Polyvinylalcohol Microgel

Takashi Fukutomi,* Kazuaki Asakawa, and Nobuhiro Kihara
Department of Polymer Chemistry, Faculty of Engineering, Tokyo Institute of Technology, Oookayama, Meguro-ku, Tokyo 152

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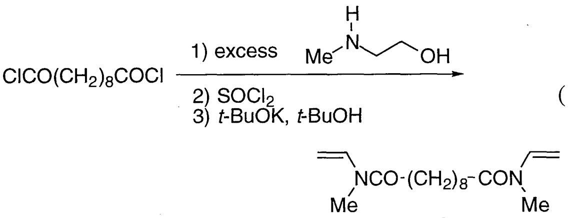
Soap-free copolymerization of vinyl acetate and N,N'-dimethyl-N,N'-divinyl-sebacoyldiamide followed by alkaline hydrolysis afforded poly(vinyl alcohol) microgel.

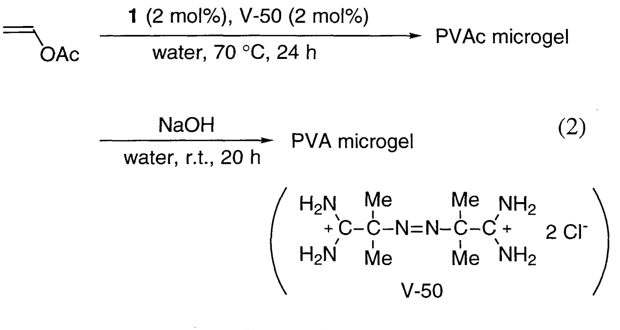
Recently, much attention have been focused on spherical polymeric microgels because of monodispersity, biomedical and microelectronics application, and low viscosity of their emulsions.[1] Microgels can be easily synthesized by emulsion copolymerization in the presence of suitable crosslinker. Although a microgel of polyvinylalcohol (PVA) is expected to be one of the most promising hydrophilic microgel, PVA microgel was scarcely known because common divinyl compounds hardly copolymerize with vinyl acetate. Although Brasch and Burchard reported PVA microgel by partial crosslinking of PVA by glutaraldehyde,[2] high dilution condition was necessary to prevent macrogelation. Thus, we designed a novel crosslinker **1** because N-vinyl amides are good comonomer of vinyl ester,[3] and an ester can be selectively hydrolyzed in the presence of an amide. In this paper, we wish to report simple and effective preparation of PVA microgel.



(1)

1
(2% in three steps)

N,N'-Divinyl-diamide **1** was synthesized as shown in eq (1).[4,5] The low yield of **1** was due to high hydrophilicity of hydroxyamide intermediate, and the yield was not optimized. The preparation of microgel of poly(vinyl acetate) (PVAc) was accomplished by the soap-free copolymerization of vinyl acetate with 2 mol% of **1** dispersed in water to afford white suspension.[6] Adition of another hydrophilic monomer was not necessary to obtain stable suspension.



(2)

The suspension was directly hydrolyzed by the addition of sodium hydroxide at room temperature for 6 h. The IR spectra of PVAc and PVA microgels purified by dialysis are shown in Figure 1. The peak of $\nu_{C=O}$ of ester group observed at 1735 cm^{-1} almost disappeared, while the peak of $\nu_{C=O}$ of amide group observed at 1645 cm^{-1} as a shoulder remained, indicating that ester group was selectively hydrolyzed to afford PVA microgel. The SEM photograph of the microgel is shown in Figure 2. Although the microgels were coagulated to each other during the isolation process, spherical microgels whose average diameter was about 230 nm were obtained.

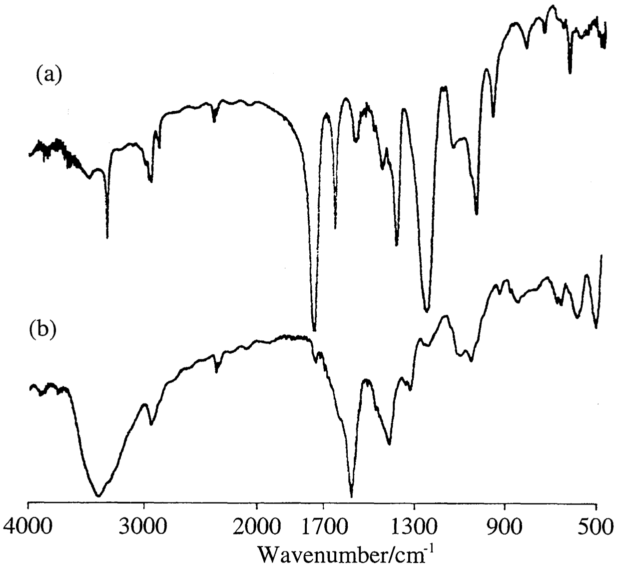


Figure 1. IR spectra of (a) PVAc and (b) PVA microgel.

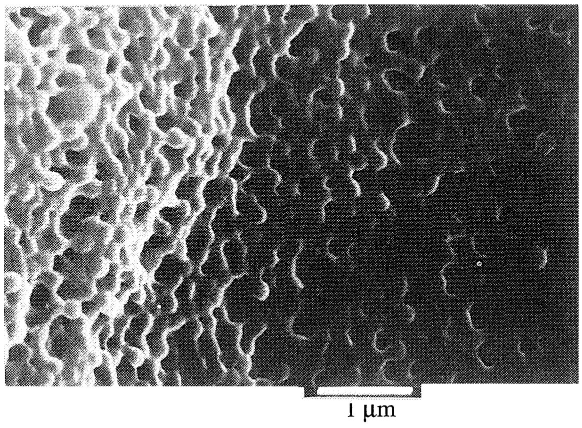


Figure 2. SEM photograph of PVA microgel.

Because of usefulness of **1** as a good crosslinker of PVA, various PVA gels are expected to be prepared using **1**. Further investigations using **1** and PVA microgel are in progress.

References and Notes

1 H. Kawaguchi, *Yuki Gosei Kagaku Kyokaishi,* **42**, 922 (1984).

2 U. Brasch and W. Burchard, *Macromol. Chem. Phys.*, **197**, 223 (1996).

3 In "Polymer Handbook," third edition, ed by J. Brandrup and E. H. Immergut, John Wily & Sons, New York (1989), II/234.

4 B. Pvetzer, L. Katz, and L. Horwitz, *J. Am. Chem. Soc.*, **74**, 4959 (1952).

5 mp: 69.0-70.0 °C (methanol-water). ^{1}H-NMR (60 MHz, CCl_4): δ 6.67 (dd, J = 9.2 and 14.8 Hz, 2H), 4.43-4.00 (m, 4H), 2.96 (s, 6H), 2.36 (t, J = 6.6 Hz, 4H), and 1.93-1.03 (m, 12H) ppm. Anal. Found: C, 68.06; H, 9.69; N, 9.72%. Calcd for $C_{16}H_{28}N_2O_2$: C, 68.53; H, 10.06; N, 9.99%.

6 Y. Ohtsuka, H. Kawaguchi, and Y. Sugi, *J. Appl. Polym. Sci.*, **26**, 1637, 1649 (1981).