CLAIMS

What is claimed is:

1. A method of preparing a multigraft copolymer, said method comprising:

(a) providing a macromonomer comprising one or more polymeric chains attached to a polymerizable terminal group, wherein the one or more polymeric chains comprise constitutional units from at least a first monomer, wherein the first monomer comprises a vinyl group;

(b) preparing an emulsion comprising the macromonomer, a second monomer, and a polymerization initiator; and

(c) copolymerizing the macromonomer and the second monomer to form the multigraft copolymer;

further wherein providing the macromomonomer comprises:

(i) providing the first monomer;

(ii) polymerizing the first monomer via anionic polymerization to provide a carbanion-containing polymeric chain;

(iii) terminating the anionic polymerization by contacting the carbanion-containing polymeric chain with an epoxide and a protic solvent to provide a hydroxyl-terminated polymeric chain; and

(iv) esterifying the hydroxyl group of the hydroxyl-terminated polymeric chain by contacting it with a vinyl-substituted carboxylic acid to provide a single-chain macromonomer or with a vinyl-substituted dicarboxylic acid to provide a double-chain macromonomer.

2. The method of claim 1, wherein polymerizing the first monomer via anionic polymerization comprises contacting the first monomer with an alkyl lithium reagent or a Grignard reagent in a non-polar organic solvent at a temperature of between about 20 degrees Celsius and about 25 degrees Celsius to initiate anionic polymerization.

3. The method of claim 1, wherein the first monomer is selected from the group consisting of a styrene, α-methylstryene, ethene, vinylchloride, vinyl pyridine, and cyclohexadiene.

4. The method of claim 1, wherein esterifying the hydroxyl group of the hydroxyl-terminated polymeric chain comprises contacting the hydroxyl-terminated polymeric chain with 4-vinylbenzoic acid to provide the single-chain macromonomer; or contacting the hydroxyl-terminated polymeric chain with 5-(4-vinylbenzyloxy)isophthalic acid to provide the double-chain macromonomer; further wherein the esterifying is performed in the presence of a carbodiimide and dimethylaminopyridine (DMAP) in a solvent, wherein the solvent is tetrahydrofuran (THF), at a temperature between about 5 degrees Celsius and about 0 degrees Celsius.

5. The method of claim 1, wherein preparing the emulsion comprises adding the macromonomer and the second monomer to an organic solvent to prepare a homogeneous solution; adding the homogeneous solution to an aqueous solution comprising one or more surfactants to provide a mixture; and agitating the mixture to provide a homogeneous emulsion, wherein preparing the emulsion further comprises adding a polymerization initiator to one or both of the homogeneous solution and the mixture.

6. The method of claim 1, wherein the second monomer is selected from isoprene and an alkyl acrylate.

7. The method of claim 1, wherein the polymerization initiator comprises a radical initiator and copolymerizing the macromonomer and the second monomer comprises heating the emulsion prepared in step (b).

8. The method of claim 7, wherein the heating comprises heating the emulsion to a temperature between about 50 degrees Celsius and about 90 degrees Celsius for about eight hours.

9. The method of claim 1, further comprising drying and/or purifying the multigraft copolymer.

10. A multigraft copolymer prepared according to the method of claim 1, wherein providing a macromonomer in step (a) comprises providing a double-chain macromonomer.

11. The multigraft copolymer of claim 10, wherein the multigraft copolymer comprises a rubbery polymeric main chain and a plurality of glassy or semi-crystalline polymeric side chains, wherein the main chain comprises a plurality of randomly spaced branch points and wherein each of the plurality of glassy or semi-crystalline polymeric side chains is attached to the main chain at one of the plurality of randomly spaced branch points.

12. The multigraft copolymer of claim 11, wherein the second monomer is n-butyl acrylate and the rubbery polymeric main chain comprises poly(n-butyl acrylate).

13. The multigraft copolymer of claim 11, wherein the first monomer is styrene and the glassy or semi-crystalline polymeric side chains comprise polystyrene.

14. A thermoplastic elastomer comprising the multigraft copolymer of claim 10.

15. An adhesive comprising the multigraft copolymer of claim 10.

16. A random multigraft copolymer comprising a poly(alkyl acrylate) main chain and a plurality of glassy or semi-crystalline polymeric side chains, wherein said main chain comprises a plurality of randomly spaced branch points, and wherein each of the plurality of polymeric side chains is attached to the main chain at one of the plurality of randomly spaced branch points, wherein the copolymer comprises a centipede architecture, and wherein the poly(alkyl acrylate) main chain is poly(methyl acrylate), poly(propyl acrylate), poly(n-butyl acrylate), poly(pentyl acrylate) or poly(hexyl acrylate).

17. The random multigraft copolymer of claim 16, wherein the copolymer has a weight-average molecular mass (M_w) greater than about 500,000 grams per mole (g/mol).

18. The random multigraft copolymer of claim 16, wherein the copolymer has a M_w of about 1,000,000 g/mol or more.

19. The random multigraft copolymer of claim 16, wherein the copolymer comprises between about 15 and about 43 weight % polystyrene.

20. The random multigraft copolymer of claim 16, wherein the copolymer comprises between about 26 and about 32 weight % polystyrene.

21. The random multigraft copolymer of claim 16, wherein the copolymer has a glass transition temperature (T_g) of between about -13 degrees C (°C) and about -42°C.

22. The random multigraft copolymer of claim 16, wherein the copolymer has at least about 12 branch points per molecule.

23. The random multigraft copolymer of claim 16, wherein the copolymer has between about 15 and about 22 branch points per molecule.

24. The random multigraft copolymer of claim 16, wherein the poly(alkyl acrylate) main chain is poly(n-butyl acrylate).

25. The random multigraft copolymer of claim 16, wherein the polymeric side chains comprise polystyrene.

26. A thermoplastic elastomer comprising the random multigraft copolymer of claim 16.

27. An adhesive comprising the random multigraft copolymer of claim 16.

28. A multigraft copolymer prepared according to the method of claim 1, wherein said multigraft copolymer has a weight-average molecular mass (M_w) of at least about 1,000,000 grams per mole (g/mol).

29. A multigraft copolymer prepared according to the method of claim 1, wherein said multigraft copolymer has at least about 15 branch points per molecule.

30. A multigraft copolymer prepared according to the method of claim 1, wherein esterifying the hydroxyl group of the hydroxyl-terminated polymeric chain is performed by contacting it with a vinyl-substituted aryl carboxylic acid.