CLAIMS

What is claimed is:

1. An article of manufacture comprising a polymeric substrate having a surface and a grafted polymer layer on the substrate surface, the grafted polymer layer having a global average dry thickness of at least about 50 nanometers, the substrate surface and the grafted polymer layer, in combination, constituting a modified surface having a fibrinogen adsorption of less than about 125 ng/cm^2 in a fibrinogen binding assay in which the modified surface is incubated for 60 minutes at 37 °C in a composition containing 70 µg/ml fibrinogen derived from human plasma and 1.4 µg/ml I-125 radiolabeled fibrinogen, provided the article (i) is other than a non-luminal polyurethane rod and (ii) has a length greater than 5 centimeters when the article is a double lumen catheter.

2. The article of claim 1 wherein modified surface has a fibrinogen adsorption of less than about 90 ng/cm^2 in a fibrinogen binding assay in which the modified surface is incubated for 60 minutes at 37 °C in a composition containing 70 µg/ml fibrinogen derived from human plasma and 1.4 µg/ml I-125 radiolabeled fibrinogen.

3. The article of claim 1 wherein modified surface has a fibrinogen adsorption of less than about 50 ng/cm^2 in a fibrinogen binding assay in which the modified surface is incubated for 60 minutes at 37 °C in 70 µg/ml fibrinogen derived from human plasma containing 1.4 µg/ml I-125 radiolabeled fibrinogen.

4. The article of each of claims 1-3 wherein modified surface has a static contact angle of less than 25 degrees.

5. The article of claims 1-4 wherein the grafted polymer layer has a global average dry thickness wherein the standard deviation of the global average dry thickness of the grafted polymer layer does not exceed 100% of the global average dry thickness of the grafted polymer layer.

6. The article of each of claim 1-5 wherein the grafted polymer layer has a global average dry thickness of at least 100 nanometers.

7. A process for grafting a polymer from an article comprising a substrate having a surface, a bulk beneath the surface, and a near-surface zone lying

between the surface and the bulk, the process comprising incorporating a polymerization initiator into the near-surface zone and graft polymerizing a polymer from the substrate surface to form a grafted polymer layer comprising the grafted polymer, the grafted polymer layer having a global average dry thickness that is at least equal to the global average R_{rms} surface roughness of the substrate surface, provided the article (i) is other than a non-luminal polyurethane rod and (ii) has a length greater than 5 centimeters when the article is a double lumen catheter.

8 The process of claim 7 wherein at least the portion of the substrate into which the polymerization initiator is incorporated is not significantly swelled by the polymerization mixture.

9. The process of each of claims 7-8 wherein the polymerization monomers and the initiator(s) incorporated into the substrate have limited solubility in the solvent system.

10. The process of each of claims 7-9 wherein the substrate polymer does not swell more than 30 % by volume at 25 °C under equilibrium conditions in the polymerization mixture solvent system.

11. The process of each of claims 7-10 wherein the substrate polymer does not swell more than 15% by volume at 25 °C under equilibrium conditions in the polymerization mixture solvent system.

12. The process of each of claims 7-11 wherein the substrate polymer does not not swell more than 5% by volume at 25 °C under equilibrium conditions in the polymerization mixture solvent system.

13. The process of each of claims 7-12 wherein the substrate polymer does not swell under equilibrium conditions in the polymerization mixture solvent system.

14. The process of each of claims 7-13 wherein the substrate is a composite of materials, the substrate comprises a coating of a precoat material overlying a metal, ceramic, glass or semi-metallic material, and the coating of the precoat material not swell more than 30% by volume at 25 °C under equilibrium conditions in the polymerization mixture solvent system.

15. The process of each of claims 7-14 wherein at least the portion of the substrate into which the polymerization initiator is incorporated is not significantly swelled by the polymerization mixture.

16. The process of each of claims 7-15 wherein the initiator(s) incorporated into the substrate have a 10 hour T1/2 decomposition temperature of 25-175 °C.

17. The process of each of claims 7-15 wherein the incorporated initiator(s) have a 10 hour T1/2 decomposition temperature of 70-130 °C.

18. The process of each of claims 7-15 wherein the initiator comprises a redox pair.

19. The process of claim 18 wherein at least one member of such pair has a limited solubility in the polymerization mixture solvent system.

20. The process of claim 18 wherein both members of the redox pair have limited solubility in the polymerization mixture solvent system.

21. The process of claim 18 wherein one member of the pair is soluble in the polymerization mixture solvent system but the other has limited solubility in the polymerization mixture solvent system.

22. The process of each of claims 7-21 wherein one member of a redox pair is soluble in the polymerization mixture solvent system, the other has limited solubility in the polymerization mixture solvent system, the two are phase separated, and initiation is enhanced at the interface of the two phases.

23. The process of each of claims 7-22 wherein either member of the redox pair may be hydrophobic and either member of the pair may be hydrophilic, provided at least one of the members has limited solubility in the polymerization mixture solvent system.

24. The process of each of claims 7-23 wherein a hydrophobic oxidizer is paired with a hydrophilic reducing agent.

25. The process of each of claims 7-24 wherein a hydrophilic oxidizer is paired with a hydrophobic reducing agent.

26. The process of each of claims 7-25 wherein the redox pair comprises a peroxide and a reducing agent wherein the peroxide has limited solubility in the polymerization solvent system and the reducing agent has high solubility in the polymerization solvent system.

27. The process of claim 26 wherein the peroxide has a log P partition coefficient greater than or equal to 3 for hydrophobic substrates and phases and a log P partition coefficient less than 3 for hydrophilic substrates and phases.

28. The process of each of claim 26 wherein the peroxide has a log P partition coefficient greater than or equal to 5 for hydrophobic substrates and phases and a log P partition coefficient less than 1 for hydrophilic substrates and phases.

29. The process of each of claims 26-28 wherein the peroxide has a log P partition coefficient greater than or equal to 7 for hydrophobic substrates and phases and a log P partition coefficient less than -1 for hydrophilic substrates and phases.

30. The process of each of claims 26-28 wherein the peroxide has a log P partition coefficient greater than or equal to 9 for hydrophobic substrates and phases and a log P partition coefficient less than -3 for hydrophilic substrates and phases.

31. The invention of each of claims 1-30 wherein the grafted polymer is a carboxyammonium polymer or a sulfoammonium polymer.

32. The invention of each of claims 1-30 wherein the grafted polymer is a carboxyammonium polymer.

33. The invention of each of claims 1-30 wherein the grafted polymer is a sulfoammonium polymer.

34. The invention of each of claims 1-30 wherein the grafted polymer is a zwitterionic polymer.

35. The invention of each of claims 1-30 wherein the grafted polymer is a carboxybetaine polymer.

36. The invention of each of claims 1-30 wherein the polymer is a sulfobetaine polymer.

37. The invention of each of the preceding claims wherein the substrate comprises a metal, ceramic, glass, polymer, biological tissue, woven fiber, non-woven fiber, semi-metal, or a combination thereof.

38. The invention of each of the preceding claims wherein substrate comprises a polyamide, polyamine, polyanhydride, polyazine, poly(carbonate), polyester, polyether, polyetheretherketone (PEEK), polyguanidine, polyimide, polyketal, poly(ketone), polyolefin, poly(orthoester), polyphosphazine, polysaccharide, polysiloxane, polysulfone, polyurea, polyurethane, halogenated polymer, silicone, aldehyde crosslinked resin, epoxy resin, phenolic resin, latex, or a copolymer or blend thereof.

