BROMINATED STYRENIC POLYMERS AND THEIR PREPARATION

TECHNICAL FIELD

[0001] This invention relates to brominated styrenic polymers with improved melt flow properties, such as improved melt flow and/or low color values, their preparation, and their use.

BACKGROUND

[0002] Commonly-owned U.S. Pat. Nos. 5,677,390, 5,686,538, 5,767,203, 5,852,131, 5,852,132, 5,916,978, ~~6,113,381~~, 6,207,765, 6,232,393, 6,232,408, 6,235,831, 6,235,844, 6,326,439, and 6,521,714 describe what is believed to be the best known prior process technology for producing brominated styrenic polymers such as brominated polystyrene having the best known properties of any previously-known brominated styrenic polymer. In this connection, the terms "brominated styrenic polymer" and "brominated polystyrene" as used in the specification and in the claims hereof refer to a brominated polymer produced by bromination of a pre-existing styrenic polymer such as polystyrene or a copolymer of styrene and at least one other vinyl aromatic monomer, as distinguished from an oligomer or polymer produced by oligomerization or polymerization of one or more brominated styrenic monomers, the properties of the latter oligomers or polymers typically being considerably different from brominated polystyrene in a number of respects.

[0003] Over the years considerable efforts have been made by various parties to improve upon the properties of brominated styrenic polymers, such as improved melt flow and/or low color values. Despite their best efforts, it appears that no party has been able to produce or provide a brominated styrenic polymer having the high melt flow values and/or low color values, much less the combination of excellent properties, of the brominated styrenic polymers producible and provided by this invention. Nor has a prior party found the processing relationships that make possible the production of such improved brominated styrenic polymers.

BRIEF SUMMARY OF THE INVENTION

[0004] It has now been discovered, *inter alia*, that in the aluminum halide catalyzed bromination of a styrenic polymer, reaction time has a profound influence on the type of product formed. More specifically, if the bromination reaction mixture is formed and exists for a very short period of time at a suitably low temperature and then the reaction is promptly terminated, a brominated styrenic polymer is formed having improved melt flow and/or color properties as compared to products produced in a reaction mixture that exists for a longer period of time, such as during a feed period of 30 minutes and a cook period of 5 minutes, the shortest residence times referred to in commonly-owned U.S. Pat. Nos. ~~6,113,381~~, 6,232,393,

a	-0.53	0.38	-0.51	0.24	-0.21	-0.04
b	2.59	-0.13	2.27	1.07	1.63	1.83
ΔE	2.84	0.18	2.35	1.32	1.77	1.93
DSC, T_g (°C)	159.9	158.2	160.6	155.6	169.2	161.8
TGA 1% wt loss temp, N_2 (°C)	351.1	343.7	349.6	350.7	359.0	350.8
BrAPS GPC						
M_n	12,100	12,400	13,200	13,000	18,200	15,300
M_w	13,100	13,000	22,400	22,100	29,600	28,700
% Aromatic rings with ortho-Br (NMR)	77.8	67.4	82.4	68.0	81.6	70.8
MFI (g/10 min, ~~220 °C/2.61 kg~~)	9.5	19.0	3.3	12.1	1.0	2.4

[0072] The brominated anionic polystyrenes of Examples 1 and 2 are novel products of this invention having extremely low initial solution ΔE values. These brominated anionic polystyrenes also possess other highly desirable properties such as high bromine contents, high thermal stabilities in the 320 °C Thermal Stability Test, and GPC weight average and GPC number average weights in ranges which enable them to be readily blended with a wide variety of thermoplastic polymers. So far as is presently known, the lowest value initial solution ΔE value reported for a brominated anionic polystyrene is 1.74, and that polymer had a far inferior thermal stability in the Thermal Stability Test even though conducted at 300 °C rather than at 320 °C as in Examples 1 and 2 above, and a significantly higher GPC weight average molecular weight. See in this connection, U.S. Pat. No. 6,521,714, *e.g.*, Column 33, lines 55-67, Column 34, lines 32-67, and Table VI, Example CE-6.

