



US006765030B2

(12) **United States Patent**
DeSimone et al.

(10) **Patent No.:** US 6,765,030 B2
(45) **Date of Patent:** Jul. 20, 2004

(54) **METHODS OF FORMING POLYMERIC STRUCTURES USING CARBON DIOXIDE AND POLYMERIC STRUCTURES FORMED THERAPY**

(75) Inventors: **Joseph M. DeSimone**, Chapel Hill, NC (US); **Sara Naomi Paisner**, Carrboro, NC (US)

(73) Assignee: **The University of North Carolina at Chapel Hill**, Chapel Hill, NC (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **10/109,588**

(22) Filed: **Mar. 28, 2002**

(65) **Prior Publication Data**

US 2003/0180522 A1 Sep. 25, 2003

Related U.S. Application Data

(60) Provisional application No. 60/367,141, filed on Mar. 22, 2002.

(51) **Int. Cl.**⁷ **C08J 9/02**; C08J 9/08

(52) **U.S. Cl.** **521/77**; 521/61; 521/64; 521/97

(58) **Field of Search** 521/61, 64, 97, 521/77

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,136,137	A	1/1979	Hsieh et al.
5,281,666	A	1/1994	Hoxmeier
5,451,633	A	9/1995	DeSimone et al.
5,589,105	A	12/1996	DeSimone et al.
5,639,836	A	6/1997	DeSimone et al.
5,674,957	A	10/1997	DeSimone et al.
5,676,705	A	10/1997	Jureller et al.
5,683,977	A	11/1997	Jureller et al.
5,783,082	A	7/1998	DeSimone et al.
6,319,858	B1	11/2001	Lee et al.
2002/0020946	A1	2/2002	Hirakoa et al.

FOREIGN PATENT DOCUMENTS

EP	1 085 041	3/2001	C08J/9/26
EP	1 211 280	6/2002	C08J/9/28

OTHER PUBLICATIONS

Chen, Vanessa Z.-H., et al., *Ordered Bicontinuous Nanoporous and Nanorelief Ceramic Films from Self Assembling Polymer Precursors*, *Science*, vol. 286, pp. 1716-1719 (Nov. 26, 1999).

Dang, T.D. et al., *Synthesis and Characterization of Fluorinated Benzoxazole Polymers with High T_g and Low Dielectric Constant*, *Journal of Polymer Science*, vol. 38, pp. 1991-2003 (2000).

Hedrick, J.L., et al., *High-temperature polyimide nanofoams for microelectronic applications*, *Reactive & Functional Polymers*, vol. 30, pp. 43-53 (1996).

Hyatt, John A., *Liquid and Supercritical Carbon Dioxide as Organic Solvents*, *Journal of Organic Chemistry*, vol. 49, No. 26, pp. 5097-5101 (1984).

Maier, Gerhard, *Polymers for microelectronics, materistoday*, pp. 22-33 (Sep./Oct. 2001).

Maier, G., *Low dielectric constant polymers for microelectronics*, *Progress in Polymer Science*, vol. 26, pp. 3-65 (2001).

Milner, Scott, T., et al., *Analytical Weak-Segregation Theory of Bicontinuous Phases in Diblock Copolymers*, *J. Phys. II France*, vol. 7, pp. 249-255 (1997).

Olmsted, Peter D., et al., *Fluctuation Corrections to Mean-Field Theory for Homopolymer-Copolymer Phase Separation: Sequence Distribution Effects*, *Macromolecules*, vol. 27, pp. 1964-1967 (1994).

Olmsted, P.D. et al., *Lifshitz points in blends of AB and BC diblock copolymers*, *Europhysics Letters*, vol. 45, No. 1, pp. 83-89 (1999).

Olmsted, Peter D., et al., *Strong-Segregation Theory of Bicontinuous Phases in Block Copolymers*, *Physical Review Letters*, vol. 72, No. 6, pp. 936-941 (Feb. 7, 1994).

Olmsted, Peter D., et al., *Errata, Strong-Segregation Theory of Bicontinuous Phases in Block Copolymers*, *Physical Review Letters*, vol. 74, No. 5, p. 829 (Jan. 30, 1995).

Olmsted, Peter D., et al., *Strong-Segregation Theory of Bicontinuous Phases in Block Copolymers*, *Macromolecules*, vol. 31, pp. 4011-4022 (1998).

Rajagopal, A., et al., *Surface characterization of a low dielectric constant polymer-SiLK* polymer, and investigation of its interface with Cu*, *J. Vac. Sci. Technol.*, vol. B 17, No. 5, pp. 2336-2340 (Sep/Oct 1999).

Rockford, L., et al., *Propagation of Nanopatterned Substrate Templated Ordering of Block Copolymers in Thick Films*, *Macromolecules*, vol. 34, pp. 1487-1492 (2001).

Sroog, C.E., *Polymides*, *Progress in Polymer Science*, vol. 16, pp. 561-694 (1991).

Zalusky, Andrew S., et al., *Mesoporous Polystyrene Monoliths*, *J. Am. Chem. Soc.*, vol. 123, pp. 1519-1520 (2001). *Low dielectric constant materials for advanced microelectronics*, www.almaden.ibm.com/st/projects/lowk, 3 pages.

Primary Examiner—Morton Foelak

(74) *Attorney, Agent, or Firm*—Myers Bigel Sibley & Sajovec, P.A.

(57) **ABSTRACT**

Methods of forming a polymeric structure having a plurality of cells therein that include contacting a polymeric material that includes a first phase and a second phase with a composition comprising carbon dioxide to form the polymeric structure having a plurality of cells therein are described. Polymeric materials and microelectronic devices formed by such methods are also described.

62 Claims, 4 Drawing Sheets