Makromol. Chem. 177, 2647-2655 (1976)

Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sumiyoshi-ku, Osaka, Japan

Radical Polymerization by Silyl Radicals. Photopolymerization of Styrene by Bis(trimethylsilyl)mercury

Hisayoshi Ikeda, Yozo Miura, and Masayoshi Kinoshita

(Date of receipt: November 25, 1975)

SUMMARY:

The photopolymerization of styrene (St) by bis(trimethylsilyl)mercury (1) was studied. Kinetic studies indicated that the rate of polymerization can be expressed by the following equation:

$$R_{\rm p} = k[1]^{1/2}[{\rm St}]$$

IR and NMR spectra of the polymer indicated that trimethylsilyl groups were incorporated. By reaction of 1 with an equimolar amount of St in benzene under UV irradiation a radical coupling product, 2,2,7,7-tetramethyl-4,5-diphenyl-2,7-disilaoctane (2) was formed in 22% yield. By spin trapping technique using 2,4,6-tri-*tert*-butylnitrosobenzene (3) as a trapping agent, N-trimethylsiloxy-2,4,6-tri-*tert*-butylanilino radicals were obtained.

On the basis of these results, it was concluded that the polymerization was initiated by trimethylsilyl radicals formed by photodecomposition of 1.

ZUSAMMENFASSUNG:

Die Photopolymerisation von Styrol (St) durch Bis(trimethylsilyl)quecksilber (1) wurde untersucht. Die kinetische Untersuchung zeigte, daß die Polymerisation durch folgende Formel beschrieben wird :

$$R_{\rm p} = k[1]^{1/2}[{\rm St}]$$

IR- und NMR-Spektren des Polymeren zeigten, daß Trimethylsilylgruppen in dem Polymeren enthalten waren. Durch die Reaktion äquimolarer Mischungen von 1 und St unter UV-Bestrahlung wurde das Radikalkupplungsprodukt 2,2,7,7-Tetramethyl-4,5-diphenyl-2,7-disilaoctan (2) in 22 % Ausbeute erhalten. Bei Abfangexperimenten ("spin trapping") mit 2,4,6-Tri-*tert*-butylnitrosobenzol (3) wurden *N*-Trimethylsiloxy-2,4,6-tri-*tert*-butyl-anilino-Radikale nachgewiesen.

Aus den Ergebnissen wird geschlossen, daß die Polymerisation durch die bei der Photozersetzung von 1 entstandenen Radikale ausgelöst wird.

Introduction

A number of examples of radical polymerizations initiated by carbon-centered, and oxygen-centered radicals have so far been presented. However, only a few examples initiated by silyl radicals have been reported, e.g. the polymerization of styrene (St) and methyl methacrylate in the presence of trihalogenosilanes or trialkylsilanes under UV irradiation¹). A recently reported thermodynamic consideration on the addition of silyl radicals to olefins indicates that the addition reaction is favorable and is irreversible²).

Bis(trimethylsilyl)mercury (1) is reported to decompose to trimethylsilyl radicals and mercury under UV irradiation (Eq. (1))³⁾. This procedure is one of the most elegant generation methods of silyl radicals. In the reaction of 1 with 1-hexene, the formation of addition products was ascertained⁴⁾. Therefore, it is expected that vinyl monomers can be initiated in the presence of 1 under UV irradiation.

In this paper, the photopolymerization of St in the presence of 1 is described.

$$\begin{array}{cccc} & CH_3 & CH_3 & CH_3 \\ CH_3 - Si - Hg - Si - CH_3 & \xrightarrow{h\nu} & 2 CH_3 - Si + Hg \\ & CH_3 & CH_3 & CH_3 & CH_3 \end{array}$$
(1)

Experimental Part

All the melting points are uncorrected. The IR spectra (KBr method) were run on a Jasco IR-G type spectrometer. The ¹H-NMR spectra were recorded with a Hitachi-Perkin-Elmer apparatus Model R-20, using tetramethylsilane as an internal standard. The ESR spectra were recorded under degassed conditions with a JES-ME-3X spectrometer, equipped with 100 kHz field modulation. Mass spectra were obtained with a Jeol JMS-OISG-2 Mass Spectrometer.

