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(54) **Title:** TRANSLUCENT OR TRANSPARENT FLAME RETARDED THERMOPLASTIC POLYMER COMPOSITIONS AND BROMINATED TELOMERIC FLAME RETARDANTS

(57) **Abstract:** Described are new translucent or transparent flame retarded thermoplastic polymer compositions and new flame retardant additive compositions for use in forming such flame retarded thermoplastic compositions. The flame retardant additives are brominated styrenic telomer distributions having a bromine content in the range of 60 to 75 wt% and a percent transmission in optically clear styrene-acrylonitrile copolymer in the CIE L* test method as described herein of at least 60, desirably at least 75, and more desirably at least 90. These distributions are made from a vinyl aromatic hydrocarbon, e.g., styrene, and a methyl substituted aromatic hydrocarbon having from 1-4 methyl substituents on the ring(s), e.g., toluene or xylene. The brominated styrenic telomer distributions can be non- polymeric or polymeric compositions. The flame retardants described are at least comparable to the only generally known commercially available melt blendable flame retardant satisfying the translucency requirements of HIPS and ABS.



**TRANSLUCENT OR TRANSPARENT FLAME RETARDED THERMOPLASTIC
POLYMER COMPOSITIONS AND BROMINATED TELOMERIC FLAME
RETARDANTS**

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TECHNICAL FIELD

[0001] This invention relates to non-opaque flame retarded polymer compositions, *i.e.*, translucent or transparent flame retarded polymer compositions. This invention also relates to translucent or transparent brominated telomeric flame retardant additive compositions useful in forming such non-opaque flame retarded polymer compositions.

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BACKGROUND

[0002] Most flame retardants for thermoplastic polymers are either particulate solids tending to interfere with or even prevent passage of light through the resultant polymer composition into which they are blended or are polymers that form domains which can also interfere with or prevent the passage of light. Thus, while the base resin may be translucent, many flame retardant additives and flame retardant synergists tend to form finished plastic items such as electronic enclosures that are opaque or minimally translucent. Nano-sized synergists such as antimony trioxide or pentoxide tend to help the translucency. Nevertheless, at present, there is only one generally known commercially-available melt blendable flame retardant that satisfies the translucency requirements of HIPS and ABS when used in combination with submicron-sized antimony synergists.

[0003] It would be highly desirable if a way could be found of providing new translucent or transparent flame retarded thermoplastic polymer compositions and also new flame retardant additive compositions which can be effectively used in forming such flame retarded thermoplastic compositions. Especially desirable from the commercial standpoint would be the provision of brominated flame retardants meeting the classification of polymers and having a good balance of physical, thermal and mechanical properties as well as having high translucency/transparency properties.

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BRIEF NON-LIMITING SUMMARY OF THE INVENTION

[0004] This invention provides new flame retarded thermoplastic polymer compositions and also new translucent or transparent flame retardant additive compositions which can be effectively used in forming such flame retarded thermoplastic compositions. The flame retardant additive compositions used are brominated styrenic telomer distributions having

a bromine content in the range of about 60 to about 75 wt% and a specified high light transmission percentage value in a test method as described herein. These distributions are made from a vinyl aromatic hydrocarbon, most desirably styrene, and an aromatic hydrocarbon having 1, 2, 3 or 4 methyl substituents on the ring or a mixture of two or more of these aromatic hydrocarbons, most desirably one or more of (i) toluene, (ii) o-xylene, (iii) p-xylene, (iv) m-xylene.

[0005] As used herein, the terms “translucent” and “translucency” refer to a percentage value of light transmission through a test plaque when using the CIE L* test method as described herein. These percentage values vary depending on the material under discussion. The test value is at least about 60 in the case of the brominated styrenic telomer distributions used as flame retardants in this invention. On the other hand, the test value can be lower or higher than about 60 as regards the host polymer being flame retarded by use of a flame retardant of this invention. For example, the additive-free host polymer may have a value of as low as about 15 or as high as about 100 in the case of an optically clear thermoplastic polymer such as SAN. Desirably, the additive-free host polymer will have a value of at least about 25. Translucency and transparency are regarded herein as constituting a continuum with transparency being in the higher regions of light transmission.

FURTHER DETAILED DESCRIPTION OF THIS INVENTION

[0006] Provided by this invention is a flame retarded thermoplastic polymer composition which comprises at least one transparent or translucent thermoplastic polymer and a brominated styrenic telomer distribution having a bromine content in the range of about 50 to about 75 wt%, and a percent transmission in optically clear styrene-acrylonitrile copolymer in the CIE L* test method as described herein of at least about 60, desirably at least about 75, and more desirably at least about 90; wherein such brominated telomer distribution has an M_w of about 422 to about 4,000, an M_n of about 420 to about 2,400, an M_z of about 436 to about 4,800, a polydispersity in the range of about 1.01 to about 2.0, a standard deviation of about 29.0 to about 2,000, and an asymmetry of about 90 to about 0.6, a glass transition temperature (T_g) in the range of about 25°C to about 100°C, a 5% weight loss by thermogravimetric analysis (TGA) under nitrogen greater than about 270°C, and a thermal HBr value at 300°C of less than about 500 ppm.

[0007] Also provided by this invention is a flame retarded thermoplastic polymer composition as described above wherein said brominated styrenic telomer distribution additionally has (i) a thermal color value after heating for 15 minutes under nitrogen at 250°C of less than about 35, (ii) a thermal color value after heating for 20 minutes under nitrogen at 300°C of less than about 40, and (iii) as a 10 wt% solution in chlorobenzene, a ΔE value of less than about 25.

[0008] Still another embodiment of this invention is flame retarded thermoplastic polymer compositions which comprise (1) at least one translucent or transparent thermoplastic polymer (*i.e.*, a non-opaque polymer of suitable transparency, viz., a percent of light transmission as measured in the CIE L* test method as described herein of at least about 15 and desirably at least about 25) with which has been blended (2) a brominated styrenic telomer distribution having a bromine content in the range of about 50 to about 75 wt%, and a percent of light transmission in the CIE L* test method as described herein of at least about 60, desirably at least about 75, and more desirably at least about 90; wherein such telomer distribution is formed from:

A) a vinyl aromatic hydrocarbon, and
B) at least one aromatic hydrocarbon having from one to three aromatic rings per molecule and containing from one to four methyl substituents bound to the aromatic ring(s) thereof; and wherein such telomer distribution has, prior to bromination, an M_w in the range of about 211 to about 1000, an M_n in the range of about 210 to about 600, an M_z in the range of about 216 to about 1200, a standard deviation in the range of about 20 to about 350, and asymmetry in the range of about 1 to about 11.

[0009] The flame retarded thermoplastic polymer compositions of this invention are thus blends comprising (1) at least one non-opaque (*i.e.*, translucent or transparent) thermoplastic polymer (sometimes referred to hereinafter as a “host polymer”) and (2) a brominated styrenic telomer distribution having a percent of light transmission in transparent styrene-acrylonitrile copolymer in the CIE L* test method as described herein of at least about 60, desirably at least about 75, and more desirably at least about 90. It will be understood therefore that the transparency value in the CIE L* test method as described herein, is a qualifying property of the brominated styrenic telomer distributions that are used as additives in the practice of this invention. Once the transparency value is known for a given brominated styrenic telomer distribution of this invention in optically clear styrene-acrylonitrile copolymer (SAN), it is not necessary thereafter to measure the

light transmission value of a brominated styrenic telomer distribution made in the same way using the same materials in the same proportions and under the same conditions.

[0010] The brominated flame retardant additive compositions of this invention comprise a translucent or transparent brominated styrenic telomer distribution as described above which when blended with a thermoplastic polymer (*i.e.*, a host polymer) results in the formation of a flame retarded polymer composition. Optionally, one or more other additive components may be included in the flame retardant additive compositions of this invention.

[0011] Thus, in one of its embodiments, this invention provides a flame retardant additive composition which comprises a brominated styrenic telomer distribution having a bromine content in the range of about 50 to about 75 wt% and a percent transmission in optically clear styrene-acrylonitrile copolymer in the CIE L* test method as described herein of at least about 60, desirably at least about 75, and more desirably at least about 90, wherein such brominated telomer distribution has an M_w of about 422 to about 4,000, an M_n of about 420 to about 2,400, an M_z of about 436 to about 4,800, a polydispersity in the range of about 1.01 to about 2.0, a standard deviation of about 29.0 to about 2,000, and an asymmetry of about 90 to about 0.6, a glass transition temperature (T_g) in the range of about 25°C to about 100°C, a 5% weight loss by thermogravimetric analysis (TGA) under nitrogen greater than about 270°C, and a thermal HBr value at 300°C of less than about 500 ppm.

[0012] In another embodiment of this invention, these compositions further comprise a flame retardant additive composition wherein the brominated styrenic telomer distribution has (i) a thermal color value after heating for 15 minutes under nitrogen at 250°C of less than about 35, (ii) a thermal color value after heating for 20 minutes under nitrogen at 300°C of less than about 40, and (iii) as a 10 wt% solution in chlorobenzene, a ΔE value of less than about 25.

[0013] As indicated above, two components, A) and B), are used in preparing the telomer distributions which in turn are brominated to form the brominated telomer distributions used in the practice of this invention. Desirably component A) is styrene and component B) is one or more of (i) toluene, (ii) o-xylene, (iii) p-xylene, (iv) m-xylene. Use of these components provides additive compositions of this invention which, after bromination, have the highest values in the CIE L* test method as described herein when tested in optically clear styrene-acrylonitrile copolymer (SAN).

[0014] While this invention provides and utilizes telomer distributions that, after bromination, are either polymeric or non-polymeric, the more desirable type of flame retardants in the marketplace are polymeric flame retardants. Thus, the polymeric brominated telomer distributions of this invention are preferred. Such polymeric brominated telomer distributions are formed from styrene, and one or more of (i) toluene, (ii) o-xylene, (iii) p-xylene, (iv) m-xylene; wherein the telomer distribution has, prior to bromination, an M_w in the range of about 400 to about 1000, an M_n in the range of about 500 to about 600, an M_z in the range of about 600 to about 1250, a standard deviation in the range of about 130 to about 350, and asymmetry in the range of about 1.5 to about 2.6; and wherein such polymeric brominated telomer distributions of this invention often have percent light transmission values as measured in SAN by the CIE L* test method as described herein as high as about 75 or above.

[0015] The bromine content of the brominated telomer distributions used in the practice of this invention is typically in the range of about 50 to about 75 wt% and desirably in the range of about 65 to about 74 wt%. The flame retarded thermoplastic polymer compositions of this invention typically contain an amount of bromine provided by the brominated telomer distributions of this invention sufficient to provide suitable flame retardancy to the host polymer. An effective flame retardant amount of a flame retardant additive of this invention may vary depending upon the host polymer being flame retarded, specifications developed by the user of the flame retardant, and so on. Generally speaking however, an effective flame retardant amount is an amount of the flame retardant that provides a bromine content in the range of about 2 to about 20 wt% of bromine based on the total weight of the finished translucent or transparent polymer composition.