39. The invention of each of the preceding claims wherein the substrate comprises polyurethane.

40. The invention of each of the preceding claims wherein the substrate is a composite comprising a precoat overlying a second material, the precoat comprising a polyamide, polyamine, polyanhydride, polyazine, poly(carbonate), polyester, polyether, polyetheretherketone (PEEK), polyguanidine, polyimide, polyketal, poly(ketone), polyolefin, poly(orthoester), polyphosphazine, polysaccharide, polysiloxane, polysulfone, polyurea, polyurethane, halogenated polymer, silicone, aldehyde crosslinked resin, epoxy resin, phenolic resin, latex, or a copolymer or blend thereof, and the second material comprises a metal, ceramic, glass, polymer, biological tissue, woven fiber, non-woven fiber, or semi-metal.

41. The invention of each of the preceding claims wherein the substrate comprises a polyurethane precoat layer overlying a polyurethane bulk.

42. The invention of claim 41 wherein the polyurethane precoat layer comprises an initiator.

43. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the substrate surface and the grafted polymer layer, in combination, constitute a modified surface having a static contact angle of less than 24 degrees.

44. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the substrate surface and the grafted polymer layer, in combination, constitute a modified surface having a static contact angle of less than 20 degrees.

45. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the substrate surface and the grafted polymer layer, in combination, constitute a modified surface having a static contact angle of less than 15 degrees.

46. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, the substrate surface and the grafted polymer layer, in combination, constitute a modified surface, and the grafted polymer layer has a global average dry thickness and a standard deviation of the global average dry thickness wherein the standard deviation of the global average dry thickness does not exceed 50% of the global average dry thickness of the grafted polymer layer.

47. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the substrate surface and the grafted polymer layer, in combination, constitute a modified surface having a global average dry thickness and a standard deviation of the global average dry thickness wherein the standard deviation of the global average dry thickness does not exceed 20% of the global average dry thickness of the grafted polymer layer.

48. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the substrate surface and the grafted polymer layer, in combination, constitute a modified surface having a global average dry thickness and a standard deviation of the global average dry thickness wherein the standard deviation of the global average dry thickness does not exceed 10% of the global average dry thickness of the grafted polymer layer.

49. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, the grafted polymer layer has a global average dry thickness of at least about 50 nm and the magnitude of the difference between the global average dry thickness of the

layer as determined by scanning electron microscopy (SEM) and the global average humidified thickness of the grafted polymer layer as determined by environmental scanning electron microscopy (ESEM) is less than 200% of the global average dry thickness.

50. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, the grafted polymer layer has a global average dry thickness of at least about 50 nm, and the magnitude of the difference between the global average dry thickness of the grafted polymer layer as determined by scanning electron microscopy (SEM) and the global average humidified thickness of the grafted polymer layer as determined by environmental scanning electron microscopy (ESEM) is less than 100% of the global average dry thickness.

51. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, the grafted polymer layer has a global average dry thickness of at least about 50 nm, and the magnitude of the difference between the global average dry thickness of the grafted polymer layer as determined by scanning electron microscopy (SEM) and the global average humidified thickness of the grafted polymer layer as determined by environmental scanning electron microscopy (ESEM) is less than 50% of the global average dry thickness.

52. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, the grafted polymer layer has having a global average dry thickness of at least about 50 nm, and the magnitude of the difference between the global average dry thickness of the grafted polymer layer as determined by scanning electron microscopy (SEM) and average humidified the thickness of the grafted polymer layer as determined by environmental scanning electron microscopy (ESEM) is less than 20% of the global average dry thickness.

53. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, the grafted polymer layer has a global average dry thickness of at least about 50 nm, and the magnitude of the difference between the global average dry thickness of the grafted polymer layer as determined by scanning electron microscopy (SEM)

and the global average humidified thickness of the grafted polymer layer as determined by environmental scanning electron microscopy (ESEM) is less than 10% of the global average dry thickness.

54. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, the grafted polymer layer has a global average dry thickness of at least about 50 nm, and the magnitude of the difference between the global average dry thickness of the grafted polymer layer as determined by scanning electron microscopy (SEM) and the global average humidified thickness of the grafted polymer layer as determined by environmental scanning electron microscopy (ESEM) is less than 5% of the global average dry thickness.

55. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, the grafted polymer layer has a global average dry thickness of at least about 50 nm, and the magnitude of the difference between the global average dry thickness of the grafted polymer layer as determined by scanning electron microscopy (SEM) and the global average humidified thickness of the grafted polymer layer as determined by environmental scanning electron microscopy (ESEM) is less than 1% of the global average dry thickness.

56. The invention of each of the preceding claims wherein the article further comprises a solvent extractable polymerization initiator or a degradation product thereof.

57. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the grafted polymer layer has a global average dry thickness that is at least equal to the global average R_{rms} surface roughness of the substrate surface.

58. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the grafted polymer layer has a global average dry thickness that is at least 110% of the global average R_{rms} surface roughness of the substrate surface.

59. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the grafted

polymer layer has a global average dry thickness that is at least 200% of the global average R_{rms} surface roughness of the substrate surface.

60. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the grafted polymer layer has a global average dry thickness that is at least 500% of the global average R_{rms} surface roughness of the substrate surface.

61. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the grafted polymer layer has a global average dry thickness less than 1 micrometer.

62. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the grafted polymer layer has a global average dry thickness less than 500 nm.

63. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the grafted polymer layer has a global average dry thickness in the range of about 100 nm to about 1,000 nm.

64. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the grafted polymer layer has a global average dry thickness of about 300 nm to about 600 nm.

65. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the grafted polymer layer has a global average dry thickness of about 200 nm to about 400 nm.

66. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the substrate surface and the grafted polymer layer, in combination, constitute a modified surface having a global average R_{rms} surface roughness that is less than the global average R_{rms} surface roughness of the substrate surface.

67. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the substrate surface and the grafted polymer layer, in combination, constitute a modified

surface having a global average R_{rms} surface roughness that is less than 50% of the global average R_{rms} surface roughness of the substrate surface.

68. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the substrate surface and the grafted polymer layer, in combination, constitute a modified surface having a global average R_{rms} surface roughness that is less than 25% of the global average R_{rms} surface roughness of the substrate surface.

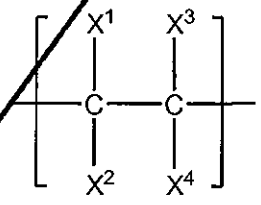
69. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the substrate surface and the grafted polymer layer, in combination, constitute a modified surface having a global average R_{rms} surface roughness that is less than 10% of the global average R_{rms} surface roughness of the substrate surface.

70. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the substrate surface and the grafted polymer layer, in combination, constitute a modified surface having a global average R_{rms} surface roughness that is less than 5% of the global average R_{rms} surface roughness of the substrate surface.

71. The invention of each of the preceding claims wherein the grafted polymer, non-fouling polymer, zwitterionic polymer, carboxybetaine polymer or sulfobetaine polymer is a chain growth addition polymer.

72. The invention of each of the preceding claims wherein the grafted polymer, non-fouling polymer, zwitterionic polymer, carboxybetaine polymer or sulfobetaine polymer is a polyolefin.

