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### Photoinitiators with Functional Groups. Part I. Polymer Photoinitiators

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## PHOTOINITIATORS WITH FUNCTIONAL GROUPS. PART I. POLYMER PHOTOINITIATORS

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### ABSTRACT

A series of new polymerizable photoinitiators (PIs) based on hydroxyalkylphenones has been synthesized by Grignard reaction of 4-vinylphenylmagnesiumchloride with suitable carbonyl compounds. Radical homopolymerization and copolymerization of the PIs with various vinyl monomers yielded polymer PIs compatible with either hydrophilic or hydrophobic resin systems. The PI monomers and polymers are characterized by excellent photoinitiating activity comparable with the most efficient known PIs and exhibit high migration stability.

### INTRODUCTION

In recent years the use of UV-photocurable compositions has largely increased in various areas of industrial applications [1–4]. The essential component of UV-curable systems is the photoinitiator (PI) [2, 5–7] generating free radicals by irradiation. The main requirements for technical applications of PIs are high photoinitiating activity, good compatibility with the photopolymerizable system, low toxicity, and migration stability.

In UV curing with commercial low-molecular PIs, difficulties arise such as migration of residual unreacted PI and its decomposition prod-

ucts causing impairment of the properties of the hardened coatings as well as environmental problems.

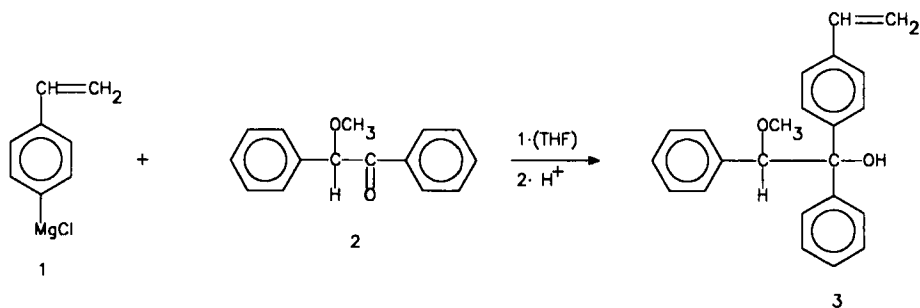
Polymeric systems containing photoinitiating residues covalently bonded to a macromolecular backbone [8–14] exhibit better migration stability but suffer from low reactivity and poor compatibility with many resin systems, and generally they are available only by tedious syntheses.

Based on the known exceptionally reactive hydroxyalkylphenones [6, 15, 16], we have synthesized a number of new polymerizable PIs as well as their homo- and copolymers.

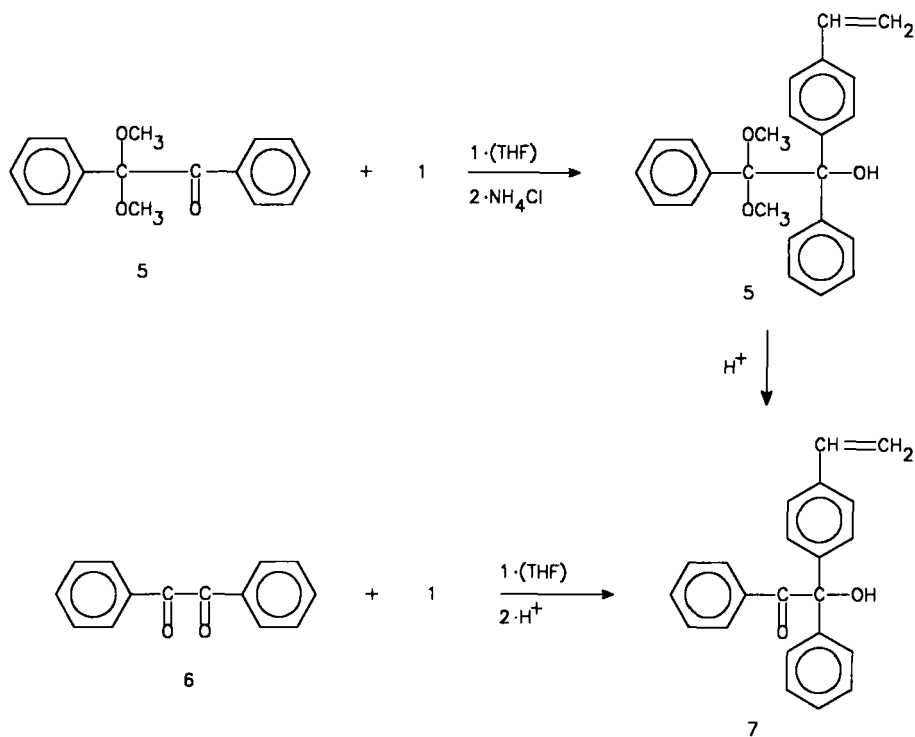
## RESULTS AND DISCUSSION

PIs containing 4-vinylphenyl residues on C atom 1 of the basic hydroxyalkylphenone structure were synthesized by Grignard reactions of 4-vinylmagnesiumchloride (1) with ketones. In a model, reaction 1 was first reacted with the PI benzoinmethylether (2) yielding 3 which is not photoactive because of the lack of the keto group (Scheme 1).

The polymerizable PI 7 has been synthesized by reaction of 1 with benzildimethyl ketal (4) and subsequent hydrolysis of the ketal 5. Using benzil (6) as starting substance, 7 could be synthesized by a one-step reaction with 1 (Scheme 2). Reaction of 1 with phenylpropandion (8) afforded a photoactive mixture of the isomers 9 and 10, which was difficult to separate (Scheme 3). Pure isomer 9 could be obtained by reaction of 1 with 1,1-dimethoxy-1-phenylpropan-2-one (11) and subsequent hydrolysis of the ketal 12. Using 2,2-dimethoxy-2-phenylacetal-



SCHEME 1.