Materials

Bis(trimethylsilyl)mercury (1) was prepared by the reaction of trimethylsilyl chloride (4,7 g, 43 mmol) with sodium amalgam (Na 1 g, Hg 200 g) in cyclohexane (15 ml) under nitrogen at room temperature according to the literature⁵), and purified by sublimation; yield 40% (3,0g, 8,6 mmol), mp 102–103 °C (lit.⁵⁾ 102–104 °C). 2,4,6-Tri-*tert*-butylnitrosobenzene (3) was prepared by treating 2,4,6-tri-*tert*-butylaniline (0,75 g, 2,9 mmol) with *m*-chloroperoxybenzoic acid (1,0g, 5,8 mmol) according to the method of *Inamoto* et al.⁶); yield 77% (0,61 g, 2,2 mmol); mp 167–168 °C (lit.⁶) 167–168 °C). Trimethylsilane was prepared by treating trimethylchlorosilane with LiAlH_4^{7} . Di-*tert*-butyl diperoxyoxalate was prepared by treating oxalyl chloride with *tert*-butyl hydroperoxide in anhydrous pentane⁸. St and benzene were distilled from CaH₂ before use.

Polymerization procedure

The required amounts of St, 1, and benzene were placed in a tube in a nitrogen filled dry-box. The tube was cooled in a dry-ice-methanol bath, and sealed after the content was degassed. The tube was then placed on a merry-go-round equipped with a Toshiba 100 W high-pressure mercury lamp (SHL-100).

After irradiation for a given time, the content was poured into an excess of methanol, giving colorless poly(St) and mercury. After the deposited mercury had been removed by decantation, the poly(St) was filtered off and dried i. vac. The rates of polymerization were calculated from the weight of polymer.

Molecular weight

The viscosity of poly(St) was determined using an Ubbelohde dilution viscometer in benzene at 30° C. The number-average degrees of polymerization of poly(St) were estimated by the following equation⁹⁾:

$$\bar{P}_{n} = 1,77 \cdot 10^{3} [\eta]^{1,40}$$

The reaction of 1 with an equivalent amount of St

A mixture of 1 (2,2 g, 6,4 mmol) and St (0,66 g, 6,4 mmol) in benzene (5 ml) was placed in a glass-tube in a nitrogen filled dry-box. The content was degassed and irradiated at 30 °C for 48 h, using a Toshiba 100 W high-pressure mercury lamp (SHL-100). After the formed mercury (1,3 g, 100%) had been removed by decantation, the benzene was evaporated and the residue was recrystallized from ethanol to give 2,2,7,7-tetramethyl-4,5-diphenyl-2,7-disilaoctane (2); yield 22% (0,25 g) based on St; mp 97–98 °C.

¹H-NMR (CCl₄): $\delta = -0.42$ (s, 18H), 0.52–0.79 (b, 4H), 2.55–2.84 (b, 2H), and 6.95–7.48 (b, 10H) ppm.

MS (m/e) 354 (M^+) .

C22H34Si2	(354,7)	Calc.	C 74,50	H 9,66
		Found	C 73,98	H 9,77

Spin trapping of trimethylsilyl radical using 3

a) 1 (0,50 mg, $1,5 \cdot 10^{-3}$ mmol), 3 (1,4 mg, $5,1 \cdot 10^{-3}$ mmol), and benzene (1 ml) were placed in a glass-tube attached to an ESR tube in a nitrogen-filled dry-box. The content

was degassed and transferred into the ESR tube, which was then cut off. ESR measurement was carried out under UV irradiation at room temperature.

b) A degassed benzene solution (1 ml) of trimethylsilane (20 mg, 0,27 mmol), di-*tert*-butyl diperoxyoxalate (8,1 mg, $3,5 \cdot 10^{-3}$ mmol), and 3 (1,4 mg, $5,1 \cdot 10^{-3}$ mmol) was put in an ESR tube according to the similar method described above, and ESR measurement was carried out at room temperature.

Results and Discussion

Kinetic study of the photopolymerization of St by 1

The photopolymerization of styrene (St) in the presence of bis(trimethylsilyl)mercury (1) was carried out in bulk or in benzene at 30°C, using a high-pressure



Fig. 1. Comparison of the initiating ability of bis(trimethylsilyl)mercury (1) with those of the related compounds in the photopolymerization of styrene. Styrene 5 ml, 30 °C. (\triangle): 1, 2,09 · 10⁻² mol/l, (\bigcirc): diphenylmercury, 2,00 · 10⁻² mol/l, (\bigcirc): hexamethyldisilane, 2,00 · 10⁻² mol/l, (\triangle): mercury, 30 mg, (\square): no additive

