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Photoacid generators (PAGs) based on *N*-acyl-*N*-phenylhydroxylamines for carboxylic and sulfonic acids

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ABSTRACT

Simple and efficient photoacid generators (PAGs) for carboxylic and sulfonic acids based on *N*-acyl-*N*-phenylhydroxylamines have been demonstrated. Irradiation of *o*-carboxylates and thermally rearranged *o*-arenesulfonates of *N*-acyl-*N*-phenylhydroxylamines using UV light (≥254 nm) in aqueous methanolic solution resulted in efficient generation of carboxylic and sulfonic acids, respectively. The carboxylic acid generation ability of *N*-acyl-*N*-phenylhydroxylamines was found to be dependent on their *N*-acyl substituents. Further, polymer bearing *o*-arenesulfonates of *N*-acyl-*N*-phenylhydroxylamine was synthesized and demonstrated as PAG for sulfonic acids.

1. Introduction

The growing demand to generate photoresist materials with high resolution[1] and high sensitivity[2] for lithography have sparkled the interest in photoacid generators (PAGs).[3,4] PAGs can be classified into two group's namely ionic and non-ionic type.[5] Non-ionic PAGs have gained much attention over ionic type due to its wide range of solubility in organic solvents and in polymer films.[6] A variety of non-ionic PAGs have been reported for the generation of sulfonic acids,[7,8] carboxylic acids,[9] phosphoric acids[10] and hydrogen halides.[11,12]

In the past years, significant progress has been made in the field of photoinduced cleavage of N–O bond due to its potential applications in the areas like radical generation,[13] protecting groups for biological molecules,[14] photopolymerisation[15] and also for the synthesis of several biologically important heterocyclic compounds.[16] In recent times, homolytic cleavage of the weak N–O bond by direct or sensitized photolysis shows growing interest in the area of PAGs. So far, only certain sulfonate esters derived from *N*-hydroxyamides,[17] *N*-hydroxyimides[3] and few imino sulfonates[18] were reported to generate sulfonic acids on photolysis via homolytic N–O bond cleavage. Hence, in search of simple organic molecules, which can act as efficient PAGs for both carboxylic and sulfonic acids by photoinduced homolytic N–O bond cleavage led us to explore *N*,*O*-diacyl-*N*-phenylhydroxylamines.

Considerable research has been undertaken to understand the mechanistic mode of N–O bond cleavage of *N*,*O*-diacyl-*N*-phenylhydroxylamines in connection to its photoaroyloxy rearrangement.[19] Sakurai and his co-workers[19] showed that direct photolysis of *N*,*O*-diacyl-*N*-phenylhydroxylamines undergoes efficient homolytic N–O bond cleavage from its singlet excited state to form 1,3 and 1,5 aroyloxy rearranged products via 'in-cage' reaction of aroyloxyl and amido radicals, along with fragmentation products, such as arenecarboxanilide, carboxylic acid and hydrocarbons through 'cage-escape' reaction of the above said radicals. Interestingly, the same group further showed that photolysis of *N*,*O*-diacyl-*N*-phenylhydroxylamines in hydrogen donor solvents produced largely fragmentation products (carboxylic acid and carboxanilide) via efficient hydrogen atom abstractions by aroyloxyl and amido radicals from the solvent by cage escape mechanism.[19,20] Considering the above result to produce carboxylic acids as a major product in hydrogen donor solvents, together with our recent research interest on exploring the applications of homolytic N–O bond cleavage of *N*,*O*-diacyl-*N*-phenylhydroxylamines,[21] made us to investigate *N*,*O*-diacyl-*N*-phenylhydroxylamines as PAGs.

Herein, we report *o*-carboxylates and thermally rearranged *o*-arenesulfonates of *N*-acyl-*N*-phenylhydroxylamines as simple and efficient PAGs for carboxylic and sulfonic acids, respectively. The synthesis and the characterization of the PAGs were discussed. The generation of carboxylic and sulfonic acids was achieved by irradiating their corresponding PAGs using UV light (≥254 nm). The

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effect of different *N*-acyl substituents on the acid generation ability of the PAGs was investigated. Further, we also synthesized polymers bearing *o*-arenesulfonyloxyanilide and showed that irradiation of these polymers in thin films resulted in the generation of sulfonic acids.

2. Results and discussion

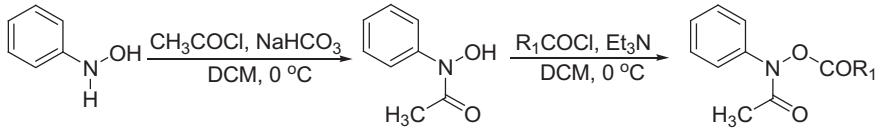
2.1. Carboxylates of *N*-acyl-*N*-phenylhydroxylamines as PAGs for carboxylic acids

*2.1.1. Synthesis of carboxylates of N-acetyl-N-phenylhydroxylamine (**3a**–**h**).* We have synthesized carboxylate esters of *N*-acetyl-*N*-phenylhydroxylamine (**3a**–**h**) as outlined in Scheme 1. The carboxylates were synthesized, initially by carrying out N-acetylation of *N*-phenylhydroxylamine (**1**) with acetyl chloride in presence of $NaHCO_3$ in dry DCM at 0 °C to yield *N*-acetyl-*N*-phenylhydroxylamine (**2**).[22] Treatment of **2** with various acid chlorides in presence of triethylamine in dry DCM resulted in quantative yield of carboxylates of *N*-acetyl-*N*-phenylhydroxylamine (**3a**–**h**, Table 2). All the carboxylates were characterized by ^1H, ^{13}C NMR, IR and mass spectral analysis.

Table 2
Synthetic yield, UV/vis and photolysis data of the carboxylate esters of *N*-acetyl-*N*-phenylhydroxylamine (**3a**–**h**)

Entry	Carboxylate	Synthetic yield[a] (%)	UV/vis		Photogeneration of carboxylic acids		
			λ (nm)[b]	log ε[c]	Time (min.)[d]	Yield[e] (RCO_2H)	Quantum yield (φ)[f]
1	**3a**[g]	90	230	4.17	60	91	0.042
2	**3b**	91	277	4.31	90	90	0.028
3	**3c**[g]	90	246	4.27	120	95	0.022
4	**3d**[g]	92	243	4.29	100	95	0.026
5	**3e**[g]	90	261	4.24	50	93	0.051
6	**3f**	95	298	4.57	30	95	0.088
7	**3g**[g]	90	243	4.20	110	92	0.023
8	**3h**[g]	93	246	4.22	140	85	0.017

[a] Based on isolated yield.
[b] Maximum absorption wavelength.
[c] Molar absorption coefficient.
[d] Time for photolysis.
[e] Photolysis yield based on HPLC.
[f] Quantum yield for the generation of various carboxylic acids at room temperature (error limit within ±5%).
[g] Carboxylates for which the photoproducts were isolated and compared with authentic samples.



1 **2** **3a-h**

R_1 = $CH_2C_6H_5$ (**3a**), $C_2H_2C_6H_5$ (**3b**), C_6H_5 (**3c**), *p*-MeC_6H_4 (**3d**), *p*-$MeOC_6H_4$ (**3e**), *p*-EtO(*m*-MeO)C_6H_3 (**3f**), *p*-ClC_6H_4 (**3g**), *p*-$NO_2C_6H_4$ (**3h**).

Scheme 1. Synthesis of carboxylate esters of *N*-acetyl-*N*-phenylhydroxylamine.

2.2. Photolysis of carboxylate esters of *N*-acetyl-*N*-phenylhydroxylamine (3a–h) to form carboxylic acids

Initially, we investigated the photolysis of carboxylate (**3c**) in methanolic solution using a 125-W medium pressure Hg lamp with quartz sleeve and we found homolytic N–O bond cleavage occurred to produce benzoic acid and acetanilide in good yields. This observation encouraged us to find the best solvent system for the efficient generation of carboxylic acids in high yield. We carried out the photolysis of **3c** (0.05 mM) in various solvents including methanol (MeOH), acetonitrile (ACN), tetrahydrofuran (THF), MeOH/H_2O (9:1) and ACN/H_2O (9:1) for 2 h and the results are tabulated in Table 1.

Table 1
Photolysis of carboxylate (**3c**) in various solvents

Entry	Solvent system	% of Acid generated[a]	Quantum yield (φ)[b]
1	MeOH	80	0.019
2	ACN	70	0.016
3	THF	75	0.017
4	ACN/H_2O (9:1)	75	0.017
5	MeOH/H_2O (9:1)	95	0.022

[a] Photolysis yield based on HPLC.
[b] Quantum yield for the generation of benzoic acid at room temperature (error limit within ±5%).

Among the above solvents, we found carboxylate (**3c**) generated benzoic acid in relatively high quantum yield and chemical yield in MeOH/H_2O (9:1) compared to other solvents used for the study.

Hence, we irradiated the carboxylate esters of *N*-acetyl-*N*-phenylhydroxylamine (**3a**–**h**) in MeOH/H_2O (9:1) solution and we found the corresponding carboxylic acids to be generated in nearly quantative yield as summarized in Table 2. In each case the photolysis was stopped when conversion reached at least 95% (as indicated by HPLC). For the carboxylates indicated in Table 2, their photoproducts (carboxylic acid and acetanilide) were isolated and characterized by ^1H NMR spectra with corresponding authentic samples. Quantum yield for the generation of various carboxylic acids were found to be in the range of 0.017–0.088 using valerophenone as an actinometer.[23]

As a representative example, we have shown in Fig. 1a HPLC analysis of photolyzed **3d**. The HPLC data clearly shows the depletion of the peak at t_R 17.48 min with increase in irradiation time, indicating the photodecomposition of the carboxylate (**3d**). On the other hand, we noticed gradual increase of two new major peaks at t_R 5.76 min and t_R 10.03 min corresponding to the photoproducts *p*-toluic acid and acetanilide, respectively.

