

Three series of multifunctional polysiloxane attached with charge-transporting agents and electro-optical chromophores

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Abstract

Three series of multifunctional polysiloxanes containing charge-transporting agents and electro-optical chromophores have been prepared for the photorefractive application. The structural characterization of these polymers is presented by IR, UV, ¹H-NMR spectra and elemental analysis. The poled films of polymer 1, 3, 8 reveal resonant d_{33} values of 21, 31 and 19 pm/V by second harmonic generation (SHG) measurements.

Keywords: polysiloxane, multifunctional polymer, synthesis, non-linear optical methods

1. Introduction

It is well known that photorefractive (PR) materials can be used in coherent optical systems including holographic data storage, real-time image processing and optical switching. Up to 1990, the family of PR materials investigated was solely inorganic crystals. Since the first observation of PR effect in polymer films in 1991[1], more and more efforts have been dedicated to the research and development of PR polymers due to their several advantages over the inorganic crystals such as large nonlinearities, low dielectric constants and ease of processing. Great strides have been achieved in the optimization of these materials, and their performances are now comparable to those of the best PR inorganics[2]. To generate PR effects, the polymer must be photoconductive in addition to electro-optical active. It would be easier to dope charge-transporting agents and electro-optical chromophores into a polymer to form guest-host polymeric systems. However, there are inherent problems of phase separation and sublimation in these composite systems, which adversely limit their commercial application. Multifunctional polymers where both functional species are covalently linked to the polymer backbone perhaps can effectively minimize these problems usually occurring in

guest-host polymeric systems. Such polymers are more stable against phase separation and sublimation during sample preparation.

Recently we have synthesized several series of multifunctional polysiloxanes. Carbazolyl group offers the charge-transporting agent and azo dye group acts as the electro-optical chromophore. The resulting polymers were expected to possess a potential photorefractivity. In this paper, we report the synthesis, structural characterization and second non-linear optical (NLO) properties of this kind of polymers.

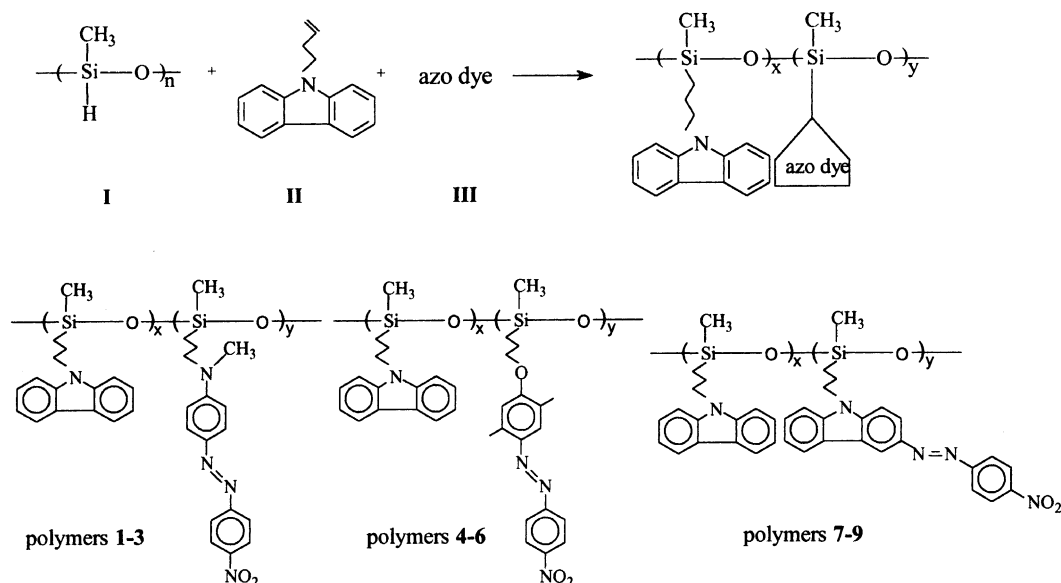
2. Experimental

2.1. Materials

Solvents were dried by using common methods. All reagents were used as received without further purification. 9-allylcarbazole was prepared according to the method of Heller[3]. Dichlorodicyclopentadiene platinum was prepared in the similar way as described by Chatt[4]. The synthesis of all the azo dye compounds was reported elsewhere[5-6].

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Scheme 1 Synthesis route and structures of the polymers 1-9.

Table 1 The characterization data of multifunctional polysiloxanes (composition, IR, DSC, molecular weights).

	composition		IR data (cm ⁻¹)		DSC(°C)		molecular weights		
	x	y	carbazolyl	group	nitro group	T _g	T _d	M _n	M _w
polymer 1	6%	94%						8628	28989
polymer 2	13%	87%	1601,1454,	746, 721	1516, 1335	70	330	11674	36446
polymer 3	24%	76%						11441	42406
polymer 4	11%	89%						6211	23913
polymer 5	22%	78%	1595, 1452,	747, 720	1521, 1340	70	280	5241	20802
polymer 6	37%	63%						3535	14490
polymer 7	4%	96%						10778	78498
polymer 8	13%	87%	1595,1456,	747,720	1522, 1340	80	350	10815	45914
polymer 9	15%	85%						12450	62738

2.2. Characterization

¹H-NMR spectra were obtained using a JEOL FX90Q spectrometer. FTIR spectra were conducted with a NICOLET FT-IR 170SX spectrophotometer. Elemental analysis was performed by CARLOERBA-1106 micro-elemental analyzer. The UV-visible absorption spectra were recorded on a Shimadzu UV-1206 spectrometer. Molecular weights were measured with a Water HPLC instrument using polystyrene as the standard samples and THF as the mobile phase. Differential scanning calorimetry (DSC) thermogram of the polymers was taken with a NETZSCH STA-409C instrument.

2.3. Hydrosilylation procedure:

Poly(hydrogenmethylsiloxane), azo dye group and toluene were placed in a flame-purged 100ml flask with a nitrogen inlet. After the addition of a small amount of dichlorodicyclopentadiene platinum (10⁻⁴ mol/mol SiH) the mixture was agitated at 60°C for 24' hrs. Then 9-allylcarbazole was added, and the reaction kept stirring for another 24 hrs, subsequently poured into methanol. The solid was collected and extracted in Soxhlet extractor with

methanol for 4 days. Polysiloxanes with different component concentration were obtained by controlling reagents mole ratio ((I):(II):(III) = 10:9:1, 5:4:1 and 10:7:3 respectively). 9-allylcarbazole (II) was usually excessive in order to make SiH react as completely as possible.

3. Results Discussion

As shown in Scheme 1, the polysiloxanes were prepared by a hydrosilylation reaction of poly(hydrogenmethylsiloxane) (I) with the terminal double bond of the allyl side chain of 9-allylcarbazole (II) and azo dye groups (III). Azo dye groups (III) were first linked to poly(hydrogenmethylsiloxane) (I) and then excessive carbazole (II) was added in order to make SiH react as complete as possible. Dichlorodicyclopentadiene platinum [C₁₀H₈PtCl₂] instead of H₂PtCl₂ was chosen as the catalyst since it is soluble in toluene and its catalytic activity keeps high during the period of the reaction[7]. The obtained polymers are soluble in ordinary organic solvents such as toluene, chloroform and etc. The substitution degree of two functional groups in the polymers was controlled by varying the reagent ratio and determined by the elemental analysis (Table 1).

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