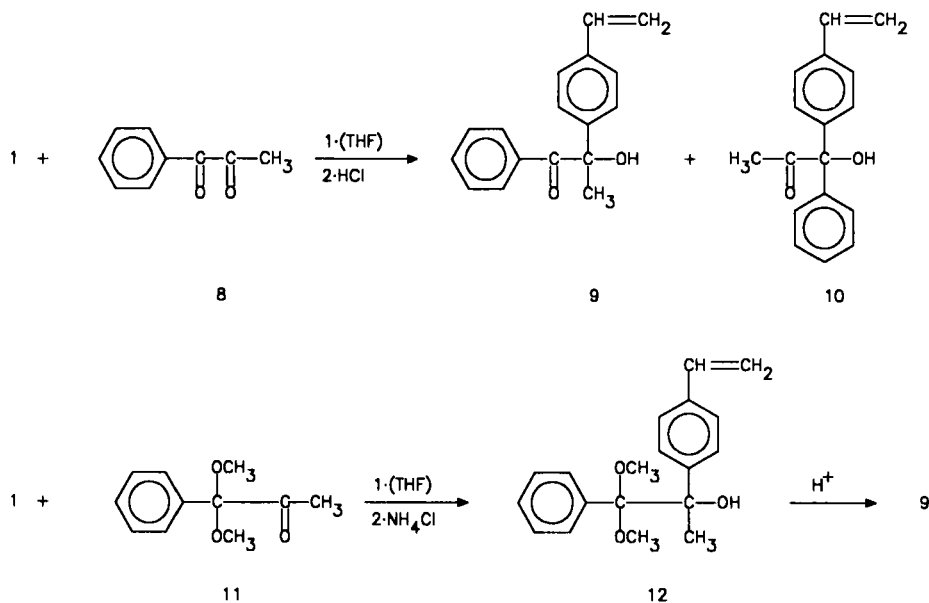
SCHEME 2.

dehyde (13) as starting compound, PI 15 was synthesized by a similar reaction sequence (Scheme 4).

PIs 18a and 18b with 4-vinylphenyl residues on C atom 2 were synthesized by reaction of 1 with cyanohydrines containing dihydropyrane-protected hydroxyl groups (17a and 17b, respectively) and subsequent splitting of the dihydropyrane residues (Scheme 5). Reaction of 1 with 17c yielded the methyl ether 19.

The photoinitiating activity of the new PIs has been compared by a standard method with 2-hydroxy-2-methyl-1-phenylpropan-1-one (DAR-OCUR 1173, Merck Co. [6]). Films based on mixtures of the PIs with epoxyacrylates were irradiated under standardized conditions, and the curing efficiency was estimated by measuring the hardness of cured films after various irradiation times.

The tests demonstrated that the efficiency of the PIs is not diminished

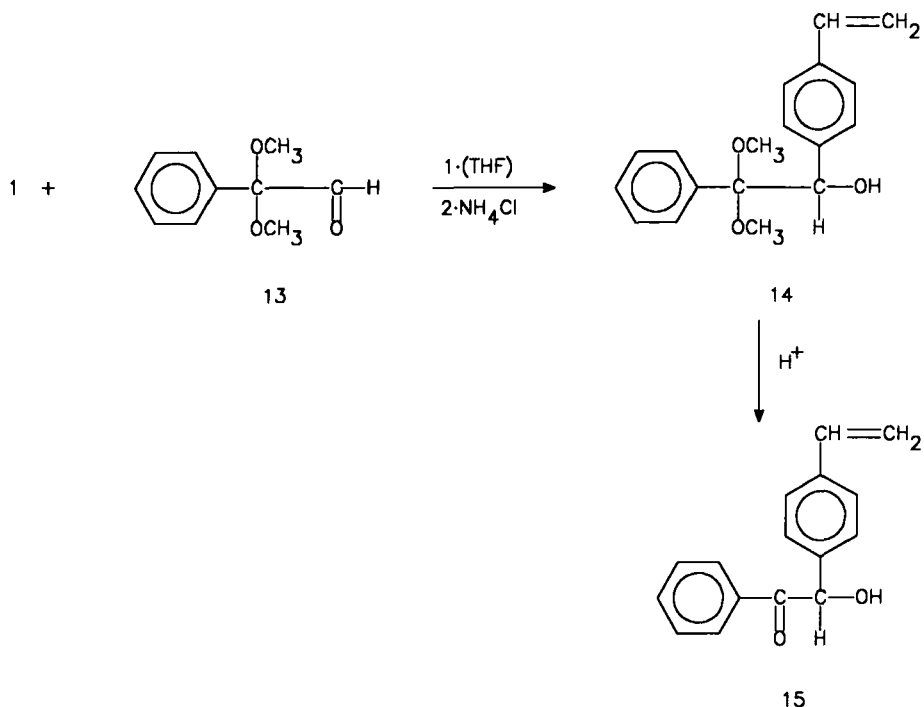


SCHEME 3.

by the polymerizable groups. Table 1 shows that PIs 7, 18a, 18b, and 19 exhibited similar activity as the standard whereas 15 was somewhat less active. The isomer mixture 9 + 10 as well as 9 were photoactive too but not soluble in the test mixture; therefore, they could not be compared with the standard PI.

Contrary to the standard PI (DAROCUR 1173) the polymerizable PIs are incorporated by covalent bonds during UV curing and thus no migration occurs, as was demonstrated by extraction experiments.

