Supporting Information

DIPEA-induced Si-H activation of siloxane for Hydrosilylation

Polymerization via Metal-Free photocatalysis

Hangcen Xie^{1,2}, Rui Xu^{1,2}, Bin Huang¹, Pingping Lou¹, Huafeng Fei^{1,2*}, Zhijie Zhang^{1*}

¹ Key Laboratory of Science and Technology on High-tech Polymer Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, P. R. China

² School of Chemical Sciences, University of Chinese Academy of Sciences, Beijing 100049, P. R. China

1. Materials

(98%, 1,1,3,3-tetramethyldisiloxane (MMH) Aladdin), 1,3-Divinyl-1,1,3,3tetramethyldisiloxane (MMVi) (97%, J&K), 1,1,3,3-tetraisopropyldisiloxane(95%, J&K), 1,1,5,5-tetramethyl-3,3-diphenyltrisiloxane(98%, J&K), Methylphenylsilane(97%, Aladdin), Diethylsilane(98+%, Alfa), Diphenylsilane (99%, 1,4-bis(dimethylsilyl)benzene(98%, J&K)), N,N'-diisopropylethylamine J&K). (DIPEA) (99%, Aladdin), N,N-diisopropylmethylamine (97%, J&K), Triethylamine (TEA) (99%, Energy Chemical), K₂CO₃ (99%, Xilong Scientific), 2,4,5,6-tetra-9Hcarbazol-9-yl-1,3-benzenedicarbonitrile (4CzIPN) (98%, J&K), 2,4,5,6-tetrakis(3,6diphenyl-9H-carbazol-9-yl) isophthalonitrile (4CzIPN-Ph) (98%, Energy Chemical), 3,4,5,6-tetrakis(3,6-di-tert-butyl-9H-carbazol-9-yl) phthalonitrile (4CzIPN-Bu) (98%, Macklin), 2,4,6-tris(diphenylamino)-3,5-difluorobenzonitrile (3DPA2FBN) (97%, Energy Chemical), 2,4,6-tris(diphenylamino)-5-fluoroisophthalonitrile (3DPAFIPN) (97%, Energy Chemical), 1,3,5-trimethoxybenzene(99%, J&K), Acetonitrile (MeCN) (99.9% anhydrous, J&K), Dichloromethane (DCM) (99.9% anhydrous, J&K), Toluene (AR, Concord technology), N, N-Dimethylformamide (DMF) (99.8% anhydrous, J&K), Tetrahydrofuran (THF) (99.9% anhydrous, J&K), 1,4-dioxane (99.8% anhydrous, J&K), 2,2,6,6-tetramethyl-1-piperinedinyloxy (TEMPO) (97%, J&K), and 1,1-diphenylethylene (97.5%, Amethyst) were used as received. The Pt catalyst was homemade in our lab. All other reagents were obtained as commercial products and used directly, unless otherwise stated. The polymerizations were carried out under irradiation with 470 nm blue light LED strips (60 W, 220 V).

2. Experiments

2.1 General Evaluation and Analytical Information

¹H NMR spectra was recorded on Bruker Avance III 400 HD (400 MHz) at room temperature using CDCl₃ or CD₂Cl₂ as solvent. ²⁹Si NMR spectra was recorded on Bruker Avance II+ 400 (400 MHz) at room temperature using CDCl₃ or toluene as

solvent. ¹⁹F NMR spectra was recorded on Bruker Avance 600 (600 MHz) at room temperature using CD₃CN as solvent. 135 DEPT ¹³C NMR spectra was recorded on Bruker Avance 600 (600 MHz) at room temperature using CDCl₃ as solvent. Gel permeation chromatography (GPC) was performed in tetrahydrofuran at 40 °C with a flow rate of 1 mL/min on a Waters Alliance HPLC system equipped with a 1515 pump and a 2414 refractive index detector. Thermogravimetric analysis (TGA) experiments were carried out on samples (5.00~10.0 mg) from 50 °C to 750 °C at a heating rate of 10 °C/min in a N₂ atmosphere using a Mettler Toledo Instruments TGA2. Differential scanning calorimetry (DSC) experiments were conducted using a Mettler Toledo Instruments DSC3 under N₂ flow. Samples (5.00~10.0 mg) were subjected to a cycle of -120 °C to 30 °C at a rate of 10 °C/min, unless otherwise stated.