REFERENCE EXAMPLE D

[0073] This batch bromination was carried out as described in Reference Example A using an anionic polystyrene having a number average molecular weight of 3400 and a weight average molecular weight of 3800. A 1.22 g (9.15 mmol) portion of aluminum chloride was suspended in 499.1 g of dry (> 15 ppm water) BCM in a 1-L, 5-necked, jacketed, glass reaction flask cooled to -5 °C by a circulating glycol bath. The reaction flask, having a flush-mount Teflon polymer bottom valve, was equipped with an overhead air stirrer and

CLAIMS

1. Brominated styrenic polymer formed by anionic polymerization having (i) a bromine content of at least about 66 wt%, (ii) a GPC weight average molecular weight in the range of about 8000 to about 50,000, and (iii) a higher melt flow index as measured using ASTM Test Method D1238-00 as compared to brominated styrenic polymers produced in a batch process in which

(a) the same quantities and proportions of a brominating agent, a solution formed from a solvent and styrenic polymer made by anionic polymerization, and aluminum halide catalyst in which the halogen atoms are bromine or chlorine with at least one such halogen atom being a bromine atom, are fed for 30 minutes to a reactor maintained at the same reaction temperature, and

(b) the reaction mixture then is held at the same temperature for a cook period of 5 minutes.

2. Brominated anionic styrenic polymer as in Claim 1 wherein said GPC weight average molecular weight is in the range of 10,000 to 30,000.

3. Brominated anionic styrenic polymer as in Claim 1 wherein said GPC weight average molecular weight is in the range of 10,000 to 20,000.

4. Brominated anionic styrenic polymer as in Claim 1 wherein said polymer has a thermal stability in the 320°C Thermal Stability Test of 300 ppm of HBr or less.

5. Brominated anionic styrenic polymer as in Claim 1 wherein said polymer has a thermal stability in the 320°C Thermal Stability Test of 125 ppm of HBr or less.

6. Brominated anionic styrenic polymer as in Claim 1 wherein said polymer has an initial Hunter Solution ΔE Color Value of 5 or less.

7. Brominated anionic styrenic polymer as in Claim 1 wherein said polymer has an initial Hunter Solution ΔE Color Value of 3 or less.

8. Brominated anionic styrenic polymer as in Claim 1 wherein said polymer has a thermal stability in the 320°C Thermal Stability Test of 300 ppm of HBr or less, wherein said polymer has a GPC weight average molecular weight in the range of 10,000 to 30,000, and wherein said polymer has an initial Hunter Solution ΔE Color Value of 5 or less.

9. Brominated anionic styrenic polymer as in Claim 1 wherein said polymer has a thermal stability in the 320°C Thermal Stability Test of 125 ppm of HBr or less, wherein

said polymer has a GPC weight average molecular weight in the range of 10,000 to 20,000, and wherein said polymer has an initial Hunter Solution ΔE Color Value of 3 or less.

10. Brominated anionic styrenic polymer as in any of Claims 1-9 wherein said polymer has a bromine content in the range of 67 to 70 wt%.

11. Brominated anionic styrenic polymer as in any of Claims 1-9 wherein said polymer is brominated anionic polystyrene.

12. Brominated anionic styrenic polymer as in any of Claims 1-9 wherein said polymer is brominated anionic polystyrene having a bromine content in the range of 67 to 70 wt%.

13. Brominated styrenic polymer formed by anionic polymerization wherein said polymer has a bromine content of at least about 66 wt% and wherein said polymer is one in which the percentage of aromatic rings having ortho bromine atoms thereon as measured by proton NMR is less than the percentage of the aromatic rings having ortho bromine atoms thereon in brominated styrenic polymers produced in a batch process in which

(a) the same quantities and proportions of a brominating agent, a solution formed from a solvent and styrenic polymer made by anionic polymerization, and aluminum halide catalyst in which the halogen atoms are bromine or chlorine with at least one such halogen atom being a bromine atom, are fed for 30 minutes to a reactor maintained at the same reaction temperature, and

(b) the reaction mixture then is held at the same temperature for a cook period of 5 minutes.

14. Brominated anionic styrenic polymer as in Claim 13 wherein the percentage of aromatic rings having ortho bromine atoms thereon is at least 5% less than the percentage of aromatic rings having ortho bromine atoms thereon in said brominated styrenic polymers formed from the same components with a feed time of 30 minutes or longer.