Radical homopolymerization of the PI monomers and copolymerization with various vinyl monomers afforded PI homo- and copolymers (Scheme 6). Homopolymer 20a exhibited almost the same photoactivity as the standard, 20b; 21–23 were photoactive too but insoluble in the test resin. Copolymerization of 18a with styrene (24), methylmethacrylate (25), acrylonitrile (29), methylvinylketone (30), and maleic acid anhydride (33) yielded photoactive hydrophobic polymers with solution properties different from those of the homopolymers (Scheme 7). Hydrophilic PI copolymers compatible with aqueous-organic systems are available by copolymerization of 18a with acrylic acid (26), methacrylic acid (27), acrylamide (28), *N*-vinylpyrrolidone (31), and 3-vinylpyridine.



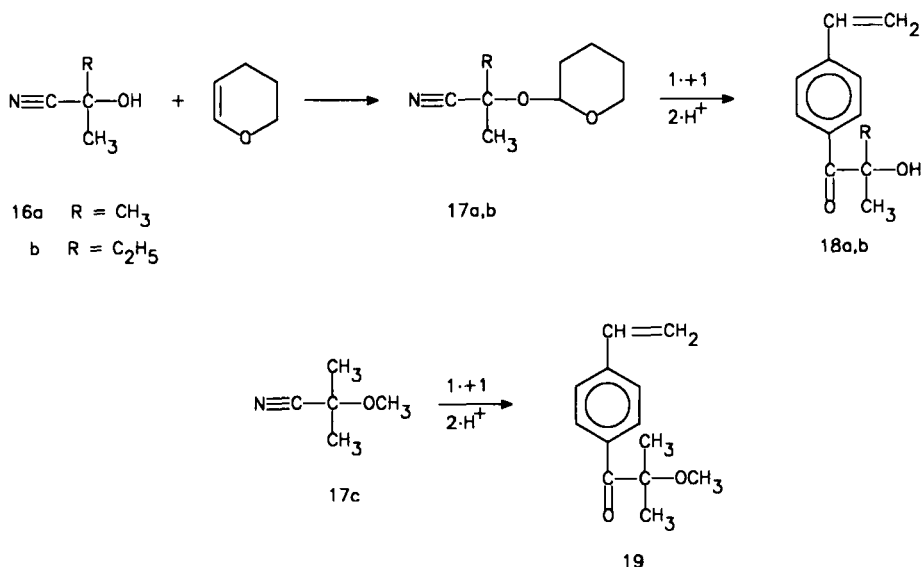
SCHEME 4.

Thus optimal compatibility of the polymer PIs with various resins can be varied by appropriated comonomers.

A polymerizable PI containing methacrylate groups (**36**, Scheme 8) has been synthesized by reacting benzil-di-2-chloroethylketal (**34**) with excess piperazine and subsequent reaction of **35** with methacryloyl chloride; **36** is a very efficient PI in UV curing of methacrylate resins.

Another methacrylic acid derivative was prepared by esterification of hydroxymethylbenzoine (**37**) with methacrylic acid chloride (Scheme 9). Using equimolar amounts of the reactants, only the primary HO-group is esterified yielding **38**, which has been homopolymerized and copolymerized with methylmethacrylate to give polymer PI **39** (Scheme 9). The HO-groups in **39** can be subsequently substituted by methacryloyl residues.

These results demonstrate that polymerizable and polymer PIs based on hydroxyalkylphenones are characterized by high photoinitiating activity comparable with the most efficient known PIs. Their compatibility



SCHEME 5.

with different hydrophobic and hydrophilic resins can be varied easily, and in contrast to low-molecular PIs, they exhibit high migration stability.

## EXPERIMENTAL

The solvents were dried and purified by common methods. 4-Vinylphenylmagnesiumchloride (**1**) was prepared according to the literature [17], yielding a solution containing 0.21 mol **1** /100 mL THF. 1-Phenyl-1,2-propanol (**8**) [18], 3,3-dimethoxy-3-phenylpropan-2-one (**11**) [19], 2,2-dimethoxy-2-phenylacetaldehyde (**13**) [20], 2-cyano-2-tetrahydropyranoxy-2-propan (**17a**) [21], 2-cyano-2-tetrahydropyranoxy-2-butan (**17b**) [21], and 2-methyl-2-methoxypropionitril (**17c**) [22], benzil-bis-(2-chlorethyl)ketal (**34**) [23], benzil-bis-(2-piperazinoethyl)ketal (**35**) [24], and 2,3-dihydroxy-1,2-diphenyl-1-propanone (**37**) [25] were prepared by known procedures.

### 1-Methoxy-1,2-diphenyl-2-(4-vinylphenyl)ethan-2-ol (**3**)

59 mmol **1** was added to a solution of benzoin methyl ether (**2**) (11.1 g, 49 mmol) in 100 mL THF at 0°C. The precipitated Grignard adduct

TABLE 1. Photoinitiating Activity of the PIs<sup>a</sup>

Speed of band conveyer (m/min) <sup>a</sup>	Hardness [s] <sup>b</sup>		
	2.5	3.75	5.0
DAROCUR 1173	203	206	208
<u>7</u>	202	179	—
<u>9</u> + <u>10</u>		<sup>c</sup>	
<u>9</u>		<sup>c</sup>	
<u>15</u>	83	—	—
<u>18a</u>	178	178	200
<u>18b</u>	198	183	195
<u>19</u>	185	179	195
<u>36</u>	200	204	—
PI polymers			
<u>20a</u>	199	203	200
<u>20b</u>	192	147	—
<u>21-23</u>		<sup>c</sup>	
PI copolymers			
<u>24</u>	207	208	207
<u>25</u>	208	211	109
<u>26-33</u>		<sup>c</sup>	

<sup>a</sup>Films were cured on glass slides passing the radiation source on a conveyor band at various speeds, thus varying the dose of radiation.