73. The invention of each of the preceding claims wherein the grafted polymer, non-fouling polymer, zwitterionic polymer, carboxybetaine polymer or sulfobetaine polymer comprises repeat units corresponding to Formula 1



Formula 1

wherein

X^1 and X^2 are independently hydrogen, hydrocarbyl, substituted hydrocarbyl, heterocyclo, or substituted carbonyl, provided, however, X^1 and X^2 are not each selected from the group consisting of aryl, heteroaryl, and heterosubstituted carbonyl,

X^3 is hydrogen, alkyl or substituted alkyl,

X^4 is $-OX^{40}$, $-NX^{41}X^{42}$, $-N^+X^{41}X^{42}X^{43}$, $-SX^{40}$, aryl, heteroaryl or acyl,

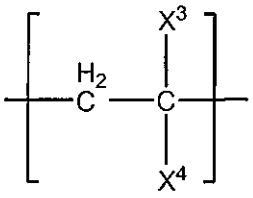
X^{40} is hydrogen, hydrocarbyl, substituted hydrocarbyl, heterocyclo or acyl, and

X^{41}, X^{42} and X^{43} are independently hydrogen, hydrocarbyl, substituted hydrocarbyl or heterocyclo.

74. The invention of claim 73 wherein X^1 and X^2 are hydrogen.

75. The invention of claim 73 or 74 wherein X^3 is hydrogen or alkyl.

76. The invention of each of the preceding claims wherein the grafted polymer, non-fouling polymer, zwitterionic polymer, carboxybetaine polymer or sulfobetaine polymer comprises at least one repeat unit corresponding to Formula 2:



Formula 2

wherein

X^3 is hydrogen, alkyl or substituted alkyl, and

X^4 is a pendant group comprising an oxylated alkylene moiety, a zwitterionic moiety, an anionic moiety, or a cationic moiety.

77. The invention of claim 76 wherein X^3 is hydrogen or alkyl.

78. The invention of claim 77 wherein X^4 is a pendant group comprising an oxylated alkylene moiety corresponding to Formula POA-1.

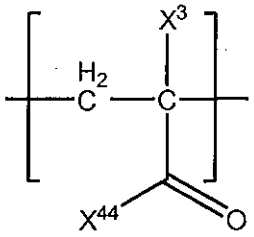
79. The invention of claim 76 wherein the repeat unit of Formula 2 is a zwitterionic repeat unit comprising a zwitterionic moiety corresponding to Formula ZI-1, ZI-2, ZI-3, ZI-4, ZI-5, ZI-6A, ZI-6B, or ZI-7.

80. The invention of claim 76 wherein the repeat unit of Formula 2 is a cationic repeat unit.

81. The invention of claim 76 wherein the repeat unit of Formula 2 is an anionic repeat unit.

82. The invention of claim 76 wherein X^3 is hydrogen or methyl and X^4 is a pendant group comprising an oxylated alkylene moiety corresponding to Formula POA-1 or a zwitterionic moiety corresponding to Formula ZI-1, ZI-2, ZI-3, ZI-4, ZI-5, ZI-6A, ZI-6B, or ZI-7.

83. The invention of each of the preceding claims wherein the grafted polymer, non-fouling polymer, zwitterionic polymer, carboxybetaine polymer or sulfobetaine polymer comprises repeat units corresponding to Formula 3:



Formula 3

wherein X^{44} comprises an oxylated alkylene moiety, a zwitterionic moiety, an anionic moiety, or a cationic moiety.

84. The invention of claim 83 wherein X^{44} is $-OX^{45}$, $-NHX^{45}$, or $-SX^{45}$, and X^{45} is a substituted hydrocarbyl or heterocyclo moiety comprising an oxylated alkylene moiety, a zwitterionic moiety, an anionic moiety, or a cationic moiety.

85. The invention of claim 83 wherein X^3 is hydrogen or alkyl.

86. The invention of claim 83 wherein X^{44} is $-OX^{45}$, or $-NX^{45}X^{46}$, X^{45} comprises an oxylated alkylene moiety corresponding to Formula POA-1 or a zwitterionic moiety corresponding to Formula ZI-1, ZI-2, ZI-3, ZI-4, ZI-5, ZI-6A,

ZI-6B, or ZI-7 and X^{46} is hydrogen, hydrocarbyl, substituted hydrocarbyl or heterocyclo.

87. The invention of claim 83 wherein the repeat units corresponding to Formula 3 comprise cationic repeat units and/or an anionic repeat units.

88. The invention of claim 83 wherein X^3 is hydrogen or methyl and X^{44} comprises an oxylated alkylene moiety corresponding to Formula POA-1 or a zwitterionic moiety corresponding to Formula ZI-1, ZI-2, ZI-3, ZI-4, ZI-5, ZI-6A, ZI-6B, or ZI-7.

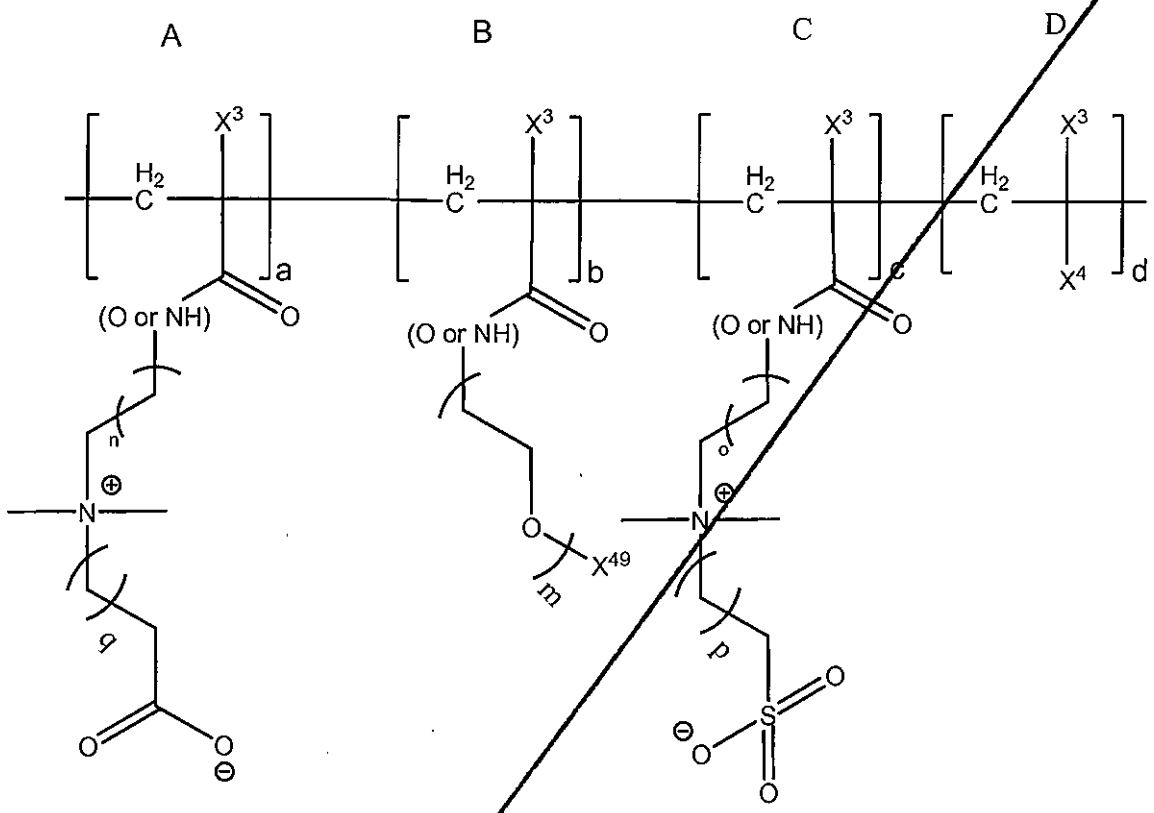
89. The invention of claim 83 wherein the polymer contains repeat units corresponding to Formula 3 and X^{44} is $-O(CH_2)_2N^+(CH_3)_2(CH_2)_nSO_3^-$, $-O(CH_2)_2N^+(CH_3)_2(CH_2)_nCO_2^-$, $-NH(CH_2)_3N^+(CH_3)_2(CH_2)_nCO_2^-$, or $-NH(CH_2)_3N^+(CH_3)_2(CH_2)_nSO_3^-$, wherein n is 1-8.

