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RATE CONSTANTS OF THE REACTION OF SILYL MACRORADICALS GENERATED BY CHAIN CLEAVAGE OF POLY(DIHEXYL SILYLENE) WITH OLEFINIC MONOMERS

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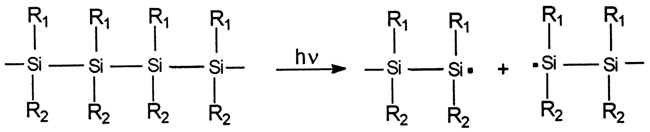
Key Words: Poly(Dihexyl Silylene), Main-Chain Cleavage, Silyl Macroradicals, Olefinic Monomers

ABSTRACT

The flash photolysis of poly(dihexyl silylene), PDHeSi, in tetrahydrofuran solution at λ_{inc} = 347 nm (flash length: 20 ns) and ambient temperature yields silyl macroradicals that strongly absorb light at 370 nm. Recording the decay of the optical density at λ_{obs} = 370 nm rate constants of reactions of the silyl macroradicals were measured. The silyl macroradicals undergo a self reaction with a rate constant $2k_{R+R} = 1.9x10^9 dm^3 mol^{(1} s^{(1)}$. Moreover, they are highly reactive towards olefinic monomers. The following rate constants k_{R+M} (in units of $dm^3 mol^{(1} s^{(1}$) were determined: $1.6x10^8$, styrene; $1.0x10^8$, acrylonitrile; $7.6x10^7$, methyl methacrylate; $6.5x10^7$, vinyl acetate; $1.6x10^7$, butyl acrylate; $7.3x10^6$, methacrylonitrile; $< 10^5$, n-butyl vinyl ether.

INTRODUCTION

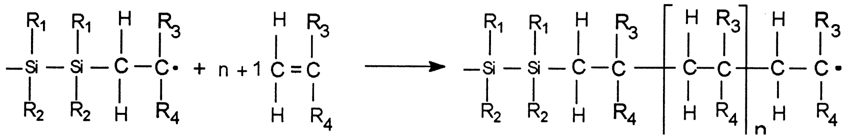
Silyl macroradicals generated by the photolysis of polysilylenes according to Reaction 1:



$$-\underset{R_2}{\overset{R_1}{Si}}-\underset{R_2}{\overset{R_1}{Si}}-\underset{R_2}{\overset{R_1}{Si}}-\underset{R_2}{\overset{R_1}{Si}}- \xrightarrow{h\nu} -\underset{R_2}{\overset{R_1}{Si}}-\underset{R_2}{\overset{R_1}{Si}}\cdot + \cdot\underset{R_2}{\overset{R_1}{Si}}-\underset{R_2}{\overset{R_1}{Si}}- \quad (1)$$

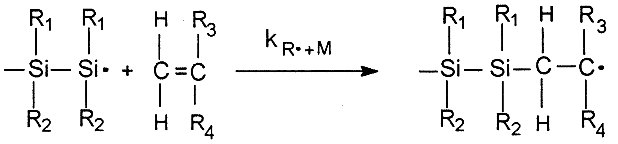
are capable of initiating the free radical polymerization of olefinic monomers such as methyl methacrylate (MMA) and styrene (St) [1-4].

The initiation step of the chain reaction leading to polymer according to Reaction 2:



$$-\underset{R_2}{\overset{R_1}{Si}}-\underset{R_2}{\overset{R_1}{Si}}-\underset{H}{\overset{H}{C}}-\underset{R_4}{\overset{R_3}{C}}\cdot + n+1\ \underset{H}{\overset{H}{C}}=\underset{R_4}{\overset{R_3}{C}} \longrightarrow -\underset{R_2}{\overset{R_1}{Si}}-\underset{R_2}{\overset{R_1}{Si}}-\underset{H}{\overset{H}{C}}-\underset{R_4}{\overset{R_3}{C}}-\left[\underset{H}{\overset{H}{C}}-\underset{R_4}{\overset{R_3}{C}}\right]_n-\underset{H}{\overset{H}{C}}-\underset{R_4}{\overset{R_3}{C}}\cdot \quad (2)$$

is thought to be the reaction of the silyl macroradical with the monome



$$-\underset{R_2}{\overset{R_1}{Si}}-\underset{R_2}{\overset{R_1}{Si}}\cdot + \underset{H}{\overset{H}{C}}=\underset{R_4}{\overset{R_3}{C}} \xrightarrow{k_{R\cdot+M}} -\underset{R_2}{\overset{R_1}{Si}}-\underset{R_2}{\overset{R_1}{Si}}-\underset{H}{\overset{H}{C}}-\underset{R_4}{\overset{R_3}{C}}\cdot \quad (3)$$

