WHAT IS CLAIMED:

1. A thermoplastic block copolymer comprising at least one PA block and at least one PB block, wherein PA represents a polymer block comprising one or more units of monomer A and PB represents a polymer block comprising one or more units of monomer B, with monomer A being a vinyl, acrylic, diolefin, nitrile, dinitrile, acrylonitrile monomer, a monomer with reactive functionality, or a crosslinking monomer, and monomer B being a radically polymerizable triglyceride or mixtures thereof, in the form of a plant oil, animal oil, or synthetic triglycerides, wherein one end or both ends of the PA block or PB block is functionalized with a thiocarbonylthio chain transfer group.

2. A telecheleic thermoplastic block copolymer having an architecture of $(PA\text{-}PB)_n$-TCTA-$(PB\text{-}PA)_n$ or $(PB\text{-}PA)_n$-TCTA-$(PA\text{-}PB)_n$, wherein:

PA represents a polymer block comprising one or more units of monomer A and PB represents a polymer block comprising one or more units of monomer B, with monomer A being a vinyl, acrylic, diolefin, nitrile, dinitrile, acrylonitrile monomer, a monomer with reactive functionality, or a crosslinking monomer, and monomer B being a radically polymerizable triglyceride or mixtures thereof, in the form of a plant oil, animal oil, or synthetic triglycerides; and

n is an integer ranging from 1 to 10,

wherein TCTA is a moiety in the PB block or PA block from a telechelic chain transfer agent used to produce the telechelic thermoplastic block copolymer.

3. The thermoplastic block copolymer of claims 1 or 2, wherein the block copolymer has a triblock polymer architecture of PA-PB-PA (or PA-PB-TCTA-PB-PA) or PB-PA-PB (or PB-PA-TCTA-PA-PB).

4. The thermoplastic block copolymer of claims 1 or 2, wherein the block copolymer has a pentablock polymer architecture of PA-PB-PA-PB-PA (or PA-PB-PA-TCTA-PA-PB-PA) or PB-PA-PB-PA-PB (or PB-PA-PB-TCTA-PB-PA-PB).

5. The thermoplastic block copolymer of claim 1, wherein the block copolymer has a $(PA\text{-}PB)_n$ architecture, wherein n is an integer ranging from 1 to 10.

6. The thermoplastic block copolymer of claim 1, wherein the block copolymer has a $(PA\text{-}PB)_n$-PA architecture, wherein n is an integer ranging from 1 to 10.

7. The thermoplastic block copolymer of claim 1, wherein the block copolymer has a PB-$(PA\text{-}PB)_n$ architecture, wherein n is an integer ranging from 1 to 10.

8. The thermoplastic block copolymer of claims 1 or 2, wherein the PA block comprises repeating units of monomer A and the PB block comprises repeating units of monomer B.

9. The thermoplastic block copolymer of claims 1 or 2, wherein the PA block comprises a polymerized linear-chain or branched-chain A monomer, or radicals thereof.

10. The thermoplastic block copolymer of claims 1 or 2, wherein the monomer A is selected from the group consisting of styrene, α-methyl styrene, t-butyl styrene, vinyl xylene, vinyl naphthalene, vinyl pyridine, divinyl benzene, methyl acrylate, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, heptyl (meth)acrylate, hexyl (meth)acrylate, acrylonitrile, adiponitrile, methacrylonitrile, butadiene, isoprene, and mixtures thereof.

11. The thermoplastic block copolymer of claim 10, wherein the monomer A is styrene.

12. The thermoplastic block copolymer of claims 1 or 2, wherein the PB block comprises a polymerized linear-chain or branched-chain plant oil or animal oil, or radicals thereof.

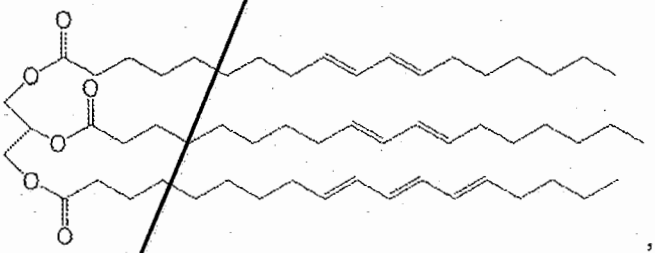
13. The thermoplastic block copolymer of claim 12, wherein the PB block comprises polymerized triglyceride or mixtures thereof.

14. The thermoplastic block copolymer of claim 13, the polymerized triglyceride or mixtures thereof comprises one or more conjugated sites.

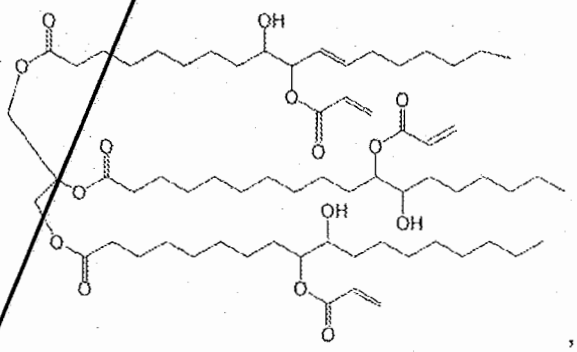
15. The thermoplastic block copolymer of claim 14, wherein the conjugated site is formed by acrylate groups.

16. The thermoplastic block copolymer of claim 14, wherein the triglyceride is acrylated epoxidized triglyceride.

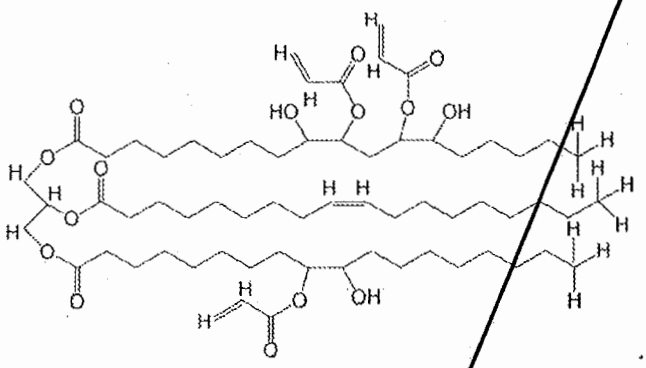
17. The thermoplastic block copolymer of claim 16, wherein the triglyceride is:



,



, or



18. The thermoplastic block copolymer of claims 1 or 2, wherein the PB block is polymerized plant oil or animal oil which is subsequently partially or fully saturated via catalytic hydrogenation post-polymerization.

