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Preparation of Poly(*N,N* '-methylenebisacrylamide) Fine Particles by Radiation-Induced Polymerization

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Preparation of fine particles of poly(*N,N* '-methylenebisacrylamide) by radiation-induced polymerization is described. The size of the obtained fine particles is 0.22 μm having a narrow distribution. This result is one of the examples of the particle formation promoted by the crosslinking polymerization. This is the first report on poly(*N,N* '-methylenebisacrylamide) fine particles.

Radiation-induced polymerization of diethylene glycol dimethacrylate (2G) in organic solvents gives monodisperese microspheres.[1] The characteristic of this method is that the solutions containing only the monomer give the monodisperse microspheres without stirring. The mechanism of the particle formation is quite different from other common methods, for example, dispersion or emulsion polymerization.[2] Radiation contributes to homogenueous initiation under the conditions without stirring. The formation of microsphere is restricted to specfic monomers such as 2G. The crosslinking reaction causes the formation of the microspheres. Therefore, it is expected that the monomers having two vinyl groups give microspheres in a suitable solvent.

There are a number of monomers having two or more vinyl groups in the molecules. We have tested ethylene glycol dimethacrylate derivatives, $CH_2=C(CH_3)COO(CH_2CH_2O)_nCO(CH_3)C=CH_2$ (n=1-4,9), but they did not give good results except for 2G.[3] Divinyl benzene, usually used as a closslinking reagent, did not give particles in benzene, toluene and ethyl acetate solutions.

N,N'-Methylenebisacrylamide is also used as a closslinking reagent, and its polymer is expected to be more stable to water than poly(diethylene glycol dimethacrylate). Before polymerization, we tested the solubility of *N,N'*- methylenebisacrylamide in various solvents, since good solvent is suitable for the preparation of microspheres.[1] The solvents tested are acetonitrile, ethyl acetate, methanol, *n*-propylamine, pyridine, THF, triethylamine and water. Fine particles were obtained only from THF solution. The monomer was also dissolved in methanol and *n* -propylamine, but the irradiation of the solutions resulted in gelation. These solvents are considered to disturb by unexpected reactions, such as chain transfer reactions.[3]

N,N'-Methylenebisacrylamide (20 mg) was dissolved in THF (2 mL) in a glass vessel with 10 mm i.d. The feed solutions were deoxgenated by nitrogen bubbling. The sample was irradiated with ^{60}Co γ rays at room temperature without stirring. The dose rate was 4 kGy h^{-1} and the irradiation time was 15 min. Teflon filters with a 0.2 μm pore size were used for the separation of the microspheres from the irradiated solutions. The microspheres were washed with THF and then dried under vacuum.

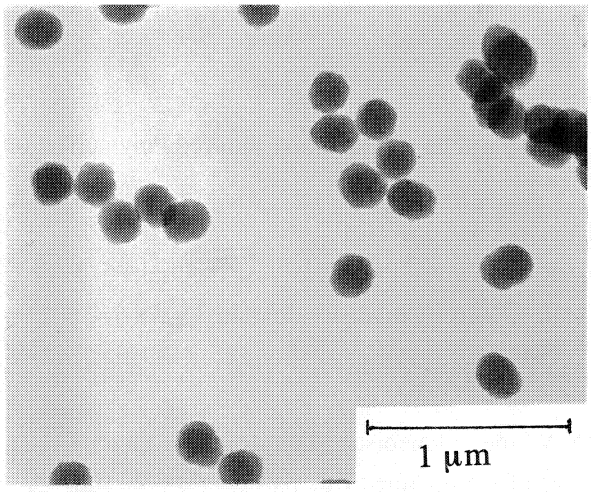

Fig.1. TEM photograph of poly(*N,N'*-methylenebisacrylamide) fine particles.

Figure 1 shows the TEM photograph of the poly(*N,N'*-methylenebisacrylamide) particles obtained from the THF solution. The shape of particles is almost sphere but the surface is rather rough compare to the 2G microspheres.[2] (We distinguish between the terms "microsphere" and "particle" according to its shape.) The narrow size distribution suggests that the mechanism is the same as the 2G microsphere case. The size of the poly(*N,N'*-methylenebisacrylamide) particles (0.22 μm) is smaller than that of 2G microspheres. The approximate number of poly(*N,N'*- methylenebisacrylamide) fine particles in the reaction vessel is 2×10^{12} mL^{-1}. This is larger than the value estimated for the 2G microspheres, of which number of particles increases with increasing monomer concentration and is at most 2×10^{11} mL^{-1}.[2] This result agrees with the tendency observed in the copolymerization of 2G and acrylamide, indicating that the acrylamide moiety contributes to the increase in the number of particles.[4] More suitable solvent must be found for the effective preparation of poly(*N,N'*-methylenebisacrylamide) fine particle.

We attempted the preparation with a freeze-melt degassing method, but it did not give particles. The difference between nitrogen bubbling and freeze-melt methods is considered to be due to the remaining oxygen concentration, although the clear explanation for the result has not yet been given.

The formation of 2G microspheres is caused by the crosslinking reaction under the special conditions. The formation of poly(*N,N'*-methylenebisacrylamide) fine particles is another example for the same type particle formation. Here, we named as "crosslinking promotion polymerization," for this type of particle formation.

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References

1) Y. Naka, I. Kaetsu, Y.Yamamoto, and K. Hayashi, *J. Polym. Sci., Part A, Polym. Chem.*, **29**, 1197 (1991).
2) Y. Naka and Y. Yamamoto, *J. Polym. Sci., Part A, Polym. Chem.*, **30**, 1287 (1992).
3) Y. Naka, Y. Yamamoto, and K. Hayashi, *Radiat. Phys. Chem.*, **40**, 83 (1992).
4) Y. Naka and Y. Yamamoto, *J. Polym. Sci., Part A, Polym. Chem.*, **30**, 2149 (1992).

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