In order to compare the efficiency of photorelease from various solutions of carboxylates, The compound **3a**, **3c**, **3e**, and **3h** (0.05 mM) in MeOH/H_2O (9:1) were irradiated using light above 254 nm and the course of the reaction was monitored by HPLC at regular interval of time. The Fig. 1b shows appearance of the carboxylic acids with respect to irradiation time. We notice that these carboxylates generates the corresponding carboxylic acids (≥85%) within 140 min of irradiation. In particular, aromatic carboxylic acids with electron donating substituent were generated more efficiently compared to aromatic carboxylic acids with electron withdrawing substituent (for example, *p*-methoxy benzoic acid was formed almost three times more efficiently compared to *p*-nitro benzoic acid).

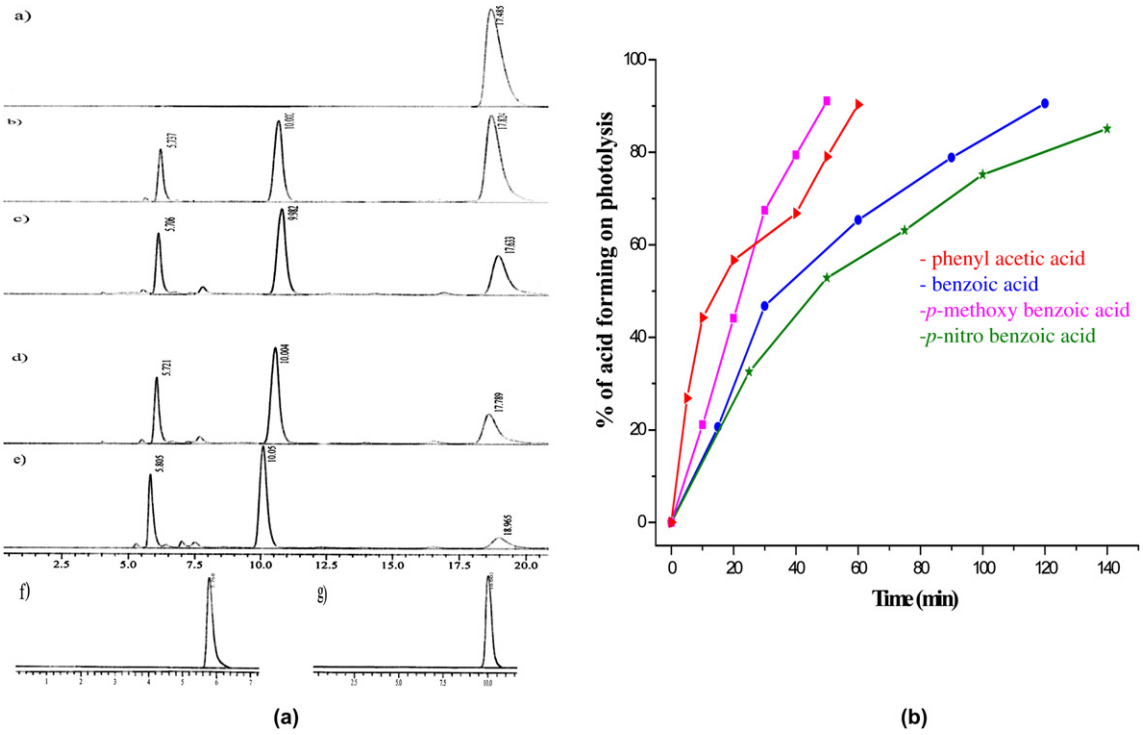


Fig. 1. a. HPLC data of photolysis of ester **3d** at regular interval of time: (a) 0 min (b) 25 min (c) 50 min (d) 75 min (e) 100 min (f) std *p*-toluic acid (g) std acetanilide. b. Comparison of efficiency for photoinduced formation of various carboxylic acids from respective carboxylates (**3a**, **3c**, **3e** and **3h**) at regular interval of photo irradiation.

2.3. Mechanism for the photogeneration of carboxylic acids

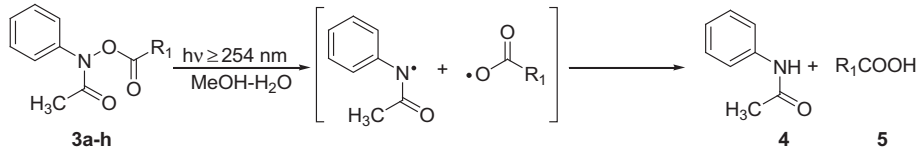
Based on the literature precedence,[24] mechanism for the photogeneration of carboxylic acid is outlined in Scheme 2. After initial excitation of the carboxylate to its singlet excited state, it undergoes homolytic N–O bond cleavage to generate carboxyl and acetanilide radical pair. The above generated radical pair, escapes from the cage and subsequently abstracts hydrogen from the solvent to produce the corresponding carboxylic acid (**5**) and acetanilide (**4**).

2.4. Effect of *N*-acyl substituents on the acid generation ability of PAGs

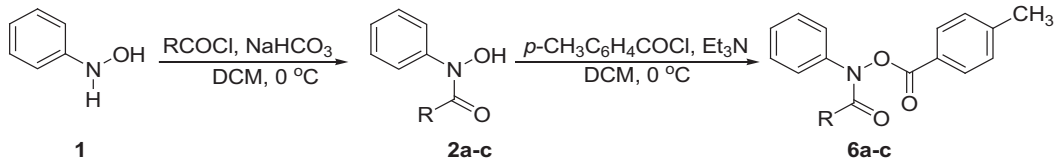
To investigate the effect of different *N*-acyl substituents on the acid generation ability of PAGs, we synthesized PAGs based on *p*-toluic esters of *N*-acyl-*N*-phenylhydroxylamines (**4a**–**c**) as described in Scheme 3.

In order to compare the efficiency of photogeneration of *p*-toluic acid by different *N*-acyl substituent PAGs, 0.05 mM solution of PAGs (**3d**, **6a**–**c**) in MeOH/H_2O (9:1) were irradiated using light source of ≥254 nm for 50 min and the photolysis was monitored by HPLC at regular interval of time. Based on HPLC data for each PAGs, the natural logarithm of the concentration of *p*-toluic acid generated (lnC) versus irradiated time was plotted. We observed a linear correlation for the generation of *p*-toluic acid, which suggested a first order reaction, obtained by linear least square methodology for a straight line (Fig. 2).

The quantum yield (ϕ) for the generation of *p*-toluic acid by PAGs (Table 3), indicate that *N*-acyl substituents have pronounced effect on the acid generation ability of PAGs. We noticed that with



Scheme 2. Mechanism for the photogeneration of carboxylic acids.



R = C_6H_5 (**6a**), *p*-$MeOC_6H_4$ (**6b**), *p*-$NO_2C_6H_4$ (**6c**).

Scheme 3. Synthesis of *p*-toluic esters of *N*-acyl-*N*-phenylhydroxylamines (**6a**–**c**).

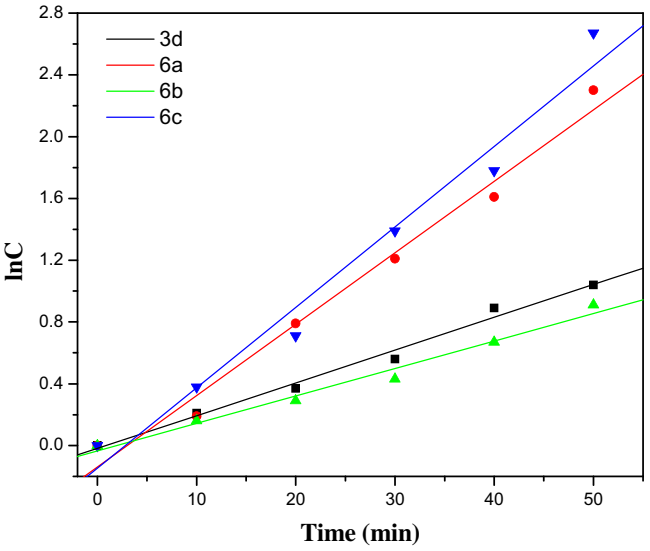


Fig. 2. Concentration of *p*-toluic acid (lnC) versus irradiation time for the PAGs (**3d**, **6a**–**c**).

Table 3
Synthetic yield, UV/vis and photolysis data of PAGs (**3d**, **6a**–**c**)

PAGs	Synthetic yield[a] (%)	UV/vis		Photogeneration of *p*-toluic acid	
		λ (nm)[b]	log ε[c]	Yield[d] (R_1CO_2H)	Quantum yield (ϕ)[e]
3d	92	243	4.29	65	0.036
6a	85	245	4.54	90	0.050
6b	91	242	4.55	60	0.039
6c	90	245	4.62	95	0.053

[a] Based on isolated yield.
[b] Maximum absorption wavelength.
[c] Molar absorption coefficient.
[d] Photolysis yield based on HPLC.
[e] Quantum yield for the generation of *p*-toluic acid at room temperature (error limit within ±5%).

increased electron withdrawing group on the *N*-acyl substituents of PAGs, quantum yield (ϕ) for the generation of *p*-toluic acid increases. Since, stronger electron withdrawing acyl substituent stabilizes generated acyl aminyl radicals.[25–27]

3. *N*-Acyl-*N*-phenylhydroxylamines as PAGs for sulfonic acids

The photoinduced generation of strong acids, such as sulfonic acids is essentially important since they afford high sensitivity resists.[28] Hence we investigated the application of *N*-acyl-*N*-phenylhydroxylamines as PAGs for sulfonic acids.

