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Synthesis of Polyacrylonitrile Based Nanoparticles via Aqueous Dispersion Polymerization

Jung-Min Lee

Jeonju Institute of Machinery and Carbon Composites, Jeonbuk 561-844, Korea

Shin-Jae Kang

Department of Mechanical Design Engineering, Chonbuk National University, Jeonbuk 561-756, Korea

Soo-Jin Park*

Department of Chemistry, Inha University, Incheon 420-751, Korea

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Introduction

The monodisperse and controlled polymer nanoparticles have attracted much attention in academic and industrial fields. Due to small size and extremely large specific surface area, nanoparticles could be used to the fields of drug delivery system, microencapsulation, chromate graphy, catalyst, organic/inorganic hybrid materials, and templates for porous inorganic materials.[1,2]

The dispersion polymerization has been known for useful method to prepare micro or submicron scale monodisperse polymer particles in a single step.[3-6] In this polymerization, all reaction materials are dissolved in the reaction medium at the beginning stage of the polymerization, then insoluble spherical polymer particles stabilized by steric stabilizer molecules are formed and dispersed in the reaction medium. However, this polymerization have some faults which is the number-average molecular weight (M_n) of the synthesized polymers is reported to be relatively smaller than 200,000 g/mol.[7] Poly(vinyl alcohol) (PVA) is a well-known protective stabilizer used in suspension polymerization. However, PVA has been rarely used in dispersion polymerization due to its very poor solubility in polymerization media, i.e., usually alcohols. The first application of pure PVA as a stabilizer dates back only to 2005 in the polymerization of vinyl acetate in which a mixture of ethanol and water was used as the polymerization medium.[8] Since then, methyl mathacrylate and styrene have been polymerized through dispersion polymerization used pure PVA as the stabilizer in aqueous media.[9] Acrylonitrile (AN) is a commonly used monomer for producing acrylic fiber and also acts as comonomer in the synthesis of engineering plastics because of its high chemical resistance, barrier property, and high reactivity with other monomers such as vinylidene chloride and styrene. Among the application of polyacrylonitrile (PAN), carbon fiber precursor has found significant interest due to the high tensile strength and modulus and low specific gravity. It is well known that high molecular weight and narrow polydispersity are essential requirements for high performance PAN fibers.[10] AN is a polar organic compound and it has a substantial solubility in water (7.35 w/v% at 20 °C) compared to that of other oil-soluble monomers.[11]

In this study, poly(acrylonitrile-*co*-itaconicacid-*co*-methylacrylate) nanoparticles were successfully synthesized by aqueous dispersion polymerization using hydrophilic PVA in a water/*N*,*N*-dimethylformamide mixture media. Then the characteristic of the nanoparticles were investigated in terms of the polymerization time and concentration of stabilizer.

Experimental

The dispersion polymerization ingredients were acrylonitrile (Dongyang Chemical, Korea), methylacrylate (MA; Junsei Chemical, Japan), itaconic acid (IA; Junsei Chemical, Japan), 2,2-azobis(isobutyronitrile) (AIBN; Junsei Chemical, Japan), poly(vinyl alcohol)(PVA; Aldrilch, USA, M_w: 109,000 g/mol), double distilled (DDI) water, and *N*,*N*-dimethylformamide (DMF; Aldrich, USC).

The general polymerization recipe used in this study is given in Table I. The polymerization involved two steps; first, the AN, IA, MA, AIBN, and DMF were charged into the reactor flask with bubbling nitrogen gas. The solution was sealed and completely sunk into an oil bath at 60 °C for 10 min. Second, the solution of DDI water and PVA was added into the reactor flask at 60 °C for 24 h. The resultant mixture was centrifuged and dispersed in water. The remnant of sample was dried in vacuum oven.

The chemical structure of the synthesized poly(AN-*co*-IA-*co*-MA) terpolymer was confirmed by 500-MHz ^{1}H NMR (Bruker advance) and FTIR spectrum (Bruker equinox 55 FTIR spectroscopy). The molecular weight was characterized using a Waters GPC (gel permeation chromatography). A Hitachi SEM (scaning electron microscopy) S-4200 was used to observe the morphology of the poly(AN-*co*-IA-*co*-MA) nanomethersized particle. The size distribution was measured using a particle size analyzer (LS230®, Beckman Coulter, USA).

