

Soluble and Conductive Polypyrrole Copolymers Containing Silicone Tegomers

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ABSTRACT: Soluble and processable conductive copolymers of silicone tegomers and pyrrole were developed. This was easily accomplished by the oxidative polymerization of pyrrole monomer by Ce(IV) salt in the presence of silicone tegomers with hydroxyl chain ends. The resulting copolymers were soluble in dimethylformamide. The products

were characterized by Fourier transform infrared, ¹H-NMR, and four-point probe conductivity, and their surface properties were investigated with contact-angle measurements. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2896–2901, 2003

Key words: polypyrroles; silicones; conducting polymers

INTRODUCTION

Conductive polypyrrole (PPy) has received considerable attention because it can be prepared both electrochemically¹ and by chemical oxidation^{2,3} and because it has relatively good stability in the conducting oxidized form. However, PPy is a hard, brittle, and non-processable solid that is insoluble in common solvents.

Neutral polymers are introduced to the polymerization media to overcome the solubility problem of PPy, which is adsorbed in the colloid form onto neutral polymers by the interaction of opposite charges of two macromolecules⁴ or by matrix polymerization.^{5–7} In the latter case, the polymerization products have low conductivities (10^{–6} S/cm) because of the very low conductivity of the matrix polymer [for poly(acrylic acid), 10^{–8} S/cm].⁸

The other method for improving the mechanical properties of PPy is the preparation of composites from a conducting polymer and an insulating polymer.^{9–11} This method improves the mechanical properties of PPy rather than the solubility properties.

The oxidative polymerization of pyrrole (Py) by ceric(IV) ammonium nitrate, in the presence of methyl ethyl ketone/formaldehyde resin was studied,¹² and soluble PPy copolymers were produced. These soluble copolymers had conductivity values as high as 10^{–2} S/cm. Ce(IV) salt oxidized both Py and methylol groups of ketonic resins, and block copolymers were formed by the termination reaction of growing PPy radicals with the radicals produced in the ketonic resin by Ce(IV).¹³ The polymerization of vinyl mono-

mers with a redox initiator system of silicone tegomer and Ce(IV) salt resulted in polymers with silicone tegomer chain ends.¹⁴ Ce(IV) oxidized hydroxymethyl groups of silicone tegomers and yielded radicals that initiated the polymerization of vinyl monomers.¹⁴ Crosslinked copolymers of Py and silicone compounds were produced electrochemically.¹⁵ However, this method included a number of steps for producing Py-terminated silicone tegomers, and only crosslinked copolymers could be produced. In this work, the oxidative polymerization of Py by ceric(IV) ammonium nitrate, in the presence of silicone tegomers with hydroxyl chain ends, was studied with the aim of producing copolymers with higher elasticity, higher solubility, and higher contact angles than PPy. The effect of the concentrations of silicone tegomers, Py, and Ce(IV) on the yield, conductivity, and physical properties of the product was investigated.

EXPERIMENTAL

Materials

Py, acetonitrile, dimethylformamide (DMF), acetone, and ceric ammonium nitrate (CAN) were all reagent-grade chemicals of the highest purity, and they were used without further purification. All the solutions were freshly prepared before each run.

α,ω -Hydroxy poly(dimethylsiloxane)s (tegomers) were products of Goldschmidt Chemical Corp. (Essen, Germany). The molecular weights of tegomers H-Si 2111 and H-Si 2311 were 950 ± 80 and 2500 ± 250, respectively.

Analyses

IR spectra were recorded on a Jasco 5300 Fourier transform infrared (FTIR) spectrometer (Japan).

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TABLE I
The Role of Concentration on the Conductivity, Solubility, and Yield of the Copolymers

Copolymer	[Tegomer 2111]	[CAN]	[Py]	Conductivity (S/cm)	Yield (g)	Solubility	
						DMF	Acetone
Blank (PPy)	—	0.01	0.232	7.5	0.03	i	i
1	0.0344	0.022	0.232	2×10^{-1}	0.08	sl	sl
2	0.0344	0.176	0.232	1×10^{-5}	0.70	s	s
3	0.0344	0.022	0.464	3×10^{-1}	0.07	sl	sl
4	0.0688	0.022	0.232	1×10^{-5}	0.50	s	s
5	0.0344	0.01	0.232	3×10^{-4}	0.09	s	i
6	0.0344	0.005	0.232	6×10^{-5}	0.04	s	s
7	0.0344	0.05	0.232	5×10^{-2}	0.18	s	i
8 ^a	0.0344	0.05	0.232	6.1	0.31	s	i

i = insoluble, sl = slightly soluble; s = soluble.