[0016] The compositions of this invention preferably contain a flame retardant synergist, *i.e.* a substance which is in the form of a finely divided powder, preferably in the form of submicron-sized particles, and which enhances the effectiveness of the flame retardant used. Among synergists which can be used in the practice of this invention are antimony trioxide, antimony pentoxide, zinc borate, zinc hydroxystannate, zinc stannate, sodium antimonite, zinc oxide, titanium dioxide, tin oxide, bismuth oxide, mixed oxides of boron and zinc, alkaline earth borate (preferably calcium borate), and alkaline earth metal oxides (such as calcium oxide, strontium oxide, barium oxide), barium sulfate, zinc sulfide, dodecaboron tetrazinc docosaoxide heptahydrate, magnesium orthoborate, magnesium

pyroborate, strontium tetraborate, and suitable mixtures of two or more of these materials, each of which is preferably of submicron size or should be reduced to submicron size. Of these flame retardant synergists, submicron-sized antimony trioxide, submicron-sized antimony pentoxide or mixtures of them are presently preferred. In the case of the flame retardant additive compositions of this invention, amounts of such synergists in the range of about 1 to about 10 wt% should be used. The flame retarded polymer compositions of this invention will typically contain in the range of about 3 to about 25 wt% based on the weight of the total flame retarded polymer composition.

[0017] Thermoplastic polymers in which the additive compositions of this invention are blended include polystyrene, styrene-acrylonitrile copolymer (SAN), polycarbonate, polyphenylene oxide (PPO), polymethylmethacrylate (PMMA), high-impact polystyrene (HIPS), acrylonitrile-butadiene-styrene terpolymer, polyesters (*e.g.*, polyethylene terephthalate (PET), polybutylene terephthalate (PBT), *etc.*), polyamides (*e.g.*, polyamide 6, polyamide 66, *etc.*) or blends or alloys thereof, especially blends of PPO and HIPS and blends of polycarbonate and ABS. The preferred polymers are HIPS and ABS.

[0018] Highly desirable flame retarded compositions of this invention are those in which HIPS or ABS contains a brominated styrenic telomer distribution of this invention, especially a telomer distribution made from styrene and toluene or one or more xylene isomers, especially when the composition also contains at least one suitable flame retardant synergist such as submicron-sized antimony trioxide, submicron-sized antimony pentoxide, or a mixture of both of them.

[0019] When forming flame retarded polymer blends of this invention a brominated flame retardant additive composition of this invention comprising a brominated styrenic telomer distribution is blended with the host polymer, typically using a melt blend procedure. When the flame retarded polymer blend of this invention is to additionally contain a flame retardant submicron-sized synergist, a brominated flame retardant additive composition of this invention comprising a brominated styrenic telomer distribution and a submicron-sized synergist can be used. Alternatively, the brominated flame retardant telomer distribution and the submicron-sized synergist can be blended as separate components to the host polymer. When forming blends containing the submicron-sized synergist, the use of an additive of this invention containing a brominated flame retardant telomer distribution and the submicron-sized synergist is more desirable since it reduces the likelihood of blending errors and reduces the complexity of the blending operations.

Test Equipment and General Description of CIE L* Test Method

[0020] The CIE L* test method as described herein involves use of the following equipment: A Hunter labs ColorQuest XE colorimeter is used to measure the CIE L*a*b*¹ color space coordinates of the plastic plaques. The measurements are made in transmission using a D65 light source and a 10 degree observer. This light source approximates mid-day sunlight and the observer angle defines the field of view for the light detector. The translucency is reported as the L* coordinate as it has been observed that this parameter correlated best with the way samples are ranked by eye.

[0021] The CIE L*a*b*¹ color space is an international standard specified by the International Commission on Illumination (CIE = Commission Internationale d'Eclairage). This is a difference measurement where a standard is defined as having coordinates of L* = 100, a* = 0 and b* = 0. Then the sample is measured relative to the standard. Usually air is used as the standard in transmission measurements on solid samples. L* is the lightness and is derived from the total light intensity measured by the detector. If no light propagates through the sample then L* = 0. If the sample is colorless, free of voids and perfectly transparent then L* would be very close to 100, being slightly less due to losses from scattering when the light rays enter and leave the sample. The coordinates a* and b* relate to color shifts (a* = +red / -green, b* = +yellow / -blue) due to parts of the white light spectrum being preferentially absorbed by the sample.

[0022] The plaques must be held in the light path in a reproducible manner for consistent results. To accomplish this a 33 mm path length rectangular glass cell is positioned in front of the transmission port (source of incident light) of the colorimeter. Then the sample plaques are pressed up against the cell and the measurements made. Therefore the sample plaques are positioned slightly more than 33mm from the transmission port. For the standard measurement (L* = 100, a* = 0, b* = 0) only the glass cell is in the light path. Hence the measured L* values for the plastic plaques are approximately relative to air.

Preparation of Test Plaques for Use in the CIE L* Test Method

[0023] This test method can be used for different purposes in the practice of this invention:

[0024] A) One use is as a means of determining whether a given brominated styrenic telomer distribution has sufficient light transmission properties to be suitable for use as flame retardant additive in the practice of this invention, *i.e.*, whether the test plaque of the

brominated styrenic telomer distribution provides a CIE L* light transmission test value of about 60 or above. In this situation the test plaques are formed from the brominated styrenic telomer distribution and optically clear SAN by forming a uniform blend of these materials in powder form such as by hand mixing or by use of a tumble mixer (about 350-365g). The mixture is added to the mixing chamber of a Brabender Plasti-corder machine heated at about 190-200°C and the rotor speed is set at 25 rpm. Depending on the plasticizing effect of the flame retardant additive (which normally tracks the T_g of the flame retardant additive), the temperature is lowered and mixing continued. When the torque increases indicating that good mixing is achieved, the rotor speed is then increased to 50 rpm and mixing continued for 5 minutes. The rotors are stopped and the mixing chamber is then opened to collect the formulated resin. The material is then pressed between two hot plates at 150-200°C under a pressure of up to 20,000 psi using a 1/32" mold followed by cooling to room temperature. The total time for the compression molding is about 5 minutes. The finished test plaques, after release from the mold and after cooling, have a thickness of approximately 1/32 of an inch (approximately 0.8mm).

[0025] B) Another use of this test method is as a means of determining the light transmission properties of a flame retarded thermoplastic polymer composition of this invention comprising a blend of (i) one or more than one host polymer, (ii) a brominated styrenic telomer distribution, suitable for use as a flame retardant additive in the practice of this invention because it meets or exceeds the test value in A) above, and optionally (iii) one or more additives suitable for use in the thermoplastic polymer, such as a flame retardant synergist and/or other type(s) of additive components. In this situation the test plaques are formed from such flame retarded thermoplastic polymer of this invention by forming a uniform blend of these materials by extrusion compounding. The host polymer resin and flame-retardant(s) are hand mixed in a plastic bag prior to extrusion. The compounding is conducted on a Werner & Pfleiderer ZSK30 twin-screw extruder at 175 rpm. The feed rate is 8 kg/hr and the temperature profiles are set between 190-220°C. The extruded strand is pelletized on-line. The pellets are then compression molded to 1/32" (approx 0.8mm) plaques as described in A). Alternatively this same procedure can be used for preparing test plaques of other flame retardants for comparative purposes.

[0026] C) Still another use of this test method is as a means of determining whether a given thermoplastic polymer has sufficient light transmission properties to be suitable for use as a host resin in the practice of this invention, *i.e.*, whether the test plaque of the host

polymer provides a CIE L* test value of at least about 15. In this situation the test plaques are formed from such thermoplastic polymer under consideration for use as a host polymer. The compounding of the resin and additives and molding of the test pieces are conducted as in the procedure described in B).

5 [0027] Except for thermal color analysis, applicable analytical methods for assaying properties of the styrenic telomer distributions, and the brominated styrenic telomer distributions (BrSSTD) are set forth in International Publication Number WO 2008/154453 A1 having an International Publication Date of 18 December 2008. The procedure for thermal color analysis is as follows: A custom made metal heating block
10 from J-Kem Scientific (St. Louis, MO) featuring 12 heating ports with diameters to snugly fit 20 ml flat bottom scintillation vials is used. The heating block is placed in a in a nitrogen-purged glove box and heated to the test temperature (either 250 or 300°C). Duplicate 5-gram samples of the BrSSTD powder are placed in 20 ml scintillation vials to be heat treated in the heating block. The material in the vials are heated for the specified
15 time (15 minutes at 250°C or 20 minutes at 300°C). Upon completion of the heat treatment or thermal aging period, the samples are immediately removed from the block and cooled under nitrogen. The samples are dissolved to make a 10 wt% solution in chlorobenzene. The solution color is of the dissolved sample in terms of L, a, b and Delta E is measured and compared to a chlorobenzene blank standard (L=100, a=0, b=0) using a
20 Hunter Lab ColorQuest XE Colorimeter (Reston, VA).

[0028] Methods for producing the brominated telomer distributions of this invention and their beneficial properties are illustrated by the following Examples in which all brominations were conducted in the bromination equipment described below:

[0029] A 5 L oil jacketed flask (bromination reactor) was equipped with an overhead
25 glass stirrer shaft, PTFE stirring paddle, a water-cooled condenser, thermowell, nitrogen inlet, and bottom drain valve. The reactor was vented through a calcium sulfate moisture trap to a well-stirred caustic scrubber to absorb co-product HBr and entrained Br₂. Additionally the reactor was outfitted with three inlet lines: 1) ¼" (6.4 mm) O.D. PTFE BCM feed for initial feed of BCM to the reactor; 2) ⅛" (3.2 mm) O.D. substrate/BCM
30 subsurface feed line; and 3) ⅛" (3.2 mm) O.D. Br₂ subsurface feed line. The Br₂ and SSTD/BCM feed lines are secured such that both inlet lines discharge their contents in close proximity creating a locally high reagent concentration. The bromination reactor was completely covered with aluminum foil to exclude light and the reaction was conducted in a darkened ventilation hood.

[0030] The bromination reactor was placed above a 6-liter water quench vessel with a $\frac{3}{8}$ " (9.5 mm) O.D. PTFE drain line that connects the bottom drain valve of the bromination reactor to the quench vessel to allow for direct transfer of the bromination reactor's contents. The quench vessel was oil jacketed and equipped with an over-head stirring mechanism, thermowell and was baffled for intimate mixing of organic and aqueous phases. The quench vessel had a nitrogen inlet and was purged to a caustic scrubber. The quench vessel had a bottom drain valve to enable transfer of the pot's contents to an intermediate 5-liter storage vessel.

