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A water-soluble poly(methylphenylsilylene) derivative as a photoinitiator of radical polymerization of hydrophilic vinyl monomers

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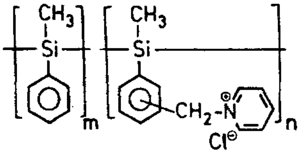
Summary

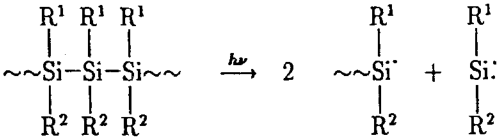
Radicals formed during photoscission of the pyridinium salt of partially chloromethylated poly(methylphenylsilylene) (Q-PMPSi) in aqueous solution are capable of initiating the polymerization of hydrophilic vinyl monomers, e.g. acrylic and methacrylic acid, acrylamide, 2-hydroxyethyl methacrylate and 1-vinyl-2-pyrrolidone.



(Q-PMPSi)

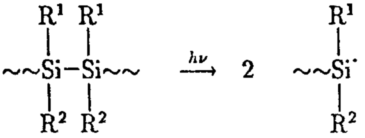
Introduction

Polysilanes, σ-conjugated polymers of the general formula $(SiR^1R^2)_n$, strongly absorb radiation in the UV region (1) between about 295 and 400 nm (depending on the nature of the substituents R^1 and R^2). Rapid photoscission takes place during UV irradiation of these materials, sometimes accompanied by photocrosslinking (1). Polymeric silyl radicals are formed by two routes:



$$\sim\sim\underset{R^2}{\overset{R^1}{Si}}-\underset{R^2}{\overset{R^1}{Si}}-\underset{R^2}{\overset{R^1}{Si}}\sim\sim \xrightarrow{h\nu} 2\ \sim\sim\underset{R^2}{\overset{R^1}{Si^{\cdot}}} + \underset{R^2}{\overset{R^1}{Si\colon}}$$

or



$$\sim\sim\underset{R^2}{\overset{R^1}{Si}}-\underset{R^2}{\overset{R^1}{Si}}\sim\sim \xrightarrow{h\nu} 2\ \sim\sim\underset{R^2}{\overset{R^1}{Si^{\cdot}}}$$

These radicals have been proved to be capable of initiating the free radical polymerization of acrylates, methacrylates and styrene (2) (naturally, dissolution of the polysilane in the reaction medium is neccessary). It was reported (2) that the comparatively low photoinitiation efficiency of silyl radicals (about 0.001) is partially compensated by the high molar absorptivities of polysilanes (usually 2 x 10^3 - 10^4 $l.mol^{-1}cm^{-1}$ per Si unit at λ_{max}). Poly(methylphenylsilylene) (PMPSi, R^1= Me, R^2=Ph) was found to be the most effective photoinitiator, which is in accordance with a high quantum yield (2) of silyl radical formation for this polymer ($\phi = 0.97$).

Notably, the relative insensitivity of polysilane photoinitiating systems toward oxygen was claimed (2). This effect was ascribed to the formation of effective oxygen scavengers (probably silene moieties, $>Si=CH_2$) by side reactions during irradiation. The resistance of this photoinitiating system to oxygen inhibition could be of a considerable practical importance, together with a possibility of tuning the optical properties of polysilanes by proper substitution and degree of polymerization (2).

Previously (3), partially chloromethylated PMPSi (degree of substitution 15 - 45 %) was used for the quaternization of pyridine. This reaction proceeded almost quantitaviley. The resulting polymeric pyridinium derivatives (Q-PMPSi) were soluble in lower alcohols, water-alcohol mixtures and even in water. It is suggested, therefore, that Q-PMPSi could serve as a water- or alcohol-soluble radical photoinitiator. Our attempts to induce polymerization of some hydrophilic vinyl monomers by UV light in the presence of Q-PMPsi, either in aqueous solution or in bulk, are reported in this paper.

Experimental Part

The preparation of the Q-PMPSi (degree of substitution 20 mol%) is described elsewhere (3). The polymer can be dissolved in water by boiling for ca. 30 min. The resulting solution is usually slightly opalescent. Colloid particles which might be responsible for this opalescence can neither be removed by centrifugation (15 000 rpm, 1 h) nor by microfiltration. 5 wt.% stock solution of Q-PMPSi in water was used for the polymerization experiments. The monomers used were free from inhibitor.

The photopolymerizations were performed in flat bottom glass vessels covered with transparent polyethylene foil. The reaction mixture was irradiated through this foil, which also served as a protecting cover for experiments under nitrogen atmosphere. The thickness of the exposed layer was app. 5 mm for aqueous solution and app. 500 µm for monomer films. A high pressure mercury vapour lamp (input 150 W) served as a light source. Light of wavelenghts shorter than 310 nm was filtered off by a 2 mm glass. The distance between the light source and the irradiated solution was about 17 cm. The photon flux at the surface of the polymerized layer, measured with a Radiometer 580, EG & G, was 1,5 x 10^{-10} Einstein/cm^2 s at 317 nm.

