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cis–trans photoisomerization of silylene-vinylene-*p*-phenylene polymers and their model compounds

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Abstract

The emission and photochemical properties of the poly[dimethylsilylene-*p*-phenylene-dimethylsilylene-(*E*)-vinylene-*p*-phenylene-(*E*)-vinylene] (*trans*-P) and its model compound (*E*,*E*)-{1,4-bis(2-dimethylphenylsilyl)ethenyl}benzene (*trans*-ST) were investigated in a quantitative manner. It was shown that both compounds exhibit similar properties indicating that the 2-dimethylphenylsilylethenylbenzene chromophore is responsible for the absorption and emission processes and for the reactivity in the lowest excited singlet states. The fluorescence quantum yields measured in dichloromethane were found to be small and equal to 0.032 and 0.008 for *trans*-P and *trans*-ST, respectively. On the other hand the *cis*-ST isomer was shown to be a nonfluorescent species. The model compounds and the polymer undergo the same type of efficient photochemical reaction, i.e. the *cis–trans* isomerization leading to the photo-stationary state depending on the excitation wavelengths. The photoisomerization reaction was studied quantitatively using UV and HPLC analyses. The initial isomerization quantum yields were relatively large (in the range of 0.14–0.49 depending on the excitation wavelengths and the solvent used). Quantum yields $\Phi_{trans \rightarrow cis}$ for the polymer *trans*-P and its model compounds *trans*-ST were found to be similar within the experimental errors (0.23 and 0.26, respectively, for irradiation with the monochromatic light $\lambda_{exc} = 313$ nm in dichloromethane). During prolonged irradiations, a photodegradation reaction of low efficiency (the quantum yield $<1 \times 10^{-2}$) was also observed in dichloromethane. It was shown that the UV absorption spectroscopy and the procedure applied can successfully be used for a quantitative description of the *cis–trans* photoisomerization mechanism of silylene-vinylene-*p*-phenylene polymers and its model compounds.

Keywords: *cis–trans* photoisomerization; Photostationary state; Photodegradation; Silylene-vinylene-*p*-phenylene polymers; Poly[dimethylsilylene-*p*-phenylene-dimethylsilylene-(*E*)-vinylene-*p*-phenylene-(*E*)-vinylene]; (*E*,*E*)-{1,4-Bis(2-dimethylphenylsilyl)ethenyl}benzene

1. Introduction

Polymers with silylene-bridged π-systems have been the subject of intense studies due to their potential applications in optoelectronic functional materials. In particular, phenylene-silylene-vinylene polymers with well-defined structures are of growing interest due to their efficient photo- and electroluminescent properties [1–7]. Therefore, Masuda and Kwak [8] have recently reported results on the photoisomerization of *trans*- and *cis*-poly(dimethylsilylenephenylenevinylene)s. They found that UV irradiation of these polymers and their model compounds led to photoproducts with various *cis*/*trans* concentration ratios. In their experiments, however, polychromatic UV light in the range 200–400 nm was used, and the photoreaction was analyzed only by means of UV absorption spectroscopy. This permitted only a qualitative description of the *cis–trans* photoisomerization of the silylenephenylenevinylene derivatives. The use of monochromatic irradiation light allowed not only for determination of initial quantum yields of isomerization, but also it is necessary to study the kinetics of the photoisomerizations and the formation of the photo-stationary state (see Eq. (1)) due to different absorption spectra of *trans* and *cis* isomers.

We have previously reported the syntheses of the first stereoregular *trans*-phenylene-silylene-vinylene polymers as well as their model compounds, *trans*-silylene-phenylene-vinylene, both polymer and model having well-defined structures. The polymer and its model were effectively synthesized via silylative coupling co(poly)condensation of bis(vinyldimethylsilylarenes)

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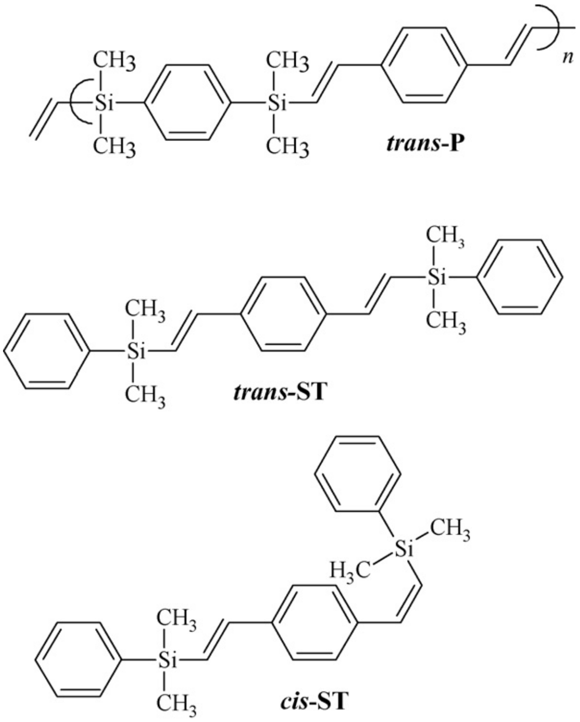


Scheme 1.

or condensation of vinylphenyldimethylsilane, respectively, with 1,4-divinylbenzene catalyzed by RuH(Cl)CO)(PCy$_3$)$_2$ [9–11].

The aim of this work is to present a detailed quantitative study of the photochemistry of such well-defined products as poly[dimethylsilylene-*p*-phenylene-dimethylsilylene-(*E*)-vinylene-*p*-phenylene-(*E*)-viny-lene] (*trans*-P) and its model compound: (*E*,*E*)-{1,4-bis(2-dimethylphenylsilyl)ethenyl}benzene (*trans*-ST) in solution (see Scheme 1). It was found that *cis*/*trans* isomerization was the main photoreaction leading to the formation of a photo-stationary state. When CH$_2$Cl$_2$ was used as the solvent, additional photoreactions – photodegradations of the irradiated compounds – were observed.

2. Experimental

2.1. Materials

The chemicals were obtained from the following sources: toluene, pentane, hexane, 1,4-bromobenzene, sodium hydride, calcium hydride were purchased from Fluka, CDCl$_3$ from Dr Glaser A.G. Basel, and vinylphenyldimethylsilane from Gelest. Vinyl bromide was purchased from Aldrich. Toluene and pentane were dried by distillation from sodium hydride; similarly, hexane was distilled from calcium hydride under argon. All liquid substrates were also dried and degassed by bulb-to-bulb distillation. The ruthenium complex RuH(Cl)(CO)(PCy$_3$)$_2$ was prepared on the basis of the procedure described in the literature [12]. Pure 1,4-divinylbenzene (DVB) was synthesized by a Ni-catalyzed coupling reaction between vinyl bromide and 1,4-bis(bromomagnesium)benzene [13]. The synthesis of poly[dimethylsilylene-*p*-phenylene-dimethylsilylene-(*E*)-vinylene-*p*-phenylene-(*E*)-vinylene] (P) was prepared according to the procedure described previously [9–11]. The molecular weight was determined by gel permeation chromatography (GPC): weight average molecular weight M_w is 17,600 and number average molecular weight M_n is 8800, the polydispersity index (PDI = $M_\mathrm{w}/M_\mathrm{n}$) is 2.0 and the number of mers n is 28.

