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PHOTOINITIATORS WITH FUNCTIONAL GROUPS. PART IV. WATER-SOLUBLE PHOTOINITIATORS CONTAINING QUATERNARY AMMONIUM GROUPS

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ABSTRACT

The syntheses and properties of a series of new water-soluble hydroxyalkylphenone-based photoinitiators (PIs) for UV curing of waterborne systems is described. By reaction of tosyl- (**2**), chloro- (**3**), and dimethylamino- (**4**) derivatives of the commercially available PI 2-hydroxy-1-[4-(2-hydroxy-ethoxy)phenyl]-2-methylpropan-1-one (**1**, Darocur 2959) with tertiary amines and halogenides, respectively, PIs containing quaternary ammonium groups exhibiting high water solubility were obtained. Preliminary photocalorimetric tests of the activity demonstrated excellent efficiencies for the PIs in a commercial water-based acrylate formulation, exceeding the photoactivity of the reference PI (**1**) substantially.

INTRODUCTION

With respect to the growing commercial activity in UV-curing of coatings and printing inks, the synthesis of new photoinitiators (PIs) has received increasing interest in recent years [1–5]. In previous articles of this series we reported the preparation and characterization of new polymerizable and polymeric PIs and of PIs containing functional groups capable of reacting with resin components [6, 7].

As a result of the new trend concerning the development of water-borne UV-curable formulations [1, 2], attention has shifted to the synthesis and investigation of water-soluble PIs. Problems such as reduced activity and poor solubility arise with conventional PIs in aqueous systems. Enhancement of the solubility of PIs is generally achieved by substitution of conventional oil-soluble PIs based on benzophenone, benzil, thioxanthone, or hydroxyalkylphenones with ionic groups, such as carboxyl, sulfonic acid, or ammonium groups [8-12].

We recently reported the preparation and characterization of water-soluble PIs synthesized by covalent bonding of carbohydrate residues such as D-glucose, sucrose, maltose, 1-amino-D-sorbitol, and D-gluconic acid-δ-lactone to the commercially available PI 2-hydroxy-1-[4-(2-hydroxy-ethoxy)phenyl]-2-methylpropan-1-one (Darocur 2959) (**1**) [13].

This article is concerned with the synthesis of new water-soluble PIs based on α-hydroxy-alkylphenones by linking ionic groups such as NR_4^+ X^- (X = Cl, H_3C-C_6H_4-SO_3) to **1**. In addition, results of preliminary tests of the photoactivity of the PIs compared to the reference PI (**1**) are presented.

EXPERIMENTAL

The solvents were dried and purified by common methods.

4-Toluene sulfonic acid-2-[4-(2-hydroxy-2-methyl-1-oxopropyl)-phenoxy]-ethyl ester **2** was prepared and purified as described in Ref. 13.

2-Hydroxy-1-[4-(2-chloro-ethoxy)-phenyl]-2-methyl-propan-1-one (3)

20 g (53 mmol) **2**, 8.96 g (212 mmol) LiCl, and 250 mL *t*-butanol were refluxed for 12 hours. The solvent was removed under reduced pressure, and the residue was treated with water and CH_2Cl_2. The organic phase was washed with water several times, dried over anhydrous Na_2SO_4, and the solvent was removed by distillation. The product was dried under vacuum at 40°C.

Yield: 11.8 g **3** (92%), mp 38-40°C. ^{1}H-NMR ($CDCl_3$): δ = 8.5 (d, 2H); 6.92 (d, 2H); 4.26 (t, 2H); 3.82 (t, 2H); 1.55 (s, 6H). Elemental analysis: calculated: C 59.39, H 6.23, Cl 14.61%; found C 60.06, H 6.45, Cl 13.89%.

2-Hydroxy-1-[4-(2-*N,N*-dimethylamino-ethoxy)-phenyl]-2-methyl-propan-1-one (4)

A mixture of 30 g (79.3 mmol) **2**, 23.8 g dimethyl amine (60% in water) (317 mmol), and 50 mL ethanol was refluxed for 4 hours. 150 mL NaOH (30%) was added and the reaction mixture was stirred for 3 hours at 40°C. The phases were separated and ethyl acetate was added to the organic phase. The solution was washed with water three times and the amine **4** was extracted with 2 N HCl. The HCl phases were cooled to 0°C, alkylized by adding 2 N NaOH, and **4** was isolated by repeated extraction with CH_2Cl_2. The extracts were washed with water and dried over anhydrous Na_2SO_4. The solvent was removed by distillation, and the product was dried under vacuum at 40°C.

