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Preparation of Monodisperse Poly(*N*-vinylformamide) Particles by Dispersion Polymerization in Methanol Solvent

Hiroshi UYAMA, Hisataka KATO, and Shiro KOBAYASHI*
Department of Molecular Chemistry and Engineering, Faculty of Engineering,
Tohoku University, Aoba, Sendai 980

Dispersion polymerization of *N*-vinylformamide (NVF) was performed in methanol using a hydrophilic polymer or a poly(2-methyl-2-oxazoline) macromonomer as a stabilizer. The polymerization of NVF using poly(2-ethyl-2-oxazoline) as stabilizer gave relatively monodisperse polymer particles in the size of micron range. In using the macromonomer, monodisperse PNVF particles in the sub-micron range were obtained.

Monodisperse polymer particles have received much attention in technical and biomedical field. Micron-size monodisperse particles of hydrophobic polymers such as polystyrene and poly(methyl methacrylate) have been prepared by a dispersion polymerization in polar media.[1-3] The polymerization usually needs a polymeric stabilizer.

Poly(vinylamine) (PVAm) is an important industrial material for chelating and agglomerating agents.[4] Recently, highly pure PVAm has been prepared by radical polymerization of *N*-vinylformamide (NVF)[5] followed by acidic hydrolysis.[6] Polymerization of NVF and functional polymers based on PNVF have not been investigated so far. This communication deals with preparation of monodisperse PNVF particles by the dispersion polymerization in methanol. NVF is soluble in water and polar solvents, however, PNVF is soluble only in water. To our knowledge, this study is the first example of preparation of monodisperse particles of highly hydrophilic polymers in the micron range.[7]

The dispersion polymerization of NVF was carried out in methanol using 2,2'-azobis(2,4-dimethylvaleronitrile) at 56 °C for 24 h under argon to produce a stable dispersion. Polymeric stabilizers used were poly(2-ethyl-2-oxazoline) (PEtOZO, Mw=5.0x10^5), poly(vinyl methyl ether) (PVME, Mw=4.6x10^4), poly(*N*-vinylpyrrolidone) (PNVP, Mw=3.6x10^5), and poly(ethylene glycol) (PEG, Mw=5.0x10^4). The polymer particles were separated by centrifugation of the dispersion and were analyzed by scanning electron microscope (SEM).

Figure 1 shows SEM photograph of PNVF particles prepared by using 20 weight % of PEtOZO. The particles were relatively monodisperse in the micron range. With PVME, PNVP or PEO, however, particles with narrow size distribution were not obtained (Table 1).

Very recently, we have found that poly(2-methyl-2-oxazoline) macromonomer (**1**) was a very efficient stabilizer for the dispersion polymerization of MMA; the concentration of **1**, necessary for the preparation of monodisperse PMMA particles, was much lower than that of a homopolymer-type stabilizer in conventional

dispersion polymerization.[8] In this study, macromonomer **1** having a polymerizable styryl group (Mw=4.8x10^3) was used as a stabilizer. In using **1** of 2 weight % for NVF, relatively monodisperse particles with the diameter of 0.3 μm (D_w/D_n=1.02) were obtained. The concentration of **1** was lower than that of PEtOZO and the resulting particle was smaller in size, indicating that the macromonomer is efficient as a comonomer as well as a stabilizer of the present dispersion polymerization. The different efficiency of the stabilizer is because the macromonomer acts not only as a stabilizer but also as a comonomer, and hence, the stabilizer polymer chain is chemically fixed on the polymer particle.

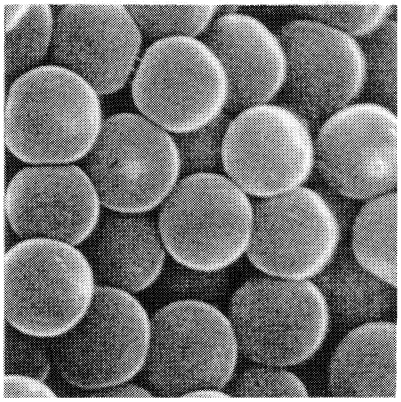
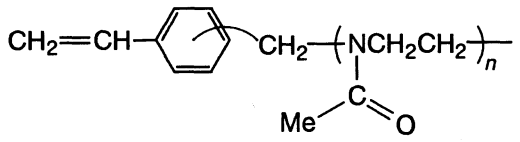


Fig. 1. SEM photograph of PNVF particles obtained by using 20 % of PEtOZO.

Table 1. Dispersion polymerization of NVF

Stabilizer[a]	Yield / %	Diameter[b] / μm
PEtOZO	95	1.2 (1.02)
PVME	98	0.4-0.8
PNVP	100	0.3-0.8
PEG	79	0.6-2.0

a) Concn of stabilizer = 20 weight % for NVF.
b) Determined by SEM. The value in the parenthesis is the particle size distribution (D_w/D_n).



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In conclusion, monodisperse PNVF particles were prepared by the dispersion polymerization in methanol. The more detailed studies including the control of particle size and preparation of particles from other highly hydrophilic polymers such as poly(acrylamide) are now in progress.

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