The polymer yield was determined gravimetrically: after removing water and monomer, the resulted solid was dried in vacuo at 60 °C for 24 h and weighed.

Molar masses of polymers were measured using gel permation chromatography (GPC), column TESSEK HEMA-BIO 1000, eluent 1 M NaCl solution in water buffered with 0.05 M NaH_2PO_4. Calibration with poly [N^5-(2-hydroxyethyl)-L-glutamin] standards was applied.

Results and Discussion

Characterization of of Q-PMPSi

The measurement of the molar mass of Q-PMPsi using GPC in water solution of NaCl failed because the polymer was eluted at the low molar mass limit. The degree of polymerization of Q-PMPSi, however, can be estimated as follows:

In the previous paper (3), the conversion of chloromethylated PMPSi to its pyridinium salt Q-PMPSi is described as well as the subsequent Kroehnke transformation of the pendent quaternary ammonium groups in Q-PMPSi to nitrone groups. Both the chloromethylated PMPSi and the nitrone derivative (in contrast to Q-PMPSi) are soluble in tetrahydrofuran (THF) and their M_w, as determined by GPC in THF using polystyrene standards calibration, were 15000 and 7000, respectively (the polydispersity was about 4). One can judge, therefore, that M_w of Q-PMPSi is between 7000 and 15000.

Similarly, the degree of chloromethylation (20 mol%) was determined by H-NMR and quantitative conversion of chloromethylated PMPSi ---> Q-PMPSi ---> nitrone derivative was checked by elemental analysis and UV-vis spectra of the nitrone derivative (see ref. 3) The degree of substitution in Q-PMPSi, therefore, should be about 20 mol %.

Photrodegradation of Q-PMPSi

In Fig. 1, The UV absorption spectra of the Q-PMPSi in aqueous solution during UV irradiation are shown. The experimental conditions were the same as those for the photopolymerization. A blue-shift of λ_{max} as well as a strong decrease in absorbance during UV illumination are typical of polysilanes (1) and indicate photoscission with formation of silyl radicals. It should be pointed out here that a similar photodegradation pattern was obtained also with the parent (non-modified) PMPSi, i.e., the rates of production of silyl radicals are comparable in both cases. From the comparision of the absorption spectrum of Q-PMPSi and the emission spectrum of the used UV source it follows, that the strong emission line at about 317 nm is predominantly responsible for the observed photodegradation (together with the weaker line at 339 nm)

Table 1. Photopolymerization of hydrophilic vinyl monomers in 5 wt.% aqueous solutions initiated with Q-PMPSi, irradiated at 317 nm

Monomer	Q-PMPSi concentration (wt.%)	Irradiation time (min)	Polymer yield (%)
AA 1	0.01	10	44
AA 2	0.01	20	54.4
AA 3	0.01	40	64.6
AA 4	0.05	10	72
AA 5	0.0025	10	30
MMA	0.01	10	50
AM	0.01	10	41
HEMA	0.01	10	22.6
VP	0.01	10	11

AA - Acrylic Acid; MMA - Methacrylic Acid; AM - Acryl Amide; HEMA - 2-Hydroxyethyl Methacrylate; VP - 1-Vinyl-2-pyrrolidone

Photopolymerization in aqueous solutions

Preliminary experiments showed that silyl radicals formed by photodegradation of Q-PMPSi are able to initiate the polymerization of acrylic acid (AA), methacrylic acid (MMA), their sodium salts, acrylamide (AM), 2-hydroxyethyl methacrylate (HEMA) and 1-vinyl-2-pyrrolidone (VP) (concentrations of Q-PMPSi between 0.0025 and 0.05 wt.% were used).

For more detailed experiments AA was chosen as a representative monomer. When the irradiated 5 % solution of AA in water containing Q-PMPSi was not stirred, the photopolymerization took place even in air. When stirred, however, the diffusion of oxygen into the reaction mixture was quite rapid and the polymerization was inhibited. Therefore, the main set of experiments with AA was performed under nitrogen. Due to the high molar absorptivity of Q-PMPSi (ϵ = 2100 $l.mol^{-1}.cm^{-1}$ at 317 nm) we preferred stirring during photopolymerization, in order to maintain the uniform irradiation of the solution.

The results are summarized in Tab. 1 and Fig. 2. One can see (curve 1) that after reaching a certain value (about 0.005 wt.%) the yield of poly(acrylic acid) (PAA) depends only slightly on the Q-PMPSi concentration. It is possible to attribute this effect (at least partly) to the high initial absorbances of concentrated Q-PMPSi solutions: The initial absorbance of a 0.05 wt.% solution of Q-PMPSi was about 4.4 at λ_{max} and, therefore, not all Q-PMPSi molecules were simultaneously irradiated in this case. Also, at high Q-PMPSi concentration the recombination of radicals may occur more frequently.

