CLAIMS

1. A method of forming a three-dimensional object, comprising:

providing an adhesion stage and a member, the member having a dewetting phase thereon, the dewetting phase having a build surface, the adhesion stage and the build surface defining a build region therebetween;

providing a polymerizable liquid in the build region, wherein the polymerizable liquid is immiscible with the dewetting phase;

cooling at least one of the member, dewetting phase, or polymerizable liquid; and

undergoing polymerization of the polymerizable liquid by exposing the build region to energy through at least a portion of the dewetting phase to form a solid polymer from the polymerizable liquid and advancing the adhesion stage away from the build surface to form the three-dimensional object comprised of the solid polymer,

wherein

the dewetting phase is not a liquid.

2. A method of forming a three-dimensional object, comprising

providing an adhesion stage, a member, and a cooling apparatus, the member having a dewetting phase thereon, the member between the cooling apparatus and the dewetting phase, the dewetting phase having a build surface, the adhesion stage and the build surface defining a build region therebetween;

providing a polymerizable liquid in the build region, wherein the polymerizable liquid is immiscible with the dewetting phase; and

undergoing polymerization of the polymerizable liquid by exposing the build region to energy through at least a portion of the cooling apparatus and through at least a portion of the dewetting phase to form a solid polymer from the polymerizable liquid and advancing the adhesion stage away from the build surface to form the three-dimensional object comprised of the solid polymer.

3. The method of claim 2, wherein the cooling apparatus is optically transparent.

4. The method of any one of claims 1 to 3, wherein the member is optically transparent.

5. The method of any one of claims 1 to 4, wherein the member allows transduction or transmission of energy provided by an energy source selected from the group consisting of electrical, chemical, magnetic, electromagnetic, photonic, acoustic, heating, and combinations thereof.

6. The method of any one of claims 1 to 5, wherein the dewetting phase and the polymerizable liquid have a contact angle of greater than 60°.

7. The method of claim 6, wherein the dewetting phase and the polymerizable liquid have a contact angle of greater than 60° when the polymerizable liquid is substantially free of surfactant.

8. The method of any one of claims 1 to 7, wherein the polymerization liquid further comprises a surfactant.

9. The method of any one of claims 1 to 8, wherein the polymerizable liquid does not include a dead zone.

10. The method of any one of claims 1 to 9, wherein the polymerization liquid comprises an aqueous polymerization liquid.

11. The method of claim 10, wherein the polymerization liquid comprises a monomer or oligomer selected from the group consisting of acrylics, methacrylics, urethanes, acrylesters, polyesters, cyanoesters, acrylamides, maleic anhydride, functionalized PEGS, dimethacrylate oligomer, and a combination thereof.

12. The method of any one of claims 1 to 9, wherein the polymerization liquid comprises an organic polymerization liquid.

13. The method of claim 12, wherein the polymerization liquid comprises a monomer or oligomer selected from the group consisting of olefins, halogenated olefins, cyclic alkenes, alkenes, alkynes, and a combination thereof.

14. The method of any one of claims 1 to 13, wherein the dewetting phase comprises a gel.

15. The method of claim 14, wherein the gel is selected from the group consisting of an organo-gel, a silicone-gel, an aqueous hydro-gel, a fluoro-gel, and a combination thereof.

16. The method of claim 15, wherein the gel is an aqueous hydro-gel and the aqueous hydro-gel is selected from the group consisting of agar, agarose gels, polyacrylamide gels, starch gels, cationic gels, anionic gels, and combinations thereof.

17. The method of claim 16, wherein the gel is a fluoro-gel and the fluoro-gel comprises 2-(perfluorohexyl)ethyl acrylate swelled with perfluoropolyether.

18. The method of any one of claims 1 to 13, wherein the dewetting phase comprises a solid.

19. The method of claim 18, wherein the solid is selected from the group consisting of an organic solid, an aqueous solid, a per-fluorinated solid, and a combination thereof.

20. The method of claim 19, wherein the solid is an organic solid and the organic solid is selected from the group consisting squalane, squalene, solid hexadecane, and a combination thereof.

21. The method of claim 19, wherein the solid is an aqueous solid and the aqueous solid is selected from the group consisting of ice, solid tetraethylene glycol, solid PEG-300, solid PEG-400, solid PEG-600, and combinations thereof.