19. The thermoplastic block copolymer of claims 1 or 2, wherein the monomer B is a radically polymerizable plant oil monomer selected from the group consisting of soybean oil, linseed oil, corn oil, flax seed oil, and rapeseed oil.

20. The thermoplastic block copolymer of claims 1 or 2, wherein the block copolymer has a PA-PB-PA (or PA-PB-TCTA-PB-PA) triblock polymer architecture, with the PA block being a linear-chain polystyrene or radicals thereof, and the PB block being a linear-chain or branched-chain polymerized vegetable oil or radicals thereof.

21. The thermoplastic block copolymer of claim 20, wherein the vegetable oil is acrylated epoxidized vegetable oil, wherein the vegetable oil is soybean oil, linseed oil, corn oil, flax seed oil, or rapeseed oil.

22. The thermoplastic block copolymer of claim 20, wherein the block copolymer has a molecular weight ranging from 7 kDa to 10,000 kDa.

23. The thermoplastic block copolymer of claim 20, wherein the PB block has a glass transition temperature (T_g) below -15 °C.

24. The thermoplastic block copolymer of claim 23, wherein the PB block has a T_g ranging from -60 °C to -28 °C.

25. The thermoplastic block copolymer of claim 20, wherein the block copolymer comprises 5 wt % to 95 wt % of PA block and 95 wt % to 5 wt % of PB block.

26. In an elastomeric composition, the improvement comprising the thermoplastic block copolymer of claims 1 or 2.

27. An elastomer composition comprising the thermoplastic block copolymer of claims 1 or 2, wherein the block copolymer is vulcanized, cross-linked, compatibilized, and/or compounded with one or more other elastomer, additive, modifier and/or filler.

28. In a toughened engineering thermoplastic composition, the improvement comprising the thermoplastic block copolymer of claims 1 or 2.

29. In an asphalt composition, the improvement comprising the thermoplastic block copolymer of claims 1 or 2 as an asphalt additive, modifier, and/or filler.

30. The asphalt composition of claim 29, wherein the asphalt composition comprises 1 to 5 wt% of the thermoplastic block copolymer.

31. The asphalt composition of claim 29 further comprising a bitumen component.

32. An adhesive composition comprising:
the thermoplastic block copolymer of claims 1 or 2 and
a tackifier and/or a plasticizer.

33. In a vehicle tire, the improvement comprising the thermoplastic block copolymer of claims 1 or 2.

34. The vehicle tire of claim 33, wherein the tire is vulcanized, cross-linked, compatibilized, and/or compounded with one or more other material.

35. A thermoplastic statistical copolymer having a general formula of:

$[A_i\text{-}B_j\text{-}C_k]_q$,

wherein:

A represents monomer A, which is a vinyl, acrylic, diolefin, nitrile, dinitrile, acrylonitrile monomer, a monomer with reactive functionality, or a crosslinking monomer;

B represents monomer B, which is a radically polymerizable triglyceride or mixture thereof, in the form of a plant oil, animal oil, or synthetic triglycerides;

C represents monomer C, which is a vinyl, acrylic, diolefin, nitrile, dinitrile, acrylonitrile monomer, a monomer with reactive functionality, or a crosslinking monomer; or a radically polymerizable triglyceride or mixtures thereof, in the form of a plant oil, animal oil, or synthetic triglycerides, provided monomer C is different than the monomer A or monomer B;

i, j, and k are average number of repeating units of monomer A, monomer B, and monomer C, respectively, such that i and j are each greater than 0 and less than 1, k is 0 to less than 1, provided $i + j + k = 1$; and

q represents the number average degree of polymerization and ranges from 10 to 100,000.

36. The thermoplastic statistical copolymer of claim 35, wherein the monomer A and the monomer C, if present, are each independently vinyl, acrylic, diolefin, nitrile, dinitrile, acrylonitrile monomers, a monomer with reactive functionality, or a crosslinking monomer.

37. The thermoplastic statistical copolymer of claim 35, wherein the monomer A and the monomer C, if present, are each independently selected from the group consisting of styrene, α-methyl styrene, t-butyl styrene, vinyl xylene, vinyl naphthalene, vinyl pyridine, divinyl benzene, vinyl acetate, N-vinylpyrrolidone, methyl acrylate, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, heptyl (meth)acrylate, hexyl (meth)acrylate, acrylonitrile, adiponitrile, methacrylonitrile, butadiene, isoprene, and mixtures thereof.

38. The thermoplastic statistical copolymer of claim 35, wherein the monomer A and the monomer C, if present, are each independently styrene or methyl (meth)acrylate.

39. The thermoplastic statistical copolymer of claim 35, wherein the monomer B is a radically polymerizable plant oil monomer selected from the group consisting of soybean oil, corn oil, linseed oil, flax seed oil, and rapeseed oil.

40. The thermoplastic statistical copolymer of claim 35, wherein the triglyceride comprises one or more conjugated sites.

41. The thermoplastic statistical copolymer of claim 35, wherein the triglyceride is an acrylated epoxidized triglyceride.

42. The thermoplastic statistical copolymer of claim 35, wherein the monomer C is a radically polymerizable triglyceride or mixtures thereof, in the form of a plant oil, animal oil, or synthetic triglycerides, wherein the monomer C is from a different plant oil or animal oil than the monomer B, or the triglycerides of the monomer C have a different degree of conjugation than that of monomer B.

43. The thermoplastic statistical copolymer of claim 35, wherein the monomer A is styrene, the monomer B is soybean oil, linseed oil, corn oil, flax seed oil, or rapeseed oil, and the monomer C, if present, is a linear chain-extending monomer.

44. In an elastomeric composition, the improvement comprising the thermoplastic statistical copolymer of claim 35.

45. An elastomer composition comprising the thermoplastic statistical copolymer of claim 35, wherein the statistical copolymer is vulcanized, cross-linked, compatibilized, and/or compounded with one or more other elastomer, additive, modifier and/or filler.

46. In a toughened engineering thermoplastic composition, the improvement comprising the thermoplastic statistical copolymer of claim 35.

47. In an asphalt composition, the improvement comprising the thermoplastic statistical copolymer of claim 35 as an asphalt additive, modifier, and/or filler.

48. The asphalt composition of claim 47 further comprising a bitumen component.

49. An adhesive composition comprising:
the thermoplastic statistical copolymer of claim 35 and
a tackifier and/or a plasticizer.