Since nothing has been reported so far on the reactivity of silyl macroradicals generated by main-chain cleavage of polysilylenes according to Reaction 1, it was attempted in this work to measure the bimolecular rate constant k_{R+M}.

For this purpose, two methods were employed:

Method A. Polysilylene was irradiated in tetrahydrofuran (THF) solution with single light flashes emitted from a ruby laser λ_{inc} = 347 nm) and formation and decay of the transient absorption of the silyl macroradical at 370 nm was monitored in the absence and presence of monomer. At sufficiently high monomer concentration [M] the decay of the silyl macroradical absorption follows pseudo-1st order kinetics and the rate constant k_{R+M} is calculated from the slope of the straight line obtained by plotting k_1(pseudo) vs. the monomer concentration according to Equation 4:

$$k_1(\text{pseudo}) = k_0 + k_{R+M}[M] \tag{4}$$

Upon employing this method care had to be taken to avoid disturbances due to the simultaneous absorption of intermediates different from silyl macroradicals at the detection wavelength (370 nm). In this connection, two species have to be considered: silyl macroradical ions and silylene (SiR_2) [5]. Whereas, the latter species absorbs light only negligibly at 370 nm, silyl macroradical ions, although generated with a rather low quantum yield are quite strong light absorbers in the case of some polysilylenes because of high extinction coefficients [6]. This applies especially to polysilylenes with aromatic side groups. Therefore, formation and decay of macroradical ions were measured independently by photo-current measurements.

Method B. In several cases, the decay of the absorption at 370 nm of the silyl macroradical is accompanied by the build-up of a new absorption due to the formation of carbon-centered radicals according to reaction (3) which can be written in the general form of Equation 3a:

$$R\bullet + M \longrightarrow R\text{-}M\bullet \tag{3a}$$

Because of the long lifetime of the R-M• radicals their optical absorption remains practically constant in the 100 µs range, i.e. the transient absorption decays after the flash at first according to the consumption of silyl macroradicals and later reaches a plateau corresponding to the R-M• radicals. Considering that silyl macroradicals either recombine with a rate constant k_{R+R} or react with monomer with a rate constant k_{R+M} the fraction f_{R+M} of silyl macroradicals undergoing Reaction 3 is given by Equation 5:

$$f_{R+M} = k_{R+M}[M]/(k_{R+M}[M] + k_{R+R}[R\bullet]_0) \tag{5}$$

Taking into account that the following relationships hold

$$[R\bullet]_0 = [R\text{-}M\bullet]_\infty = OD_\infty(\text{sat})/\varepsilon d \tag{6}$$

$$f_{R+M}[R\bullet]_0 = [R\text{-}M\bullet]_M = OD_\infty(M)/\varepsilon d \tag{7}$$

it turns out that

$$f_{R+M} = OD_\infty(M)/OD_\infty(sat) \qquad (8)$$

and Equation 9 results by combining Equations 5 and 8:

$$OD_\infty(sat)/OD_\infty(M) = 1 + (k_{R+R}[R\bullet]_0/k_{R+M}[M]) \qquad (9)$$

Here, the following denotations are used:

$[R\bullet]_0$: initial concentration of silyl macroradicals. $[R\text{-}M\bullet]_\infty = OD_\infty(sat)/\varepsilon d$: concentration of growing chain radicals at total conversion of silyl radicals into R-M• radicals, i.e. at high monomer concentration. $[R\text{-}M\bullet]_M = OD_\infty(M)/\varepsilon d$: concentration of growing chain radicals at partial conversion of macrosilyl radicals into R•M• radicals.