[0031] The intermediate storage vessel was piped to transfer its contents to a wash kettle. The wash kettle was a 6-liter oil-jacketed, baffled reactor outfitted with an over-head stirrer, thermocouple and bottom drain valve. Product isolation is conducted in an oil jacketed resin kettle outfitted with a stainless steel stirring shaft, a pitched blade turbine impeller and a high torque stirring motor. The product is stripped of BCM first at ambient pressure until the pot temperature reaches about 120°C. Vacuum is then applied gradually and to remove residual bromination solvent with ending conditions of about 5 mmHg vacuum and 170°C. Upon completion of the vacuum strip the resin kettle is then restored to atmospheric pressure with N₂ and the contents discharged through a bottom drain valve into a Pyrex® tray having a PTFE sheet liner. Upon cooling the product is recovered as a resin, which is then finely ground prior to use in the CIE L* test method as described herein.

[0032] Three groups of runs were made to prepare the styrenic telomer distributions to be brominated by the above bromination procedure. In the first group, the following apparatus was employed:

[0033] A spherical glass 12 liter creased reactor with oil jacket was equipped with a reflux condenser, distillation head, submerged thermal couple, bottom drain valve, and stainless steel internal cooling coils. Temperature was tightly maintained at a set point via PID controller that regulates water flow to the cooling coils. Vigorous agitation was accomplished by means of a overhead stirring assembly comprised of 19 mm OD glass shaft with two sets of glass impellers, one set pitched and the other flat, fused to the shaft. The reactor is essentially free of all wetted PTFE parts or other polymeric fluorinated materials or elastomers.

[0034] The reactor was maintained under an inert dry N₂ atmosphere during all operations. The reactor was charged with the chain transfer agent(s) through a dip leg by means of a diaphragm pump. Alkyl lithium, additional solvents and the amine promoter

(TMEDA) were all fed subsurface to the stirred chain transfer agent(s) through the same dip leg. Styrene was pumped into the reactor by means of a metering pump through a 3" cylindrical column (1.75" dia. $\approx$ 100 g) of basic aluminum oxide (EMD Chemicals, aluminum oxide 90, mesh 70-230, column chromatography grade) and delivered as a fine stream or spray above the surface of the reaction mixture through two 1/16" OD feed nozzles.

EXAMPLE 1

Stripped Styrenic Telomer Distribution 1 (SSTD 1)

10 [0035] Toluene 5795 g, (6.7 liters, 62.89 mol) was charged to the reactor described above previously heated to reflux and azeotropically dried over a 4 hour period. The dried toluene was heated to 110° C with the oil jacket and PID controller operating the coiling coils both set at that temperature. Upon heating to the set point temperature, 76.5 g n-BuLi solution (2M in cyclohexane, 0.197 mol) was charged through the dip leg below the surface of the gently agitated (300 rpm) toluene reaction mixture. The feed line was then
15 flushed with 75 ml of anhydrous toluene. Next, 24.49 g of *N,N,N',N'*-tetramethylethylenediamine (TMEDA, 0.211 mol) was charged to the reactor through the subsurface feed line forming the characteristic bright red color of TMEDA complexed benzyl lithium anion with concomitant off gassing of butane. The subsurface line was
20 flushed with a second 75 ml aliquot of anhydrous toluene via metering pump. Additionally 350 ml of anhydrous toluene was fed at a constant rate during the anionic chain transfer polymerization process. Reactor agitation was increased to 510 rpm and 2323 g of styrene (99+%, 22.31 mol) were fed over 120 minutes. The well-calibrated metering pump was
25 programmed to feed at a constant rate of 19.4 g/min. Anhydrous cyclohexane (2x200 ml) was charged to the styrene feed system to flush the alumina bed. The styrene feed to the reactor was deemed complete when no further heat of reaction was observed generally signified by the closing of the automated control valve on the coiling coils.

[0036] The set point of PID temperature controller was maintained at 115°C and water was fed through the cooling coils as needed while the flow of the hot oil was altered to
30 bypass the reactor jacket. The reaction mixture was quenched at 80°C with a 50 ml aliquot of deoxygenated water resulting in a water white turbid mixture. The reaction mixture was washed with deoxygenated water (3 x 650 ml). Phase cuts were rapid and required little settling time. Water and any rag or emulsion was removed through the bottom drain valve.

[0037] The temperature of the oil jacket was increased to 130°C while the control valve to the cooling coils turned off. Cyclohexane, residual moisture and toluene are distilled through a simple distillation head (1 atm.) until a pot temperature of 115°C was observed. An aliquot was removed for analysis via GPC (M_p : 195, M_n : 313, M_w : 456, M_z : 815, PD: 1.46, Standard Deviation: 212, Asymmetry α_3 : 4.608).

[0038] The crude reaction mixture, 8875 g, was stripped via continuous operation of excess toluene to yield 3868 g of an intermediate product stream that had the following GPC analysis: M_p : 195, M_n : 303, M_w : 438, M_z : 763, PD: 1.44, Standard Deviation: 202, Asymmetry α_3 : 4.383. The continuous stripping was accomplished by means of wiped film evaporator (WFE, aka. Pope Still). WFE operating conditions were as follows: feed rate = 1.33 L/hr, oil jacket temperature = 110°C, Pressure = 100 mmHg and condenser temperature = 0°C. Additionally 247 g of toluene was collected in a dry ice trap, while the cold finger condensed 4854 g of a mixture of toluene and 1,3-diphenylpropane.

[0039] A second pass of 1237g of the concentrate through the WFE produced 794 g of a telomeric mixture with the following GPC profile M_n : 374, M_w : 528, M_z : 880, Standard Deviation: 240, Asymmetry α_3 : 4.112. WFE operating conditions were as follows: feed rate = 1.33 L/hr, oil jacket temperature = 220°C, Pressure = 25 mmHg and condenser temperature = 0°C. A mixture (50 g) of 1,3-Diphenylpropane and its structural isomers (methylated diphenylethanes) were collected as a distillate.

Brominated Stripped Styrenic Telomer Distribution 1 (BrSSTD-1)

[0040] To the 5 L bromination reactor described above was charged 3000 g of dry BCM (23 ppm moisture, Karl Fisher) and 4.14 g of $AlCl_3$. The BCM was cooled in the dark to -10 °C and a previously prepared 25 wt % solution comprised of 333 g of a distilled SSTD-11 mixture (M_w = 698) and 1000 g of dry BCM was charged to a dry, 2000 mL N_2 blanketed graduated cylinder outfitted with a 1/8" (3.2 mm) O.D. PTFE feed line placed to transfer the entire content of the cylinder by means of a peristaltic metering pump to the bromination reactor. The bromine (1397.4 g) was transferred via a peristaltic pump into a 1.5 liter graduated cylinder. This feed vessel was maintained under a N_2 atmosphere and was outfitted with a 1/8" (3.2 mm) O.D. PTFE feed line placed to transfer the desired amount of bromine solution by means of a peristaltic metering pump to the bromination reactor.

[0041] The two reagents were co-fed at predetermine relative rates such that the entire content of the two feeds were charged and simultaneously completed in 180 minutes with an average residence time of 90 minutes. Ample cooling was provided through out the operation such that the reaction temperature remains close to -5°C . Upon completion of the feed the reaction was allowed to stir for an additional 15 minutes and gradually warmed to 7°C to allow unreacted bromine to be consumed. The reaction mixture was transferred (gravity) to the 6 L quench vessel through the bottom drain valve and the $\frac{3}{8}$ " (9.5 mm) O.D. PTFE transfer line.

[0042] The quench vessel was previously charged with 1000 mL tap water (25°C) containing 10 grams of hydrazine hydrate and stirred at 400 rpm to assure intimate mixing of the organic and aqueous phase. The quench was exothermic and a 10°C temperature rise was observed. Agitation was slowed to 20 rpm and the organic phase was allowed to settle. The light colorless HBr aqueous phase gradually separated forming the top layer. The lower organic phase was transferred to a 5L storage vessel containing 1000 mL of 1 wt% NaBH_4 and 10% aqueous NaOH .

[0043] This two-phase system was then transferred to the 6 L wash kettle and refluxed (62°C) for 30 minutes. Agitation was interrupted and the bottom organic layer cut from the reactor. The organic layer was returned to the completely drained kettle and washed with 1000 mL of tap water until a pH of 10 was observed. The bromination solvent was removed until the volume was reduced to 1.2 liters. The concentrated product solution was transferred to the resin kettle, concentrated as described above and upon isolation yield 1040g of BrSSTD-1. The analytical data and results for the Translucency Test are reported in Table 1.

EXAMPLE 2

Stripped Styrenic Telomer Distribution 2 (SSTD 2)

[0044] The procedure as in Example 1 was repeated except that 2523 g of styrene (99+%, 24.22 mol) was fed to a reaction mixture comprised of 5191 g of toluene (6 liters, 56.34 mol), 94.27 g TMEDA (0.811 mol), 18.3 g potassium *t*-butoxide (0.163 mol) and 63.9 g *n*-BuLi solution (2M in cyclohexane, 0.165 mol) over a period of 153 minutes, a feed rate of 16.5 g/min. GPC results of the unstripped reaction mixture excluding toluene were M_p : 195, M_n : 377, M_w : 446, M_z : 517, PD: 1.18, Standard Deviation: 161, Asymmetry α_3 : 0.936.

[0045] The crude reaction mixture, 7027 g, was stripped via continuous operation of excess toluene to yield 4924 g of an intermediate product stream that had the following GPC analysis: M_p : 195, M_n : 377, M_w : 446, M_z : 517, PD: 1.18, Standard Deviation: 161, Asymmetry α_3 : 0.936. The continuous stripped was accomplished by means of wiped film evaporator (WFE, *aka.* Pope Still). WFE operating conditions were as follows: feed rate = 1.33 L/hr, oil jacket temperature = 120°C, Pressure = 250 mmHg and condenser temperature = 0 °C. Additionally 0 g of toluene was collected in a dry ice trap, while the cold finger condensed 2103 g of a mixture of toluene and 1,3-diphenylpropane.

[0046] A second pass of the concentrate through the WFE produced 3231 g of a telomeric mixture with the following GPC profile: M_p : 300, M_n : 367, M_w : 483, M_z : 634, PD: 1.32, Standard Deviation: 206, Asymmetry α_3 : 1.831. WFE operating conditions were as follows: feed rate = 1.33 L/hr, oil jacket temperature = 185°C, Pressure = 50 mmHg and condenser temperature = 0 °C. Additionally 440 g of toluene was collected in a dry ice trap, while the cold finger condensed 1177 g of a mixture of toluene and 1,3-diphenylpropane.

Brominated Stripped Styrenic Telomer Distribution 2 (BrSSTD 2)

[0047] A 333 g of SSTD 2 was brominated with 1530 g of bromine as described above for Example 1. This yielded 1110 g of a clear light yellow resin. Analytical results including transparency data are reported in Table 1.