The hydrochloride **4a** was obtained by dissolving **4** in dry THF, precipitating with gaseous HCl, and drying in vacuo at 40°C.

Yield: 17.3 g **4** (87%), mp 76–79.5°C (mp **4a** 150–163°C). ^{1}H-NMR ($CDCl_3$): δ = 8.05 (d, 2H); 6.9 (d, 2H); 4.5 (s, 1H, OH); 4.05 (t, 2H); 2.7 (t, 2H); 2.23 (s, 6H); 1.55 (s, 6H). Elemental analysis: calculated: C 66.91, H 8.42, N 5.57%; found C 66.74, H 8.19, N 5.56%.

Synthesis of the Quaternary Ammonium Compounds 5–19

Solutions of the starting products were stirred at 25–115°C for 12–96 hours. Molar ratios (amine: RX), solvents, reaction times, temperatures, and yields are summarized in Table 1.

TABLE 1. Experimental Data

PI	Amine	RX	Molar ratio	Solvent	Reaction time, hours	Reaction temperature, °C	Yield, %
5	Pyridine	**2**	10:1	–	15	60	90
6	Triethylamine	**2**	20:1	–	15	90	74
7	*N*,*N*-Dimethyl ethanolamine	**2**	1:1	DMF	36	50	72
8	*N*-Methyl diethanolamine	**2**	1:1	DMF	72	60	79
9	Methacrylic acid-2-dimethylamino-ethyl ester	**2**	1:1	DMF	36	50	41
10	Pyridine	**3**	20:1	–	12	115	86
11	*N*,*N*-Dimethyl ethanolamine	**3**	1:1	DMF	72	60	50
12	**4**	Chloroacetic acid methyl ester	1:4	THF	24	45	94
13	**4**	Benzyl chloride	2:3	THF	18	25	86
14	**4**	Chloromethyl styrene	2:3	THF	40	25	63
15	**4**	Chloroacetic acid	3:1	Absolute DMF	96	40	47
16	**4**	4-Chloromethyl benzoic acid	1:2	Dioxane	70	40	81
17	**4**	Allylchloride	1:5	Dioxane	15	40	86
18	**4**	**2**	1:1	DMF	40	50	87
19	**4**	**3**	1:1	Absolute DMF	36	60	24

The quaternary ammonium compounds **5**–**19** were isolated and purified in the following ways:

5, **12**, **13**, **16**, **17**, and **18** precipitated during the reaction; the white crystals were filtered, and **12**, **13**, and **16** were washed with the solvent, and **5**, **17** and **18** with ethyl acetate. All products were finally washed with diethyl ether and dried under vacuum at 40°C.

6 was obtained by removing excess triethylamine by distillation. The tacky residue was purified and crystallized by treating it several times with THF and diethyl ether.

7 and **9** were isolated by pouring the reaction mixtures into ethyl acetate and diethyl ether, respectively. The milky solutions obtained were allowed to stand for 1–3 hours. The crystallized products were filtered, washed with ethyl acetate and finally with diethyl ether, and dried under vacuum.

Adding ethyl acetate to the reaction mixtures containing **8** and **11** afforded oily precipitates. The solvents were decanted, and the residues were treated with ethyl acetate several times and dried under vacuum. **8** could only be obtained as an oily product, whereas **11**, covered with a layer of ethyl acetate, crystallized within 2 days.

10 was isolated by removing excessive pyridine by distillation, and purified and crystallized by treating the oily residue with CH_2Cl_2.

15 was isolated by diluting the reaction mixture with a small amount of methanol and pouring the solution into diethyl ether. The precipitated product was filtered, treated with dioxane:diethyl ether (1:1) and then with diethyl ether, and finally dried in vacuo.

Treating the reaction mixture containing **19** with ethyl acetate afforded an oily precipitate. **19** was purified by decanting the solvent, dissolving the raw product in a small amount of methanol, and precipitating the product in ethyl acetate.

