



# Synthesis of organic-inorganic polymer hybrids utilizing *in-situ* anionic hydrogen-transfer polymerization of acrylamide



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## ABSTRACT

Homogeneous polymer hybrid consisting of poly( $\beta$ -alanine) and silica gel was synthesized by an *in-situ* anionic polymerization method. Acrylamide (AAM) as an organic monomer was introduced into a sol–gel reaction of tetramethoxysilane (TMOS). The polymerization of AAM was initiated by potassium *tert*-butoxide (*t*-BuOK), while sol–gel reaction of TMOS proceeded to generate a silica gel matrix. The obtained polymer hybrid was optically transparent and no phase separation was observed by SEM measurement. From the <sup>1</sup>H and <sup>13</sup>C NMR analysis, the anionic polymerization of AAM proceeded *via* a hydrogen-transfer process under *in-situ* hybridization conditions.

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## 1. Introduction

Composite materials are used to create novel materials and much attention is being paid to these composite materials because new materials can be created without using new chemicals. In particular, organic-inorganic polymer hybrids are one of the notable materials having high performance such as transparency, thermal stability, mechanical property, and so on [1–4]. In recent years, transparent materials have been applied to various optical applications [5–9], and organic-inorganic polymer hybrids have the potential for use in many optical applications. This is because they provide not only high optical transparency but also combine both organic and inorganic properties which could lead to the fabrication of more reliable optical devices [10]. The sol–gel reaction of alkoxy silanes is the most typical technique for the synthesis of polymer hybrids [11–18]. Generally, organic-inorganic polymer hybrids can be prepared by mixing organic polymer into the sol–gel reaction. However, homogeneous and transparent organic-inorganic polymer hybrids, in which organic polymer is dispersed within an inorganic matrix on the nano or molecular scale, can not be synthesized without suitable interactions between organic

polymer and inorganic matrix. There are no suitable interactions between organic polymer and inorganic matrix, and thus the polymer hybrids obtained are phase separated. The *in-situ* polymerization method is an excellent method to obtain homogeneous and transparent organic-inorganic polymer hybrids. Previously, we reported the synthesis of polystyrene/silica gel polymer hybrids starting from styrene monomer and tetramethoxysilane by an *in-situ* polymerization method [19]. To overcome the phase separation between organic polymer and inorganic matrix, an *in-situ* polymerization method is a coinstantaneous polymerization of organic monomer during the formation of inorganic matrix from metal alkoxides. However, only a few examples using this *in-situ* polymerization method has been reported [19,20]. It is caused that water is generally employed as a sol–gel catalyst when organic-inorganic hybrids are synthesized on the basis of the sol–gel reaction. Namely, it means that the water-sensitive polymerization methods such as anionic polymerization are difficult to employ for the synthesis of organic-inorganic polymer hybrids. Usually, anionic polymerizations are terminated under protonic compounds such as water. Therefore, special precautions have to be taken to exclude moisture in the anionic polymerization conditions. This difficulty may be surmounted by employing vinyl monomers having active hydrogens.

Vinyl monomers having active hydrogens such as acrylamide and its derivatives are known to undertake hydrogen-transfer

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polymerization under anionic polymerization conditions [21–24]. In this polymerization system, the *N*-anions as the propagating species might be terminated by the deprotonation of the amidic proton from the monomer and/or polymer (Scheme 1). However, when the terminated polymers are regenerated by deprotonation, the regenerated *N*-anions are expected to be associated with anionic polymerization. Therefore, utilizing the propagation reaction resulting from regeneration of *N*-anions may become an effective method for the preparation of polymer hybrid materials derived from other polyamides. In this study, we describe a novel *in-situ* hybridization method based on the anionic polymerization of acrylamide (AAM) involving a hydrogen-transfer process (Scheme 2).

## 2. Experimental procedure

### 2.1. Materials

Acrylamide (AAM) was purchased from Wako Pure Chemical Industries, Ltd. AAM was purified by recrystallization from methanol and dried *in vacuo*. Tetramethoxysilane (TMOS) was distilled and stored under nitrogen. *N,N*-Dimethylformamide (dehydrated grade) was purchased from Wako Pure Chemical Industries, Ltd. Potassium *tert*-butoxide (*t*-BuOK), 1.0 *M* solution in tetrahydrofuran was purchased from Sigma–Aldrich, Inc. Other solvents and reagents were used as supplied.

