

ANIONIC POLYMERIZATION OF HEXAFLUORO-1,3-BUTADIENE

T. Narita

Department of Environmental Engineering, Saitama Institute of Technology, Okabe-machi, Osato-gun, Saitama 369-02, Japan

As has previously been reported briefly, hexafluoro-1,3-butadiene (HFBD) which is hardly polymerized under radical polymerization conditions is easily polymerized with cesium fluoride as an initiator[1]. The present paper is concerned with the more detailed results of anionic polymerization of HFBD with several initiators possessing cesium or rubidium as counter-cation. Cesium fluoride, *tert*-C₄H₉OCs, Cs⁺(α -methylstyrene)_n²⁻Cs⁺, cesium naphthalene, rubidium fluoride, *tert*-C₄H₉ORb, Rb⁺(α -methylstyrene)_n²⁻Rb⁺, and rubidium naphthalene are found to show surprisingly high activity since the yields of poly(HFBD) were over 70% within 3 hours at 60°C. The ionic radius of the counter-cations might thus be important in the anionic polymerization of HFBD. The initiation reaction of HFBD with *tert*-C₄H₉OCs in THF at 0°C was examined by the measurement of the concentration of *tert*-C₄H₉OCs. The reaction was found to be completed within 5 minutes although the reactions were carried out at much lower temperature than that of the polymerization reaction. The initiation reaction was, therefore, inferred to take place in an anionic fashion by adding *tert*-butoxide anion to HFBD.

Poly(HFBD) obtained was white powdery substance which was insoluble in any solvents except hexafluorobenzene. The beginning of decomposition and the softening point of poly(HFBD) yielded with CsF in toluene were about 360°C and 339°C, respectively. The softening point measured after heating the same sample at 400°C for 10 hours was 417°C, which was 78°C higher than the case of no treatment. The thermal expansion coefficient of the polymer was about one third of that of poly(tetrafluoroethylene). These coefficients scarcely changed as a function of temperature.

[1] T. Narita, et al., Macromolecules, **22**, 2025(1989); T. Narita et al., Makromol. Chem., in press.