14, which was obtained as an oily residue during the reaction, was purified in the same way as **19**.

The melting points of the new initiators, the results of elemental analysis (% N, Cl, S), and ^{1}H-NMR data are summarized in Table 2.

Test Methods

The PIs were tested by measuring the maximum heat flow upon irradiation with a high pressure mercury lamp (Heraeus, TQ-150, λ = 200–600 nm, distance from the substrate 15 cm) using a modified DuPont 910 Differential Scanning Calorimeter. Solutions containing 3 wt% PI in a water-based acrylate resin (Merck test mixture ZLI 5252 containing an emulsion of polyester acrylate/50 wt% water) were prepared. Samples of 30 mg were dried for 5 minutes at 100°C, and UV-curing was started after 10 minutes. The time to reach the maximum heat flow—corresponding to the maximum rate of polymerization—was detected and compared with **1** as the standard PI. The percentage differences of reaction times were calculated. The results of the photocalorimetric measurements and the water solubilities of the PIs are summarized in Table 3.

TABLE 2. Analytical Data

		%N		%Cl		%S		
PI	mp, °C	Calc.	Found	Calc.	Found	Calc.	Found	^{1}H-NMR (DMSO), δ (ppm)
5	156–159	3.06	2.97	–		7.01	7.03	9.2 (d, 2H); 8.7 (t, 1H); 8.2 (d, 4H); 7.55 (d, 2H); 7.15 (d, 2H); 7.0 (d, 2H); 5.75 (s, 1H); 5.15 (t, 2H); 4.65 (t, 2H); 2.3 (s, 3H); 1.4 (s, 6H)
6[a]	80–97	2.92	2.77	–		5.99	6.06	8.25 (d, 2H); 7.5 (d, 2H); 7.0–7.25 (2d, 4H); 5.7 (s, 1H); 4.45 (t, 2H); 3.7 (t, 2H); 3.4 (q, 6H); 2.3 (s, 3H); 1.4 (s, 6H); 1.2 (t, 9H)
7	91–95	3.00	2.80	–		6.86	6.91	8.25 (d, 2H); 7.5 (d, 2H); 7.0–7.25 (2d, 4H); 4.6 (t, 2H); 3.8–4.05 (m, 4H); 3.6 (t, 2H); 3.25 (s, 6H); 2.35 (s, 3H); 1.45 (s, 6H)
8	Oil	2.81	2.63	–		6.44	6.39	8.25 (d, 2H); 7.55 (d, 2H); 7.0–7.25 (2d, 4H); 5.7 (s, 1H); 5.3–5.55 (s, 2H); 4.55 (t, 2H); 3.85–4.05 (m, 6H); 3.65 (t, 4H); 3.25 (s, 3H); 2.35 (s, 3H); 1.4 (s, 6H)
9	110–115	2.61	2.44	–		5.99	6.06	[D_2O] 8.15 (d, 2H); 7.7 (d, 2H); 7.35 (d, 2H); 7.05 (d, 2H) 6.2 (s, 1H); 5.8 (s, 1H); 4.6–4.8 (m, 4H); 3.95 (t, 4H); 3.35 (s, 6H); 2.4 (s, 3H); 1.95 (s, 3H); 1.55 (s, 6H)
10	176–180	4.41	4.23	11.16	11.38	–		[D_2O] 8.95 (d, 2H); 8.52 (t, 1H); 8.05 (t, 2H); 7.88 (d, 2H); 6.88 (d, 2H); 5.02 (t, 2H); 4.55 (t, 2H); 1.45 (s, 6H)
11[a]	30–65	4.22	4.06	10.68	10.25	–		8.25 (d, 2H); 7.15 (d, 2H); 5.85 (s, 1H); 5.72 (s, 1H); 4.6 (t, 2H); 3.8–4.1 (m, 4H); 3.65 (t, 2H); 3.35 (s, 6H); 2.45 (s, 6H)
12	156–160	3.89	3.74	9.85	9.82	–		8.22 (d, 2H); 7.0 (d, 2H); 5.85 (s, 1H); 4.75 (s, 2H); 4.5–4.7 (s, 2H); 4.05–4.25 (s, 2H); 3.75 (s, 3H); 3.4 (s, 6H); 1.4 (s, 6H)