2.2 Survey of the hydrosilylation polymerization reaction conditions

entry	[DIPEA] (mol%)	Solvent	Conv ^a (%)
1	10	acetonitrile	22
2	20	acetonitrile	47
3	30	acetonitrile	52
4	40	acetonitrile	71
5	50	acetonitrile	89
6	60	acetonitrile	68

Table S1. Optimization of the DIPEA concentration for the hydrosilylation

1	1	•	
no	VIMO	11701	tion
DU		ILLa	uon
	2		

7	70	acetonitrile	44
8	80	acetonitrile	57
9	90	acetonitrile	65
10	100	acetonitrile	72

a. Conversion rate of dienes based on crude ¹H NMR analysis, using 1,3,5-trimethoxybenzene as an internal standard;

entry	[DIPEA] (mol%)	[PC] (mol%)	Solvent	Conv ^a (%)
1	50	3	1,4-dioxane	trace
2	50	3	THF	51
3	50	3	toluene	0
4	50	3	dichloromethane	20
5	50	3	acetonitrile	89

Table S2.	Optimization	of the solvent	for the h	hydrosilvlation	polymerization
14010 52.	optimization	or the borrent	101 0110 1	i jai obli jiacioli	Polymenzation

a. Conversion rate of dienes based on crude $^1\mathrm{H}$ NMR analysis, using 1,3,5-trimethoxybenzene as an internal standard;

Table S3. Optimization of the catalyst concentration for the hydrosilylationpolymerization				
entry	[DIPEA] (mol%)	[PC] (mol%)	Solvent	Conv ^a (%)

1	50	3	THF	51
2	50	1.5	THF	59
3	50	3	acetonitrile	89
4	50	1.5	acetonitrile	75

a. Conversion rate of dienes based on crude ¹H NMR analysis, using 1,3,5-trimethoxybenzene as an internal standard;

entry	Base	Solvent	Conv ^a (%)
1	TEA	acetonitrile	67
2	K ₂ CO ₃	acetonitrile	NR
3	N, N-Diisopropylmethylamine	acetonitrile	84

Table S4. Optimization of the base for the hydrosilylation polymerization

a. Conversion rate of dienes based on crude ¹H NMR analysis, using 1,3,5-trimethoxybenzene as an internal standard;

2.3 Model Hydrosilylation Reaction



Scheme S1. Model hydrosilylation reaction conditions

To a 25 mL single necked flask equipped with a magnetic stir bar was added the photocatalyst **5a** 3DPAFIPN (0.0036 mmol) and anhydrous acetonitrile (2.0 mL). The flask was sealed and filled with N_2 for 30 min. After that, MMH (0.12 mmol), MMVi

(0.12 mmol) and DIPEA (0.06 mmol) were added sequentially by means of syringe. Then the reaction was placed under a blue LED with a nitrogen balloon and irradiated for 24 h. The solvent was removed on a rotary evaporator under reduced pressure. The resulting mixture was added dropwise to 10 equal volume of methanol solution for three times in order to give the hydrosilylation product.

2.4 Gram scale reaction



Scheme S2. Equipment for large-scale synthesis

In a 50 ml round bottom flask equipped with a stir bar was added anhydrous acetonitrile (20 mL), DIPEA (6 mmol, 0.5 equiv.), 3DPAFIPN (0.036 mmol, 0.03 equiv.) and filled with N_2 for 2 h. After that, MMH (12 mmol) and MMVi (12 mmol) were added sequentially by means of syringe. The mixture was stirred at room temperature with a nitrogen balloon for 36 h under blue light LED (60W). After the reaction, the mixture was extracted with methanol solution for three times and concentrated in vacuo.

2.5 Pt catalyzed hydrosilylation polymerization

In a 25 ml round bottom flask equipped with a stir bar was added anhydrous acetonitrile (2 mL), DIPEA (0.06mmol, 0.5 equiv.), Pt catalyst (2 wt%) and filled with N₂ for 2 h. After that, MMH (0.12 mmol) and MMVi (0.12 mmol) were added sequentially by means of syringe. The mixture was stirred at 65 °C for 24 h under N₂ atmosphere. After the reaction, the mixture was extracted with methanol solution for three times and concentrated in vacuo.

2.6 The reusability of base

In a 25 ml round bottom flask equipped with a stir bar was added the upper clear solution derived from the solution of the completed gram-scale hydrosilylation reaction of MePhSiH₂ (10 mL), and filled with N₂ for 2 h. After that, MMH (6 mmol) and MMVi (6 mmol) were added sequentially by means of syringe. The mixture was stirred at room temperature with a nitrogen balloon for 24 h under blue light LED (60 W). Take the liquid before and after the reaction for ¹H NMR. ¹H NMR spectra was recorded on Bruker Avance III 400 HD (400 MHz) at room temperature using CDCl₃ as a solvent. The conversion rate of the reaction can reach 43%.