^a Prepared with method II.

¹H-NMR spectra were obtained from CS₂ solutions on a Bruker AC (250 MHz) (Germany).

The electrical conductivities of the solid products were measured with the four-point probe technique.

The contact-angle measurements of the copolymer pellets were done on a Kernco model GIII contact-angle meter (El Paso, TX) at room temperature with distilled water.

Preparation of the silicone tegomer/PPy copolymers

Method I

First, silicone tegomer, CAN, and Py were dissolved in acetonitrile separately. Then, the CAN solution was added to the tegomer solution dropwise under stirring. The color of the solution changed from pale yellow to orange. Finally, the Py solution was added to the mixture. A black powder formed almost instantaneously. After 1 h, the precipitate was filtered, washed with acetonitrile and then boiling water several times, and dried at room temperature. The polymerization experiments were carried out at 25°C during stirring with a magnetic stirrer. The reaction volume was 40 mL in all the experiments.

Method II

Silicone tegomer and Py were dissolved in acetonitrile, and into this solution, a CAN solution was added slowly for 30 min with vigorous stirring. The stirring was continued for 1 h at 25°C. The solution changed from being colorless to black. After 1 h, the precipitate was filtered, washed with acetonitrile, boiling water, and alcohol several times, and dried at room temperature. The reaction volume was 40 mL in all the experiments.

Conductivity measurements

For the measurement of the electrical conductivity of the products, thin pellets were prepared by the compaction of the polymer powders under 10 tons of pressure. The typical sample dimension was 13 mm, and the thickness was 0.8 mm. The conductivity measurements were performed with the four-point probe technique and calculated with the following equation:

$$\sigma = V^{-1} \cdot I(\ln 2 / \pi d_n) \quad (1)$$

where V is the potential (V), I is the current (A), and d_n is the thickness of the samples (cm).

TABLE II
The Role of Concentration on the Solubility, Conductivity, and Yield of the Copolymers

Copolymer	[Tegomer 2311]	[CAN]	[Py]	Conductivity (S/cm)	Yield (g)	Solubility	
						DMF	Acetone
101	0.0344	0.022	0.232	6×10^{-2}	0.21	s	s
102	0.0344	0.176	0.232	2×10^{-5}	3.20	s	s
103	0.0344	0.022	0.464	—	—	s	s
104	0.0688	0.022	0.232	2×10^{-4}	0.90	s	s
105	0.0344	0.01	0.232	—	0.01	s	sl
106	0.0344	0.005	0.232	—	0.003	s	s
107	0.0344	0.05	0.232	10^{-5}	0.25	s	sl
108 ^a	0.0344	0.05	0.232	1.8×10^{-1}	0.47	s	i

s = soluble; sl = slightly soluble; i = insoluble.

^a Prepared with method II.

RESULTS AND DISCUSSION

Solvent-soluble Py copolymers were produced with silicone tegomers containing hydroxyl groups; this involved a redox reaction with Ce(IV). The reaction mechanism was probably similar to the mechanism proposed earlier.¹³

The solid-state conductivities and solubilities of the polymers at room temperature are listed in Tables I and II according to the effect of the CAN, Py, and tegomer concentrations.

Effect of the CAN concentration

The effects of the CAN concentration on the polymerization yields and conductivities are shown in Figures 1 and 2, respectively.

The conductivities of the copolymers obtained from tegomer 2111 and tegomer 2311 increased with the Ce(IV) concentration up to 0.022M. Above this value, the yield continued to increase, but the conductivity decreased drastically. This probably occurred because linear chain termination by Ce(IV) became dominant at high initial Ce(IV) concentrations, short PPy chains formed, and a copolymer with low conductivity and high solubility was produced. Moreover, a larger amount of silicone tegomer in the redox reaction gave a copolymer with a higher yield and a lower conductivity if the initial Ce(IV) concentration was high. This could clearly be seen in the FTIR spectra of the copolymers (Figs. 3(b) and 4(b)).