The polymerization kinetics of AA in the presence of 0.01 wt. % of Q-PMPSi (A=0.87) are presented by curve 2 in Fig. 2. As the irradiation proceeds, Q-PMPSi is split into short chains with low absorptivity at 317

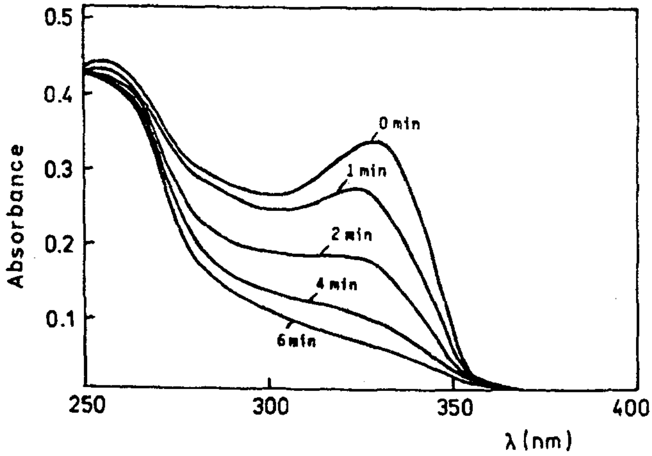


Figure 1: UV spectra of 0.002 wt.% aqueous solution of Q-PMPSi recorded during UV irradiation at 317 nm, photon flux 1.5 x 10^{-10} Einstein / cm^2.s.

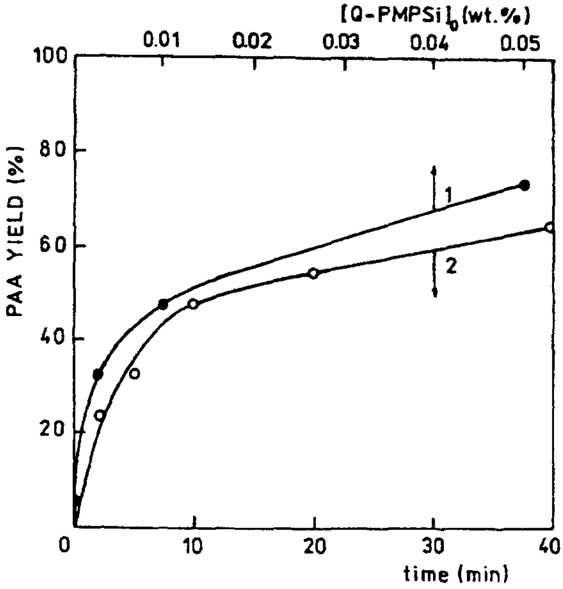


Figure 2: Polymer yield in the photopolymerization of acrylic acid at 317 nm, photon flux 1.5 Einstein / cm^2.s.; curve 1: dependence on initial concentration of photoinitiator [Q-PMPSi]$_0$, at 10 min of irradiation; curve 2: time dependence, [Q-PMPSi]$_0$ = 0.01 wt.%

nm (see Fig. 1) and the production of radicals is reduced. Consequently, the polymerization is also slowed down after app. 10 min.

Our attempts to determine the molar mass of the PAA using GPC in aqueous NaCl solution failed due to the considerable tendency of PAA to form aggregates.

Experiments with other hydrophilic monomers in aqueous solutions are also summarized in Table 1. The yields of PAM and PMMA polymers are comparable with those of PAA, whereas the PVP and PHEMA yields are lower. As expected, PHEMA precipitated from the solution during irradiation. Molar masses were determined by GPC using aqueous NaCl solution as eluent for PAM (M_w = 124000) and PVP (M_w = 120000).

Photopolymerization in monomer films

Whereas Q-PMPSi is practically insoluble in AA and VP, its aqueous solutions are easily miscible with these monomers, provided the content of water in the resulting mixture is at least 5 wt.%. Probably, water acts as a compatibilizing agent.

In the experiments with AA layers, 50 μl of 5 wt.% aqueous solution of Q-PMPSi was dissolved in 500 μl of monomer. A solid non-sticky film of PAA was formed during 5 min of irradiation under nitrogen. In air, however, practically no polymerization occured. The inhibition of polymerization by diffusing oxygen is obviously quite efficient in this case. Since some amines were reported to stabilize certain radical photoinitiator systems, including those containing polysilanes, towards oxygen (2) , we added triethanolamine (TEA) to the reaction mixture. However, TEA had no apparent effect.

In conclusion, Q-PMPSi is capable of polymerizing app. 500 μm thick AA films, but only under inert atmosphere. Similar results were obtained with MAA. For comparison, we used the commercial photoinitiator Irgacure 500 (1:1 mixture of benzophenone and 1-hydroxycyclohexyl phenyl ketone, CIBA Geigy) under the same conditions. In this case the sensitivity toward oxygen was similar to that observed with the Q-PMPSi initiator. Therefore, regarding the sensitivity of the polysilane photoinitiator system to oxygen, our results are not in agreement with those of West et al. (2). If any oxygen scavenging species is formed at all in our reaction system during irradiation, its concentration is not high enough to prevent inhibition by the diffusing oxygen.

References

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