22. The method of claim 19, wherein the solid is a per-fluorinated solid and the per-fluorinated solid comprises a solid perfluoropolyether, a fluorinated ethylene propylene, or a polytetrafluoroethylene.

23. The method of any one of claims 1 to 13, wherein the dewetting phase comprises a gas.

24. The method of any one of claims 2 to 13, wherein the dewetting phase comprises a liquid.

25. The method of claim 24, wherein the liquid is an aqueous liquid, organic liquid, silicone liquid, or fluoro liquid.

26. The method of claim 25, wherein the aqueous liquid comprises water, deuterium oxide, a densified salt solution, or a densified sugar solution.

27. The method of claim 25, wherein the organic liquid comprises organic oils.

28. The method of claim 25, wherein the silicone liquid comprises silicone oils.

29. The method of claim 25, wherein the fluoro liquid comprises fluorinated oils.

30. The method of any one of claims 1 to 29, wherein the polymerization liquid comprises a particulate or colloidal matter capable of binding together.

31. The method of any one of claims 1 to 30, wherein the polymerization liquid comprises metal ions capable of depositing to form a bulk metallic.

32. The method of any one of claims 1 to 31, wherein the dewetting phase is optically transparent.

33. The method of any one of claims 1 to 32, wherein the dewetting phase is curvilinear.

34. The method of any one of claims 1 to 33, wherein the member is not oxygen permeable.

35. The method of any one of claims 1 to 34, wherein the polymerization is performed by electromagnetic irradiation.

36. The method of any one of claims 1 to 35, wherein the polymerization is performed by electricity.

37. The method of any one of claims 1 to 36, wherein the polymerization is performed by thermal activation.

38. The method of any one of claims 1 to 37, wherein the polymerization is performed by magnetic activation.

39. The method of any one of claims 1 to 38, wherein the method is performed in parallel using a multi-tip array, and the tip of the multi-tip array comprises the member.

40. The method of claim 39, wherein the multi-tip array is part of a beam-pen lithography system.

41. The method of claim 39, wherein the multi-tip array is part of a polymer pen lithography system.

42. The method of any one of claims 1 to 38, wherein the member and dewetting phase are attached to a fiber optic projector, and the fiber optic projector delivers the energy for polymerization.

43. The method of any one of claims 1 to 42, wherein the printing occurs omnidirectional.

44. The method of any one of claims 1 to 43, wherein advancing the adhesion stage away from build surface comprises advancing the adhesion stage away from the build surface at a constant rate.

45. The method of any one of claims 1 to 43, wherein advancing the adhesion stage away from the build surface comprising advancing the adhesion stage away from the build surface at a variable rate.

46. The method of any one of claims 1 to 43, wherein advancing the adhesion stage away from the build surface comprises advancing the adhesion stage away from the build surface at a constant rate for a fixed distance and is then paused for a fixed amount of time, and optionally repeated.

47. The method of any one of claims 1 to 43, wherein advancing the adhesion stage away from the build surface comprises advancing the adhesion stage away from the build surface at a variable rate for a fixed distance and is then paused for a fixed amount of time, and optionally repeated.

48. The method of any one of claims 1 to 43, wherein advancing the adhesion stage away from build surface comprises advancing the adhesion stage away from the build surface in an oscillating manner.

49. The method of claim 48, wherein advancing the adhesion stage away from the build surface in an oscillating manner comprises a cycle comprising (i) advancing the adhesion stage away from the build surface, and (ii) advancing the adhesion stage back toward the build surface.

50. The method of claim 49, further comprising pausing the adhesion stage between advancing the adhesion stage away from the build surface and advancing the adhesion stage back toward the build surface.

51. The method of claim 49 or claim 50, further comprising pausing the adhesion stage after advancing the adhesion stage back toward the build surface.

52. An apparatus for forming a three-dimensional object from a polymerizable liquid, comprising:

a support;

an adhesion stage operatively associated with the support on which adhesion stage the three-dimensional object is formed;

a member having a layer of a dewetting phase thereon, the dewetting phase having a build surface, wherein the dewetting phase is not a liquid, with the build surface and adhesion stage defining a build region therebetween;

a polymerizable liquid supply operatively associated with the build surface and configured to supply polymerizable liquid into the build region for solidification or polymerization, wherein the polymerizable liquid is immiscible with the dewetting phase;

an energy source configured to deliver energy to the build region through the member to form a solid polymer from the polymerizable liquid;

an optically transparent cooling apparatus; and

at least one controller operatively associated with the energy source for delivering energy to the build region, the at least one controller also operatively associated with the adhesion stage for advancing the adhesion stage away from the build surface at a rate that is dependent on energy intensity to form the three-dimensional object from the solid polymer.

