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Preparation of a novel class of phthalocyanine containing cross-linked polymers and their thin films

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Abstract

Prepolymers containing vanadyl phthalocyanines, prepared by the reaction of amino-substituted vanadyl phthalocyanines and diglycidyl ether of biphenol A, can be cured to give transparent network polymeric films, which show absorptions at 780 nm and 820 nm, respectively. The films are stable to organic solvents, inorganic bases and acids. Ultrafast optical responses were observed for both polymers with typical decay time of about 240 fs.

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1. Introduction

Phthalocyanines have been widely used as dyes and pigments due to their high thermal stability and chemical stability. They now draw interest as materials for optical recording media, nonlinear optical application, light absorption, electric conduction, photoconduction, energy conversion, electrode and catalyst. Synthesis of phthalocyanines able to be fabricated into thin films has received much attention for practical reason. Phthalocyanine compounds with varied substituted groups have been synthesized [1]. They are soluble in organic solvent and thus can be doped into suitable polymers to form functional films. Soluble phthalocyanine polymers were also reported, in which phthalocyanine or metallophthalocyanine ring is chemical bonded to the polymer main chains [2] or side chains [3]. Network phthalocyanine polymers usually possess high thermal stability [4], but they are difficult to process due to poor solubility in organic solvents. Here, we report a novel class of phthalocyanine-containing cross-linked polymers. Thin solid films with good optical quality can be fabricated. The polymers are stable to acids, bases and organic solvents. Ultrafast optical Kerr effects (OKE) were observed from their thin films. Their thermal stability, chemical stability and near IR absorption characteristics make them interesting materials for potential application in many research fields.

2. Experimental details

2,9,16,23-tetraamino vanadyl phthalocyanine (1) and 1,8,15,22-tetraamino vanadyl phthalocyanine (2) were prepared by the procedure described in our previous work [5].

2.1. Prepolymers 1 and 2

2,9,16,23-tetraamino vanadyl phthalocyanine (1) (0.021 g, 3.1×10^{-5} mol) and diglycidyl ether of bisphenol A (DGEBPA; 0.34 g, 1.0×10^{-3} mol) were mixed. The mixture was stirred at 180 °C under nitrogen for 24 h. Chloroform was added to dissolve the product. After filtration and concentration, the solid obtained was dried at 30 °C under vacuum for 24 h to give dark purple prepolymer 1, with yield 45% (vanadyl phthalocyanine content: 6.5 wt.%). Prepolymer 2 can be prepared by similar procedure (vanadyl phthalocyanine content: 1.3 wt.%).

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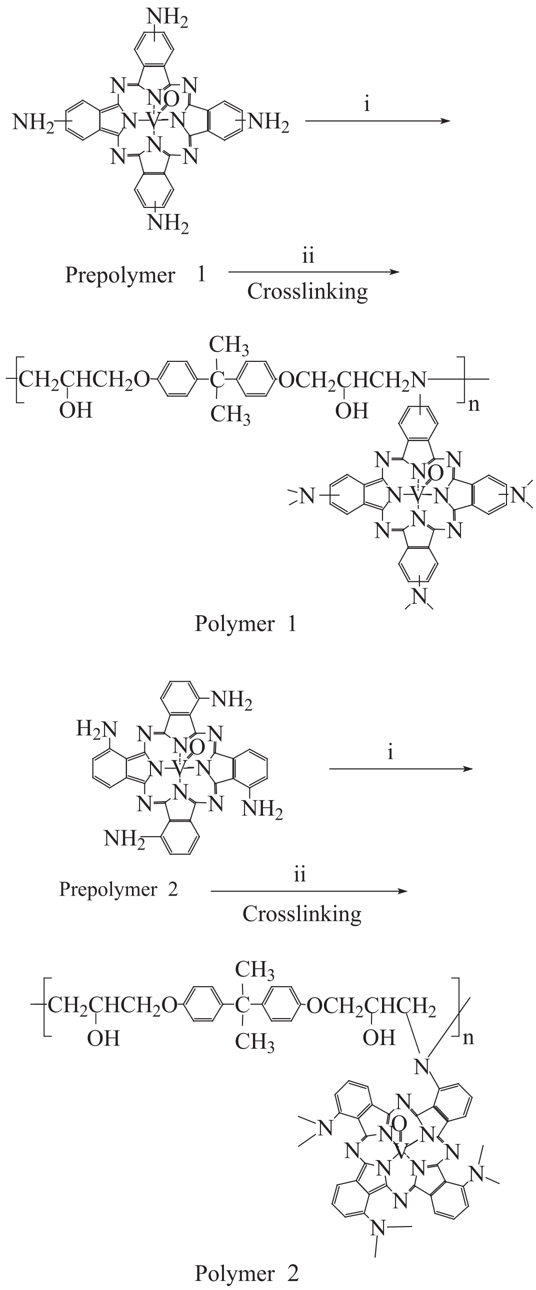