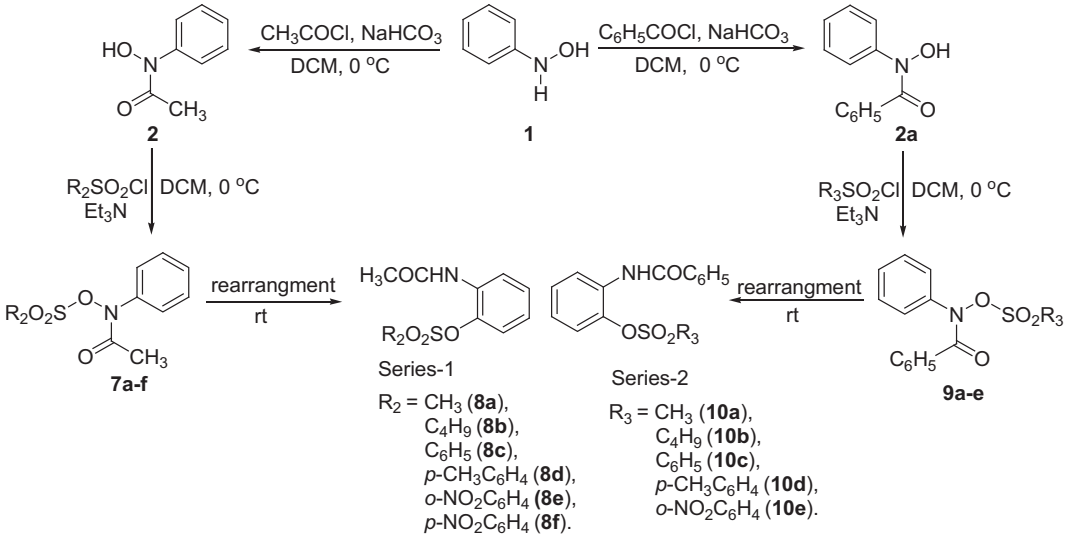
3.1. Synthesis of *o*-arenesulfonyloxyacetanilide (8a–f) and *o*-arenesulfonyloxybenzanilide (10a–e)

We synthesized two series of *o*-arenesulfonyloxyanilide as outlined in Scheme 4. The *series*-1 consists of *o*-arenesulfonyloxyacetanilides and the *series*-2 has *o*-arenesulfonyloxybenzanilides. The sulfonates of *series*-1 were synthesized by carrying out N-acetylation of *N*-phenylhydroxylamine (**1**) to yield *N*-acetyl-*N*-phenylhydroxylamine (**2**). However, treatment of **2** with various sulfonyl chlorides in presence of Et_3N in dry DCM at 0 °C resulted in thermally unstable *N*-sulfonyl-*N*-acetyl-*N*-phenylhydroxylamines (**7a**–**f**), which then efficiently rearranged to form *o*-arenesulfonates of *N*-acetyl-*N*-phenylhydroxylamine in excellent yields[29] (Table 4, **8a**–**f**). Similarly in the case of *series*-2, *N*-phenylhydroxylamine (**1**) was benzoylated and then treated with various sulfonyl chlorides to yield rearranged *o*-arenesulfonyloxybenzanilide (Table 4, **10a**–**e**).

3.2. Irradiation of *o*-arenesulfonyloxyacetanilides (8a–f) and *o*-arenesulfonyloxybenzanilides (10a–e) for the generation of sulfonic acids

Irradiation of the methanolic solution of sulfonates (**8a**–**f**, **10a**–**e**) using the similar procedure as described for the generation of carboxylic acids (Section 2.2), resulted in efficient S–O bond cleavage to generate their corresponding sulfonic acids in high yield (Scheme 5, Table 4). The photolysis was monitored using ^{1}H NMR spectroscopy and the reaction was stopped when the conversion reached about 95%. In all the cases, sulfonic acid was isolated as the only significant photoproduct along with *o*-hydroxyacetanilide or *o*-hydroxybenzanilide (**11**). As anticipated, the *o*-arenesulfonyloxybenzanilide (**10a**–**e**, Table 4, entries 7–11) generated sulfonic acids more efficiently with higher quantum yield compared to *o*-arenesulfonyloxyacetanilide (**8a**–**f**, Table 4, entries 1–6).

As a representative example, we have shown in Fig. 3a the ^{1}H NMR spectra of sulfonate (**10d**) at regular interval of irradiation. From the ^{1}H NMR spectra we observed signal at 2.38 ppm corresponding to the methyl group of sulfonate decreases with

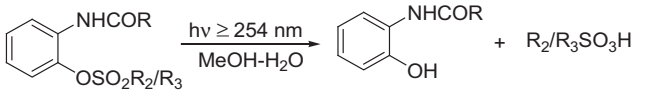


Scheme 4. Synthesis of *o*-arenesulfonyloxyacetanilides (**8a**–**f**) and *o*-arenesulfonyloxybenzanilides (**10a**–**e**).

Table 4
Synthetic yield, UV/vis and photolysis data of the *o*-arenesulfonyloxyacetanilide (**8a**–**f**) and o-arenesulfonyloxybenzanilide (**10a**–**e**)

Entry	Sulfonate	Synthetic yield[a] (%)	UV/vis		Photogeneration of sulfonic acids		
			λ (nm)[b]	log ε[c]	Time (min.)[d]	Yield[e] (RSO_3H)	Quantum yield (ϕ)[f]
1	**8a**	83	236	4.05	45	95	0.058
2	**8b**	80	237	4.12	60	85	0.039
3	**8c**	91	246	4.08	90	90	0.027
4	**8d**	90	227	4.47	50	93	0.051
5	**8e**	85	240	4.21	75	90	0.033
6	**8f**	90	241	4.38	100	90	0.025
7	**10a**	85	249	4.05	35	95	0.075
8	**10b**	80	245	4.12	45	92	0.057
9	**10c**	91	246	4.08	40	90	0.062
10	**10d**	90	242	4.47	50	90	0.050
11	**10e**	82	250	4.21	45	95	0.058

[a] Based on isolated yield.
[b] Maximum absorption wavelength.
[c] Molar absorption coefficient.
[d] Time for photolysis.
[e] Photolysis yield based on ^1H NMR.
[f] Quantum yield for the generation of various sulfonic acids at room temperature (error limit within ±5%).



8a-f or **10a-e** **11** **12a-f** or **13a-e**

Scheme 5. Photogeneration of sulfonic acids from *o*-arenesulfonyloxyanilide.

bearing *o*-arenesulfonyloxyanilide as PAG for sulfonic acids, since they can be used as photoresist materials for lithography.

4.1. Synthesis of monomer *o*-(styrenesulfonoxy) acetanilide (SSAI)

The monomer *o*-(styrenesulfonoxy) acetanilide (**16**) was synthesized by treating *p*-styrenesulfonyl chloride[30] (**14**) with

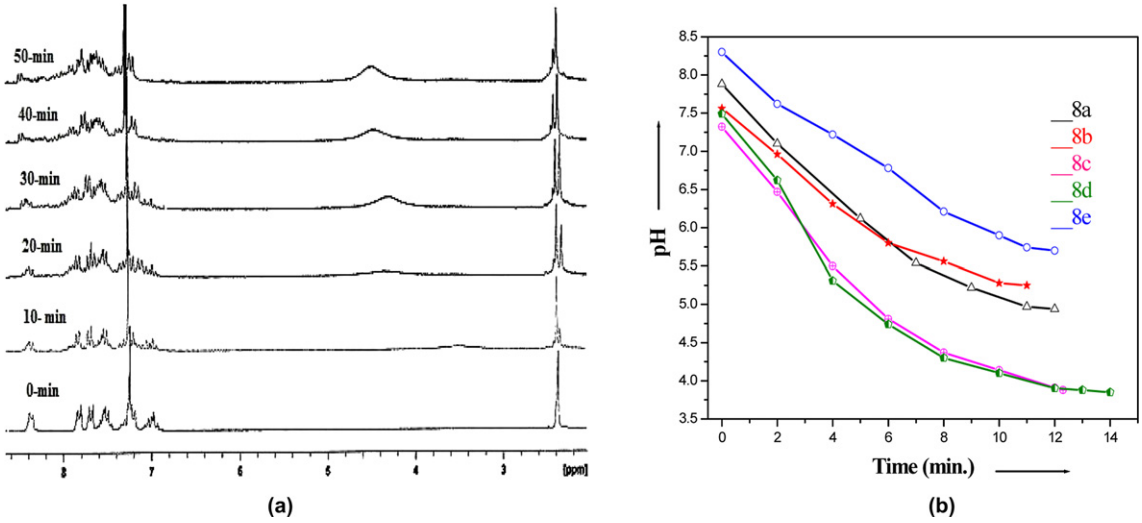


Fig. 3. a. ^1H NMR spectra of sulfonate (**10d**) at regular interval of irradiation. b. Change of pH on photolysis of sulfonate esters (**8a**–**e**) at regular interval of irradiation.

irradiation time, indicating the photodecomposition of **10d**. On the other hand, we can notice gradual increase of a signal at 2.35 ppm corresponding to the methyl peak of *p*-toluic sulfonic acid with increase in irradiation time. In addition, we also observed gradual appearance of a broad singlet at 4.38 ppm of –OH proton, which disappeared on D_2O exchange confirming the formation of *p*-toluic sulfonic acid.