(continued)

TABLE 2. Continued

PI	mp, °C	%N		%Cl		%S		^{1}H-NMR (DMSO), δ (ppm)
		Calc.	Found	Calc.	Found	Calc.	Found	
13	132–137	3.71	3.39	9.38	9.26		—	8.25 (d, 2H); 7.45–7.75 (m, 5H); 7.1 (d, 2H); 5.8 (s, 1H); 4.82 (s, 2H); 4.68 (s, 2H); 3.88 (s, 2H); 3.1 (s, 6H); 1.4 (s, 6H)
14	118–123	3.47	3.18	8.78	8.72		—	8.25 (d, 2H); 7.4–7.85 (m, 4H); 7.1 (d, 2H); 6.65–6.95 (m, 1H); 5.85–6.05 (m, 1H); 5.8 (s, 1H); 5.35 (d, 1H); 4.8 (s, 2H); 4.65 (s, 2H); 3.9 (s, 2H); 3.1 (s, 6H); 1.4 (s, 6H)
15[b]	112–130	4.20	4.31	7.08	6.90		—	8.2 (d, 2H); 7.05 (d, 2H); 4.5 (d, 2H); 4.05 (d, 2H); 3.58 (s, 2H); 3.3 (s, 3H); 2.85 (s, 3H); 1.45 (s, 6H)
16[c]	126–150	3.67	2.99	7.15	7.05		—	8.25 (d, 2H); 8.05 (d, 2H); 7.75 (d, 2H); 7.1 (d, 2H); 4.9 (s, 2H); 4.7 (s, 2H); 3.98 (s, 2H); 3.15 (s, 6H); 1.45 (s, 6H)
17	147–151	4.27	4.27	10.81	10.79		—	8.25 (d, 2H); 7.15 (d, 2H); 6.0–6.25 (m, 1H); 5.6–5.85 (m, 2H); 4.65 (t, 2H); 4.25 (d, 2H); 3.9 (t, 2H); 3.25 (s, 6H); 1.4 (s, 6H)
18	198–203	2.22	2.13		—	5.09	5.15	8.25 (d, 4H); 7.5 (d, 2H); 7.0–7.2 (m, 6H); 5.75 (s, 2H); 4.6 (s, 4H); 4.0 (s, 4H); 3.3 (s, 6H); 2.25 (s, 3H); 1.45 (s, 12H)
19	168–173	2.84	2.56	7.18	6.82		—	8.25 (d, 4H); 7.1 (d, 4H); 5.75 (s, 2H); 4.63 (s, 4H); 4.0 (s, 4H); 3.3 (s, 6H); 1.4 (s, 6H)

[a] Waxy, extremely hygroscopic.

[b] Mixture of **15** and 50% betaine, **15a**.

[c] Mixture of **16** and 30% betaine, **16a**.

TABLE 3. Properties of the PIs

PI	Molecular weight	Solubility in water, g/100 mL	$t_{\max}$,[a] S	Δt,[b] %
1	224.26	0.17	34	
			28.6[c]	
4a	287.79	56	26.6	+21.8
5	457.55	16	28.7	+15.6
6	479.64	72	27.4	+19.4
7	467.59	>60	29.5	+13.2
8	497.61	>100	32.7	+3.8
9	535.66	>20	37.5	−10.3
			25.2[c]	+11.9
10	312.8	>80	32.5	+4.4
11	331.84	>80	27.7	+18.5
12	359.8	76	31.3	+7.9
13	377.91	53	35	−2.9
14	403.95	>40	34.6	−1.8
			28.2[c]	+1.4
15	345.8	34	25.6	+24.7
16	389.93	58	32.5	+4.4
17	327.85	57	29.2	+14.1
18	629.77	<0.1	62.1	−82.6
19	494.03	0.15	36.2	−6.5

[a] $t_{\max}$ = time to reach the maximum heat flow.

[b] $\Delta t = (t_{\max}(\mathbf{1}) - t_{\max})100/t_{\max}$.

[c] Times reached without predrying.