50. In a vehicle tire, the improvement comprising the thermoplastic statistical copolymer of claim 35.

51. The vehicle tire of claim 50, wherein the tire is vulcanized, cross-linked, compatibilized, and/or compounded with one or more other material.

52. A method of preparing a thermoplastic block copolymer, said method comprising:
providing a radically polymerizable monomer, represented by A, or a polymer block PA comprising one or more units of monomer A;

providing a radically polymerizable triglyceride or mixture thereof, in the form of a plant oil, animal oil, or synthetic triglycerides, in the form of a plant or animal oil, represented by B; and

polymerizing monomer A or the polymer block PA with monomer B via reversible addition-fragmentation chain-transfer polymerization (RAFT), in the presence of a free radical initiator and a chain transfer agent, to form the thermoplastic block copolymer, wherein said polymerizing is carried out under conditions effective to achieve a number average degree of polymerization (N_n) for the thermoplastic block copolymer of up to 100,000 without gelation.

53. The method of claim 52, wherein said polymerizing comprises:

a) polymerizing monomer A via RAFT in a solvent suitable for dissolving PA; and

b) polymerizing monomer B via RAFT in a solvent suitable for dissolving PA and a polymer block PB comprising one or more units of monomer B, with PA from step a) being a macro chain transfer agent, to form a diblock copolymer PA-PB.

54. The method of claim 52, wherein said chain transfer agent is a telechelic chain transfer agent, and wherein said polymerizing comprises:

a) polymerizing monomer A via RAFT in a solvent suitable for dissolving PA; and

b) polymerizing monomer B via RAFT in a solvent suitable for dissolving PA and a polymer block PB comprising one or more units of monomer B, with PA from step a) being a telechelic macro chain transfer agent, to form a symmetrical triblock copolymer PA-PB-TCTA-PB-PA, wherein TCTA is a moiety in the PB block derived from the telechelic chain transfer agent.

55. A method of preparing a thermoplastic block copolymer, said method comprising:

providing a radically polymerizable triglyceride or mixture thereof, in the form of a plant oil, animal oil, or synthetic triglycerides, represented by B, or a polymer block PB comprising one or more units of monomer B;

providing a radically polymerizable monomer, represented by A; and

polymerizing monomer B or the polymer block PB with monomer A via reversible addition-fragmentation chain-transfer polymerization (RAFT), in the presence of a free radical initiator and a chain transfer agent, to form the thermoplastic block copolymer, wherein said polymerizing is carried out under conditions effective to achieve a number average degree of polymerization (N_n) for the thermoplastic block copolymer of up to 100,000 without gelation.

56. The method of claim 55, wherein said polymerizing comprises:

a) polymerizing monomer B via RAFT in a solvent suitable for dissolving PB; and

b) polymerizing monomer A via RAFT in a solvent suitable for dissolving a polymer block PA comprising one or more units of monomer A and PB, with PB from step a) being a macro chain transfer agent, to form a diblock copolymer PB-PA.

57. The method of claim 55, wherein said chain transfer agent is a telechelic chain transfer agent, and wherein said polymerizing comprises:

a) polymerizing monomer B via RAFT in a solvent suitable for dissolving PB; and

b) polymerizing monomer A via RAFT in a solvent suitable for dissolving a polymer block PA comprising one or more units of monomer A and PB, with PB from step a) being a telechelic macro chain transfer agent, to form a symmetrical triblock copolymer PB-PA-TCTA-PA-PB, wherein TCTA is a moiety in the PA block derived from the telechelic chain transfer agent.

58. The method of claims 53 or 56 further comprising:

c) polymerizing monomer A or monomer B via RAFT with the formed block copolymer in step b) as a macro chain transfer agent, thereby adding an additional polymer block to the block copolymer formed in step b).

59. The method of claims 54 or 57 further comprising:

c) polymerizing monomer A or monomer B via RAFT with the formed block copolymer in step b) as a telechelic macro chain transfer agent, thereby adding additional symmetrical polymer blocks to the triblock copolymer formed in step b).

60. The method of claims 58 or 59, wherein the monomer A or monomer B in said polymerizing step c) is each independently the same or different monomer than the monomer A or monomer B used in said polymerizing step a) or b).

61. The method of claims 58 or 59 further comprising:

d) repeating said polymerizing step c) to form a multiple block copolymer.

62. The method of claims 52 or 55, wherein said polymerizing is carried out at a molar ratio of the chain transfer agent to the monomer ranging from 1:1 to 50:1.

63. The method of claims 52 or 55 further comprising:

catalytically hydrogenating reactive unsaturated sites in the PA or PB block to partial or full saturation after said polymerizing.

64. The method of claims 52 or 55, wherein the monomer A is vinyl, acrylic, diolefin, nitrile, dinitrile, acrylonitrile monomer, a monomer with reactive functionality, or a crosslinking monomer.

65. The method of claims 52 or 55, wherein the monomer A is selected from the group consisting of styrene, α-methyl styrene, t-butyl styrene, vinyl xylene, vinyl naphthalene, vinyl pyridine, divinyl benzene, vinyl acetate, N-vinylpyrrolidone, methyl acrylate, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, heptyl (meth)acrylate, hexyl (meth)acrylate, acrylonitrile, adiponitrile, methacrylonitrile, butadiene, isoprene, and mixtures thereof.

66. The method of claim 65, wherein the monomer A is styrene or methyl (meth)acrylate.

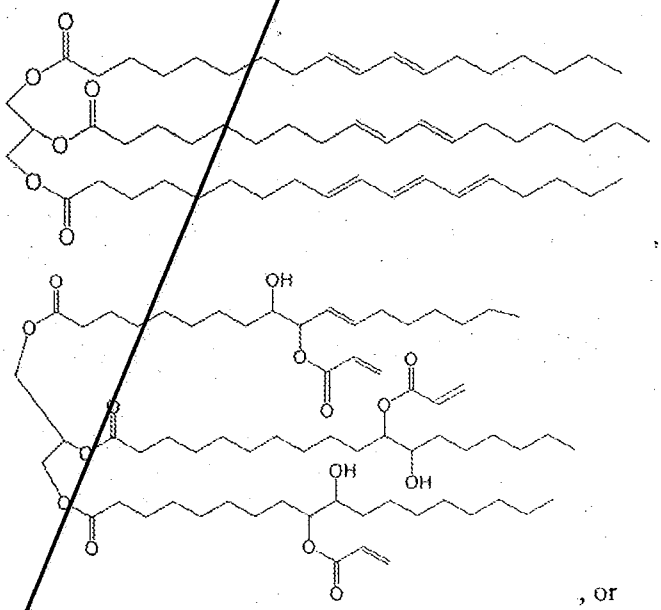
67. The method of claims 52 or 55, wherein the monomer B is a radically polymerizable plant oil monomer selected from the group consisting of soybean oil, corn oil, linseed oil, flax seed oil, and rapeseed oil.