Furthermore, the generation of sulfonic acids from their corresponding sulfonates (**8a**–**e**) was also studied by monitoring the pH change of the photolysate at regular interval of irradiation (Fig. 3b).

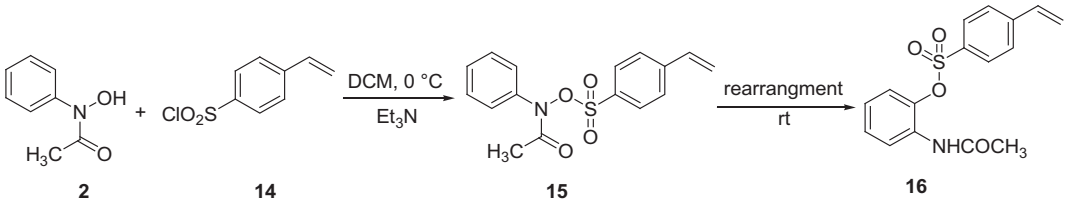
4. Polymers derived from *o*-arenesulfonyloxyacetanilide as sulfonic acid generators

After successfully demonstrating *o*-arenesulfonyloxyanilides as PAGs for sulfonic acids, we were interested to develop polymers

N-hydroxyacetanilide (**2**) in presence of Et_3N in dry DCM under nitrogen atmosphere as outlined in Scheme 6.

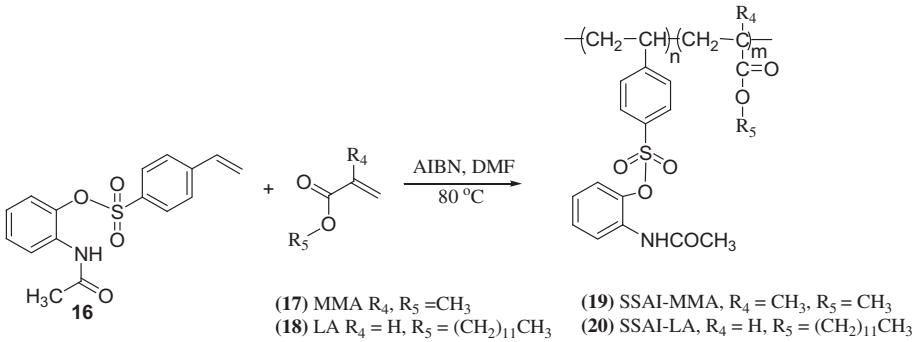
4.2. Synthesis of *o*-(styrenesulfonoxy) acetanilide–methylmethcrylate (SSAI–MMA) and *o*-styrenesulfonyloxy acetanilide–lauryl acrylate (SSAI–LA) polymers

Polymerization was carried out by free radical method using AIBN as an initiator.[31] The monomer *o*-(styrenesulfonoxy) acetanilide (**16**) and methylmethcrylate (MMA) (**17**) or lauryl acrylate (LA) (**18**) were dissolved in THF and AIBN was added (molar ratio of monomer: AIBN was 200:1) under nitrogen atmosphere. The reaction mixture was heated at 80 °C for 3 h to yield the corresponding polymers SSAI–MMA (**19**) and SSAI–LA (**20**) (Scheme 7).



2 14 15 16

Scheme 6. Synthesis of monomer *o*-(styrenesulfonyloxy) acetanilide.



16

(17) MMA R_4, R_5 =CH_3 **(19)** SSAI-MMA, R_4 = CH_3, R_5 = CH_3
(18) LA R_4 = H, R_5 = $(CH_2)_{11}CH_3$ **(20)** SSAI-LA, R_4 = H, R_5 = $(CH_2)_{11}CH_3$

Scheme 7. Synthesis of polymer SSAI–MMA and SSAI–LA.

4.3. Characterisation of the polymers

Molecular weights and the polydispersity of the polymers SSAI–MMA (**19**) and SSAI–LA (**20**) were recorded by gel permeation chromatography (GPC) and the results are tabulated in Table 5. GPC was carried out at ambient temperature using a Viscotek-GPC system equipped with two GMH HR-H non polar organic columns in series. Tetrahydrofuran was used as an eluant at a flow rate of 1 ml/min. Polystyrene standards in the M_n range of 955–37,15,000 was used for calibrations (Fig. 4).

The FTIR spectra (Fig. 5a) indicated photodecomposition of polymer films (SSAI–MMA) on irradiation at 254 nm. We noticed the peak at 1375, 1195 and 1180 cm^{-1} (νSO_2) due to aminosulfonate unit decreases on irradiation, indicating the photodecomposition of the polymer. The above fact was also noticed in the UV/vis spectra from the decrease in the absorbance around 250 nm, which corresponds to aminosulfonate unit (for UV/vis spectra see Supplementary data).

On the other hand, the generation of sulfonic acid by the polymer films was confirmed by using acid-catalyzed polysiloxane

Table 5
Polymerization conditions and characterization of polymer

Compound	Sample name	SSAI	MMA (gm)	LA (gm)	AIBN (gm)	M_w[a]	M_w/M_n
19	SSAI–MMA copolymer	0.75 (2.365 mmol)	0.238 (2.375 mmol)	—	0.002 (0.012 mmol)	18,432	1.95
20	SSAI–LA copolymer	0.75 (2.365 mmol)	—	0.568 (2.363 mmol)	0.002 (0.012 mmol)	13,339	1.86
21	Homo polymer	0.75 (2.365 mmol)	—	—	0.002 (0.012 mmol)	10,859	1.74

[a] Measured against polystyrene standards.

Further the polymers were also characterized by UV, IR and ^1H NMR spectroscopy.

4.4. Photogeneration of sulfonic acid from polymers

To investigate the polymers as PAG, the SSAI–MMA (**19**) polymer was spin coated onto silicon wafers using a headway research spinner (Spin Coating Unit SCU 2005). The photoresist films were then baked at 90 °C for 5 min in an oven. The film thicknesses were measured with a dektak-150 film thickness measurement gauge and were in the range of 0.5–0.8 μm. Irradiation of the polymer thin films at 254 nm by the use of low pressure Hg lamp (The incident photon flux (I0) at 254 nm is 1.8×10^{17} photon s^{-1} cm^{-2}) at room temperature in air resulted in homolytic S–O bond cleavage followed by hydrogen abstraction from the residual solvent in the film or polymer molecule leading to the generation of sulfonic acids.

formation technique.[32] From the FTIR spectra (Fig. 5b) we can notice changes of irradiated film before and after treatment with methyltriethoxysilane (MTEOS). The appearance of new peaks at 780 (Si–CH_3), 900 (Si–OH), 1000–1200 (Si–O–Si) and 3200–3500 (Si–OH) on the irradiated film shows the formation of silanol, which indicates hydrolysation of MTEOS under humid condition by the newly generated sulfonic acids.

5. Conclusions

We have showed simple carboxylates of *N*-acyl-*N*-phenylhydroxylamines to act as efficient PAGs for carboxylic acids. We demonstrated that by altering the *N*-acyl substituents, the acid generation ability of *N*-acyl-*N*-phenylhydroxylamines can be easily tuned. Furthermore, *o*-arenesulfonates of *N*-acyl-*N*-phenylhydroxylamines (rearranged product) and the polymers bearing *o*-arenesulfonyl *N*-acyl phenylhydroxylamines were demonstrated as PAG for sulfonic acids.

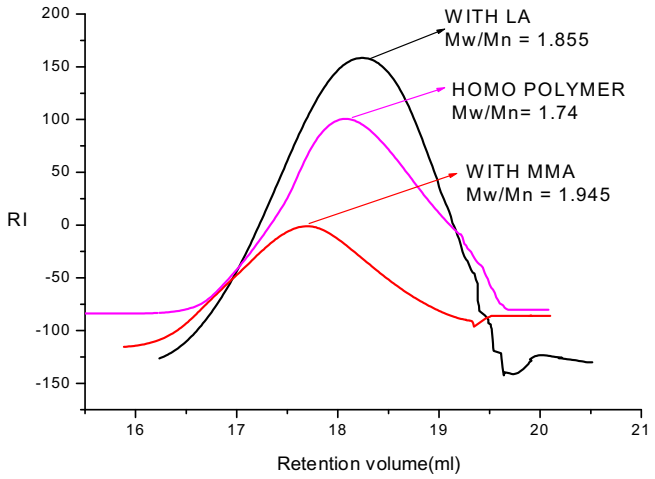


Fig. 4. GPC chromatogram of HOMO polymer of SSAI (**21**) and copolymers SSAI–MMA (**19**) and SSAI–LA (**20**).