Figure S1. ¹H NMR spectrum of (a) the liquid mixture before the recycled reaction; (b) the liquid mixture after the recycled reaction.

3. Mechanistic Investigations

1)Radical inhibition experiments



a. The results based on crude ²⁹Si NMR analysis

Scheme S3. Radical inhibition experiments conditions

2) ¹⁹F NMR spectroscopic evidence for ConPET process

Add 3DPAFIPN (6.5 mg, 1 mmol) to the nuclear magnetic tube (NMR tube). Then, the NMR tube was transferred to the glovebox and CD_3CN (0.6 mL) were subsequently added to the tube.

Step 1: The ¹⁹F NMR spectrum of the photocatalyst were recorded.

Step 2: The ¹⁹F NMR spectrum were recorded after the solution was irradiated with 60 W blue LED lamps (1 cm away) for 5 min.

Step 3: Then, DIPEA (40 μ L) was added to the solution in the glovebox. The ¹⁹F NMR spectrum were recorded.

Step 4: Place the solution in step 3 under the blue LED lamps (1 cm away) for 5 min. The ¹⁹F NMR spectrum were recorded.



Figure S2. ¹⁹F NMR spectrum for ConPET process

3) Stern-Volmer experiments

First, N, N-diisopropylethylamine was dissolved in CH₃CN in a 5 mL volumetric flask to give concentrations of 0.10 mM, 0.20 mM and 0.30 mM. The photocatalyst 3DPAFIPN was also dissolved in CH₃CN (50 mL) to adjust the concentration to 0.1 mM. N, N-diisopropylethylamine was added to a solution of 3DPAFIPN (0.1 mM) in CH₃CN, and the resulting solution was made to a fixed concentration in a volumetric flask. Subsequently, the combined solutions should be transferred to a capped quarts cuvette. Samples were irradiated at 416 nm.



Figure S3. Fluorescence intensity of 3DPAFIPN solution with different DIPEA concentrations

4) Kinetic Studies of the Hydrosilylation Polymerization

To a 25 mL single necked flask equipped with a magnetic stir bar was added the photocatalyst **5a** 3DPAFIPN (0.018 mmol) and anhydrous acetonitrile (10.0 mL). The flask was sealed and filled with N₂ for 30 min. After that, MMH (0.6 mmol), MMVi (0.6 mmol) and DIPEA (0.3 mmol) were added sequentially by means of syringe. Then the reaction was placed under a blue LED with a nitrogen balloon and irradiated for 24 h. During the reaction process, use a syringe to take a small amount of the reaction solution every 2 h for GPC and ¹H NMR test. Conversions of the diene were based on crude ¹H NMR analysis. M_n and dispersity of the polymer (D) were determined by GPC calibrated with PS standards in THF at 40 °C. Figure S4 shows the data.



Figure S4. Kinetic studies of the hydrosilylation polymerization:(a) conversion of C=C bonds vs. time (first 400 minutes); (b) conversion of C=C bonds vs. time; (c) the average molecular weight of polymers M_n vs. the conversion rate of C=C bonds, the dispersity of the polymer D vs. the conversion rate of C=C bonds; (d) The variation pattern of retention time in GPC test

5) DFT calculation results

All density functional theory (DFT) and time-dependent DFT (TD-DFT) computations were executed using the Gaussian 16 suite of programs. Geometry optimizations and frequency analyses for all compounds were performed at the M06-2X/def2-SVP level, ensuring the attainment of stable structures devoid of imaginary frequencies. The SMD model, specifically employing acetonitrile as the solvent, was employed to simulate solvent effects. For the radical systems, the DFT calculations were performed within the unrestricted formalism using the unrestricted Kohn-Sham (UKS) theory.

A systematic conformational search was conducted utilizing xTB software package. The conformation with the lowest energy was then selected as the initial structure of the P for subsequent calculations.