90. The invention of claim 83 wherein the polymer contains repeat units corresponding to Formula 3 and X^{44} is $-NH(CH_2)_mN(CH_2)_nCH_3(CH_2)_pSO_3$, $,-NH(CH_2)_mN(CH_2)_nCH_3(CH_2)_pCO_2$, $-NH(CH_2)_mN^+[(CH_2)_nCH_3]_2(CH_2)_pSO_3$, $-NH(CH_2)N^+[(CH_2)_nCH_3]_2(CH_2)_pCO_2$, $-NH(CH_2)_mNcyclo-(CH_2)_pCO_2$, or $-NH(CH_2)_mNcyclo-(CH_2)_pSO_3$, (Ncyclo- is a heterocyclic structure or a heterocyclic derivative containing at least one nitrogen element), wherein m is 1-8; n is 0-5; and p is 1-8.

91. The invention of claim 83 wherein the polymer contains repeat units corresponding to Formula 3 and X^{44} is $-O(CH_2)_mN(CH_2)_nCH_3(CH_2)_pSO_3$, $-O(CH_2)_mN(CH_2)_nCH_3(CH_2)_pCO_2$, $-O(CH_2)_mN^+[(CH_2)_nCH_3]_2(CH_2)_pSO_3$, $-O(CH_2)N^+[(CH_2)_nCH_3]_2(CH_2)_pCO_2$-$O(CH_2)_mNcyclo-(CH_2)_pCO_2$, or $-O(CH_2)_mNcyclo-(CH_2)_pSO_3$, wherein m is 1-8; n is 0-5; and p is 1-8.

92. The invention of claim 83 wherein the polymer contains repeat units corresponding to Formula 3 and X^{44} is $-O(CH_2)_2N^+(CH_3)_2(CH_2)_3SO_3$, $-O(CH_2)_2N^+(CH_3)_2(CH_2)_2CO_2$, $-NH(CH_2)_2N^+(CH_3)_2(CH_2)_3SO_3$, $-NH(CH_2)_2N^+(CH_3)_2(CH_2)_2CO_2$, $-NH(CH_2)_3N^+(CH_3)_2(CH_2)_3SO_3$, $-NH(CH_2)_3N^+(CH_3)_2(CH_2)_2CO_2$, $-O(CH_2)_2N^+(CH_2CH_3)_2(CH_2)_3SO_3$, $-O(CH_2)_2N^+(CH_2CH_3)_2(CH_2)_2CO_2$, $-O(CH_2)_2N^+(CH_2CH_2CH_2CH_3)_2(CH_2)_3SO_3$, $-O(CH_2)_2N^+(CH_2CH_2CH_2CH_3)_2(CH_2)_2CO_2$ or $-NH(CH_2)_3Ncyclo-(CH_2)_3SO_3$.

93. The invention of each of the preceding claims wherein the grafted polymer, non-fouling polymer, zwitterionic polymer, carboxybetaine polymer or sulfobetaine polymer comprises repeat units corresponding to Formula 4:



Formula 4

wherein

a is 0-1;

b is 0-1;

c is 0-1;

d is 0-1;

m is 1-20

n and o are independently 0-11;

p and q are independently 0-11;

X^3 is hydrogen, alkyl or substituted alkyl,

X^4 is $-OX^{40}$,$-NX^{41}X^{42}$, $-SX^{40}$, aryl, heteroaryl or acyl;

X^{40} is hydrogen, hydrocarbyl, substituted hydrocarbyl, heterocyclo or acyl;

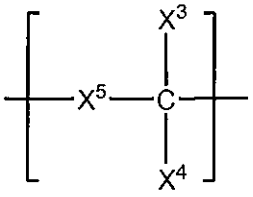
X^{41} and X^{42} are independently hydrogen, hydrocarbyl, substituted hydrocarbyl or heterocyclo; and

X^{49} is hydrogen, hydrocarbyl or substituted hydrocarbyl,

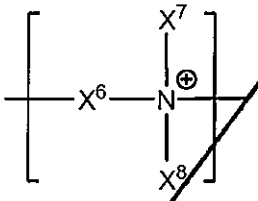
provided the sum of a, b, c and d is greater than 0 and X^4 of repeat unit D differs from the corresponding pendant group of repeat units A, B and C.

94. The invention of claim 93 wherein X^3 is hydroxyalkyl.

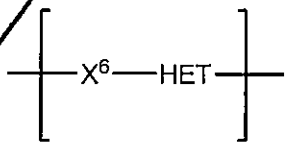
95. The invention of each of the preceding claims wherein the grafted polymer, non-fouling polymer, zwitterionic polymer, carboxybetaine polymer or sulfobetaine polymer comprises repeat units corresponding to Formula 5, Formula 6, Formula 7, Formula 8, or Formula 9:



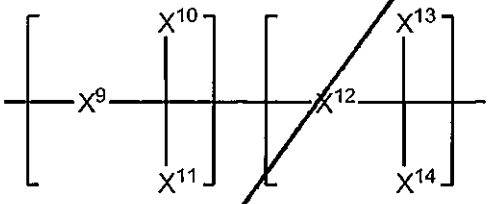
Formula 5



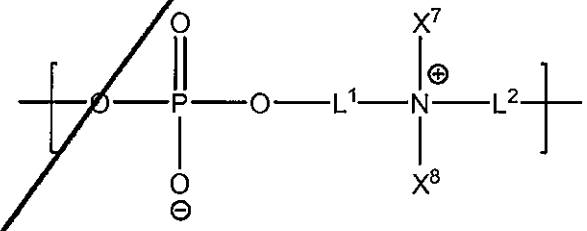
Formula 6



Formula 7



Formula 8



Formula 9

wherein

HET is part of a heterocyclic structure,

X^3 is hydrogen, alkyl or substituted alkyl,

X^4 is $-OX^{40}$,$-NX^{41}X^{42}$, $-SX^{40}$, aryl, heteroaryl or acyl,

X^5 is ester, anhydride, imide, amide, ether, thioether, thioester, hydrocarbylene, substituted hydrocarbylene, heterocyclo, urethane, or urea;

X^6 is hydrocarbylene, substituted hydrocarbylene, heterocyclo, amide, anhydride, ester, imide, thioester, thioether, urethane, or urea;

X^7 is hydrogen, alkyl or substituted alkyl;

X^8 is an anionic moiety;

X^9 is hydrocarbylene, substituted hydrocarbylene, heterocyclo, amide, anhydride, ester, imide, thioester, thioether, urethane, or urea;

X^{10} is hydrogen, alkyl or substituted alkyl;

X^{11} is a cationic moiety;

X^{12} is hydrocarbylene, substituted hydrocarbylene, heterocyclo, amide, anhydride, ester, imide, thioester, thioether, urethane, or urea;

X^{13} is hydrogen, alkyl or substituted alkyl;

X^{14} is an anionic moiety;

L^1 and L^2 are independently hydrocarbylene, substituted hydrocarbylene, heterocyclo, amide, anhydride, ester, imide, thioester, thioether, urethane, or urea; and

X^{40} is hydrogen, hydrocarbyl, substituted hydrocarbyl, heterocyclo or acyl, and

X^{41} and X^{42} are independently hydrogen, hydrocarbyl, substituted hydrocarbyl or heterocyclo.

96. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the substrate surface and the grafted polymer layer, in combination, constitute a modified surface having a fibrinogen adsorption of less than about 30 ng/cm^2 in a fibrinogen binding assay in which the modified surface is incubated for 60

minutes at 37 °C in 70 µg/ml fibrinogen derived from human plasma containing 1.4 µg/ml I-125 radiolabeled fibrinogen.

97. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the substrate surface and the grafted polymer layer, in combination, constitute a modified surface having a fibrinogen adsorption of less than about 20 ng/cm^2 in a fibrinogen binding assay in which the modified surface is incubated for 60 minutes at 37 °C in 70 µg/ml fibrinogen derived from human plasma containing 1.4 µg/ml I-125 radiolabeled fibrinogen.

98. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the substrate surface and the grafted polymer layer, in combination, constitute a modified surface having a fibrinogen adsorption of less than about 15 ng/cm^2 in a fibrinogen binding assay in which the modified surface is incubated for 60 minutes at 37 °C in 70 µg/ml fibrinogen derived from human plasma containing 1.4 µg/ml I-125 radiolabeled fibrinogen.

99. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the substrate surface and the grafted polymer layer, in combination, constitute a modified surface having a fibrinogen adsorption of less than about 12 ng/cm^2 in a fibrinogen binding assay in which the modified surface is incubated for 60 minutes at 37 °C in 70 µg/ml fibrinogen derived from human plasma containing 1.4 µg/ml I-125 radiolabeled fibrinogen.

100. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the substrate surface and the grafted polymer layer, in combination, constitute a modified surface having a fibrinogen adsorption of less than about 10 ng/cm^2 in a fibrinogen binding assay in which the modified surface is incubated for 60 minutes at 37 °C in 70 µg/ml fibrinogen derived from human plasma containing 1.4 µg/ml I-125 radiolabeled fibrinogen.

101. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the substrate

surface and the grafted polymer layer, in combination, constitute a modified surface having a fibrinogen adsorption of less than about 8 ng/cm^2 in a fibrinogen binding assay in which the modified surface is incubated for 60 minutes at 37 °C in 70 µg/ml fibrinogen derived from human plasma containing 1.4 µg/ml I-125 radiolabeled fibrinogen.

102. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the substrate surface and the grafted polymer layer, in combination, constitute a modified surface having a fibrinogen adsorption of less than about 6 ng/cm^2 in a fibrinogen binding assay in which the modified surface is incubated for 60 minutes at 37 °C in 70 µg/ml fibrinogen derived from human plasma containing 1.4 µg/ml I-125 radiolabeled fibrinogen.

103. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the substrate surface and the grafted polymer layer, in combination, constitute a modified surface having a fibrinogen adsorption of less than about 4 ng/cm^2 in a fibrinogen binding assay in which the modified surface is incubated for 60 minutes at 37 °C in 70 µg/ml fibrinogen derived from human plasma containing 1.4 µg/ml I-125 radiolabeled fibrinogen.

104. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the substrate surface and the grafted polymer layer, in combination, constitute a modified surface having a fibrinogen adsorption of less than about 2 ng/cm^2 in a fibrinogen binding assay in which the modified surface is incubated for 60 minutes at 37 °C in 70 µg/ml fibrinogen derived from human plasma containing 1.4 µg/ml I-125 radiolabeled fibrinogen.

105. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the substrate surface and the grafted polymer layer, in combination, constitute a modified surface having a fibrinogen adsorption of less than about 1 ng/cm^2 in a fibrinogen binding assay in which the modified surface is incubated for 60 minutes at 37 °C in 70 µg/ml fibrinogen derived from human plasma containing 1.4 µg/ml I-125 radiolabeled fibrinogen.

106. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the substrate surface and the grafted polymer layer, in combination, constitute a modified surface having a fibrinogen adsorption of less than about 0.5 ng/cm^2 in a fibrinogen binding assay in which the modified surface is incubated for 60 minutes at 37 °C in 70 µg/ml fibrinogen derived from human plasma containing 1.4 µg/ml I-125 radiolabeled fibrinogen.

107. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the substrate surface and the grafted polymer layer, in combination, constitute a modified surface having a fibrinogen adsorption of less than about 0.25 ng/cm^2 in a fibrinogen binding assay in which the modified surface is incubated for 60 minutes at 37 °C in 70 µg/ml fibrinogen derived from human plasma containing 1.4 µg/ml I-125 radiolabeled fibrinogen.

108 The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the substrate surface and the grafted polymer layer, in combination, constitute a modified surface exhibiting a reduction in thrombus formation relative to a reference substrate that is substantially identical but lacks the grafted polymer layer in an assay in which the article and the reference substrate are exposed to freshly harvested bovine blood, heparinized, with radiolabeled platelets, and circulated in a flow loop at a rate from of about 200mL/min to 2.5L/min. for 60 to 120 min.

109. The invention of claim 108 wherein the thrombus formation for the article with the grafted polymer layer is no more than 20% of the thrombus formation for the reference article.

110. The invention of claim 108 wherein the thrombus formation for the article with the grafted polymer layer is no more than 10% of the thrombus formation for the reference article.

111. The invention of claim 108 wherein the thrombus formation for the article is no more than 2% of the thrombus formation for the reference article.

112. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the substrate surface and the grafted polymer layer, in combination, constitute a modified

surface exhibiting a reduction in thrombus formation relative to a reference article that is substantially identical but lacks the grafted polymer layer in an assay in which the article and the reference substrate are exposed to sterile citrated human plasma for at least 55 days with the plasma replaced weekly and then exposed to freshly harvested bovine blood, heparinized, with radiolabeled platelets, and circulated in a flow loop at a rate from of about 200mL/min to 2.5L/min. for 60 to 120 min.

113. The invention of claim 112 wherein the thrombus formation for the article is no more than 20% of the thrombus formation for the reference substrate.

114. The invention of claim 112 wherein the thrombus formation for the article is no more than 10% of the thrombus formation for the reference substrate.

115. The invention of claim 112 wherein the thrombus formation for the article is no more than 2% of the thrombus formation for the reference substrate.

116. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the substrate surface and the grafted polymer layer, in combination, constitute a modified surface having a contact angle and the contact angle is stable for at least 30 days in at least one of phosphate buffered saline containing protein, media, or serum, or *in vivo*. .

117. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the substrate surface and the grafted polymer layer, in combination, constitute a modified surface having non-fouling activity and the non-fouling activity is stable for at least 30 days in at least one of phosphate buffered saline containing protein, media, or serum, or *in vivo*.

118. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the substrate surface and the grafted polymer layer, in combination, constitute a modified surface having anti-thrombogenic activity and the anti-thrombogenic activity is stable for at least 30 days in at least one of phosphate buffered saline containing protein, media, or serum, or *in vivo*.

119. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the substrate surface and the grafted polymer layer, in combination, constitute a modified surface having antimicrobial activity and the actimicrobial activity is stable for at least 30 days in at least one of phosphate buffered saline containing protein, media, or serum, or *in vivo*.

120. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the substrate surface and the grafted polymer layer, in combination, constitute a modified surface exhibiting antibiofilm activity of at least 1 log.

121. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the substrate surface and the grafted polymer layer, in combination, constitute a modified surface exhibiting antibiofilm activity of at least 1 log after the article has been exposed to PBS for at least 30 days at 37 °C.

122. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the substrate surface and the grafted polymer layer, in combination, constitute a modified surface exhibiting antibiofilm activity of at least 1 log after the article has been exposed to PBS for at least 90 days at 37 °C.

123. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the substrate surface and the grafted polymer layer, in combination, constitute a modified surface exhibiting antibiofilm activity of at least 1 log after the article has been exposed to sterile citrated human plasma for at least 30 days at 37 °C.

