containing 1.01 mmol/g of MAPO co-units, (\blacklozenge) poly(MAPO), and (\diamond) PIVPO.

photoinitiating activity, measured by different methods such as curing rate, pendulum hardness, and solvent resistance of the cross-linked coatings, was slightly lower for poly(MAPO) and poly(MAPO-co-MMA)s than for PIVPO. However, the performance, in terms of yellowness and whiteness properties, of the pigmented coatings after UV curing by the polymeric photoinitiators was similar to

that observed by using PIVPO under the same irradiation conditions (Table IV).

CONCLUSIONS

On the basis of the results obtained, some conclusions can be drawn:

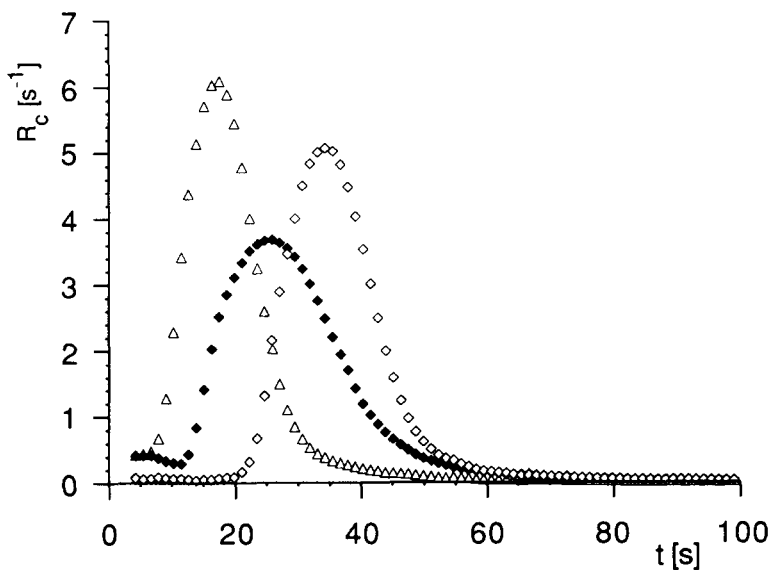


Figure 8 Polymerization rate (R_c) as a function of irradiation time in the photoinitiated HDDA/BA polymerization by (Δ) poly(MAPO-co-MMA) containing 1.01 mmol/g of MAPO co-units, (\blacklozenge) poly(MAPO), and (\diamond) PIVPO.

Table III Kinetic Data of UV-initiated Polymerization under Nitrogen of HDDA/BA Equimolar Mixture in the Presence of High and Low Molecular Weight Photoinitiators Based on Acyldiphenylphosphin oxide Moiety

Photoinitiator	Acyldiphenylphosphin oxide Moiety (mmol/g)	t_0^a (s)	$t_{1/2}^b$ (s)	$(R_p)_{max}^c$ (s ⁻¹)
PIVPO	3.49	23.4	35.4	5.1
Poly(MAPO)	1.78	12.6	28.2	3.7
Poly(MAPO-co-MMA)	1.53	14.4	27.6	4.2
Poly(MAPO-co-MMA)	1.97	15.0	24.6	6.2
Poly(MAPO-co-MMA)	1.01	7.8	18.0	6.1
Poly(MAPO-co-MMA)	0.20	12.6	32.4	3.0

^a Induction period of the photoinitiated polymerization process.

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

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

- The synthesis of polymeric systems containing side-chain acyldiphenylphosphin oxide moieties is readily achieved. However, the functionalization of poly(MAC) and poly(MAC-co-MMA)s by methoxydiphenylphosphine is not quantitative as unreacted MAC co-units remain present to an appreciable extent.
- The MAPO co-units partially undergo photolytic degradation, giving rise to low molecular weight byproducts such as diphenylphosphin oxide and diphenylphosphinic acid and its anhydride, which remain embedded as impurities in the polymeric photoinitiators. For this reason, a more accurate evaluation of photo-reactive units in the polymeric systems was performed by UV analysis.
- The photoinitiating activity of poly(MAPO) and poly(MAPO-co-MMA)s in the curing of both clear and pigmented coating formulations is not strictly related to the content of MAPO

co-units, thus suggesting that each photoreactive moiety behaves as an isolated one. The comparison between polymeric systems and PIVPO indicates that high and low molecular weight photoinitiators containing the acyldiphenylphosphin oxide group exhibit similar photoinitiating activity. However, a more detailed analysis of the results indicates that in the UV curing of clear coatings the polymeric systems are to be preferred for their higher productivity, due to an appreciable reduction of the induction period of the polymerization and cross-linking reactions. In pigmented coatings, no appreciable gain of productivity is obtained by using the polymeric photoinitiators; the ultimate properties of the coating are similar or slightly poorer than those obtained by using PIVPO.

- The polymeric photoinitiators based on acyldiphenylphosphin oxide moieties show a signif-

Table IV UV Curing Activity of TiO₂-pigmented Coating Formulation Based on Epoxyacrylate in the Air by Low and High Molecular Weight Photoinitiators Containing the Acylphosphin oxide Moiety and Properties of the Resulting Surface Coatings

Photoinitiator	Acyldiphenylphosphin oxide Moiety ^a (mmol/g)	Curing Rate ^b	Pendulum Hardness ^c (s)	Solvent Resistance ^d	Y.I. ^e	W.I. ^e
PIVPO	3.49	3	145	150	-10.3	76.2
Poly(MAPO)	1.78	4	135	127	-9.3	76.8
Poly(MAPO-co-MMA)	1.97	3	140	138	-5.1	73.3

^a As determined by UV spectroscopy.

^b Expressed as number of passes at 8 m/min under the same irradiation conditions, in order to obtain a nontacky surface coating.

^c Expressed as oscillation time of the Koenig pendulum after three passes under the same irradiation conditions.

^d Expressed as number of double-rubs by an MEK-soaked cotton-wool.

^e Yellowness and whiteness indexes.

icant higher stability than does the low molecular weight structural model, both under light exposure and in hydrolytic conditions, thus making them more promising for potential technological applications in the area of UV-curable coatings as they can overcome problems of stability during formulation storage. This behavior can be explained by a "cage" effect due to the polymer backbone on the primary radicals produced by photofragmentation.

- The stability of these polymeric photoinitiators is not completely satisfactory for practical applications. More stable photoinitiators should be obtained by anchoring the acyldiphenylphosphinoyl moiety to a polymer matrix bearing side-chain aromatic groups. Work is in progress in this direction.

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