# Polymeric Photoinitiators Bearing Side-Chain Benzoyldiphenylphosphinoxide Moieties for UV Curable Coatings

LUIGI ANGIOLINI, DANIELE CARETTI, and CARLO CARLINI*

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

## SYNOPSIS

Polymeric photoinitiators bearing side-chain benzoyldiphenylphosphinoxide moieties have been prepared by reacting poly(4-vinylbenzoic acid) or 4-vinylbenzoic acid/methyl methacrylate copolymers with thionyl chloride followed by methoxydiphenylphosphine. The activity of the above polymeric systems has been checked in the UV curing of the acrylic clear-coating formulation HDDA/BA and compared with that of the low molecular weight model 4-isopropylbenzoyldiphenylphosphinoxide. The stability to light and to hydrolytic conditions of the polymeric photoinitiators with respect to the model has also been tested. The results obtained are discussed in terms of composition and structural features of these systems. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

The use of polymers having side-chain photoreactive moieties has, in recent years, increased in interest as photoinitiators for UV-curable surface coatings, due to their improved performances in terms of nonyellowing and low-odor properties.[1-3] Quite recently, the synthesis of low molecular weight photoinitiators based on the acyldiphenylphosphinoxide moiety has been reported.[4] They are claimed to work with a Norrish I-type fragmentation mechanism[5,6] and to be very active in the UV curing of TiO$_2$-pigmented coatings[7] as well as of thick-walled glass fiber-reinforced polyesters.[8]

In a previous article,[9] we extended our research, devoted to a better comprehension of structure/activity relations in polymeric photoinitiators based on different photoreactive groups,[10-13] to macromolecular systems containing pendant aliphatic acyldiphenylphosphinoxide moieties. Indeed, poly(methacryloyldiphenylphosphinoxide) [poly(MAPO)] and poly(methacryloyldiphenylphosphinoxide-co-methyl methacrylate) [poly(MAPO-co-MMA)] copolymers, having variable contents of

photosensitive moieties, were prepared and found to display substantially the same photoinitiation activity as that of the corresponding low molecular weight structural model, pivaloyldiphenylphosphinoxide. However, an appreciable reduction of the induction time of UV curing and a significantly higher stability both under light exposure and in hydrolytic conditions were observed in the polymeric systems.

Taking into account that in the case of low molecular weight acyldiphenylphosphinoxides the best performances, in terms of stability and photoinitiation activity, are observed when the acyl group is linked to a phenyl ring,[14,15] it appeared interesting to prepare polymeric systems containing side-chain benzoyldiphenylphosphinoxide moieties with the aim of improving the overall features of this type of photoinitiator. Thus, the present article deals with the synthesis of poly(VBPO) and poly(VBPO-co-MMA)s (Scheme 1), obtained, respectively, from the corresponding homopolymer of 4-vinyl benzoic acid [poly(VBA)] and its copolymers with MMA [poly(VBA-co-MMA)s], by treatment with thionyl chloride followed by functionalization with methoxydiphenylphosphine, according to the Michaelis–Arbuzov reaction.[16]

The activity of the above polymeric photoinitiators has been tested in the UV curing of a 1,6-hex-
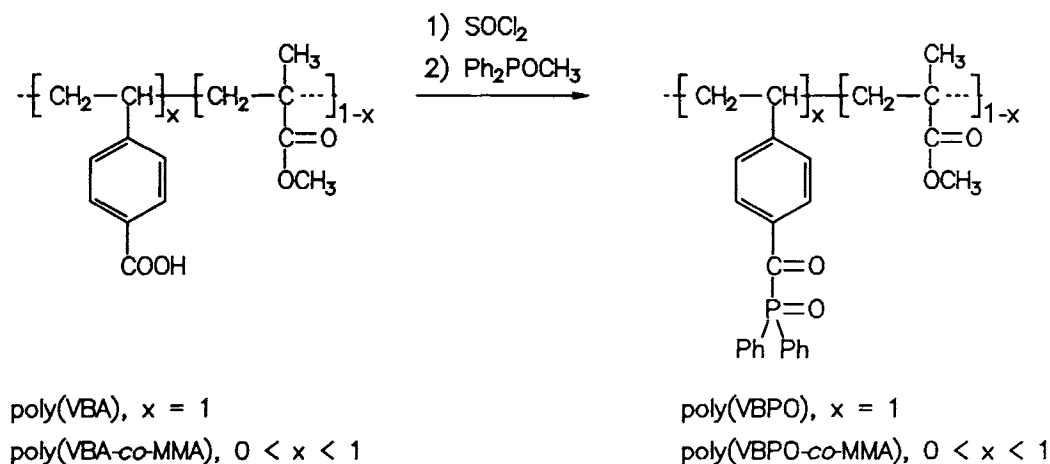
**Scheme 1**

anediol–diacrylate (HDDA)/n-butyl acrylate (BA) equimolar mixture and compared with those of the low molecular weight structural model 4-isopropylbenzoyldiphenylphosphinoxide (IBPO) and the previously reported[9] poly(MAPO) and poly (MAPO-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. BA and MMA (Fluka) were washed with 5% aq NaHCO$_3$, dried over anhydrous Na$_2$SO$_4$, and then distilled under nitrogen just before use.

4-Vinyl benzoic acid (VBA) was synthesized starting from (2-bromoethyl)benzene (BB) (Aldrich), according to what previously reported.[17,18] This procedure involves the Friedel–Crafts acylation



IBPO

of BB with acetyl chloride[17] to give 4-(2-bromoethyl)acetophenone, its oxidation with NaOBr[18] to yield 4-(2-bromoethyl) benzoic acid, and, finally, its dehydrohalogenation[18] with KOH in ethanol to the pure VBA (mp = 140°C).
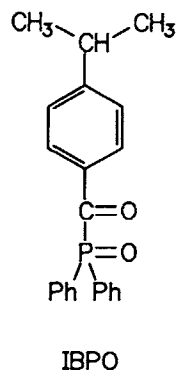
$^1$H-NMR (CDCl$_3$): 8.1 (d, 2 H, aromatic protons in the *ortho* position to the CO group), 7.5 (d, 2 H, aromatic protons in the *ortho* position to the vinyl group), 6.8 (q, 1 H, —CH$=$CH$_2$), and 5.9 and 5.4 (2 d, 2 H, —CH$=$CH$_2$) ppm.

