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Dehydrogenative polycondensation of telechelically bis(dimethylsilyl)functionalized oligo(dimethylsiloxane)s or aromatics and 1,3,3,5,5,7,7,7-octamethyltetrasiloxane

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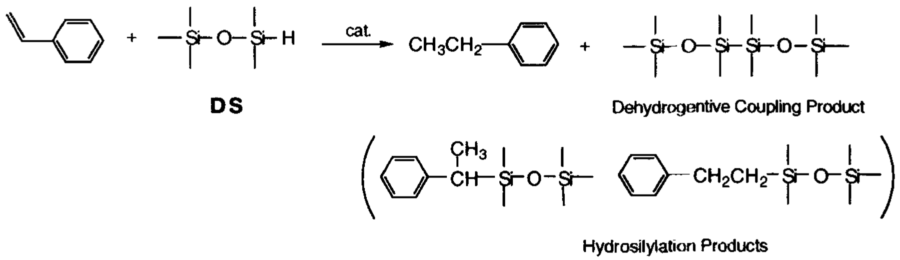
Summary

Telechelically bis(hydrodimethylsilyl)-functionalized oligo(dimethylsiloxane)s or aromatics were found to give polymers constituting of alternating disilylene and oligodimethylsiloxane or 4,4'-diylaromatics as repeating units by dehydrogenative coupling reaction in the presence of palladium dibenzylideneacetone complex. The same catalyst gave polysilylenes with trisiloxane pendant from 1,1-dihydro-1,3,3,5,5,7,7,7-octamethyltetrasiloxane.

Introduction

We recently reported the synthesis of 1-hydro-(1, 3 or 7)-functionalized di- or tetrasiloxanes(1-3). The bifunctional di- and tetrasiloxanes with unsaturated bond thus prepared gave polymers via polyaddition by platinum catalyzed hydrosilylation(2). During the study of the reaction between styrene and 1-hydro-1,1,3,3,3-pentamethyldisiloxane(**DS**) as a model reaction, we found that ethylbenzene was formed during the reaction which strongly suggested the formation of disilylene derivative from 1-hydro-1,1,3,3,3-pentamethyldisiloxane by the cleavage of Si-H bond, especially with high (2 mol % or higher) concentration of the catalyst, even with Pt-divinyltetramethyldisiloxane complex(Pt-DVTMDS)(4). Whole reaction scheme might be written as shown in Scheme 1.



Scheme 1. Formation of ethylbenzene during hydrosilylation.

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This is a quite unfavorable side reaction in hydrosilylation, but if the dehydrogenative coupling reaction proceeds selectively, the reaction may become an efficient synthetic route to poly(disilylene-*alt*-oligosiloxane)s from α,ω-bis(hydrosilane)-functionalized oligosiloxanes. Although dehydrogenative coupling of trihydro or dihydrosilanes are well known(5-16), interested in our findings on effective coupling of monohydrosilanes, efficient and selective catalysts were further explored, and here we report on the synthesis of poly(disilylene-*alt*-oligodimethylsiloxane or 4,4'-diylaromatics) and polysilylenes.

Experimental

General

^{1}H and ^{29}Si NMR spectra were recorded on Varian NMR spectrometers model Gemini 300(300 MHz for ^{1}H) and Unity 400(79.5 MHz for ^{29}Si). Molecular weights of the polymer were determined by a JASCO gel permeation chromatography (GPC) model 980 at 40 °C equipped with Shodex KF-800P (precolumn), KF-801 (exclusion molecular weight polystyrene Mn = 1,500) and KF-804 (exclusion molecular weight polystyrene Mn = 400,000) columns and JASCO 875-UV, 830-RI detectors using THF as an eluent (1 mL/min). The molecular weight was calibrated using standard polystyrenes.