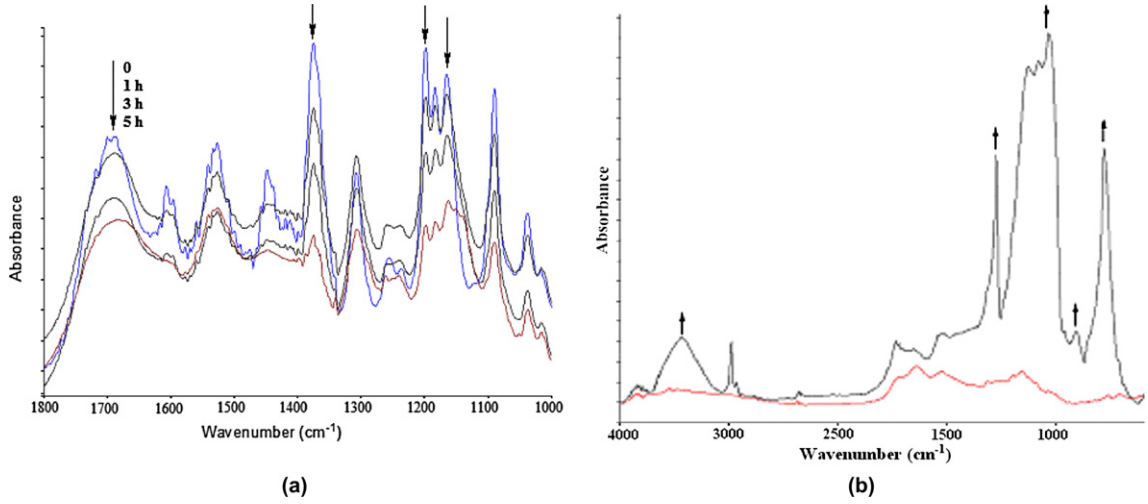


Fig. 5. a. FTIR spectral change of SSAI–MMA film on irradiation at 254 nm. Film thickness: 0.2 μm. b. FTIR spectral change of the SSAI–MMA film before (red) and after (black) treatment with MTEOS vapour for 20 min. Film thickness: 0.2 μm.

6. Experimental section

6.1. General

^{1}H NMR (200 MHz) spectra were recorded on a BRUKER-AC 200 MHz spectrometer. Chemical shifts are reported in parts per million from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: 7.26 ppm). Data are reported as follows: chemical shifts, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, dd=doublet of doublet, m=multiplet), coupling constant (Hz). ^{13}C NMR (50 MHz) spectra were recorded on a BRUKER-AC 200 MHz Spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: 77.0 ppm). Chromatographic purification was done with 60–120 mesh silica gel (Merck). For reaction monitoring, precoated silica gel 60 F_{254} TLC sheets (Merck) were used. UV/vis absorption spectra were recorded on a Shimadzu UV-2450 UV/vis spectrophotometer. FTIR spectra were recorded on a Perkin–Elmer RXI spectrometer. High-resolution mass spectra (HRMS) were recorded using LCT micro mass spectrometer. HPLC was performed using Shimadzu Prominence (LC 20 AT) liquid chromatography on a C_{18} column (4.5 mm×250 mm) with a UV/vis detector. GPC was carried out at ambient temperature using a Vistek-GPC system equipped with two GMH HR-H non polar organic columns in series. Photolysis of all the ester were carried out using 125 W medium pressure mercury lamp supplied by SAIC (India).

6.2. General procedure for the synthesis of carboxylate esters of *N*-acetyl-*N*-phenylhydroxylamine (3a–h)

To the *N*-acetyl-*N*-phenylhydroxylamine (500 mg, 3.31 mmol) in dry DCM, acid chloride (3.98 mmol), was added, to the reaction mixture Et_3N (0.92 ml, 6.61 mmol) was slowly added over a period of 5 min at 0 °C. The reaction mixture was stirred for further 12 h at room temperature. After the completion of the reaction (as indicated by TLC), it was quenched by ice cold water, diluted with DCM. The organic layer was separated, dried over Na_2SO_4 and the solvent was removed under vacuum.

*6.2.1. O-Phenylethanoyl-N-phenyl-acetohydroxamic acid (**3a**).* The crude product was purified by column chromatography (20% ethyl acetate/hexane) to give the title compound **3a** (90%) as brown liquid; R_f (30% ethyl acetate/hexane) 0.45; FTIR (neat) ν_{max} (cm^{-1}): 1648, 1793; ^{1}H NMR ($CDCl_3$, 200 MH_Z) δ: 2.01 (s, 3H), 3.78 (s, 2H), 7.29–7.32 (m, 5H), 7.39 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 21.3, 38.5, 127.5, 128.7 (2C), 129.2 (4C), 129.6 (4C), 139.1, 168.4, 168.6; MS *m*/*z*: 292 (72%, MNa^+), 270 (100%, MH^+), 214 (18%); HRMS (ES^+) calcd for $C_{16}H_{16}NO_3$ [$M+H^+$] 270.1125, found 270.1128.

*6.2.2. O-Cinnamoyl-N-phenyl-acetohydroxamic acid (**3b**).* The dark yellow crude product on purification by column chromatography (30% ethyl acetate/hexane) resulted the title compound **3b** (91%) as pale yellow solid; R_f (30% ethyl acetate/hexane) 0.54; mp: 65–67 °C; FTIR (KBr) ν_{max} (cm^{-1}): 1699, 1763; ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 2.13 (m, 3H), 6.53 (d, 1H, *J*=16 Hz), 7.26–7.43 (m, 6H), 7.51–7.56 (m, 4H), 7.86 (d, 1H, *J*=16 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 21.5, 113.2, 128.3 (4C), 128.9 (4C), 129.3, 131.6, 133.6, 139.4, 148.50, 164.1, 164.3; MS *m*/*z*: 305 (19%), 304 (80%, MNa^+), 282 (100%, MH^+), 214 (35%); HRMS (ES^+) calcd for $C_{17}H_{16}NO_3$ [$M+H^+$] 282.1125, found 282.1127.

*6.2.3. O-Benzoyl-N-phenyl-acetohydroxamic acid (**3c**).* The crude product was purified by column chromatography (30% ethyl acetate/hexane) to give the title compound **3c** (90%) as brown liquid; R_f (40% ethyl acetate/hexane) 0.50; FTIR (neat) ν_{max} (cm^{-1}): 1687, 1757; ^{1}H

NMR ($CDCl_3$, 200 MHz) δ: 2.17 (m, 3H), 7.37–7.50 (m, 5H), 7.57 (d, 2H, J=8 Hz), 7.63 (m, 1H), 8.11 (d, 2H, J=7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 21.6, 128.7 (2C), 129.3 (4C), 129.7 (4C) 134.2, 139.4, 164.0, 164.3; MS m/z: 278 (100%, MNa^+), 256 (42%, MH^+), 214 (19%); HRMS (ES^+) calcd for $C_{15}H_{14}NO_3$ [M+H$^+$] 256.0968, found 256.0971.

*6.2.4. O-(4-Methylbenzoyl)-N-phenyl-acetohydroxamic acid (**3d**).* On purification of crude product by column chromatography (40% ethyl acetate/hexane) gives title compound **3d** (92%) as light brown solid; R_f (30% ethyl acetate/hexane) 0.35; mp: 53–55 °C; FTIR (KBr) ν_{max} (cm^{-1}): 1690, 1755; ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 2.16 (m, 3H), 2.42 (s, 3H), 7.30–7.42 (m, 5H), 7.55 (d, 2H, J=2.8 Hz), 7.90 (d, 2H, J=8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 21.5, 21.7, 123.8, 129.0, 129.2 (4), 130.0 (4C), 139.4, 145.3, 164.0, 164.1; HRMS (ES^+) calcd for $C_{16}H_{16}NO_3$ [M+H$^+$] 270.1125, found 270.1129.

*6.2.5. O-(4-Methoxybenzoyl)-N-phenyl-acetohydroxamic acid (**3e**).* The compound **3e** (90%) was obtained as pale yellow solid on purification of the crude product through column chromatography (40% ethyl acetate/hexane); R_f (20% ethyl acetate/hexane) 0.25; mp: 65–67 °C; FTIR (KBr) ν_{max} (cm^{-1}): 1692, 1750; ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 2.16 (m, 3H), 3.87 (s, 3H), 6.95 (d, 2H, J=9.0 Hz), 7.38–7.55 (m, 3H), 7.58 (d, 2H, J=1.8 Hz), 8.06 (d, 2H, J=2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 21.6, 55.5, 114.1, 118.8, 129.2 (4C), 132.3 (4C), 139.5, 145.5, 163.7, 164.4; HRMS (ES^+) calcd for $C_{16}H_{16}NO_4$ [M+H$^+$] 286.1074, found 286.1078.

*6.2.6. O-(4-Ethoxy-2-methoxybenzoyl)-N-phenyl-acetohydroxamic acid (**3f**).* On purification of crude product by column chromatography (40% ethyl acetate/hexane) yielded title compound **3f** (95%) as white solid; R_f (30% ethyl acetate/hexane) 0.52; mp: 90–93 °C; FTIR (KBr) ν_{max} (cm^{-1}): 1683, 1762; ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.5 (t, 3H, J=6.8 Hz), 2.17 (br s, 3H), 3.98 (s, 3H), 4.17 (q, 2H, J_1=7.2, J_2=14 Hz), 6.90 (d, 1H, J=8 Hz), 7.42 (m, 3H), 7.56 (m, 3H), 7.75 (d, 1H, J=8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 14.4, 21.6, 56.0, 64.5, 111.3 (2C), 112.4 (2C), 118.5, 123.4, 124.7 (2C), 129.2, 139.4, 149.0, 153.5, 164.5, 163.8; HRMS (ES^+) calcd for $C_{18}H_{20}NO_5$ [M+H$^+$] 330.1336, found 330.1339.

*6.2.7. O-(4-Chlorobenzoyl)-N-phenyl-acetohydroxamic acid (**3g**).* The dark white solid compound **3g** (90%) was obtained on purification of the crude product by column chromatography (40% ethyl acetate/hexane); R_f (50% ethyl acetate/hexane) 0.55; mp: 67–69 °C; FTIR (KBr) ν_{max} (cm^{-1}): 1690, 1760; ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 2.17 (m, 3H), 7.41–7.58 (m, 7H), 8.04 (d, 2H, J=8.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 21.6, 125.3, 129.1 (4C), 129.5, 131.5 (4C), 139.3, 140.9, 163.3, 163.5; MS m/z: 312 (50%), 290 (100%, MH^+), 214 (32%); HRMS (ES^+) calcd for $C_{15}H_{13}ClNO_3$ [M+H$^+$] 290.0578, found 290.0580.