15. Brominated anionic styrenic polymer as in Claim 13 wherein said polymer has a bromine content in the range of 67 to 69 wt% and wherein the percentage of aromatic rings having ortho bromine atoms thereon is at least 10% less than the percentage of aromatic rings having ortho bromine atoms thereon in said brominated styrenic polymers formed from the same components with a feed time of 30 minutes or longer.

16. Brominated anionic styrenic polymer as in Claim 13 wherein said polymer has a thermal stability in the 320°C Thermal Stability Test of 300 ppm of HBr or less.

17. Brominated anionic styrenic polymer as in Claim 13 wherein said polymer has a thermal stability in the 320°C Thermal Stability Test of 200 ppm of HBr or less.

18. Brominated anionic styrenic polymer as in Claim 13 wherein said polymer has a thermal stability in the 320°C Thermal Stability Test of 125 ppm of HBr or less.

19. Brominated anionic styrenic polymer as in Claim 13 wherein said polymer has an initial ΔE Color Value of 5 or less.

20. Brominated anionic styrenic polymer as in Claim 13 wherein said polymer has an initial Hunter Solution ΔE Color Value of 3 or less.

21. Brominated anionic styrenic polymer as in Claim 13 wherein the percentage of aromatic rings having ortho bromine atoms thereon is at least 5% less than the percentage of aromatic rings having ortho bromine atoms thereon in said brominated styrenic polymers formed from the same components with a feed time of 30 minutes or longer, and wherein said polymer has a thermal stability in the 320°C Thermal Stability Test of 300 ppm of HBr or less.

22. Brominated anionic styrenic polymer as in Claim 13 wherein said polymer has a thermal stability in the 320°C Thermal Stability Test of 300 ppm of HBr or less and wherein said polymer has an initial Hunter Solution ΔE Color Value of 5 or less.

23. Brominated anionic styrenic polymer as in Claim 13 wherein said polymer has a thermal stability in the 320°C Thermal Stability Test of 200 ppm of HBr or less and wherein said polymer has an initial Hunter Solution ΔE Color Value of 5 or less.

24. Brominated anionic styrenic polymer as in Claim 13 wherein said polymer has a thermal stability in the 320°C Thermal Stability Test of 125 ppm of HBr or less and wherein said polymer has an initial Hunter Solution ΔE Color Value of 3 or less.

25. Brominated anionic styrenic polymer as in any of Claims 13, 14, or 16-24 wherein said polymer has a bromine content in the range of 67 to 70 wt%.

26. Brominated anionic styrenic polymer as in any of Claims 13-24 wherein said polymer is brominated anionic polystyrene.

27. Brominated anionic styrenic polymer as in any of Claims 13-24 wherein said polymer has a GPC weight average molecular weight in the range of 8,000 to 50,000.

28. Brominated anionic styrenic polymer as in Claim 27 wherein said polymer has a GPC weight average molecular weight in the range of 10,000 to 30,000.

29. Brominated anionic styrenic polymer as in Claim 27 wherein said polymer has a GPC weight average molecular weight in the range of 10,000 to 20,000.

30. A flame retardant composition which comprises a blend of at least one thermoplastic polymer and a flame retardant amount of at least one brominated anionic styrenic polymer as in any of Claims 1-29.

31. A composition as in Claim 30 wherein said thermoplastic polymer is a thermoplastic styrenic polymer, a thermoplastic acrylonitrile-butadiene-styrene polymer, a thermoplastic polyester, or a thermoplastic polyamide.

32. A method of flame retarding a thermoplastic polymer or a thermoset resin, which method comprises blending therewith or applying a coating thereon of at least one brominated styrenic polymer as in any of Claims 1-29.

33. Brominated anionic styrenic polymer wherein said polymer has an initial Hunter Solution ΔE value in the range of up to 1.50, determined as a 10 wt% solution in chlorobenzene using a transmission cell having a 20-mm transmission length.

34. Brominated anionic styrenic polymer as in Claim 33 wherein said initial ΔE value is in the range of 0.15 to 1.40.

35. Brominated anionic styrenic polymer as in Claim 33 wherein said initial ΔE value is in the range of 0.18 to 1.32.

36. Brominated anionic styrenic polymer as in any of Claims 33-35 wherein said polymer additionally has (1) a GPC weight average molecular weight in the range of 8,000 to 50,000, or (2) a thermal stability in the 320°C Thermal Stability Test of 300 ppm of HBr or less, or (3) a bromine content of at least about 66 wt%, or (4) a combination of any two, or all three, of (1), (2), (3).

