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Preparation of Narrow or Monodisperse Polymer Microspheres with Cyano Group by Distillation-Precipitation Polymerization

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Summary

Narrow- or monodisperse poly(divinylbenzene-co-acrylonitrile) (poly(DVB-co-AN)) microspheres with reactive cyano group were prepared by distillation-precipitation polymerization of divinylbenzene (DVB) and acrylonitrile (AN) in neat acetonitrile with 2,2′-azobis(isobutyronitrile) (AIBN) as initiator in the absence of any stabilizer or additive without stirring. The effects of the comonomer feed on the morphology and the size of poly(DVB-co-AN) microspheres were investigated. All the polymer microspheres were characterized with scanning electron microscopy and FT-IR spectra.

Introduction

Functional crosslinked polymer microspheres have received increasing attention in many fields of scientific research as well as for industrial importance, especially with the regard to their application in waste-water treatment. The resins based on acrylonitrile are easy to prepare and present a reactive pendant group (cyano group), which can be modified by different kinds of reagents through the nucleophilic addition and cycloaddition reaction, such as the chemical modifications of cyano groups with hydroxylamine, hydrazine, and ethanolamine to afford amidoxime, amidazone, and oxazoline groups, respectively [1-6]. The main fields of application of such functional resins are the removal of undesired ions and molecules from solutions and extraction of useful substances. Furthermore, the utilization of functional polymer as catalysts in organic synthesis and for the chromatographic separation of metals and organic compounds has been into a general use on a technical scale during the last a few years. AN/DVB copolymer beads in millimeter range with broad-size distribution as the precursors of the amidoxime resins have been synthesized by a suspension polymerization process [10-12]. It was difficult to control the particle size and size distribution of these copolymer beads through a dynamic equilibrium of mechanism of droplet breakdown and coalescence, which was affected by the inert diluent, stirring conditions, temperature and initiator for the polymerization. Irregular submicron-sized polyacrylonitrile particles were prepared by dispersion polymerization of acrylonitrile in supercritical carbon dioxide [13]. Monodisperse submicrometer microspheres with cyano group were obtained by emulsifier-free emulsion copolymerization of styrene and acrylonitrile [14].

Recently, we reported the distillation-precipitation polymerization as a novel technique to afford monodisperse poly(DVB) [15], poly(DVB-co-chloromethyl styrene) (poly(DVB-co-CMSt)) [16] microspheres in neat acetonitrile. We also succeeded in obtaining core-shell structure polymer microspheres with different functional groups by two-stage distillation-precipitation polymerization [17]. Neither steric nor electrostatic stabilizers were added to these systems to get crosslinked monodisperse micron-sized polymer particles with a clean, stabilizer-free surface. In the present work, we described the preparation of monodisperse poly(DVB-*co*-AN) microspheres in micrometer and sub-micrometer size range containing the reactive cyano functional group with smooth and clean surface by distillation-precipitation copolymerization of DVB and AN in neat acetonitrile with AIBN as initiator.

Experimental

Chemicals. Divinylbenzene (DVB80, containing 80% of DVB isomers, Shengli Chemical Factory, Shandong, China) was washed with 5% aqueous sodium hydroxide solution, water and then dried over anhydrous magnesium sulfate prior to use. Acrylonitrile (Chemical grade, Tianjin Chemical Reagents II Co.) was washed through an alumina column and purified by vacuum distillation. 2,2′-Azobis(isobutyronitrile) (AIBN, Chemical Factory of Nankai University) was recrystallized from methanol. Acetonitrile (analytical grade, Tianjin Chemical Reagents II Co.) was dried with calcium hydride and purified by distillation before utilization. All the other reagents were analytical grade and used as received without any further purification.

