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European Polymer Journal 43 (2007) 1573–1579
EUROPEAN POLYMER JOURNAL
www.elsevier.com/locate/europolj

Short communication

Multi-step sol–gel process and its effect on the morphology of polyethylene oxide (PEO)/SiO_2 anion-exchange hybrid materials

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Received 6 December 2006; accepted 28 December 2006
Available online 13 January 2007

Abstract

Polyethylene oxide (PEO)/SiO_2 anion-exchange hybrid materials were prepared through the sol–gel process of alkoxysilane functionalized PEO-1000 (PEO-[Si(OCH_3)$_3$]$_2$) and *N*-[3-(trimethoxysilyl)propyl] ethylene diamine (A-1120). The influence of the multi-step sol–gel processing procedure, i.e. the pre-hydrolysis of either of the two precursors on the homogeneity of the hybrid materials was investigated. Results showed that the sol–gel reaction of A-1120 and PEO-[Si(OCH_3)$_3$]$_2$ from the same time would result in hybrid materials with the highest homogeneity, and pre-hydrolysis of A-1120 or PEO-[Si(OCH_3)$_3$]$_2$ could only decrease the materials' compatibility.

Keywords: Hybrid materials; Organic–inorganic materials; Anion-exchange; Sol–gel; Polyethylene oxide (PEO)

1. Introduction

Since their emergence in the 1980s, the organic–inorganic hybrid materials have attracted a great deal of attention [1–4]. One important route for preparing the hybrid materials is through the sol–gel process of alkoxysilane functionalized polymers and/or other lower-molecular-weight precursors, including organically modified alkoxysilanes or metal alkoxides [5–7].

When different precursors are used in one sol–gel system, reaction conditions should be carefully controlled to obtain a homogeneous distribution of all the precursors throughout the gel. In previous researches, multi-step approaches are commonly utilized, i.e., the precursor of lower reaction rate is allowed to hydrolyze and condense for some time before adding the other(s) [8–10]. For the sol–gel systems of metal alkoxides or organically modified alkoxysilanes, kinetics study has been conducted and the results show that the multi-step approaches

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doi:10.1016/j.eurpolymj.2006.12.042

can actually contribute to the copolymerization and homogeneity [10]. For the sol–gel systems containing alkoxysilane functionalized polymers, on the other hand, influence of the multi-step approaches on the morphology of the hybrid materials has been very seldom explored.

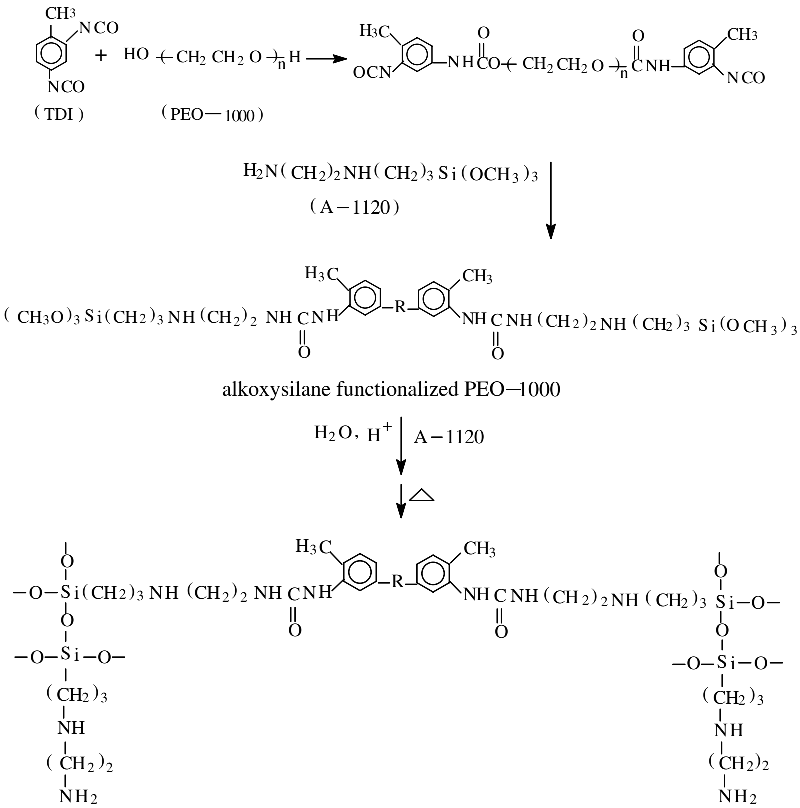
Here, we chose the sol–gel reaction system of alkoxysilane functionalized polyethylene oxide (PEO)-1000 (PEO-[Si(OCH_3)$_3$]$_2$) and *N*-[3-(trimethoxysilyl)propyl] ethylene diamine (A-1120) as an example and investigated the effect of the multi-step reactions on the homogeneity of the hybrid materials.

2. Experimental

Alkoxysilane functionalized PEO-1000, signified as PEO-[Si(OCH_3)$_3$]$_2$ was prepared through the reaction of PEO-1000 ($\overline{M}_n = 1200$, determined through titration of the end –OH groups) with 2,4-diisocyanate toluene (TDI) and *N*-[3-(trimethoxysilyl) propyl] ethylene diamine (A-1120) in sequence (Scheme 1). The preparation procedure was similar to that in our previous paper [11]. DMF was used as the solvent and the concentration of PEO-[Si(OCH_3)$_3$]$_2$ was 13.8 g/mL.

The molar ratio of PEO-[Si(OCH_3)$_3$]$_2$: A-1120 was set to be 1:2 or 1:4.6 and thus two series (series A or B) of sol–gel reaction systems were conducted. For either series, seven samples of reactions (A1–A7 or B1–B7) were performed. In samples 1–3, the PEO-[Si(OCH_3)$_3$]$_2$ was allowed to react for 50, 30 or 10 min and then A-1120 was added, while in samples 5–7, A-1120 pre-reacted for 10, 30 or 50 min before the addition of PEO-[Si(OCH_3)$_3$]$_2$. In sample 4, PEO-[Si(OCH_3)$_3$]$_2$ and A-1120 were mixed before the sol–gel reaction started.

The reaction procedures for the different samples was as following: Acidic water diluted with equal volume of DMF was dropped within 2 min into one precursor (PEO-[Si(OCH_3)$_3$]$_2$ or A-1120) (Si:H_2O:HCl (molar ratio) = 1:3:10^{-3}) and stirred for 50, 30 or 10 min (for samples 1–3) or 10, 30, 50 min (for samples 5–7). Then, the other precursor and additional acidic water (Si:H_2O:HCl (molar



Scheme 1. The synthesis of alkoxysilane functionalized polyethylene oxide (PEO) (PEO-[Si(OCH_3)$_3$]$_2$) and its reaction with *N*-[3-(trimethoxysilyl)propyl] ethylene diamine (A-1120).