53. An apparatus for forming a three-dimensional object from a polymerizable liquid, comprising:

a support;

an adhesion stage operatively associated with the support on which adhesion stage the three-dimensional object is formed;

a member having a layer of a dewetting phase thereon, the dewetting phase having a build surface, with the build surface and adhesion stage defining a build region therebetween;

an optically transparent cooling apparatus that spans the build region;

a polymerizable liquid supply operatively associated with the build surface and configured to supply polymerizable liquid into the build region for solidification or polymerization, wherein the polymerizable liquid is immiscible with the dewetting phase;

an energy source configured to deliver energy to the build region through the member to form a solid polymer from the polymerizable liquid; and

at least one controller operatively associated with the energy source for delivering energy to the build region, the at least one controller also operatively associated with the cooling apparatus for cooling the build region, the at least one controller also operatively associated with the adhesion stage for advancing the adhesion stage away from the build surface at a rate that is dependent on energy intensity to form the three-dimensional object from the solid polymer.

54. The apparatus of any one of claims 52 to 53, wherein the member is optically transparent.

55. The apparatus of any one of claims 52 to 53, wherein the member allows transduction or transmission of energy provided by an energy source selected from the group consisting of electrical, chemical, magnetic, electromagnetic, photonic, acoustic, heating, and combinations thereof.

56. The apparatus of any one of claims 52 to 55, wherein the apparatus does not include a dead zone.

57. The apparatus of any one of claims 52 to 56, wherein the optically transparent cooling apparatus is operatively associated with at least one of the member, dewetting phase, and polymerizable liquid.

58. The apparatus of any one of claims 52 to 57, wherein the optically transparent cooling apparatus is a heat exchanger.

59. The apparatus of any one of claims 52 to 58, wherein the at least one controller is operatively associated with the optically transparent cooling apparatus and configured to maintain the dewetting phase in a non-liquid state.

60. The apparatus of any one of claims 52 to 59, wherein the dewetting phase is curvilinear.

61. The apparatus of any one of claims 52 to 60, wherein the energy source is configured to provide energy to the build region through the member to form a solid polymer from the polymerizable liquid.

62. The apparatus of any one of claims 52 to 61, wherein the adhesion stage is operatively associated with an actuation arm configured to advance the adhesion stage away from the build stage.

63. The apparatus of any one of claims 52 to 62, wherein the energy source is a light engine.

64. The apparatus of claim 63, wherein the light engine has a light source selected from the group consisting of a mercury light source, LED source, halogen light, and laser.

65. The apparatus of any one of claims 52 to 62, wherein the energy source is a thermal controller.

66. The apparatus of any one of claims 52 to 62, wherein the energy source is selected from the group consisting of electrical, chemical, magnetic, electromagnetic, photonic, acoustic, heating, and combinations thereof.

67. The apparatus of any one of claims 52 to 66, wherein the member is not oxygen permeable.

68. The apparatus of any one of claims 52 to 67, wherein the build surface is a horizontal surface.

69. The apparatus of any one of claims 52 to 67, wherein the build surface is a vertical surface.

70. The apparatus of any one of claims 52 to 67, wherein the build surface is omnidirectional.

71. A method of forming a three-dimensional object, comprising:

providing an adhesion stage and a member, the member having a mobile phase thereon, the mobile phase having a build surface, the adhesion stage and the build surface defining a build region therebetween;

providing a polymerizable liquid in the build region, wherein the polymerizable liquid is immiscible with the mobile phase; and

undergoing polymerization of the polymerizable liquid by exposing the build region to energy through at least a portion of the mobile phase to form a solid polymer from the

polymerizable liquid and advancing the adhesion stage away from the build surface to form the three-dimensional object comprised of the solid polymer,

wherein during polymerization the mobile phase is in motion, thereby providing a shear force at the interface of the solid polymer and the mobile phase.

72. The method of claim 71, wherein the mobile phase comprises a moving solid phase, a moving gel phase, a flowing fluid, or a combination of the foregoing.