IR (KBr): 3300–2500 ($\nu_{OH}$), 1680 ($\nu_{C=O}$), 1630 ($\nu_{C=C}$, vinyl group), 1610, 1565 ($\nu_{C=C}$, phenyl ring), 1420 ($\delta_{CH_2}$, vinyl group), 1290 ($\nu_{C-O}$), 990, 905 ($\delta_{CH}$, vinyl group), 920 ($\delta_{OH}$), and 860 ($\delta_{CH}$, 1,4-disubstituted phenyl ring) cm$^{-1}$.

Methoxydiphenylphosphine was prepared as previously reported,[4] 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

4-Isopropylbenzoyldiphenylphosphinoxide (IBPO) was prepared starting from 4-isopropyl benzoic acid (IBA) in two steps: First, IBA was converted to 4-isopropylbenzoyl chloride by reaction with thionyl chloride in 1,2-dichloroethane as solvent and in the presence of few drops of dimethylformamide (DMF) as catalyst. Then, the so-obtained chloride derivative was allowed to react in toluene solution, under inert atmosphere and in the dark, with a slight excess (10 mol %) of methoxydiphenylphosphine, according to a general procedure described for the preparation of

acyldiphenylphosphinoxides.[4] The final product was isolated by precipitation with anhydrous cyclohexane, dried, and stored in the dark under dry argon.

$^1$H-NMR (CDCl$_3$): 8.4 (d, 2 H, aromatic protons in the *ortho* position to the CO group), 8.2–7.9 (m, 4 H, aromatic protons in the *ortho* position to the PO group), 7.6–7.2 (m, 8 H, residual aromatic protons), 2.9 (hept, 1 H, CH$_3$—C$\underline{\text{H}}$), and 1.2 (d, 6 H, CH$_3$) ppm.

$^{31}$P-NMR (CDCl$_3$): 19.7 (PO) ppm.

IR (KBr): 3057 ($\nu_{CH}$, aromatic), 2961, 2930, 2870 ($\nu_{CH}$, aliphatic), 1641 ($\nu_{C=O}$), 1598 ($\nu_{C=C}$, phenyl ring), 1463 ($\nu_{P-Ph}$), 1385, 1365 ($\delta_{CH}$, gem. methyl groups), 1195 ($\nu_{P=O}$), 842 ($\delta_{CH}$, 1,4-disubstituted phenyl ring), and 749 and 698 ($\delta_{CH}$, monosubstituted phenyl rings) cm$^{-1}$.

UV (CHCl$_3$): $\varepsilon_{max}$ = 255 at 389 nm.

## Polymeric Photoinitiators

### Synthesis of Precursors Poly(VBA) and Poly(VBA-co-MMA)s

The title compounds were prepared by free radical homo- and copolymerization in benzene, using 2,2'-azobisisobutyronitrile (AIBN) as initiator (0.5 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 60°C for 120 h; then, the reaction mixture was poured into a large excess of petroleum ether and the coagulated polymer was redissolved in tetrahydrofuran (THF), precipitated again in petroleum ether, filtered, and dried at reduced pressure. All the polymers were characterized by $^1$H-

**Table I  Synthesis and Characterization of Poly(VBA) and Poly(VBA-co-MMA)s[a]**

| Run | Feed VBA (Mol %) | Conversion[b] (%) | Polymeric Product VBA Co-units[c] (Mol %) |
|---|---|---|---|
| 1 | 100 | 60 | 100 |
| 2 | 75 | 93 | 85 |
| 3 | 60 | 61 | 72 |
| 4 | 50 | 80 | 64 |
| 5 | 40 | 53 | 63 |
| 6 | 30 | 60 | 46 |
| 7 | 20 | 70 | 27 |
| 8 | 10 | 75 | 12 |

[a] In benzene at 60°C using AIBN as free-radical initiator. Duration: 120 h.
[b] Calculated as (wt of polymer/wt of monomers) × 100.
[c] Determined by $^1$H-NMR analysis.

NMR and FTIR analyses. In particular, the $^1$H-NMR spectrum of poly(VBA) in CDCl$_3$ displays broad signals at 8.0–7.5 and 7.0–6.2, as well as at 2.4–1.0 ppm, related to the aromatic and aliphatic protons, respectively, of VBA units. An additional signal at 3.6 ppm, having its relative intensity dependent on the composition, due to the ester CH$_3$ group of MMA units, was also present in the copolymers. Moreover, signals in the 2.3–1.3 and 1.2–0.5 ppm regions, connected with the CH$_2$ and $\alpha$-CH$_3$ groups, respectively, of MMA co-units forming triads of different tacticity, were observed. The composition of poly(VBA-co-MMA)s samples was determined by matching the integrated areas of the resonances of the ester CH$_3$ groups in MMA co-units with those of the aromatic protons of VBA co-units. The most relevant properties of the polymers are reported in Table I.

### Synthesis of poly(VBPO) and poly(VBPO-co-MMA)s

The polymers were dissolved in a large excess of SOCl$_2$ in the presence of few drops of DMF and the mixture refluxed for several hours (usually 16–20 h) until a complete conversion was obtained. The progress of the reaction was monitored by IR analysis following the progressive depletion of the band at 1680 cm$^{-1}$, related to the CO stretching vibration of the carboxyl group of VBA co-units, and the contemporary progressive increase of the band at 1770 cm$^{-1}$, connected with the corresponding vibration of the acyl chloride group in the functionalized product.

Because of their sensitivity to hydrolysis, the chlorinated polymers were not isolated, but immediately submitted to the successive reaction after distillation of the excess thionyl chloride. Thus, the polymeric material was dissolved with dry THF and allowed to react, under nitrogen and in the dark, with a small excess (10 mol %) of methoxydiphenylphosphine at 60°C until the complete disappearance (usually after 1 h) of the IR band at 1770 cm$^{-1}$ was observed in test samples drawn from the reaction mixture. The contemporary appearance in the IR spectrum of bands at 1634, 1434, and 1198 cm$^{-1}$, typical of the acyldiphenylphosphinoxide moiety, confirmed the occurrence of the functionalization reaction.

The polymeric products were isolated by precipitation with anhydrous cyclohexane and filtered under inert atmosphere, thus obtaining a white powdery material that was thoroughly washed with anhydrous petroleum ether, dried under vacuum, and, finally, stored under dry argon, in the dark.