Insertion of $[R\bullet]^0 = \Phi_R D_{abs}$ into Equation 9 yields Equation 10:

$$OD_\infty(sat)/OD_\infty(M) = 1 + (k_{R+R}\Phi_R D_{abs}/k_{R+M}[M]) \qquad (10)$$

Accordingly, k_{R+M} is calculated from the slope of the straight line obtained by plotting OD_∞ (sat)/OD_∞(M) vs. 1/[M] according to Equation 11:

$$k_{R+M} = k_{R+R}\Phi_R D_{abs}/\text{slope} \qquad (11)$$

EXPERIMENTAL

Materials

Methyl methacrylate, MMA, vinyl acetate, VA, and styrene, St, were purchased from E. Merck. Butyl acrylate, BA, and methacrylonitrile, MAN, were obtained from Fluka and butyl vinyl ether, BVE, from Aldrich. All monomers were distilled prior to use. Those containing a stabilizer were washed with NaOH solution and with water several times and then dried over $CaCl_2$ prior to distillation. Tetrahydrofuran (Uvasol, E.Merck) passed through an Al_2O_3 column prior to use.

Poly(dihexyl silylene), PDHeSi, was prepared with the aid of the Wurtz coupling method by reacting dichlorodihexylsilane with metallic sodium dispersed in toluene at 110°C. The polymer was extracted with diethyl ether to remove the low molar mass fraction and reprecipitated from THF solution with 2-propanol.

Flash Photolysis

All experiments were performed with a ruby laser (Korad model K1 QS2) that was operated in conjunction with an ADP frequency doubler (flash length: 20 ns, λ_{inc} = 347 nm). A flow system containing a rectangular quartz cell with two platinum electrodes was used. By directing the analytical light beam generated by a xenon lamp through the space between the electrodes it was possible to measure simultaneously changes in the optical density and in the electrical conductivity (R = 333 Ω) of the solution in the cell. Generally, the experiments were performed at [PDHeSi] = $4x10^{-3}$ base mol dm^{-3} corresponding to OD = 0.2 ($\varepsilon_{347\ nm}$(PDHeSi) = 100 $dm^3mol^{-1}cm^{-1}$, d = 0.5 cm). The absorbed dose per flash was determined with the aid of the benzophenone/naphthalene actinometer [$\varepsilon_{425\ nm}$(T) = $1.51x10^4$ dm^3 $mol^{-1}cm^{-1}$, (ΦT) = 1.0].

Theoretical Calculations

The geometrical structures of certain carbon-centered and silicon-centered radicals were calculated with the aid of semiempirical and *ab initio* methods. A detailed description of the methods used has been given previously [7].

RESULTS AND DISCUSSION

Experiments were performed with several polysilylenes in THF solution at room temperature, but this paper exclusively reports results obtained with poly(dihexyl silylene). It appears that in this case the transient absorption at 370 nm is almost completely due to silyl macroradicals and that the decay rate of this absorption in the presence of monomers clearly reflects the reaction of the silyl macroradical with the monomer. This was shown by simultaneously measuring the optical density (OD) and the photocurrent (i_{photo}) in the absence and presence of monomer. As can be seen from Figure 1 both transients, i_{photo} and OD, are formed during the 20 ns flash both in the absence and presence of monomer. In the absence of monomer the photocurrent decays much faster than the optical density. Moreover, in the presence of monomer (in this case, BA) the decay of the transient OD is strongly influenced by the monomer in contrast to the decay of i_{photo} that is not affected by the monomer. It is, therefore, concluded that the decay of the transient absorption in the presence of monomer reflects solely the reaction of silyl macroradicals and not that of silyl macroradical ions. In the text below the determination of the bimolecular rate constant k_{R+M} of silyl macrorad-