(*E*,*E*)-{1,4-bis(2-dimethylphenylsilyl)ethenyl}benzene (*trans*-ST) was synthesized according to the following procedure: RuH(Cl)(CO)(PCy$_3$)$_2$ complex (19.5 mg, 2.69×10^{-2} mmol), toluene (5.4 ml), DVB (0.35 g, 2.69 mmol), and vinylphenyldimethylsilane (0.92 g, 5.65 mmol) were placed in a 15 ml mini-reactor with a condenser connected with a bubbler. Then, the reaction mixture was stirred and heated at 80 °C under an argon flow for 24 h. The reaction progress was monitored by GC and GC–MS. After that, this mixture was cooled to room temperature, and the excess solvent was removed under vacuum. The final product was isolated by the use of column chromatography with silica, using hexane as an eluent (R_f = 0.55), to yield *trans*-ST 0.944 g (2.38 mmol, 88% yield) as a white powder.

2.1.1. Analytical data

^{1}H NMR (CDCl$_3$; δ (ppm)): 0.42 (s, 12H, –CH_3); 6.56 (d, 2H, J_HH = 19.1 Hz, Si–*H*C=CH– C$_6$H$_4$–); 6.91 (d, 2H, J_HH = 19.1 Hz, Si–HC=C*H*–C$_6$H$_4$–); 7.23–7.33 (m, 6H, *m*,*p*-C$_6H_5$); 7.38 (s, 4H, –C$_6H_4$–); 7.58 (d, 4H, J_HH = 2.1 Hz, *o*-C$_6H_5$). ^{13}C NMR (CDCl$_3$; δ (ppm)): −2.40 (–CH$_3$); 126.81 (–C_6H$_4$–); 127.04 (*p*-C_6H$_5$); 127.12 (Si–HC=*C*H–C$_6$H$_4$–); 129.10 (*m*-C_6H$_5$); 134.16 (*o*-C_6H$_5$); 137.92 (C_i at –C$_6$H$_4$–); 138.65 (C_i at –C$_6$H$_5$); 144.81 (Si–H*C*=CH–). ^{29}Si NMR (CDCl$_3$; δ (ppm)): −11.15. MS(EI) [*m*/*z* (rel. int. (%)] = 398 (M$^{+\bullet}$) (10), 383 (17), 367 (2), 320 (100), 305, 279, 262, 247, 218, 203, 187, 161, 135, 121, 105, 91, 75. HRMS calcd. for C$_{26}$H$_{30}$Si: 398.18860, found: 398.18845. Anal. calcd. for C$_{26}$H$_{30}$Si: C, 78.33; H, 7.58, found: C, 78.28; H, 7.52. mp: 90.0–91.2 °C. UV–vis λ_max = 299 nm in hexane.

(*E*,*Z*)-{1,4-bis(2-Dimethylphenylsilyl)ethenyl}benzene (*cis*-ST) was obtained in the photoisomerization reaction of *trans*-ST by chromatographic isolation of the proper isomer from the reaction mixture after the irradiation. Details of the irradiation procedure and the HPLC analysis are described in Section 2.3. Several fractions containing isomer (*cis*-ST) were collected, and the solvent, hexane, was evaporated.

2.1.2. Analytical data

^{1}H NMR (CDCl$_3$; δ (ppm)) 0.28 (s, 6H, –CH_3, at fragment *Z*); 0.43 (s, 6H, –CH_3, at fragment *E*); 6.00 (d, 1H, J_HH = 15.3 Hz, Si–HC=C*H*– C$_6$H$_4$–, *Z*); 6.55 (d, 1H, J_HH = 19.1 Hz, Si–HC=C*H*–C$_6$H$_4$–, *E*); 6.88 (d, 1H, J_HH = 19.1 Hz, Si–*H*C=CH–C$_6$H$_4$–, *E*); 7.31–7.40 (m, 6H, *m*,*p*-C$_6H_5$, *E*,*Z*); 7.41 (s, 4H, –C$_6H_4$–, *E*,*Z*); 7.44 (d, 1H, J_HH = 15.3 Hz, Si–*H*C=CH–C$_6$H$_4$–, *Z*); 7.56–7.60 (m, 4H, *o*-C$_6H_5$, *E*,*Z*). MS(EI) [*m*/*z* (rel. int. (%)]: 398 (M$^{+\bullet}$) (7), 383 (16), 367 (1), 320 (100), 305 (36), 279 (4), 262 (13), 247 (21), 218 (43), 203 (10), 187 (6), 161 (19), 135 (70), 121 (26), 105 (13), 91 (5), 75 (15). UV–vis λ_max = 289 nm in hexane.

2.2. *Spectral and analytical methods*

UV–vis spectra were measured at room temperature using a Cary 300 Bio Varian spectrophotometer, and fluorescence spectra were measured on a Perkin-Elmer MPF3 spectrofluorimeter. The quinine sulphate in 1N H_2SO_4 was used as a standard for fluorescence quantum-yield determinations ($\Phi_f = 0.54$) [14]. ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR, and DEPT spectra were recorded on a Varian XL 300 MHz spectrometer in $CDCl_3$. Chemical shifts are reported in δ (ppm) with reference to the residue portion of the solvent ($CHCl_3$) peak for ^{1}H, and ^{13}C. HPLC measurements were performed on a Waters 600E Multisolvent Delivery System pump. The detection system consisted of a Waters 996 photodiode array UV–vis detector. Analytical HPLC was carried out on a PrepNova-Pak HR Silica column (3.9 mm × 300 mm) and a PrepNova-Pak HR Silica (7.8 mm × 300 mm), eluent: hexane, flow rate: 1 ml/min. Authentic reference samples of *cis*-ST and *trans*-ST isomers were used in the quantitative analysis of the isomeric compositions during irradiations. Gas chromatographic analysis was performed on a HP 5890 II series instrument equipped with a FID using a ULTRA 1 column.

