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[45] **Date of Patent:** Oct. 21, 1997[54] **HETEROGENEOUS POLYMERIZATION IN CARBON DIOXIDE**[75] **Inventors:** Joseph M. DeSimone; Elise E. Maury, both of Chapel Hill; James R. Combes, Carboro; Yusuf Z. Menceloglu, Chapel Hill, all of N.C.[73] **Assignee:** The University of North Carolina at Chapel Hill, Chapel Hill, N.C.[21] **Appl. No.:** 760,939[22] **Filed:** Dec. 6, 1996**Related U.S. Application Data**

[60] Continuation of Ser. No. 443,478, May 18, 1995, Pat. No. 5,589,105, which is a division of Ser. No. 378,550, Jan. 25, 1995, Pat. No. 5,506,317, which is a division of Ser. No. 299,516, Sep. 1, 1994, Pat. No. 5,451,633, which is a division of Ser. No. 198,224, Feb. 17, 1994, Pat. No. 5,382,623, which is a division of Ser. No. 99,905, Jul. 30, 1993, Pat. No. 5,312,882.

[51] **Int. Cl.⁶** C08F 2/00; B01F 17/00; B01F 1/00[52] **U.S. Cl.** 524/529; 252/351; 252/364; 526/201[58] **Field of Search** 526/201; 252/351, 252/364[56] **References Cited****U.S. PATENT DOCUMENTS**3,522,228 7/1970 Fukui et al. 260/94.9
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57-149367 9/1982 Japan .
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WO96/01851 1/1996 WIPO .**OTHER PUBLICATIONS**J.M. DeSimone et al.; *Dispersion Polymerizations in Supercritical Carbon Dioxide*; *Science* 265:356-359 (1994).K. A. Shaffer et al.; *Chain Polymerizations in Inert Near and Supercritical Fluids*; *TRIPS* 3 No. 5:146-153 (1995).J. M. DeSimone et al.; *Synthesis of Fluoropolymers in Supercritical Carbon Dioxide*; *Science* 257:945-947 (1992).Cosani et al., *Observations on the Solubility of Surfactants and Related Molecules in Carbon Dioxide at 50° C.*, *J. Supercrit. Fluid* 3:51 (1990).*Primary Examiner*—Joseph L. Schofer*Assistant Examiner*—N. Sarofim*Attorney, Agent, or Firm*—Bell, Seltzer, Park & Gibson[57] **ABSTRACT**The heterogeneous polymerization of water-insoluble polymer in CO₂ is disclosed. The method comprises providing a heterogeneous reaction mixture comprising CO₂, a monomer, and a surfactant, then polymerizing the monomer to form a water-insoluble polymer.**27 Claims, 2 Drawing Sheets**