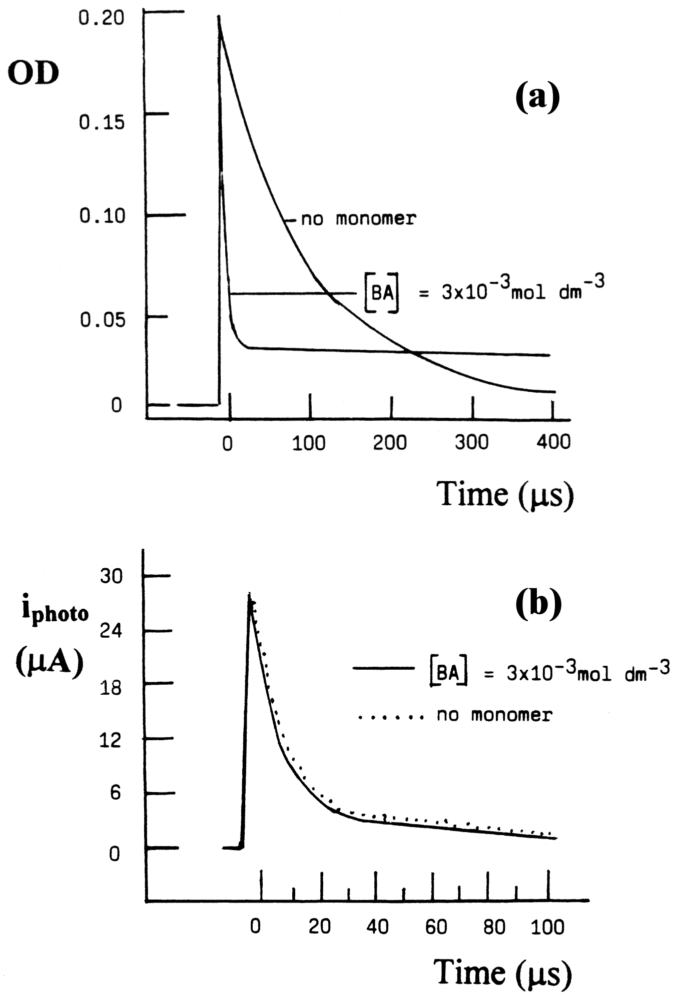


Figure 1. Photolysis of PDHeSi ($4x10^{-3}$ base mol dm^{-3}) in ar-saturated THF solution Dabs = $3.6x10^{-5}$ Einstein dm^{-3}. Kinetic traces depicting formation and decay of the transient absorption at 370 nm (a) and of the transient photocurrent (b) in the absence and presence of BA ($3x10^{-3}$ mol dm^{-3}).

icals generated from PDHeSi with butyl acrylate is described in detail as a typical example. Analogously, rate constants were determined with other monomers and the results of these determinations are compiled in Table 1. As can be seen from Equation 10, the determination of k_{R+M} according to method B requires the knowledge of k_{R+R}, the bimolecular rate constant for the self reaction of silyl macroradicals. Since the value of k_{R+R} is not available from the literature its determination was attempted and this is dealt with in the next section.

TABLE 1. Rate Constants of the Reaction of Silyl Macroradicals Generated by the Photolysis of PDHeSi with Various Olefinic Monomers, Measured in THF Solution at Ambient Temperature

Monomer	k_{R+M} (Method A) ($dm^3mol^{-1}s^{-1}$)	k_{R+M} (Method B) ($dm^3mol^{-1}s^{-1}$)
St	$1.6x10^8$	
AN	$1.0x10^8$	
MMA	$7.6x10^7$	$7.9x10^7$
VA	$6.5x10^7$	
BA	$1.6x10^7$	$9.1x10^7$
MAN	$7.3x10^6$	
BVE	$< 10^5$	

Determination of the Rate Constant k_{R+R}

The bimolecular rate constant for the self reaction of silyl macroradicals k_{R+R} was determined by measuring the decay of the absorption of silyl macroradicals at 370 nm in the absence of additives. This decay follows 2nd order kinetics. Plots of the reciprocal optical density vs. time recorded at various laser intensities yielded straight lines indicating that Equation 12, which is derived from Equation 13, holds:

$$1/OD_t \;=\; 1/OD_0 \;+\; (2k_{R+R}/ed)t \qquad (12)$$

$$1/[R\bullet]_t \;=\; 1/[R\bullet]_0 \;+\; 2k_{R+R}{}^{t} \qquad (13)$$

As can be seen from Figure 2, the first halflife $(\tau 1/2)^1$ depends linearly on the reciprocal absorbed dose per flash, D_{abs}. This dependence is expected from Equation 14 that holds if 2nd order kinetics apply:

$$(\tau 1/2)^1 = 1/(2\,k_{R+R}[R\bullet]_0) = 1/(2\,k_{R+R}\;(\Phi_R\,D_{abs}) \qquad (14)$$