EXAMPLE 3

Stripped Styrenic Telomer Distribution 3 (SSTD 3)

[0048] The procedure as in Example 1 was repeated except that 3004 g of styrene (99+%, 28.84 mol) was fed to a reaction mixture comprised of 3366 g of toluene (3.9 liters, 36.53 mol), 66.7 g TMEDA (0.574 mol), and 142.6 g n-BuLi solution (2M in cyclohexane, 0.367 mol) over a period of 113 minutes, a feed rate of 26.6 g/min. GPC results of the unstripped reaction mixture excluding toluene were M_p : 194, M_n : 253, M_w : 296, M_z : 361, PD: 1.17, Standard Deviation: 104, Asymmetry α_3 : 2.276.

[0049] The crude reaction mixture, 6471 g, was stripped via continuous operation of excess toluene to yield 4566 g of an intermediate product stream that had the following GPC analysis: M_p : 194, M_n : 254, M_w : 297, M_z : 360, PD: 1.17, Standard Deviation: 105, Asymmetry α_3 : 2.145. The continuous stripped was accomplished by means of wiped film evaporator (WFE, *aka.* Pope Still). WFE operating conditions were as follows: feed

rate = 1.33 L/hr, oil jacket temperature = 170°C, Pressure = 60 mmHg and condenser temperature = 0 °C. Additionally 226 g of toluene was collected in a dry ice trap, while the cold finger condensed 1631 g of a mixture of toluene and 1,3-diphenylpropane.

[0050] A second pass of the concentrate through the WFE produced 2069 g of a telomeric mixture with the following GPC profile: M_p : 301, M_n : 367, M_w : 403, M_z : 451, PD: 1.10, Standard Deviation: 115, Asymmetry α_3 : 1.795. WFE operating conditions were as follows: feed rate = 1.33 L/hr, oil jacket temperature = 165°C, Pressure = <0.1 mmHg and condenser temperature = 0 °C. A mixture (2459 g) of 1,3-diphenylpropane and its structural isomers (methylated diphenylethanes) were collected as a distillate.

[0051] A third pass of the concentrate through the WFE produced 796 g of a distillate with a GPC profile: M_p : 301, M_n : 301, M_w : 304, M_z : 308, PD: 1.01, Standard Deviation: 30, Asymmetry α_3 : 3.57. WFE operating conditions were as follows: feed rate = 1.33 L/hr, oil jacket temperature = 195°C, Pressure = <0.1 mmHg and condenser temperature = 0 °C. A mixture (1264 g) of a telomeric mixture was collected in the bottoms.

EXAMPLE 3 - Part A

Brominated Stripped Styrene Telomeric Distribution 3 (BrSSTD 3A)

[0052] A 333 g of SSTD 3 was brominated with 1397 g of bromine as described above for Example 1. This yielded 1040 g of a clear light yellow resin. Analytical results including transparency data are reported in Table 1.

EXAMPLE 3 - Part B

Brominated Stripped Styrenic Telomer Distribution 3 (BrSSTD 3B)

[0053] A 333 g of SSTD 3 was brominated with 1764 g of bromine as described above in Example 1. This yielded 1233 g of a clear light yellow resin. Analytical results including transparency data are presented in Table 1.

EXAMPLE 4

Stripped Styrenic Telomer Distribution 4 (SSTD 4)

[0054] The procedure as in Example 1 was repeated except that 5176 g of styrene (99+%, 49.70 mol) was fed to a reaction mixture comprised of 2200 g of *o*-xylene (2.5 liters, 20.72 mol), 38.6 g TMEDA (0.332 mol), and 128.4 g n-BuLi solution (2M in cyclohexane, 0.331 mol) over a period of 180 minutes, a feed rate of 32.4 g/min. GPC

results of the unstripped reaction mixture excluding *o*-xylene M_n : 340, M_w : 402, M_z : 483, PD: 1.18, Standard Deviation: 145, Asymmetry α_3 : 1.703.

[0055] The crude reaction mixture, 4259 g was stripped via continuous operation of excess *o*-xylene to yield 3617 g of an intermediate product stream that had the following GPC analysis: M_n : 346, M_w : 405, M_z : 480, PD: 1.17, Standard Deviation: 143, Asymmetry α_3 : 1.595. The continuous stripped was accomplished by means of wiped film evaporator (WFE, aka. Pope Still). WFE operating conditions were as follows: feed rate = 1.33 L/hr, oil jacket temperature = 130°C, Pressure = 30 mmHg and condenser temperature = 0 °C. Additionally the cold finger condensed 620 g of a mixture of *o*-xylene and 1-methyl-2-(3-phenylpropyl)benzene.

[0056] A second pass of the concentrate through the WFE produced 2874 g of a telomeric mixture with the following GPC profile: M_n : 387, M_w : 438, M_z : 505, PD: 1.13, Standard Deviation: 140, Asymmetry α_3 : 1.704. WFE operating conditions were as follows: feed rate = 1.33 L/hr, oil jacket temperature = 220°C, Pressure = 10 mmHg and condenser temperature = 0 °C. A mixture (713 g) of 1-methyl-2-(3-phenylpropyl)benzene and its structural isomers (dimethylated diphenylethanes) were collected as a distillate.

Brominated Stripped Styrenic Telomer Distribution 4 (BrSSTD 4)

[0057] A 333 g of SSTD 4 was brominated with 1397 g of bromine as described above in Example 1. This yielded 1041 g of a clear light yellow resin. Analytical results including transparency data are presented in Table 1.

[0058] In the second group of runs the following apparatus was employed: A 316 stainless steel 2-gallon Parr autoclave having thermal couple, bottom drain valve, cooling coils, heating mantle and twin pitch-blade turbine impellers was further equipped with diaphragm pump, nitrogen purged 250 ml stainless charge vessel, a well calibrated metering pump and a 1/16th inch OD subsurface feed line. The reactor was vented to a 3-liter water-jacketed flask with condenser. The bottom drain valve was plumbed to a 6 liter oil jacketed creased wash vessel having a bottom drain and outfitted for overhead stirring and distillation.

[0059] Bulk solvent (usually one and the same as the chain transfer agent) was charged to the reactor via diaphragm pump, TMEDA, butyllithium and any additional co-catalyst if used were charged to the reactor separately through the charging vessels. Each charge was flushed with a 100 ml aliquot of the solvent. Styrene is fed via metering pump at

predetermined constant rate through the 1/16th inch OD feed line. The tip was modified such that the styrene was fed with a velocity of 18-22 ft/s and delivered in close proximity to the bottom turbine impeller. Reaction temperature was tightly maintain at a predetermined set point using the Parr 4841 controller which balanced the out put to the heating mantle with that of a solenoid valve to the cooling coils.

[0060] The reactor was prepared by charging 4 liters of the reaction solvent (in most cases one and the same as the chain transfer agent) and heating to 155°C under super atmospheric conditions. Super heated solvent ($\approx$ 200 ml) was then flashed overhead to the 3-liter reactor. The bulk of the solvent was then cooled, removed from the reactor and analyzed for moisture (Karl Fischer). All transfers of catalyst components were made via syringe under inert atmosphere. Styrene (99%, Across), TMEDA (Aldrich), butyllithium (Aldrich) were each used as received from the vendor.

EXAMPLE 5

Stripped Styrenic Telomer Distribution 5 (SSTD 5)

[0061] *o*-Xylene 1214 g, ($\approx$ 1.38 liters, 11.44 mol) was mixed with 295g of recycled styrene *o*-xylene mono-adduct then was charged to the reactor; Karl Fischer moisture analysis indicated 28 ppm residual H₂O, this was dried with 7.55 g of n-BuLi solution. The dried *o*-xylene solution was heated to 95° C with the autoclave heater and PID controller operating the coiling coils. Upon reaching the set point temperature, 70.51 g n-BuLi solution (2M in cyclohexane, 0.182 mol) was charged through the dip leg below the surface of the gently agitated (300 rpm) *o*-xylene reaction mixture. The feed line was then flushed with 88 g of *o*-xylene. Next, 56.91 g of *N,N,N',N'*-tetramethylethylenediamine (TMEDA, 0.490 mol) was charged to the reactor through the subsurface feed line forming the TMEDA complexed benzyl lithium anion with concomitant off gassing of butane. The subsurface line was flushed with a second 88 g of *o*-xylene via metering pump. Reactor agitation was increased to 846 rpm and 2531 g of styrene (99+%, 42.08 mol) diluted with 1175 g of recycled styrene *o*-xylene mono-adduct was fed over 180.5 minutes. The well-calibrated metering pump was programmed to feed at a constant rate of 20.53 g/min. When the styrene tank was empty, *o*-xylene (100 ml) was charged to the styrene feed system to flush the line. The styrene feed to the reactor was deemed complete when no further heat of reaction was observed generally signified by the closing of the automated control valve on the coiling coils.

[0062] The temperature was controlled using a Parr 4841 controller. The temperature was maintained at 95°C with water fed through the cooling coils and heat added to the reactor jacket as needed. The reaction mixture was quenched at 80°C with a 12.9 g of isopropanol in 25 ml of *o*-xylene.

5 [0063] The reaction mixture was transferred to the glass oil-heated wash kettle and washed with deoxygenated water (3 x 200 mL). Phase cuts were rapid and required little settling time. Water and any rag or emulsion was removed through the bottom drain valve. The temperature of the oil jacket was increased to 160°C. Cyclohexane, residual moisture and *o*-xylene are distilled through a simple distillation head (1 atm.) until a pot
10 temperature of 140°C was observed. The resin was cooled and drained into a nitrogen-purged bottle (5596 g).

[0064] An aliquot was removed for analysis via GPC (M_p : 317, M_n : 298, M_w : 337, M_z : 388, PD: 1.13, Standard Deviation: 108, Asymmetry α_3 : 1.685).

[0065] The reaction mixture, 5596 g, was stripped via continuous operation of 551 g
15 excess *o*-xylene to yield 5060 g of an intermediate product stream. The continuous stripped was accomplished by means of wiped film evaporator (WFE, aka. Pope Still). WFE operating conditions were as follows: feed rate = 1.33 L/hr, oil jacket temperature = 150°C, Pressure = 30 mmHg and condenser temperature = 0 °C.

[0066] A 5032 g sample of the concentrate was run through the WFE produced 3207 g
20 of a telomeric mixture with the following GPC profile: M_p : 320, M_n : 372, M_w : 398, M_z : 431, PD: 1.07, Standard Deviation: 98, Asymmetry α_3 : 1.618. WFE operating conditions were as follows: feed rate = 1.33 L/hr, oil jacket temperature = 160°C, Pressure = <0.1 mmHg and condenser temperature = 0 °C. A mixture (1825 g) of 1-methyl-2-(3-phenylpropyl) benzene and its structural isomers were collected as a distillate.