If the same Ce(IV) concentration was added dropwise for 30 min to a mixture of the tegomer and Py (method II), both the polymerization yield and the conductivity of the product were very high. In this case, the extent of the oxidative dimerization reaction increased, and long PPy chains formed. Similar results were observed earlier for the homopolymerization of Py.¹⁶

Effect of the tegomer and Py concentration

The conductivities of the copolymers obtained with different tegomers under the same experimental conditions (copolymers 1 and 101) were about 10^{-1} S/cm, although their solubilities in acetone were rather different. Tegomer 2311 gave much more soluble copolymers because the chain length of tegomer 2311 was 2.5 times higher than that of tegomer 2111. Increasing the tegomer concentration resulted in an increasing copolymer yield and decreasing conductivity. However, increasing the Py concentration (copolymers 1, 3, 101, and 103) did not seem to affect the yield and conductivity considerably because there was not enough Ce(IV) salt for oxidation.

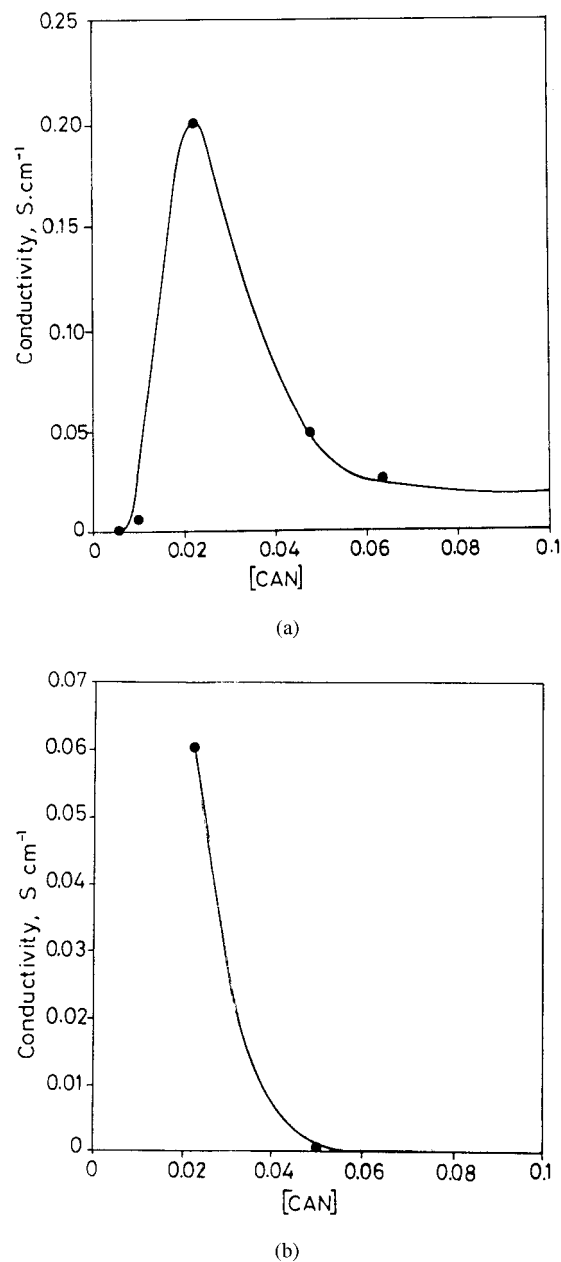


Figure 1 Effect of the CAN concentration on the conductivity of (a) the copolymer of tegomer 2111 and PPy and (b) the copolymer of tegomer 2311 and PPy.

Spectroscopic study

FTIR spectra of chemically prepared PPy–tegomer copolymers are shown in Figures 3 and 4. The peak at 1384 cm^{-1} was due to a NO_3^- ligand incorporated into the polymer. This peak was always observed as a sharp band in the spectrum of the copolymer. Three bands appearing around 3350 , 1030 , and 800 cm^{-1} were due to $-\text{OH}$, $\text{Si}-\text{O}$, and $\text{Si}-\text{CH}_3$ groups of tegomer blocks, respectively. These bands appeared quite clearly in the spectra of copolymers 4 and 107 (Figs. 3 and 4).