2 k_{R+R}= $1.9x10^9$ dm^3 mol^{-1} s^{-1} was calculated from the slope of the straight line in Figure 2 using ($\Phi_R = 2\Phi(S) = 1.76$. (ΦS) = 0.88 main-chain scissions per photon were determined upon continuous irradiation of PDHeSi in THF solution with the aid of size exclusion measurements performed with the irradiated poly-

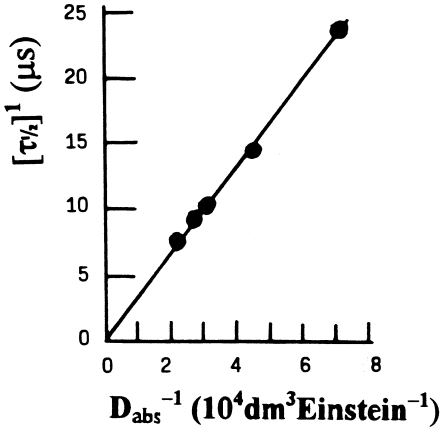


Figure 2. Photolysis of PDHeSi ($4x10^{-3}$ base mol dm^{-3}) in Ar-saturated THF solution. Plot of the halflife of the decay of the OD at 370 nm vs. the reciprocal absorbed dose per flash.

mer [8]. Provided the observed decrease in the average molar mass results exclusively from main-chain scissions giving rise to the formation of two silyl macroradicals per scission (Φ_R is equal to 2Φ (S)).

Determination of k_{R+M} with the Aid of Method A

All monomers except BVE significantly affected the decay of the absorption of the silyl macroradical at 370 nm. Typical kinetic traces recorded with BA are shown in Figure 3. The results obtained with the other monomers are included in Figure 4 where the pseudo-1st order rate constant k_1(pseudo) of the decay of the absorption at 370 nm is plotted *vs.* the monomer concentration. The values of k_{R+M} calculated with the aid of the slopes of the straight lines using Equation 4 are compiled in Table 1. From the rather high values, it is inferred that silyl macroradicals generated by the photolysis of PDHeSi are quite reactive towards several olefinic monomers. In this connection it must be pointed out that carbon-centered radicals generated with commonly used photoinitiators for free radical polymerization are much less reactive [9]. Notably, butyl vinyl ether did not affect the decay of the OD at 370 nm at concentrations up to $3x10^{-3}$ mol dm^{-3}. Therefore, it can be concluded that k_{R+M} is lower than about 10^5 dm^{3}mol^{-1}s^{-1} in this case.

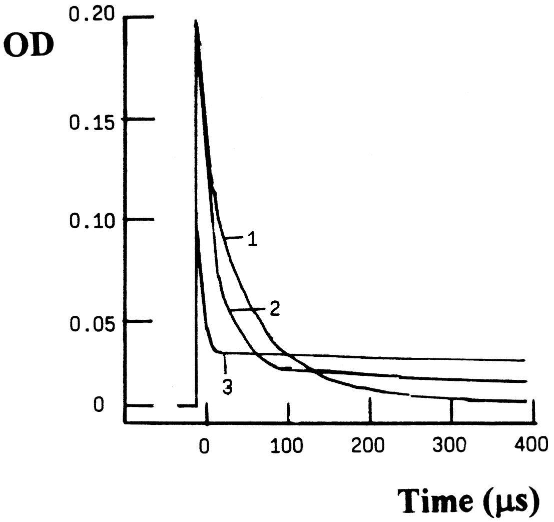


Figure 3. Photolysis of PDHeSi ($4x10^{-3}$ base mol dm^{-3}) in Ar-saturated THF solution containing BA (in mol dm^{-3}): $2x10^{-4}$ (1), 1x10-3 (2) and $3x10^{-3}$ (3). D_{abs} = $3.6x10^{-5}$ Einstein dm^{-3}. Plots of the OD at 370 nm vs. the time after the flash.