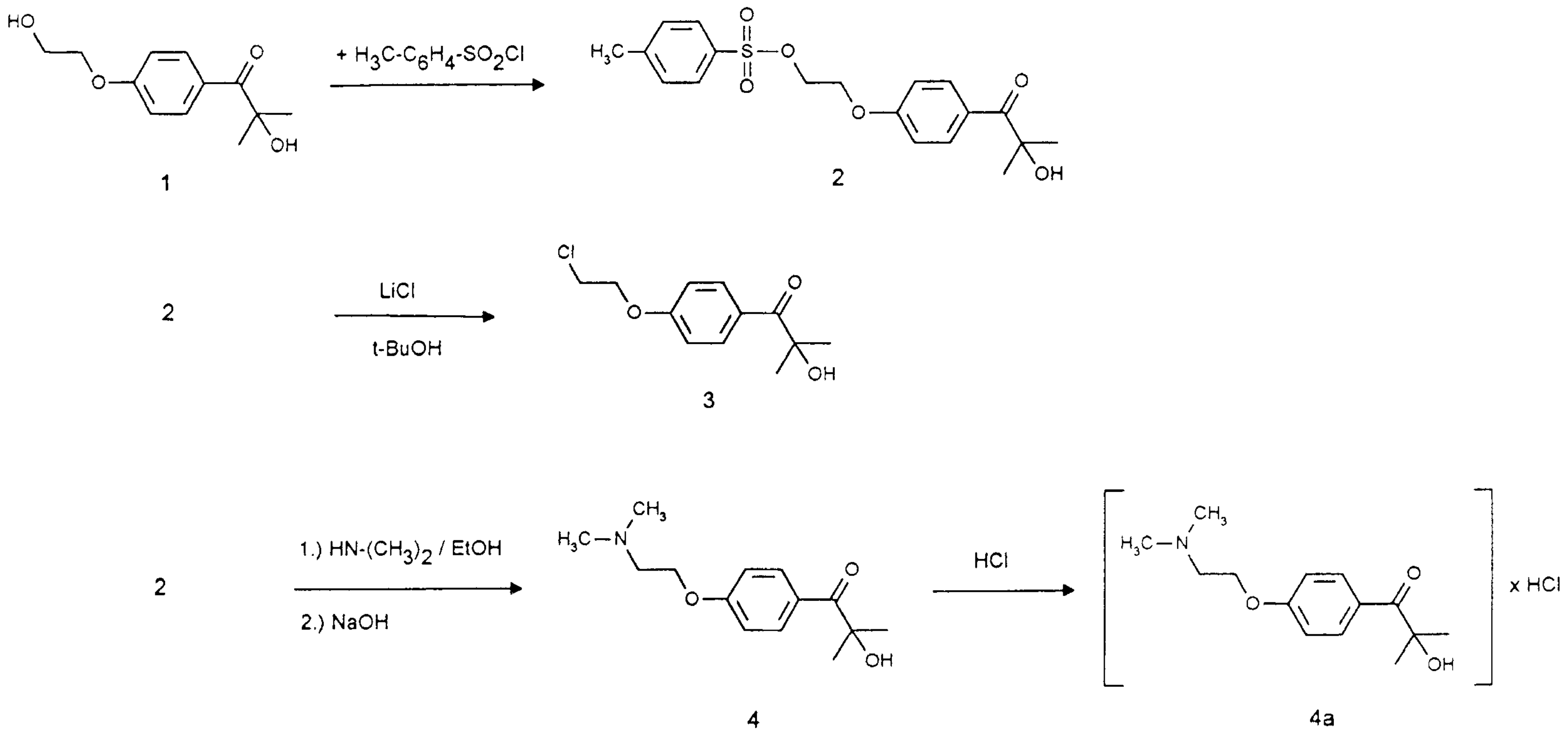
Analysis

^{1}H-NMR spectra were recorded on a Bruker AC-E-200 FT-NMR spectrometer.

RESULTS AND DISCUSSION

The water-soluble PIs were synthesized from the functional PI derivatives **2**, **3**, and **4**, based on the commercially available PI 2-hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methyl-propan-1-one (**1**, Darocur 2959).