68. The method of claims 52 or 55, wherein the triglyceride comprises one or more conjugated sites.

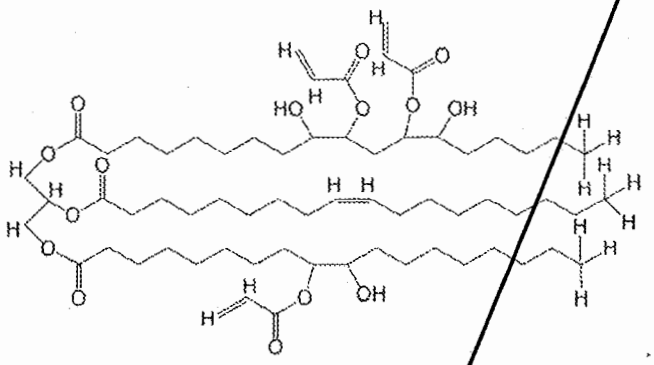
69. The method of claim 68, wherein the one or more conjugated site are formed by acrylate groups.

70. The method of claim 68, wherein the triglyceride is an acrylated epoxidized triglyceride.

71. The method of claim 70, wherein the triglyceride is:



, or



72. The method of claims 52 or 55, wherein the monomer A is styrene, and the monomer B is soybean oil, linseed oil, corn oil, flax seed oil, or rapeseed oil.

73. The method of claims 52 or 55, wherein said polymerizing is carried out at a temperature of 0 to 150 °C.

74. The method of claims 52 or 55, wherein said polymerizing is carried out in a solvent at a temperature of 50 to 85 °C.

75. The method of claim 74, wherein the solvent is toluene, THF, chloroform, cyclohexane, dioxane, dimethyl sulfoxide, dimethyl formamide, acetone, acetonitrile, n-butanol, n-pentnaol, chlorobenzene, dichloromethane, diethylether, tert-butanol, 1,2,-dichloroethylene, diisopropylether, ethanol, ethylacetate, ethylmethylketone, heptane, hexane, isopropylalcohol, isoamylalcohol, methanol, pentane, n-propylacohol, pentachloroethane, 1,1,2,2,-tetrachloroethane, 1,1,1,-trichloroethane, tetrachloroethylene, tetrachloromethane, trichloroethylene, water, xylene, benzene, nitromethane, or a mixture thereof.

76. The method of claim 75, wherein the monomer B has a concentration, when dissolved in the solvent, ranging from 5 % to 100 wt%.

77. The method of claim 75, wherein the monomer B has a concentration, when dissolved in the solvent, ranging from 10 % to 40 wt%.

78. The method of claims 52 or 55, wherein the initiator is benzoyl peroxide or azobisisobutyronitrile.

79. The method of claims 52 or 55, wherein the chain transfer agent is a thiocarbonylthio compound, a dithioester compound, a trithiocarbonate compound, a dithiocarbamate comound, or a xantate compound capable of reversible association with polymerizable free radicals.

80. The method of claim 79, wherein the chain transfer agent is 1-phenylethyl benzodithioate or 1-phenylethyl 2-phenylpropanedithioate.

81. The method of claims 54 or 57, wherein the telechelic chain transfer agent is dibenzyl carbonotrithioate

82. The method of claim 53, wherein said polymerizing of step a) forms a PA block having a molecular weight of 1 to 1000 kDa.

83. The method of claims 53 or 56, wherein the diblock copolymer PA-PB or PB-PA has a molecular weight of 5 to 10,000 kDa.

84. The method of claim 58, wherein said polymerizing of step c) forms a block copolymer PA-PB-PA having a molecular weight of 7 to 10,000 kDa.

85. A method of preparing a thermoplastic homopolymer, said method comprising:

providing a radically polymerizable triglyceride or mixture thereof, in the form of a plant oil, animal oil, or synthetic triglycerides; and

polymerizing said plant oil monomer or animal oil monomer via reversible addition-fragmentation chain-transfer polymerization (RAFT), in the presence of a free radical initiator and a chain transfer agent, to form the thermoplastic homopolymer, wherein said polymerizing is carried out under conditions effective to achieve a number average degree of polymerization (N_n) for the thermoplastic homopolymer of up to 100,000 without gelation.

86. The method of claim 85, wherein the chain transfer agent to the monomer molar ratio ranges from 1:1 to 50:1.

87. The method of claim 85 further comprising:

catalytically hydrogenating reactive unsaturated sites in the thermoplastic homopolymer to partial or full saturation after said polymerizing.

88. The method of claim 85, wherein the monomer is a radically polymerizable plant oil monomer selected from the group consisting of soybean oil, linseed oil, corn oil, flax seed oil, and rapeseed oil.

89. The method of claim 85, wherein the triglyceride comprises one or more conjugated sites.

90. The method of claim 85, wherein the triglyceride is an acrylated epoxidized triglyceride.

91. The method of claim 85, wherein said polymerizing is carried out at a temperature of 0 to 150 °C.

92. The method of claim 85, wherein said polymerizing is carried out in a solvent at a temperature of 50 to 85 °C.

93. The method of claim 85, wherein said polymerizing is carried out in a solvent with the solvent being toluene, THF, chloroform, cyclohexane, dioxane, dimethyl sulfoxide, dimethyl formamide, acetone, acetonitrile, n-butanol, n-pentnaol, chlorobenzene, dichloromethane, diethylether, tert-butanol, 1,2,-dichloroethylene, diisopropylether, ethanol, ethylacetate, ethylmethylketone, heptane, hexane, isopropylalcohol, isoamylalcohol, methanol, pentane, n-propylacohol, pentachloroethane, 1,1,2,2,-tetrachloroethane, 1,1,1,-trichloroethane, tetrachloroethylene, tetrachloromethane, trichloroethylene, water, xylene, benzene, nitromethane, or a mixture thereof.

94. The method of claim 85, wherein said polymerizing is carried out in a solvent with the monomer having a concentration, when dissolved in the solvent, ranging from 5 % to 100 wt%.