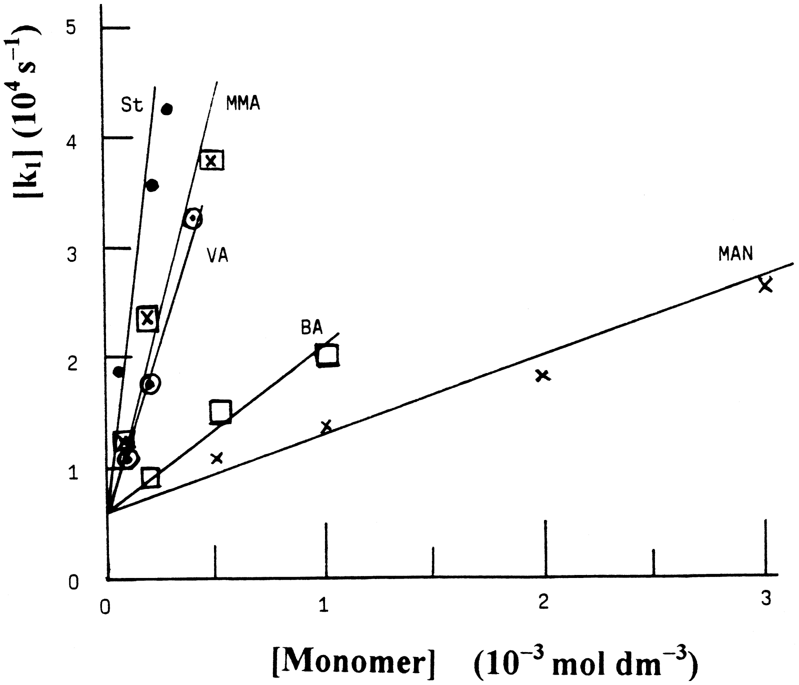


Figure 4. Determination of rate constants k_{R+M}. Plots of the 1st-order rate constant of the decay of the OD at 370 nm vs. the monomer concentration for variuos monomers (as indicated in the graph). D_{abs} = $3.6x10^{-5}$ Einstein dm^{-3}.

Determination of k_{R+M} with the Aid of Method B

This method was applicable only in those cases where the carbon-centered growing chain radical is substantially light-absorbing at 370 nm. This applies to MMA, BA and MAN. However, only in the cases of MMA and BA the evaluation of k_{R+M} was attempted. In the case of MAN, the absorption was extraordinarily high which might be due to the existence of radicals differing from growing chain radicals. Typically, the results obtained with BA are discussed here. Figure 3 shows kinetic traces recorded at various BA concentrations. It is clearly seen that the OD attained after several hundred microseconds increases with increasing monomer concentration. Figure 5a depicts how the reciprocal OD recorded at 400 μs increases with increasing reciprocal BA concentration. The intersection of the straight line with the ordinate corresponds to $OD_\infty(sat)$. With the aid of this value the ratio $OD_\infty(sat)/OD_\infty(M)$ was obtained and plotted vs. the reciprocal concentration of BA according to Equation 10). This plot is shown in Figure 5b. From the slope of the resulting straight line $k_{R+M} = 9.1x10^7$ $dm^3mol^{-1}s^{-1}$ is obtained using Equation 11 with $\Phi_R = 1.76$ and $D_{abs} = 3.6x10^{-5}$ Einstein dm^{-3}. The value of k_{R+M} determined in this way is about six times higher than that obtained with method A. Proceeding analogously, $k_{R+M} = 7.9x10^7$ $dm^3mol^{-1}s^{-1}$ is found in the case of MMA. This value is almost equal to that determined by method A. Generally, it is expected that method B yields less accurate values than method A. However, both methods give values of the same order of magnitude and, in this way, the high reactivity of silyl radicals towards several olefinic monomers is substantiated.

The high reactivity of silyl macroradicals generated by the photolysis of poly(dihexyl silylene) towards vinyl monomers is remarkable. In this connection, it is seemly to refer to earlier work by C. Chatgilialoglu *et al.* [10] concerning the reactivity of small silyl radicals. In that work, the rate constant of the reaction of triethylsilyl radicals with various compounds containing unsaturated groups was measured employing an indirect (competitive) method. Actually, the reaction of the triethylsilyl radical with benzil resulting in an adduct carbon-centered radical strongly absorbing at 378 nm was followed. This was necessary, because the triethylsilyl radical absorbs light only very weakly in the wavelength range appropriate for recording changes in the optical absorption as a function of time.