### 2.2. Instruments

Scanning electron microscopy (SEM) measurements were conducted using a JEOL JSM-5600B system. Thermogravimetric analysis (TGA) was performed using a TG/DTA6200, SEIKO Instruments, Inc., with a heating rate of 10 °C/min in air. <sup>1</sup>H NMR spectra were recorded on a JEOL JNM-EX400 (<sup>1</sup>H NMR: 400 MHz) spectrometer and Oxford Instruments Pulsar (<sup>1</sup>H NMR: 60 MHz) spectrometer. <sup>13</sup>C NMR spectra were recorded on a JEOL ECA-500 spectrometer. FT-IR spectra were measured on a JASCO FT/IR-4200 spectrometer.

### 2.3. Measurement of monomer conversion (typical procedure)

AAM (0.25 g, 3.52 mmol), *t*-BuOK 1.0 *M* solution in THF (0.11 mL, 0.11 mmol) as an initiator of anionic polymerization, *N*-phenyl- $\beta$ -naphthylamine (1 mol%, an inhibitor for radical polymerization), and a sol–gel catalyst were dissolved in 7 mL of DMF with TMOS (0.68 g, 4.47 mmol), and distilled water (35  $\mu$ L, 1.94 mmol) as a sol–gel reaction initiator, and tetralin (0.10 g) as an internal standard. After the stated time, the reaction mixture (100  $\mu$ L) was poured into chloroform-*d* (0.5 mL). The chloroform-*d* solution was used as a sample for the <sup>1</sup>H NMR analysis. Monomer conversion was determined by the integral ratio of the vinyl protons of AAM and aromatic protons of tetralin in the <sup>1</sup>H NMR spectra.

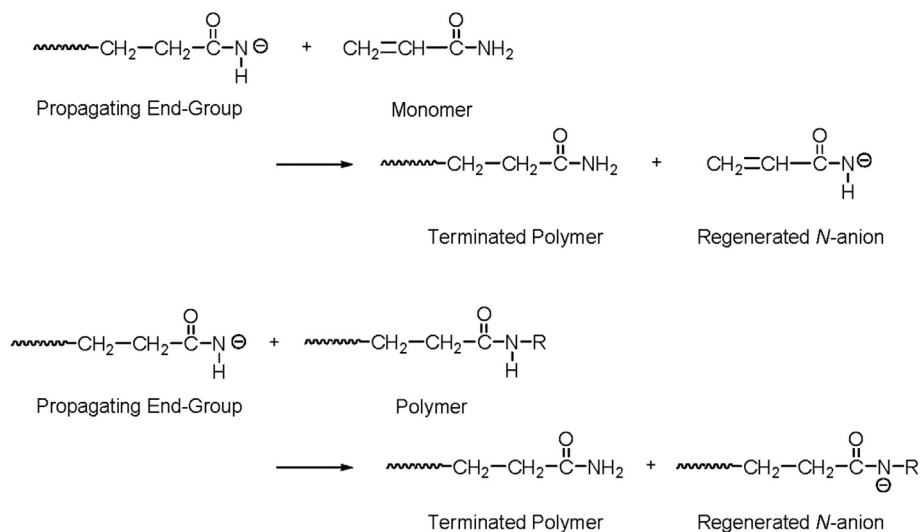
### 2.4. Synthesis of organic-inorganic polymer hybrids from AAM and TMOS (typical procedure)

AAM (0.25 g, 3.52 mmol), *t*-BuOK 1.0 *M* solution in THF (0.11 mL, 0.11 mmol) as an initiator of anionic polymerization, *N*-phenyl- $\beta$ -naphthylamine (1 mol%, an inhibitor for radical polymerization), and a sol–gel catalyst were dissolved in 7 mL of DMF with TMOS (0.68 g, 4.47 mmol), and distilled water (35  $\mu$ L, 1.94 mmol) as a sol–gel reaction initiator. After being stirred at 80 °C for 72 h, the mixture was placed in a polypropylene vessel covered with a wiping paper and left in air at 60 °C for 2 weeks. The obtained polymer hybrid was dried *in vacuo* at 60 °C for 2 days.

### 2.5. Isolation of organic polymer from organic-inorganic polymer hybrids

The obtained polymer hybrid (105 mg) was dissolved in 2 mL of DMF. After being stirred at room temperature for 24 h, the insoluble substance was filtrated off. The filtrate was poured into ethyl ether and the precipitated polymer was dried *in vacuo*.

IR (KBr): 3387, 3208, 3092, 2948, 1665, 1556, 1441, 1413, 1372 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>/CF<sub>3</sub>COOD (v/v = 4/1), 400 MHz)  $\delta$ : 2.60–2.80 (m, 2H, –CH<sub>2</sub>–CH<sub>2</sub>–CO–), 3.25–3.99 (m, 2H,



**Scheme 1.** Plausible Regeneration Mechanism of *N*-Anion in Hydrogen-Transfer Polymerization.

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