25

Brominated Stripped Styrenic Telomer Distribution 5 (BrSSTD 5)

[0067] A 333 g of SSTD 5 was brominated with 1530 g of bromine as described above in the general bromination procedure. This yielded 1110 g of a clear light yellow resin. Analytical results including transparency data are presented in Table 1.

EXAMPLE 6**Stripped Styrenic Telomer Distribution 6 (SSTD 6)**

[0068] The procedure as in Example 5 was repeated except 3250 g of styrene (99+%, 31.20 mol) diluted with 444 g of *o*-xylene (4.18 mol),) was fed to a reaction mixture comprised of 1690 g of *o*-xylene (1.9 liters, 15.92 mol), 68.1 g TMEDA (0.586 mol) and 93.92 g n-BuLi solution (2M in cyclohexane, 0.242 mol) over a period of 190 minutes at 87°C, a feed rate of 19.4 g/min. The GPC results of the unstripped reaction mixture excluding *o*-xylene were M_p : 315, M_n : 323, M_w : 381, M_z : 457, PD: 1.18, Standard Deviation: 137, Asymmetry α_3 : 1.711. The reaction mass (5384 g) was collected in nitrogen purged glass bottles.

[0069] The reaction mixture, 3000 g, was stripped via continuous operation of 324 g excess *o*-xylene to yield 2671 g of an intermediate product stream. The continuous stripped was accomplished by means of wiped film evaporator (WFE, aka. Pope Still). WFE operating conditions were as follows: feed rate = 1.33 L/hr, oil jacket temperature = 150°C, Pressure = 30 mmHg and condenser temperature = 0 °C.

[0070] A 2658 g sample of the concentrate was run through the WFE produced 1983 g of a telomeric mixture with the following GPC profile: M_p : 313, M_n : 384, M_w : 431, M_z : 492, PD: 1.12, Standard Deviation: 134, Asymmetry α_3 : 1.655. WFE operating conditions were as follows: feed rate = 1.33 L/hr, oil jacket temperature = 140°C, Pressure = <0.1 mmHg and condenser temperature = 0 °C. A mixture (676 g) of 1-methyl-2-(3-phenylpropyl) benzene and its structural isomers were collected as a distillate.

Brominated Stripped Styrenic Telomer Distribution 6 (BrSSTD 6)

[0071] A 333 g of SSTD 6 was brominated with 1397 g of bromine as described above in Example 1. This yielded 1054 g of a clear light yellow resin. Analytical results including transparency data are presented in Table 1.

EXAMPLE 7**Stripped Styrenic Telomer Distribution 7 (SSTD 7)**

[0072] The procedure as in Example 5 was repeated except that 2034 g of styrene (99+%, 19.53 mol) diluted with 863 g of *o*-xylene (8.13 mol),) was fed to a reaction mixture comprised of 1690 g of *o*-xylene (1.9 liters, 15.92 mol), 70.2 g TMEDA (0.604 mol), 5.33 g potassium *t*-butoxide (0.048 mol) and 77.30 g n-BuLi solution (2M in cyclohexane, 0.199 mol) over a period of 136 minutes at 80°C, a feed rate of 21.3 g/min.

The GPC results of the unstripped reaction mixture excluding *o*-xylene were M_p : 210, M_n : 358, M_w : 457, M_z : 592, PD: 1.28, Standard Deviation: 188, Asymmetry α_3 : 1.934. The reaction mass (4509 g) was collected in nitrogen purged glass bottles.

[0073] The reaction mixture, 4484 g, was stripped via continuous operation of 1600 g excess *o*-xylene to yield 2884 g of an intermediate product stream. The continuous stripped was accomplished by means of wiped film evaporator (WFE, aka. Pope Still). WFE operating conditions were as follows: feed rate = 1.33 L/hr, oil jacket temperature = 141°C, Pressure = 25 mmHg and condenser temperature = 0 °C.

[0074] A 2814 g sample of the concentrate was run through the WFE produced 2399 g of a telomeric mixture with the following GPC profile: M_p : 316, M_n : 405, M_w : 498, M_z : 621, PD: 1.23, Standard Deviation: 194, Asymmetry α_3 : 1.786. WFE operating conditions were as follows: feed rate = 1.33 L/hr, oil jacket temperature = 140°C, Pressure = <0.1 mmHg and condenser temperature = 0 °C. A mixture (412 g) of 1-methyl-2-(3-phenylpropyl) benzene and its structural isomers were collected as a distillate.

[0075] A 1866 g sample of the first pass was run through the WFE produced 1601 g of a telomeric mixture with the following GPC profile: M_p : 316, M_n : 455, M_w : 531, M_z : 634, PD: 1.17, Standard Deviation: 186, Asymmetry α_3 : 1.832. WFE operating conditions were as follows: feed rate = 1.33 L/hr, oil jacket temperature = 140°C, Pressure = <0.1 mmHg and condenser temperature = 0 °C. A mixture (252 g) of 1-methyl-2-(3-phenylpropyl) benzene and its structural isomers were collected as a distillate.

Brominated Stripped Styrene Telomeric Distribution 7 (BrSSTD 7)

[0076] A 333 g of SSTD 7 was brominated with 1279 g of bromine as described above in Example 1. This yielded 979 g of a clear light yellow resin. Analytical results including transparency data are presented in Table 2.

EXAMPLE 8

Stripped Styrenic Telomer Distribution 8A(SSTD 8A)

[0077] The procedure as in Example 5 was repeated except 3163 g of styrene (99+%, 30.37 mol) diluted with 430 g of *p*-xylene (4.05 mol),) was fed to a reaction mixture comprised of 1677 g of *p*-xylene (2.0 liters, 15.80 mol), 30.4 g TMEDA (0.262 mol) and 41.51 g n-BuLi solution (2M in cyclohexane, 0.107 mol) over a period of 181 minutes at 95°C, a feed rate of 19.8 g/min. The GPC results of the unstripped reaction mixture excluding *p*-xylene were M_p : 209, M_n : 340, M_w : 415, M_z : 512, PD: 1.22, Standard

Deviation: 160, Asymmetry α_3 : 1.702. The reaction mass (5333 g) was collected in nitrogen purged glass bottles.

5 [0078] The reaction mixture, 4730 g, was stripped via continuous operation of 1109 g excess *p*-xylene to yield 3603 g of an intermediate product stream. The continuous stripped was accomplished by means of wiped film evaporator (WFE, aka. Pope Still). WFE operating conditions were as follows: feed rate = 1.33 L/hr, oil jacket temperature = 155°C, Pressure = 30 mmHg and condenser temperature = 0 °C.

10 [0079] A 1207.6 g sample of the concentrate was run through the WFE produced 880 g of a telomeric mixture with the following GPC profile: M_p : 313, M_n : 430, M_w : 492, M_z : 578, PD: 1.14, Standard Deviation: 163, Asymmetry α_3 : 1.926. WFE operating conditions were as follows: feed rate = 1.33 L/hr, oil jacket temperature = 165°C, Pressure = <0.1 mmHg and condenser temperature = 0 °C. A mixture (321 g) of 1-methyl-4-(3-phenylpropyl) benzene and its structural isomers were collected as a distillate.

Stripped Styrenic Telomer Distribution 8B (SSTD 8B)

15 [0080] The procedure as in Example 5 was repeated except 3166 g of styrene (99+%, 30.40 mol) diluted with 431 g of *p*-xylene (4.06 mol),) was fed to a reaction mixture comprised of 1692 g of *p*-xylene (2.0 liters, 15.94 mol), 20.9 g TMEDA (0.180 mol) and 29.18 g n-BuLi solution (2M in cyclohexane, 0.075 mol) over a period of 184 minutes at 95°C, a feed rate of 19.9 g/min. The GPC results of the unstripped reaction mixture
20 excluding *p*-xylene were M_p : 212, M_n : 398, M_w : 523, M_z : 687, PD: 1.31, Standard Deviation: 223, Asymmetry α_3 : 1.852. The reaction mass (5004 g) was collected in nitrogen purged glass bottles.

[0081] The reaction mixture, 3993 g, was stripped via continuous operation of 1753 g excess *p*-xylene to yield 2221 g of an intermediate product stream. The continuous
25 stripped was accomplished by means of wiped film evaporator (WFE, aka. Pope Still). WFE operating conditions were as follows: feed rate = 1.33 L/hr, oil jacket temperature = 155°C, Pressure = 35 mmHg and condenser temperature = 0 °C.

[0082] A 1118 g sample of the concentrate was run through the WFE produced 904 g of a telomeric mixture with the following GPC profile: M_p : 314, M_n : 495, M_w : 625, M_z : 810,
30 PD: 1.26, Standard Deviation: 254, Asymmetry α_3 : 2.067. WFE operating conditions were as follows: feed rate = 1.33 L/hr, oil jacket temperature = 165°C, Pressure = <0.1 mmHg and condenser temperature = 0 °C. A mixture (205 g) of 1-methyl-4-(3-phenylpropyl) benzene and its structural isomers were collected as a distillate.

Brominated Stripped Styrenic Telomer Distribution 8 (BrSSTD 8)

[0083] 313.1 g of SSTD 8A was blended with 189.5 g of SSTD 8B to form a composite with the following molecular weight distribution as determined by GPC: M_n : 459, M_w : 555, M_z : 701, PD: 1.21, Standard Deviation: 134, Asymmetry α_3 : 1.655. A 333 g of this blend was brominated with 1279 g of bromine as described above in Example 1. This yielded 1009 g of a clear light yellow resin. Analytical results including transparency data are presented in Table 2.

EXAMPLE 9

Brominated Stripped Styrene Telomer 9 (BrSST 9)

[0084] A 333 g sample of a styrenic telomer distribution recovered from the wiped film evaporator strip of Examples 5 and 6 having a molecular weight distribution of M_n : 210, M_w : 212, M_z : 216, PD: 1.01 as determined by GPC was brominated with 1530 g of bromine as described above in Example 1. The work up procedure was as above except that the product solution was not concentrated but instead allowed to crystallize. The product was recovered by filtration and upon drying yielded 600 grams of a solid resin. Analytical results including transparency data are presented in Table 2.

EXAMPLE 10

Brominated Stripped Styrene Telomer 10 (BrSST 10)

[0085] A 333 g sample of a styrenic telomer distribution recovered from the wiped film evaporator strip of Examples 5 through 6 having a molecular weight distribution of M_n : 210, M_w : 212, M_z : 216, PD: 1.01 as determined by GPC was brominated with 1853 g of bromine as described above in Example 1. The work up procedure was as above except that the product solution was not concentrated but instead allowed to crystallize. The product was recovered by filtration and upon drying yielded 700 grams of a solid resin. Analytical results including transparency data are presented in Table 2.