By contrast, silyl macroradicals generated by the photolysis of PDHeSi absorb light rather strongly and therefore, their reaction could be followed directly. Interestingly, also the triethylsilyl radical was found to be highly reac-

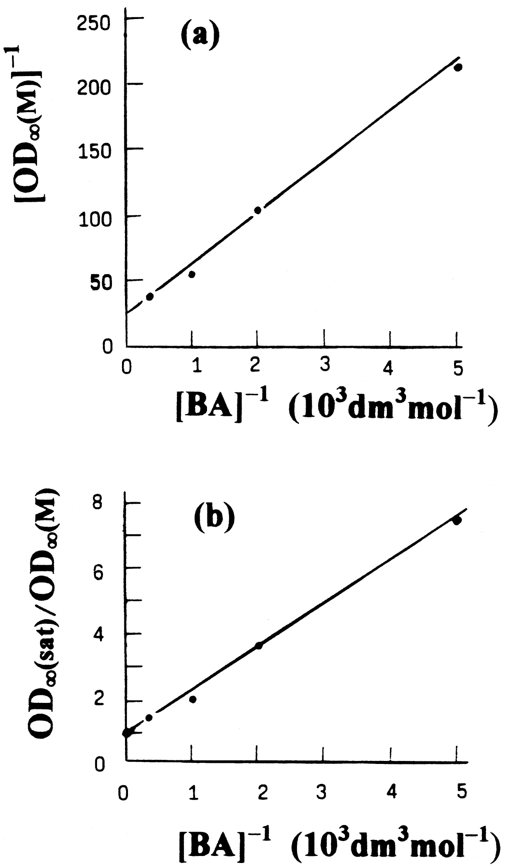
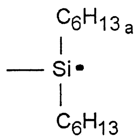
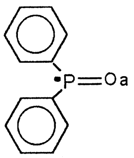
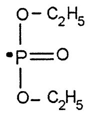
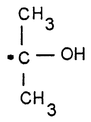
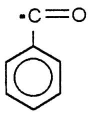


Figure 5. Photolysis of PDHeSi ($4x10^{-3}$ base mol dm^{-3}) in Ar-saturated THF solution containing BA at various concentrations. (a) Plot of the reciprocal OD_∞ (M) values measured at 370 nm (see Figure 3) vs. the reciprocal concentration of BA. (b) Plot of OD_∞(sat)/OD_∞(M) vs. the reciprocal concentration of BA according to Equation 10.

tive. The following bimolecular rate constants (all in units of $dm^3mol^{(1}s^{(1})$ were reported: $k_{R+M} = 2.2x10^8$ (St) and $k_{R+M} = 4.6x10^8$ (MMA). These values are to be compared with $k_{R+M} = 1.6x10^8$ (St) and $k_{R+M} = 7.6x10^7$ (MMA) determined in the present work. Whereas the agreement in the case of styrene is remarkably good, the large discrepancy in the case of MMA is puzzling and unexplainable, at present.

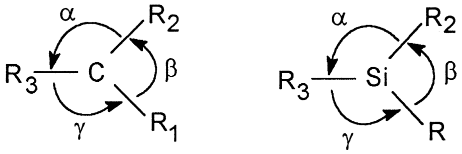
Another interesting aspect is the large difference beween the k_{R+M} values found for silicon- and carbon-centered radicals. As can be seen from Table 2 the

TABLE 2. Rate Constants of the Reaction of Various Radicals with Olefinic Monomers, Measured at Ambient Temperature (in Units of $dm^3mol^{-1}s^{-1}$)

Monomer					
St	$1.6x10^8$	$6.0x10^7$	$2.5x10^8$	$3.5x10^5$	$1.2x10^5$
MMA	$7.6x10^7$	$8.0x10^7$	$5.3x10^7$	$5.4x10^5$	$0.9x10^5$
AN	$1.0x10^8$	$2.0x10^7$	$2.6x10^6$	$1.6x10^5$	$0.2x10^5$
MAN	$7.3x10^6$	$5.0x10^7$	$1.1x10^8$		
BVE	$< 10^5$	$5.0x10^6$			