124. The invention of each of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the substrate surface and the grafted polymer layer, in combination, constitute a modified surface exhibiting antibiofilm activity of at least 1 log after the article has been exposed to sterile citrated human plasma for at least 90 days at 37 °C.

125. The invention of each of the preceding claims wherein the article, and aqueous and organic extracts of the article have no detectable level of bypiridine as determined by HPLC or UV analysis.

126. The invention of each of the preceding claims wherein the grafted polymer layer contains >30% zwitterionic monomers.

127. The invention of each of the preceding claims wherein the grafted polymer layer contains >50% zwitterionic monomers.

128. The invention of each of the preceding claims wherein the grafted polymer layer contains >75% zwitterionic monomers.

129. The invention of each of the preceding claims wherein the grafted polymer layer contains >90% zwitterionic monomers.

130. The invention of each of the preceding claims wherein the grafted polymer layer is a homopolymer of zwitterionic monomers.

131. The invention of each of the preceding claims wherein the grafted polymer layer contains less than 50 mole% of the residue of a polyvalent crosslinker.

132. The invention of each of the preceding claims wherein the grafted polymer layer contains less than 25 mole% of the residue of a polyvalent crosslinker.

133. The invention of each of the preceding claims wherein the grafted polymer layer contains less than 10 mole% of a polyvalent crosslinker.

134. The invention of each of the preceding claims wherein the grafted polymer layer contains less than 5 mole% of the residue of a polyvalent crosslinker.

135. The invention of each of the preceding claims wherein the grafted polymer layer contains less than 3 mole% of a polyvalent crosslinker.

136. The invention of each of the preceding claims wherein the grafted polymer layer contains less than 0.1 mole% of the residue of a polyvalent crosslinker.

137. The invention of each of the preceding claims wherein the grafted polymer layer contains no residue of a polyvalent crosslinker.

AMENDED CLAIMS
received by the International Bureau on 10 May 2012 (10.05.12)

Please amend the claims as follows:

1. An article of manufacture comprising a polymeric substrate having a surface and a grafted polymer layer on the substrate surface, the grafted polymer layer having a global average dry thickness of at least about 50 nanometers, the substrate surface and the grafted polymer layer, in combination, constituting a modified surface having a fibrinogen adsorption of less than about 125 ng/cm^2 in a fibrinogen binding assay in which the modified surface is incubated for 60 minutes at 37 °C in a composition containing 70 μg/ml fibrinogen derived from human plasma and 1.4 μg/ml I-125 radiolabeled fibrinogen, provided the article (i) is other than a non-luminal polyurethane rod and (ii) has a length greater than 5 centimeters when the article is a double lumen catheter.

2 - 3. Canceled.

4. The article of claim 1 wherein modified surface has a static contact angle of less than 25 degrees.

5. The article of claim 1 or 4 wherein the grafted polymer layer has a global average dry thickness wherein the standard deviation of the global average dry thickness of the grafted polymer layer does not exceed 100% of the global average dry thickness of the grafted polymer layer.

6. The article of any one of the preceding claims wherein the grafted polymer layer has a global average dry thickness of at least 100 nanometers.

7. A process for grafting a polymer from an article comprising a substrate having a surface, a bulk beneath the surface, and a near-surface zone lying between the surface and the bulk, the process comprising incorporating a polymerization initiator into the near-surface zone and graft polymerizing a polymer from the substrate surface to form a grafted polymer layer comprising the grafted polymer, the grafted polymer layer having a global average dry thickness that is at least equal to the global average R_{rms} surface roughness of the substrate surface, provided the article (i) is other than a non-luminal polyurethane rod and (ii) has a length greater than 5 centimeters when the article is a double lumen catheter.

8 The process of claim 7 wherein at least the portion of the substrate into which the polymerization initiator is incorporated is not significantly swelled by the polymerization mixture.

9. canceled.

AMENDED SHEET (ARTICLE 19)

10. The process of claim 7 or 8 wherein the substrate polymer does not swell more than 30 % by volume at 25 °C under equilibrium conditions in the polymerization mixture solvent system.

11 -13. Canceled.

14. The process of claim 7, 8 or 10 wherein the substrate is a composite of materials, the substrate comprises a coating of a precoat material overlying a metal, ceramic, glass or semi-metallic material, and the coating of the precoat material not swell more than 30% by volume at 25 °C under equilibrium conditions in the polymerization mixture solvent system.

15 – 17. Canceled.

18. The process of claim 7, 8, 10 or 14 wherein the initiator comprises a redox pair.

19. The process of claim 18 wherein at least one member of such pair has a limited solubility in the polymerization mixture solvent system.

20. The process of claim 18 wherein both members of the redox pair have limited solubility in the polymerization mixture solvent system.

21. The process of claim 18 wherein one member of the pair is soluble in the polymerization mixture solvent system but the other has limited solubility in the polymerization mixture solvent system.

22 – 25. Canceled

26. The process of claim 7, 8, 10, 14, 18 or 19 wherein the redox pair comprises a peroxide and a reducing agent wherein the peroxide has limited solubility in the polymerization solvent system and the reducing agent has high solubility in the polymerization solvent system.

27. The process of claim 26 wherein the peroxide has a log P partition coefficient greater than or equal to 3 for hydrophobic substrates and phases and a log P partition coefficient less than 3 for hydrophilic substrates and phases.

28 – 30. Canceled.

31. The article or process of any one of the preceding claims wherein the grafted polymer is a carboxyammonium polymer or a sulfoammonium polymer.

32 – 33. Canceled.

AMENDED SHEET (ARTICLE 19)

34. The article or process of any one of the preceding claims wherein the grafted polymer is a zwitterionic polymer.

35. The article or process of any one of the preceding claims wherein the grafted polymer is a carboxybetaine polymer or a sulfobetaine polymer.

36 – 37. Canceled..

38. The article or process of any one of the preceding claims wherein substrate comprises a polyamide, polyamine, polyanhydride, polyazine, poly(carbonate), polyester, polyether, polyetheretherketone (PEEK), polyguanidine, polyimide, polyketal, poly(ketone), polyolefin, poly(orthoester), polyphosphazine, polysaccharide, polysiloxane, polysulfone, polyurea, polyurethane, halogenated polymer, silicone, aldehyde crosslinked resin, epoxy resin, phenolic resin, latex, or a copolymer or blend thereof.

39. Canceled.

40. The article or process of any one of the preceding claims wherein the substrate is a composite comprising a precoat overlying a second material, the precoat comprising a polyamide, polyamine, polyanhydride, polyazine, poly(carbonate), polyester, polyether, polyetheretherketone (PEEK), polyguanidine, polyimide, polyketal, poly(ketone), polyolefin, poly(orthoester), polyphosphazine, polysaccharide, polysiloxane, polysulfone, polyurea, polyurethane, halogenated polymer, silicone, aldehyde crosslinked resin, epoxy resin, phenolic resin, latex, or a copolymer or blend thereof, and the second material comprises a metal, ceramic, glass, polymer, biological tissue, woven fiber, non-woven fiber, or semi-metal.

41 – 45. Canceled

46. The article or process of any one of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, the substrate surface and the grafted polymer layer, in combination, constitute a modified surface, and the grafted polymer layer has a global average dry thickness and a standard deviation of the global average dry thickness wherein the standard deviation of the global average dry thickness does not exceed 50% of the global average dry thickness of the grafted polymer layer.

47 – 55. Canceled

56. The article or process of any one of the preceding claims wherein the article further comprises a solvent extractable polymerization initiator or a degradation product thereof.

AMENDED SHEET (ARTICLE 19)

57. The article or process of any one of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the grafted polymer layer has a global average dry thickness that is at least equal to the global average R_{rms} surface roughness of the substrate surface.