95. The method of claim 85, wherein said polymerizing is carried out in a solvent with the monomer having a concentration, when dissolved in the solvent, ranging from 10 % to 40 wt%.

96. The method of claim 85, wherein the initiator is benzoyl peroxide or azobisisobutyronitrile.

97. The method of claim 85, wherein the chain transfer agent is a thiocarbonylthio compound, a dithioester compound, a trithiocarbonate compound, a dithiocarbamate comound, or a xantate compound capable of reversible association with polymerizable free radicals.

98. The method of claim 97, wherein the chain transfer agent is 1-phenylethyl benzodithioate, 1-phenylethyl 2-phenylpropanedithioate, or dibenzyl carbonotrithioate.

99. A method of preparing a thermoplastic statistical copolymer, said method comprising:

providing a radically polymerizable monomer, represented by A;

providing a radically polymerizable triglyceride or mixture thereof, in the form of a plant oil, animal oil, or synthetic triglycerides, represented by B; and

polymerizing monomer A and monomer B simultaneously, via reversible addition-fragmentation chain-transfer polymerization (RAFT), in the presence of a free radical initiator and a chain transfer agent to form the thermoplastic statistical copolymer, wherein said polymerizing is carried out under conditions effective to achieve a number average degree of polymerization (N_n) for the thermoplastic statistical copolymer of up to 100,000 without gelation.

100. The method of claim 99 further comprising, prior to said polymerizing:

providing a radically polymerizable monomer, represented by C, wherein monomer C is different than monomer A or monomer B, wherein said polymerizing comprises polymerizing monomer A, monomer B, and monomer C simultaneously, via RAFT, in the presence of the free radical initiator and the chain transfer agent to form the thermoplastic statistical copolymer.

101. The method of claims 99 or 100, wherein said polymerizing is carried out at a molar ratio of the chain transfer agent to the monomer ranging from 1:1 to 50:1.

102. The method of claims 99 or 100 further comprising:

catalytically hydrogenating reactive unsaturated sites in the thermoplastic statistical copolymer to partial or full saturation after said polymerizing.

103. The method of claims 99 or 100, wherein the monomer A and the monomer C, if present, are each independently vinyl, acrylic, diolefin, nitrile, dinitrile, acrylonitrile monomer, a monomer with reactive functionality, or a crosslinking monomer .

104. The method of claim 103, wherein the monomer A and the monomer C, if present, are each independently selected from the group consisting of styrene, α-methyl styrene, t-butyl styrene, vinyl xylene, vinyl naphthalene, vinyl pyridine, divinyl benzene, vinyl acetate, N-vinylpyrrolidone, methyl acrylate, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, heptyl (meth)acrylate, hexyl (meth)acrylate, acrylonitrile, adiponitrile, methacrylonitrile, butadiene, isoprene, and mixtures thereof.

105. The method of claim 104, wherein the monomer A and the monomer C, if present, are each independently styrene or methyl (meth)acrylate.

106. The method of claims 99 or 100, wherein the monomer B is a radically polymerizable plant oil monomer selected from the group consisting of soybean oil, corn oil, linseed oil, flax seed oil, and rapeseed oil.

107. The method of claims 99 or 100, wherein the triglyceride comprises one or more conjugated sites.

108. The method of claims 99 or 100, wherein the triglyceride is an acrylated epoxidized triglyceride.

109. The method of claim 100, wherein the monomer C is a radically polymerizable triglyceride or mixture thereof, in the form of a plant oil, animal oil, or synthetic triglycerides, wherein the monomer C is from a different plant oil or animal oil than the monomer B, or the triglycerides of the monomer C have a different degree of conjugation than the monomer B.

110. The method of claims 99 or 100, wherein the monomer A is styrene, the monomer B is soybean oil, and the monomer C, if present, is a linear chain-extending monomer.

111. The method of claims 99 or 100, wherein said polymerizing is carried out at a temperature of 0 to 150 °C.

112. The method of claims 99 or 100, wherein said polymerizing is carried out in a solvent at a temperature of 50 to 85 °C.

113. The method of claims 99 or 100, wherein said polymerizing is carried out in a solvent with the solvent being toluene, THF, chloroform, cyclohexane, dioxane, dimethyl sulfoxide, dimethyl formamide, acetone, acetonitrile, n-butanol, n-pentnaol, chlorobenzene, dichloromethane, diethylether, tert-butanol, 1,2,-dichloroethylene, diisopropylether, ethanol, ethylacetate, ethylmethylketone, heptane, hexane, isopropylalcohol, isoamylalcohol, methanol, pentane, n-propylacohol, pentachloroethane, 1,1,2,2,-tetrachloroethane, 1,1,1,-trichloroethane,

tetrachloroethylene, tetrachloromethane, trichloroethylene, water, xylene, benzene, nitromethane, or a mixture thereof.

114. The method of claim 112, wherein said polymerizing is carried out in a solvent with the monomers being dissolved in the solvent at a concentration ranging from 5 % to 100 wt%.

115. The method of claim 112, wherein said polymerizing is carried out in a solvent with the monomers being dissolved in the solvent at a concentration ranging from 10 % to 40 wt%.

116. The method of claims 99 or 100, wherein the initiator is benzoyl peroxide or azobisisobutyronitrile.

117. The method of claims 99 or 100, wherein the chain transfer agent is a thiocarbonylthio compound, a dithioester compound, a trithiocarbonate compound, a dithiocarbamate comound, or a xantate compound capable of reversible association with polymerizable free radicals.

118. The method of claims 99 or 100, wherein the chain transfer agent is 1-phenylethyl benzodithioate or 1-phenylethyl 2-phenylpropanedithioate.

WHAT IS CLAIMED:

1. A thermoplastic block copolymer comprising at least one PA block and at least one PB block, wherein PA represents a polymer block comprising one or more units of monomer A and PB represents a polymer block comprising one or more units of monomer B, with monomer A being a vinyl, acrylic, diolefin, nitrile, dinitrile, acrylonitrile monomer, a monomer with reactive functionality, or a crosslinking monomer, and monomer B being a radically polymerizable triglyceride or mixtures thereof, in the form of a plant oil, animal oil, or synthetic triglycerides, wherein one end or both ends of the PA block or PB block is functionalized with a thiocarbonylthio chain transfer group.

