

Preparation and Polymerization of 4-Hydroxy-4'-vinylbiphenyl

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ABSTRACT: A new monomer of 4-hydroxy-4'-vinylbiphenyl (HVB) was prepared from 4-hydroxybiphenyl as starting material through acetylation, reduction and dehydroxylation. HVB was found to be stable at room temperature in air in contrast with 4-hydroxystyrene (PHS). The polymerization of HVB with AIBN was shown to proceed by the normal radical polymerization mechanism on the basis of kinetic results, and to give polymers with molecular weight of 25000—87000. The rate of polymerization increased in going from THF to MeOH. From the application of linear solvation energy relationships proposed by Kamlet and Taft, it seems that the polymerization is affected mainly by polarity and HBD effects of the solvent. The monomer reactivity ratio, Q and e values of HVB were determined from radical copolymerization with several vinyl monomers. An alternating copolymer was obtained by the copolymerization of HVB with maleic anhydride. The polymer of HVB was also obtained by use of cationic catalysts.

KEY WORDS 4-Hydroxy-4'-vinylbiphenyl / *p*-Hydroxybiphenyl / Radical Polymerization / Radical Copolymerization / Alternating Copolymer / Solvent Effect / Cationic Polymerization /

4-Hydroxystyrene (PHS) has been known to be a versatile monomer and numerous applications have been reported.¹⁻⁵ The preparation of pure PHS, however, is difficult in high yield, and spontaneous polymerization occurs even at low temperature to give a low molecular weight polymer.⁶ The radical polymerization of PHS has been studied by several authors.⁷⁻⁹ Kato⁷ has demonstrated that the radical polymerization proceeds by the usual manner. However, recent work has pointed out the involvement of a non-radical process.⁸ These polymerizations also gave low molecular weight polymers. Some attempts to prepare the high molecular weight polymer of PHS have been made by protection with the *t*-butoxycarbonyl¹⁰ or trialkylsilyl group¹¹ at the hydroxy group of PHS.

We found that 4-hydroxy-4'-vinylbiphenyl (HVB) is stable at room temperature and can be polymerized readily to give a high molecular weight polymer by a radical initiator.

This polymer would be expected to be useful material such as a curing agent for epoxy compounds. The present paper deals with the preparation of HBV, solvent effect on the radical polymerization, and copolymerization with vinyl monomer. Furthermore, cationic polymerization will be described.

EXPERIMENTAL

Materials

Styrene (St), methyl methacrylate (MMA), acrylonitrile (AN), methacrylic acid (MA), and maleic anhydride (MAN) were purified by the usual manners. Solvents were purified and dried by the ordinary methods. Other chemicals were of highest commercially available grade, and used without further purification.

Preparation of Monomer

*4-Acetoxy-4'-acetyl*biphenyl (AAB). 4-Hydroxybiphenyl (80 g, 0.47 mol) was added

to an ice-cold solution of acetyl chloride (110 g, 1.4 mol) and AlCl_3 (160 g, 1.2 mol) in 500 ml of methylene chloride with stirring over a period of 30 min. The reaction mixture was stirred for 3 h at room temperature and poured into ice water. The methylene chloride solution was separated, washed with water, and dried over sodium sulfate. After removal of the solvent, the resulting residue was recrystallized from methanol to give AAB (115 g 96%): mp 124.5–126°C; IR (Nujol) 1750 (ester) and 1675 cm^{-1} (ketone); ^1H NMR (CDCl_3) δ 2.3 (3H, s, $-\text{OCOCH}_3$), 2.6 (3H, s, $-\text{COCH}_3$), and 7.0–8.0 ppm (8H aroma); ^{13}C NMR (CDCl_3) δ 21.0 (q), 26.5 (q), 122.1 (d), 127.0 (d), 128.2 (d), 128.8 (d), 135.8 (s), 137.3 (s), 144.6 (s), 150.8 (s), 169.2 (s), and 187.4 ppm (s); *Anal.* Calcd for $\text{C}_{12}\text{H}_{14}\text{O}_3$: C, 75.57%; H, 5.55%. Found: C, 75.76%; H, 5.57%.

