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Short communication

Synthesis and characterization of phenylacetylene-terminated poly(silyleneethynylene-4,4′-phenylethereneethynylene)s

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Abstract

Two kinds of phenylacetylene-terminated poly(silyleneethynylene-4,4′-phenylethereneethynylene)s, $\{C_6H_5{-}C{\equiv}C{-}[Si(R)_2{-}C{\equiv}C{-}C_6H_4{-}O{-}C_6H_4{-}C{\equiv}C]_n{-}C_6H_5\}$ wherein R represents methyl or phenyl, were synthesized by condensation reaction between dichlorosilanes and 4,4′-diethynyldiphenyl ether using organomagnesium reagents. The polymers were characterized by NMR, IR, gel permeation chromatography, thermogravimetric analysis, and differential scattering calorimetry.

Keywords: Phenylacetylene; Poly(silyleneethynylene-4,4′-phenylethereneethynylene)s; Gel permeation chromatography; Thermogravimetric analysis; Differential scattering calorimetry

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1. Introduction

In the last decade, organosilicon polymers having an alternating arrangement of an organosilicon unit and a π-electron system, have received a great deal of attention because of their potential applications as advanced materials, such as ceramics precursors [1], organic semiconductors [2], hole-transporting materials [3], thermally stable polymers [4], liquid crystalline polymers [5]. In addition, polymers having ethynylene units in the π-electron system have been extensively studied [6]. An example includes the synthesis of poly [(hydrosilylene) ethynylene (phenylene) ethynylene]s with excellent heat-resistant and flame-resistant properties, reported by Itoh and his co-workers [7], which is fusible and soluble in most common organic solvents. In this paper, we report the synthesis of two kinds of new resins phenylacetylene-terminated poly(silyleneethynylene-4,4′-phenyl etherene ethynylene)s (**1a** and **1b**, Fig. 1), which are highly heat-resistant, low moisture sensitive and highly processable polymers. Selecting appropriate monomers can further enhance specific and desirable properties.

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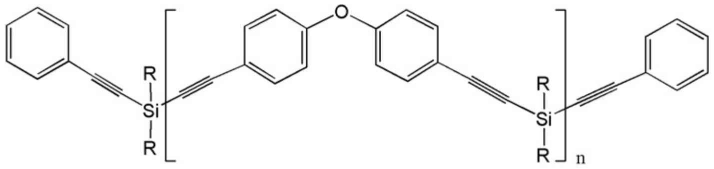


1a R=Me
1b R=Ph

Fig. 1. Phenylacetylene-terminated poly(silyleneethynylene-4,4′-phenylethereneethynylene)s.

2. Experimental section

2.1. Materials

All chemicals and solvents were purchased from Shanghai Reagent Company and distilled or dried when necessary using standard procedures.

2.2. Instrument

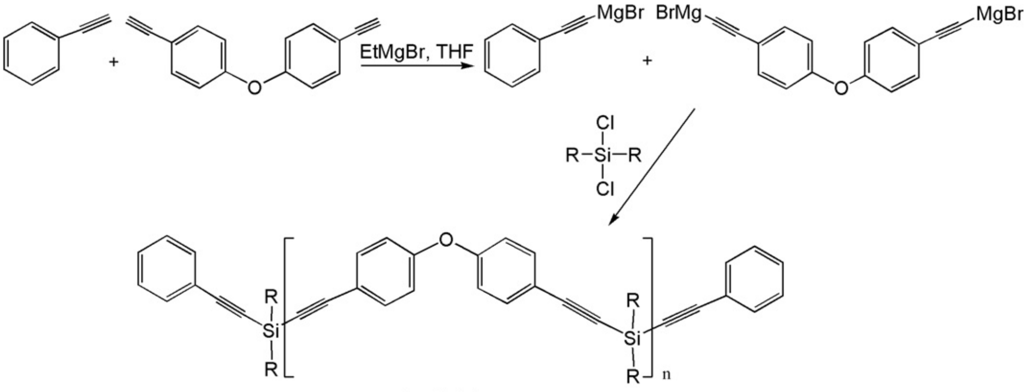
IR spectra were recorded on a Nicolet spectrophotometer. ^{1}H NMR spectra were obtained on a Bruker AVANCE 500 spectrometer operating at 500 MHz: chemical shifts were quoted downfield of TMS. Molecular weight distribution curves of polymers were determined by gel permeation chromatography (GPC) using 10^5, 10^4 and 10^3 Å μ-Styragel columns at 35 °C. Polymers were eluted with tetrahydrofuran and detected using a refractive index detector (Waters. Model R4000). Polystyrene standards of molecular weight ranging from 750 to 233,000 g/mol were used for calibrating GPC columns for hydrodynamic volume versus elution volume. Differential scattering calorimetries (DSC) were performed on a DSC50 Shimadzu (10 °C/min). The thermo gravimetric analyses were performed on a Setaran TGA 24 (10 °C/min).

