Long wavelength photoinitiated cationic polymerization using diphenyliodonium salt and catena-poly(phenyl-4-phenylphenylsilicon)

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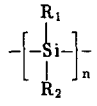
The photolysis of catena-poly(phenyl-4-phenylphenylsilicon) at $\lambda_{inc} = 365-400$ nm leads to products (probably free radicals) which are oxidized by diphenyliodonium ions. The resulting ionic species is capable of readily initiating the cationic polymerization of tetrahydrofuran, n-butyl vinyl ether, cyclohexene oxide and *N*-vinylcarbazol.

(Keywords: cationic photopolymerization; polysilanes)

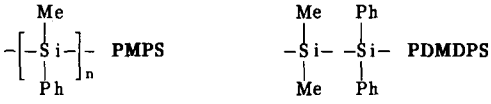
Introduction

Recently, it has been shown that, in conjunction with *N*-ethoxypyridinium hexafluorophosphate ($EMP^+PF_6^-$), catena-poly(alkyl aryl silicon)s, commonly denoted as poly(alkylarylsilane)s, of the general structure:



can be used as photoinitiators for the cationic polymerization of cyclic ethers, such as cyclohexene oxide (CHO), and vinyl ethers, such as n-butyl vinyl ether (BVE)[1].

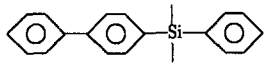
The polysilanes used so far as photoinitiators for cationic polymerizations, catena-poly(methylphenylsilicon), PMPS, and catena-poly(dimethyldiphenylsilicon), PDMDPS, have absorption maxima around 340 nm.



Repeating units of statistical copolymer

For practical applications, catena-polysilicons absorbing light at much longer wavelengths should be more appropriate than PMPS or PDMDPS, because most commercially available lamps emit strongly at $\lambda > 350$ nm.

As will be reported below, catena-poly(phenyl-4-phenylphenylsilicon), PPBPS, that has been synthesized recently in our laboratory fulfils this requirement.



Repeating unit of PPBPS

As can be seen from *Figure 1*, the absorption spectrum of PPBPS extends to wavelengths exceeding 400 nm with a maximum at ~382 nm. It turned out that PPBPS is decomposed upon irradiation at $\lambda_{inc} = 370$ nm. At this wavelength, diphenyliodonium ions (Ph_2I^+) that have strong oxidation power [$E^{red}_{1/2} = -0.2$ V (vs. SCE)] do not absorb light. Therefore, irradiations of monomer systems containing both $Ph_2I^+PF_6^-$ and PPBPS were performed at 370 nm and it was found that the polymerization of tetrahydrofuran (THF), *N*-vinylcarbazol (NVC), BVE and CHO was readily initiated.

Experimental

Monomers and solvents. THF (Aldrich) was stored over NaOH for 24 h, filtered and distilled from CaH_2. Subsequently, it was refluxed under N_2 with sodium and distilled again. BVE (EGA) was washed with aqueous NaOH solution. After drying with $CaCl_2$ and Na_2SO_4

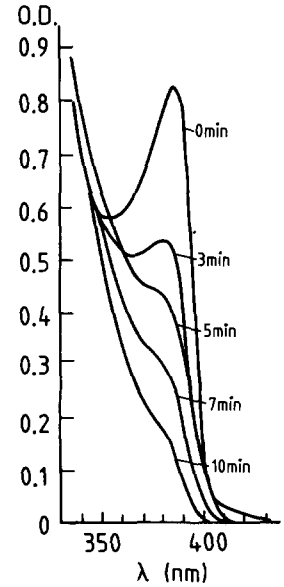


Figure 1 Irradiation of PPBPS at $\lambda_{inc} = 370$ nm in THF solution at room temperature. Optical absorption spectra recorded after various irradiation times. [PPBPS] = 4.8×10^{-5} mol dm^{-3}

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it was distilled from CaH_2 at 94°C. CHO (Aldrich) was washed with aqueous NaOH solution, dried over $CaCl_2$ and distilled over CaH_2. NVC (Fluka) was recrystallized from ethanol. CH_2Cl_2 (Aldrich) was dried over CaH_2 and distilled. Diphenyliodonium hexafluorophosphate was prepared as described previously[2].

Synthesis of phenyl-4-phenylphenyl dichlorosilane. Phenyltrichlorosilane (0.2 mol) was reacted with 4-bromomagnesium biphenyl (0.17 mol) in boiling diethyl ether. After MgClBr was filtered off, diethyl ether and unreacted phenyltrichlorosilane were distilled off at $\sim 6.7 \times 10^3$ Pa.