Reagents

Commercial styrene, **DS**, 1,4-bis(hydrodimethylsilyl)benzene, 1,1-dihydro-1,1,3,3-tetramethyldisiloxane, benzoquinone, and palladium dibenzylideneacetone[$Pd_2(dba)_3{\bullet}CHCl_3$] complex were used. 1,7-Dihydro-1,1,3,3,5,5,7,7-octamethyltetrasiloxane was synthesized by reducing 1,7-dichloro-1,1,3,3,5,5,7,7-octamethyltetrasiloxane with lithium aluminum hydride. 4,4'-Bis(hydrodimethylsilyl)biphenyl(**4**) was synthesized from 4,4'-dibromobiphenyl through Grignard reaction followed by quenching with dimethylchlorosilane(Yield 51 %). 1,1-Dihydro-1,3,3,5,5,7,7,7-octamethyltetrasiloxane(**5**) was synthesized by the reduction of 1-chloro-1-hydro-1,3,3,5,5,7,7,7-octamethyltetarasiloxane obtained from lithium heptamethyltrisiloxanolate and methyldichlorosilane by lithium aluminum hydride. Bis(cyclopentadienyl)diphenyltitanium(Cp_2TiPh_2) was synthesized as reported(17,18).

Reaction Procedure

Typical procedures of model reaction and polycondensation are given.

*Palladium Catalyzed Reaction of **DS** with Styrene*

To $Pd_2(dba)_3{\bullet}CHCl_3$ (0.0052 g, 0.005 mmol) in a 10 ml test tube, **DS**(0.18 ml, 1.0 mmol) and styrene (0.11 ml, 1.0 mmol) were added at room temperature under argon atmosphere, and the reaction mixture was stirred at 50 °C. The extent of the reaction was monitored by following the disappearance of Si*H* by ^{1}H NMR.

Palladium Catalyzed Polycondensation in the Presence of an Acceptor

1,4-Bis(hydrodimethylsilyl)benzene(5 mmol) and $Pd_2(dba)_3{\bullet}CHCl_3$ (0.025 mmol) were heated in the presence or absence of benzoquinone (5 mmol) as a possible hydrogen acceptor.

The reaction was monitored by the disappearance of Si*H*.

Results and Discussion

^{1}H NMR spectrum of the reaction mixture of **DS** and styrene with $Pd_2(dba)_3{\bullet}CHCl_3$(run 6) revealed that ethylbenzene had been formed almost selectively with the consumption of styrene. Change in ^{29}Si chemical shift of the reaction product(7.6ppm, s, Me_3*Si*O; -22.0 ppm, s, *SiSi*) from **DS**(9.0 ppm, s, Me_3*Si*O; -7.0 ppm, d, J=202 Hz, *Si*H) supports the formation of 1,1,1,3,3,4,4,6,6,6-decamethyl-2,5-dioxahexasilylene. Based on this, it was concluded that the reaction between **DS** and styrene in the presence of $Pd_2(dba)_3{\bullet}CHCl_3$ actually proceeded as shown in Scheme 1. The results of the reaction between **DS** and styrenein the presence of various catalysts are summarized in Table 1. The selectivity of α- and β- addition was deterimined by ^{1}H NMR as reported(2).

Table 1. Selectivity in Reaction of **DS** with Styrene

Run	Cat. (mol%)	Solv.	Temp (°C)	Time (h)[a)]	Ratio (α/β/EB)[b)]
1	PtDVTMDS (2.0)	bulk	r.t.	0.1	24/63/13
2	PtDVTMDS (0.01)	bulk	r.t.	1	30/70/0
3	$Rh(PPh_3)_3Cl$ (0.5)	Tol.	50	18	23/48/29
4	$[Rh(COD)Cl]_2$ (0.5)	Tol.	50	24	10/48/42
5	$Pd(PPh_3)_2Cl_2$ (1.0)	Tol.	50	14	0/0/100
6	$Pd_2(dba)_3{\bullet}CHCl_3$ (0.5)	Tol.	50	10	0/0/100
7	Cp_2TiPh_2 (0.5)	Tol.	80	48	0/0/100

a) Pentamethyldisiloxane was completely consumed.

b) α , β and EB indicate α and β adduct of the hydrosilylation and ethylbenzene, respectively.