<sup>b</sup>Hardness (DIN 53157) of cured films based on 2.5% PI (or 2.5% related to active substance of PI polymers) in epoxyacrylate LAROMER EA 81 (BASF), UB radiation 80 W/cm.

<sup>c</sup>PI insoluble in the test mixture.

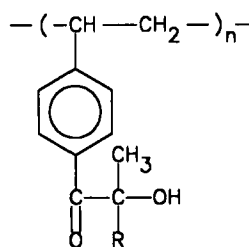
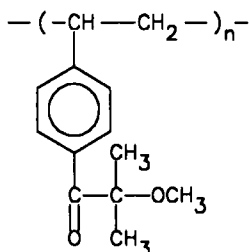
was filtered under nitrogen and treated with ice water. The product was washed with water several times and dried.

Yield: 11.9 g (73%), mp 166–167°C

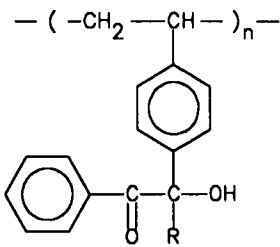
IR(KBr): 908, 985, 1630, 1103, 2824–2984, 3010–3063, 3441 cm<sup>-1</sup>

<sup>1</sup>HNMR: 1.6 (s, 1H, C—H), 3.4 (s, 3H, —OCH<sub>3</sub>), 4.8 (s, 1H, —C—OH), 5.0–7.1 (m, 3H, —CH=CH<sub>2</sub>), 7.1–8.0 ppm (m, 14H, benzene ring)

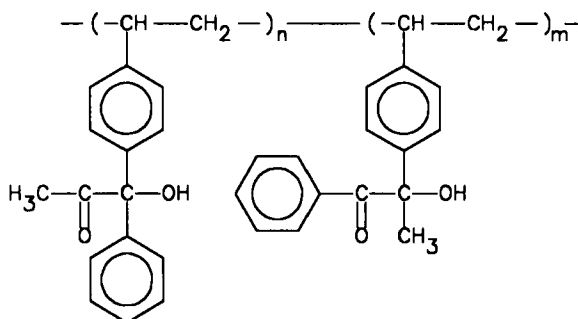


20a R = CH<sub>3</sub>20b R = C<sub>2</sub>H<sub>5</sub>

21



22a R = H

22b R = CH<sub>3</sub>22c R = 

23

SCHEME 6.

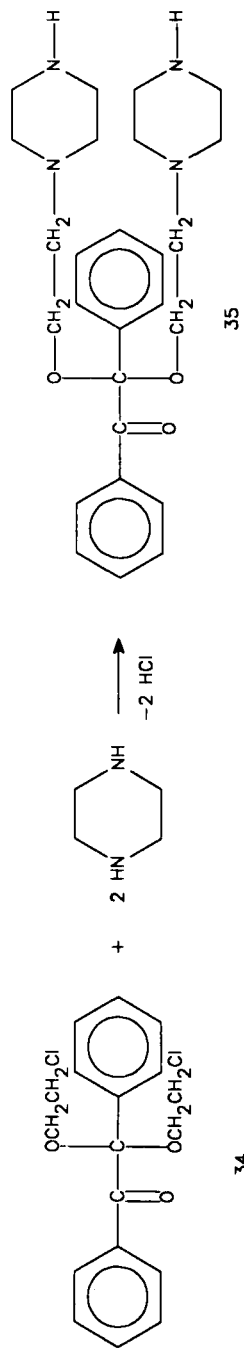
Elemental analysis: calc.	C 83.59	found	83.51
	H 6.71		6.73
	O 9.68		9.72

### 1,2-Diphenyl-2-hydroxy-2-(4-vinylphenyl)ethan-1-one (7)

#### From Benzildimethyl Ketal (4)

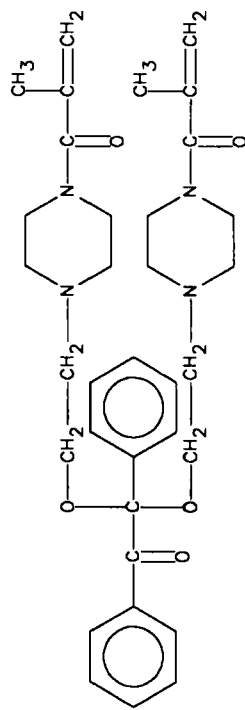
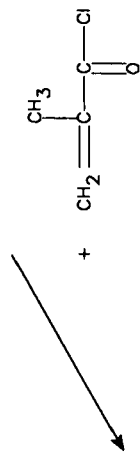
To a precooled ( $-20^{\circ}\text{C}$ ) solution of 4 (34.95 g, 136 mmol) in 60 mL THF **1** (163 mmol) was added slowly and stirred at  $20^{\circ}\text{C}$  for 3 h; 60 mL THF was added and the precipitated Grignard adduct was filtered under





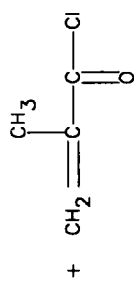
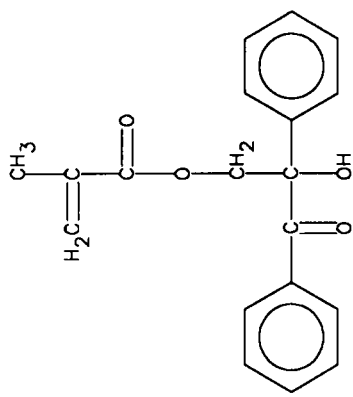
35

34



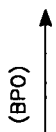
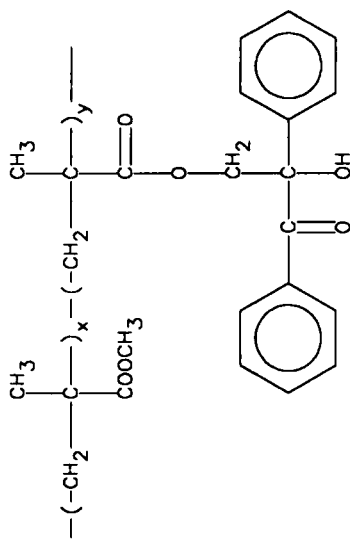
36

SCHEME 8.