**Table II   Synthesis and Characterization of Poly(VBPO) and Poly(VBPO-co-MMA)s**

| | Starting Polymer | Functionalized Polymer | | | | | | |
| | | Content of VBPO Co-units | | | | | | |
| Sample | VBA Co-units (Mol %) | $^1$H-NMR (Mol %) | UV[a] (Mol %) | UV[a] (mmol/g) | VBC Co-units[b] (Mol %) | $\bar{M}_n$[c] | $\bar{M}_w/\bar{M}_n$[c] |
|---|---|---|---|---|---|---|---|
| Poly(VBA) | 100 | n.d. | 57 | 2.28 | 22 | n.d. | n.d. |
| Poly(VBA-co-MMA) | 64 | 42 | 44 | 2.07 | 5 | 13,000 | 1.7 |
| Poly(VBA-co-MMA) | 63 | 37 | 39 | 1.93 | 4 | 12,300 | 2.2 |
| Poly(VBA-co-MMA) | 46 | 28 | 33 | 1.83 | 4 | 16,000 | 2.4 |
| Poly(VBA-co-MMA) | 27 | 18 | 17 | 1.17 | 2 | 14,600 | 2.0 |
| Poly(VBA-co-MMA) | 12 | 11 | 8 | 0.70 | 3 | 15,400 | 1.8 |

[a] Evaluated assuming that VBPO co-units in the polymeric samples display the same molar extinction coefficient as IBPO ($\varepsilon_{389}$ = 255 L mol$^{-1}$ cm$^{-1}$).

[b] Determined on the basis of chlorine content, assuming that VBPO, VBC, VBA, and MMA (except for the homopolymer) co-units are present. The VBPO content obtained from UV determination has been considered. (VBC = 4-vinylbenzoyl chloride co-units.)

[c] Determined by gel permeation chromatography (GPC) measurements.

All the functionalized polymers have been characterized in terms of composition by $^1$H-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. First, formulations of the HDDA/BA equimolar mixture containing 0.1 mol % of benzoyldiphenylphosphinoxide moiety were prepared in order to compare the activity of the newly prepared photoinitiators with that of the photoinitiators based on the aliphatic acyldiphenylphosphinoxide moiety previously measured[9] at the same concentration. Although the systems described in the present article did not result completely soluble in the formulation, exception made for the model compound IBPO, the curing of the above mixtures was performed at 25°C, under dry nitrogen, on a film matrix (200 $\mu$m) by UV irradiation at 330 nm ($I_0$ = 53 W/m$^2$).

To overcome the solubility problems, a second set of curing experiments was carried out on formulations constituted by $\frac{2}{3}$ wt % of chloroform and $\frac{1}{3}$ wt % of HDDA/BA equimolar mixture containing 0.12 mol % of photoinitiator in terms of the benzoyldiphenylphosphinoxide moiety. Under these conditions, all the polymeric photoinitiators were soluble and the formulations were subjected to UV irradiation in the same above-described way.

In both cases, the time evolution of the curing reaction was followed by microwave dielectrometry at 9.5 GHz in terms of $\varepsilon''$ (loss factor), as previously reported.[11,19]

## Physicochemical Measurements

$^1$H-NMR spectra were performed at 200 MHz on samples in CDCl$_3$ solution, with TMS as internal standard, by a Varian FT-NMR Gemini 200 spectrometer. $^{31}$P-NMR spectra were recorded at 30 MHz by a Varian FT-80A spectrometer on samples in CDCl$_3$ solution, by using H$_3$PO$_4$ 85% as external standard.

UV absorption spectra of the photoinitiators were recorded at 25°C in CHCl$_3$ solution on a Kontron Instruments Model UVICON 860 spectrophotometer. The spectral region between 450 and 300 nm was investigated by using a cell path length of 1 cm and concentrations of acyldiphenylphosphinoxide moieties in the 0.8–1.5 mmol/L range; $\varepsilon$ values are expressed in L mol$^{-1}$ cm$^{-1}$.

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

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

ANAL: Found: Poly(VBPO): Cl, 2.98%; poly(VBPO-co-MMA) [36%]: Cl, 0.87%; poly(VBPO-co-MMA) [37%]: Cl, 0.98%; poly(VBPO-co-MMA) [54%]: Cl, 0.79%; poly(VBPO-co-MMA) [73%]: Cl, 0.58%; poly(VBPO-co-MMA) [88%]: Cl, 1.01%,

where the percentage in square brackets represents the content of MMA co-units in the copolymers.

Average molecular weights of the polymeric samples were determined by a HPLC Waters Millipore 590 apparatus equipped with an injector Model U6K, a TSK column gel-G4000HXL, and a refractive index detector Waters Model R401. $CHCl_3$ was used as eluent. The calibration curve was obtained by using several monodisperse polystyrene standards.

## RESULTS AND DISCUSSION

### Poly(VBA) and Poly(VBA-co-MMA)s

As reported in Table I, the copolymers are enriched in VBA units, with respect to the corresponding feed, in the whole range of compositions. This result fits quite well with the data previously obtained[20] for the free-radical copolymerization of VBA with MMA, whose reactivity ratios were found to be equal to 4.878 and 0.305, respectively. The content of VBA co-units in the copolymers, calculated from the copolymerization equation[21] on the basis of these reactivity ratios (Fig. 1), is higher than that observed in our copolymeric samples, but the difference can be readily attributed to the high degree of conversion (> 50%) adopted in our experiments. A confirmation of this comes from runs 4 and 5 (Table I), where conversions of 80 and 53% allow one to
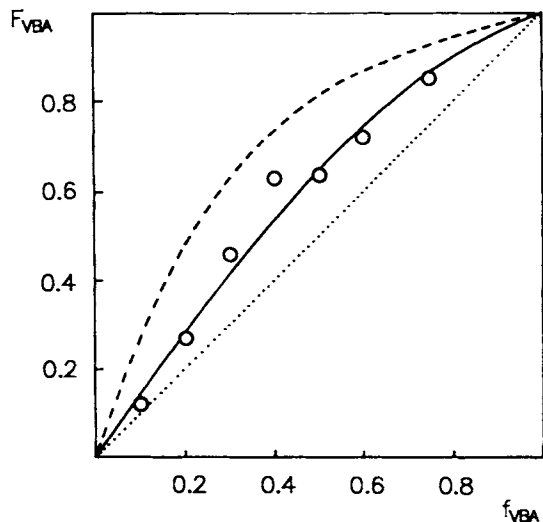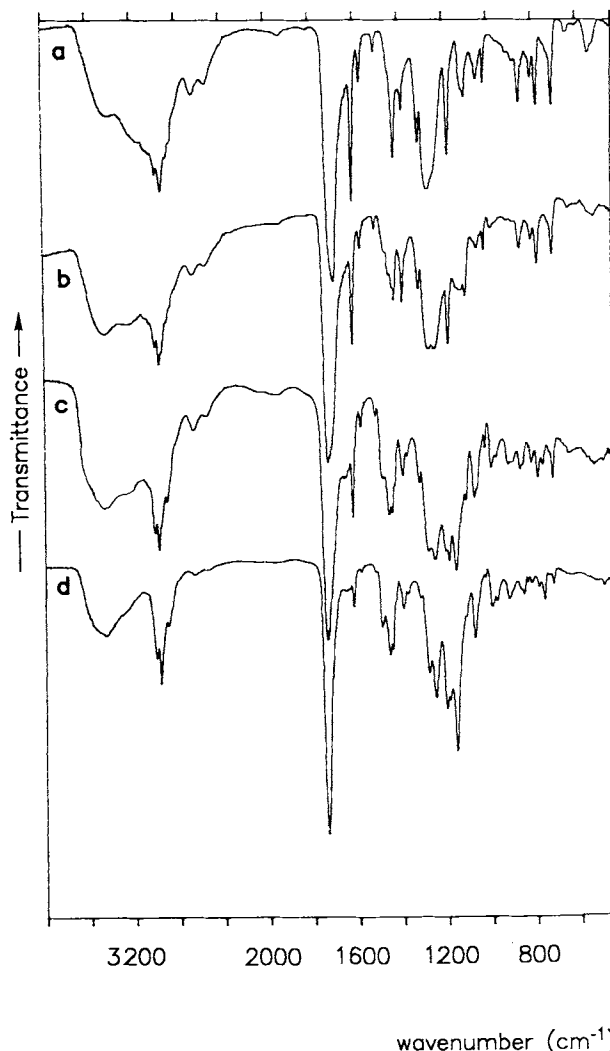
Figure 2  FTIR spectra of (a) poly(VBA) and of poly(VBA-co-MMA)s containing (b) 64, (c) 46, and (d) 12 mol % of VBA co-units, respectively.