37. Brominated anionic styrenic polymer as in Claim 36 wherein said polymer has a combination of any two of (1), (2), (3).

38. Brominated anionic styrenic polymer as in Claim 37 wherein said polymer has a combination of all three of (1), (2), (3).

39. Brominated anionic styrenic polymer as in any of Claims 36-38 wherein the GPC weight average molecular weight of (1) is in the range of 10,000 to 30,000, wherein the thermal stability in the 320°C Thermal Stability Test of (2) is 200 ppm of HBr or less, and wherein the bromine content of (3) is in the range of about 67-70 wt%.

40. Brominated anionic styrenic polymer as in Claim 39 wherein said polymer has a combination of any two of (1), (2), (3).

41. Brominated anionic styrenic polymer as in Claim 39 wherein said polymer has a combination of all three of (1), (2), (3).

42. Brominated anionic styrenic polymer as in any of Claims 36-38 wherein said polymer is brominated anionic polystyrene.

43. Brominated anionic styrenic polymer as in any of Claims 39-41 wherein said polymer is brominated anionic polystyrene.

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[0003] Over the years considerable efforts have been made by various parties to improve upon the properties of brominated styrenic polymers, such as improved melt flow and/or low color values. Despite their best efforts, it appears that no party has been able to produce or provide a brominated styrenic polymer having the high melt flow values and/or low color values, much less the combination of excellent properties, of the brominated styrenic polymers producible and provided by this invention. Nor has a prior party found the processing relationships that make possible the production of such improved brominated styrenic polymers.

BRIEF SUMMARY OF THE INVENTION

[0004] It has now been discovered, *inter alia*, that in the aluminum halide catalyzed bromination of a styrenic polymer, reaction time has a profound influence on the type of product formed. More specifically, if the bromination reaction mixture is formed and exists for a very short period of time at a suitably low temperature and then the reaction is promptly terminated, a brominated styrenic polymer is formed having improved melt flow and/or color properties as compared to products produced in a reaction mixture that exists for a longer period of time, such as during a feed period of 30 minutes and a cook period of 5 minutes, the shortest residence times referred to in commonly-owned U.S. Pat. Nos. 6,133,381, 6,232,393,

a	-0.53	0.38	-0.51	0.24	-0.21	-0.04
b	2.59	-0.13	2.27	1.07	1.63	1.83
ΔE	2.84	0.18	2.35	1.32	1.77	1.93
DSC, T_g (°C)	159.9	158.2	160.6	155.6	169.2	161.8
TGA 1% wt loss temp, N_2 (°C)	351.1	343.7	349.6	350.7	359.0	350.8
BrAPS GPC						
M_n	12,100	12,400	13,200	13,000	18,200	15,300
M_w	13,100	13,000	22,400	22,100	29,600	28,700
% Aromatic rings with ortho-Br (NMR)	77.8	67.4	82.4	68.0	81.6	70.8
MFI (g/10 min, 220°C/2.16 kg)	9.5	19.0	3.3	12.1	1.0	2.4

[0072] The brominated anionic polystyrenes of Examples 1 and 2 are novel products of this invention having extremely low initial solution ΔE values. These brominated anionic polystyrenes also possess other highly desirable properties such as high bromine contents, high thermal stabilities in the 320°C Thermal Stability Test, and GPC weight average and GPC number average weights in ranges which enable them to be readily blended with a wide variety of thermoplastic polymers. So far as is presently known, the lowest value initial solution ΔE value reported for a brominated anionic polystyrene is 1.74, and that polymer had a far inferior thermal stability in the Thermal Stability Test even though conducted at 300°C rather than at 320°C as in Examples 1 and 2 above, and a significantly higher GPC weight average molecular weight. See in this connection, U.S. Pat. No. 6,521,714, *e.g.*, Column 33, lines 55-67, Column 34, lines 32-67, and Table VI, Example CE-6.