Mass spectra of the monomers were obtained by GC–MS analysis (Varian Saturn 2100T, equipped with a BD-5 capillary column (30 m) and an ion-trap detector. High-resolution mass spectroscopic (HRMS) analyses were performed on an AMD-402 instrument. Melting points are uncorrected and were determined using a Melting Point Apparatus SMP3 (BIBBY Stuart Scientific, UK).

2.3. *Steady-state irradiations and analysis*

Steady-state photolysis experiments were carried out in a 1 cm × 1 cm rectangular UV cell on a standard optical bench system. A low-pressure mercury lamp (Original Hanau TNN 15/30) was used as the excitation source for the 254-nm irradiation. A high-pressure mercury lamp (HBO 200) was used for the 313-nm irradiations in combination with a BC-4 glass filter and a 313-nm interference filter (Zeiss). The irradiation, $\lambda > 300$ nm, was performed using the BC-4 filter. All solutions were deoxygenated by bubbling them with oxygen-free argon. Quantum yields were calculated based on the decrease in the concentration of the substrate or the increase in appropriate products using analytical methods such as UV spectroscopy and HPLC. Uranyl oxalate actinometry was used to measure the light intensity. The quantum yields for this actinometry were taken to be 0.602 and 0.561 for the 254-nm and the 313-nm irradiations, respectively [15]. The intensities of incident light were determined to be $I_0 = 3.74 \times 10^{-5}$ and 1.0×10^{-4} Einstein dm^{-3} min^{-1}, respectively. All quantum yields reported in this paper represent initial quantum yields obtained by extrapolation to zero irradiation time.

The photoisomerization processes in P and *trans*- and *cis*-ST were monitored by UV–vis absorption spectroscopy and HPLC analysis in the case of model compounds. Photoisomerizations were also studied by ^{1}H NMR analysis of reaction mixtures after irradiation ($\lambda > 300$ nm) of *trans*-ST and the polymer P.

2.3.1. *^{1}H NMR data of trans-ST after prolonged irradiation*

^{1}H NMR ($CDCl_3$; δ (ppm)): 0.28 (s, 6H, –CH_3, *E,Z*); 0.35 (s, 6H, –CH_3, at siloxane); 0.42 (s, 12H, –CH_3, *E,E*); 0.43 (s, 6H, –CH_3, *E,Z*); 6.00 (d, 1H, J_{HH} = 15.3 Hz, Si–HC=CH–C$_6$H$_4$–, *E,Z*); 6.56 (d, 2H, J_{HH} = 19.1Hz, Si–HC=CH–C$_6$H$_4$–, *E,E*); 6.58 (d, 1H, J_{HH} = 18.7 Hz, Si–HC=CH–C$_6$H$_4$–, *E,Z*); 6.88 (d, 2H, J_{HH} = 19.1 Hz, Si–HC=CH–C$_6$H$_4$–, *E,E*); 6.92 (d, 1H, J_{HH} = 18.7 Hz, Si–HC=CH–C$_6$H$_4$–, *E,Z*); 7.23–7.33 (m, 6H, *m,p*-C$_6H_5$, *E,E*); 7.32–7.37 (m, 6H, *m,p*-C$_6H_5$, *E,Z*); 7.38 (s, 4H, –C$_6H_4$–, *E,E*); 7.44 (d, 1H, J_{HH} = 15.3 Hz, Si–HC=CH–C$_6$H$_4$–, *E,Z*); 7.56–7.60 (m, 4H, J_{HH} = 2.1 Hz, *o*-C$_6H_5$, *E,E* and *E,Z* + siloxane) (see Fig. 7).

2.3.2. *^{1}H NMR data of polymer P before irradiation*

^{1}H NMR ($CDCl_3$; δ (ppm)): 0.33 (s, 12H, –CH_3, external), 0.41 (s, 12H, –CH_3, internal); 5.75 (dd, J_{HH} = 4, 24 Hz, SiCH=CH_2, trace); 6.04 (dd, J = 4, 15 Hz, Si–CH=CH_2, trace); 6.27(dd, J_{HH} = 15, 20 Hz, >C–HC=CH–Si–, trace); 6.56 (d, 1H, J_{HH} = 19.0 Hz, >C–CH=CH–Si–); 6.92 (d, 1H, J_{HH} = 19.0 Hz, >C–HC=CH–Si–); 7.36 (s, 4H, –C$_6H_4$–); 7.56 (s, 4H, –Si–C$_6H_4$–Si–).

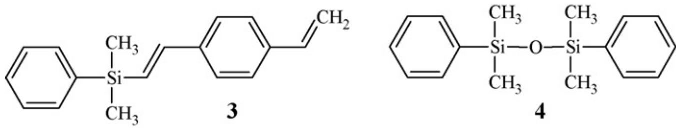
2.3.3. *^{1}H NMR data of polymer P after irradiation*

^{1}H NMR ($CDCl_3$; δ (ppm)): 0.27 (s, 6H, –CH_3, *E,Z*); 0.33 (s, 12H, –CH_3, external, *E,E*); 0.41 (s, 12H, –CH_3, internal, *E,E*); 5.75 (dd, J_{HH} = 4, 24 Hz, SiCH=CH_2, trace); 5.91 (d, 1H, J_{HH} = 14.8 Hz, >C–CH=CH–Si–, *E,Z*); 6.04 (dd, J = 4, 15 Hz, Si–CH=CH_2, trace); 6.27 (dd, J_{HH} = 15, 20 Hz, >C–HC=CH–Si–, trace); 6.54 (d, 1H, J_{HH} = 19.2 Hz, >C–CH=CH–Si–, *E,Z*); 6.56 (d, 1H, J_{HH} = 19.2 Hz, >C–CH=CH-Si-, *E,E*); 6.89 (d, 1H, J_{HH} = 19.2 Hz, >C–CH=CH–Si–, *E,Z*); 6.92 (d, 1H, J_{HH} = 19.2 Hz, >C–HC=CH–Si–, *E,E*); 7.39 (s, 4H, –C$_6H_4$–, *E,E*); 7.40 (s, 4H, –C$_6H_4$–, *E,Z*); 7.54 (s, 4H, –Si–C$_6H_4$–Si–, *E,E*); 7.57 (s, 4H, –Si–C$_6H_4$–Si–, *E,Z*); 7.67 (d, 1H, J_{HH} = 14.3 Hz, >C–HC=CH–Si–, *E,Z*) (see Fig. 8).