Crude phenyl-4-phenylphenyl dichlorosilane was twice distilled over a Vigreux column (b.p. ~200°C at ~67 Pa). The yield was 10%.

Synthesis of catena-poly(phenyl-4-phenylphenylsilicon). Phenyl-4-phenylphenyl-dichlorosilane (5.8 g, 0.0176 mol) was added dropwise to a dispersion of sodium (5 g, 0.065 mol) in boiling toluene. After 15 min the dark greenish reaction mixture was cooled down to room temperature and 2-propanol (20 cm^3) and then water (100 cm^3) were slowly added. The precipitated polymer was extracted with toluene. The insoluble portion was separated by centrifugation (30 min at 15 000 rev min^{-1}). Finally, 1.3 g polymer, corresponding to a yield of 29%, were precipitated with methanol. Apart from THF the polymer is soluble in benzene, toluene, $CHCl_3$ and CH_2Cl_2. The average molar mass is relatively low: $M_w = 2500$ (g.p.c., polystyrene calibration). U.v. absorption: $\lambda_{max} = 382$ nm, $\varepsilon_{382} = 1900$ dm^3 mol^{-1} cm^{-1}. I.r. absorption bands (cm^{-1}): 3040 (m), 3020 (m, phenyl stretching), 2920 (terminal 2-propoxyl group), 1590 (m), 1480 (m), 1425 (Ph–Si, m), 1380 (m), 1090 (Ph–Si), 825 (m), 758 (s), 735 (s), 695 (Si–Si, vs) 650 (m), 555 (m), 465 (Si–Si, broad, m). ^1H n.m.r. δ: 7.2 ppm (with a broad shoulder).

Polymerizations. Neat THF containing given amounts of PPBPS and $Ph_2I^+PF_6^-$ was polymerized in rectangular quartz ampoules (optical path length 1 cm) at room temperature. Prior to irradiation at $\lambda_{inc} = 370$ nm the ampoules were degassed in a high vacuum system and sealed. BVE, CHO and NVC were polymerized in CH_2Cl_2 solutions containing given amounts of PPBPS and $Ph_2I^+PF_6^-$. Prior to irradiation at $\lambda_{inc} = 370$ nm, Ar was bubbled through the solutions. For the irradiations a xenon lamp (Osram, XBO 450 W) in conjunction with a monochromator (Polytech, model GM 252) was used. Poly(n-butyl vinyl ether), poly(cyclohexene oxide) and poly(*N*-vinylcarbazol) formed during the irradiation were precipitated with methanol. Poly(tetrahydrofuran) was precipitated with water. Weight average molar masses were determined by light scattering measurements ($\lambda_{obs} = 546$ nm) using a Sofica apparatus.

Results

Photolysis of PPBPS in THF solution. PPBPS was irradiated at $\lambda_{inc} = 370$ nm in dilute Ar-saturated THF solution and the change in the optical absorption spectrum was recorded as a function of irradiation time. *Figure 1* shows optical absorption spectra of PPBPS recorded in THF solution before irradiation and after various irradiation times. One can see that, with increasing irradiation time, the maxima of the absorption spectra are shifted to lower wavelengths. This behaviour is typical of catena-polysilicons undergoing main-chain scission[3]. It originates from the fact, that λ_{max} decreases with decreasing molar mass (chain length) of the polymer. This behaviour was also found with other catena-polysilicons studied in our laboratory: catena-poly(methylphenylsilicon)[4] and catena-poly[(dimethyl-silicon)(diphenylsilicon)][1]. Therefore, it is concluded that PPBPS also degrades very effectively upon u.v. irradiation in THF solution.

Polymerization of THF. THF containing only $Ph_2I^+PF_6^-$ did not polymerize upon irradiation at $\lambda_{inc} \geqslant 365$ nm. However, polymerization took place upon addition of PPBPS. This can be seen from the conversion–time plot in *Figure 2* and also from *Table 1*. The conversion increases linearly with irradiation time after an induction period, as is seen from *Figure 2*. The induction period may be due to an impurity which is present in a small amount and which is consumed in the initial stages of the polymerization. The data in *Table 1* demonstrate that the polymerization of THF is initiated by irradiation in the wavelength range 365–400 nm. The average molar mass is relatively high (1.3×10^5–2.7×10^5). It is known that the cationic polymerization of THF exhibits living character with neither termination nor transfer taking place[5,6] provided impurities are absent. In most cases, small amounts of nucleophilic impurities are present in the polymerizing system, which terminate the growing chains.