4-Hydroxy-4'-hydroxyethylbiphenyl (HEB). A solution of AAB (50 g, 0.2 mol) and NaBH_4 (7.5 g, 0.2 mol) in 150 ml of methanol was stirred at room temperature for 2 h. Most of methanol was distilled off from the reaction mixture and 400 ml of ethyl acetate was added to the residue. The ethyl acetate solution was washed with dilute hydrochloric acid and water, and dried over sodium sulfate. The solvent was removed, and the resulting residue was recrystallized from ethyl acetate to give 41 g (98%) of HEB: mp 145–146°C; IR (Nujol) 3400 (carbinol) and 3150 cm^{-1} (phenol); ^1H NMR ($\text{DMSO}-d_6$) δ 1.5 (3H, d, $-\text{CH}_3$), 4.9 (1H, q, CH), and 7.0–7.6 ppm (8H, aroma); ^{13}C NMR ($\text{DMSO}-d_6$) δ 26.1 (q), 68.6 (d), 116.3 (d), 126.2 (d), 126.4 (d), 128.2 (d), 131.6 (s), 139.1 (s), 145.6 (s), and 157.2 ppm (s); *Anal.* Calcd for $\text{C}_{14}\text{H}_{14}\text{O}_2$: C, 78.48%; H, 6.59%. Found: C, 78.09%; H, 6.63%.

4-Hydroxy-4'-vinylbiphenyl (HVB). A mixture of HEB (100 g) and zinc chloride (20 g) in 300 ml of DMSO was heated to 180°C for 20 min. After adding trichloroacetic acid (20 g), the mixture was kept at the same temperature for an additional 3 min, allowed to cool to room temperature and poured into

water. The resulting precipitate was dissolved in acetone and the acetone solution was extracted with hexane several times. The combined hexane extracts were concentrated and the resulting residue was recrystallized from chloroform and then from benzene to give 60 g of HVB in a yield of 60%: mp 190.0–191.5°C; UV_{max} (THF) 289 nm ($\epsilon=27500$); IR (Nujol) 3350 ($-\text{OH}$), 1620, 995, and 900 cm^{-1} ($-\text{CH}=\text{CH}$); ^1H NMR (CDCl_3) δ 4.6–5.0 (1H, $-\text{OH}$), 5.2–6.7 (3H, $-\text{CH}=\text{CH}_2$), and 6.9–7.6 ppm (8H, aroma); ^{13}C NMR ($\text{DMSO}-d_6$) δ 114.3 (t), 116.3 (d), 126.5 (d), 127.1 (d), 128.1 (d), 131.0 (s), 135.7 (s), 136.6 (d), 140.0 (s), and 157.5 ppm (s); *Anal.* Calcd for $\text{C}_{14}\text{H}_{12}\text{O}$: C, 85.68%; H, 6.16%. Found: C, 85.79%; H, 6.03%.

Polymerization of HVB

The radical polymerization of HVB was carried out with AIBN in pyrex glass tube sealed under high vacuum after repeated degassing processes. The homopolymers were obtained by pouring the reaction mixture into a large amount of benzene. The polymer was dried at 40°C and weighed. The copolymers of HVB were obtained by use of a mixture of benzene and hexane as precipitant. The cationic polymerization of HVB was carried out at room temperature under a dry nitrogen atmosphere. HVB and dry solvent distilled before use were placed in a flask, and the mixture was bubbled with dry nitrogen to remove air, and then a catalyst solution was added with stirring. The reaction mixture was treated similarly as described above. The purification of polymers by reprecipitation was repeated until no HVB in the filtrate was detected by TLC.

Measurement

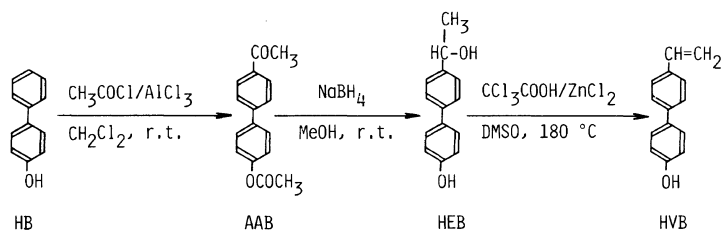
NMR-spectra were taken by a JEOL FX-100 spectrometer using TMS as an internal standard. UV-spectra were recorded on a Shimadzu-UV 260 spectrophotometer. IR spectra were recorded on a Shimadzu IR-420

spectrophotometer. The molecular weights of polymer were measured on a Shimadzu LC-3A gel permeation chromatography by use of THF as eluent. The calibration curve was made by plotting the molecular weight of the polymer measured on a Knauer vapor pressure osmometer against the elution volume.