Figure 1  Copolymerization diagram for the VBA/ MMA system; $F_{VBA}$ and $f_{VBA}$ represent the VBA content (molar fraction) in the copolymerization product and in the feed, respectively: (———) experimental data; (– – –) curve determined from literature reactivity ratios.

afford copolymers having substantially the same content of VBA co-units starting from feeds containing 50 and 40 mol % of VBA, respectively. 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.

FTIR spectra (Fig. 2) confirm the expected structure of the copolymers. Indeed, bands around 3400 ($\nu_{OH}$), 1610, 1509, 1422 ($\nu_{C=C}$ phenyl ring), and 856 ($\delta_{C-H}$ 1,4-disubstituted phenyl ring), typical of VBA co-units, as well as bands at 1732 ($\nu_{C=O}$) and 1266 ($\nu_{O-CH_3}$) $cm^{-1}$, connected with the methyl ester group of MMA co-units, are present with relative intensities related to the composition of the

copolymer sample. In poly(VBA), the band at 1697 ($\nu_{C=O}$) cm$^{-1}$, belonging to carboxy group, obscured in the copolymers by the more intense band at 1732 cm$^{-1}$ of MMA ester group, is also observed.

## Poly(VBPO) and Poly(VBPO-co-MMA)s

$^1$H-NMR spectra of poly(VBPO) and poly(VBPO-co-MMA)s show the appearance at 8.4 ppm of the signal typical of the aromatic protons in the *ortho* position to the CO group of VBPO co-units, as found for the structural model IBPO (see Experimental). The integrated area of the above signal, compared with that of the signal at 3.6 ppm, related to the methyl ester group of MMA co-units, has been used for the determination of the composition of the copolymeric products. The calculation is based on the reasonable assumption that the content of MMA co-units in the copolymers remains unchanged after the functionalization reaction. The results, reported in Table II, clearly indicate that the two-step functionalization reaction is uncomplete, as confirmed by the elemental analysis of chlorine content, which suggests the presence of significant amounts of residual 4-vinylbenzoyl chloride (VBC) co-units. In addition, appreciable amounts of VBA co-units, calculated by difference, are also present, due to residual VBA co-units after the chlorination step or produced by partial hydrolysis of unreacted VBC co-units during the manipulation of the polymeric products for their spectroscopic characterization. In conclusion, $^1$H-NMR and elemental analyses suggest that poly(VBPO) has to be actually considered as a terpolymer constituted by VBPO, VBC, and VBA co-units, whereas poly(VBPO-co-MMA)s consist of four repeating units, as they include also MMA co-units.

In accordance with the above-proposed structures, the FTIR spectra (Fig. 3) of poly(VBPO) and poly(VBPO-co-MMA)s show a broad band centered at 3400 cm$^{-1}$, attributable to the carboxylic hydroxy group of VBA co-units, which is particularly evident in poly(VBPO). A band at 1775 cm$^{-1}$, characteristic of the COCl group of VBC co-units, is also visible in the spectrum of poly(VBPO), but is not observable in the spectra of poly(VBPO-co-MMA)s, due to overlapping with the more intense band of the carbonyl group in the methyl ester moiety of MMA co-units at 1732 cm$^{-1}$. Bands at 1697 and 1634 cm$^{-1}$, related to the carbonyl-stretching vibration of carboxylic acid and benzoylphosphinoxide moieties in the VBA and VBPO co-units, respectively, are, moreover, observed in the FTIR spectra of all the polymeric samples.
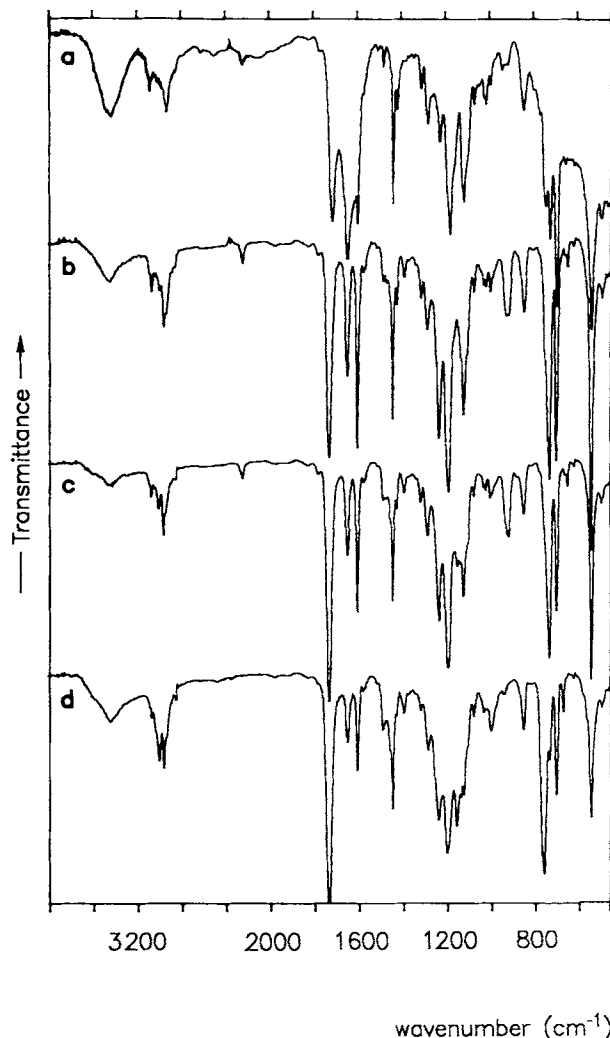