The basic reactions used for the synthesis of phenylacetylene-terminated poly(silyleneethynylene-4,4′-phenylethereneethynylene)s are shown in Scheme 1.

General synthesis for phenylacetylene-terminated poly(silyleneethynylene-4,4′-phenylethereneethynylene)s was condensation reaction using organometallic reagents. All the operations were carried out under inert atmosphere conditions using pure argon. Solvents and reagents were dried and distilled.

2.3. *Synthesis of phenylacetylene-terminated poly(dimethylsilyleneethynylene-4,4′-phenylethereneethynylene)s (**1a**)*

Ethyl bromide (21.8 g, 0.2 mol) in tetrahydrofuran (50 ml) was added dropwise to a stirred mixture of magnesium powder (5.76 g, 0.24 mol) in tetrahydrofuran (50 ml) at room temperature for 30 min. The reaction mixture was heated at reflux for 2 h, followed by the dropwise addition of a solution of bis-(4-ethynyl-phenyl) ether (17.44 g, 0.08 mol) and phenylacetylene (2.04 g, 0.02 mol) in tetrahydrofu-



1a R=Me
1b R=Ph

Scheme 1.

ran (50 ml), After another 1 h reflux, the mixture turned from a clear solution to a suspension. Then dimethyldichlorosilane (11.61 g, 0.09 mol) in tetrahydrofuran (50 ml) was added dropwise, and stirred at reflux for another 1 h. The reaction mixture was cooled, then treated with 0.1 M HCl (50 ml) and separated into two layers, the organic phase was isolated and the solvent was evaporated under reduced pressure. The residue was extracted by using chloroform, neutralized with 0.1 M NaOH, washed with water and dried over anhydrous magnesium sulfate. The solvent was evaporated under reduced pressure, to give 23.3 g resin **1a** (**II**) (yield 94%) as a pale yellow viscous oil. $M_w = 2430$ ($M_w/M_n = 1.67$). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm). 0.15 (Me_2Si), 6.85–7.38(phenylene). ^{13}C NMR (500 MHz, $CDCl_3$): 158, 132, 128, 119, 118, 106, 91, 78(TMS), 1.5. IR ν(KBr) 2157 cm^{-1} (C$\equiv$C).

Table 1
The molecular masses of **1a** controlled by phenylacetylene

No.	The mol. ratio of phenylacetylene to 4,4′-diethynyldiphenyl ether	M_n	M_w	Polydispersity index
I	0	2131	3452	1.62
II	1:4	1455	2430	1.67
III	1:1	980	1564	1.60

Table 2
The molecular masses of **1b** controlled by phenylacetylene

No.	The mol. ratio of phenylacetylene to 4,4′-diethynyldiphenyl ether	M_n	M_w	Polydispersity index
IV	0	3068	5827	1.90
V	1:4	1341	2200	1.64
VI	1:1	1028	1543	1.50