37

38



38 + MMA

39

SCHEME 9.

nitrogen. After washing with THF, the adduct was treated with ice water and the pH was adjusted to 7 by addition of cold  $\text{NH}_4\text{Cl}$  solution. The aqueous phase was extracted several times with diethylether. The extracts were washed with water and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed under reduced pressure, yielding an oily substance crystallizing after several hours.

Yield: 35 g **5** (71%), mp 81–83°C

IR(KBr): 684, 705, 827, 912, 981, 1630, 2837–2978, 3008–3057, 3501  $\text{cm}^{-1}$

$^1\text{H}$ NMR: 3.3 (s, 6H,  $-\text{OCH}_3$ ), 3.9 (s, 1H,  $-\text{C}-\text{OH}$ ), 5.1–6.9 (m, 3H,  $-\text{CH}=\text{CH}_2$ ), 7.0–8.9 ppm (m, 14H, benzene ring)

Elemental analysis: calc.	C 79.97	found	79.81
	H 6.72		6.81
	O 13.31		13.38

A solution of **5** (30 g, 0.83 mol) in 90 mL  $\text{CHCl}_3$  was stirred with 30 mL 1 M HCl at 30°C for 20 h and then at 50°C for 4 h. The organic phase was washed with and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed under reduced pressure and the residual oil was purified by flash chromatography using benzene as an eluent.

Yield: 22.5 g (86%), mp 63–64°C; IR(KBr): 3435: 3062–3005, 1674, 1226, 981, 912, 827, 705, 684  $\text{cm}^{-1}$

$^1\text{H}$ NMR ( $\text{CDCl}_3$ ): 5.51 (s, 1H,  $-\text{C}-\text{OH}$ ), 5.3–7.3 (m, 3H,  $-\text{CH}=\text{CH}_2$ ), 7.6–8.2 (m, 14H, benzene ring).

Elemental analysis: calc.	C 84.07	found	83.92
	H 5.73		5.81
	O 10.19		10.27

### From Benzil (**6**)

To a precooled ( $-15^\circ\text{C}$ ) solution of **6** (13.87 g, 65 mmol) in 25 mL THF **1** (72 mmol) was added slowly and stirred at 20°C for 4 h. The reaction mixture was poured into ice water, acidified with diluted HCl, and extracted several times with diethylether. The extracts were washed with water and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed under reduced pressure and the residual oil was purified by flash chromatography using benzene as an eluent. Yield: 10.7 g (66%); mp, IR,  $^1\text{H}$ NMR, and elemental analysis identical with the product from benzildimethylketal.

**Reaction of 1-Phenyl-1,2-propanedione (8) with 1**

To a precooled (0°C) solution of **8** (6.98 g, 47 mmol) in 20 mL THF **1** (52 mmol) was added slowly and stirred at 20°C for 3 h. The reaction mixture was poured into ice water, acidified with diluted HCl, and extracted several times with diethylether. The extracts were washed with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure, yielding 12 g of a raw product containing **9** and **10**; 1 g was purified by flash chromatography using chloroform as an eluent, yielding 0.76 g (64%) of a mixture of 45% **9** and 55% **10** (determined by <sup>1</sup>HNMR).

IR: 912, 991, 1630, 1682, 1709, 2860–2924, 3010–3057, 3450 cm<sup>-1</sup>

<sup>1</sup>HNMR: 1.9 (s, 3H, COCH<sub>3</sub>), 2.3 [s, 3H, C(OH)CH<sub>3</sub>], 4.8–5 (d, 2H, C–OH), 5.2–7.1 (m, 3H, –CH=CH<sub>2</sub>), 7.2–8.0 ppm (m, 18H, benzene ring)

Elemental analysis: calc	C 80.91	found	81.19
	H 6.37		6.49
	O 12.68		12.32

**1,1-Dimethoxy-1,2-diphenyl-2-(4-vinylphenyl)ethan-2-ol (12) and 1,2-Diphenyl-2-hydroxy-2-(4-vinylphenyl)ethan-1-one (9)**

212 mmol **1** was added slowly to a solution of **11** (31.6 g, 163 mmol) in 50 mL THF at 20°C and stirred for 10 h. The mixture was refluxed for 5 h, cooled, and divided into two parts. One-half of the solution was poured into cold aqueous NH<sub>4</sub>Cl solution. The aqueous phase was extracted several times with diethylether. The extracts were washed with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure, yielding 17.5 g (72%) **12**; 4 g of the raw product **12** was purified by flash chromatography using benzene as an eluent.

Yield: 1.0 g

IR: 912, 991, 1630, 1682, 1030–1105, 2860–2924, 3010–3057, 3450 cm<sup>-1</sup>

<sup>1</sup>HNMR: 2.3 (s, 3H, –C–CH<sub>3</sub>), 3.1–3.3 [d, 6H, –C(OCH<sub>3</sub>)], 4.8 (s, 1H, C–OH), 5.1–7.0 (m, 3H, –CH=CH<sub>2</sub>), 7.3–8.1 ppm (m, 9H, benzene ring)

Elemental analysis: calc.	C 76.46	found	76.54
	H 7.44		7.49
	O 16.09		15.92

The second part of the solution was poured in cold diluted  $\text{H}_2\text{SO}_4$  and stirred for 24 h at  $20^\circ\text{C}$  and for 16 h at  $45^\circ\text{C}$ . The aqueous phase was extracted several times with diethylether. The extracts were washed with water and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed under reduced pressure, yielding 14 g (68%) **9**: 5 g of the raw product was purified by flash chromatography using benzene as an eluent. Recrystallization from petrol ether yielded 0.7 g (17%) of pure **9**.