The analyses of the stable photoproducts formed during photolysis ($\lambda > 300$ nm) of *trans*-ST in nondeuterated and deuterated dichloromethane and chloroform were performed by GCMS and HPLC analyses. In addition to finding the *cis*-ST isomer, two additional products were detected. Their MS spectra are presented below:

- [(*E*)-4-(*Dimethylphenylsilyl*)*ethenyl*]*styrene* (**3**): MS(EI) [*m/z* (rel. int. (%)] = 264 ($M^{+\bullet}$) (100), 249 (42), 236 (1), 223 (5), 207 (2), 189 (3), 171 (98), 161 (4), 145 (36), 135 (10), 121 (20), 105 (19), 91 (7), 77 (4).
- *1,3-Diphenyl-1,1,3,3-tetramethyldisiloxane* (**4**): MS(EI) [*m/z* (rel. int. (%)] = 286 ($M^{+\bullet}$) (10), 271 (100), 256 (4), 211 (10), 193 (86), 179 (1), 163 (2), 135 (5), 121 (1), 105 (2), 91 (10), 77 (5), 65 (2).

The mechanism of their formation (photodegradation reaction) was investigated in additional trapping experiments with methanol. Immediately after prolonged irradiation ($\lambda > 300$ nm) of *trans*-ST in dichloromethane, methanol was added to the



Scheme 2.

irradiated solution ending up with a 1:1 (v/v) CH_2Cl_2/MeOH mixture. After several hours in the dark, a methoxy derivative, methoxydimethylphenylsilane, Ph-$Si(CH_3)_2OCH_3$, was detected by GC–MS analysis together with the absence of siloxane **4** and the presence of **3** (Scheme 2). The MS spectrum of Ph-$Si(CH_3)_2OCH_3$ is presented below: MS(EI) [*m/z* (rel. int. (%)] = 166 ($M^{+\bullet}$) (0), 152 (11), 151 (100), 135 (2), 121 (46), 105 (4), 91 (34), 77 (4) and corresponds to the MS spectrum and the fragmentation pattern presented in Ref. [16].

3. Results and discussion

3.1. Spectroscopic properties of polymer (trans-P) and its model compounds in solution

The UV–vis absorption and fluorescence spectra for *trans*-P and *trans*-ST in dichloromethane solution are presented in Fig. 1. The values of the molar absorption coefficients measured at $\lambda_{max} = 301$ nm were determined to be 39,100 $dm^3\ mol^{-1}\ cm^{-1}$ for *trans*-ST and 27,900 $dm^3\ mol^{-1}\ cm^{-1}$ for P (calculated per one monomer unit) in dichloromethane. These strong absorption bands can be attributed to the π–π^* transition of the 2-dimethylphenylsilylethenylbenzene chromophore. The fluorescence spectrum of *trans*-P is shifted slightly to longer wavelengths ($\lambda_{f,max} = 354$ nm) in comparison to the spectrum of *trans*-ST ($\lambda_{f,max} = 350$ nm). The fluorescence quantum yields, determined in CH_2Cl_2, were equal to 0.032 and 0.008 for *trans*-P and *trans*-ST, respectively. Fig. 1 shows that the spectroscopic properties of the polymer and its model compound (*trans*-ST) are very similar, suggesting, as expected, that the 2-dimethylphenylsilylethenylbenzene chromophore (see Scheme 1) is responsible for the absorption and emission properties in both compounds.

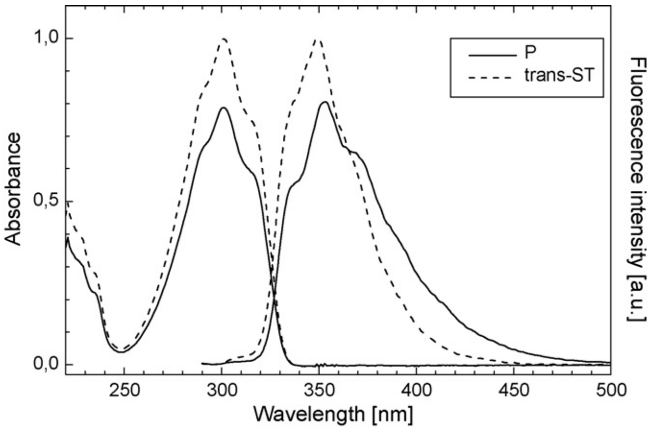


Fig. 1. Absorption and fluorescence spectra of polymer (*trans*-P) and *trans*-ST in dichloromethane ($\lambda_{exc} = 280$ nm, $c = 2.5 \times 10^{-5}$ M, $l = 1$ cm).

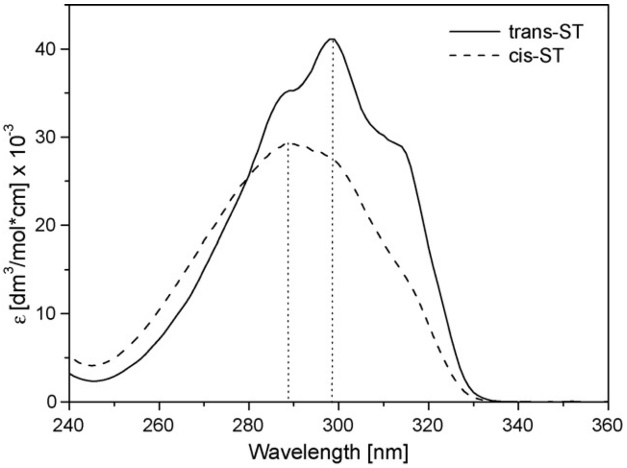


Fig. 2. UV absorption spectra of *trans*-ST and *cis*-ST in hexane.

In changing the position of one of the dimethylphenylsilyl groups, forming the *cis* from the *trans* isomer, one would expect some changes in the absorption spectra of the model compound. These changes are presented in Fig. 2 and indicate that there was a blue shift of the absorption maxima for the *cis* isomer, in addition to the lost of vibrational structure for this isomer. Changing solvent from hexane to the more polar dichloromethane led to a small red shift observed for both isomers (in hexane: λ_{max}(*cis*-ST) = 289 nm, λ_{max}(*trans*-ST) = 299 nm; in dichloromethane: λ_{max}(*cis*-ST) = 292 nm, λ_{max}(*trans*-ST) = 301 nm).

trans-ST exhibits fluorescence with a low quantum yield (0.008). On the other hand, the *cis*-isomer, *cis*-ST, was shown to be nonfluorescent. The limit of its fluorescence quantum yield in dichloromethane was determined to be $\Phi_{fl} < 1 \times 10^{-4}$. The efficient *cis*–*trans* photoisomerization, occurring even in the spectrofluorometer, during fluorescence measurements did not allow us to determine the Φ_{fl} limit for *cis*-ST with better accuracy. This behaviour is analogous to that reported for the emission properties of the *cis* and *trans* isomers of stilbene [17] and of the poly(dimethylsilylenephenylenevinylene)s [8]. The photophysical properties of *trans*-ST, *cis*-ST, and *trans*-P are summarized in Table 1. All compounds studied are characterized by low fluorescence efficiencies. Thus, nonradiative processes (internal conversion and intersystem crossing) are mainly responsible for the deactivation of their lowest excited singlet states although efficient isomerization reactions also contribute significantly to nonradiative pathways (*vide infra*).