*Corresponding Author. E-mail: sjpark@inha.ac.kr

Table I. Standard Recipe Used in Dispersion Polymerization at 60 °C for 24 h

Ingredient	Amount (g)	Remark
Acrylonitrile	28.5	95 wt% relative to total monomer
Itaconic acid	0.6	2 wt% relative to total monomer
Methylacrylate	0.9	3 wt% relative to total monomer
AIBN	0.3	1 wt% relative to monomer
PVA	3	10 wt% relative to monomer
DDI water	300	91 wt% relative to total medium
DMF	30	9 wt% relative to total medium

Results and Discussion

^{1}H NMR and FTIR spectra are used to confirm the chemical structure of the poly(AN-*co*-IA-*co*-MA) terpolymer in synthesized PAN-based nanoparticles. Figure 1 showed the ^{1}H NMR spectrum of the terpolymer using DMSO-d_6 as the solvent. The characteristic peaks of the -CH_2- and -CHR- protons were observed at 1.95-2.2 and 3.02-3.23 ppm, respectively in Figure 1(a) and 1(b). The multiplet at 3.6-3.7 ppm for 3 protons of ester methyl in polymethyl acrylate unit was observed in Figure 1(c).

Figure 2(a) and 2(b) show the FTIR spectra of nanomether-sized particle with the standard recipe (Table I) and resin prepared by solution polymerization with AN, IA, MA and AIBN in DMF, respectively. These spectrums show the representative characteristic peaks of aliphatic -CH- and -CH_2- stretching at 2900-3000 cm^{-1}. A strong adsorption peak at 2240 cm^{-1}, characteristic peak of C≡N stretching of AN repeating unit is observed. In addition, the carbonyl (C=O)

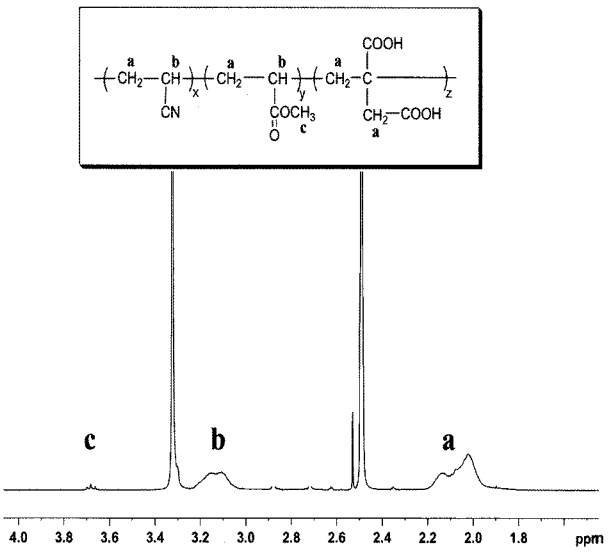

Figure 1. ^{1}H NMR spectrum of PAN-based terpolymer by dispersion polymerization.

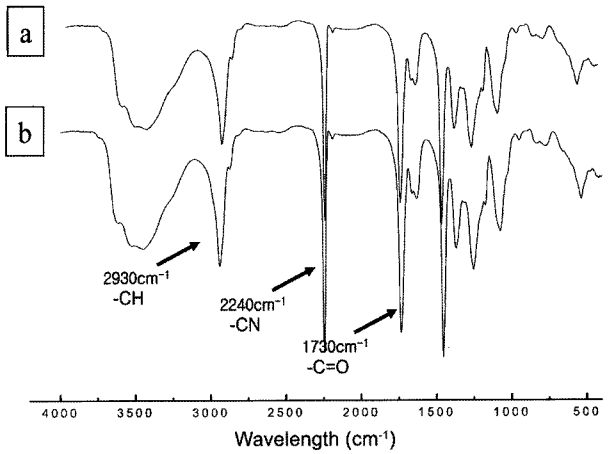

Figure 2. FTIR spectra of the PAN-based terpolymer prepared by (a) dispersion and (b) solution polymerization.

peak of polyitaconicacid and polymethylacrylate is appeared at 1730 cm^{-1}. This FTIR spectrum of PAN-based nanoparticles was identical to spectrum of PAN-based resin. In addition, the GPC traces of the synthesized poly(AN-*co*-IA-*co*-MA) nanoparticles showed a symmetrical and unimodal distribution without other peaks, which means that there is no significant homopolymer or other impurities in the terpolymer. And the weight-average molecular weight of the terpolymer is about 785,235 g/mol. Based on the ^{1}H NMR, FTIR, and GPC spectrums, it was confirmed that poly(AN-*co*-IA-*co*-MA) terpolymer was successfully synthesized.