*6.2.8. O-(4-Nitrobenzoyl)-N-phenyl-acetohydroxamic acid (**3h**).* The compound **3h** (93%) was obtained on purification of the crude product through column chromatography (40% ethyl acetate/hexane) as dark yellow solid; R_f (40% ethyl acetate/hexane) 0.50; mp: 115–117 °C; FTIR (KBr) ν_{max} (cm^{-1}): 1710, 1769; ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 2.13 (m, 3H), 7.29–7.59 (m, 5H), 8.24–8.33 (m, 4H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 21.8, 124.0 (4C), 129.9 (2C), 131.5 (3C), 132.7, 139.4, 151.3, 162.1, 162.6; HRMS (ES^+) calcd for $C_{15}H_{13}N_2O_5$ [M+H$^+$] 301.0819, found 301.0821.

6.3. General procedure for the synthesis of carboxylate ester of *N*-acyl-*N*-phenylhydroxylamine (6a–c)

To the mixture of *N*-acyl-*N*-phenylhydroxylamine and *p*-toluic chloride in dry DCM, Et_3N was added slowly at 0 °C. Then the reaction mixture was stirred for overnight at room temperature. After the completion of the reaction (as indicated by TLC), it was quenched by ice cold water, diluted with DCM. The organic layer was separated, dried over Na_2SO_4 and the solvent was removed under vacuum.

*6.3.1. O-(4-Methylbenzoyl)-N-phenyl-benzohydroxamic acid (**6a**).* *N*-Benzoyl-*N*-phenylhydroxylamine (250 mg, 1.17 mmol) reacts with (272 mg, 1.77 mmol) of *p*-methyl benzoyl chloride in presence of Et_3N (0.23 ml, 2.34 mmol) as base to give the crude product. The dark yellow crude product on purification by column chromatography (30% ethyl acetate/hexane) gives title compound **6a** (85%) as white solid; R_f (40% ethyl acetate/hexane) 0.42; mp: 120–121 °C; FTIR (KBr) ν_{max} (cm^{-1}): 1683, 1762; ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 2.35 (m, 3H), 7.18–7.31 (m, 8H), 7.40 (d, 2H, J=1.6 Hz), 7.59 (d, 2H, J=6.4 Hz), 7.94 (d, 2H, J=8.2 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 21.7, 124.1, 126.4 (2C), 127.2 (2C), 128.1 (2C), 128.7 (3C), 129.1 (2C), 129.4 (2C), 131.0, 133.5, 140.7, 145.1, 164.2, 167.2; HRMS (ES^+) calcd for $C_{21}H_{18}NO_3$ [M+H$^+$] 332.1281, found 332.1285.

*6.3.2. O-(4-Methylbenzoyl)-N-phenyl-4-methoxybenzohydroxamic acid (**6b**).* By the reaction of (210 mg, 0.86 mmol) of *p*-methoxy-*N*-benzoyl-*N*-phenylhydroxylamine with (200 mg, 1.29 mmol) of *p*-methyl benzoyl chloride in presence of Et_3N (0.16 ml, 1.15 mmol) gives the light brown crude product, on purification of crude product by column chromatography (40% ethyl acetate/hexane) gives the title compound **6b** (91%) as white solid; R_f (30% ethyl acetate/hexane) 0.41; mp: 85–87 °C; FTIR (KBr) ν_{max} (cm^{-1}): 1673, 1758; ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 2.36 (m, 3H), 3.69 (m, 3H), 6.75 (dd, 2H, J=1.6, J=8.6 Hz), 7.20–7.33 (m, 5H), 7.42 (d, 2H, J=8.0 Hz), 7.60 (d, 2H, J=7.4 Hz), 7.98 (d, 2H, J=6.8 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 22.0, 55.4, 113.7 (2C), 124.4, 125.5, 126.7 (2C), 128.3, 129.4 (2C), 192.6 (2C), 130.3 (2C), 131.3 (2C), 141.5, 145.3, 162.1, 164.5, 167.1; HRMS (ES^+) calcd for $C_{22}H_{19}NO_4$ [M+H$^+$] 362.1387, found 362.1388.

*6.3.3. O-(4-Methylbenzoyl)-N-phenyl-4-nitrobenzohydroxamic acid (**6c**).* On reaction of (150 mg, 0.58 mmol) of *p*-nitro-*N*-benzoyl-*N*-phenylhydroxylamine with (0.134 mg, 0.86 mmol) of *p*-methyl benzoyl chloride in presence of Et_3N (0.16 ml, 1.15 mmol) produces the crude product, then it was purified by column chromatography (25% ethyl acetate/hexane) to give the title compound **6c** (90%) as pale yellow solid; R_f (30% ethyl acetate/hexane) 0.43; mp: 110–111 °C; FTIR (KBr) ν_{max} (cm^{-1}): 1691, 1772; ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 2.35 (m, 3H), 7.19–7.35 (m, 5H), 7.41–7.44 (m, 2H), 7.74 (d, 2H, J=8.8 Hz), 7.90 (d, 2H, J=7.8 Hz), 8.08 (d, 2H, J=8.6 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 21.7, 123.3 (4C), 126.4, 128.9, 129.4 (4C), 129.6 (4C), 139.6, 144.4, 145.6, 148.9, 165.2, 171.5; HRMS (ES^+) calcd for $C_{20}H_{15}N_2O_5$ [M+H$^+$] 363.0975, found 363.0979.

6.4. Photogeneration of carboxylic acids and its quantum yield measurement

Carboxylates (**3a**–**h** and **6a**–**c**) (0.05 mmol) was dissolved in MeOH/H_2O (9:1), and it was irradiated using 125 W medium pressure Hg lamp using quartz filter. In each case the photolysis was stopped when conversion reached at least 95% (as indicated by HPLC). After the completion of the photolysis, the solvent was removed under vacuum and the photoproducts (carboxylic acids and carboxyanilide) were separated by column chromatography using ethyl acetate/hexane as eluant.

The quantum yield of photogeneration of carboxylic acids was analyzed by employing valerophenone as an actinometer. The progress of the photolysis was monitored by taking 5 μl of aliquot at regular interval of time and analyzed by HPLC, using eluant hexane/isopropanol (9:1), at a flow rate of 1 ml/min (detection: UV 254 nm). The % of carboxylic acid generated was determined by calculating the gradual increase in the peak area of the carboxylic acid.

6.5. General procedure for the synthesis of *O*-arenesulfonyloxyacetanilide (*Series*-1 8a–f)

To the mixture of sulfonyl chloride (2.38 mmol) and *N*-acetyl-*N*-phenylhydroxylamine (300 mg, 1.98 mmol) in dry DCM, Et_3N (0.55 ml, 3.97 mmol) was added drop by drop at 0 °C. The reaction mixture was then stirred for overnight at room temperature. After the completion of the reaction (as indicated by TLC), it was quenched by ice cold water, diluted with DCM. The organic layer was separated, dried over Na_2SO_4 and the solvent was removed under vacuum.

*6.5.1. o-(Methanesulfonoxy) acetanilide (**8a**).* The dark yellow crude solid on purification by column chromatography (40% ethyl acetate/hexane) gives title compound **8a** (83%) as light yellow solid; R_f (40% ethyl acetate/hexane) 0.50; mp: 105–107 °C; FTIR (KBr) ν_{max} (cm^{-1}): 3234, 1650, 1363; ^1H NMR ($CDCl_3$, 400 MHz) δ: 2.21 (s, 3H), 3.26 (s, 3H), 7.14 (t, 1H, J=7.4 Hz), 7.27 (m, 1H), 7.32 (t, 1H, J=8 Hz), 7.83 (br s, 1H), 8.24 (d, 1H, J=8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 24.5, 37.7, 122.5, 123.8, 124.9, 128.1, 131.0, 138.7, 168.7; MS *m*/*z*: 230 (100%, MH+), 214 (58%), 187 (55%); HRMS (ES^+) calcd for $C_9H_{12}NO_4S$ [M+H^+] 230.0482, found 230.0486.

*6.5.2. o-(Butanesulfonoxy) acetanilide (**8b**).* The blackish crude solid was purified using column chromatography (40% ethyl acetate/hexane) gives the title compound **8b** (80%) as yellow solid; R_f (30% ethyl acetate/hexane) 0.45; mp: 75–76 °C; FTIR (KBr) ν_{max} (cm^{-1}): 3231, 1654, 1354; ^1H NMR ($CDCl_3$, 200 MHz) δ: 1.01 (t, 3H, J=7.4), 1.52–1.54 (m, 2H), 1.93–2.08 (m, 2H), 2.20 (s, 3H), 3.34–3.41 (m, 2H), 7.12–7.25 (m, 2H), 7.31–7.35 (m, 1H), 7.9 (br s, 1H), 8.24 (d, 1H, J=8.4 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 13.3, 21.3, 24.4, 25.4, 50.7, 122.7, 123.7, 124.8, 127.8, 131.2, 138.5, 168.6; MS *m*/*z*: 294 (15%), 272 (100%, MH^+), 230 (59%), 214 (20%); HRMS (ES^+) calcd for $C_{12}H_{17}NO_4S$ [M+H^+] 272.0951, found 272.0955.