Table 1
Photophysical properties of *trans*-ST, *cis*-ST and *trans*-P in dichloromethane at room temperature

Compound	λ_a (max)	$\varepsilon_{\lambda max}$	λ_{fl} (max)	Φ_{fl}	Φ_n[a]
trans-ST	301	39,100	350	0.008	0.76
cis-ST	292	29,100	–	<0.0001	0.86
trans-P	301	27,900[b]	354	0.032	0.71

[a] Quantum yields of nonradiative processes (internal conversion and intersystem crossing processes) equal to $(1 - \Phi_{fl} - \Phi_{isom})$. The values of initial isomerization quantum yields were taken from Table 2.

[b] Calculated per one monomer.

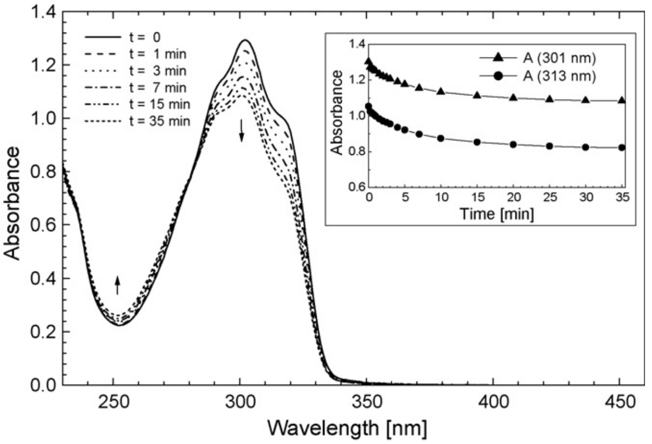


Fig. 3. Absorption spectra of *trans*-P in dichloromethane during irradiation $\lambda_{exc} = 313$ nm; insert: changes in absorbance measured at 301 nm and 313 nm with irradiation time.

3.2. Photoisomerization of P and trans-ST—absorption spectra

Studies on the photoisomerization of *trans*-P and its model compound, *trans*-ST, were first performed by means of UV absorption spectroscopy. Changes in the absorption spectra during 313-nm irradiations of *trans*-P and *trans*-ST in dichloromethane are presented in Figs. 3 and 4, respectively. Dichloromethane was used as a solvent due to the low solubility of *trans*-P in other solvents. In both cases, the 300-nm absorption bands initially decreased with irradiation time, and the absorption bands were shifted toward shorter wavelengths. After longer irradiation, a photo-stationary state was attained, and the spectra of the reaction mixtures did not change with further irradiation, see insets to Figs. 3 and 4. These results can be rationalized by the existence of *trans*–*cis* isomerization occurring in these systems leading to the same photo-stationary state regardless of whether the *cis* or the *trans* isomer were being irradiated (see the ratios of c_{cis}/c_{trans} concentrations in the photostationary state, in Table 2). In addition, absorption spectral changes during irradiations of either *trans*-P or *trans*-ST were found to be very similar. This suggests similar pathways for the photoisomerizations of the polymer and its model compound.

Table 2
Isomerization quantum yields for model compounds (and *trans*-P) disappearance (Φ_{dis}), appropriate isomer formation (Φ_{form}) and ratios of *cis*/*trans* concentrations in the photo-stationary state for irradiation with $\lambda_{irr} = 313$ nm and 254 nm

Compound	Solvent	Method	Φ_{dis}	Φ_{form}	c_{cis}/c_{trans}
trans-ST[a]	C_6H_{14}	HPLC (UV)	0.28 (0.28)	0.27 (0.29)	2.49
cis-ST[a]	C_6H_{14}	HPLC (UV)	0.18 (0.19)	0.19 (0.20)	2.60
trans-ST[a]	CH_2Cl_2	UV	0.23	0.23	2.01
cis-ST[a]	CH_2Cl_2	UV	0.14	0.15	1.98
trans-ST[b]	C_6H_{14}	HPLC (UV)	0.49 (0.46)	0.49 (0.47)	0.88
cis-ST[b]	C_6H_{14}	HPLC (UV)	0.37 (0.36)	0.37 (0.35)	0.92
trans-P[a]	CH_2Cl_2	UV	0.26[c]	–	–

[a] ($\lambda_{irr} = 313$ nm), estimated error of quantum yield ±10%.
[b] ($\lambda_{irr} = 254$ nm), estimated error of quantum yield ±15%.
[c] Calculated on the bases of results presented in the inset of Fig. 3 and Table 1.

Since there are more analytical tools available for the model compounds compared to the polymer, the *cis*–*trans* isomerization mechanism could be studied more quantitatively using model compounds (*trans*-ST and *cis*-ST).

3.3. Photoisomerization of trans- and cis-ST in hexane

Photoisomerization of *trans*-ST was studied quantitatively in hexane using UV spectroscopy and HPLC as analytical methods (Fig. 5). As expected, changing the solvent from dichloromethane to hexane did not affect the reaction pattern (compare Figs. 4 and 5). The HPLC analysis indicated formation of the *cis* isomer as the only photoproduct (see Section 2). Thus, knowing the molar absorption coefficients for *trans*- and *cis*-ST (that were determined in separate experiments), the concentrations of both isomers could be determined from the changes in the absorption spectra during the irradiations.

The changes in the concentrations of the *trans* and *cis* isomers during irradiation, as measured both by UV and HPLC methods, are presented in the inset of Fig. 5. These results indicate that the same concentration profiles were obtained from both analytical

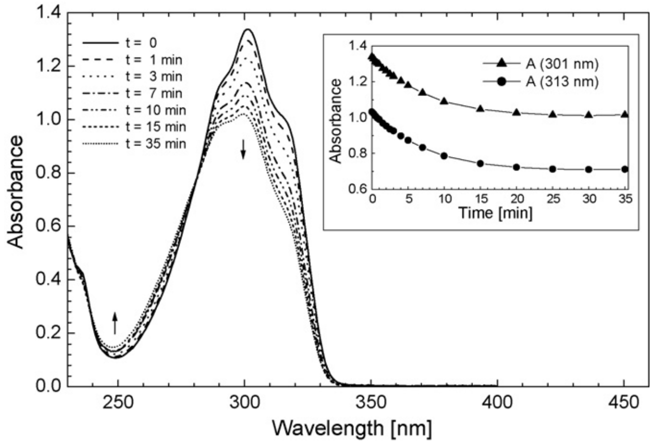


Fig. 4. Absorption spectra of *trans*-ST in dichloromethane during irradiation $\lambda_{exc} = 313$ nm; insert: changes in absorbance measured at 301 nm and 313 nm with irradiation time.