IR(KBr): 912, 991, 1630, 1682, 2860–2924, 3010–3057,  $3450\text{ cm}^{-1}$

$^1\text{H}$ NMR: 2.3 (s, 3H,  $-\text{C}-\text{CH}_3$ ), 4.8 (s, 1H,  $\text{C}-\text{OH}$ ), 5.1–7.0 (m, 3H,  $-\text{CH}=\text{CH}_2$ ), 7.3–8.1 ppm (m, 9H, benzene ring)

Elemental analysis: calc.	C 80.95	found	80.74
	H 6.37		6.45
	O 12.68		12.82

### 1,1-Dimethoxy-1-phenyl-2-(4-vinylphenyl)ethan-2-ol (**14**)

124 mmol **1** was added slowly to a solution of **13** (21.1 g, 103 mmol) in 150 mL THF at  $0-5^\circ\text{C}$  and stirred at  $20^\circ\text{C}$  for 10 h. The precipitated adduct was filtrated under nitrogen, washed with THF, and poured into ice water. The pH was adjusted to 7 by addition of cold  $\text{NH}_4\text{Cl}$  solution, and the aqueous phase was extracted several times with diethylether. The extracts were washed with water and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed under reduced pressure and the residual product was treated with petrol ether, filtered, and dried under vacuum.

IR(KBr): 1045–1118, 906, 999, 1630, 2840–2944, 3010–3057,  $3490\text{ cm}^{-1}$

$^1\text{H}$ NMR( $\text{CDCl}_3$ ): 2.1 (s, 1H,  $-\text{CH}$ ), 3.3–3.6 [d, 6H,  $\text{C}(\text{OCH}_3)$ ], 4.7 (s, 1H,  $-\text{C}-\text{OH}$ ), 5.1–7.0 (m, 3H,  $-\text{CH}=\text{CH}_2$ ), 7.1–7.6 ppm (m, 9H, benzene ring)

Elemental analysis: calc.	C 76.03	found	75.87
	H 7.09		7.18
	O 16.88		16.95

### 1-Phenyl-2-hydroxy-2-(4-vinylphenyl)ethan-1-one (**15**)

The Grignard adduct resulting from the reaction of **1** with **13** was treated with diluted HCl and the mixture was extracted several times with diethylether. The extracts were washed with water and dried over

anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed under reduced pressure and the residual product was treated with petrol ether, filtered, and dried under vacuum.

Yield: 20.2 g 15 (72%), mp 120–122°C

IR(KBr): 923, 1001, 1630, 2900–2984, 3010–3057, 3490  $\text{cm}^{-1}$

$^1\text{H}$ NMR( $\text{CDCl}_3$ ): 2.1 (s, 1H,  $-\text{CH}$ ), 4.8 (s, 1H,  $-\text{C}-\text{OH}$ ), 5.1–7.0 (m, 3H,  $-\text{CH}=\text{CH}_2$ ), 7.1–8 ppm (m, 9H, benzene ring)

Elemental analysis: calc.	C 80.45	found	80.64
	H 5.92		6.02
	O 13.43		13.23

### 2-Hydroxy-2-methyl-1-(4-vinylphenyl)propan-1-one (18a)

0.49 mol 1 was added to a precooled (0°C) solution of 17a (64.2 g, 0.41 mol) in 50 mL THF. The mixture was stirred at 20°C for 4 h, then at 65°C for 1 h, and poured into ice water. After hydrolysis with diluted HCl for 20 h at 45°C, the aqueous phase was extracted several times with diethylether. The extracts were washed with water and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed under reduced pressure and the residual product was distilled.

Yield: 42.6 g 18a (60%), bp 83–86°C/0.01 mm

IR: 918, 989, 1630, 1669, 2900–2984, 3010–3092, 3458  $\text{cm}^{-1}$

$^1\text{H}$ NMR: 1.6 (s, 6H,  $\text{CH}_3$ ), 4.2 (s, 1H,  $-\text{C}-\text{OH}$ ), 5.3–7.2 (m, 3H,  $-\text{CH}=\text{CH}_2$ ), 7.4–8.3 ppm (m, 4H, benzene ring)

Elemental analysis: calc.	C 75.89	found	75.64
	H 7.37		7.47
	O 16.73		16.83

### 2-Hydroxy-2-methyl-1-(4-vinylphenyl)butan-1-one (18b)

0.29 mol 1 was added to a solution of 17b (48.1 g, 0.29 mol) in 50 mL THF at 20°C. The mixture was refluxed for 90 min, cooled, and poured into cold diluted HCl. The mixture was stirred at 30°C for 15 h and the aqueous phase was extracted several times with diethylether. The extracts were washed with water and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed under reduced pressure and the residual product was distilled.