*6.5.3. o-(Benzanesulfonoxy) acetanilide (**8c**).* The crude product was purified by column chromatography (30% ethyl acetate/hexane) to give the title compound **8c** (91%) as white solid; R_f (25% ethyl acetate/hexane) 0.40; mp: 120–123 °C; FTIR (KBr) ν_{max} (cm^{-1}): 3221, 1695, 1366; ^1H NMR ($CDCl_3$, 200 MHz) δ: 2.06 (s, 3H), 6.88–7.03 (m, 2H), 7.20 (m, 1H), 7.56 (t, 3H, J=7.6 Hz), 7.69–7.77 (m, 1H), 7.83–7.87 (m, 2H), 8.16 (d, 1H, 8.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 24.4, 122.6, 122.9, 124.3, 127.8, 128.3 (3C), 129.3 (2C), 131.0, 134.8, 138.8, 168.1; MS *m*/*z*: 314 (20%, MNa^+), 292 (100%, MH^+), 214 (24%), 157 (22%); HRMS (ES^+) calcd for $C_{14}H_{14}NO_4S$ [M+H^+] 292.0638, found 292.0640.

*6.5.4. o-(p-Tolylsulfonoxy) acetanilide (**8d**).* On purification of crude product by column chromatography (40% ethyl acetate/hexane) yield the desired compound **8d** (90%) as white solid; R_f (30% ethyl acetate/hexane) 0.45; mp: 120–125 °C; FTIR (KBr) ν_{max} (cm^{-1}): 3235, 1679, 1367; ^1H NMR ($CDCl_3$, 400 MHz) δ: 2.07 (s, 3H), 2.46 (s, 3H), 6.89 (d, 1H, J=8.4 Hz), 6.98 (t, 1H, J=8.4 Hz), 7.23 (m, 1H), 7.34 (d, 2H, J=8 Hz), 7.54 (m, 1H), 7.72 (d, 2H, J=8.4 Hz), 8.18 (d, 1H, J=8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 21.3, 24.4, 122.7, 122.8, 124.2, 127.5, 128.4 (2C), 130.0 (2C), 131.0, 131.6, 138.8, 146.2, 168.1; MS *m*/*z*: 328 (10%, MNa^+), 306 (100%, MH^+), 264 (52%), 214 (22%); HRMS (ES^+) calcd for $C_{15}H_{16}NO_4S$ [M+H^+] 306.0795, found 306.0798.

*6.5.5. o-(2-Nitrobenzenesulfonoxy) acetanilide (**8e**).* The crude product on purification by column chromatography (50% ethyl acetate/hexane) gives the title compound **8e** (85%) as brown solid; R_f (40% ethyl acetate/hexane) 0.40; mp: 105–106 °C; FTIR (KBr) ν_{max} (cm^{-1}): 3254, 1699, 1368; ^1H NMR ($CDCl_3$, 400 MHz) δ: 2.06 (s, 3H), 7.10 (t, 1H, J=8 Hz), 7.28–7.30 (1H, m), 7.45 (d, 1H, J=8.4 Hz), 7.67–7.71 (m, 1H), 7.85–7.90 (m, 3H), 8.13 (br s, 1H), 8.31 (d, 1H, J=8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 24.3, 122.0, 122.8, 124.0, 124.7, 127.7, 128.3, 131.0, 132.3, 132.5, 136.0, 137.6, 148.4, 168.4; HRMS (ES^+) calcd for $C_{14}H_{13}N_2O_6S$ [M+H^+] 337.0489, found 337.0490.

*6.5.6. o-(4-Nitrobenzenesulfonoxy) acetanilide (**8f**).* The yellow solid compound **8f** (90%) was obtained by the purification of the crude product using column chromatography (50% ethyl acetate/hexane); R_f (30% ethyl acetate/hexane) 0.35; mp: 120–123 °C; FTIR (KBr) ν_{max} (cm^{-1}): 3249, 1668, 1363; ^1H NMR ($CDCl_3$, 400 MHz) δ: 2.14 (s, 3H), 6.82 (d, 1H, J=7.2 Hz), 6.99–7.02 (m, 1H), 7.28–7.31 (m, 1H), 7.52–7.55 (m, 1H), 8.08 (d, 2H, J=8.4 Hz), 8.16–8.18 (m, 1H), 8.41 (d, 2H, J=8.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 24.3, 122.1, 123.9, 124.4, 124.7, 128.3, 128.8, 129.9, 130.9, 136.0, 137.6, 140.2, 151.2, 168.4; MS *m*/*z*: 337 (100%, MH^+), 294 (85%), 214 (64%), 158 (30%); HRMS (ES^+) calcd for $C_{14}H_{13}N_2O_6S$ [M+H^+] 337.0489, found 337.0489.

6.6. General procedure for the synthesis of *o*-arenesulfonyloxybenzanilide (*Series*-2 10a–e)

To the reaction mixture of *N*-benzoyl *N*-phenyl hydroxyl amine (400 mg, 1.88 mmol) and sulfonyl chloride (2.87 mmol) in dry DCM, Et_3N (0.52 ml, 3.75 mmol) was added drop wise at 0 °C. The reaction mixture was then stirred for 12 h at room temperature. After the completion of the reaction (as indicated by TLC), it was quenched by ice cold water, diluted with DCM. The organic layer was separated, dried over Na_2SO_4 and the solvent was removed under vacuum.

*6.6.1. o-(Methanesulfonoxy) benzanilide (**10a**).* The crude product was purified by column chromatography (50% ethyl acetate/hexane) to give the title compound **10a** (85%) as white solid; R_f (30% ethyl acetate/hexane) 0.32; mp: 115–120 °C; FTIR (KBr) ν_{max} (cm^{-1}): 3233, 1654, 1350; ^1H NMR ($CDCl_3$, 400 MHz) δ: 3.25 (s, 3H), 7.12–7.39 (m, 4H), 7.43–7.58 (m, 2H), 7.91 (d, 2H, J=6.4 Hz), 8.38 (d, 1H, J=8.2 Hz), 8.67 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 37.9, 122.9, 124.0, 125.1, 127.2 (2C), 128.3, 128.9 (2C), 131.4, 132.2, 134.1, 138.9, 165.5; MS *m*/*z*: 314 (23%, MNa^+), 292 (100%, MH^+), 214 (27%), 157 (25%); HRMS (ES^+) calcd for $C_{14}H_{14}NO_4S$ [M+H^+] 292.0638, found 292.0636.

*6.6.2. o-(Butanesulfonoxy) benzanilide (**10b**).* On purification of crude product by column chromatography (20% ethyl acetate/hexane) gives the desired compound **10b** (80%) as white solid; R_f (25% ethyl acetate/hexane) 0.45; mp: 95–100 °C; FTIR (KBr) ν_{max} (cm^{-1}): 3221, 1654, 1354; ^1H NMR ($CDCl_3$, 200 MHz) δ: 0.79 (t, 3H, J=16.2), 1.44–1.47 (m, 2H), 1.89–2.04 (m, 2H), 3.18–3.44 (m, 2H), 7.11–7.25 (m, 3H), 7.30–7.38 (m, 1H), 7.44–7.54 (m, 2H), 7.71–7.78 (m, 2H), 8.61 (d, 1H, J=5.6 Hz), 8.85 (br s, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 13.3, 21.3, 25.5, 50.9, 123.2, 123.8, 125.0, 127.2 (2C), 128.1, 128.8 (2C), 131.6, 132.1, 134.1, 138.5, 165.4; HRMS (ES^+) calcd for $C_{17}H_{20}NO_4S$ [M+H^+] 334.1108, found 334.1110.

*6.6.3. o-(Benzanesulfonoxy) benzanilide (**10c**).* The crude product was purified by column chromatography (30% ethyl acetate/hexane) to give the title compound **10c** (91%) as off white solid; mp: 70–72 °C; R_f (25% ethyl acetate/hexane) 0.40; FTIR (KBr) ν_{max} (cm^{-1}): 3225, 1683, 1360; ^1H NMR ($CDCl_3$, 200 MHz) δ: 6.90–7.07 (m, 2H), 7.26–7.34 (m, 1H), 7.40–7.65 (m, 6H), 7.81–7.85 (m, 4H), 8.34–8.39 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 122.9, 123.1, 124.6, 127.1(2C), 128.0, 128.3 (2C), 128.8 (2C), 129.4 (2C), 131.2, 132.2, 134.1, 134.5, 134.9, 139.3, 165.1; HRMS (ES^+) calcd for $C_{19}H_{16}NO_4S$ [M+H^+] 354.0795, found 354.0797.

*6.6.4. o-(p-Tolylsulfonoxy) benzanilide (**10d**).* The crude product on purification by column chromatography (30% ethyl acetate/hexane) yielded the title compound **10d** (90%) white solid; R_f (40% ethyl

acetate/hexane) 0.51; mp: 120–125 °C; FTIR (KBr) ν_{max} (cm^{-1}): 3251, 1678, 1366; ^1H NMR ($CDCl_3$, 400 MHz) δ: 2.39 (s, 3H), 6.98–7.04 (m, 2H), 7.19–7.23 (m, 2H), 7.27–7.31 (m, 1H), 7.41–7.59 (m, 3H), 7.69 (d, 2H, J=8.4 Hz), 7.83(d, 2H, J=9.4 Hz), 8.35–8.40 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 21.7, 123.0, 123.1, 124.6, 127.1 (2C), 127.8, 128.2 (2C), 128.7 (2C), 130.1 (2C), 131.2, 131.5, 132.1, 134.0, 139.3, 146.2, 164.9; MS m/z: 368 (100%, MH+), 214 (30%); HRMS (ES^+) calcd for $C_{20}H_{18}NO_4S$ [M+H^+] 368.0951, found 368.0955.