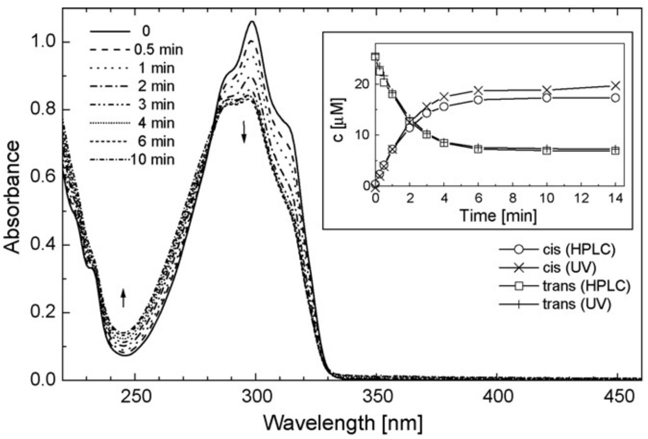


Fig. 5. Changes in the absorption spectra of *trans*-ST during its irradiation ($\lambda_{exc} = 313$ nm) in hexane; insert: changes in concentration of *cis*- and *trans*-ST isomers with irradiation time measured using HPLC and UV analysis.

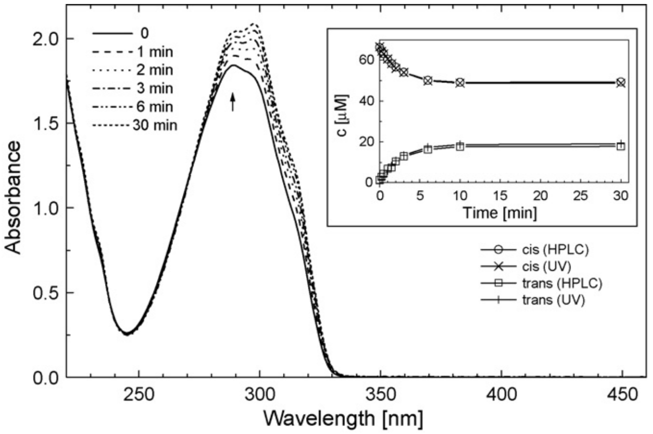


Fig. 6. Changes in the absorption spectra of *cis*-ST during its irradiation ($\lambda_{exc} = 313$ nm) in hexane; insert: changes in the concentrations of *cis*- and *trans*-ST isomers with irradiation time as measured by HPLC and UV analysis.

methods within experimental error. Thus, the UV absorption spectroscopic method is a reliable method to study quantitatively the photoisomerization reaction. UV detection can then be used to study photoisomerization of the polymer *trans*-P.

The irradiation of *cis*-ST in hexane led to formation of a photo-stationary state, as in the case of *trans* isomer, and the results are presented in Fig. 6. Also for this system, UV and HPLC analytical methods led to the same results (see the inset of Fig. 6). Comparing the results presented in the insets of Figs. 5 and 6, one can conclude that regardless of which isomer was used as the initial substrate, after a certain period of irradiation, the same photo-stationary state was obtained (the same ratio of the concentrations of *cis*/*trans* isomers).

3.4. Photoproduct analysis

In addition to the UV absorption studies presented above, stable products in the photoreaction studied were also analyzed by means of HPLC and GC methods. In these cases, however, irradiations were performed with wavelengths λ > 300 nm, and, in addition, longer irradiation times (1 h) were used to check for the possibility of photodegradation of the model compound ST in hexane and dichloromethane.

The results on the photochemistry of the model compounds, *trans*-ST and *cis*-ST, indicate that *cis*–*trans* photoisomerization was the main reaction pathway in both solvents. In dichloromethane, however, a photodegradation reaction occurred with low efficiency ($\Phi \leq 10^{-2}$). Photodegradation was observed by the detection of two additional photoproducts **3** and **4** (Scheme 2). The structure of product **3** was assigned to [(*E*)-4-(dimethylphenylsilyl)ethenyl]styrene and product **4** to 1,3-diphenyl-1,1,3,3-tetramethyl-disiloxane using GCMS analysis. The presence of these compounds indicates there was a cleavage of a C–Si bond as a primary mechanism of the photodegradation reaction. A pre-existing interaction between the chlorine atom of the solvent and the Si atom in the ground state of *trans*-ST could facilitate a cleavage of the C–Si bond following photoexcitation. In deuterated dichloromethane or chloroform, no deuterium effect was observed in **3** or **4** which suggests the photodegradation mechanism must go to completion with fragments from the substrate and not the solvent. A post-irradiation trapping experiment with methanol (see Section 2) led to the formation of Ph–Si$(CH_3)_2OCH_3$ together with the absence of siloxane **4** and the presence of **3**, which may indicate that silene, Ph-Si(CH_3)=CH_2, is involved in the photodegradation mechanism. A similar reaction of silene with methanol, leading to methoxydimethylphenylsilane, was discussed in Ref. [18]. However, a definitive mechanism for the photodegradation requires further studies and will be discussed elsewhere.

The ^{1}H NMR spectroscopy can also be used to confirm formation of the *cis* isomer during the irradiation of the model compound *trans*-ST and the polymer *trans*-P. In these ^{1}H NMR experiments, the spectra of the reaction mixtures obtained after prolonged irradiations λ > 300 nm were compared with the spec-