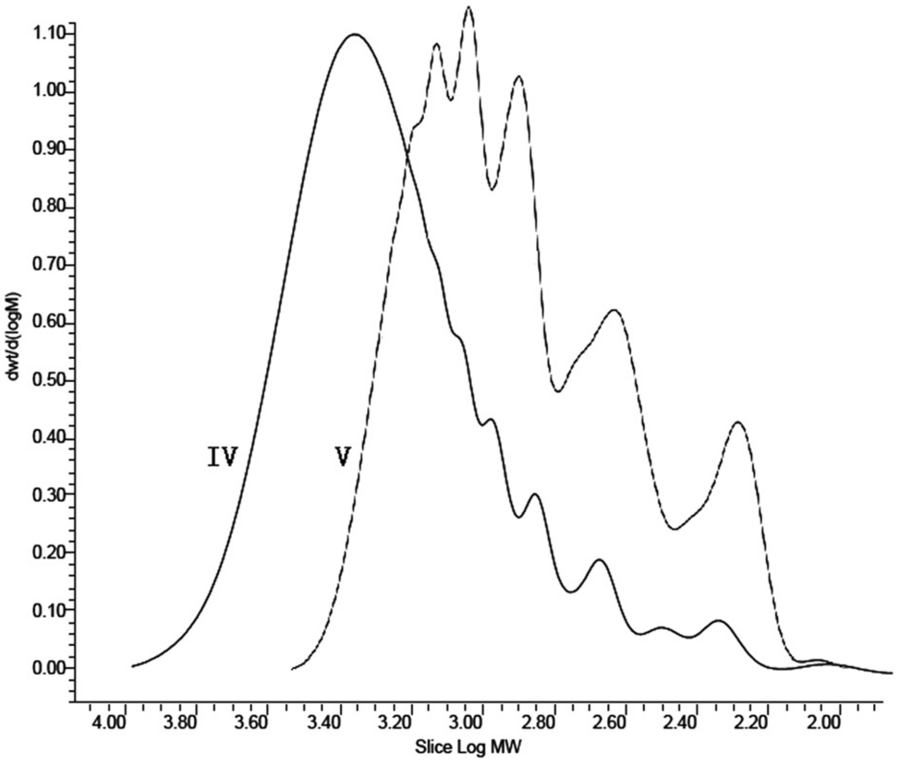


Fig. 2. GPC naves of polymers **IV** and **V**.

2.4. Synthesis of phenylacetylene-terminated poly(diphenylsilyleneethynylene-4,4′-phenylethereneethynylene)s (1b)

Using essentially the same procedure and employing diphenyldichlorosilane (22.77 g, 0.09 mol), 33.0 g resin **1b** (**V**) (yield 92%) was obtained as a pale yellow viscous oil. $M_w = 2200$ ($M_w/M_n = 1.64$). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm). 6.85–7.54 (phenylene). ^{13}C NMR (500 MHz, $CDCl_3$): 158, 135, 128, 122, 119, 117, 108, 88, 78(TMS). IR ν(KBr) 2150 cm^{-1}($C{\equiv}C$).

3. Results and discussion

Phenyl acetylene-terminated poly(silyleneethynylene-4,4′-phenylethereneethynylene)s, $\{C_6H_5{-}C{\equiv}C{-}[Si(R)_2{-}C{\equiv}C{-}C_6H_4{-}O{-}C_6H_4{-}C{\equiv}C]_n{-}C_6H_5\}$ wherein R represents methyl or phenyl, were synthesized by condensation reaction between dichlorosilanes and 4,4′-diethynyldiphenyl ether using organic magnesium reagents. These reactions proceeded smoothly. Chemical structures of the polymers have been determined by ^{1}H NMR. They are in good agreement with the desired structures.

With addition of phenylacetylene to 4,4′-diethynyldiphenyl ether, the control of the molecular masses of the macromoleculars shown in Tables 1 and 2.

By gel permeation chromatography (GPC), molecular mass distributions of some polymers were determined. As presented in Fig. 2, polymer **IV** possesses unimodal molecular mass distribution, whereas polymer **V** shows multimodal molecular mass distribution.