Figure S5. The structures in DFT simulation calculations (obtained by Gaussian software)

Substance	G(a.u.)
1	-814.546881
2	-969.112818
DIPEA(A)	-370.337107
DIPEA*+(B)	-370.156443
DIPEA-H ⁺ (C)	-370.838724
PC(III)	-2065.48278
PC ⁻ (II)	-2065.58604
PC*(I)	-2065.37419
P_anion	-1783.14835
1_radical	-813.909338
P_radical	-1783.05397
Р	-1783.69364
H^{+}	-0.397948

Table S5. Gibbs free energy values of each substance calculated by DFT theory

4. Cross-linking of polyvinyl silicone oil with disiloxane

The polyvinyl silicone oil (5000 cp) was utilized as the precursor for the crosslinking reaction, and a suitable quantity of the 3DPAFIPN, DIPEA and disiloxane were incorporated prior to irradiation with blue light for a period of 24 h.

entry	[3DPAFIPN] (mol%)	[DIPEA] (mol%)	[Si-H] ₀ /[C=C] ₀	product	Solvent
1ª	3	50	0	liquid	THF
2	3	50	1	gels	THF
3	1.5	50	1	gels	THF
4	3	50	1.1	gels	THF
5	1.5	50	1.1	gels	THF
6	3	50	1.5	gels	THF
7	3	50	0.5	liquid	THF
8	3	50	1	liquid	toluene
9	3	50	1	liquid	DCM
10	3	50	1	liquid	1,4-dioxane

Table S6. Gel results under different conditions

a. without disiloxane

5. Analytical Data of the Polymers

Due to the relatively complex composition of the product, all final product structures presented below are distinguished by the trans addition structure.

5.1 GPC trace



Figure S6. Retention time of the addition reaction product of MMVi and reactant 2b in GPC test



Figure S7. Retention time of the addition reaction product of MMVi and reactant 3b in GPC test



Figure S8. Retention time of the addition reaction product of MMVi and reactant 4b in GPC test



Figure S9. Retention time of the addition reaction product of MMVi and reactant 6b in GPC test

5.2 ¹H NMR spectrum



Figure S10. ¹H NMR spectrum of addition reaction product of MMVi and reactant 2b (solvent: CDCl₃)



Figure S11. ¹H NMR spectrum of addition reaction product of MMVi and reactant 3b (solvent: CDCl₃)



Figure S12. ¹H NMR spectrum of addition reaction product of MMVi and reactant 4b (solvent: $CDCl_3$)



Figure S13. ¹H NMR spectrum of addition reaction product of MMVi and reactant 5b (solvent: $CDCl_3$)



Figure S14. ¹H NMR spectrum of addition reaction product of MMVi and reactant 6b (solvent: CDCl₃)



Figure S15. ¹H NMR spectrum of addition reaction product of MMVi and reactant 7b (solvent: CDCl₃)



Figure S16. ¹H NMR spectrum of addition reaction product of MMVi and reactant 7b using Pt as catalyst (solvent: CD₂Cl₂)

5.2 ²⁹Si NMR spectrum



Figure S17. ²⁹Si NMR spectrum of addition reaction product of MMVi and reactant 2b (solvent: CDCl₃)



Figure S18. ²⁹Si NMR spectrum of addition reaction product of MMVi and reactant 3b (solvent: toluene)



Figure S19. ²⁹Si NMR spectrum of addition reaction product of MMVi and reactant 4b (solvent: toluene)



Figure S20. ²⁹Si NMR spectrum of addition reaction product of MMVi and reactant 5b (solvent: CDCl₃)



Figure S21. ²⁹Si NMR spectrum of addition reaction product of MMVi and reactant 6b (solvent: CDCl₃)



re S22. ²⁹Si NMR spectrum of addition reaction product of MMVi and reactant 7b (solvent: CDCl₃)



Figure S23. ²⁹Si NMR spectrum of addition reaction product of MMVi and reactant 4b using Pt as catalyst (solvent: CDCl₃)



Figure S24. ²⁹Si NMR spectrum of addition reaction product of MMVi and reactant 5b using Pt as a catalyst (solvent: CDCl₃)



Figure S25. ²⁹Si NMR spectrum of addition reaction product of MMVi and reactant 6b using Pt as catalyst (solvent: CDCl₃)



Figure S26. ²⁹Si NMR spectrum of spectrum of addition reaction product of MMVi and reactant 7b using Pt as catalyst (solvent: toluene)

5.3 135 DEPT ¹³C NMR spectrum



Figure S27. 135 DEPT ¹³C NMR spectrum of addition reaction product of MMVi and reactant 3b (solvent: CDCl₃)



Figure S28. 135 DEPT ¹³C NMR spectrum of addition reaction product of MMVi and reactant 3b (solvent: CDCl₃)



Figure S29. 135 DEPT ¹³C NMR spectrum of addition reaction product of MMVi and reactant 5b (solvent: CDCl₃)



Figure S30. 135 DEPT ¹³C NMR spectrum of addition reaction product of MMVi and reactant 5b (solvent: CDCl₃)

5.4 TGA and DSC data of the polymers

