The $^1\text{H-NMR}$ spectrum of a PPy–tegomer copolymer with a lower conductivity showed a characteristic

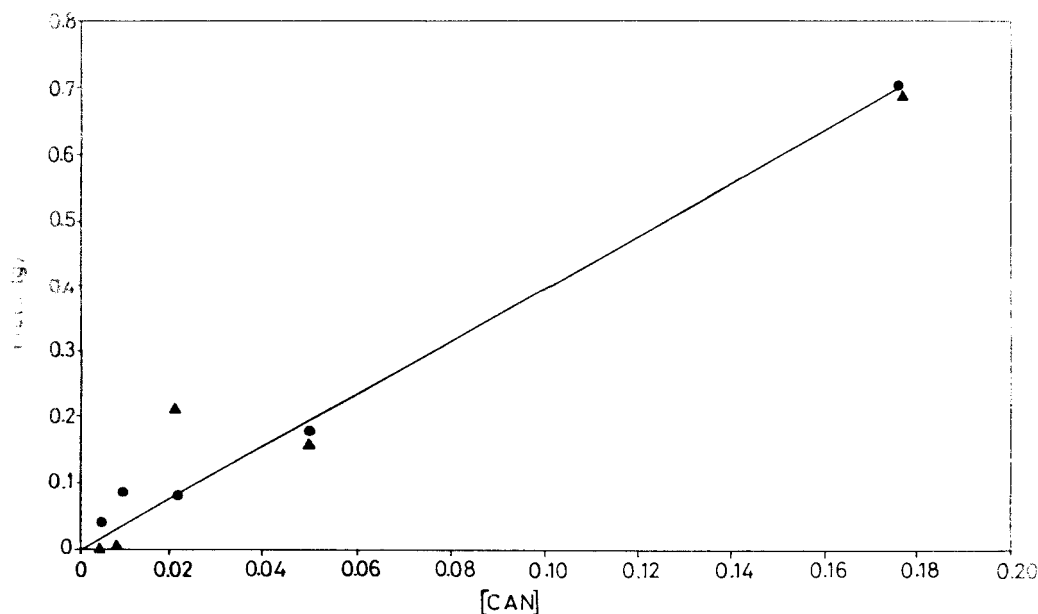


Figure 2 Effect of the CAN concentration on the yield of (●) the copolymer of tegomer 2111 and PPy and (▲) the copolymer of tegomer 2311 and PPy.

singlet at about 0.08 ppm due to protons of Si—CH₃ groups and a doublet at 5.8 ppm due to protons in the 3- and 4-positions of Py rings. The absence of another doublet near this doublet showed that the polymerization of Py occurred via 2,5-coupling only (Fig. 5).

Contact-angle measurements

The contact-angle measurements were performed on pellets of the copolymer with a thickness of about 1

mm. The results are given in Table III. As expected, the elastic pellets of the copolymers showed much higher contact-angle values than PPy.

Mechanism

The polymerization in solution proceeded via the oxidation of Py by Ce(IV) and produced radical cations that dimerized with the expulsion of protons.¹⁷ The second mechanistic possibility in the initiation step

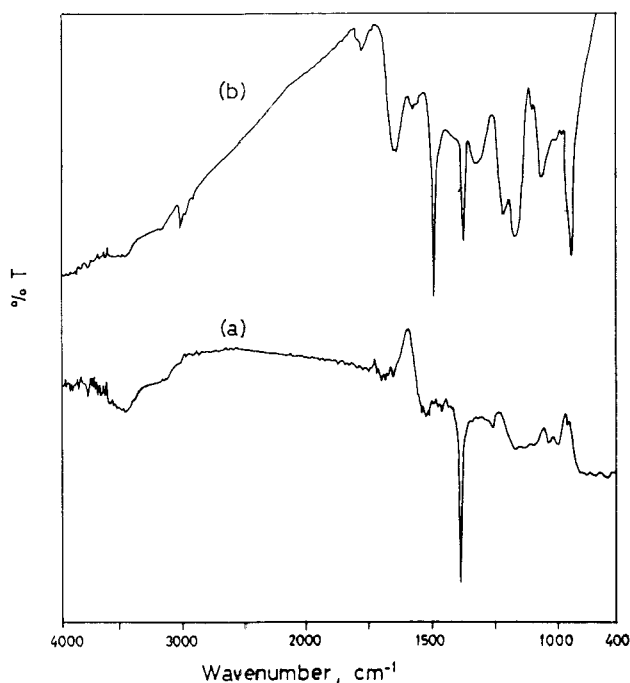


Figure 3 FTIR spectra of copolymers (a) 3 and (b) 4.