[0086] The third series of runs were conducted in a semi-commercial scale using the equipment described below:

[0087] A glass-lined, 200-gallon jacketed reactor equipped with an overhead condenser, submerged thermal well/ thermal couple and a bottom drain valve. Temperature was maintained at a set point by controlling the temperature of the water flowing through the jacket using a steam control valve. Vigorous agitation was accomplished by means of a

three-blade, retreat-curve agitator on a variable speed drive. The reactor is essentially free of all wetted PTFE parts or other polymeric fluorinated materials or elastomers.

[0088] The reactor was maintained under an inert dry N₂ atmosphere during all operations. The reactor was charged with the chain transfer agent(s) through a dip leg by means of pressure transfer from a portable tank. Alkyl lithium, additional solvents and the amine promoter (TMEDA) were all fed subsurface to the stirred chain transfer agent(s) through the same dip leg. Styrene was pressure transferred from a portable, pressure vessel by means of a metering valve and delivered as a fine stream or spray above the surface of the reaction mixture through a full-cone spray nozzle.

EXAMPLE 11

Stripped Styrenic Telomer Distribution 11 (SSTD 11)

[0089] Toluene 202 pounds, (995 mol) was charged to the reactor and agitation began. Upon reaching the set point temperature, 5.2 pounds of N,N,N',N'-tetramethylethylenediamine (TMEDA, 20.4 mol) was charged to the reactor through the dip leg below the surface of the agitated toluene reaction mixture. The feed line was then flushed with 14.4 pounds (71 mol) of anhydrous toluene. Next, 10.6 lb n-BuLi solution (10 wt% in toluene) (7.5 mol n-BuLi) was charged through the subsurface feed line forming the characteristic bright red-orange color of TMEDA complexed benzyl lithium anion with concomitant off gassing of butane. The feed line was then flushed with 14.4 pounds (71 mol) of anhydrous toluene. The solvent was heated to 88° C by applying tempered water to the vessel jacket. 555 lb of styrene (99+%, 2423 mol, American Styrenics) were fed over 153 minutes. When the styrene feed began, a temperature rise to 92°C was observed. The reaction temperature oscillated between 88 and 92°C for the duration of the styrene feed. The styrene was added by means of pressure transfer from a nitrogen regulated portable tank through a metering valve at a constant feed rate of 3.6 lb/min. The reactor was allowed to ride for 5 minutes to make certain the reaction was complete.

[0090] The reaction mixture was quenched at 70°C with 15 gallons of 1.1 wt% ammonium chloride solution which had been deoxygenated overnight. The reaction mixture was washed two times with an additional 12 gallons of deoxygenated water each. Phase cuts were rapid and required little settling time. Water and any rag or emulsion was removed through the bottom drain valve.

[0091] The reactor was cooled to 50°C. Vacuum was applied to the vessel and the reactor was heated to boiling point. Steam was then applied to the reactor jacket to increase the temperature of the reactor jacket to 140°C. Vacuum was used to decrease the reactor pressure to 100 mm Hg. Residual moisture and toluene boiled and condensed in the overhead condenser, then drained to a drum until a pot temperature of 135°C was observed. An aliquot was removed from the reactor for analysis via GPC (M_p : 196, M_n : 353, M_w : 471, M_z : 636, PD: 1.3, Standard Deviation: 204, Asymmetry α_3 : 2.076). An additional charge of 58 pounds (286 mol) of anhydrous toluene was made to the 200-gallon reactor. The reaction mass (869 lbs) was collected in a 350-gallon tote bin.

[0092] The reaction mixture, 3682 g, was stripped via continuous operation of 475 g excess toluene to yield 3192 g of an intermediate product stream. The continuous stripped was accomplished by means of wiped film evaporator (WFE, aka. Pope Still). WFE operating conditions were as follows: feed rate = 1.33 L/hr, oil jacket temperature = 145°C, Pressure = 30 mmHg and condenser temperature = 0 °C.

[0093] A 3186 g sample of the concentrate was run through the WFE produced 2411 g of a telomeric mixture with the following GPC profile: M_p : 300, M_n : 452, M_w : 546, M_z : 678, PD: 1.21, Standard Deviation: 206, Asymmetry α_3 : 1.983. WFE operating conditions were as follows: feed rate = 1.33 L/hr, oil jacket temperature = 145°C, Pressure = <0.1 mmHg and condenser temperature = 0 °C. A mixture (747 g) of 1,3-diphenylpropane and its structural isomers were collected as a distillate.

EXAMPLE 11 - Part A

Brominated Stripped Styrenic Telomer Distribution 11A (BrSSTD 11A)

[0094] A 333 g of SSTD 11 was brominated with 1397 g of bromine as described above in Example 1. This yielded 1040 g of a clear light yellow resin. Analytical results including transparency data are presented in Table 2.

EXAMPLE 11 - Part B

Brominated Stripped Styrenic Telomer Distribution 11B (BrSSTD 11B)

[0095] A 333 g of SSTD 11 was brominated with 1279 g of bromine as described above in Example 1. This yielded 988 g of a clear light yellow resin. Analytical results including transparency data are presented in Table 2.

TABLE 1

Example (BrSSTD)	1	2	3A	3B	4	5	6
SSTD	1	2	3	3	4	5	6
Starting Methylbenzene	Toluene	Toluene	Toluene	Toluene	<i>o</i> -Xylene	<i>o</i> -Xylene	<i>o</i> -Xylene
SSTD GPC Results							
M _n	374	367	301	301	387	372	384
M _w	528	483	304	304	438	398	431
M _z	880	634	308	308	505	431	492
PD	1.41	1.32	1.01	1.01	1.13	1.67	1.12
Standard Deviation	240.0	206.3	30.0	30.0	140.5	98.35	134.34
Asymmetry	4.12	1.83	3.57	3.57	1.69	1.62	1.66
% Br	68	70	69	74	68	70.0	68.4
DSC							
Tg (°C) (DSC)	43.23	43.6	36.6	25.91	53.6	57.80	54.38
TGA							
1% Wt. Loss (°C)	224.4	260.3	277.81	124.34	276.5	297.70	270.94
5% Wt. Loss (°C)	298.84	307.3	329.16	314.16	326.92	346.81	327.56
10% Wt. Loss (°C)	331.33	330.6	348.23	349.89	346.65	361.89	349.41
50% Wt. Loss (°C)	386.78	390.1	391.33	395.05	393.25	396.66	395.95
Thermal HBr-FP 300°C (ppm)	213	<50	206	384	329	<50	<50
BrSSTD GPC							
M _n	1270	1470	1094	1189	1480	1126	980
M _w	1400	1730	1107	1193	1620	1146	1320
M _z	1650	2061	1126	1196	1875	1169	1690
PD	1.11	1.18	1.01	1.003	1.09	0.00	1.35
Color							
L	95.69	0.96	99.4	99.04	95.86	99.32	99.54
a	-1.58	-0.23	-0.24	-0.31	-3.21	-0.65	-0.39
b	13.97	3	1.72	3.25	18.26	2.76	1.33
Delta E	14.8	3.15	1.91	3.93	18.9	2.92	1.58
Thermal Color							
250°C 15 minutes	22.64	5.82	NA	9.95	30.53	7.50	3.73
300°C 20 minutes	34.60	9.68	NA	18.45	35.51	17.75	11.15
CIE L* Test Method Using the CIE L* Test Procedure as Described Herein, Plaques Formed as in A)							
Test value	79.7	59.5	96.4	96.7	96.6	64.07	95.4

TABLE 2

Example (BrSSTD)	7	8	9	10	11A	11B
SSTD	7	8	9	10	11	11
Starting Methylbenzene	<i>o</i> -Xylene	<i>p</i> -Xylene	<i>o</i> -Xylene	<i>o</i> -Xylene	Toluene	Toluene
SSTD GPC Results						
M _n	455	459	210	210	452	452
M _w	531	555	212	212	546	546
M _z	634	701	216	216	678	678
PD	1.17	1.21	1.01	1.01	1.21	1.21
Standard Deviation	185.96	209.91	20.49	20.49	206.13	206.13
Asymmetry	1.83	2.29	10.54	10.54	1.98	1.98
% Br	66.0	66.1	70.3	74.4	68.0	66.3
DSC						
MP (°C) (DSC)			152.90	169.40		
Tg (°C) (DSC)	60.18	52.10			60.37	49.90
TGA						
1% Wt. Loss (°C)	272.77	278.19	238.68	269.73	289.90	267.99
5% Wt. Loss (°C)	341.86	338.68	272.80	305.83	341.91	336.46
10% Wt. Loss (°C)	357.53	356.14	288.23	322.70	356.63	353.41
50% Wt. Loss (°C)	395.46	392.58	329.73	370.24	391.30	388.79
Thermal HBr 300°C (ppm)	<50	<50	<50	94	<50	<50
BRSSSTD GPC						
M _n	1354	1417	736	Not Soluble	1580	1242
M _w	1544	1640	750	Not Soluble	1970	1507
M _z	1829	2013	766	Not Soluble	2720	1856
PD	1.14	1.16	1.02	Not Soluble	1.25	1.21
Color (Solution)						
L	99.79	91.54	Not Soluble	Not Soluble	98.87	99.69
a	-0.19	-0.55	Not Soluble	Not Soluble	-0.53	-0.19
b	0.98	6.95	Not Soluble	Not Soluble	3.34	1.06
Delta E	1.04	13.13	Not Soluble	Not Soluble	3.58	1.13
Thermal Color						
250 °C/15min	2.44	22.54	Not Soluble	Not Soluble	7.63	3.98
300 °C/20min	7.03	34.21	Not Soluble	Not Soluble	20.13	13.56
CIE L* Test Method Using the CIE L* Test Procedure as Described Herein, Plaques Formed as in A)						
Test value	96.7	62.3	97.4	85	96.0	96.3

[0096] From the translucency test data in Tables 1 and 2, it can be seen that in all cases the CIE L* test values were at least about 60, the 59.5 value of Example 2 is a value that rounds to 60.

5 [0097] The trend that becomes apparent from the translucency test data in Tables 1 and 2 is the importance of styrenic telomer microstructure with respect to performance in the CIE L* test method as described herein. Materials formed exclusively from toluene and styrene form telomeric distributions that after bromination, exhibit increased transparency test performance over a broad range of molecular weight distributions and higher bromine
10 content. Because toluene has only one methyl group a telomer formed from toluene and styrene cannot readily form a branch and the structure remains linear. Xylene-based styrenic telomer distributions have a propensity under certain process conditions to have branch points. Nevertheless, using certain novel process conditions such as shown in Examples set forth above results in novel xylene-based styrenic telomer distributions
15 which, after bromination, provide flame retardant additives and flame retardant compositions exhibiting high transparency. The trends observed in our laboratory are that with an increase in branched microstructure content there is a decrease in miscibility and as exhibited by a greatly reduced transparency, *e.g.*, the light transmission values in the CIE L* test method as described herein are significantly below 60 and typically as low as
20 40 or below.