58 – 62. Canceled.

63. The article or process of any one of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the grafted polymer layer has a global average dry thickness in the range of about 100 nm to about 1,000 nm.

64 – 65. Canceled.

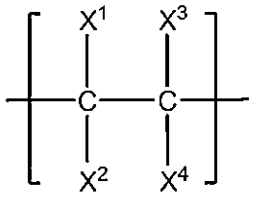
66. The article or process of any one of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the substrate surface and the grafted polymer layer, in combination, constitute a modified surface having a global average R_{rms} surface roughness that is less than the global average R_{rms} surface roughness of the substrate surface.

67 – 70. Canceled.

71. The article or process of any one of the preceding claims wherein the grafted polymer, non-fouling polymer, zwitterionic polymer, carboxybetaine polymer or sulfobetaine polymer is a chain growth addition polymer.

72. Canceled.

73. The article or process of any one of the preceding claims wherein the grafted polymer, non-fouling polymer, zwitterionic polymer, carboxybetaine polymer or sulfobetaine polymer comprises repeat units corresponding to Formula 1



Formula 1

wherein

AMENDED SHEET (ARTICLE 19)

X^1 and X^2 are independently hydrogen, hydrocarbyl, substituted hydrocarbyl, heterocyclo, or substituted carbonyl, provided, however, X^1 and X^2 are not each selected from the group consisting of aryl, heteroaryl, and heterosubstituted carbonyl,

X^3 is hydrogen, alkyl or substituted alkyl,

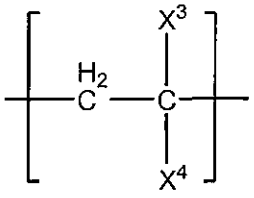
X^4 is $-OX^{40}$, $-NX^{41}X^{42}$, $-N^+X^{41}X^{42}X^{43}$, $-SX^{40}$, aryl, heteroaryl or acyl,

X^{40} is hydrogen, hydrocarbyl, substituted hydrocarbyl, heterocyclo or acyl, and

X^{41}, X^{42} and X^{43} are independently hydrogen, hydrocaryl, substituted hydrocarbyl or heterocyclo.

74 – 75. Canceled.

76. The article or process of any one of the preceding claims wherein the grafted polymer, non-fouling polymer, zwitterionic polymer, carboxybetaine polymer or sulfobetaine polymer comprises at least one repeat unit corresponding to Formula 2:



Formula 2

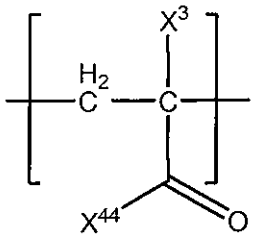
wherein

X^3 is hydrogen, alkyl or substituted alkyl, and

X^4 is a pendant group comprising an oxylated alkylene moiety, a zwitterionic moiety, an anionic moiety, or a cationic moiety.

77 – 82. Canceled.

83. The article or process of any one of the preceding claims wherein the grafted polymer, non-fouling polymer, zwitterionic polymer, carboxybetaine polymer or sulfobetaine polymer comprises repeat units corresponding to Formula 3:



Formula 3

wherein X^3 is hydrogen, alkyl or substituted alkyl, and X^{44} comprises an oxylated alkylene moiety, a zwitterionic moiety, an anionic moiety, or a cationic moiety.

84. The article or process of claim 83 wherein X^{44} is $-OX^{45}$, $-NHX^{45}$, or $-SX^{45}$, and X^{45} is a substituted hydrocarbyl or heterocyclo moiety comprising an oxylated alkylene moiety, a zwitterionic moiety, an anionic moiety, or a cationic moiety.

85 – 107. Canceled.

108. The article or process of any one of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the substrate surface and the grafted polymer layer, in combination, constitute a modified surface exhibiting a reduction in thrombus formation relative to a reference substrate that is substantially identical but lacks the grafted polymer layer in an assay in which the article and the reference substrate are exposed to freshly harvested bovine blood, heparinized, with radiolabeled platelets, and circulated in a flow loop at a rate from of about 200mL/min to 2.5L/min. for 60 to 120 min.

109- 111. Canceled.

112. The article or process of any one of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the substrate surface and the grafted polymer layer, in combination, constitute a modified surface exhibiting a reduction in thrombus formation relative to a reference article that is substantially identical but lacks the grafted polymer layer in an assay in which the article and the reference substrate are exposed to sterile citrated human plasma for at least 55 days with the plasma replaced weekly and then exposed to freshly harvested bovine blood, heparinized, with radiolabeled platelets, and circulated in a flow loop at a rate from of about 200mL/min to 2.5L/min. for 60 to 120 min.

113 – 124. Canceled.

125. The article or process of any one of the preceding claims wherein the article, and aqueous and organic extracts of the article have no detectable level of bypiridine as determined by HPLC or UV analysis.

126. The article or process of any one of the preceding claims wherein the grafted polymer layer contains >30% zwitterionic monomers.

127 – 130. Canceled.

131. The article or process of any one of the preceding claims wherein the grafted polymer layer contains less than 50 mole% of the residue of a polyvalent crosslinker.

132 – 137. Canceled.

CLAIMS

What is claimed is:

1. An article of manufacture comprising a polymeric substrate having a surface and a grafted polymer layer on the substrate surface, the grafted polymer layer having a global average dry thickness of at least about 500 nanometers, the substrate surface and the grafted polymer layer, in combination, constituting a modified surface having a fibrinogen adsorption of less than about 125 ng/cm^2 in a fibrinogen binding assay in which the modified surface is incubated for 60 minutes at 37 °C in a composition containing 70 µg/ml fibrinogen derived from human plasma and 1.4 μg/ml I-125 radiolabeled fibrinogen and a water contact angle of less than 40 degrees, provided the article (i) is other than a non-luminal polyurethane rod and (ii) has a length greater than 5 centimeters when the article is a double lumen catheter.

2. The article of claim 1 wherein modified surface has a static contact angle of less than 25 degrees.

3. The article of claim 1 or 2 wherein the grafted polymer layer has a global average dry thickness wherein the standard deviation of the global average dry thickness of the grafted polymer layer does not exceed 100% of the global average dry thickness of the grafted polymer layer.

4. The article of any one of the preceding claims wherein the grafted polymer layer has a global average dry thickness of at least 100 nanometers.

5. A process for grafting a polymer from an article comprising a substrate having a surface, a bulk beneath the surface, and a near-surface zone lying between the surface and the bulk, the process comprising incorporating a polymerization initiator into the near-surface zone and graft polymerizing a polymer from the substrate surface to form a grafted polymer layer comprising the grafted polymer, the grafted polymer layer having a global average dry thickness that is at least equal to the global average R_{rms} surface roughness of the substrate surface, provided the article (i) is other than a non-

luminal polyurethane rod and (ii) has a length greater than 5 centimeters when the article is a double lumen catheter.

6. The process of claim 5 wherein at least the portion of the substrate into which the polymerization initiator is incorporated is not significantly swelled by the polymerization mixture.

7. The process of claim 5 or 6 wherein the substrate polymer does not swell more than 30 % by volume at 25 °C under equilibrium conditions in the polymerization mixture solvent system.

8. The process of claim 5, 6 or 7 wherein the substrate is a composite of materials, the substrate comprises a coating of a precoat material overlying a metal, ceramic, glass or semi-metallic material, and the coating of the precoat material not swell more than 30% by volume at 25 °C under equilibrium conditions in the polymerization mixture solvent system.

9. The process of claim 5, 6, 7 or 8 wherein the initiator comprises a redox pair.

10. The process of claim 9 wherein at least one member of such pair has a limited solubility in the polymerization mixture solvent system.