2. A telecheleic thermoplastic block copolymer having an architecture of $(PA\text{-}PB)_n$-TCTA-$(PB\text{-}PA)_n$ or $(PB\text{-}PA)_n$-TCTA-$(PA\text{-}PB)_n$, wherein:

PA represents a polymer block comprising one or more units of monomer A and PB represents a polymer block comprising one or more units of monomer B, with monomer A being a vinyl, acrylic, diolefin, nitrile, dinitrile, acrylonitrile monomer, a monomer with reactive functionality, or a crosslinking monomer, and monomer B being a radically polymerizable triglyceride or mixtures thereof, in the form of a plant oil, animal oil, or synthetic triglycerides; and

n is an integer ranging from 1 to 10,

wherein TCTA is a moiety in the PB block or PA block from a telechelic chain transfer agent used to produce the telechelic thermoplastic block copolymer.

3. The thermoplastic block copolymer of claims 1 or 2, wherein the block copolymer has a triblock polymer architecture of PA-PB-PA (or PA-PB-TCTA-PB-PA) or PB-PA-PB (or PB-PA-TCTA-PA-PB).

4. The thermoplastic block copolymer of claims 1 or 2, wherein the block copolymer has a pentablock polymer architecture of PA-PB-PA-PB-PA (or PA-PB-PA-TCTA-PA-PB-PA) or PB-PA-PB-PA-PB (or PB-PA-PB-TCTA-PB-PA-PB).

5. The thermoplastic block copolymer of claim 1, wherein the block copolymer has a $(PA\text{-}PB)_n$ architecture, wherein n is an integer ranging from 1 to 10.

6. The thermoplastic block copolymer of claim 1, wherein the block copolymer has a $(PA\text{-}PB)_n\text{-}PA$ architecture, wherein n is an integer ranging from 1 to 10.

7. The thermoplastic block copolymer of claim 1, wherein the block copolymer has a $PB\text{-}(PA\text{-}PB)_n$ architecture, wherein n is an integer ranging from 1 to 10.

8. The thermoplastic block copolymer of claims 1 or 2, wherein the PA block comprises repeating units of monomer A and the PB block comprises repeating units of monomer B.

9. The thermoplastic block copolymer of claims 1 or 2, wherein the PA block comprises a polymerized linear-chain or branched-chain A monomer, or radicals thereof.

10. The thermoplastic block copolymer of claims 1 or 2, wherein the monomer A is selected from the group consisting of styrene, α-methyl styrene, t-butyl styrene, vinyl xylene, vinyl naphthalene, vinyl pyridine, divinyl benzene, methyl acrylate, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, heptyl (meth)acrylate, hexyl (meth)acrylate, acrylonitrile, adiponitrile, methacrylonitrile, butadiene, isoprene, and mixtures thereof.

11. The thermoplastic block copolymer of claim 10, wherein the monomer A is styrene.

12. The thermoplastic block copolymer of claims 1 or 2, wherein the PB block comprises a polymerized linear-chain or branched-chain plant oil or animal oil, or radicals thereof.

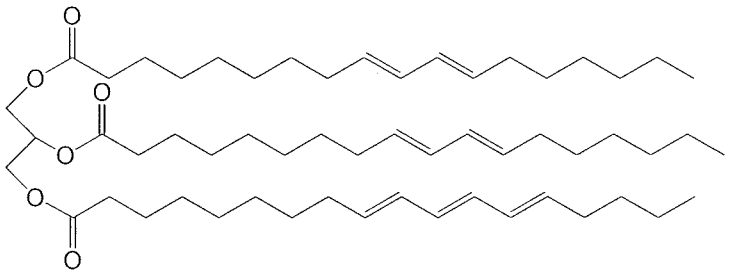
13. The thermoplastic block copolymer of claim 12, wherein the PB block comprises polymerized triglyceride or mixtures thereof.

14. The thermoplastic block copolymer of claim 13, the polymerized triglyceride or mixtures thereof comprises one or more conjugated sites.

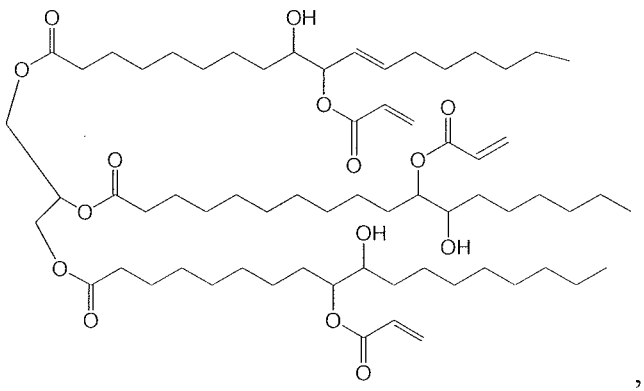
15. The thermoplastic block copolymer of claim 14, wherein the conjugated site is formed by acrylate groups.

16. The thermoplastic block copolymer of claim 14, wherein the triglyceride is acrylated epoxidized triglyceride.

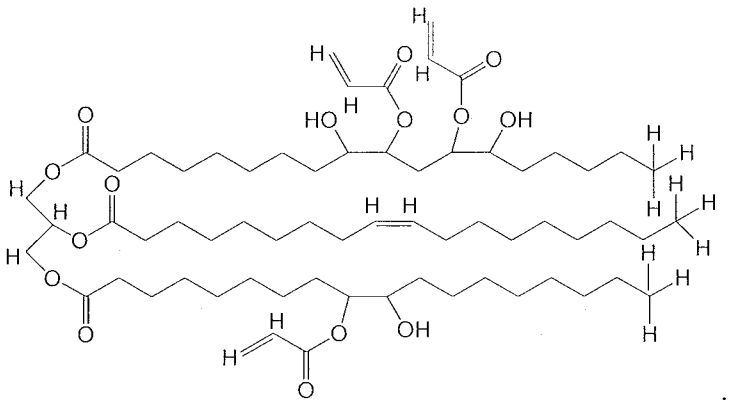
17. The thermoplastic block copolymer of claim 16, wherein the triglyceride is:



,



, or



18. The thermoplastic block copolymer of claims 1 or 2, wherein the PB block is polymerized plant oil or animal oil which is subsequently partially or fully saturated via catalytic hydrogenation post-polymerization.

19. The thermoplastic block copolymer of claims 1 or 2, wherein the monomer B is a radically polymerizable plant oil monomer selected from the group consisting of soybean oil, linseed oil, corn oil, flax seed oil, and rapeseed oil.