[0098] In order to still further demonstrate the advantages available from the practice of this invention, a group of comparative tests were conducted in HIPS and ABS using the CIE L* test method as described herein

[0099] The HIPS resin and flame-retardants were hand mixed in a plastic bag prior to
25 extrusion. The compounding was conducted on a Werner & Pfleiderer ZSK30 twin-screw extruder at 175 rpm. The feed rate was 8 kg/hr. The temperature profile was 175-175-190-215-215°C. The extruded strand was pelletized on-line. All formulations were injection molded at a Battenfeld BA350 CD injection-molding machine. The temperature profile was 195-195-205°C. The mold temperature was 40°C.

30 [0100] The ABS resin was dried for four hours at 80°C prior to being weighed. The powders and pellets were hand mixed in a plastic bag prior to extrusion. The compounding was conducted on a Werner & Pfleiderer ZSK30 twin-screw extruder at 175 rpm. The temperature profile was 190-210-210-220-220°C. The extruded strand was

pelletized on-line. The ABS compounds were dried for four hours at 80°C and then injection molded at a Battenfeld BA350 CD injection-molding machine. The temperature profile was 204-216-221 °C. The mold temperature was 40°C.

[0101] Evaluation of the test samples was performed on samples according to the following ASTM test standards: Tensile Strength (D638) specimen type 1; Flexural Strength (D790) method 1; Heat Deflection Temperature under Load (D648) 1/8" at 264 psi; Vicat softening temperature (D1525) 1/8" at 1 Kg; Notched-Izod Impact Strength (D256) method A; Gardner Impact Strength (D3029) method G; and Melt Flow Rate (D1238) procedure A, 200°C/5Kg for HIPS and 230°C/3.8 Kg for ABS. The color measurements were made using HunterLab scale, D65 illuminant, 10° observer, and integrated-sphere geometry.

[0102] The HIPS used in these tests was a commercial HIPS product from Ineos Nova, LLC. The flame retardants used in these tests were 2,4,6-Tris(2,4,6-tribromophenoxy)-1,3,5 triazine commonly referred to as FR245, a widely used translucent flame retardant from ICL Industrial Products, and two brominated flame retardant additives of this invention. One of these was brominated stripped styrenic telomer distribution 7 (BrSSTD 7) produced in Example 7 hereof and the other was brominated stripped styrenic telomer distribution 11A (BrSSTD 11A) produced in Example 11 hereof. Each HIPS polymer blend contained antimony trioxide (ATO) in the form of a white powder but not of submicron size (Brightsun HB; M Chemical Company, Inc.). The make-up of the test compositions and the test results are summarized in Table 3.

TABLE 3

Ingredient		Units	Comparative Example A	Example 12	Example 13
Ineos Nova 495F HIPS		Wt %	81.1	80.8	80.8
FR-245		Wt %	14.9		
BrSSTD 7		Wt %		15.2	
BrSSTD 11A		Wt %			15.2
Brightsun HB (ATO)		Wt %	4.0	4.0	4.0
Property	Conditions	Units			
Flammability					
UL-94	UL94 1/8"	Rating	V-0	V-0	V-0
		seconds	16	30	13

Thermal Properties					
Melt Flow Index	ASTM D1238	200°C/5kg g/10 min	17.8	18.4	20.0
HDT	ASTM D648 at 120°C/hr	°C	70.5	68.0	66.4
VICAT	ASTM D648 at 50°C/hr	°C	94.5	91.4	89.8
Physical Properties					
Gloss	60°	n/a	64.4	64.8	64.1
Initial Color on discs	LAV, UV excluded 10° D65 YI: 2°C	L	93.65	93.36	93.24
		a	-0.43	-0.41	-0.43
		b	3.23	3.64	3.39
		YI (D1925)	5.86	6.70	6.20
Mechanical Properties					
Tensile Strength	ASTM D638	psi X 10^3	3.7	3.8	3.7
Tensile Modulus	ASTM D638	psi X 10^5	3.1	3	3.1
Elongation at yield	ASTM D638	%	1.5	1.55	1.47
Elongation at Break	ASTM D638	%	18.27	13.07	10.56
Flexural Strength	ASTM D790	psi X 10^3	6.8	7.4	6.7
Flexural Modulus	ASTM D790	psi X 10^5	3.7	3.3	3.3
Izod Impact	ASTM D256	ft-lb/in	1.746	1.702	1.671
Optical Property					
CIE L* Value	As described herein ¹	%	21.31	21.84	22.05

¹ Plaques Formed as in

[0103] The ABS used in these tests was a commercial ABS product from SABIC Innovative Plastics. This particular resin is identified as SABIC MG47. The flame retardants used in these tests were 2,4,6-Tris(2,4,6-tribromophenoxy)-1,3,5 triazine commonly referred to as FR245, a widely used translucent flame retardant from ICL Industrial Products, and two brominated flame retardant additives of this invention. One of these was brominated stripped styrenic telomer distribution 7 (BrSSTD 7) produced in Example 7 hereof and the other was brominated stripped styrenic telomer distribution 11A (BrSSTD 11A) produced in Example 11 hereof. Each ABS polymer blend contained antimony trioxide in the form of a white powder not of submicron size (Brightsun HB; M Chemical Company, Inc.) and a 1:1 blend of penterthritol tetrakis (3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate) and tris-(2,4-di-tert-butylphenyl)phosphate, an antioxidant-

stabilizer blend (ALBlend[®] 181 antioxidant: Albemarle Corporation). The make-up of the test compositions and the test results are summarized in Table 4.

TABLE 4

Ingredient		Units	Comparative Example B	Example 14	Example 15
SABIC MG47		Wt%	75.0	77.2	77.2
FR-245		Wt%	17.9		
BrSSTD 7		Wt%		18.2	
BrSSTD 11A		Wt%			18.2
Brightsun HB (ATO)		Wt%	4.5	4.5	4.5
AT 181		Wt%	0.1	0.1	0.1
Property	Conditions	Units			
Flammability					
UL-94	UL94 1/8"	Rating	V-0	V-2*	V-2*
		seconds	7	53	84
Thermal Properties					
Melt Flow Index	ASTM D1238	230°C/3.8 kg; g/10 min	12.3	12.8	12.2
VICAT	ASTM D648 at 50°C/hr	°C	102.8	100.5	100.2
Physical Properties					
Gloss	60°	n/a	96.1	95.8	95.6
Initial Color	LAV, UV excluded 10° D65 YI: 2° C	L	87.40	88.21	87.77
		a	0.19	0.37	0.44
		b	9.88	9.71	9.80
		YI (D1925)	20.55	20.21	20.58
Mechanical Properties					
Tensile Strength	ASTM D638	psi X 10^3	7	6.9	7
Tensile Modulus	ASTM D638	psi X 10^5	3.5	3.4	3.6
Elongation at yield	ASTM D638	%	2.69	2.79	2.76
Elongation at Break	ASTM D638	%	5.37	6.72	5.39
Flexural Strength	ASTM D790	psi X 10^3	11.6	11.9	12.2
Flexural Modulus	ASTM D790	psi X 10^5	3.8	3.9	3.9
Izod Impact	ASTM D256	ft-lb/in	1.036	1.429	1.811
Gardner Impact	ASTM D3209	in.lb/in	283	930	915
Optical Property					
CIE L* Value	As described herein	%	17.92	18.85	19.28

*A few samples had dripped and ignited the cotton during the second ignition indicating the borderline loading and/or non-homogeneity of the samples.

[0104] In another group of tests, HIPS (Ineos Nova 495F) was used as the host polymer. The flame retardants used in these tests were 2,4,6-Tris(2,4,6-tribromophenoxy)-1,3,5 triazine commonly referred to as FR245, a widely used translucent flame retardant from ICL Industrial Products, and two brominated flame retardant additives of this invention.

One of these was brominated stripped styrenic telomer distribution 7 (BrSSTD 7) produced in Example 7 hereof and the other was brominated stripped styrenic telomer distribution 11A (BrSSTD 11A) produced in Example 11 hereof. The three HIPS polymer blends contained nanosized antimony pentoxide (APO) (BurnEX 6220; Nyacol Nano Technologies, Inc.) Additionally, a comparative example was conducted on the “as received” HIPS as a control run. The make-up of the test compositions and the test results are summarized in Table 5.

TABLE 5

Ingredient	Units	Comparative Example C	Comparative Example D	Example 16	Example 17
Ineos Nova 495F HIPS	Wt%	100	81.1	80.8	80.8
FR-245	Wt%		17.9		
BrSSTD 7	Wt%			15.2	
BrSSTD 11A	Wt%				15.2
BurnEX 6620 APO*	Wt%		4.0	4.0	4.0
CIE L* Value ¹	%	31.64	28.41	29.44	29.57

¹Using the CIE L* test procedure as described herein

[0105] As seen from the results in Examples 16 and 17 in Table 5, the brominated flame retardant additives used therein had only minimal effect on the light transmission of the host polymer. The reduction in these examples, as compared to the control value of Comparative Example C, was less than 10 percent.

[0106] Still another group of tests was conducted in which acrylonitrile-butadiene-styrene polymer (ABS) designated as Sabic Mg47 from Saudi Basic Industries Corporation was used as the host polymer. The flame retardants used in these tests were the same as in those used in the tests reported in Table 5, viz. FR245 and two brominated flame retardant additives of this invention, brominated stripped styrenic telomer distribution 7 (BrSSTD 7) produced in Example 7 hereof and brominated stripped styrenic telomer distribution 11A (BrSSTD 11A) produced in Example 11 hereof. The three HIPS polymer blends contained nanosized antimony trioxide (ATO) (BurnEX 6620; Nyacol

Nano Technologies, Inc.) Additionally, a Comparative Example was conducted on the “as received” ABS as a control run. The make-up of the test compositions and the test results are summarized in Table 6.

5

TABLE 6

Ingredient	Units	Comparative Example E	Comparative Example F	Example 18	Example 19
Sabic Mg47 ABS	Wt%	100	77.6	77.3	77.3
FR-245	Wt%		17.9		
BrSSTD 7	Wt%			18.2	
BrSSTD 11A	Wt%				18.2
BurnEX 6620 APO	Wt%		4.5	4.5	4.5
CIE L* Value ¹	%	30.18	27.28	29.50	30.38

¹Using the CIE L* test procedure as described herein

[0107] As seen from the results in Examples 18 and 19 in Table 6, the brominated flame retardant additives used therein had only minimal effect on the light transmission of the host polymer. The reduction in Example 18 was less than 5%, as compared to the control value of Comparative Example E. In the case of Example 19, there was no significant change in light transmission relative to the control value of Comparative Example E.