The toluene sulfonic acid ester **2** was prepared by the reaction of **1** with 4-toluene sulfonylchloride as described recently [13] (Scheme 1). The chloride **3** was obtained from **2** and lithium chloride in 92% yield, whereas attempts to react **1** with thionyl chloride were not successful. The chloride **3** has already been claimed in a patent, but no experimental and analytical data are available [14]. The dimethylamino derivative **4** was obtained in 87% yield by reaction of **2** with dimethyl amine. By


+ H_3C-C_6H_4-SO_2Cl
1
2
LiCl
t-BuOH
3
1.) HN-$(CH_3)_2$ / EtOH
2.) NaOH
4
HCl
x HCl
4a

SCHEME 1.

conversion of **4** to the hydrochloride **4a**, a PI with excellent solubility in water was obtained.

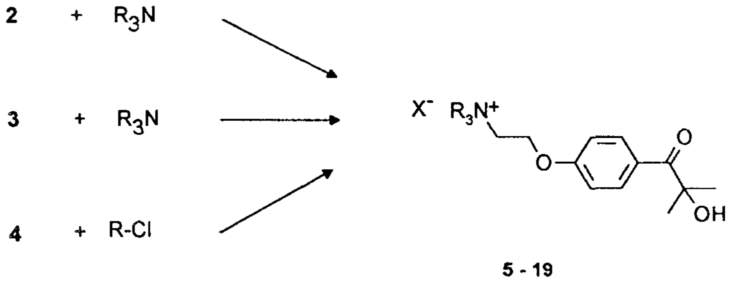
PIs containing quarternary ammonium groups were prepared by reaction of **2** and **3** with various tertiary amines as well as by reaction of **4** with alkyl chlorides (Scheme 2). The structures of the PIs are summarized in Table 4.

The pyridinium compound **5** and the triethylammonium salt **6** were obtained in 90 and 74% yield by reaction of **2** with excess pyridine and triethylamine, respectively. Reaction of *N*,*N*-dimethyl ethanolamine, *N*-methyl diethanol amine and methacrylic acid-2-dimethylamino-ethyl ester with **2** (molar ratio 1:1, solvent DMF) yielded 72% **7**, 79% **8**, and 41% **9**.

In accordance with the known low reactivity of β-halogenated ethers [15], **3** was found to be much less reactive toward tertiary amines than **2**. Attempts to react **3** with triethylamine, *N*-methyl diethanol amine and methacrylic acid-2-dimethylamino-ethyl ester afforded oily, impure products in low yields. Only the reactions of **3** with pyridine and *N*,*N*-dimethyl ethanolamine were successful. The pyridinium compound **10** was obtained in 86% yield, using an excess of pyridine. Reaction of *N*,*N*-dimethyl ethanolamine with **3** (molar ratio: 1:1, solvent DMF) yielded 50% **11**.

Quaternization of **4** with alkyl chlorides yielded the new initiators **12–19**. By reaction of **4** with chloroacetic acid methyl ester and benzyl chloride, the quaternary ammonium compounds **12** and **13** were obtained in high yields (94 and 86%, respectively). The polymerizable initiator **14** was synthesized in 63% yield by reaction of **4** with chloromethyl styrene. Attempts to improve the yield by variation of the reaction conditions yielded mixtures of **14** and polymers with poor solubility in water.

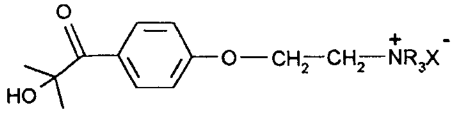
Reaction of **4** with chloroacetic acid afforded a mixture of the quaternary ammonium compound **15** and the corresponding betaine **15a** (Scheme 3). Treatment of the mixture with hydrochloric acid to convert **15a** to the hydrochloride **15** resulted in elimination of the tertiary hydroxy group of the photoinitiator. Therefore the mixture of **15** and **15a** – containing about 50% **15a** – was used for photocalorimetric tests. Similar results were obtained with 4-chloromethyl benzoic acid as with alkyl chloride, affording a mixture of the quaternary ammonium compound **16** and about 30% of the corresponding betaine **16a**. The allyl ammonium chloride was obtained in 86% yield from **4** and allyl chloride. Reaction of **4** with **2** and **3** (molar ratio 1:1, solvent DMF) yielded the bifunctional initiators **18** and **19** (yields 87 and 24%, respectively).