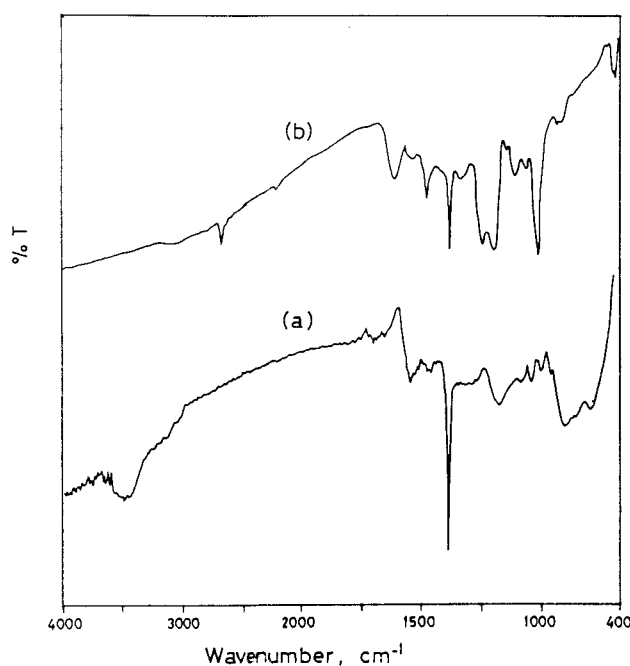


Figure 4 FTIR spectra of copolymers (a) 101 and (b) 107.

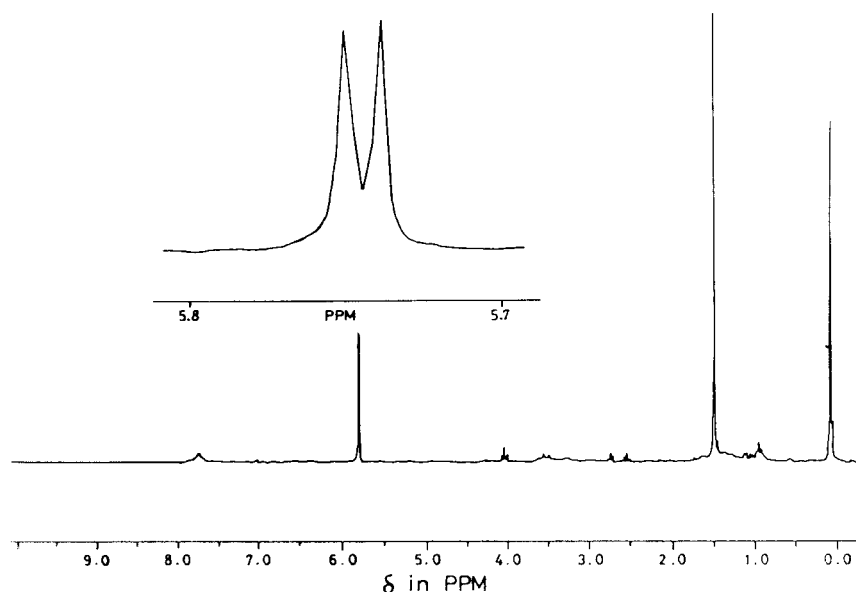


Figure 5 $^1\text{H-NMR}$ spectrum of copolymer 101.

was the proton loss of radical cations, which formed radicals that attacked another Py molecule,¹⁸ and the PPy chain continued to grow as long as Py and Ce(IV) were available. In the presence of the tegomer, Ce(IV) also attacked $-\text{CH}_2\text{OH}$ groups of the tegomer and produced radicals on carbon or oxygen atoms.¹⁴ The oxidation of Py and silicone tegomer by Ce(IV) started simultaneously, and the copolymer probably formed by a combination reaction between growing PPy chains and tegomer radicals. (Scheme 1).

CONCLUSIONS

PPy/silicone tegomer copolymers were prepared with Ce(IV) as an oxidation agent in a single step. The solubility and conductivity of the copolymer depended on the type of tegomer, the addition rate of Ce(IV), and the tegomer/Ce(IV)/Py ratio during the preparation.

Soluble copolymers with a conductivity of 6 S/cm were produced. The soluble copolymers were easily examined with NMR. A signal due to silicone tegomers at 0.08 ppm and a characteristic doublet at 5.8 ppm were observed in the NMR spectrum of a

soluble PPy–tegommer copolymer, and this indicated that 2,5-coupling between Py rings occurred. These soluble and conductive copolymers may overcome difficulties in the applications of PPy homopolymers and open new application areas in which the contact angle is also important. Therefore, the copolymers may find a number of new application areas as well as existing PPy applications.