**Figure 3**   FTIR spectra of (a) poly(VBPO) and of poly(VBPO-co-MMA)s containing (b) 2.07, (c) 1.83, and (d) 0.70 mmol/g of VBPO co-units, respectively.

The presence of diphenylphosphinoxide as impurity in poly(VBPO) and poly(VBPO-co-MMA)s, at least for the samples having a high content of VBPO co-units, is evidenced by a low-intensity doublet centered at 8.1 ppm, assigned[22,23] to the P—H proton ($J_{PH}$ = 482 Hz) and by the occurrence, in the FTIR spectra, of a weak band at 2322 cm$^{-1}$, due to the stretching vibration of the P—H bond.[24] Small amounts of low molecular weight impurities containing the Ph$_2$PO group are ascertained also by $^{31}$P-NMR spectrometry on dark-adapted CDCl$_3$ solutions of poly(VBPO-co-MMA)s, which show, in addition to the signal at 20.1 ppm, belonging to the benzoyldiphenylphosphinoxide moiety of VBPO co-units,[25] two signals at 26.8 and 32.5 ppm, assigned to diphenylphosphinoxide[26] and diphenylphosphinic acid,[27] respectively.

Considering that the photoinitiation activity of poly(VBPO) and poly(VBPO-co-MMA)s has to be compared with that of the structural model IBPO at the same concentration of benzoyldiphenylphosphinoxide moiety in the coating formulation, the accurate determination of the content of VBPO co-units in the above polymeric systems is essential. As the above identified low molecular weight phosphorus-containing impurities do not display any absorption band in the spectral region related to the $n \rightarrow \pi^*$ electronic transition of the acyl group of benzoyldiphenylphosphinoxide moiety,[9] the quantitative analysis of VBPO co-units by UV spectroscopy could appear more reliable, provided that the molar extinction coefficient of the $n \rightarrow \pi^*$ band in VBPO co-units is equal to that found for IBPO.

This hypothesis usually holds for isolated VBPO co-units. On increasing the content of VBPO co-units, electronic interactions between neighboring benzoyldiphenylphosphinoxide moieties along the polymer chain could give a progressive hypochromic effect,[28,29] in accordance with what reported for copolymers containing side-chain aromatic chromophores.[30,31] However, this behavior is generally associated with a slight hypsochromic effect.[30-32] Taking into account that poly(VBPO) and poly(VBPO-co-MMA)s show practically identical UV spectra, regardless the composition, consisting of a structured absorption band with a maximum centered at 392 nm with a slight bathochromic effect with respect to IBPO ($\lambda_{max}$ = 389) (Fig. 4), it may be reasonably concluded that no appreciable interaction occurs
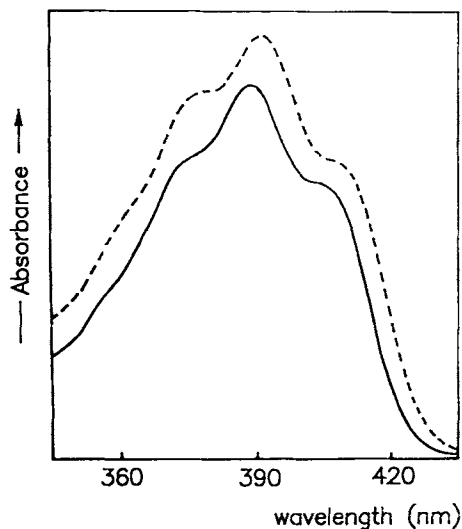


**Figure 4** UV spectra in chloroform solution of (———) IBPO and (- - -) poly(VBPO-co-MMA) containing 1.17 mmol/g of VBPO co-units.

between benzoyldiphenylphosphinoxide moieties in our polymeric samples, thus allowing to use the molar extinction coefficient of IBPO ($\varepsilon$ = 255 L mol$^{-1}$ cm$^{-1}$) for calculating the VBPO co-units content in the polymeric samples. The results, reported in Table II, appear in good agreement with those obtained from $^1$H-NMR measurements, thus indicating a substantial reliability of both the analytical methods employed.

The average molecular weights of poly(VBPO-co-MMA)s result in the 12,000–16,000 range without any particular trend related to composition, whereas the molecular weights distribution (MWD), expressed by $\bar{M}_w/\bar{M}_n$, falls in the 1.7–2.4 range usually found in free-radical copolymerizations and appears slightly broader for the intermediate compositions (Table II). This could be ascribed to enhanced competition, in the initial copolymerization step producing the polymeric precursors, between the two different termination mechanisms, namely, disproportionation and coupling, respectively, preferred by MMA and VBA growing chain radicals.[33,34] Indeed, when one comonomer is largely prevailing in the feed, only one type of termination mechanism should predominantly occur, thus narrowing the MWD values of the resulting copolymers.

## Stability of Polymeric Photoinitiators

It is well known[35-38] that low molecular weight acyl-diphenylphosphinoxides are quite unstable under the combined action of light, humidity, heating, and air, giving rise, particularly in solution, to degradation products as a consequence of both homolytic and heterolytic reactions involving free radicals as well as ionic species. We have, however, observed[9] that anchoring the acyldiphenylphosphinoxide moiety to an aliphatic polymeric chain, as in poly(MAPO) and poly(MAPO-co-MMA)s, a remarkable increase of stability to light and hydrolysis with respect to the corresponding low molecular weight counterpart is obtained. This was tentatively explained[9] on the basis of a "cage effect" by the polymer backbone on the free radicals formed by photofragmentation of the CO—PO bond. Similarly, the reduced reactivity toward hydrolysis was attributed to the protective action exerted by the polymer chain as a consequence of its steric hindrance.

