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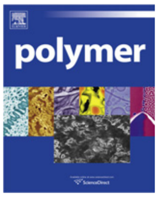

Preparation of polyacrylonitrile nanoparticles via dispersion polymerization of acrylonitrile using a poly(*N*-vinyl pyrrolidone)-cobalt complex in an aqueous system

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ABSTRACT

Monodisperse spherical polyacrylonitrile (PAN) nanoparticles were successfully prepared for the first time by dispersion polymerization of acrylonitrile (AN) in water using well-defined poly(*N*-vinyl pyrrolidone) (PVP) that was end-capped by a cobalt(II) acetylacetonate ($Co(acac)_2$) complex (PVP-$Co(acac)_2$) as both a macroinitiator and a colloidal stabilizer. The well-defined PVP-$Co(acac)_2$ ($M_n = 14,000$ g/mol, PDI = 1.25) was synthesized by the bulk cobalt-mediated radical polymerization of *N*-vinyl pyrrolidone at 20 °C using 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) as an initiator and $Co(acac)_2$ as a regulating agent. The PVP macroradicals generated at 30 °C by the homolytic cleavage of the C–Co bonds in PVP-$Co(acac)_2$ initiated the dispersion polymerization of AN, as well as successfully stabilized the growing PAN particles. The average diameters of PAN nanoparticles synthesized with 20, 30, 40, and 50 wt% of PVP-$Co(acac)_2$ at 30 °C for 24 h were 263.5, 163.1, 157.3, and 143.5 nm, respectively. The PAN nanoparticles had a slightly crumpled spherical appearance, and the degree of crystallinity of the PAN nanoparticles prepared using 30 wt% of PVP-$Co(acac)_2$ was 31.2%. The mol% of VP units in the PAN nanoparticles was about 6 mol%, and the PVP chains were present on the surface of the PAN nanoparticles as a stabilizing layer. The PVP hairy chains could successfully stabilize very small Ag nanoparticles on the surface of the PAN nanoparticles.

1. Introduction

Polyacrylonitrile (PAN) nanoparticles have potential applications in enzyme immobilization, pigmentation, separation processes, and as carbon sources [1–4]. In order to prepare monodisperse spherical PAN nanoparticles, a variety of polymerization techniques, such as dispersion, miniemulsion, and dispersion/emulsion polymerizations, have been investigated [5–8]. However, PAN nanoparticles prepared by these polymerization techniques exhibited a crumpled appearance with some crystalline structure. Since PAN is not soluble in acrylonitrile (AN), it is hard to form swollen, intermediate PAN particles during these polymerization processes. The PAN chains precipitate and crystallize in the nucleated PAN particles, resulting in polydisperse PAN particles with some crystalline structure. Interestingly, monodisperse spherical PAN particles were only produced via dispersion polymerization in compressed liquid dimethyl ether by utilizing polydimethylsiloxane-*g*-pyrrolidonecarboxylic acid as a stabilizer [8]. Their average sizes were in the range of 350–500 nm.

There are several reports demonstrating the production of polymer particles via dispersion polymerization using a macroazoinitiator (MAI) as both an initiator and a colloidal stabilizer [9–13]. MAIs are known to be useful initiators for synthesis of block copolymers via radical polymerization. MAIs based on poly(dimethylsiloxane) (PDMS) or poly(ethylene glycol) (PEG) are commercially available, and simple free radical polymerizations using these MAIs yield PDMS or PEG block copolymers. Okubo et al. [10] synthesized polymer particles composed of poly(methyl methacrylate) (PMMA) cores and PDMS hairy shells by the dispersion polymerization of methyl methacrylate (MMA) using a PDMS-based MAI in supercritical carbon dioxide. Similarly, Kimoto et al. [11] obtained PMMA particles with PEG hairy chains by the dispersion polymerization of MMA in ethanol/H_2O solutions with a PEG-based MAI. In the present study, PAN nanoparticles were synthesized via dispersion polymerization of AN in water using a well-defined poly(*N*-vinyl pyrrolidone) (PVP)-cobalt complex as a macroinitiator and a colloidal stabilizer. Cobalt-mediated radical polymerization (CMRP) has recently been

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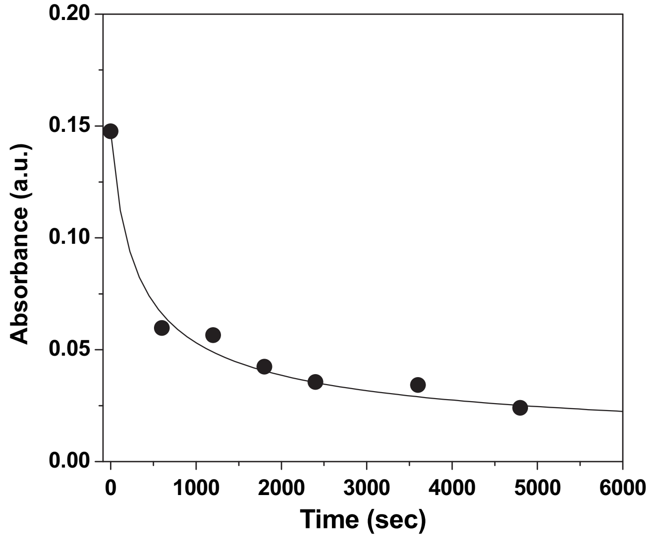

Fig. 1. Homolytic cleavage of PVP-Co(acac)$_2$: PVP MRs were scavenged by TEMPOL.

reported to be one of the most promising controlled radical polymerization processes for achieving controlled polymerization of non-conjugated monomers, such as vinyl acetate (VAc) and *N*-vinyl pyrrolidone (VP) [14–27]. The PVP obtained via CMRP has its cobalt complex at its ω end, and the carbon-cobalt (C–Co) bonds can be homolytically cleaved by thermal activation to yield PVP macroradicals (MRs) [24–27], which initiate the dispersion polymerization of AN. To the best of our knowledge, this article is the first report suggesting the applications of PVP–cobalt complexes as a macroinitiator and a colloidal stabilizer for the dispersion polymerization of vinyl monomers.

