US006423372B1

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

(10) **Patent No.: US 6,423,372 B1**
(45) **Date of Patent: Jul. 23, 2002**

(54) **TAILORING THE GRAFTING DENSITY OF ORGANIC MODIFIERS AT SOLID/LIQUID INTERFACES**

(75) Inventors: **Jan Genzer**; **Kirill Efimenko**, both of Raleigh, NC (US)

(73) Assignee: **North Carolina State University**, Raleigh, 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.: **09/736,675**

(22) Filed: **Dec. 13, 2000**

(51) **Int. Cl.**[7] **C23C 16/04**; C23C 16/02

(52) **U.S. Cl.** **427/250**; 427/255.4; 427/255.6; 427/282; 427/299; 427/301; 427/307; 427/322; 427/553

(58) **Field of Search** 427/250, 255.4, 427/255.6, 282, 299, 301, 307, 322, 553

(56) **References Cited**

U.S. PATENT DOCUMENTS

5,512,131 A	4/1996	Kumar et al.	.....	156/655.1
5,661,092 A	8/1997	Koberstein et al.	.....	427/515
5,962,079 A	10/1999	Koberstein et al.	.....	427/508

OTHER PUBLICATIONS

Alexander; "Adsorption Of Chain Molecules With A Polar Head A Scaling Description," *Journal De Physique* 38:8 983–987 (Aug. 1977).

Andersson et al.; "Microtextured Surfaces: Towards Macrofouling Resistant Coatings," *Biofouling* 14(2):167–178 (1999).

Biesalski et al.; "Preparation And Characterization Of A Polyelectrolyte Monolayer Covalently Attached To A Planar Solid Surface," *Macromolecules* 32:7 2309–2316 (1999).

Bowden et al.; "Spontaneous Formation Of Ordered Structures In Thin Films Of Metals Supported On An Elastomeric Polymer," *Nature* 393:146–149 (May 1998).

Chaudhury et al.; Correlation Between Surface Free Energy And Surface Constitution, *Science* 255:1230–1232 (Mar. 1992).

Chaudhury; "Self–Assembled Monolayers On Polymer Surfaces," *Biosensor & Bioelectronics* 10:785–788 (1995).

Chaudbury; "Inferfacila Interaction Between Low–Energy Surfaces," *Materials Science and Engineering* R16:97–159 (1996).

Chaudbury; "Adhesion And Friction Of Self–Assembled Organic Monolayers," *Current Opinion in Colloid & Interface Science* 2:65–69 (1997).

Chidsey et al.; "Chemical Functionality In Self–Assembled Monolayers: Structural And Electrochemical Properties," *Langmuir* 6:3 682–691 (1990).

de Gennes; "Scaling Theory Of Polymer Adsorption," *Journal De Physics* 37:12 1445–1452 (Dec. 1976).

de Gennes; "Conformations Of Polymers Attached To An Interface," *Macromolecules* 13:5 1069–1075 (Sep.–Oct. 1980).

Ejaz et al.; "Controlled Graft Polymerization Of Methyl Methacrylate On Silicon Substrate By The Combined Use Of The Langmuir–Blodgett And Atom Transfer Radical Polymerization Techniques," *Macromolecules* 31:17 5934–5936 (1998).

Fischer et al.; "Functional Group Orientation In Surface And Bulk Polystyrene Studied By Ultra Soft X–Ray Absorption Spectroscopy," *Applied Surface Science* 133:58–64 (1998).

Fujiki et al.; "Radical Grafting From Glass Fiber Surface: Graft Polymerization Of Vinyl Monomers Initiated By Azo Groups Introduced Onto The Surface," *Journal of Polymer Science: Part A: Polymer Chemistry* 37:2121–2128 (1999).

Gaboury et al.; "Microwave Plasma Reactions Of Solid Monomers With Silicone Elastomer Surfaces: A Spectroscopic Study," *Langmuir* 9:11 3225–3233 (1993).

Genzer et al.; "Temperature Dependence Of Molecular Orientation On The Surfaces Of Semifluorinated Polymer Thin Films" *Langmuir* 16:4 1993–1997 (2000).

Genzer et al.; "The Orientation Of Semifluorinated Alkanes Attached To Polymers At The Surface Of Polymer Films" *Macromolecules* 33:5 1882–1887 (2000).

Genzer et al.; "Creating Long–Lived Superhydrophobic Polymer Surfaces Through Mechanically Assembled Monolayers," *Science* 290:2130–2133 (Dec. 2000).

Hillborg et al.; "Hydrophobicity Changes In Silicon Rubbers," *IEEE Transactions on Dielectrics and Electrical Insulation* 6:5 703–717 (Oct. 1999).

Huang et al.; "Surface–Confined Living Radical Polymerization for Coatings In Capillary Electrophoresis," *Anal. Chem.* 70:19 4023–4029 (Oct. 1998).

Huang et al.; "Make Ultrathin Films Using Surface–Confined Living Radical Polymerization," *Chemtech* 19–25 (Dec. 1998).

Huang et al.; "Surface Initiation Of Living Radical Polymerization For Growth Of Tethered Chains Of Low Polydispersity," *Macromolecules* 32:5 1694–1696 (1999).

Huck et al.; "Ordering Of Spontaneously Formed Buckles On Planar Surfaces," *Langmuir* 16:7 3497–3501 (2000).

(List continued on next page.)

Primary Examiner—Timothy Meeks
(74) *Attorney, Agent, or Firm*—Myers Bigel Sibley & Sajovec

(57) **ABSTRACT**

A method of depositing a functional group on a surface portion of an elastic substrate comprises the steps of:

(a) stretching an elastic substrate having an initial surface portion to form an enlarged surface portion from the initial surface portion; then

(b) conjugating a functional group on the enlarged surface portion; and then (c) releasing the substrate to form a reduced surface portion from the enlarged surface portion, with the reduced surface portion having an area less than the enlarged surface portion, and with the reduced surface portion having the functional group deposited therein at a greater density than the enlarged surface portion.

38 Claims, 8 Drawing Sheets