[0108] Components referred to by chemical name or formula anywhere in the specification or claims hereof, whether referred to in the singular or plural, are identified as they exist prior to coming into contact with another substance referred to by chemical name or chemical type (*e.g.*, another component, a solvent, or *etc.*). It matters not what chemical changes, transformations and/or reactions, if any, take place in the resulting mixture or solution as such changes, transformations, and/or reactions are the natural result of bringing the specified components together under the conditions called for pursuant to this disclosure.

[0109] The invention may comprise, consist, or consist essentially of the materials and/or procedures recited herein.

[0110] Except as may be expressly otherwise indicated, the article "a" or "an" if and as used herein is not intended to limit, and should not be construed as limiting, a claim to a single element to which the article refers. Rather, the article "a" or "an" if and as used herein is intended to cover one or more such elements, unless the text expressly indicates otherwise.

[0111] Each and every patent or publication referred to in any portion of this specification is incorporated *in toto* into this disclosure by reference, as if fully set forth herein.

5 [0112] This invention is susceptible to considerable variation in its practice. Therefore the foregoing description is not intended to limit, and should not be construed as limiting, the invention to the particular exemplifications presented hereinabove.

CLAIMS:

1. A flame retarded thermoplastic polymer composition which comprises at least one transparent or translucent thermoplastic polymer and a brominated styrenic telomer distribution having a bromine content in the range of about 50 to about 75 wt%, and a percent transmission in optically clear styrene-acrylonitrile copolymer in the CIE L* test method as described herein of at least about 60, desirably at least about 75, and more desirably at least about 90; wherein such brominated telomer distribution has an M_w of about 422 to about 4,000, an M_n of about 420 to about 2,400, an M_z of about 436 to about 4,800, a polydispersity in the range of about 1.01 to about 2.0, a standard deviation of about 29.0 to about 2,000, and an asymmetry of about 90 to about 0.6, a glass transition temperature (T_g) in the range of about 25°C to about 100°C, a 5% weight loss by thermogravimetric analysis (TGA) under nitrogen greater than about 270°C, and a thermal HBr value at 300°C of less than about 500 ppm.
2. A flame retarded thermoplastic polymer composition as in Claim 1 wherein said brominated styrenic telomer distribution has (i) a thermal color value after heating for 15 minutes under nitrogen at 250°C of less than about 35, (ii) a thermal color value after heating for 20 minutes under nitrogen at 300°C of less than about 40, and (iii) as a 10 wt% solution in chlorobenzene, a ΔE value of less than about 25.
3. A flame retarded thermoplastic polymer composition which comprises (1) at least one transparent or translucent thermoplastic polymer with which has been blended (2) a brominated styrenic telomer distribution having a bromine content in the range of about 50 to about 75 wt%, and a percent transmission in optically clear styrene-acrylonitrile copolymer in the CIE L* test method as described herein of at least about 60, desirably at least about 75, and more desirably at least about 90; wherein such telomer distribution is formed from:
- A) a vinyl aromatic hydrocarbon, and
 - B) at least one aromatic hydrocarbon having from one to three aromatic rings per molecule and containing from one to four methyl substituents bound to the aromatic ring(s) thereof; and wherein such telomer distribution has, prior to bromination, an M_w in the range of about 211 to about 1000, an M_n in the range of about 210 to about 600, an M_z

in the range of about 216 to about 1200, a standard deviation in the range of about 20 to about 350, and asymmetry in the range of about 1 to about 11.

4. A composition as in any of Claims 1-3 wherein component A) used in forming the telomer distribution is styrene and component B) used in forming the telomer distribution is one or more of (i) toluene, (ii) o-xylene, (iii) p-xylene, (iv) m-xylene.

5. A composition as in Claim 4 wherein said telomer distribution has, prior to bromination, an M_w in the range of about 400 to about 1000, an M_n in the range of about 500 to about 600, an M_z in the range of about 600 to about 1250, a standard deviation in the range of about 130 to about 350, and asymmetry in the range of about 1.5 to about 2.6.

6. A flame retarded composition as in any of Claims 1-5 wherein said brominated styrenic telomer distribution has a bromine content in the range of from about 62 to less than 69 wt%.

7. A flame retarded composition as in any of Claims 1-6 wherein said flame retarded composition additionally contains at least one flame retardant synergist, or optionally at least one flame retardant synergist which is a finely divided, non-submicron-sized powder.

8. A flame retarded composition as in Claim 7 wherein said synergist is submicron-sized antimony trioxide or submicron-sized antimony pentoxide, or both.

9. A flame retarded composition as in any of Claims 1-8 wherein said at least one thermoplastic polymer is polystyrene, SAN, polycarbonate, polyphenylene oxide (PPO), PMMA, HIPS, ABS, polyester, polyamide, or a combination or alloy of any two or more of these.

10. A flame retarded composition as in Claim 9 wherein said thermoplastic polymer is HIPS.

11. A flame retarded composition as in Claim 9 wherein said thermoplastic polymer is ABS.

12. A flame retarded composition as in Claim 9 wherein said thermoplastic polymer is SAN.

13. A flame retarded composition as in Claim 9 wherein said flame retarded composition contains at least one submicron-sized flame retardant synergist, and wherein said synergist comprises submicron antimony trioxide or submicron antimony pentoxide, or both of them.

14. A flame retarded composition as in any of Claims 1-5 wherein:

A. brominated styrenic telomer distribution has a bromine content in the range of from about 62 to less than 69 wt%;

5 B. said flame retarded composition contains at least one flame retardant synergist, or optionally at least one flame retardant synergist which is a finely divided, non-submicron-sized powder; and

C. said at least one transparent or translucent thermoplastic polymer is polystyrene, SAN, polycarbonate, polyphenylene oxide (PPO), PMMA, HIPS, ABS, polyester, polyamide or a combination or alloy of any two or more of these.

10 15. A flame retarded composition as in Claim 14 wherein said flame retardant synergist comprises submicron-sized antimony trioxide, submicron-sized antimony pentoxide, or both of them.

16. A flame retardant additive composition which comprises a brominated styrenic telomer distribution having a bromine content in the range of about 50 to about 75 wt%
15 and a percent transmission in optically clear styrene-acrylonitrile copolymer in the CIE L* test method as described herein of at least about 60, desirably at least about 75, and more desirably at least about 90, wherein such brominated telomer distribution has an M_w of about 422 to about 4,000, an M_n of about 420 to about 2,400, an M_z of about 436 to about 4,800, a polydispersity in the range of about 1.01 to about 2.0, a standard deviation of
20 about 29.0 to about 2,000, and an asymmetry of about 90 to about 0.6, a glass transition temperature (T_g) in the range of about 25°C to about 100°C, a 5% weight loss by thermogravimetric analysis (TGA) under nitrogen greater than about 270°C, and a thermal HBr value at 300°C of less than about 500 ppm.

17. A flame retardant additive composition as in Claim 16 wherein said brominated
25 styrenic telomer distribution has (i) a thermal color value after heating for 15 minutes under nitrogen at 250°C of less than about 35, (ii) a thermal color value after heating for 20 minutes under nitrogen at 300°C of less than about 40, and (iii) as a 10 wt% solution in chlorobenzene, a ΔE value of less than about 25.

18. A flame retardant additive composition which comprises a brominated styrenic
30 telomer distribution having a bromine content in the range of about 50 to about 75 wt% and a percent transmission in optically clear styrene-acrylonitrile copolymer in the CIE L* test method as described herein of at least about 60, desirably at least about 75, and more desirably at least about 90;

wherein said telomer distribution is formed from:

- A) a vinyl aromatic hydrocarbon, and
- B) at least one aromatic hydrocarbon having from one to three aromatic rings per molecule and containing from one to four methyl substituents bound to the aromatic ring(s) thereof; and

wherein said telomer distribution has, prior to bromination, an M_w in the range of about 211 to about 1000, an M_n in the range of about 210 to about 600, an M_z in the range of about 216 to about 1200, a standard deviation in the range of about 20 to about 350, and asymmetry in the range of about 1 to about 11.

19. An additive composition as in Claim 18 wherein component A) used in forming the telomer distribution is styrene and component B) used in forming the telomer distribution is one or more of (i) toluene, (ii) o-xylene, (iii) p-xylene, (iv) m-xylene.

20. An additive composition as in Claim 19 wherein said telomer distribution has, prior to bromination, an M_w in the range of about 400 to about 1000, an M_n in the range of about 500 to about 600, an M_z in the range of about 600 to about 1250, a standard deviation in the range of about 130 to about 350, and asymmetry in the range of about 1.5 to about 2.6; and wherein said percent transmission in optically clear styrene-acrylonitrile copolymer is at least about 75, and more desirably at least about 90.

21. An additive composition as in any of Claims 16-20 wherein said brominated styrenic telomer distribution has a bromine content in the range of from about 62 to less than 69 wt%.

22. An additive composition as in any of Claims 16-21 wherein said additive composition contains at least one submicron-sized flame retardant synergist.

23. An additive composition as in Claim 22 wherein said synergist comprises submicron-sized antimony trioxide or submicron-sized antimony pentoxide, or both.

24. An additive composition as in any of Claims 16-20 wherein said brominated styrenic telomer distribution has a bromine content in the range of from about 62 to less than 69 wt% and wherein said additive composition contains at least one submicron-sized flame retardant synergist.

25. An additive composition as in Claim 24 wherein said synergist comprises submicron-sized antimony trioxide or submicron-sized antimony pentoxide, or both.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2011/036827

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F8/22 C08K5/03
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08K C07C C09K C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2008/154453 A1 (ALBEMARLE CORP [US]; LAYMAN WILLIAM J JR [US]; MACK ARTHUR G [US]; KOL) 18 December 2008 (2008-12-18) cited in the application page 42; examples 1-3,7-10; table 1 page 44; examples 11-14; table 1 page 48 - page 51; table II claims 1,2,5-8,10-25,27-31 -----	1-25
X	WO 2009/148464 A1 (ALBEMARLE CORP [US]; LAYMAN WILLIAM J JR [US]; MACK ARTHUR G [US]; KOL) 10 December 2009 (2009-12-10) examples 1-3,6-14; table 1 table II claims ----- -/-	1-25



Further documents are listed in the continuation of Box C.



See patent family annex.

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INTERNATIONAL SEARCH REPORT

International application No

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	WO 2010/065468 A1 (ALBERMARLE CORP [US]; LAYMAN WILLIAM J [US]; KOLICH CHARLES H [US]; MA) 10 June 2010 (2010-06-10) tables 10-20 claims -----	1-25
X,P	WO 2010/065467 A1 (ALBEMARLE CORP [US]; LAYMAN WILLIAM J [US]; KOLICH CHARLES H [US]; MAC) 10 June 2010 (2010-06-10) examples 21-29,32-36; table 4 table 5 table 6 claims -----	1-25

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