Thus, the stability to the light of the newly obtained photoinitiators has been tested on freshly prepared chloroform solutions of poly(VBPO-co-MMA)s containing 1.83 and 1.93 mmol/g of VBPO co-units and compared with that of an analogous

solution of IBPO. The samples have been maintained under dry argon atmosphere and submitted to the same cyclic exposure to daylight and dark. The corresponding dark-adapted solutions have been also used as reference samples. Contrarily to what previously observed for poly(MAPO-co-MMA)s, poly(VBPO-co-MMA)s exhibit a lower light stability with respect to the low molecular weight model IBPO, as checked by the faster depletion of their UV absorption maximum at about 390 nm (Fig. 5). At the same time, the presence of turbidity in the solution, due to the formation of cross-linked material, is observed in the polymeric samples. A reduction of about the 50% of the UV absorbance at the same wavelength is also observed after 2 weeks in the dark-adapted reference samples of poly(VBPO-co-MMA)s, whereas no appreciable variation of the UV absorbance occurs after the same period of time in the dark for the IBPO reference sample.

These results may be therefore attributed to the occurrence, in the copolymers, also of heterolytic degradation promoted by the presence of residual acidic VBA co-units. Indeed, whereas dark-adapted chloroform solutions of poly(VBPO-co-MMA)s and IBPO are substantially stable when treated with about 3% by volume of methanol, a sharp reduction of the content of benzoyldiphenylphosphinoxide moieties is displayed by the same samples on addition of 3% by volume of hydrochloric acid saturated methanol (Fig. 6), thus demonstrating the sensitivity of these systems to the presence of acidic species.

It would therefore appear that light and residual acidic groups of the polymers concurrently act as promoters of degradation so as to reduce their stability with respect to the low molecular weight
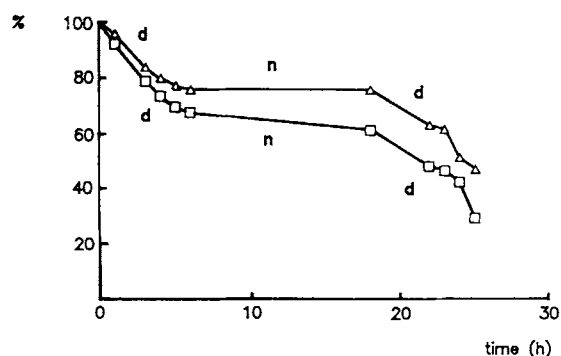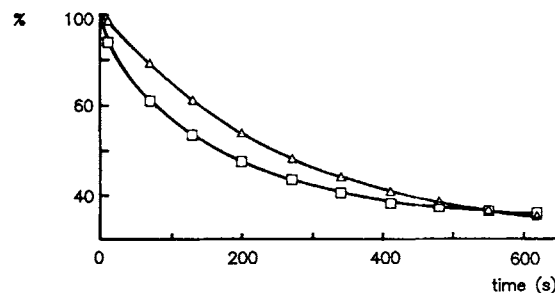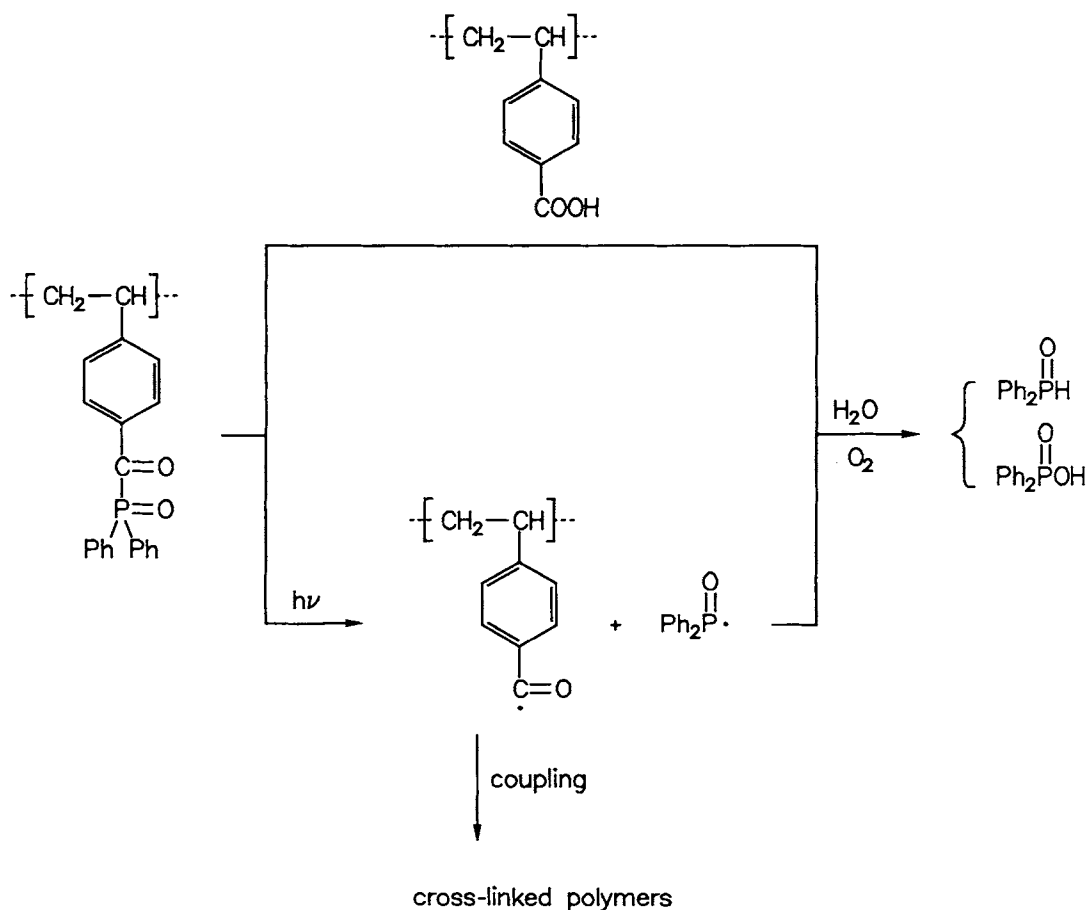


**Figure 6** Residual benzoyldiphenylphosphinoxide moieties (%) in dark-adapted chloroform solutions of ($\square$) poly(VBPO-co-MMA) containing 1.83 mmol/g of VBPO co-units and ($\triangle$) IBPO as a function of time after treatment with 3% by volume of hydrochloric acid saturated methanol.

model. Taking into consideration the nature of the above-described phosphorus-containing impurities identified in the polymers, a possible mechanism of degradation, in the presence of traces of air and humidity in the solution, could be depicted as in Scheme 2.