Yield: 23.8 g 18b (42%), bp 90–93°C/0.01 mm



IR: 923, 1001, 1630, 1250, 1669, 2900–2984, 3010–3092, 3490  $\text{cm}^{-1}$

$^1\text{H}$ NMR: 0.8–1.1 (t, 3H,  $-\text{CH}_2-\text{CH}_3$ ), 1.6 (s, 3H,  $-\text{C}-\text{CH}_3$ ), 1.8–2.1 (m, 2H,  $-\text{CH}_2-\text{CH}_3$ ), 4.3 (s, 1H,  $-\text{C}-\text{OH}$ ), 5.3–7.1 (m, 3H,  $-\text{CH}=\text{CH}_2$ ), 7.3–8.1 ppm (m, 4H, benzene ring)

Elemental analysis: calc.	C 76.44	found	76.64
	H 7.90		8.01
	O 15.66		15.33

## 2-Methyl-2-methoxy-1-(4-vinylphenyl)propan-1-one (19)

0.21 mol **1** was added to a solution of **17c** (25 g, 0.25 mol) in 30 mL THF. The mixture was stirred at 65°C for 1 h and poured into cold diluted HCl. The aqueous phase was extracted several times with diethyl-ether. The extracts were washed with water and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed under reduced pressure and the residual product was distilled.

Yield: 36 g **19** (84%), bp 72–74°C/0.05 mm

IR: 908, 986, 1630, 1078, 1676, 2831–2989, 3010–3092  $\text{cm}^{-1}$

$^1\text{H}$ NMR: 1.6 (s, 3H,  $-\text{CH}_3$ ), 3.3 (s, 3H,  $-\text{C}-\text{OCH}_3$ ), 5.3–7.1 (m, 3H,  $-\text{CH}=\text{CH}_2$ ), 7.3–8.4 ppm (m, 4H,  $-\text{benzene ring}$ )

Elemental analysis: calc.	C 75.76	found	75.51
	H 7.41		7.54
	O 16.82		16.97

## Homopolymerizations

The monomers **3**, **9**, **9/10**, **15**, **19**, **18a**, and **18b** (20 mmol) were polymerized in 15 mL benzene with AIBN (0.8 mmol) under nitrogen at 60°C for 12 h and precipitated with petrol ether. They were purified by the benzene/petrol ether system three times and finally dried in vacuum at 50°C.

Polymers (yield %): **20a** (83), **20b** (81), **21** (78), **22a** (81), **22b** (75), **22c** (76)

## Copolymerizations of **18a** with vinyl monomers

Copolymers containing **18a** and comonomer in calculated molar ratios of 1:3, 3:1, and 2:1 were prepared by radical copolymerization in benzene at 60°C using AIBN (4 mol%) as initiator. The molar ratios of

monomers were calculated assuming approximately the value of styrene for the reactivity ratio  $r_1$  of 18a.  $r_2$  values were taken from the literature. The copolymers were purified by precipitation with appropriated solvents.

The relative amounts of the monomers incorporated into the polymers were calculated from the elemental analyses (see Tables 2 and 3).

### Methacryloylation of 35

A solution of methacrylic acid chloride (14.4 g, 0.16 mol) in 20 mL benzene was added to a solution of 35 (24 g, 0.053 mol) and triethylamine (32.4 g, 0.32 mol) in 100 mL benzene at 5°C. The mixture was stirred at 20°C for 20 h and filtered. The solution was washed several times with diluted NaOH and with water. The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuum. The residue was purified by flash chromatography.

Yield: 15 g (50%)

IR: 1695 (C=O)

<sup>1</sup>HNMR: 1.8 (s, 6H, CH<sub>2</sub>), 2.2–2.7 (m, 20H, –N–CH<sub>2</sub>), 3.3–3.7 (m, 4H, –OCH<sub>2</sub>), 4.9–5.0 (m, 4H, –CH=CH<sub>2</sub>), 7.1–7.6 ppm (m, 10H, benzene ring)

Elemental analysis: calc.	C 68.43	found	68.23
	H 7.43		7.54
	N 10.70		11.00
	O 13.40		13.19

### Methacryloylation of 37

A solution of methacrylic acid chloride (2.16 g, 21 mmol) in 20 mL THF was added to a solution of 37 (5 g, 21 mmol) and triethylamine (2.1 g, 21 mmol) in 50 mL THF at 5°C. The mixture was stirred at 20°C for 5 h and filtered from hydrochloride. The solution was concentrated under vacuum and the residue treated with petrol ether. The crystals were filtered and dried.

Yield: 6 g 38 (88%)

<sup>1</sup>HNMR: 1.8–2.0 (s, 3H, CH<sub>3</sub>), 4.7 (s, 2H, –O–CH<sub>2</sub>), 4.9 (s, 1H, –C–OH), 5.0–6.1 (m, 2H, –C=CH<sub>2</sub>), 7.1–8.2 ppm (m, 10H, benzene ring)

TABLE 2. Copolymers of 18a

Copolymer	Comonomer <sup>a</sup>	Monomer ratio <sup>b</sup>	Monomer ratio in copolymer		Solubility <sup>c</sup>	
			Calc. <sup>c</sup>	Found <sup>d</sup>	s	i
<u>24a</u>	St	1:3	1:3	1:3	b,me,a c	pe
<u>b</u>		1:6	1:6	1:6		
<u>c</u>		2:1	2:1	2:1		
<u>25a</u>	MMA	1:3	1:3	1:3	b, ac	pe
<u>b</u>		1:6	1:6	1:6		
<u>c</u>		2:1	2:1	2:1		
<u>26a</u>	AA	1:9,8	1:3	1:3,1	NaOH	w
<u>b</u>		1:20	1:6	1:5,5	NaOH	w
<u>c</u>		1,7:1	2:1	4:1		w,NaOH
<u>27a</u>	MA	1:3,5	1:3	1:3	NaOH,me	w
<u>b</u>		1:5,7	1:6	1:6	NaOH,me,ac	w
<u>c</u>		2,5:1	2:1	2,3:1		w,NaOH
<u>28a</u>	AAM	1:3	1:3	1:3	d/w(3:1) ac/2(3:1)	
<u>b</u>		1:6	1:6	1:5,9		w
<u>c</u>		2:1	2:1	2:1		w
<u>29a</u>	AN	1:50,2	1:3	1:7	DMF	me
<u>b</u>		2,5:1	2:1	2,6:1		
<u>30a</u>	MVK	1:6,25	1:3	1:2,8	me,ac	pe
<u>b</u>		1:14,7	1:6	1:6		
<u>c</u>		2,3:1	2:1	2:1,3		
<u>31a</u>	NVP	1:27,3	1:3	1:1,1	HCl	w
<u>b</u>		1:4,5	2:1	2:1		HCl,w
<u>32a</u>	VP	1:3,6	1:3	1:3	HCl	
<u>b</u>		1:6,8	1:6	1:6,1	HCl	
<u>c</u>		2,3:1	2:1	2:0,9		HCl
<u>33</u>	MAA	1:1	1:1	1:1,1	b	w