RESULTS AND DISCUSSION

Preparation of HVB

HVB was prepared from 4-hydroxybiphenyl (HB) according to the following scheme. In the



Scheme 1.

reaction of HB with 2 times the molar amounts of AlCl_3 and acetyl chloride in CH_2Cl_2 , 4-acetoxy-4'-acetyl biphenyl (AAB) was obtained quantitatively. The use of equimolar amounts of AlCl_3 and acetyl chloride gave only 4-biphenyl acetate, and 4-hydroxy-4'-acetyl biphenyl or AAB was not obtained. Additional acetylation of 4-biphenyl acetate using AlCl_3 (2 mol) and acetyl chloride (1 mol) gave AAB quantitatively, indicating that the acetylation of 4-hydroxybiphenyl proceeds through the formation of 4-biphenyl acetate followed by acetylation of the acetate. Among the combination of catalysts and solvents examined, the use of AlCl_3 in CH_2Cl_2 was found to be most effective for the formation of AAB as described above. The use of ferric chloride, stannic chloride or titanium tetrachloride in CCl_4 , CHCl_3 , CS_2 or nitrobenzene gave AAB in low yield. The method of the acetylation of 4-hydroxybiphenyl could be applied to the preparation of 4-acyloxy-4'-acylniphenyl by use of various acyl chloride.

The dehydration of HEB by KHSO_4 at 200°C under reduced pressure gave only polymeric material. A combination of ZnCl_2 and CCl_3COOH in DMSO is the most convenient method for the preparation of HVB.

The HVB obtained was quite stable at room

temperature and could be stored without any care in contrast with the analogous monomer, PHS. It should be noted that various attractive monomers can be prepared from HVB by reacting with alkyl or acyl halides in basic medium. For example, glycidyoxy, allyloxy, cinnamoyloxy, and methacryloyloxy derivatives were prepared. The details of the polymerization of these monomers will be reported.

Radical Polymerization of HVB

The polymerization of HVB with AIBN in THF gave a white polymer with T_m of about 210°C . The polymer was soluble in CH_3OH , acetone, DMF and THF, and insoluble in benzene, CHCl_3 and ether, and had $\bar{M}_n = 25000$ — 87000 (Table I). The values of \bar{M}_n decreased with an increase in initiator concentration. Thus, the polymerization of HVB affords high molecular weight polymer without the protection of a hydroxy group. The UV, IR, and NMR spectra of the polymer were identical to those of the polymer obtained by the polymerization of 4-acetoxy-4'-vinylbiphenyl (ACVB) with AIBN followed by hydrolysis. The UV spectrum of the polymer of HVB showed λ_{max} at 264 nm which was close to that of 4-ethyl-4'-hydroxybiphenyl

Table I. Radical polymerization of HVB in THF

[HVB]	[I] × 10 ²	Temp	Time	Conversion	$\bar{M}_n \times 10^{-4}$
mol dm ⁻³	mol dm ⁻³	°C	h	%	
1.5	1.5	60	3	14.9	7.5
1.5	1.5	60	6	30.4	8.7
1.5	1.5	65	3	27.5	7.9
1.5	1.5	70	3	37.9	6.7
0.4	0.2	60	13	20.2	4.9
0.4	1.5	60	5	18.3	3.3
0.4	4.0	60	3.5	17.8	2.5

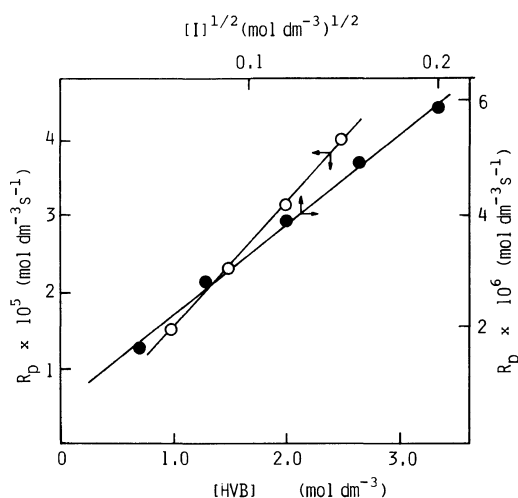


Figure 1. Relationship between R_p and initiator or monomer concentration: ●, [HVB], 0.4 mol dm⁻³; ○, [I], 1.5 × 10⁻² mol dm⁻³; temp, 60°C.