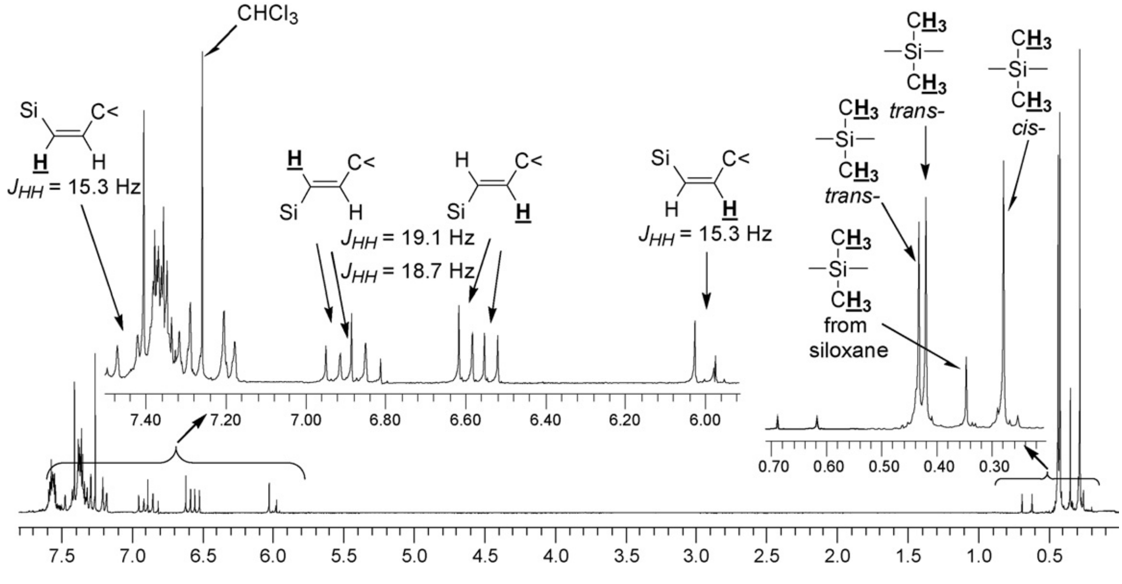


Fig. 7. ^{1}H NMR spectrum of *trans*-ST after prolonged irradiation λ > 300 nm.

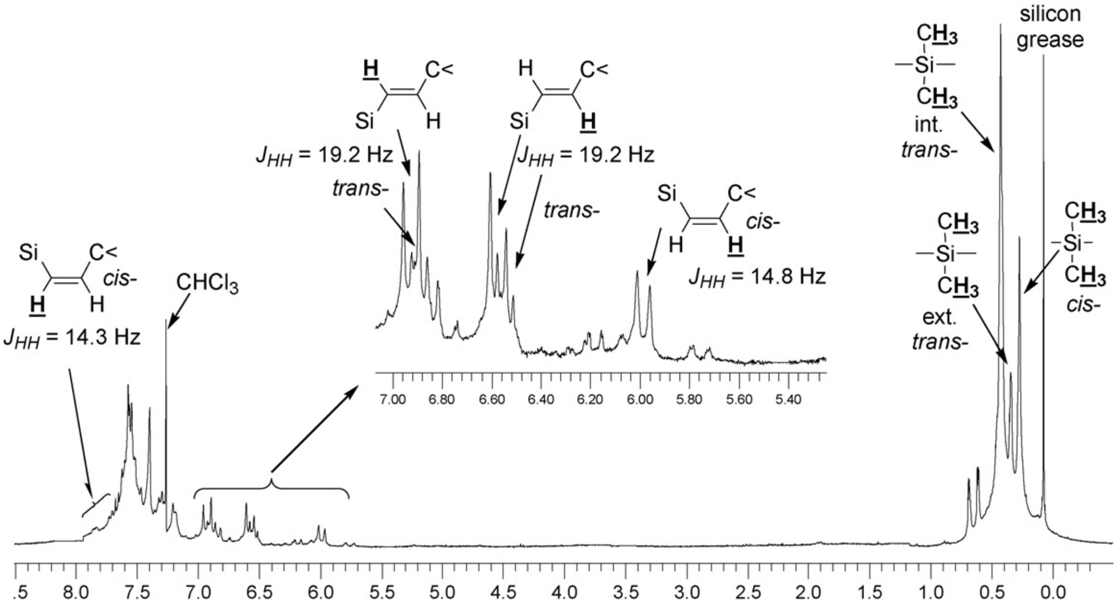


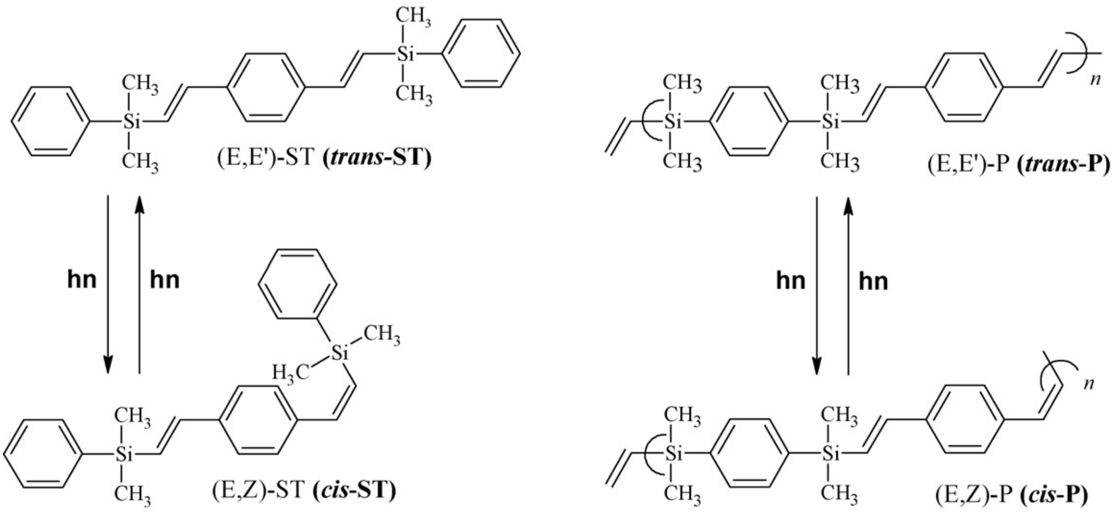
Fig. 8. ^{1}H NMR spectrum of the polymer *trans*-P after prolonged irradiation λ > 300 nm.

tra of the substrates before the irradiations (see Section 2). These comparisons of the ^{1}H NMR spectra measured before and after irradiation of the model compound *trans*-ST and the irradiation of the polymer led to the identification of *cis*- and *trans*-fragments for both substrates. By assigning proton–proton coupling constants (for *trans*- in the range J_{HH} = 19.0–19.2 Hz and for *cis*- J_{HH} = 14.3–15.3 Hz) for the individual vinylene fragments, it was possible to identify adequate signals (doublets) corresponding to the *cis* and *trans* isomers (see Section 2.3 and Figs. 7 and 8). Minor olefin signals obtained after prolonged irradiation of the *trans*-P can be attributed to photodegradation products (with terminal vinyl groups) similar to the product **3** obtained during prolonged irradiation of the model compound *trans*-ST.

The resulting analysis of the changes occurring in the UV absorption spectra of *trans*-ST and *trans*-P during their irradiations (see Figs. 3 and 4) and the resulting NMR analysis presented above indicate that the same photoisomerization reaction occurring for the polymer and the model compounds (Scheme 3). Similar to Kliger's results for isomerization of 1,4-diphenylbutadienes by direct excitation [19], we found for the compounds studied the isomerization of only one bond leading to appropriate *cis*-ST (*E*,*Z*-isomer) or *trans*-ST (*E*,*E*′-isomer). No measurable (*Z*,*Z*′) isomer was found in the experimental conditions used.