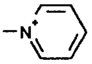
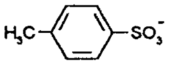
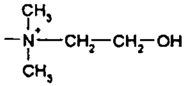
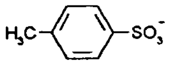
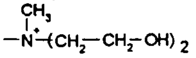
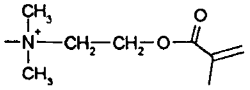
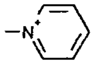
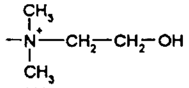
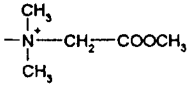
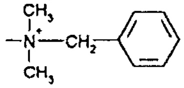
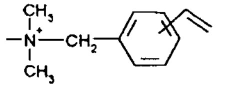
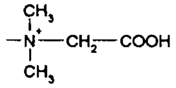
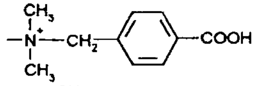
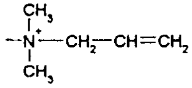
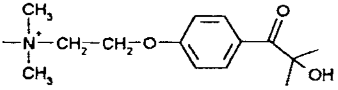
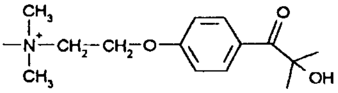


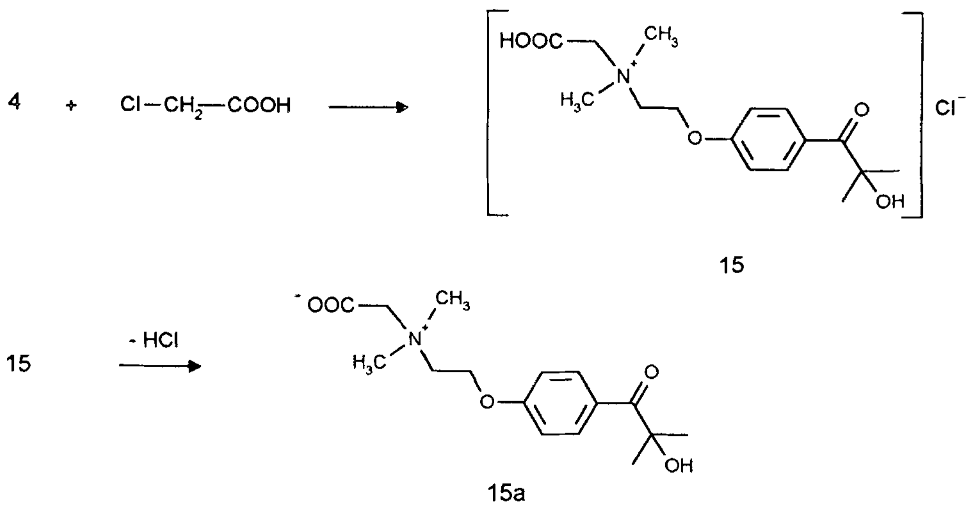
SCHEME 2.

TABLE 4. Structures of the Photoinitiators **5–19**

General Formula:



PI	NR_3^+	X^-
5		
6	$-N^+(CH_2-CH_3)_3$	
7	 $-\overset{CH_3}{\underset{CH_3}{N^+}}-CH_2-CH_2-OH$	
8	 $-\overset{CH_3}{N^+}(CH_2-CH_2-OH)_2$	
9		
10		Cl^-
11	 $-\overset{CH_3}{\underset{CH_3}{N^+}}-CH_2-CH_2-OH$	Cl^-
12	 $-\overset{CH_3}{\underset{CH_3}{N^+}}-CH_2-COOCH_3$	Cl^-
13		Cl^-
14		Cl^-
15	 $-\overset{CH_3}{\underset{CH_3}{N^+}}-CH_2-COOH$	Cl^-
16		Cl^-
17	 $-\overset{CH_3}{\underset{CH_3}{N^+}}-CH_2-CH=CH_2$	Cl^-
18		
19		Cl^-



SCHEME 3.