Fig. 2. Time-conversion curves in the photopolymerization of styrene in the presence of 1. Styrene, 8,72 mol/l, 30 °C. $10^2 \cdot [1] = 3,56$ (\odot), 2,09 (\blacktriangle), 1,31 (\Box), 0,695 (\blacklozenge), 0,319 mol/l (\triangle), (\blacksquare): none

2650



Fig. 3. Relationship between $\log R_p$ and $\log[1]$ in the photopolymerization of styrene. Styrene 8,72 mol/l, 30 °C (R_p : rate of polymerization)

Fig. 4. Relationship between $\log R_p$ and $\log[St]$ in the photopolymerization of styrene (St) in benzene. $[1] = 1,45 \cdot 10^{-2} \text{ mol/l}, 30 \text{ °C}$

mercury lamp. The behavior of the polymerization in the presence of 1 was compared with those of the related compounds, e.g. diphenylmercury or the compounds which are formed on the photodecomposition of 1 (hexamethyldisilane and mercury). The results are given in Fig. 1. As can be seen, only 1 possesses a large initiating ability. In this case, as the polymerization proceeded, mercury deposited as a droplet at the bottom of the glass tube. However, the amount was only a trace, thus the mercury did not disturb the kinetic studies. The time-conversion curves in the presence of various concentrations of 1 are shown in Fig. 2. From this Fig. the logarithm of the rate of polymerization, $\log R_p$, is plotted againist $\log[1]$ (Fig. 3). The slope of 0,50 in Fig. 3 indicates that R_p is of square root dependence on the concentration of 1. The polymerization was also carried out, changing the concentrations of St from 1,25 to 6,23 mol/l, and keeping the concentration of 1 (1,45 \cdot 10⁻² mol/l) constant. The results are shown in Fig. 4, and the slope of 1,26 shows that R_p was approximately of first order dependence on the concentration of St.

H. Ikeda, Y. Miura, and M. Kinoshita

On the basis of the results obtained, R_p can be expressed by the following equation:

$$R_{\rm p} = k[1]^{1/2}[{\rm St}]$$

It is obvious that this equation holds only for a given and constant irradiation intensity which is involved in the constant k.

The above kinetic results indicate that this photopolymerization proceeds via a usual radical polymerization mechanism.



Fig. 5. Relationship between $1/\overline{P}_n - 12,3 R_p$ and [1]/[styr-ene] in the photopolymerization of styrene (\overline{P}_n : number average degree of polymerization; R_p : rate of polymerization)

Tab. 1. Chain-transfer constant of 1, C_i , in the photopolymerization of styrene $(St)^{a}$

$\frac{10^2 \cdot [1]}{\text{mol } 1^{-1}}$	$\frac{[1]}{[St]} \cdot 10^3$	Conversion in %	$\frac{R_{\rm p} \cdot 10^5}{\rm mol \ l^{-1} \ s^{-1}}$	[η]	$ar{P}_n$	$\frac{1}{\overline{P}_{n}} \cdot 10^{3}$	C _i
0,391	0,448	3,2	3,8	0,35	410	2,4)	
0,695	0,797	5,1	5,4	0,22	220	4,5	25
1,31	1,50	8,4	7,5	0,19	180	5,6	2,3
2,09	2,39	10,0	9,2	0,14	120	8,3	

^{a)} Conditions: $[St] = 8,72 \text{ mol/l}, 30 \degree \text{C}.$

The chain-transfer constant (C_i) of 1 was next determined. Based on the results given in Tab. 1, Fig. 5 illustrates plot of [1]/[St] against $[1/\bar{P}_n - 12,3R_p]$ (\bar{P}_n : degree of polymerization). The value of C_i is calculated from the slope in the Fig. 5 to be 2,5, which is considerably large in comparison with widely used initiators, e.g. benzoylperoxid ($C_i = 0,1$ at $22^{\circ}C$)¹⁰. Thus, the

chain-transfer reaction from the propagating radical to 1 would occur frequently in this system.

IR and NMR analyses of poly(St)

The IR absorption at 1253 cm⁻¹ due to the Si-CH₃ bond and the NMR absorption at -0.33 ppm due to the trimethylsilyl protons observed for the obtained polymer (Fig. 6) indicate the presence of trimethylsilyl groups in the polymer. As mentioned above, 1 acts not only as an initiator but also as a chain



Fig. 6. ¹H-NMR spectrum (CDCl₃, standard: TMS) of the polystyrene obtained in the photopolymerization of styrene in the presence of 1

transfer agent; thus a part of the trimethylsilyl groups in the polymer seems to be incorporated through the chain-transfer reaction.