<sup>a</sup>St, styrene; MMA, methylmethacrylate; AA, acrylic acid; MA, methacrylic acid; AAM, acrylamide; AN, acrylonitrile; MVK, methylvinylketone; NVP, *N*-vinylpyrrolidone; VP, 3-vinylpyridine; MAA, maleic acid anhydride.

<sup>b</sup>Calculated from reactivity ratios  $r_1$  ( $r_1 = r_1$  styrene,  $r_2$  taken from literature).

<sup>c</sup>From elemental analysis.

<sup>d</sup>s, soluble; i, insoluble; b, benzene; me, methanol; ac, acetone; pe, petrol ether; w, water; d, dioxane.

Elemental analysis: calc. C 73.55      found 73.53  
                                  H 5.86                      5.97

### Polymerization of 38

1 g 38 was polymerized in 10 mL THF at 70°C with 0.01 g dibenzoylperoxide as initiator for 15 h. The polymer was precipitated several times with methanol and dried under vacuum.

Yield: 0.9 g

Elemental analysis: calc. C 73.55      found 73.43  
                                  H 5.86                      6.06

### Copolymerization of 38 with MMA

Mixtures of MMA (30 g, 0.3 mol) and 38 (9.3 g, 0.03 mol) were polymerized in THF at 70°C with dibenzoylperoxide for 15 h. The copolymers were precipitated with methanol and dried under vacuum.

Yield: 37 g

Elemental analysis: calc. C 63.47      found 63.60  
                                  H 7.44                      7.20

### Test Methods

PIs were tested by Merck Co. using a standard method. Films (50  $\mu\text{m}$ ) on glass plates were prepared using a solution of 2.5% PI in a resin based on epoxacylates (LAROMER EA 81). The glass plates were placed on a conveyor band and the coatings were hardened by two 80 W/cm lamps. The radiation dose is determined by the speed of the conveyor band. The hardness of cured films (DIN 53157) is a measure for photoactivity.

### Analysis

$^1\text{H-NMR}$  spectra were recorded on JEOL JNM-PMX 60 spectrometer using TMS as internal standard. IR spectra were recorded on a NICOLET FT-IR 5 spectrometer.

TABLE 3. Yields and Analysis of Copolymers

Copolymer	Yield (%)	Elemental analysis (%)								
		Calc.			Found					
		C	H	N	O	C	H	N	O	
<u>24a</u>	88	85.82	7.63		6.31	85.61	7.50		6.61	
<u>b</u>	87	88.23	7.71		3.94	88.42	7.63		3.63	
<u>c</u>	79	78.93	7.45		13.32	78.88	7.63		12.93	
<u>25a</u>	85	66.21	7.82		25.72	66.01	8.03		25.32	
<u>b</u>	92	63.85	7.90		29.12	63.77	8.06		27.83	
<u>c</u>	68	72.17	7.93		19.89	72.46	8.10		19.11	
<u>26a</u>	28	62.63	6.78		30.43	62.45	6.47		29.89	
<u>b</u>	29	58.53	6.18		34.98	58.61	6.33		34.71	
<u>c</u>	60	73.53	7.26		19.01	73.53	7.52		18.71	
<u>27a</u>	89	64.36	7.14		31.42	64.11	7.11		31.72	
<u>b</u>	89	61.26	7.14		31.43	60.98	7.19		31.72	
<u>c</u>	61	72.49	7.34		20.16	72.55	7.66		19.79	

<u>28a</u>	84	62.65	7.32	10.61	19.50	62.43	7.44	10.91	19.22
<u>b</u>	91	58.65	7.21	13.63	20.51	58.45	7.36	13.38	20.80
<u>c</u>	70	71.03	8.37	3.07	17.53	71.25	8.26	2.80	17.69
<u>29a</u>	28	70.33	6.31	17.54	5.62	69.94	6.30	17.55	5.90
<u>b</u>	28	75.00	7.26	2.55	15.19	74.68	7.52	2.28	15.52
<u>30a</u>	24	72.62	8.64		18.51	72.94	8.68		17.96
<u>b</u>	29	71.28	8.03		19.93	72.05	8.24		19.27
<u>c</u>	73	74.38	7.64		17.78	74.32	7.75		17.83
<u>31a</u>	29	71.26	7.62	5.16	15.93	70.98	7.76	4.88	16.80
<u>b</u>	28	73.28	7.59	2.85	16.28	73.38	7.55	2.48	16.59
<u>32a</u>	91	79.81	7.10	6.65	6.38	79.63	7.17	6.49	6.58
<u>b</u>	82	78.92	6.89	10.38	3.80	78.75	6.96	10.64	3.35
<u>c</u>	74	76.06	7.43	2.72	13.79	75.79	7.18	2.76	14.27
<u>33</u>	85	65.17	6.50		27.82	64.82	6.67		27.64

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