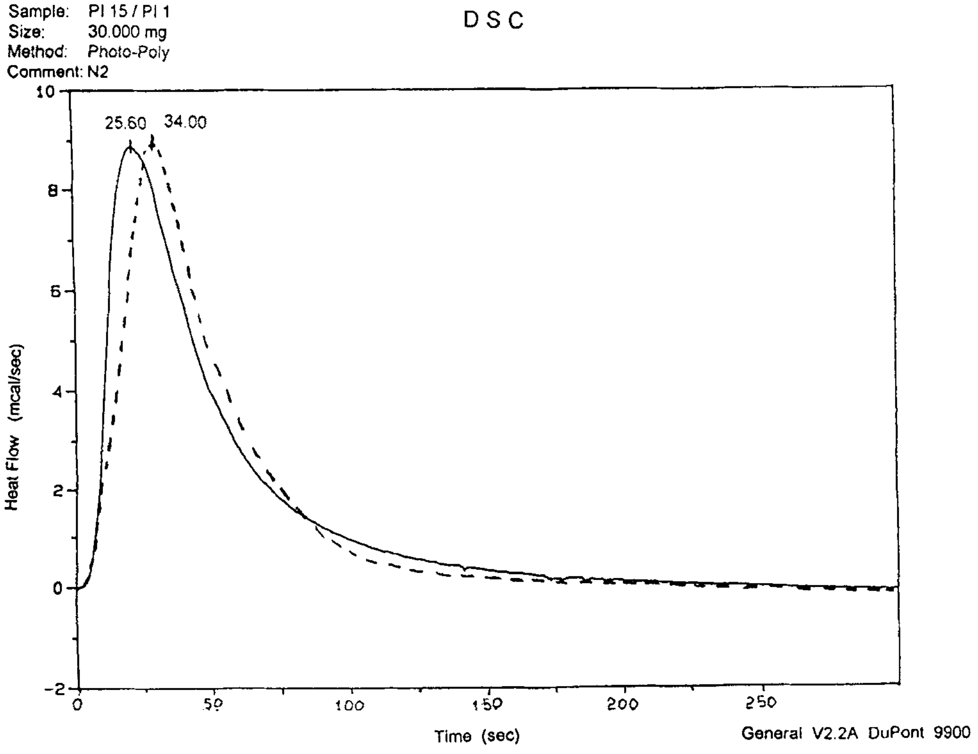


FIGURE 1. Photo-DSC of formulations containing **15** (——) and **1** (---).

Properties of the PIs

As expected, all PIs except **18** and **19** generally exhibit substantially higher solubility in water than the standard PI **1** (Table 3).

The photoinitiating activity of the new PIs was studied comparatively with Darocur 2959 (**1**) as the reference PI using a modified differential scanning calorimeter [16, 17]. The PIs were dissolved in an commercial test mixture consisting of a 50% aqueous emulsion based on polyester acrylate. After drying the mixtures for 5 minutes at 100°C, they were exposed to UV-irradiation under standard conditions. As usual in industrial applications, equal concentrations of 3 wt% PI were used without consideration of the nonphotoactive residue. The curing efficiency was evaluated by detecting the time (t_{max}) to reach the maximum heat flow, which corresponds to the maximum rate of polymerization. The time t_{max} was related to **1** as the reference PI, and the percentage difference was calculated.

For example, the photo-DSC traces of formulations containing **1** and **15** are shown in Fig. 1. The tests demonstrated that with the exception of **9**, **13**, and **14**, all of the new PIs with a water solubility higher than **1** exhibit even higher photoactivity than the standard PI **1**, although equal weight concentrations were used without considering the nonphotoactive residue (Table 4). The polymerizable initiators **9** and **14** were found to have a higher photoactivity than **1** when tested without drying. In dried samples the activity decreased due to the lower water solubility of polymers formed during the drying process. The low photoactivity of **18** and **19** could also be explained by the poor water solubility. The best results were obtained with **4a**, **5**, **6**, **11**, **15**, and **17** (a 14 to 25% acceleration compared to **1**).

More detailed investigations concerning the properties of the PIs, such as the range of overall percent conversion of the acrylate groups and the photoinitiating activity in various water-borne systems, will be discussed in a future article.

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