

CLAIMS

1. A method of preparing a polymer under solution polymerization conditions in a reaction zone comprising:
 - (a) charging a monovinylaromatic monomer and an initiator in the presence of a randomizer; which is an ether, thioether, or a tertiary amine; thereafter
 - (b) charging an initiator and a monovinylaromatic monomer; thereafter
 - (c) charging a mixture of a monovinylaromatic monomer and a conjugated diene monomer; thereafter
 - (d) optionally charging a mixture of a monovinylaromatic monomer and a conjugated diene monomer; and thereafter
 - (e) charging the reaction mixture with a coupling agent,wherein in steps (a) and (b) 0.005 - 1.5 parts by weight per 100 parts by weight of total monomers each of initiator, and 20 - 60 parts by weight per 100 parts by weight of total monomers each of the monovinylaromatic monomer are employed, and wherein in each of steps (a) to (d) polymerization is conducted until essentially no free monomer is present.
2. The method of claim 1, consisting of steps (a), (b), (c), and (e).
3. The method of claim 1, consisting of steps (a), (b), (c), (d), and (e).
4. The method of any of claims 1 to 3, wherein each said monovinylaromatic monomer contains 8 to 12 carbon atoms and each said conjugated diene contains 4 to 6 carbon atoms, said monomers being added in a ratio of 55 to 95, preferably of 60 to 90, and most preferably of 65 to 85 weight percent, monovinylaromatic monomer to 5 to 45, preferably of 10 to 40, and most preferably of 15 to 35, weight percent conjugated diene monomer, thus giving a resinous tapered block copolymer.
5. The method of any of the preceding claims, wherein the weight ratio of the amounts of said monovinylaromatic monomer and said conjugated diene monomer in each of steps (c) and (d) is within the range of 1:0.63 to 1:2, preferably of 1:0.67 to 1:1.8, and most preferably of 1:0.8 to 1:1.5.
6. The method of any of the preceding claims, wherein said

monovinylaromatic monomer charged in step (a) is from 27 to 80, preferably from 40 to 67, and most preferably from 47 to 60, each weight percent of the total monovinylaromatic monomer charged in said method.

7. The method of any of the preceding claims, wherein said monovinylaromatic monomer charged in step (b) is from 5 to 21, preferably from 8 to 19 and most preferably from 11 to 16, weight percent of the total monovinylaromatic monomer charged in said method.

8. The method of any of claims 1, 2 and 4 to 7, wherein said monovinylaromatic monomer charged in step (c) is from 7 to 60, preferably from 27 to 40, and most preferably from 29 to 37, weight percent of the total monovinylaromatic monomer charged in said method.

9. The method of any of claims 1 and 3 to 7, wherein said monovinylaromatic monomer charged in step (c) is from 3 to 19, preferably from 5 to 16, and most preferably from 8 to 13, weight percent of the total monovinylaromatic monomer charged in said method.

10. The method of any of claims 1, 3 to 7 and 9, wherein said monovinylaromatic monomer charged in step (d) is from 13 to 36, preferably from 16 to 32, and most preferably from 20 to 25, weight percent of the total monovinylaromatic monomer charged in said method.

11. The method of any of the preceding claims, wherein said initiator in steps (a) and (b) is charged in amounts effective to provide proportionate amounts of polymeric species in said polymer such that articles made from blends of said polymer with polymers of styrene have improved impact strength.

12. The method of any of the preceding claims, wherein said initiator in steps (a) and (b) is charged in amounts effective to provide proportionate amounts of polymeric species in said polymer such that articles made from blends of said polymer with polymers of styrene have low blueness.

13. The method of any of the preceding claims, wherein said initiator in steps (a) and (b) is charged in amounts effective to provide polymer having a melt flow in the range from 2 to 50 g/10 min.

14. The method of any of the preceding claims, wherein said initiator in step (b) is present in an amount at least equal to the amount of said initiator in step (a),

preferably wherein the amount of initiator in step (b) is from 0.25 to 300 times as much, most preferably from 0.3 to 10 times as much, each based on weight, as the amount of initiator in step (a).

15. The method of any of the preceding claims, wherein each said conjugated diene monomer is 1,3-butadiene, each said monovinylaromatic monomer is styrene, said organomonoalkali metal initiator is n-butyllithium, said randomizer is one chosen from tetrahydrofuran and diethyl ether, and said coupling agent is epoxidized vegetable oil.

16. The method of any of the preceding claims, wherein polymerization is carried out in a hydrocarbon diluent;

wherein said polymerization is carried out in a substantial absence of oxygen and water at temperatures ranging from -10 to 150°C;

wherein, after said coupling agent reacts with products of said polymerization, the system is treated with a terminating agent and a stabilizer; and

wherein, after termination with said terminating agents, any remaining hydrocarbon diluent is flashed off.

17. A polymodal coupled resinous block copolymer of a monovinylaromatic compound and a conjugated diene, said copolymer having polymer chains which result from coupling a mixture comprising

S-S-B/S-B/S-Li and

S-B/S-B/S-Li

wherein

S = monovinylaromatic block

B = conjugated diene block

B/S = tapered block

Li = living polymer site or coupling site.

18. The copolymer of claim 17, having from 55 to 95, preferably from 60 to 90, and most preferably from 65 to 85, weight percent polymerized monovinylaromatic monomer, based on total weight of monomers in said copolymer.

19. Articles made from the copolymer of claim 17 or 18.

20. Blends of a polymer of styrene and the copolymer of claim 17 or 18.

21. The blend of claim 20, wherein said polymer of styrene is present in an

amount in the range from 10 to 70, preferably from 20 to 65, and most preferably from 30 to 60, weight percent, based on total weight of said blend.

22. Articles made from the blend of claim 20 or 21.