*6.6.5. o-(2-Nitrobenzenesulfonoxy) benzanilide (**10e**).* Compound **10e** (82%) was obtained on purification of the crude product by column chromatography (40% ethyl acetate/hexane) as off white solid; R_f (30% ethyl acetate/hexane) 0.40; mp: 122–125 °C; FTIR (KBr) ν_{max} (cm^{-1}): 3244, 1685, 1377; ^1H NMR ($CDCl_3$, 400 MHz) δ:7.09–7.22 (m, 1H), 7.29–7.42 (m, 5H), 7.42–7.58 (m, 1H), 7.59–7.66 (m, 2H), 7.67–7.75 (m, 2H), 7.79–7.82 (m, 1H), 8.25 (d, 1H, J=9.6 Hz), 8.52 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 123.2, 123.6, 124.9 (2C), 127.4 (2C), 128.1, 128.4, 128.6 (2C), 130.8, 131.9, 132.3, 132.5, 133.6, 135.7, 139.0, 147.9, 165.3; HRMS (ES^+) calcd for $C_{19}H_{15}N_2O_6S$ [M+H^+] 399.0645, found 399.0647.

6.7. Photolysis and quantum yield measurements of the sulfonate esters

Sulfonate ester (0.05 mmol) (**8a**–**f** and **10a**–**e**) was dissolved in MeOH/H_2O (9:1) solvent, and it was irradiated by 125 W medium pressure Hg lamp using quartz filter. The progress of the reaction was monitored by ^1H NMR analysis. After the completion of the reaction the solvent was removed under vacuum and the photo-products (sulfonic acids and *o*-hydroxyacetanilide or *o*-hydroxybenzanilide) were separated by column chromatography using ethyl acetate/hexane as an eluant.

The quantum yield of photogeneration of sulfonic acids was analyzed by ^1H NMR spectroscopy by employing valerophenone as an actinometer. The percent of acids generated was determined by calculating the gradual increase in the peak area of the sulfonic acids using anisole as internal standard.

6.8. Synthesis of monomer *o*-(styrenesulfonoxy) acetanilide (SSAI) (16)

To the mixture of *N*-acetyl-*N*-phenylhydroxylamine (2 g, 13.24 mmol) and *p*-styrenesulfonyl chloride (4 g, 19.73 mmol) in dry DCM, Et_3N (3.68 ml, 26.48 mmol) was added over a period of 5 min at 0 °C, then the reaction mixture was continuously stirred at room temperature for overnight. After the completion of the reaction it was quenched by ice cold water, diluted with DCM. The organic layer was separated, dried over Na_2SO_4 and the solvent was removed under vacuum.

*6.8.1. o-(Styrenesulfonoxy) acetanilide (SSAI) (**16**).* The monomer was got without further purification (92%) as yellow liquid, R_f (40% ethyl acetate/hexane) 0.45; FTIR (neat) ν_{max} (cm^{-1}): 3233, 1654, 1354; ^1H NMR ($CDCl_3$, 200 MHz) δ: 2.11–2.15 (s, 3H), 5.50 (d, 1H, J=11 Hz), 5.92 (d, 1H, J=17.6 Hz), 6.68–6.82 (m, 1H), 6.88–7.02 (m, 2H), 7.19–7.26 (m, 2H), 7.54 (d, 2H, J=8.4 Hz), 7.83 (d, 2H J=8.6 Hz), 8.15–8.19 (m, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 24.4, 118.9, 122.8, 123.2, 124.5, 126.9 (2C), 127.7, 128.7 (2C), 131.0, 133.2, 134.8, 139.1, 143.9, 168.5; HRMS (ES^+) calcd for $C_{21}H_{18}NO_4S$ [M+H^+] 380.0951, found 380.0958.

6.9. Preparation of polymers

Polymerization was carried out by free radical method using AIBN as initiator at 80 °C in THF under N_2 atmosphere. *o*-(styrenesulfonoxy) acetanilide (2.36 mmol) and methylmethcrylate (MMA 2.37 mmol) or lauryl acrylate (LA 2.36 mmol) were dissolved in THF in a dry, long glass tube with a magnetic stirring bar. AIBN was added (molar ratio of monomer: AIBN was 200:1) and stirred till it dissolved. The reaction mixture was degassed with nitrogen for 20 min. The polymerization was continued in nitrogen atmosphere at 80 °C in an oil bath for 3 h till it turned viscous. Reaction was stopped by taking out the tube from oil bath and placed in cold water. After stopping the reaction the reaction mixture was dissolved in THF. The solution was concentrated and the polymer was precipitated into methanol and was dried at room temperature for one day followed by drying in a vacuum oven for another 24 h.

*6.9.1. Polymer SSAI–MMA (**19**).* White solid; FTIR (KBr) ν_{max} (cm^{-1}): 3225, 1650, 1355; ^1H NMR ($CDCl_3$, 200 MHz) δ: 1.74–2.01 (br m), 2.4–2.6 (br m), 3.12–3.97 (br m), 7.14–7.92 (br m).

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Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.tet.2011.03.049.

References and notes

1. Dai, J.; Chang, S. W.; Hamad, A.; Yang, D.; Felix, N.; Ober, C. K. *Chem. Mater.* **2006**, *18*, 3404.
2. Fujigaya, T.; Sibasaki, Y.; Ando, S.; Kishimura, S.; Endo, M.; Sasago, M.; Ueda, M. *Chem. Mater.* **2003**, *15*, 1512.
3. Shirai, M.; Okamura, H. *Prog. Org. Coat.* **2009**, *64*, 175.
4. Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 3845.
5. Kim, Y. J.; Kang, H.; Leolukman, M.; Nealey, P. F.; Gopalan, P. *Chem. Mater.* **2009**, *21*, 3030.
6. Kim, K. M.; Ayothi, R.; Ober, C. K. *Polym. Bull.* **2005**, *55*, 333.
7. Naitoh, K.; Yoneyama, K.; Yamaoka, T. *J. Phys. Chem.* **1992**, *96*, 238.
8. Yamaoka, T.; Omote, T.; Adachi, H.; Kikuchi, N.; Watanabe, Y.; Shirosaki, T. *J. Photopolym. Sci. Technol.* **1990**, *3*, 275.
9. Morspool, W. M. *Synthetic Organic Photochemistry*; Plenum: New York NY, 1984.
10. Givens, R. S.; Kuepe, L. W. *Chem. Rev.* **1993**, *93*, 55.
11. Gannon, T.; McGimpsey, W. G. *J. Org. Chem.* **1993**, *58*, 913.
12. Gannon, T.; McGimpsey, W. G. *J. Org. Chem.* **1993**, *58*, 5639.
13. Nyfeler, E.; Renaud, P. *Org. Lett.* **2008**, *10*, 985.
14. Okada, K.; Okamato, K.; Oda, M. *J. Am. Chem. Soc.* **1988**, *110*, 8736.
15. Verbec, J.; Oosterhoff, P.; Hageman, J. H. *J. Photochem. Photobiol., A* **1999**, *121*, 207.
16. Buscemi, S.; Pace, A.; Pibiri, I.; Vivona, N.; Carona, T. *J. Fluorine Chem.* **2004**, *125*, 165.
17. Shirai, M.; Yatsuo, T.; Tsunooka, M. *J. Photopolym. Sci. Technol.* **1996**, *9*, 273.
18. Aveline, B. M.; Kochever, I. E.; Redmond, R. W. *J. Am. Chem. Soc.* **1995**, *117*, 9699.
19. Sakurai, T.; Yamamoto, H.; Yamada, S.; Inoue, H. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1174.
20. Keneko, T.; Kubo, K.; Sakurai, T. *Tetrahedron Lett.* **1997**, *38*, 4779.
21. Chowdhury, N.; Dutta, S.; Nishitha, B.; Dasgupta, S.; Singh, P. N. D. *Bioorg. Med. Chem. Lett.* **2010**, *20*, 5414.
22. Oxley, P. W.; Adger, B. M.; Sasse, M. J.; Forth, M. A. *Org. Synth.* **1993**, *8*, 16.
23. Wagner, P. J.; Kemppainen, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 7495.
24. White, R. C.; Selvam, T.; Ihmels, H.; Adam, W. *J. Photochem. Photobiol., A* **1999**, *122*, 7.
25. Cumaioni, D. M.; Walter, H. F.; Pratt, D. W. *J. Am. Chem. Soc.* **1973**, *95*, 4057.
26. Danen, W. C.; Neugebauer, F. A. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 783.
27. Quast, H.; Nüdling, W.; Klemm, G.; Kirschfeld, A.; Neuhaus, P.; Sander, W.; Hrovat, D. A.; Borden, W. T. *J. Org. Chem.* **2008**, *73*, 4956.
28. Schlegel, L.; Ueno, T.; Shiraishi, H.; Hayashi, N.; Iwayanagi, T. *Microelectron. Eng.* **1991**, *14*, 227.
29. Tisue, G. T.; Grassmann, M.; Lwowski, W. *Tetrahedron* **1967**, *24*, 999.
30. Berrisford, D. J.; Lovell, P. A.; Suliman, N. R.; Whiting, A. *Chem. Commun.* **2005**, 5904.
31. Gao, B.; Chen, X.; Ivan, B.; Kops, J.; Batsberg, W. *Polym. Bull.* **1997**, *39*, 559.
32. Shinozuka, T.; Shirai, M.; Tsunooka, M. *Eur. Polym. J.* **2001**, *37*, 1625.