***the rate constants of the reaction of phosphorus- and carbon-centered radicals with monomers were determined earlier (see [9])**

rate constant of the silyl radical is one to two orders of magnitude larger than that of carbon-centered radicals, viz. the benzoyl radical and the 2-hydroxy propyl radical, that are typical for radicals produced by the photolysis of commercially available photoinitiators. Notably, the reactivity of the silyl radical under investigation is quite similar to that of phosphorus-centered radicals as can be seen from Table 2, where also k_{R+M} values of the reaction of two phosphinoyl radicals with olefinic monomers are listed. As in the case of the phosphorus-centered radicals the high reactivity of silyl radicals might be explainable in terms of their pyramidal structure that contrasts the planar or strongly flattened tetrahedral structure of carbon-centered radicals. Regarding small silyl radicals it has been pointed out earlier [11, 12] that the reactivity of silicon-centered radicals is expected to surpass that of corresponding carbon-centered radicals, and this should be due to the pyramidal structure, the greater size, the polarizability and the availability of the 3p unpaired electron of the silyl radical. This has been substantiated by calculating the geometric parameters of two silicon-centered radicals, namely the trimethyl silyl radical, $\bullet Si(CH_3)_3$, and the trimethylsilyl dimethylsilyl radical, $\bullet Si(CH_3)_2(Si(CH_3)_3$, and of two carbon-centered radicals, namely the methyl radical, $\bullet CH_3$, and the dimethyl hydroxy-methyl radical $\bullet CH_2OH(CH_3)_2$. The geometry of a radical center bearing three substituent is determined by the sum Σ of the angles α, β and γ ($\Sigma = \alpha + \beta + \gamma$):



Theoretically, one obtains $\Sigma = 329.5^0$ for a sp^3 structure and $\Sigma = 360^0$ for a sp^2 structure. Both semi-empirical and *ab initio* calculations yielded $\Sigma = 331.5^0$ and $\Sigma = 304.4^0$ for the radicals $\bullet Si(CH_3)_3$ and $\bullet Si(CH_3)_2(Si(CH_3)_3$, respectively, whereas $\Sigma = 360^0$ was obtained for the carbon-centered radicals. This proves that the silicon-centered radicals possess sp^3 geometry. It is likely that this also holds for the large silyl radicals generated by the photolysis of PDHeSi or other polysilylenes.

Regarding the reactivity of the silyl macroradicals towards the various monomers investigated in this work, it is to be noted that the rate constants obtained with the aid of frontier molecular orbital calculations vary in the same order as those experimentally determined by method A. Details will be reported elsewhere [13].

A reviewer has pointed out that silyl macroradicals, apart from the addition to carbon-carbon double bonds, could also abstract hydrogen from the monomer. Actually, it should be possible to discriminate between these two possibilities with the aid of the two methods A and B employed in this work, because method A yields an integrated rate constant comprising all reactions of the silyl macroradical with the monomer whereas method B allows to determine independently the rate constants of hydrogen abstraction from the monomer and of addition of the silyl macroradical to the double bond of the monomer. Provided both hydrogen abstraction from the monomer and addition to the monomer occurred simultaneously with the self reaction of silyl macroradicals, Equation 15 should hold instead of Equation 10:

$$OD_\infty(sat)/OD_\infty(M) = 1 + (k_{R+H}/k_{R+M}) + (k_{R+R}\Phi_R D_{abs}/k_{R+M}[M]) \qquad (15)$$

Here, k_{R+H} denotes the rate constant of the hydrogen abstraction reaction.

Obviously, k_{R+M} is still obtainable from the slope of the straight line if $OD_\infty(sat)/OD_\infty(M)$ is plotted *vs.* $[M]^{-1}$. However, the straight line should not intersect the ordinate at 1.0, but at a somewhat higher value. As can be seen from Figure 5b, this does not apply to BA. It is, therefore, concluded that, if hydrogen abstraction occurs at all, its rate constant would be at least one order of magni-tude lower than k_{R+M}. It remains to say that the discrepancy of the k_{R+M} values found for BA by the two methods is still an unsolved problem. But it is certainly not due to hydrogen abstraction. In the case of MMA, on the other hand, the k_{R+M} values obtained with both methods are almost equal. Also in this case method B does not reveal indications of the occurrence of hydrogen abstraction.

The question whether or not hydrogen abstraction might play a role in the reaction of silyl radicals with carbon-carbon double bonds containing compounds came up during gas phase studies of the reaction of $H_3Si\bullet$ radicals with ethylene and propylene by Loh *et al.* [14]. Careful reading of this paper reveals that the authors discarded the primarily made assumption that $H_3Si\bullet$ radicals abstract hydrogen from propylene.

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