The poly(AN-*co*-IA-*co*-MA) nanoparticles were synthesized by aqueous dispersion polymerization. Upon the polymerization, primary particles are obtained from the precipitation of large oligomeric species. These primary particles then grow to the final particle size by the absorbing oligomers and monomers from the medium.

According to the mechanism, all reaction materials are dissolved in the polymerization medium at the beginning state of the process. In our research, the mixture of AN, IA, and MA was not fully dissolved in pure water system. However, this mixture of monomers is perfectly solved in DMF. Therefore mixture of water and DMF system was used in our polymerization system. Boguslavsky *et al.* reported the effects of DMF in dispersion/emulsion polymerization of acrylonitrile in the presence of potassium persulfate as an initiator, alkyl-sulfate and sulfonate surfactants.[12] These researchers described that the addition of small amount of DMF as the co-solvent was needed to dissolve the acrylonitrile monomers. Consequently, addition of DMF affected to the solubility of monomer and PAN-based terpolymer in reaction medium, and it is produced PAN-based particles to be successfully formed in our experimental system. In addition, more higher critical molecular weight of poly(AN-*co*-IA-*co*-MA) terpolymer chains obtained.

Figure 3 displays SEM images of the surface morphology

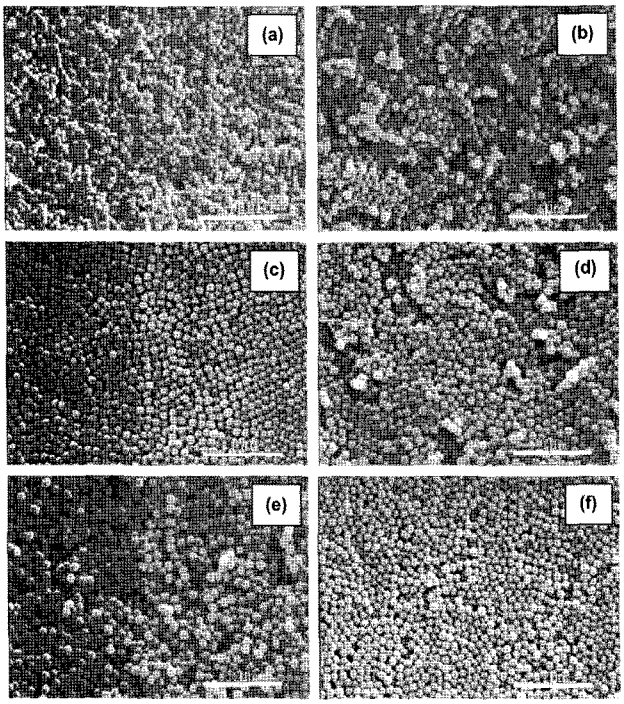

Figure 3. SEM photographs of PAN-based nanoparticles synthesized by dispersion polymerization in 10/1(w/w) water/DMF medium at various polymerization time; (a) 1, (b) 2, (c) 4, (d) 6, (e) 12, and (f) 24 h.

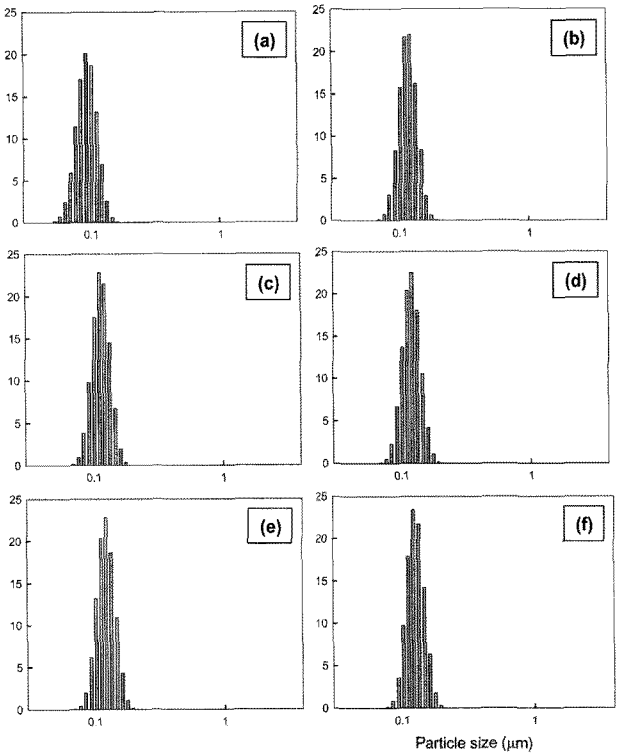

Figure 4. Particle sized distributions of PAN-based nanoparticles synthesized by dispersion polymerization in 10/1 (w/w) water/DMF medium at various polymerization times; (a) 1, (b) 2, (c) 4, (d) 6, (e)12, and (f) 24 h.