## Photoinitiation Activity of Poly(VBPO) and Poly(VBPO-co-MMA)s

The time evolution of the UV curing, under nitrogen, of the HDDA/BA equimolar mixture by polymeric photoinitiators has been monitored by microwave dielectrometry (see Experimental), which allows one to determine the induction period ($t_0$), the half-time of polymerization and cross-linking of the formulation ($t_{1/2}$), as well as the maximum polymerization rate [$(R_c)_{max}$]. To compare the photoinitiation activity of poly(VBPO) and poly(VBPO-co-MMA)s with that one previously obtained[9] for the polymers containing methacryloyldiphenylphosphinoxide co-units [poly(MAPO) and poly(MAPO-co-MMA)s], formulations of HDDA/BA (1 : 1) containing 0.1 mol %, in terms of the benzoyldiphenylphosphinoxide moiety, of polymeric and low molecular weight photoinitiators have been submitted to UV curing. Notwithstanding that the polymeric samples resulted partially soluble at the above concentration in the HDDA/BA (1 : 1) mixture, differently from IBPO, the UV curing by polymeric photoinitiators proceeds at a markedly higher rate, as checked by $(R_c)_{max}$ values, and exhibits $t_0$ values about one order of magnitude shorter with respect to the corresponding values found for poly(MAPO-co-MMA)s (Table III). Accordingly, the $t_{1/2}$ values are about $\frac{1}{3}$ less than in poly(MAPO-co-MMA)s,



**Figure 5** Residual benzoyldiphenylphosphinoxide moieties (%) as a function of light-exposure time for chloroform solutions of ($\square$) poly(VBPO-co-MMA) containing 1.93 mmol/g of VBPO co-units and ($\triangle$) IBPO (d = daylight, n = night).

**Scheme 2**

thus suggesting a reduced sensitivity of poly(VBPO-co-MMA)s to traces of oxygen in the formulation, usually responsible for the overall slowing down of

the process.[39] Such a behavior clearly indicates an enhanced productivity of the benzoyldiphenyl-phosphinoxide moiety in comparison with the

**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 the Acyldiphenylphosphinoxide Moiety**

| Photoinitiator | Acyldiphenylphosphinoxide Moiety (mmol/g) | $t_0$ [a] (s) | $t_{1/2}$ [b] (s) | $(R_c)_{max}$ [c] $(s^{-1})$ |
|---|---|---|---|---|
| IBPO | 2.87 | 1.8 | 6.4 | 13.6 |
| Poly(VBPO-co-MMA) | 0.70 | 0.6 | 9.1 | 9.4 |
| Poly(VBPO-co-MMA) | 1.17 | 2.6 | 9.5 | 9.2 |
| Poly(VBPO-co-MMA) | 1.83 | 2.9 | 8.4 | 11.0 |
| Poly(VBPO-co-MMA) | 2.07 | 1.4 | 8.9 | 9.4 |
| Poly(MAPO-co-MMA)[9] | 1.97 | 15.0 | 24.6 | 6.2 |
| Poly(MAPO-co-MMA)[9] | 1.53 | 14.4 | 27.6 | 4.2 |
| Poly(MAPO-co-MMA)[9] | 1.01 | 7.8 | 18.0 | 6.1 |
| Poly(MAPO-co-MMA)[9] | 0.20 | 12.6 | 32.4 | 3.0 |

[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.

corresponding aliphatic acyldiphenylphosphinoxide moiety of MAPO units.

A quantitative comparison between IBPO and the polymeric systems is not possible from the data of Table III, as the higher activity of IBPO is probably due to its complete solubility in the HDDA/BA mixture, which produces a higher concentration of active moieties. A more accurate check on this point has been therefore made by repeating the UV-curing experiments on the same acrylic mixture diluted with chloroform (see Experimental), so as to have the complete solubility also of the polymeric photoinitiators. Indeed, the kinetic parameters are (Table IV) substantially the same, within the limits of the experimental errors, thus demonstrating a practically equal productivity of poly(VBPO) and poly(VBPO-co-MMA)s as compared with IBPO. The photoinitiation activity of the polymers appears independent of the content of VBPO co-units, without any significant trend indicative of cooperative interactions between neighboring photosensitive moieties. Moreover, the presence in the macromolecules of variable amounts of potentially photolabile residual benzoyl chloride moieties does not seem to appreciably affect the overall photoinitiation activity of the polymeric systems.

## CONCLUSIONS

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

- The synthesis of polymers bearing side-chain benzoyldiphenylphosphinoxide moieties has been accomplished, starting from the homopolymer of 4-vinylbenzoic acid and its copolymers with methyl methacrylate, by a two-step functionalization reaction producing the desired product, which, however, contains significant amounts of residual vinylbenzoic acid and acyl chloride co-units.

- The benzoyldiphenylphosphinoxide co-units are rather unstable and give rise to small amounts of low molecular weight phosphorus containing byproducts that are found as contaminants of the polymers. For this reason, the UV analysis appears the most reliable technique for the accurate evaluation of the content of VBPO co-units in the polymeric systems.

- The stability to the light of the polymeric photoinitiators is lower than that found for the corresponding low molecular weight model IBPO. The residual vinylbenzoic acid co-units, present in the polymers, appear to play a significant role in promoting the degradation in solution by a heterolytic mechanism.

- The photoinitiation activity of poly(VBPO-co-MMA)s are much improved with respect to that found for analogous aliphatic polymeric systems bearing the acyldiphenylphosphinoxide moiety in the side chain. This is in accordance with previous investigations on low molecular weight systems, indicating a much higher activity promoted by the presence of the aromatic acyl group in the photoinitiator molecule.