Preparation of Poly(DVB-co-AN) Microspheres by Distillation-precipitation Polymerization

A typical procedure for the distillation-precipitation polymerization: DVB80 (1.2 mL, 1.1 g, 8.5 mmol) and AN (0.8 mL, 0.64 g, 12 mmol) (total comonomers as 2.5 vol% relative to the reaction medium), AIBN (0.04 g, 0.24 mmol, 2 wt% relative to the total comonomers) were dissolved in 80 mL of acetonitrile in a dried 100-mL two-necked flask, attaching with a fractionating column, Liebig condenser and a receiver. The flask was submerged in a heating mantle and the reaction mixture was heated from ambient temperature till boiling state within 30 min and the system was kept under refluxing for 20 min. Then the solvent was distilled off the reaction system. The initially homogeneous reaction mixture became milky white after boiling for 15 min. The reaction was stopped after 40 mL of acetonitrile was distilled from the reaction system within 1.5 h. After the copolymerization, the resulting poly(DVB-co-AN) microspheres were separated by vacuum filtration over a G-5 sintered glass filter and washed successively with THF and ethanol for three times. The polymeric particles were dried at 50 ^{o}C in vacuum oven till constant weight to afford 0.21 g in 12% yield.

The procedures for the other distillation-precipitation copolymerizations were much similar to that of the typical one but varying the comonomer ratio of DVB and AN, while the total comonomer concentration, the amount of AIBN and acetonitrile were kept at the same level as the above. The initially homogeneous reaction mixture became milky white after boiling for 10-40 min, depending on the comonomer ratios. The treatment for these samples was the same as the typical one.

All the yields of microspheres were determined gravimetrically. The reproducibility of the copolymerizations was confirmed by several duplicate experiments.

Particle Size Analysis

The particle size and size distribution were determined by scanning electron microscopy (SEM) using a Philips XL-30. All of the SEM size data reflect the average of about 100 particles each, which were calculated by the following formula:

$$U = D_W / D_n \qquad D_n = \sum_{i=1}^{k} n_i D_i / \sum_{i=1}^{k} n_i$$

$$D_w = \sum_{i=1}^{k} n_i D_i^4 / \sum_{i=1}^{k} n_i D_i^3$$

where, U is the polydispersity index, D_n is the number average diameter, D_w is the weight average diameter. N is the total number of measured particles, and D_i is the particle diameter of the determined microspheres.

FT-IR Analysis

Fourier-transform infrared analysis were recorded on a Bio-Rad FTS 135 FT-IR spectrometer. All samples were mixed and ground with spectroscopic grade potassium bromide prior to being placed in the sample cell, and the diffuse reflectance spectra were scanned over the range of 400-4000 cm^{-1}.

Results and Discussion

Copolymerizations of AN with DVB80 were carried out at 2.5 vol% of total comonomer loading relative to the reaction medium and 2 wt% AIBN (relative to the total comonomers) as initiator. In these experiments, the AN fraction in the comonomers feed was varied from 0 to 0.80.

The monomer feed in copolymerization had much effect on poly(DVB-co-AN) particle formation by distillation-precipitation polymerization. In addition to the monodispersed spherical particles formed in the absence of AN, two copolymerization regions can be distinguished in terms of the AN fraction in comonomer feed. One was irregular nanoparticle formed at AN fraction of 0.80 in the comonomer feed. The other was spherical particle with monodisperse distribution afforded at AN fraction from 0 to 0.60 in comonomer feed.

The SEM images of the resultant poly(DVB-co-AN) particles with different AN fraction in comonomer feed were shown in Figure 1.

Figures 1(A1)-(A5) showed the images of monodisperse particles obtained from the AN fraction of 0 to 0.60, respectively. All of these polymer particles have nearly perfect spherical shape with non-segmented surfaces. Figure 1(A6) shows the image of poly(DVB-co-AN) particles with AN fraction of 0.80, which were agglomerates of irregular nanoparticles.