11. The process of claim 9 wherein both members of the redox pair have limited solubility in the polymerization mixture solvent system.

12. The process of claim 9 wherein one member of the pair is soluble in the polymerization mixture solvent system but the other has limited solubility in the polymerization mixture solvent system.

13. The process of claim 5, 6, 7, 8, 9 or 10 wherein the redox pair comprises a peroxide and a reducing agent wherein the peroxide has limited solubility in the polymerization solvent system and the reducing agent has high solubility in the polymerization solvent system.

14. The process of claim 13 wherein the peroxide has a log P partition coefficient greater than or equal to 3 for hydrophobic substrates and phases and a log P partition coefficient less than 3 for hydrophilic substrates and phases.

15. The article or process of any one of the preceding claims wherein the grafted polymer is a carboxyammonium polymer or a sulfoammonium polymer.

16. The article or process of any one of the preceding claims wherein the grafted polymer is a zwitterionic polymer.

17. The article or process of any one of the preceding claims wherein the grafted polymer is a carboxybetaine polymer or a sulfobetaine polymer.

18. The article or process of any one of the preceding claims wherein substrate comprises a polyamide, polyamine, polyanhydride, polyazine, poly(carbonate), polyester, polyether, polyetheretherketone (PEEK), polyguanidine, polyimide, polyketal, poly(ketone), polyolefin, poly(orthoester), polyphosphazine, polysaccharide, polysiloxane, polysulfone, polyurea, polyurethane, halogenated polymer, silicone, aldehyde crosslinked resin, epoxy resin, phenolic resin, latex, or a copolymer or blend thereof.

19. The article or process of any one of the preceding claims wherein the substrate is a composite comprising a precoat overlying a second material, the precoat comprising a polyamide, polyamine, polyanhydride, polyazine, poly(carbonate), polyester, polyether, polyetheretherketone (PEEK), polyguanidine, polyimide, polyketal, poly(ketone), polyolefin, poly(orthoester), polyphosphazine, polysaccharide, polysiloxane, polysulfone, polyurea, polyurethane, halogenated polymer, silicone, aldehyde crosslinked resin, epoxy resin, phenolic resin, latex, or a copolymer or blend thereof, and the second material comprises a metal, ceramic, glass, polymer, biological tissue, woven fiber, non-woven fiber, or semi-metal.

20. The article or process of any one of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, the substrate surface and the grafted polymer layer, in combination, constitute a modified surface, and the grafted

polymer layer has a global average dry thickness and a standard deviation of the global average dry thickness wherein the standard deviation of the global average dry thickness does not exceed 50% of the global average dry thickness of the grafted polymer layer.

21. The article or process of any one of the preceding claims wherein the article further comprises a solvent extractable polymerization initiator or a degradation product thereof.

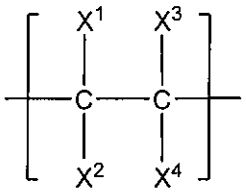
22. The article or process of any one of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the grafted polymer layer has a global average dry thickness that is at least equal to the global average R_{rms} surface roughness of the substrate surface.

23. The article or process of any one of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the grafted polymer layer has a global average dry thickness in the range of about 100 nm to about 1,000 nm.

24. The article or process of any one of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the substrate surface and the grafted polymer layer, in combination, constitute a modified surface having a global average R_{rms} surface roughness that is less than the global average R_{rms} surface roughness of the substrate surface.

25. The article or process of any one of the preceding claims wherein the grafted polymer, non-fouling polymer, zwitterionic polymer, carboxybetaine polymer or sulfobetaine polymer is a chain growth addition polymer.

26. The article or process of any one of the preceding claims wherein the grafted polymer, non-fouling polymer, zwitterionic polymer, carboxybetaine polymer or sulfobetaine polymer comprises repeat units corresponding to Formula 1



Formula 1

wherein

X^1 and X^2 are independently hydrogen, hydrocarbyl, substituted hydrocarbyl, heterocyclo, or substituted carbonyl, provided, however, X^1 and X^2 are not each selected from the group consisting of aryl, heteroaryl, and heterosubstituted carbonyl,

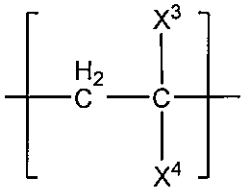
X^3 is hydrogen, alkyl or substituted alkyl,

X^4 is $-OX^{40}$, $-NX^{41}X^{42}$, $-N^+X^{41}X^{42}X^{43}$, $-SX^{40}$, aryl, heteroaryl or acyl,

X^{40} is hydrogen, hydrocarbyl, substituted hydrocarbyl, heterocyclo or acyl, and

X^{41}, X^{42} and X^{43} are independently hydrogen, hydrocaryl, substituted hydrocarbyl or heterocyclo.

27. The article or process of any one of the preceding claims wherein the grafted polymer, non-fouling polymer, zwitterionic polymer, carboxybetaine polymer or sulfobetaine polymer comprises at least one repeat unit corresponding to Formula 2:



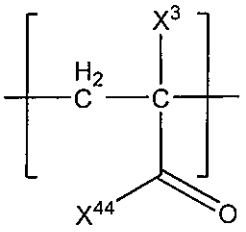
Formula 2

wherein

X^3 is hydrogen, alkyl or substituted alkyl, and

X^4 is a pendant group comprising an oxylated alkylene moiety, a zwitterionic moiety, an anionic moiety, or a cationic moiety.

28. The article or process of any one of the preceding claims wherein the grafted polymer, non-fouling polymer, zwitterionic polymer, carboxybetaine polymer or sulfobetaine polymer comprises repeat units corresponding to Formula 3:



Formula 3

wherein X^3 is hydrogen, alkyl or substituted alkyl, and X^{44} comprises an oxylated alkylene moiety, a zwitterionic moiety, an anionic moiety, or a cationic moiety.

29. The article or process of claim 28 wherein X^{44} is $-OX^{45}$, $-NHX^{45}$, or $-SX^{45}$, and X^{45} is a substituted hydrocarbyl or heterocyclo moiety comprising an oxylated alkylene moiety, a zwitterionic moiety, an anionic moiety, or a cationic moiety.

30. The article or process of any one of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the substrate surface and the grafted polymer layer, in combination, constitute a modified surface exhibiting a reduction in thrombus formation relative to a reference substrate that is substantially identical but lacks the grafted polymer layer in an assay in which the article and the reference substrate are exposed to freshly harvested bovine blood, heparinized, with radiolabeled platelets, and circulated in a flow loop at a rate from of about 200mL/min to 2.5L/min. for 60 to 120 min.

31. The article or process of any one of the preceding claims wherein the article comprises a grafted polymer layer on the substrate surface, and the substrate surface

and the grafted polymer layer, in combination, constitute a modified surface exhibiting a reduction in thrombus formation relative to a reference article that is substantially identical but lacks the grafted polymer layer in an assay in which the article and the reference substrate are exposed to sterile citrated human plasma for at least 55 days with the plasma replaced weekly and then exposed to freshly harvested bovine blood, heparinized, with radiolabeled platelets, and circulated in a flow loop at a rate from of about 200mL/min to 2.5L/min. for 60 to 120 min.

32. The article or process of any one of the preceding claims wherein the article, and aqueous and organic extracts of the article have no detectable level of bypiridine as determined by HPLC or UV analysis.

33. The article or process of any one of the preceding claims wherein the grafted polymer layer contains >30% zwitterionic monomers.

34. The article or process of any one of the preceding claims wherein the grafted polymer layer contains less than 50 mole% of the residue of a polyvalent crosslinker.