20. The thermoplastic block copolymer of claims 1 or 2, wherein the block copolymer has a PA-PB-PA (or PA-PB-TCTA-PB-PA) triblock polymer architecture, with the PA block being a linear-chain polystyrene or radicals thereof, and the PB block being a linear-chain or branched-chain polymerized vegetable oil or radicals thereof.

21. The thermoplastic block copolymer of claim 20, wherein the vegetable oil is acrylated epoxidized vegetable oil, wherein the vegetable oil is soybean oil, linseed oil, corn oil, flax seed oil, or rapeseed oil.

22. The thermoplastic block copolymer of claim 20, wherein the block copolymer has a molecular weight ranging from 7 kDa to 10,000 kDa.

23. The thermoplastic block copolymer of claim 20, wherein the PB block has a glass transition temperature (T_g) below -15 °C.

24. The thermoplastic block copolymer of claim 23, wherein the PB block has a T_g ranging from -60 °C to -28 °C.

25. The thermoplastic block copolymer of claim 20, wherein the block copolymer comprises 5 wt % to 95 wt % of PA block and 95 wt % to 5 wt % of PB block.

26. In an elastomeric composition, the improvement comprising the thermoplastic block copolymer of claims 1 or 2.

27. An elastomer composition comprising the thermoplastic block copolymer of claims 1 or 2, wherein the block copolymer is vulcanized, cross-linked, compatibilized, and/or compounded with one or more other elastomer, additive, modifier and/or filler.

28. In a toughened engineering thermoplastic composition, the improvement comprising the thermoplastic block copolymer of claims 1 or 2.

29. In an asphalt composition, the improvement comprising the thermoplastic block copolymer of claims 1 or 2 as an asphalt additive, modifier, and/or filler.

30. The asphalt composition of claim 29, wherein the asphalt composition comprises 1 to 5 wt% of the thermoplastic block copolymer.

31. The asphalt composition of claim 29 further comprising a bitumen component.

32. An adhesive composition comprising:
the thermoplastic block copolymer of claims 1 or 2 and
a tackifier and/or a plasticizer.

33. In a vehicle tire, the improvement comprising the thermoplastic block copolymer of claims 1 or 2.

34. The vehicle tire of claim 33, wherein the tire is vulcanized, cross-linked, compatibilized, and/or compounded with one or more other material.

35. A method of preparing a thermoplastic block copolymer, said method comprising:

providing a radically polymerizable monomer, represented by A, or a polymer block PA comprising one or more units of monomer A;

providing a radically polymerizable triglyceride or mixture thereof, in the form of a plant oil, animal oil, or synthetic triglycerides, in the form of a plant or animal oil, represented by B; and

polymerizing monomer A or the polymer block PA with monomer B via reversible addition-fragmentation chain-transfer polymerization (RAFT), in the presence of a free radical initiator and a chain transfer agent, to form the thermoplastic block copolymer, wherein said polymerizing is carried out under conditions effective to achieve a number average degree of polymerization (N_n) for the thermoplastic block copolymer of up to 100,000 without gelation.

36. The method of claim 35, wherein said polymerizing comprises:

a) polymerizing monomer A via RAFT in a solvent suitable for dissolving PA; and

b) polymerizing monomer B via RAFT in a solvent suitable for dissolving PA and a polymer block PB comprising one or more units of monomer B, with PA from step a) being a macro chain transfer agent, to form a diblock copolymer PA-PB.

37. The method of claim 35, wherein said chain transfer agent is a telechelic chain transfer agent, and wherein said polymerizing comprises:

a) polymerizing monomer A via RAFT in a solvent suitable for dissolving PA; and

b) polymerizing monomer B via RAFT in a solvent suitable for dissolving PA and a polymer block PB comprising one or more units of monomer B, with PA from step a) being a telechelic macro chain transfer agent, to form a symmetrical triblock copolymer PA-PB-TCTA-PB-PA, wherein TCTA is a moiety in the PB block derived from the telechelic chain transfer agent.

38. A method of preparing a thermoplastic block copolymer, said method comprising:

providing a radically polymerizable triglyceride or mixture thereof, in the form of a plant oil, animal oil, or synthetic triglycerides, represented by B, or a polymer block PB comprising one or more units of monomer B;

providing a radically polymerizable monomer, represented by A; and

polymerizing monomer B or the polymer block PB with monomer A via reversible addition-fragmentation chain-transfer polymerization (RAFT), in the presence of a free radical initiator and a chain transfer agent, to form the thermoplastic block copolymer, wherein said polymerizing is carried out under conditions effective to achieve a number average degree of polymerization (N_n) for the thermoplastic block copolymer of up to 100,000 without gelation.

39. The method of claim 38, wherein said polymerizing comprises:

a) polymerizing monomer B via RAFT in a solvent suitable for dissolving PB; and

b) polymerizing monomer A via RAFT in a solvent suitable for dissolving a polymer block PA comprising one or more units of monomer A and PB, with PB from step a) being a macro chain transfer agent, to form a diblock copolymer PB-PA.

40. The method of claim 38, wherein said chain transfer agent is a telechelic chain transfer agent, and wherein said polymerizing comprises:

a) polymerizing monomer B via RAFT in a solvent suitable for dissolving PB; and

b) polymerizing monomer A via RAFT in a solvent suitable for dissolving a polymer block PA comprising one or more units of monomer A and PB,

with PB from step a) being a telechelic macro chain transfer agent, to form a symmetrical triblock copolymer PB-PA-TCTA-PA-PB, wherein TCTA is a moiety in the PA block derived from the telechelic chain transfer agent.

41. The method of claims 36 or 39 further comprising:

c) polymerizing monomer A or monomer B via RAFT with the formed block copolymer in step b) as a macro chain transfer agent, thereby adding an additional polymer block to the block copolymer formed in step b).

42. The method of claims 37 or 40 further comprising:

c) polymerizing monomer A or monomer B via RAFT with the formed block copolymer in step b) as a telechelic macro chain transfer agent, thereby adding additional symmetrical polymer blocks to the triblock copolymer formed in step b).

43. The method of claims 41 or 42, wherein the monomer A or monomer B in said polymerizing step c) is each independently the same or different monomer than the monomer A or monomer B used in said polymerizing step a) or b).

44. The method of claims 41 or 42 further comprising:

d) repeating said polymerizing step c) to form a multiple block copolymer.

45. The method of claims 35 or 38, wherein said polymerizing is carried out at a molar ratio of the chain transfer agent to the monomer ranging from 1:1 to 50:1.