(262 nm), and about 25 nm shorter than that of HVB. This result suggests that the reaction of polymer radical with a hydroxy group in monomer and polymer may be neglected.

The conversion of monomer in the polymerization increased linearly with reaction time up to 40%, and no induction period was observed. The rate of polymerization (R_p) in THF was proportional to the concentration of monomer and the square root of the concentration of initiator as shown in Figure 1. The results indicate that the polymerization of HVB with AIBN proceeds by a normal free radical mechanism, including mutual termi-

nation of polymer radicals. The rate of polymerization (R_p) of HVB, $R_p = 3.07 \times 10^{-5}$, was large compared to that of PHS, $R_p = 1.27 \times 10^{-5}$ (mol dm⁻³ s⁻¹),⁷ showing the high reactivity of HVB in radical polymerization. The overall activation energy of polymerization of HVB (87.1) was somewhat larger than that of PHS (75.4 kJ mol⁻¹).⁷

Solvent Effect on the Radical Polymerization of HVB

The copolymerizations of HVB with several carried out in several solvents. R_p increased in going from THF to methanol (Table II). This result differs from the polymerization of *o*-hydroxystyrene, which has no solvent effect on polymerization.¹² Recently, Kamlet and Taft demonstrated the following linear solvation energy relationships (eq 1), which can serve to explain solvent effects on many reaction rate and equilibrium constants.¹³

$$XYZ = XYZ_0 + s\Pi^* + a\alpha + b\beta \quad (1)$$

where XYZ , Π^* , α , and β represent reaction rate, dipolarity/polarizability, hydrogen bond donor (HBD) acidity, hydrogen bond acceptor (HBA) basicity. The coefficients, s , a , and b are measures of the response of XYZ to changing solvent polarity, HBD acidity, and HBA basicity. The application of eq 1 to the observed R_p' which was corrected in terms of the solvent viscosity in order to exclude its influence on the polymerization rate gave a following re-

Table II. Solvent effects on the rate of polymerization of HVB^a

	CH ₃ OH	C ₂ H ₅ OH	CH ₃ CN	DMSO	DMF	Acetone	THF
$\frac{R'_p \times 10^5}{\text{mol dm}^{-3} \text{ s}^{-1}}$	1.74	1.35	1.06	1.28	0.85	0.79	0.77

^a [HVB], 0.4 mol dm⁻³; [AIBN], 1.5 × 10⁻² mol dm⁻³; temp, 60°C.

gression equation.

$$\ln R'_p = -12.52 + 1.20\pi^* + 0.82\alpha - 0.02\beta \quad (2)$$

The observed values (R'_p) are plotted against calculated values in Figure 2. From the coefficient values, it is likely that the change of polymerization rate is caused mainly by solvent polarity. This suggests polar participation of the solvent in the transition state of the propagation reaction.¹⁴ The solvent-HVB hydrogen bond interactions (HBD effect) are also important. This solvation would result in the change of monomer reactivity. In order to get information on monomer reactivity, ¹H NMR spectra were measured. The results are shown in Table III together with the rates of polymerization. These rates are related to differences in chemical shifts ($\Delta\delta$) of -OH and olefinic protons, suggesting that the interaction of HVB with solvent is also responsible for the polymerization rates. The reactivity of propagating radical would be affected by this solvation. These data are consistent with the results of polymerization of ACVB, in which there is no solvent effect on the polymerization rate; $R_p = 4.4 \times 10^{-6}$ in benzene, 4.6×10^{-6} in THF, and 4.2×10^{-6} (mol dm⁻³ s⁻¹) in DMF. It is known that the solvent effect on R_p is often caused by the difference of chain transfer to solvent and reinitiation rate by generated radical.¹⁴ However, this effect is not important because of the above result of ACVB.