Thermal properties of **II** and **V** were examined by TGA–DTA in nitrogen. Their Td_5 and final weight loss at 1000 °C are listed in Table 3. As expected, the materials obtained from the polymers exhibited excellent heat-resistant properties in nitrogen. In particular, **V** showed higher Td_5 and lower weight loss at 1000 °C (Table 3) than those of **II**. This is probably due to the larger number of Si–Me bonds in a repeating unit that are relatively unstable as indicated by the smaller bond dissociation energy of Si–Me (318 kJ/mol) to that of Si–Ph (358 kJ/mol) [2].

DTA of **V** revealed a sharp exothermic peak at 200–220 °C in Fig. 3. This signal above 200 °C is the curing temperature [7,8]. Presumably, cross-linking reactions of polymers occurred at this temperature, which would be responsible for the high heat resistance of these polymers. In fact, when polymer was heated at 210 °C in nitrogen, the polymers became insoluble in the familiar organic solvents, such as THF, DMSO, alcohol, and chloroform. The IR spectrum of **V** after being heated

Table 3
TGA of polymers **II** and **V** in nitrogen

Polymers	TGA in nitrogen[a]	
	Td_5 (°C)[b]	Weight loss (%)[c]
II	603	23
V	625	19

[a] At a rate of 10 °C/min from 25 to 1000 °C.

[b] Temperature resulting in 5% weight loss based on the initial weight.

[c] Total weight loss at 1000 °C.

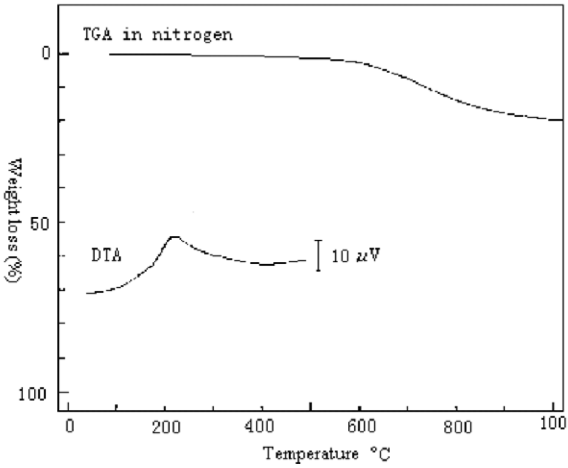


Fig. 3. TGA–DTA of polymer **V**.

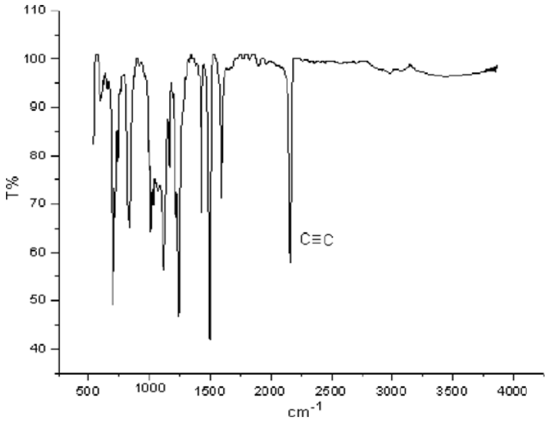


Fig. 4. IR spectra of polymer **V**.

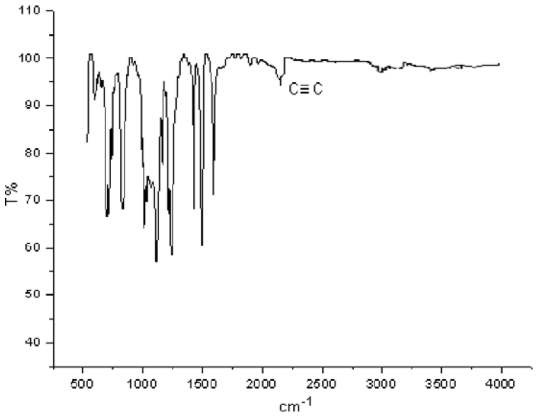


Fig. 5. IR spectra of polymer **V** after heating at 220 °C for 30 min in nitrogen.

revealed a decrease of the absorption band at around 2150 cm^{-1} due to the C≡C bond stretching frequency (Figs. 4 and 5), indicating that some cross-linking reactions [8].

Acknowledgement

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