Platinum catalyst is efficient in hydrosilylation(run 2). It is also active in reductive coupling when it is used in high concentration, but the reaction is not selective(run 1). Rhodium compounds are moderately active and less selective catalysts(run 3, 4). Not only palladium compounds, Cp_2TiPh_2 is effective in the reaction but at elevated temperature(run 7). Among the palladium compounds, $Pd_2(dba)_3{\bullet}CHCl_3$ is the better catalyst(run 5, 6). Although dehydrogenative couplings of silane with transition metal catalysts were reported(5), to our knowledge, this is the first example of the dehydrogenative coupling reaction of hydrodimethylsilyl-substituted oligodimethylsiloxane.

Polymerization of 1,3-dihydro-1,1,3,3-tetramethyldisiloxane(**1**), 1,7-dihydro-1,1,3,3,5,5,7,7-octamethyltetrasiloxane(**2**), 1,4-bis(hydrodimethylsilyl)benzene(**3**), and **4** catalyzed by $Pd_2(dba)_3{\bullet}CHCl_3$ were carried out in the presence or absence of styrene or benzoquinone as a hydrogen acceptor. For comparison, Cp_2TiPh_2 is used in the polymerizations of 1 and 3(run 4, 11). Polymerization of **5** was also carried out. The results are shown in

Table 2.

Table 2. Polycondensation of Monomer **1**, **2**, **3**, **4** and **5**.

Run	Monomer	Cat.	Acceptor	Temp (°C)	Time (d)[a]	*Mn*[b]	*Mw*/*Mn*
1	**1**	Pd	none	50	1.5	540	1.2
2			St	50	1	bimordal	
3			BQ	50	0.5	670	1.5
4		Ti	none[c]	80	1	no reaction	
5	**2**	Pd	none	50	1	6200	1.4
6			St	50	5	bimordal	
7			BQ	50	4	bimordal	
8	**3**	Pd	none	50	4	2200	1.7
9			St	50	1	1580	1.8
10			BQ	50	0.8	1310	1.5
11		Ti	none[c]	80	1	no reaction	
12	**4**	Pd	none	50	0.8	2050	2.9
13			St	50	0.8	bimordal	
14			BQ	50	0.5	bimordal	
15	**5**	Pd	none	50	0.8	2800	2.0
16			BQ	50	0.8	3000	3.2

a) Reaction time when monomer was completely consumed.
b) Collelated by standard polystyrene.
c) When acceptors were existed, the results were same, no reaction.
Pd : $Pd_2(dba)_3$•$CHCl_3$. Ti : Cp_2TiPh_2. St : Styrene. BQ : Benzoquinone.

The average molecular weights of polymers from **1**, **2**, **3**, and **4** were in the range of only hundreds, probably cyclic dimer, 6000, 2000, and 2000, respectively. In the cases of monomer **1** and **3**, when a hydrogen acceptor, styrene or benzoquinone, was present, the polycondensation reactions were faster than that without it. However, in the cases of monomer **2** and **4**, the polymerization reactions with hydrogen acceptor were slower than that without it. Sometimes even bimodal molecular weight distribution was noticed. Definite conclusion about the effect of hydrogen acceptor could not be drawn.

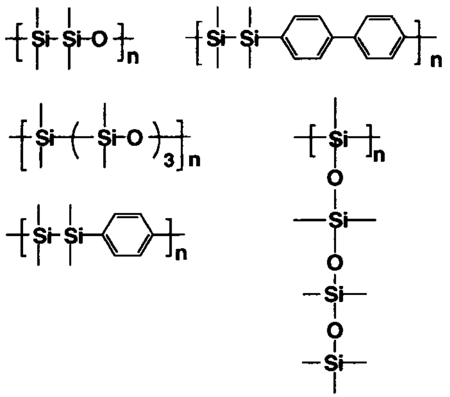

Figure 1. Structures of synthesized polymer.

Meanwhile, it is reported that polysiylenes synthesized by polycondensation of dichlorosilane with sodium metal usually have bimodal molecular weight distribution(19).

Titanocene compound was only effective in the model reaction, not in polycondensation of the monohydrosilane.

Conclusion

Polymers with unique structure such as alternating siloxane and disilylene units and polysilylenes with pendant heptamethyltrisiloxane were obtained by dehydrogenative polycondensation reaction although the molecular weights were not so high.

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