- The activity of poly(VBPO) and poly(VBPO-co-MMA)s in the curing of clear acrylic formulations is not related to the content of VBPO co-units, thus suggesting that each photoreactive group behaves as an isolated moiety, as

Table IV   Kinetic Data of UV-initiated Polymerization, Under Nitrogen, of HDDA/BA (1 : 1)/CHCl₃ Mixture in the Presence of High and Low Molecular Weight Photoinitiators Based on the Benzoyldiphenylphosphinoxide Moiety[a]

| Photoinitiator | Acyldiphenylphosphinoxide Moiety (mmol/g) | $t_0$[b] (s) | $t_{1/2}$[c] (s) | $(R_c)_{max}$[d] (s⁻¹) |
|---|---|---|---|---|
| IBPO | 2.87 | 0.5 | 7.3 | 7.9 |
| Poly(VBPO) | 2.28 | 0.5 | 8.2 | 7.3 |
| Poly(VBPO-co-MMA) | 2.07 | 1.3 | 9.7 | 6.2 |
| Poly(VBPO-co-MMA) | 1.93 | 1.0 | 8.0 | 7.7 |
| Poly(VBPO-co-MMA) | 1.83 | 1.0 | 6.0 | 7.9 |
| Poly(VBPO-co-MMA) | 1.17 | 1.7 | 9.0 | 7.2 |

[a] Mixture consisting of 1 part of HDDA/BA (1 : 1) and 2 parts of CHCl₃ (wt/wt).
[b] Induction period of the photoinitiated polymerization process.
[c] Time required for reaching 50% conversion of the HDDA/BA mixture.
[d] Maximum polymerization rate, expressed as percentage of conversion over time.

confirmed by the similar activity exhibited in comparison with the low molecular weight model IBPO. This last result appears quite promising for practical applications in the field of surface protecting pigmented coatings, provided that a significant improvement of solubility of the polymeric system is attained. Work is in progress in this direction.

# REFERENCES

1. S. Q. S. Lin, A. F. Jacobine, and L. F. Fabrizio, Eur. Pat. Appl. 0,162,572 (1975) (to Loctite Co.).
2. H. Zweifel, J. Berger, V. Kvita, and M. Roth, Eur. Pat. Appl. 0,033,721 (1985) (to Ciba Geigy AG).
3. G. Li Bassi, C. Nicora, L. Cadonà, and C. Carlini, Eur. Pat. Appl. 0,161,463 (1985) (to Fratelli Lamberti SpA. and Consiglio Nazionale delle Ricerche).
4. P. Lechtken, I. Buethe, and A. Hesse, Ger. Pat. 2,830,927 (1980) (to Basf AG).
5. T. Sumiyoshi, W. Schnabel, A. Henne, and P. Lechtken, *Polymer*, **26**, 141 (1985).
6. J. E. Baxter, R. S. Davidson, H. J. Hageman, and T. Overeem, *Makromol. Chem. Rapid Commun.*, **8**, 311 (1987).
7. M. Jacobi and A. Henne, *Radiat. Curing*, **10**, 16 (1983).
8. W. Nickolaus, A. Hesse, and D. Scholz, *Plastverarbeiter*, **31**, 723 (1980).
9. L. Angiolini, D. Caretti, C. Carlini, and N. Lelli, *J. Appl. Polym. Sci.*, **48**, 1163 (1993).
10. C. Carlini, F. Ciardelli, D. Donati, and F. Gurzoni, *Polymer*, **24**, 599 (1983).
11. C. Carlini, L. Toniolo, P. A. Rolla, F. Barigelletti, P. Bortolus, and L. Flamigni, *New Polym. Mater.*, **1**, 63 (1987).
12. L. Angiolini and C. Carlini, *Chim. Ind.*, **72**, 124 (1990).
13. C. Carlini and L. Angiolini, in *New Aspects of Radiation Curing in Polymer Science and Technology*, J. P. Fouassier and J. F. Rabek, Eds., Elsevier, Belfast, 1993, Vol. 2, Chap. 5, p. 283.
14. P. Lechtken, I. Buethe, M. Jacobi, and W. Trimborn, Ger. Pat. 2,909,994 (1980) (to Basf AG).
15. M. Jacobi and A. Henne, in *Radcure '83*, Lausanne, Switzerland, May 9–11, 1983; Technical Paper FC83-256, SME Ed., Deaborn, MI, 1983.
16. R. Engel, *Synthesis of Carbon-Phosphorus Bonds*, CRC Press, Boca Raton, FL, 1988, p. 21.
17. L. Foreman and S. M. McElvain, *J. Am. Chem. Soc.*, **62**, 1435 (1940).
18. P. Jäger and E. S. Waight, *J. Am. Chem. Soc.*, **85**, 1339 (1963).
19. C. Carlini, P. A. Rolla, and E. Tombari, *J. Appl. Polym. Sci.*, **41**, 805 (1990).
20. R. Z. Greenley, *J. Macromol. Sci.-Chem.*, **A14**, 445 (1980).
21. G. E. Ham, in *High Polymers: Copolymerization*, G. E. Ham, Ed., Interscience, New York, 1964, Vol. 18.
22. E. Lindner and M. Steinwand, *Z. Naturforsch.*, **37b**, 407 (1982).
23. R. Curci and A. M. Piepoli, *Boll. Fac. Chim. Ind. Bologna*, **27**, 237 (1969).
24. M. Sanchez, R. Wolf, and F. Mathis, *Spectrochim. Acta*, **23A**, 2617 (1967).
25. E. Lindner and D. Hübner, *Chem. Ber.*, **116**, 2574 (1983).
26. E. Fluck and H. Binder, *Z. Naturforsch.*, **22b**, 805 (1967).
27. E. Lindner and H. Kern, *Z. Naturforsch.*, **38b**, 790 (1983).
28. I. Tinoco, Jr., *J. Am. Chem. Soc.*, **82**, 4785 (1960).
29. K. Okamoto, A. Itaya, and S. Kusabayashi, *Chem. Lett.*, 1167 (1974).
30. R. Solaro, G. Galli, A. Ledwith, and E. Chiellini, in *Polymer Photophysics*, D. Phillips, Ed., Chapman and Hall, London, 1985, p. 377.
31. C. Carlini and F. Gurzoni, *Polymer*, **24**, 101 (1983).
32. A. Altomare, C. Carlini, F. Ciardelli, and R. Solaro, *Polym. J.*, **20**, 801 (1988).
33. R. P. Taylor, J. C. Bevington, and H. W. Melville, *J. Polym. Sci.*, **12**, 449 (1954).
34. Y. Yagci and Önen, *J. Macromol. Sci.-Chem.*, **A28**, 129 (1991).
35. N. J. De'ath, S. T. McNeilly, and J. A. Miller, *J. Chem. Soc. Perkin I*, 741 (1976).
36. H. Lesiecki, E. Lindner, and G. Vordermaier, *Chem. Ber.*, **112**, 793 (1979).
37. E. Lindner and H. Kern, *Chem. Ber.*, **117**, 355 (1984).
38. J. E. Baxter, R. S. Davidson, H. J. Hageman, and T. Overeem, *Makromol. Chem.*, **189**, 2769 (1988).
39. C. Decker, *Makromol. Chem.*, **180**, 2027 (1979).