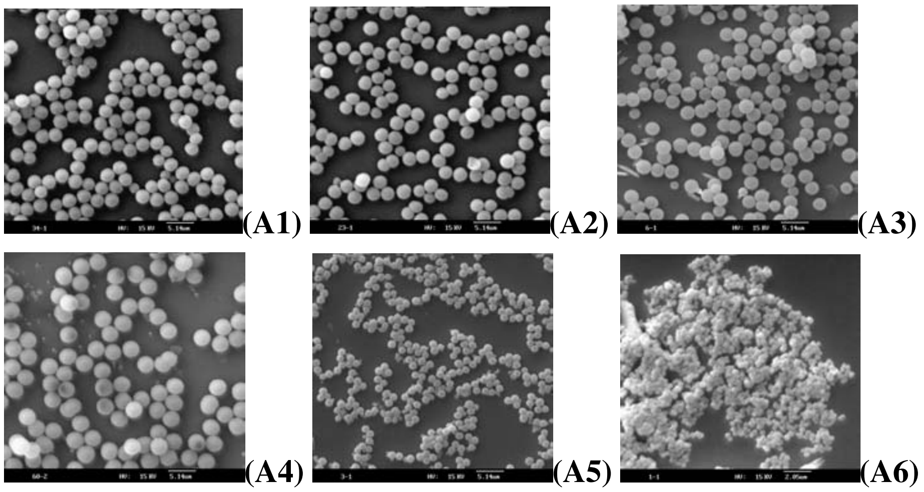

Figure 1 SEM images of poly(DVB-*co*-AN) microspheres with different AN fraction in comonomer feed with AIBN as initiator: A1: DVB only; A2: 0.10 AN; A3: 0.20 AN; A4: 0.40 AN; A5: 0.60 AN; A6: 0.80 AN

The results indicated that the morphology varied with the comonomer composition. The nuclei were formed during the distillation-precipitation copolymerization most likely by the aggregation of oligomers at the initial stage. Then the particles were grown by the radical reaction with the formation of oligomers and comonomers subsequently. The results indicated that the solvated branched or crosslinked copolymer chains at the particle surfaces were sufficient to stabilize the particles against homocoagualtion at low comonomer loading in most cases for the present distillation-precipitation copolymerization, even with the crosslinking degree as low as 0.40 in the absence of any stabilizer or stirring. The irregular nanoparticles may be attributed to the extended particle nucleation at lower crosslinking degree of 0.20 (Figure 1 (A6)).

The size, size distribution and the yield of poly(DVB-co-AN) particles with different AN fraction in comonomer feed were summarized in Table 1.

The average diameter varied from 1.27 to 3.10 μm with AN fraction in the range of 0 to 0.60 in comonomer feed. The yield of the polymer particles slightly decreased from 18% to 12% when the AN fraction in comonomer feed was increased from 0 to 0.40. On the other hand, the yield increased promptly to 20% when the AN fraction was further increased to 0.60. The low yield of polymer microspheres may be due to the low concentration of the comonomer feed for the distillation precipitation polymerization [15-16]. Otherwise, the reaction system would bump with higher loading of commoners during the distillation precipitation polymerization.

The solubility parameters of the solvent played an essential role in disseminating the successful formation of a stable spherical shape in dispersion polymerization [18-19] as well as precipitation-polymerization [20]. The solubility parameters of polyDVB, polyAN, and acetonitrile are 35.6, 53.1, 40.2 $(J/cm^3)^{1/2}$, respectively [21]. It can be said that acetonitrile is a precipitant solvent for poly(acrylonitrile) (polyAN). The final particle size was determined by the conversion of the comonomers and the number of nuclei. The solubility parameter of poly(DVB-*co*-AN) should be in the range of 35.6-53.1 (J/cm^3)$^{1/2}$, which depends on the fraction of AN in the copolymer. When AN fraction in the comonomer feed was increased from 0 to 0.40, the solubility parameter of initially formed oligomer DVB-*co*-AN became closer to the parameter of acetonitrile. In such case, the oligomers can be dissolved well in the solvent to reduce the number of nuclei and retard the formation of polymer microspheres, which had a tendency to enlarge the size of the resultant polymer particles. For the present distillation precipitation copolymerization system, acetonitrile is a poorer solvent for oligomers of AN than DVB. The larger is the fraction of AN in comonomer feed in the polymerization system, the earlier phase separation or precipitation of polymer microspheres occurs with increasing the number of nuclei at the initial stage of copolymerization, which decreased the particle size to 1.27 μm with AN fraction at 0.60 (Entry A5, Table 1). In the other words, the AN fraction of 0.40 can be regarded as a critical point for the size of the resultant poly(DVB-co-AN) microspheres due to the different solubility of oligomers DVB and AN in acetonitrile. When the AN fraction was increased further to 0.80, the formed polymer precipitated from the reaction system too quickly to be stabilized against homocoagulation, which led to the formation of aggregates of irregular nanoparticles as in Entry A6, Table 1.