The reciprocal of the number-average degree of polymerization of the polymers obtained in THF, DMF, and MeOH was plotted against R_p as shown in Figure 3. The values of $K_p/K_t^{1/2}$ calculated from the slopes of lines

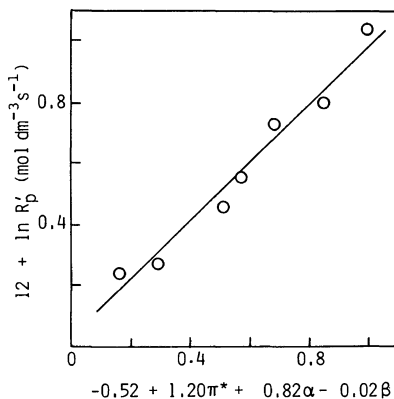



Figure 2. Observed vs. calculated rate of polymerization of HVB: [HVB], 0.4 mol dm⁻³, [I], 2.5 × 10⁻² mol dm⁻³.

Table III. Chemical shifts of HVB in various solvents

Solvent	-OH			$R'_p \times 10^5$ mol dm ⁻³ s ⁻¹
		H _a ppm	H _b ppm	
CD ₃ OD	—	5.85	5.30	1.74
DMSO- <i>d</i> ₆	9.49	5.81	5.24	1.28
CD ₃ CN	7.02	5.80	5.24	1.06
Acetone- <i>d</i> ₆	8.33	5.79	5.21	0.79
CDCl ₃	4.75	5.75	5.24	—

^a TMS was used as the internal standard.

were 8.1 in THF, 10.7 in DMF, and 14.8×10^{-2} (dm³ mol⁻¹ s⁻¹)^{1/2} in CH₃OH.

Radical Copolymerization of HVB

The copolymerizations of with several HVB conjugative monomers by AIBN were examined. The composition of the copolymers was

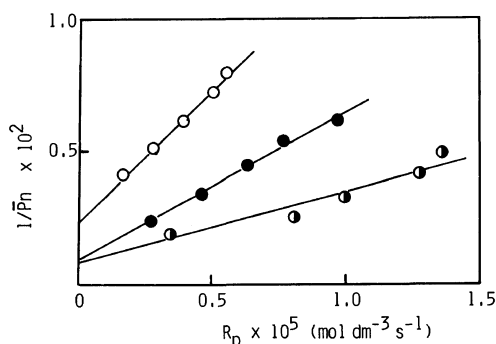


Figure 3. Relationship between $1/P_n$ and R_p ; [HVB], 0.4 mol dm^{-3} ; \circ , THF; \bullet , DMF; \ominus , CH_3OH .

Table IV. Monomer reactivity ratios (r_1, r_2) and Q - e values for HVB^a

Monomer		r_1	r_2	$r_1 r_2$	Q_1	e_1
M_1	M_2					
HVB	MMA	0.61	0.21	0.13	1.98	-1.03
HVB ^b	MMA	0.76	0.15	0.11	2.77	-1.08
HVB	MA	0.34	0.17	0.06	2.59	-1.05
HVB	AN	0.78	0.06	0.05	1.26	-0.56
HVB	St	0.53	0.54	0.29	4.48	-1.91
PHS ^c	MMA	0.25	0.34	0.09	1.14	-1.16
PHS ^c	St	1.20	0.79	0.95	1.52	-1.03

^a In THF. ^b In DMF. ^c Reference 7.

determined from the results of elemental analysis, and reactivity ratio, r_1 and r_2 , were calculated by use of the Mayo-Lewis integral equation. The e -values of HVB obtained from the copolymerization with methyl methacrylate (MMA) and methyl acrylate (MA) were similar to that of PHS, while the Q_1 -value was considerably large (Table IV).⁷ As expected, for the copolymerization with AN, an alternating tendency is greater than that of MMA. The reason why e_1 value is small for the case of AN is not clear. The rate of copolymerization with AN showed features different from those of MMA, in which the copolymerization rate had a maximum at a mole fraction of 0.3 of HVB in the monomer feed (Figure 4). This seems to be consistent with the observation of an increase of the formation of alternating polymer.