Scheme 1. The synthetic route of the polymers. Reagents and conditions: (i) DGEBPA, N_2, 180 °C; (ii) catalyst, heating.

2.2. Preparation and curing of the films

Twenty milligrams of prepolymer 1 or 2 and catalyst (1% in weight) were dissolved in 1 ml of dimethylacetamide (DMAC). Films were prepared by spin coating the solution on glass substrates. The thickness of the films is 1–5 μm. After drying under vacuum at 30 °C for 24 h, the films were heated at curing temperature to give cross-linked polymer samples.

UV/Vis spectra were taken on a Hitachi 340 UV/Vis spectrophotometer.

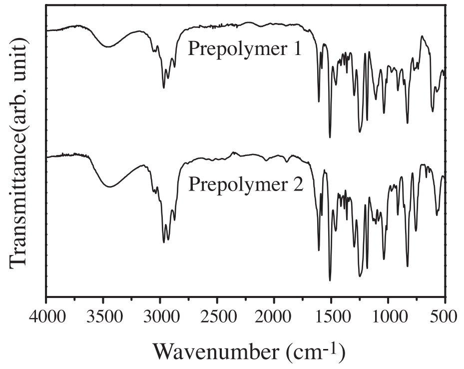

Fig. 1. IR spectra of prepolymers 1 and 2.

In femtosecond OKE measurements, a Ti/sapphire laser system was employed as the pulse source, and the output pulses were centered at 800 nm with 120 fs pulse duration. The pulse was divided into two parts by a beam splitter, and the ratio of pump and probe intensity was set to 10:1. The pump beam was chopped at a frequency of 1.6 kHz and passed through a computer-controlled optical delay line, then focused together with probe beam onto the sample. The polarization of the probe pulse was set at 45° with respect to that of the pump pulse, and an analyzer with orthogonal polarization to probe beam was used to detect OKE signal. Femtosecond pump–probe technique was employed to measure the ultrafast dynamics of excited molecules, and the setup arrangement was similar to that of OKE, except that the polarization of probe beam is set parallel to that of pump pulses, and no analyzer was in the probe path.

3. Results and discussion

The synthetic route to the network phthalocyanine-containing polymers is given in Scheme I.

Tetraaminophthalocynines 1 and 2 were prepared by reducing the corresponding tetranitro phthalocyanines. The reaction between tetraamino phthalocyanine and DGEBPA was carried out under a nitrogen atmosphere in order to avoid the oxidation of amino. Prepolymers with varied

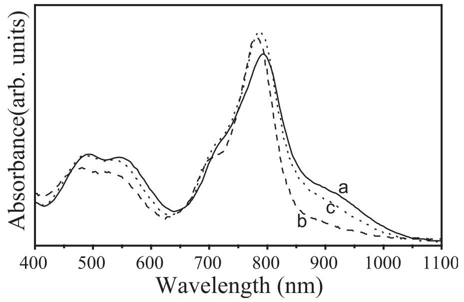

Fig. 2. Absorption spectra for (a) prepolymer 1; (b) polymer 1, obtained by quickly curing; and (c) polymer 1, obtained by slowly curing.

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