2. Experimental section

2.1. Materials

VP (Acros, 98%) and AN (Junsei, 95%) were dried over CaH_2, distilled under reduced pressure, and then degassed by performing three freeze-thawing cycles. 2,2′-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70, Wako, 96%), cobalt(II) acetylacetonate [Co(acac)$_2$, Aldrich, 97%], diethyl ether (Duksan, 99.5%), 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPOL, Aldrich, 97%), silver nitrate ($AgNO_3$, Acros, 99.85%), and sodium borohydride ($NaBH_4$, Aldrich, 98%) were used as received.

2.2. CMRP of VP

The CMRP of VP at a ratio of $[VP]_0/[V\text{-}70]_0/[Co]_0 = 200/8/1$ was performed using V-70 as an initiator and Co(acac)$_2$ as a regulating agent as follows: Degassed VP (6.8 mL, 64.0 mmol), V-70 (0.769 g, 2.56 mmol), and Co(acac)$_2$ (0.08 g, 0.32 mmol) were added to a 100 mL reaction flask equipped with a magnetic stir bar under a nitrogen atmosphere. The reaction mixture was degassed by bubbling with nitrogen for 30 min, and then stirred at 20 °C for 5 h. The resulting product was dissolved in methanol, precipitated in diethyl ether, filtered, and then dried under vacuum. The monomer conversion determined by a gravimetric method was 40.0%. The PVP chains were end-capped by a Co(acac)$_2$ complex (PVP-Co(acac)$_2$), and the number-average molecular weight (Mn) of the resulting PVP was 14,000 g/mol (polydispersity index, PDI = 1.25).

2.3. PVP MRs scavenging by TEMPOL

A PVP-Co(acac)$_2$ aqueous solution (8.3 mg/mL) was divided into 3 mL aliquots in 10 mL vials, and 1 mL of the TEMPOL aqueous solution (0.2 mg/mL) was added to each aliquot. The mixed

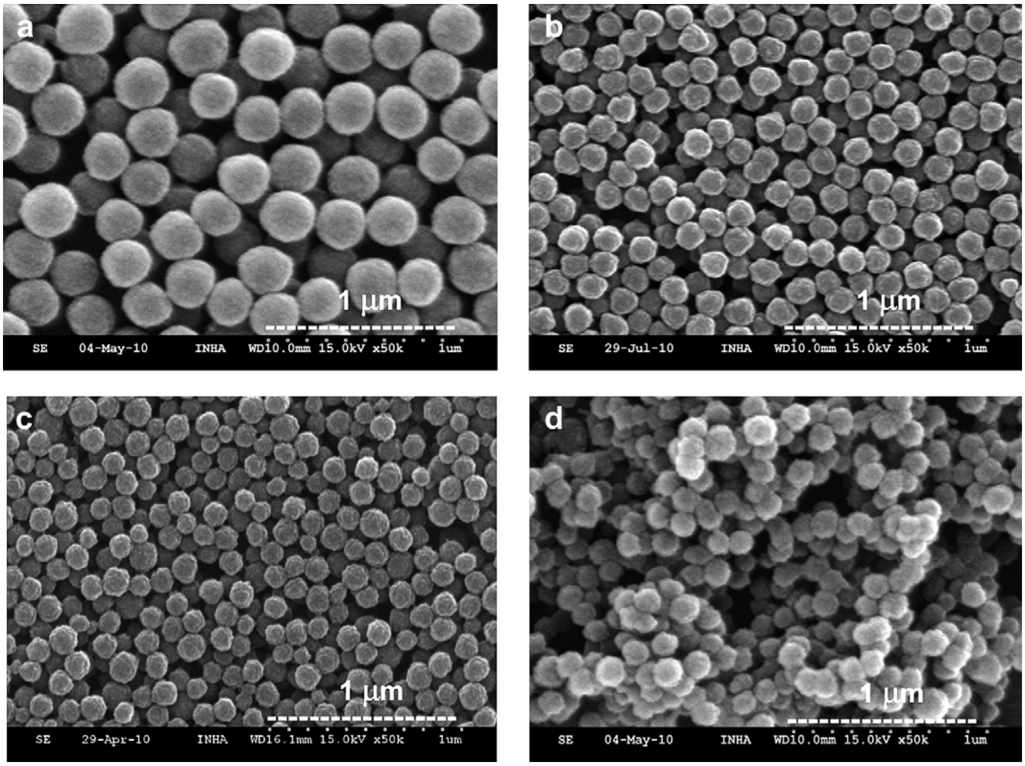

Fig. 2. SEM images of PAN nanoparticles prepared by dispersion polymerization of AN using (a) 20, (b) 30, (c) 40, and (d) 50 wt% of PVP-Co(acac)$_2$ at 30 °C for 24 h.