46. The method of claims 35 or 38 further comprising:

catalytically hydrogenating reactive unsaturated sites in the PA or PB block to partial or full saturation after said polymerizing.

47. The method of claims 35 or 38, wherein the monomer A is vinyl, acrylic, diolefin, nitrile, dinitrile, acrylonitrile monomer, a monomer with reactive functionality, or a crosslinking monomer.

48. The method of claims 35 or 38, wherein the monomer A is selected from the group consisting of styrene, α-methyl styrene, t-butyl styrene, vinyl xylene, vinyl naphthalene, vinyl pyridine, divinyl benzene, vinyl acetate, N-vinylpyrrolidone, methyl acrylate, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, heptyl (meth)acrylate, hexyl (meth)acrylate, acrylonitrile, adiponitrile, methacrylonitrile, butadiene, isoprene, and mixtures thereof.

49. The method of claim 48, wherein the monomer A is styrene or methyl (meth)acrylate.

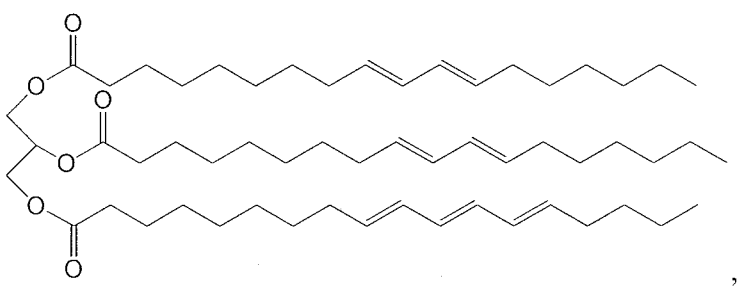
50. The method of claims 35 or 38, wherein the monomer B is a radically polymerizable plant oil monomer selected from the group consisting of soybean oil, corn oil, linseed oil, flax seed oil, and rapeseed oil.

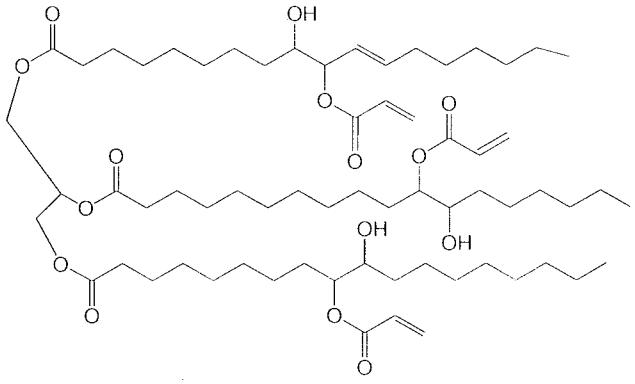
51. The method of claims 35 or 38, wherein the triglyceride comprises one or more conjugated sites.

52. The method of claim 51, wherein the one or more conjugated site are formed by acrylate groups.

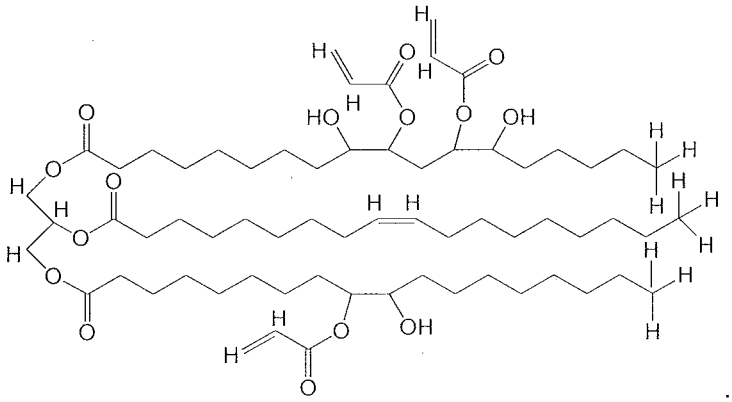
53. The method of claim 51, wherein the triglyceride is an acrylated epoxidized triglyceride.

54. The method of claim 53, wherein the triglyceride is:





, or



55. The method of claims 35 or 38, wherein the monomer A is styrene, and the monomer B is soybean oil, linseed oil, corn oil, flax seed oil, or rapeseed oil.

56. The method of claims 35 or 38, wherein said polymerizing is carried out at a temperature of 0 to 150 °C.

57. The method of claims 35 or 38, wherein said polymerizing is carried out in a solvent at a temperature of 50 to 85 °C.

58. The method of claim 57, wherein the solvent is toluene, THF, chloroform, cyclohexane, dioxane, dimethyl sulfoxide, dimethyl formamide, acetone, acetonitrile, n-butanol, n-pentnaol, chlorobenzene, dichloromethane, diethylether, tert-butanol, 1,2,-dichloroethylene, diisopropylether, ethanol, ethylacetate, ethylmethylketone, heptane, hexane, isopropylalcohol, isoamylalcohol, methanol, pentane, n-propylacohol, pentachloroethane, 1,1,2,2,-tetrachloroethane, 1,1,1,-

trichloroethane, tetrachloroethylene, tetrachloromethane, trichloroethylene, water, xylene, benzene, nitromethane, or a mixture thereof.

59. The method of claim 58, wherein the monomer B has a concentration, when dissolved in the solvent, ranging from 5 % to 100 wt%.

60. The method of claim 58, wherein the monomer B has a concentration, when dissolved in the solvent, ranging from 10 % to 40 wt%.

61. The method of claims 35 or 38, wherein the initiator is benzoyl peroxide or azobisisobutyronitrile.

62. The method of claims 35 or 38, wherein the chain transfer agent is a thiocarbonylthio compound, a dithioester compound, a trithiocarbonate compound, a dithiocarbamate comound, or a xantate compound capable of reversible association with polymerizable free radicals.

63. The method of claim 62, wherein the chain transfer agent is 1-phenylethyl benzodithioate or 1-phenylethyl 2-phenylpropanedithioate.

64. The method of claims 37 or 40, wherein the telechelic chain transfer agent is dibenzyl carbonotrithioate

65. The method of claim 36, wherein said polymerizing of step a) forms a PA block having a molecular weight of 1 to 1000 kDa.

66. The method of claims 36 or 39, wherein the diblock copolymer PA-PB or PB-PA has a molecular weight of 5 to 10,000 kDa.

67. The method of claim 41, wherein said polymerizing of step c) forms a block copolymer PA-PB-PA having a molecular weight of 7 to 10,000 kDa.