73. The method of claim 72, wherein the moving solid phase is selected from the group consisting of an organic solid, an aqueous solid, a per-fluorinated solid, and a combination thereof.

74. The method of claim 73, wherein the organic solid is selected from the group consisting of squalane, squalene, solid hexadecane, and a combination thereof.

75. The method of claim 73, wherein the aqueous solid is selected from the group consisting of ice, solid tetraethylene glycol, solid PEG-300, solid PEG-400, solid PEG-600, and a combination thereof.

76. The method of claim 73, wherein the per-fluorinated solid is selected from the group consisting of perfluoropolyether, fluorinated ethylene propylene, polytetrafluoroethylene, and a combination thereof.

77. The method of claim 72, wherein the moving gel phase is selected from the group consisting of an organo-gel, a silicone-gel, an aqueous hydro-gel, a fluoro-gel, and a combination thereof.

78. The method of claim 77, wherein the aqueous hydro-gel is selected from the group consisting of agar, agarose gels, polyacrylamide gels, starch gels, cationic gels, anionic gels, and a combination thereof.

79. The method of claim 77, wherein the fluoro-gel comprises 2-(perfluorohexyl)ethyl acrylate swelled with perfluoropolyether.

80. The method of claim 72, wherein the flowing fluid is selected from the group consisting of an aqueous liquid, an organic liquid, a silicone liquid, and a fluoro liquid.

81. The method of claim 80, wherein the flowing fluid comprises an aqueous liquid selected from the group consisting of water, deuterium oxide, a densified salt solution, and a densified sugar solution.

82. The method of claim 80, wherein the flowing fluid comprises a silicone liquid comprising a silicone oil.

83. The method of claim 80, wherein the flowing fluid comprises a fluoro liquid comprising a fluorinated oil.

84. The method of claim 80, wherein the flowing fluid comprises an organic liquid comprising an organic oil.

85. The method of any one of claims 71 to 84, wherein the mobile phase comprises a dewetting phase.

86. The method of any one of claims 71 to 85, wherein the mobile phase is recirculated through a closed loop.

87. The method of any one of claims 71 to 86, further comprising one or more of filtering, cleaning, and decontaminating the mobile phase.

88. The method of any one of claims 71 or 87, further comprising cooling the mobile phase.

89. The method of claim 88, wherein cooling the mobile phase comprises passing the mobile phase through a cooling apparatus.

90. The method of claim 88, wherein cooling the mobile phase is via a heat exchanger that spans the build region.

91. The method of any one of claims 71 to 90, further comprising oxygenating the mobile phase.

92. The method of any one of claims 71 to 91, wherein the member is optically transparent.

93. The method of any one of claims 71 to 92, wherein the member allows transduction or transmission of energy provided by an energy source selected from the group consisting of electrical, chemical, magnetic, electromagnetic, photonic, acoustic, heating, and combinations thereof.

94. The method of any one of claims 71 to 93, wherein the mobile phase and the polymerizable liquid have a contact angle of greater than 60°.

95. The method of any one of claims 71 to 94, wherein the polymerizable liquid does not include a dead zone.

96. The method of any one of claims 71 to 95, wherein the polymerization liquid is an aqueous polymerization liquid.

97. The method of claim 96, wherein the polymerization liquid comprises a monomer or oligomer selected from the group consisting of acrylics, methacrylics,

urethanes, acrylesters, polyesters, cyanoesters, acrylamides, maleic anhydride, functionalized PEGS, dimethacrylate oligomer, and a combination thereof.

98. The method of any one of claims 71 to 97, wherein the polymerization liquid is an organic polymerization liquid.

99. The method of claim 98, wherein the polymerization liquid comprises a monomer or oligomer selected from the group consisting of olefins, halogenated olefins, cyclic alkenes, alkenes, alkynes, and a combination thereof.

100. The method of any one of claims 71 to 99, wherein the polymerization liquid comprises a particulate or colloidal matter capable of binding together.

101. The method of any one of claims 71 to 199, wherein the polymerization liquid comprises metal ions capable of depositing to form a bulk metallic.

102. The method of any one of claims 71 to 101, wherein the mobile phase is optically transparent.

103. The method of any one of claims 71 to 102, wherein at least one of the polymerizable liquid and mobile phase further comprises a surfactant.

104. The method of any one of claims 71 to 103, wherein both the polymerizable liquid and the mobile phase further comprise a surfactant.