3.5. Initial quantum yields of photoisomerization

The initial quantum yields were measured for the photoisomerization of the model compounds. The quantum yields of disappearance of the substrate isomer and the formation of the product isomer were determined from the initial changes of the



Scheme 3.

appropriate isomer concentrations (e.g. see Figs. 4–6) and from the absorbed light intensities. The isomerization quantum yield for *trans*-P was estimated on the bases of initial changes in the absorption spectra during irradiation (Fig. 3) and on the known values of molar absorption coefficients calculated per one monomer unit (Table 1). The results are summarized in Table 2. The values of isomerization quantum yields did not change with bubbling of oxygen (instead of argon) through the reaction mixture.

The values of the isomerization quantum yields for ST measured by substrate disappearance and by product formation are identical, and they are the same, within experimental error, for both analytical methods used (HPLC and UV). The quantum yields are in the range 0.14–0.29 and 0.35–0.49 for the 313-nm and the 254-nm irradiations, respectively. The difference in the initial quantum yields for various irradiation wavelengths can be rationalized by the shape of the rotational potential surfaces in the excited states of *trans*- and *cis*-ST and whether the different photon energies put the molecule in an energy above or below the excited state potential barrier (analogous to the isomerization of stilbene, see [20]). The results indicate that the isomerization reaction is an efficient reaction occurring in both solvents, i.e. in hexane and dichloromethane (compare with the small observed values of the fluorescence quantum yields, Table 1). The quantum yields of photodegradation observed for irradiations of *trans*-ST and *cis*-ST in dichloromethane (quantum yields of product **3** formation were measured after prolonged irradiations with 313 nm) were determined to be $\Phi \leq 10^{-2}$. To observe the photodegradation products, the irradiation times had to be chosen several times longer than the times of reaching the photo-stationary states. As a consequence, we could not distinguish whether by-products were formed selectively from the excited *cis* and/or *trans* isomers.

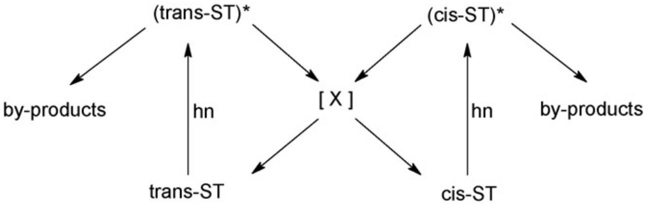
In the case of *trans*-P, the value of the initial isomerization quantum yield was estimated as 0.26 (Table 2). A comparison of this value with that for *trans*-ST ($\Phi_{trans\to cis} = 0.23$) suggests that a primary photochemical reaction (isomerization) occurs in a similar manner for both the polymer and the standard.

The composition of the photo-stationary state is given by the following equation [20]:

$$\frac{c_{cis}}{c_{trans}} = \frac{\varepsilon_{trans}^{\lambda_{exc}}\phi_{trans\to cis}^{\lambda_{exc}}}{\varepsilon_{cis}^{\lambda_{exc}}\phi_{cis\to trans}^{\lambda_{exc}}} \qquad (1)$$

in which c_{cis} and c_{trans} are the molar concentrations of *cis* and *trans* isomers in the photo-stationary state, ε_{cis} and ε_{trans} the molar absorption coefficients at the excitation wavelength, and $\Phi_{cis\to trans}$ and $\Phi_{trans\to cis}$ are the initial quantum yields for *cis*–*trans* and *trans*–*cis* isomerization, respectively.

On the bases of the known values of the molar absorption coefficients, the initial quantum yields (Table 2) and Eq. (1), one can calculate the ratio of *cis*/*trans* concentrations in the photo-stationary state. The results obtained are in good agreement with the concentrations of *cis* and *trans* isomers in the photo-stationary state as measured directly by HPLC or UV analysis (see insets of Figs. 4 and 5). As one can see from Table 2, the ratios of the initial isomerization quantum yields, $\Phi_{trans\to cis}/\Phi_{cis\to trans}$, are the same within experimental error for the 313-nm and the 254-nm irradiations. This can be additionally confirmed by calculation of these ratios from Eq. (1) using appropriate values for the molar absorption coefficients and the *cis* and *trans* ST concentrations in the photo-stationary state. The $\Phi_{trans\to cis}/\Phi_{cis\to trans}$ ratios were determined to be in the range of (1.3–1.5) for the 313-nm and the 254-nm irradiations.



Scheme 4.

On the bases of the results presented above, the suggested mechanism of the photochemical reactions of the model compounds is presented in Scheme 4. The observed lack of an oxygen effect on the photoisomerization quantum yields suggests that the excited singlet states of the ST isomers are involved in the reaction mechanism. The formation of by-products **3** and **4** (photodegradation reactions) was observed only after prolonged irradiations in dichloromethane (irradiation times several times longer than times of reaching photo-stationary states). Therefore, it was not possible to distinguish whether the by-products were formed selectively from the excited *cis* and/or *trans* isomers.

4. Conclusions

In this paper, we have quantitatively described the absorption and emission properties and *cis*–*trans* photoisomerization of the poly[dimethylsilylene-*p*-phenylene-dimethylsilylene-(*E*)-vinylene-*p*-phenylene-(*E*)-vinylene] (*trans*-P) and its model compounds (*E*,*E*)-{1,4-bis(2-dimethylphenylsilyl)ethenyl}benzene (*trans*-ST) and (*E*,*Z*)-{1,4-bis(2-dimethylphenylsilyl)ethenyl}benzene (*cis*-ST) in solution. It was shown that *trans*-P and *trans*-ST exhibit strong absorption bands at about 300 nm and weak fluorescence at about 350 nm. Changing the position of one of the dimethylphenylsilyl group to form the *cis* isomer blue-shifts the absorption maxima. It was shown that *cis*-ST is a nonfluorescent species in solution at room temperature. It was also found that the model compounds (*trans*-ST and *cis*-ST) and the polymer undergo the same type of efficient photochemical reaction, i.e. *cis*–*trans* photoisomerization leading to the formation of a photo-stationary state. The initial quantum yields of isomerization were determined to be in the range of 0.14–0.49 depending on the solvent and excitation wavelengths used. When dichloromethane was used as the solvent, a photodegradtion reaction of low efficiency ($\Phi < 1 \times 10^{-2}$) was observed. The results obtained suggest that the 2-dimethylphenylsilylethenylbenzene chromophore is responsible for the absorption and emission properties and for the *cis*–*trans* isomerization occurring in the lowest excited singlet states of both the polymer and the model compounds.

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