Polymerization of BVE, CHO and NVC. These monomers polymerized upon irradiation at $\lambda_{inc} = 370$ nm at room temperature in CH_2Cl_2 solution containing PPBPS and $Ph_2I^+PF_6^-$. In the absence of PPBPS

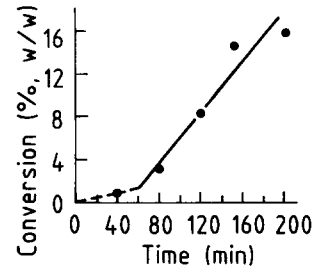


Figure 2 Photopolymerization of neat THF at room temperature ($\lambda_{inc} = 370$ nm). [PPBPS] = 1.3×10^{-3} mol dm^{-3}. [$Ph_2I^+PF_6^-$] = 5.0×10^{-3} mol dm^{-3}. Plot of the conversion of the monomer to polymer *versus* irradiation time

Table 1 Photoinitiated cationic polymerization of THF containing $Ph_2I^+PF_6^-$ (5×10^{-3} mol dm^{-3}) and PPBPS (1.32×10^{-3} mol dm^{-3}) at room temperature

λ_{inc} (nm)	Conversion[a] (wt%)	M_w[b] (g mol^{-1})
365[c]	0	–
365	10	2.1×10^5
370	15	1.3×10^5
380	10	1.7×10^5
400	6	2.7×10^5

[a]Irradiation time: 150 min
[b]Determined by light scattering measurements
[c]In the absence of PPBPS

Table 2 Polymerization of various monomers in CH_2Cl_2 solution containing PPBPS (1.32×10^{-3} mol dm^{-3}) and $Ph_2I^+PF_6^-$ (5×10^{-3} mol dm^{-3}) at room temperature ($\lambda_{inc} = 370$ nm)

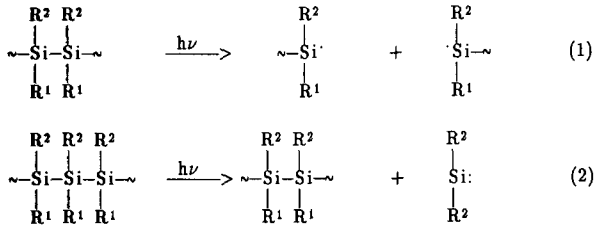
Monomer	Concentration (mol l^{-1})	t_{irr} (min)	Conversion (wt%)	M_w[a] (g mol^{-1})
BVE	7.7	5	74.7	–
CHO	5.7	120	19.6	7.3×10^4
NVC	1.0	1	76.0	7.5×10^5

[a]Determined by light scattering measurements

polymer was not generated. Typical results are presented in *Table 2*. Regarding BVE, the polymer was found to be insoluble in the reaction mixture. Poly(n-butyl vinyl ether) started to precipitate right after the onset of irradiation. Since it was difficult to purify the polymer, the molar mass was not determined in this case.

Conclusions

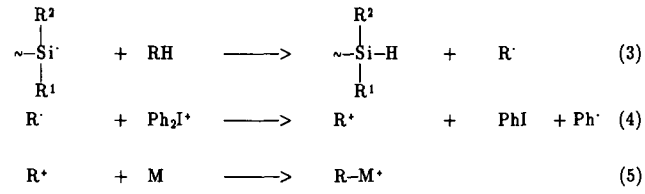
The results show that, upon irradiation at $\lambda_{inc} = 370$ nm, the system catena-poly(phenyl-4-phenylphenylsilicon)/$Ph_2I^+PF_6^-$ is capable of initiating the cationic polymerization of appropriate monomers such as THF, BVE, CHO and NVC. The present state of knowledge does not permit any conclusions on the nature of the initiating species. It is known[7] that u.v. irradiation of catena-polysilicons yields silyl radicals and silylene biradicals:



(1)

(2)

Regarding the systems studied in this work, various processes involving silicon-centred radicals and ending up in the formation of reactive cationic species can be suggested. For example, silicon-centred radicals could react with iodonium ions to give sililenium ions which attack the monomer. Moreover, hydrogen abstraction from monomer or solvent molecules by silicon-centred radicals could lead to secondary radicals capable of undergoing electron transfer reactions with iodonium ions. The resulting cations would act as initiating species:



(3)

(4)

(5)

Studies concerning the initiation mechanism are in progress in our laboratories.

Acknowledgement

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