Table 1 The size, size distribution and the yield of poly(DVB-*co*-AN) microspheres with AIBN as initiator

Entry	Fraction of AN	AIBN (g)	Dn (μm)	Dw (μm)	U	Yield
A1	0	0.04	2.30	2.31	1.009	18
A2	0.10	0.04	2.84	2.85	1.003	18
A3	0.20	0.04	2.54	2.62	1.050	14
A4	0.40	0.04	3.10	3.11	1.003	12
A5	0.60	0.04	1.27	1.33	1.031	20
A6[a]	0.80	0.04	-	-	-	-

[a] Irregular nanoparticle (600~750 nm)

The incorporation of AN to the poly(DVB-co-AN) microspheres with reactive cyano functional group was confirmed further by FT-IR spectra, as shown in Figure 2.

All the FT-IR spectra polymer particles show a narrow strong peak at 2236 cm^{-1} corresponding to the typical stretching vibration of the cyano group and the height of the peak increased dramatically with increasing fraction of AN in comonomer feed (a weak peak at 2236 cm^{-1} even for polyDVB due to the residual cyano group from AIBN initiator). There was a weak peak at 1630 cm^{-1} in FT-IR spectra of the copolymer attributing to the stretching vibration of carbon-carbon double bonds. In the other words, there were many residual double bonds on poly(DVB-co-AN) microspheres due to the rigid surface of the resultant polymer particles and low monomer concentration of comonomers for distillation-precipitation polymerization. The residual double bonds on the surface of polymer microspheres played an important role for the formation and extension of monodisperse particles, which can capture the soluble oligomers and monomers to grow the polymer particles and prevent the coagulation during the distillation-precipitation copolymerization. However, the few residual double bonds could not capture the soluble oligomers

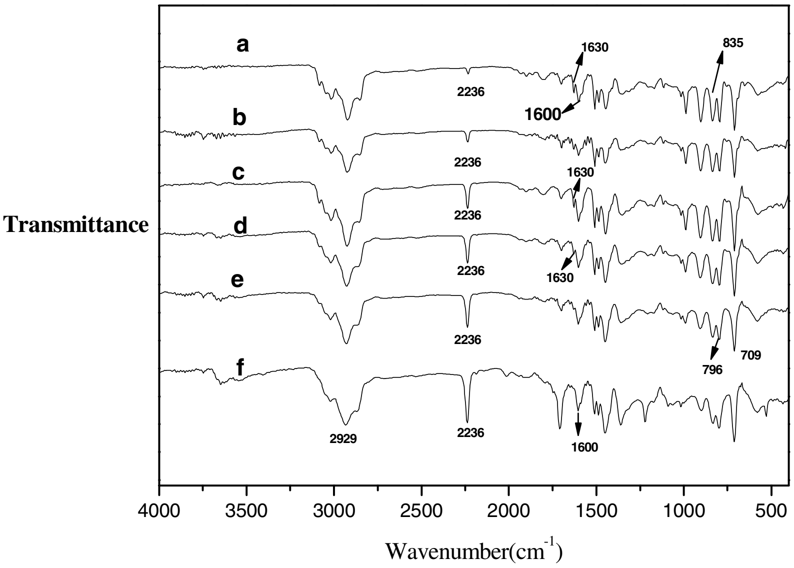

Figure 2 FT-IR spectra of poly(DVB-*co*-AN) microspheres with different AN fraction in comonomer feed with AIBN as initiator: a: DVB only; b: 0.10 AN; c: 0.20 AN; d: 0.40 AN; e: 0.60 AN; f: 0.80AN

completely such as Entry A6 in Table 1 with 0.20 of low DVB crosslinking degree. In this case, the reaction either between the active radicals and soluble oligomers or between the active radicals themselves became possible, which led to the formation of aggregation of irregular nanoparticles. The FT-IR spectra of all poly(DVB-co-AN) microspheres have a strong peak at 2929 cm^{-1} due to the vibration of the benzyl backbone.

The relationship peak ratios of 1630 to 2929, and 2236 to 2929 cm^{-1} for all the particles calculated by Kubelka-Munk units were illustrated in Figure 3.