and growth of the PAN-based nanoparticles prepared by the standard recipe given in Table I for various reaction times. By observing stable particles, the use of PVA has proven to play role as a stabilizer in our dispersion polymerization system. The relatively monodispersed particles were formed during the reaction time from the early stage of the polymerization and they progressively grew in size until the completion of polymerization except the Figure 3(a). At the early stage of polymerization (Figure 3(a)), the synthesized particles were not stable and partially coagulated. As the further reaction produced the particles size gradually increased with relatively narrow distribution of particle size. Although some doublets or triplets are still remained, almost well-shaped stable particles were obtained in whole reaction time. As the polymerization time was increased from 1 to 24 h, the average particle size was increased from 69 to 138 nm. In generally, micro or sub-micron sized particles are obtained from the dispersion polymerization. Therefore, these results are considered as unusual tendency. Also these photographs show the nonsmooth surface of the PAN-based nanoparticles. According to Boguslavsky *et al.*, this phenomenon was explained that nanocrystalline grains were existed within and on the surface.[12]

The characteristics of synthesized PAN-based nanoparticles are analyzed in Figure 4, which is showed the relationship with particle size distributions and reaction time. With increasing polymerization time, average particle size distribution graphs are narrow and shifted to the right. These behaviors are consistent to the SEM photographs in Figure 3.

Figure 5 shows the effect of the PVA concentration on the size of PAN-based nanoparticles by the dispersion polymerization using 2-15 wt% of PVA for 24 h. As the PVA concentration increased from 5, 10, to 15 wt%, the size of PAN-

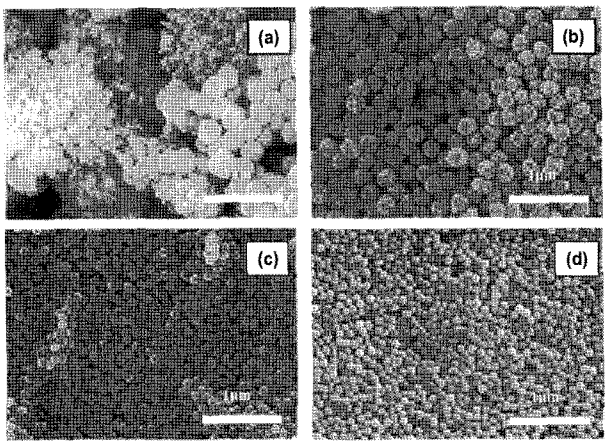

Figure 5. SEM photographs of PAN-based nanoparticles in mixture of water and DMF medium with (a) 2, (b) 5, (c) 10, and (d) 15 wt% of PVA relative to total monomer for 24 h.

based nanoparticle decreased from 253, 107, to 86 nm as shown in Figure 5(b), 5(c), and 5(d). Whereas, the nanoparticles with broad size distribution, i.e., coefficient of variation (C_v) of 15-19% are obtained. As the stabilized concentration increased, the size of synthesized particle decreased, due to the favorable formation of more primary nuclei in the early stage of polymerization at higher concentrations of the stabilizer. The unstable particles and aggregation of very tiny particles were observed when using 2 wt% of PVA as shown in Figure 5(a).

Conclusions

In this study, the aqueous dispersion polymerization of acrylonitrile, itaconic acid, and methyl acrylate has been successfully carried out using PVA as a steric stabilizer in the mixture of water and DMF medium. The formation and characterization of PAN-based nanoparticles were studied by the polymerization time and concentration of PVA. The chemical structure of the synthesized terpolymer of poly (AN-*co*-IA-*co*-MA) nanoparticle was confirmed using ^{1}H NMR, FTIR, and GPC spectra. All of the synthesized particles have the nonsmooth surface and relatively spherical shaped. The particle sizes were affected by the concentration of stabilizer concentration and reaction time. The stable PAN-based nanoparticles were successfully obtained when the concentration of the PVA increased from 5 to 15 wt% relative to the monomer and the average particle size decreased from 250 to 87 nm. The effects of PVA on the stabilization of particles and size variation are similar to the conventional stabilizers in the dispersion polymerization.

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