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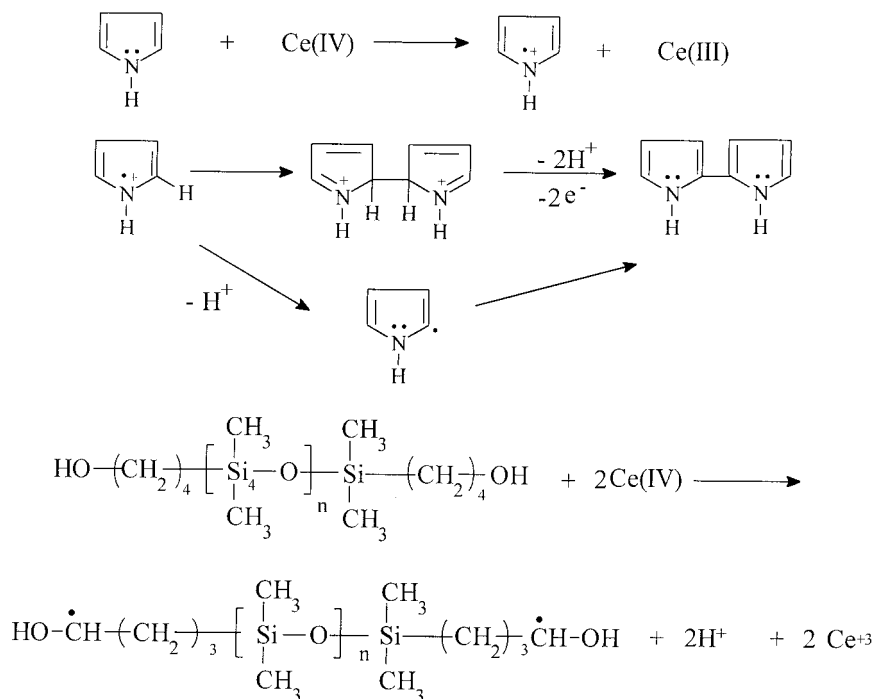
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TABLE III
Contact-Angle Measurements(θ°)

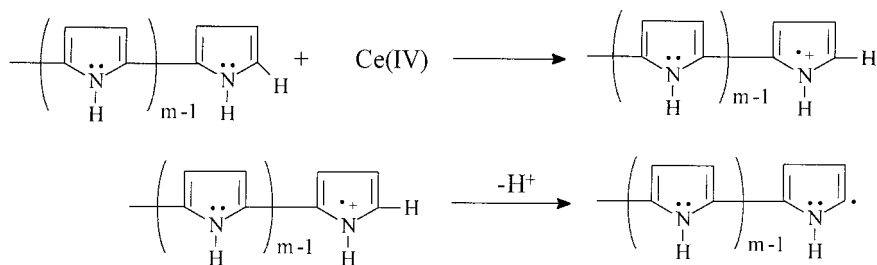
Copolymer	Tegomer type	Copolymer pellet (air side)
Polypyrrole	—	44
1	2111	65
8 ^a	2111	66
101	2311	73
102	2311	57

^a Prepared with method II.

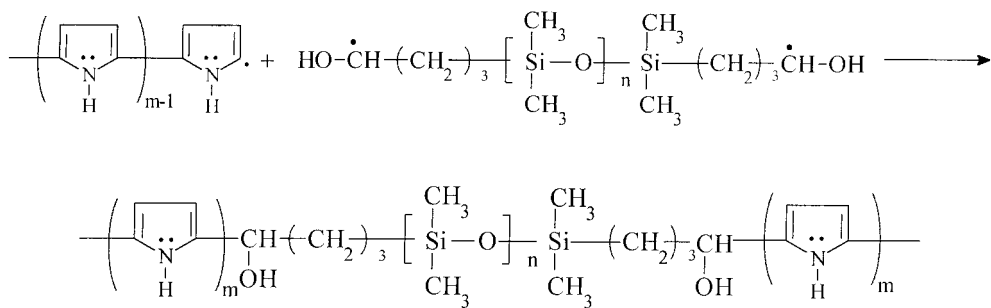
Initiation:



Propagation



Termination:



Scheme 1

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