REFERENCE EXAMPLE D

[0073] This batch bromination was carried out as described in Reference Example A using an anionic polystyrene having a number average molecular weight of 3400 and a weight average molecular weight of 3800. A 1.22 g (9.15 mmol) portion of aluminum chloride was suspended in 499.1 g of dry (> 15 ppm water) BCM in a 1-L, 5-necked, jacketed, glass reaction flask cooled to -5°C by a circulating glycol bath. The reaction flask, having a flush-mount Teflon polymer bottom valve, was equipped with an overhead air stirrer and

CLAIMS

1. Brominated anionic styrenic polymer having (i) a bromine content of at least about 66 wt%, (ii) a GPC weight average molecular weight in the range of about 8000 to about 50,000, and (iii) an initial Hunter Solution ΔE Color Value of 5 or less, determined as a 10 wt% solution in chlorobenzene using a transmission cell having a 20mm transmission length.

2. Brominated anionic styrenic polymer as in Claim 1 wherein said GPC weight average molecular weight is in the range of 10,000 to 30,000.`

3. Brominated anionic styrenic polymer as in Claim 1 wherein said GPC weight average molecular weight is in the range of 10,000 to 20,000.

4. Brominated anionic styrenic polymer as in Claim 1 wherein said polymer has a thermal stability in the 320°C Thermal Stability Test of 300 ppm of HBr or less.

5. Brominated anionic styrenic polymer as in Claim 1 wherein said polymer has a thermal stability in the 320°C Thermal Stability Test of 125 ppm of HBr or less.

6. Brominated anionic styrenic polymer as in Claim 1 wherein said polymer has an initial Hunter Solution ΔE Color Value of 3 or less.

7. Brominated anionic styrenic polymer as in Claim 1 wherein said polymer has a thermal stability in the 320°C Thermal Stability Test of 300 ppm of HBr or less, wherein said polymer has a GPC weight average molecular weight in the range of 10,000 to 30,000, and wherein said polymer has an initial Hunter Solution ΔE Color Value of 5 or less.

8. Brominated anionic styrenic polymer as in Claim 1 wherein said polymer has a thermal stability in the 320°C Thermal Stability Test of 125 ppm of HBr or less, wherein said polymer has a GPC weight average molecular weight in the range of 10,000 to 20,000, and wherein said polymer has an initial Hunter Solution ΔE Color Value of 3 or less.

9. Brominated anionic styrenic polymer as in any of Claims 1-5 or 7-8 wherein said polymer is brominated anionic polystyrene having a bromine content in the range of 67 to 70 wt%.

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10. Brominated anionic styrenic polymer wherein said polymer has a bromine content of at least about 66 wt%, wherein said polymer has an initial Hunter Solution ΔE Color Value of 5 or less, determined as a 10 wt% solution in chlorobenzene using a transmission cell having a 20mm transmission length, and wherein said polymer is one in which the percentage of aromatic rings having ortho bromine atoms thereon as measured by proton NMR is less than the percentage of the aromatic rings having ortho bromine atoms thereon in brominated styrenic polymers produced in a batch process in which

(a) the same quantities and proportions of a brominating agent, a solution formed from a solvent and styrenic polymer made by anionic polymerization, and aluminum halide catalyst in which the halogen atoms are bromine or chlorine with at least one such halogen atom being a bromine atom, are fed for 30 minutes to a reactor maintained at the same reaction temperature, and

(b) the reaction mixture then is held at the same temperature for a cook period of 5 minutes.

11. Brominated anionic styrenic polymer as in Claim 10 wherein the percentage of aromatic rings having ortho bromine atoms thereon is at least 5% less than the percentage of aromatic rings having ortho bromine atoms thereon in said brominated styrenic polymers formed from the same components with a feed time of 30 minutes or longer.

12. Brominated anionic styrenic polymer as in Claim 10 wherein said polymer has a bromine content in the range of 67 to 69 wt% and wherein the percentage of aromatic rings having ortho bromine atoms thereon is at least 10% less than the percentage of aromatic rings having ortho bromine atoms thereon in said brominated styrenic polymers formed from the same components with a feed time of 30 minutes or longer.

13. Brominated anionic styrenic polymer as in Claim 10 wherein said polymer has a thermal stability in the 320°C Thermal Stability Test of 300 ppm of HBr or less.

14. Brominated anionic styrenic polymer as in Claim 10 wherein said polymer has a thermal stability in the 320°C Thermal Stability Test of 200 ppm of HBr or less.

15. Brominated anionic styrenic polymer as in Claim 10 wherein said polymer has a thermal stability in the 320°C Thermal Stability Test of 125 ppm of HBr or less.