The results indicated that A2236/A2929 (cyano group to benzyl backbone) increased significantly from 0.007 (originated from the residual part of AIBN initiator) to 0.620 with simultaneous decrease of A1630/A2929 (residual double bonds to benzyl backbone). These results demonstrated that loading of the cyano group on the polymer microspheres increased significantly with the increase of AN fraction in the comonomer feed. In the previous work, monodisperse poly(DVB-*co*-HEMA) microspheres with the active hydroxyl groups prepared by distillation-precipitation polymerization were much reactive and easily accessible with high loading capacity from 2-4 mmol/g [23]. The reactivity ratios for *p*-DVB (monomer 1), *m*-DVB (2) and AN (3) present in the system were r_{13}=4.2, ν_{31}=0.2, r_{23}=1.55, ν_{32}=0.26, r_{12}=1.55, and ν_{21}=0.42, respectively [24]. These values suggest that the AN-DVB copolymer formed at initial stage of polymerization contains more DVB units than the monomer mixture. In the other words, more AN monomers were incorporated into the solvent-swollen gel layer than the nuclei of polymer microspheres during the distillation-precipitation polymerization. The chemical modification of the reactive and accessible cyano groups on the crosslinked resins and their application as sorbants for various metal cations will be published elsewhere in our forthcoming paper.

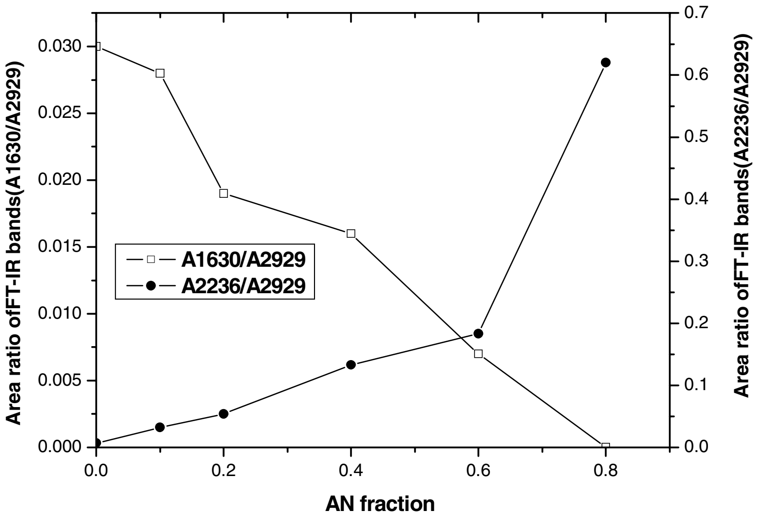

Figure 3 Relationship between the peak area of cyano group, residual double bonds to the benzyl backbone of poly(DVB-*co*-AN) microspheres with different AN fraction in comonomer feed with AIBN as initiator

Distillation precipitation copolymerization of DVB and AN involved polymerization-induced phase separation of crosslinking in the absence of any stabilizer or additive. Therefore, the surface of the polymer microspheres is clean without any contaminant. Only a powder polymer was precipitated from the reaction system with AN in the monomer feed without any crosslinking agent. The key problem in this process was to maintain the reaction system homogeneity by distilling the acetonitrile solvent off the reaction system during the copolymerization to avoid coagulation, Otherwise, the reaction system would bump under the refluxing state without distilling the solvent out of the reaction system. In the other words, the agitation caused by distilling off a portion of the polymerization solvent, acetonitrile, during the copolymerization played an essential role for the formation of the narrow- or monodisperse microspheres with reactive cyano group.

Conclusion

Narrow- or monodisperse poly(DVB-*co*-AN) microspheres with active cyano group on the surface in the range of 1.27 to 3.10 μm were prepared by distillation-precipitation polymerization in acetonitrile in the absence of any stabilizer or additive without stirring with AIBN as initiator. The SEM images indicated that the copolymer particles had spherical shapes with smooth surfaces in narrow dispersity with AN fraction in comonomer feed from 0 to 0.60. The comonomer feed ratio has much effect on the formation of the copolymer particles for the distillation-precipitation copolymerization of AN and DVB in acetonitrile. The results demonstrated that more functional cyano groups were incorporated into the outer solvent-swollen gel layer of the copolymer microspheres with increase AN fraction in comonomer feed. The distillation of a portion of the solvent out of the reaction system during the polymerization was a key problem to avoid the coagulation and form monodisperse polymer microspheres for the distillation precipitation copolymerization of DVB and AN in acetonitrile.

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