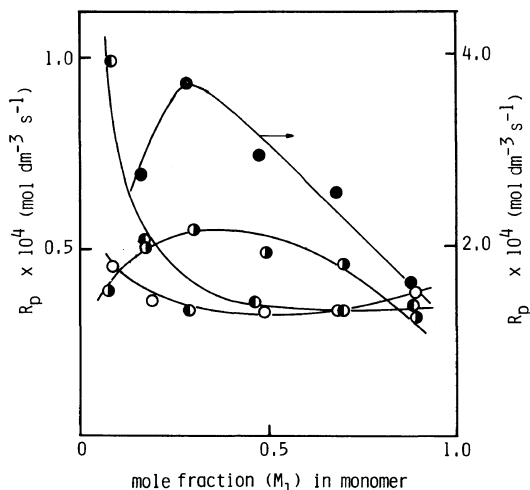


Figure 4. Rate of copolymerization vs. mole fraction in monomer feed: $[M]$, 3 mol dm^{-3} , $[I]$, $3 \times 10^{-2} \text{ mol dm}^{-3}$, THF; \circ , HVB-MMA; \bullet , HVB-MA; \ominus , HVB-AN; \bullet , HVB-MAN.

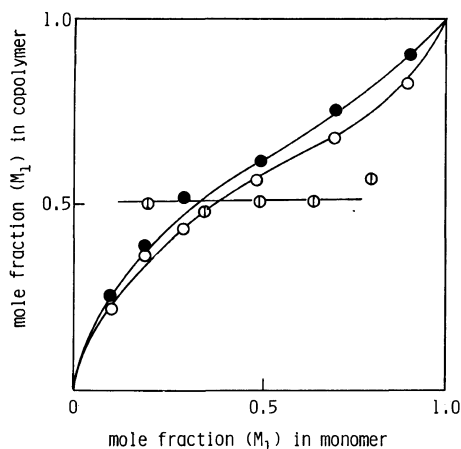


Figure 5. Copolymer composition curves of HVB with MMA and MAN: $[M]$, 3 mol dm^{-3} , $[I]$, $3 \times 10^{-2} \text{ mol dm}^{-3}$; \circ , MMA, THF; \bullet , MMA, DMF; \ominus , MAN, THF.

For the copolymerization of HVB with MAN, the alternating copolymer was obtained as shown in Figure 5. The solution of HVB and MAN in THF was pale yellow. The absorption spectra of the mixture of HVB and MAN shifted to the red region, indicating the formation of a charge-transfer complex. The continuous variation plots showed the formation

of a 1:1 complex. If the charge-transfer complex participates in the propagation step, the rate of copolymerization should maximize at a monomer feed molar ratio of unity. However, the maximum rate was found at a mole fraction of 0.3 of HVB. This suggests that the copolymerization predominantly occurs by free radical process.¹⁵ Copolymerization with styrene did not give a reasonable e -value of HVB, because of the difficulty to obtain accurate composition of the copolymers. The solvent effect also appeared in the copolymerization with MMA as shown in Figure 5. The reactivity ratio of HVB, r_1 , increased whereas r_2 decreased by changing the solvent from THF to DMF. These results may be explained by the increase of reactivity of HVB owing to the solvation with DMF.

Cationic Polymerization of HVB

The results of cationic polymerization of HVB by several catalysts are shown in Table V. Among the catalysts used, stannic chloride showed the best results in yields of polymer. The polymer was insoluble in the solvents used and precipitated from the reaction mixture during the polymerization. Therefore, the cationic polymerization of HVB in these solvents gave a low molecular weight polymer of *ca.* 5000. The structure of the polymer obtained by the cationic polymerization was confirmed to be identical with that of the polymer by radical polymerization on the basis of IR and NMR spectra, indicating that the cationic polymerization of HVB proceeds through polymerization of a vinyl function in HVB.¹⁶

In summary, HVB can be readily homo- and copolymerized with various vinyl monomers with AIBN to give high molecular weight polymers. The rate of polymerization is affected by the solvent polarity and hydrogen bond effect. HVB and its polymer may be expected to be useful materials such as antioxidants and to resist resins for microlithography.

Table V. Cationic polymerization of HVB^a

[HVB] mol dm ⁻³	Catalyst	[Cat.] mol dm ⁻³	Conversion %	\bar{M}_n
31	BF ₃ Et ₂ O	5.0	82.7	6200
25		0.4	3.3	—
		1.0	10.3	4700
		5.0	83.8	5400
		5.0 ^b	66.5	6200
25	TiCl ₄	5.0	69.1	4400
25	SnCl ₄	5.1	100	5000

^a In CH₂Cl₂; temp, 25°C, time, 20 min.

^b In ClCH₂CH₂Cl.

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