16. Brominated anionic styrenic polymer as in Claim 10 wherein said polymer has an initial Hunter Solution ΔE Color Value of 3 or less.

17. Brominated anionic styrenic polymer as in Claim 10 wherein the percentage of aromatic rings having ortho bromine atoms thereon is at least 5% less than the percentage of aromatic rings having ortho bromine atoms thereon in said brominated styrenic polymers formed from the same components with a feed time of 30 minutes or longer, and wherein said polymer has a thermal stability in the 320°C Thermal Stability Test of 300 ppm of HBr or less.

18. Brominated anionic styrenic polymer as in Claim 10 wherein said polymer has a thermal stability in the 320°C Thermal Stability Test of 125 ppm of HBr or less and wherein said polymer has an initial Hunter Solution ΔE Color Value of 3 or less.

19. Brominated anionic styrenic polymer as in any of Claims 1-5, 7-8, 10, 11, 13-15, 16-17, or 18 wherein said polymer has a bromine content in the range of 67 to 70 wt%.

20. Brominated anionic styrenic polymer as in any of Claims 1-5, 7-8, 10-15, 16-17, or 18 wherein said polymer is brominated anionic polystyrene.

21. Brominated anionic styrenic polymer as in any of Claims 10-15, 16-17, or 18 wherein said polymer has a GPC weight average molecular weight in the range of 8,000 to 50,000.

22. Brominated anionic styrenic polymer as in Claim 21 wherein said polymer has a GPC weight average molecular weight in the range of 10,000 to 30,000.

23. Brominated anionic styrenic polymer as in Claim 21 wherein said polymer has a GPC weight average molecular weight in the range of 10,000 to 20,000.

24. A flame retardant composition which comprises a blend of at least one thermoplastic polymer and a flame retardant amount of at least one brominated anionic styrenic polymer as in any of Claims 1-5, 7-8, 9-15, 16-17, or 18-23.

25. A composition as in Claim 24 wherein said thermoplastic polymer is a thermoplastic styrenic polymer, a thermoplastic acrylonitrile-butadiene-styrene polymer, a thermoplastic polyester, or a thermoplastic polyamide.

26. A method of flame retarding a thermoplastic polymer or a thermoset resin, which method comprises blending therewith or applying a coating thereon of at least one brominated styrenic polymer as in any of Claims 1-5, 7-8, 9-15, 16-17, or 18-23.

27. Brominated anionic styrenic polymer wherein said polymer has an initial Hunter Solution ΔE Color value in the range of up to 1.50, determined as a 10 wt% solution in chlorobenzene using a transmission cell having a 20-mm transmission length.

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28. Brominated anionic styrenic polymer as in Claim 27 wherein said initial Hunter Solution ΔE Color is in the range of 0.15 to 1.40.

29. Brominated anionic styrenic polymer as in Claim 27 wherein said initial Hunter Solution ΔE Color is in the range of 0.18 to 1.32.

30. Brominated anionic styrenic polymer as in any of Claims 27-29 wherein said polymer additionally has (1) a GPC weight average molecular weight in the range of 8,000 to 50,000, or (2) a thermal stability in the 320°C Thermal Stability Test of 300 ppm of HBr or less, or (3) a bromine content of at least about 66 wt%, or (4) a combination of any two, or all three, of (1), (2), (3).

31. Brominated anionic styrenic polymer as in Claim 30 wherein said polymer has a combination of any two of (1), (2), (3).

32. Brominated anionic styrenic polymer as in Claim 31 wherein said polymer has a combination of all three of (1), (2), (3).

33. Brominated anionic styrenic polymer as in any of Claims 30-32 wherein the GPC weight average molecular weight of (1) is in the range of 10,000 to 30,000, wherein the thermal stability in the 320°C Thermal Stability Test of (2) is 200 ppm of HBr or less, and wherein the bromine content of (3) is in the range of about 67-70 wt%.

34. Brominated anionic styrenic polymer as in Claim 33 wherein said polymer has a combination of any two of (1), (2), (3).

35. Brominated anionic styrenic polymer as in Claim 33 wherein said polymer has a combination of all three of (1), (2), (3).

36. Brominated anionic styrenic polymer as in any of Claims 30-35 wherein said polymer is brominated anionic polystyrene.