105. The method of any one of claims 71 to 104, wherein the member is not oxygen permeable.

106. The method of any one of claims 71 to 105, wherein the polymerization is performed by at least one of irradiation, electrical activation, thermal activation, and magnetic activation.

107. The method of any one of claims 71 to 106, wherein the method is performed in parallel using a multi-tip array, and the tip of the multi-tip array comprises the member.

108. The method of claim 107, wherein the multi-tip array is part of a beam-pen lithography system.

109. The method of claim 107, wherein the multi-tip array is part of a polymer pen lithography system.

110. The method of any one of claims 71 to 109, wherein the printing occurs omnidirectional.

111. The method of any one of claims 71 to 110, wherein advancing the adhesion stage away from build surface comprises advancing the adhesion stage away from the build surface at a constant rate.

112. The method of any one of claims 71 to 110, wherein advancing the adhesion stage away from the build surface comprising advancing the adhesion stage away from the build surface at a variable rate.

113. The method of any one of claims 71 to 110, wherein advancing the adhesion stage away from the build surface comprises advancing the adhesion stage away from the build surface at a constant rate for a fixed distance and is then paused for a fixed amount of time, and optionally repeated.

114. The method of any one of claims 71 to 110, wherein advancing the adhesion stage away from the build surface comprises advancing the adhesion stage away from the build surface at a variable rate for a fixed distance and is then paused for a fixed amount of time, and optionally repeated.

115. The method of any one of claims 71 to 110, wherein advancing the adhesion stage away from build surface comprises advancing the adhesion stage away from the build surface in an oscillating manner.

116. The method of claim 115, wherein advancing the adhesion stage away from the build surface in an oscillating manner comprises a cycle comprising (i) advancing the adhesion stage away from the build surface, and (ii) advancing the adhesion stage back toward the build surface.

117. The method of claim 116, further comprising pausing the adhesion stage between advancing the adhesion stage away from the build surface and advancing the adhesion stage back toward the build surface.

118. The method of claim 115 or claim 116, further comprising pausing the adhesion stage after advancing the adhesion stage back toward the build surface.

119. An apparatus for forming a three-dimensional object from a polymerizable liquid, comprising:

a support;

an adhesion stage operatively associated with the support on which adhesion stage the three-dimensional object is formed;

a member having a layer of a mobile phase thereon, the mobile phase having a build surface, with the build surface and adhesion stage defining a build region therebetween;

a polymerizable liquid supply operatively associated with the build surface and

configured to supply polymerizable liquid into the build region for solidification or polymerization, wherein the polymerizable liquid is immiscible with the mobile phase;

an energy source configured to deliver energy to the build region through the member to form a solid polymer from the polymerizable liquid;

at least one controller operatively associated with the energy source for delivering energy to the build region, the at least one controller also operatively associated with the adhesion stage for advancing the adhesion stage away from the build surface at a rate that is dependent on energy intensity to form the three-dimensional object from the solid polymer, wherein during polymerization the mobile phase is in motion, thereby providing a shear force at the interface of the solid polymer and the mobile phase.

120. The apparatus of claim 119, further comprising a cooling apparatus operatively associated with at least one of the member, mobile phase, and polymerizable liquid.

121. The apparatus of claim 120, wherein the cooling apparatus is optically transparent.

122. The apparatus of any one of claims 120 to 121, wherein the cooling apparatus is a heat exchanger that spans the build region.

123. The apparatus of any one of claims 120 to 122, wherein the cooling apparatus is operatively associated with at least one controller configured to control the temperature of at least one of the member, mobile phase, and polymerizable liquid.

124. The apparatus of any one of claims 119 to 123, wherein the adhesion stage is operatively associated with an actuation arm configured to advance the adhesion stage.

125. The apparatus of any one of claims 119 to 124, wherein the mobile phase comprises a moving solid phase, a moving gel phase, a flowing fluid, or a combination of the foregoing.

126. The apparatus of claim 125, wherein the moving solid phase is selected from the group consisting of an organic solid, an aqueous solid, a per-fluorinated solid, and a combination thereof.

127. The apparatus of claim 126, wherein the organic solid is selected from the group consisting of squalane, squalene, solid hexadecane, and a combination thereof.

128. The apparatus of claim 126, wherein the aqueous solid is selected from the group consisting of ice, solid tetraethylene glycol, solid PEG-300, solid PEG-400, solid PEG-600, and a combination thereof.