Reaction of 1 with an equimolar amount of St

The reaction of 1 with an equimolar amount of St was carried out in order to establish the initiation mechanism of this system. A benzene solution of 1 and St was UV-irradiated for 48 h. After the removal of solvent, 2,2,7,7-tetramethyl-4,5-diphenyl-2,7-disilaoctane (2) was isolated in 22% yield from the residue by recrystallization. This compound must be formed mainly via the following reaction path, Eq. (2): H. Ikeda, Y. Miura, and M. Kinoshita



The formation of **2** indicates the following initiation mechanism: the trimethylsilyl radical which is generated on the photodecomposition of **1** attacks St, and the resulting 3,3-dimethyl-1-phenyl-3-silabutyl radical initiates the polymerization.

Furthermore, considerable amounts of hexamethyldisilane and 2,2,5,5-tetramethyl-3-phenyl-2,5-disilahexane were detected by gas-liquid chromatography, but the amounts were not determined.

Spin trapping of the trimethylsilyl radical with 2,4,6-tri-tert-butylnitrosobenzene (3)

It has been reported by *Konaka* et al.¹¹⁾ that silyl radicals are easily trapped by **3** to give the corresponding *N*-siloxy-2,4,6-tri-*tert*-butylanilino radicals (Eq. (3)).



The ESR measurement was carried out under UV-irradiation with a degassed benzene solution containing 1 and 3. Only one radical species was observed at high concentration, and the spectrum was constituted of a triplet of triplets (Fig. 7). Thus, the observed spin-adduct is obviously the *N*-trimethylsiloxy-2,4,6-tri-*tert*-butylanilino radical. The same radical was also generated by

treating trimethylsilane with di-*tert*-butyl diperoxyoxalate in benzene in the presence of $3(a_N = 10,52 \text{ G}, a_{m-H} = 1,96 \text{ G}, g = 2,0042)$. In this system *tert*-butoxy radical generated by thermodecomposition of di-*tert*-butyl diperoxyoxalate abstracts the hydrogen from trimethylsilane, and the resulting trimethylsilyl radical is trapped by 3.



Fig. 7. ESR spectrum obtained from a benzene solution (1 ml) containing $1(1,5 \cdot 10^{-3} \text{ mmol})$ and $3(5,1 \cdot 10^{-3} \text{ mmol})$ under UV irradiation

In the system of 1 and 3, a weak signal of the *N*-trimethylsiloxy-2,4,6-tri-*tert*butylanilino radical was already observed before UV-irradiation, and the intensity of the signal rapidly increased on the UV-irradiation. Thus it seems that a part of the radicals is formed via the induced decomposition of 1 by the nitroso group of 3, but the larger part of the radicals may be formed by the reaction of 3 with the trimethylsilyl radicals generated upon the photolysis of 1.

- ¹⁾ T. Minoura, H. Toshima, J. Polym. Sci., Part A-1, 7, 2837 (1969)
- ²⁾ R. A. Jackson, J. Chem. Soc. Chem. Comm. 1974, 573
- ³⁾ C. Eaborn, R. A. Jackson, R. W. Walsingham, ibid., 1965, 300
- ⁴⁾ S. W. Bennett, C. Eaborn, R. A. Jackson, R. Pearce, J. Organometal. Chem. 15, 17 (1968)

- ⁵⁾ C. Eaborn, R. A. Jackson, R. W. Walsingham, J. Chem. Soc. C, 1967, 2188
- ⁶⁾ R. Okazaki, T. Hosogai, E. Iwadare, M. Hashimoto, N. Inamoto, Bull. Chem. Soc. Japan, **42**, 3611 (1969)
- ⁷⁾ H. Gilman, R. K. Ingham, A. G. Smith, J. Org. Chem. 18, 1731 (1953)
- ⁸⁾ P. D. Bartlett, E. P. Benzing, R. E. Pinocock, J. Amer. Chem. Soc. 82, 1762 (1960)
- ⁹⁾ R. A. Gregg, F. R. Mayo, ibid., 70, 2373 (1948)
- ¹⁰⁾ J. W. Breitenbach, A. Schindler, Monatsh. Chem. 83, 724 (1952)
- ¹¹⁾ S. Terabe, R. Konaka, J. Chem. Soc., Perkin Trans. 2, 1973, 369