129. The apparatus of claim 126, wherein the per-fluorinated solid is selected from the group consisting of perfluoropolyether, a fluorinated ethylene propylene, a polytetrafluoroethylene, and a combination thereof.

130. The apparatus of claim 125 wherein the moving gel phase is selected from the group consisting of an organo-gel, a silicone-gel, an aqueous hydro-gel, a fluoro-gel, and a combination thereof.

131. The apparatus of claim 130, wherein the aqueous hydro-gel is selected from the group consisting of agar, agarose gels, polyacrylamide gels, starch gels, cationic gels, anionic gels, and a combination thereof.

132. The apparatus of claim 130, wherein the fluoro-gel comprises 2-(perfluorohexyl)ethyl acrylate swelled with perfluoropolyether.

133. The apparatus of claim 125, wherein the flowing fluid is selected from the group consisting of an aqueous liquid, an organic liquid, a silicone liquid, and a fluoro liquid.

134. The apparatus of claim 133, wherein the aqueous liquid is selected from the group consisting of water, deuterium oxide, a densified salt solution, and a densified sugar solution.

135. The apparatus of claim 133, wherein the silicone liquid comprises a silicone oil.

136. The apparatus of claim 133, wherein the fluoro liquid comprises a fluorinated oil.

137. The apparatus of claim 133, wherein the organic liquid comprises an organic oil.

138. The apparatus of any one of claims 119 to 137, wherein the mobile phase comprises a dewetting phase.

139. The apparatus of any one of claims 119 to 138, further comprising an outlet in fluid communication with the mobile phase and an inlet in fluid communication with the mobile phase.

140. The apparatus of claim 139, wherein the outlet is in fluid communication with the inlet to provide a recirculation loop and allow a flow of mobile phase across the membrane.

141. The apparatus of any one of claims 139 to 140, further comprising an outlet distribution nozzle in fluid communication with the mobile phase and comprising the outlet,

and an inlet distribution nozzle in fluid communication with the mobile phase and comprising the inlet.

142. The apparatus of claim 140 or claim 141, further comprising a filtration unit provided along the recirculation loop between the outlet and the inlet, the filtration unit operatively associated with at least one controller configured to filter, clean, or decontaminate the mobile phase.

143. The apparatus of any one of claims 140 to 142, further comprising a cooling apparatus along the recirculation loop between the outlet and the inlet, the cooling apparatus operatively associated with at least one controller configured to control the temperature of the mobile phase.

144. The apparatus of any one of claims 140 to 143 further comprising an oxygenation unit along the recirculation loop between the outlet and the inlet, the oxygenation unit operatively associated with at least one controller configured to control the amount of oxygen provided to the mobile phase.

145. The apparatus of any one of claims 119 to 144, wherein the member is optically transparent.

146. The apparatus of any one of claims 119 to 145, wherein the member allows transduction or transmission of energy provided by an energy source selected from the group consisting of electrical, chemical, magnetic, electromagnetic, photonic, acoustic, heating, and combinations thereof.

147. The apparatus of any one of claims 119 to 146, wherein the polymerizable liquid does not include a dead zone.

148. The apparatus of any one of claims 120 to 147, wherein the recirculation loop is operatively associated with at least one controller configured to maintain a continuous flow of the mobile phase.

149. The apparatus of any one of claims 119 to 148, wherein the energy source is configured to provide energy to the build region through the member to form a solid polymer from the polymerizable liquid.

150. The apparatus of any one of claims 119 to 149, wherein the energy source is a light engine.

151. The apparatus of claim 150, wherein the light engine has a light source selected from the group consisting of a mercury light source, LED source, halogen light, and laser.

152. The apparatus of any one of claims 119 to 151, wherein the energy source is a thermal controller.

153. The apparatus of any one of claims 119 to 151, wherein the energy source is selected from the group consisting of electrical, chemical, magnetic, electromagnetic, photonic, acoustic, heating, and combinations thereof.

154. The apparatus of any one of claims 121 to 155, wherein the member is not oxygen permeable.

155. The method of any one of claims 71 to 118, wherein the mobile phase moves in a plane wherein the solid polymer is substantially normal to the plane.

156. The apparatus of any one of claims 119 to 154, wherein the mobile phase moves in a plane wherein the solid polymer is substantially normal to the plane.