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(57) Abstract

The present invention relates to selectively halogenated copolymers containing at least one polymerized α-olefin and a monomeric or polymeric alkylbenzene containing comonomer and to the preparation of crosslinked compositions therefrom.

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COPOLYMERS OF OLEFINS AND AROMATIC OLEFINS AND OF OLEFINS AND POLYMERIC AROMATIC COMPOUNDS

FIELD OF THE INVENTION

The present invention relates to selectively halogenated copolymers containing at least one polymerized α-olefin and an monomeric or polymeric alkylbenzene containing comonomer and to the preparation of crosslinked compositions therefrom.

BACKGROUND OF THE INVENTION

Amorphous copolymers containing ethylene and at least one other C_2-C_8 α-olefin comonomer are well known materials which exhibit elastomeric properties and exceptional resistance to oxidative degradation.

Crosslinked ethylene/α-olefin copolymers are particularly useful in applications such as moldings, coatings, tires, and other shaped articles where good ozone resistance and weatherability are particularly desirable.

Crosslinking of such copolymers containing no ethylenic unsaturation can be carried out through radical formation induced by peroxides or other free radical generators used alone or in conjunction with crosslinking agents such as sulfur or polyfunctional electrophilic reagents. Terpolymers containing minor amounts of a diene monomer such as alkylidene norbornene, 1,4-hexadiene, dicyclopentadiene and the like are sulfur curable as a consequence of the availability of a double bond not incorporated into the polymer chain which acts as a cure site in sulfur curing.

For example, sulfur curable elastomeric terpolymers comprising ethylene, propylene and a substituted norbornene such as 5-phenyl-2-norbornene are disclosed in U.S. Patent No. 3,478,002.

U.S. Patent No. 3,506,627 discloses the preparation of copolymers of ethylene, propylene and allyl benzene (optionally with some incorporated diene) which may be cross linked using a free radical system if the polymers are saturated, or with conventional sulfur where the polymer is unsaturated in the polymer backbone.

In addition, Holmquist et al., J. Appl. Polym. Sci., 1971, p. 2103-2114, teach the curing of terpolymers containing ethylene, propylene and 4-alkyl-1-butenes, e.g., 4-phenyl-1-butene, using a polyfunctional electrophilic crosslinking agent such as a bis benzylic halide. Crosslinking is said to occur by reaction at aromatic ring sites present along the polymer chain.

Organolithium initiators containing vinyl unsaturation have been used to initiate polymerization of anionically polymerizable monomers to produce vinyl terminated macromolecules which may be then used as a macromeric component in the preparation of copolymers by ionic or free radical polymerization techniques to product graft copolymers containing the vinyl macromonomer as pendant side chains. For example, U.S. Patent No. 3,235,626 to Waack, describes a method for preparing graft copolymers of controlled branch configuration. Waack discloses graft copolymers prepared by first preparing a prepolymer by reacting a vinyl metal compound with an olefinic monomer to obtain a vinyl terminated prepolymer. After protonation and catalyst removal, the prepolymer is dissolved in an inert solvent with a polymerization catalyst and is thereafter reacted with either a different polymer having a reactive vinyl group or a different vinyl monomer under free-radical conditions.

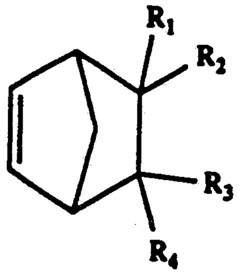
Sumitomo Chemical's Japanese Kokai 50013483-A discloses olefin copolymers prepared by the Ziegler-catalyzed reaction of ethylene and/or propylene and polystyrene end-capped with norbornene. The preparation of a styrene-ethylene graft copolymer is described in an example, wherein the polystyrene macromonomer is formed by reacting living n-BuLi capped polystyrene with 5-bromomethyl-2-norbornene.

In addition, polystyrene macromonomers capped with a norbornene group have been prepared by coupling a polystyrene anion with 5-bromomethyl-norbornene in a mixed solvent (Chemical Abstracts No. CA104(26) 225321 w, 1986) and these functional polystyrenes have been further disclosed used as a macromonomer in the Ziegler-Natta polymerization of graft copolymers comprising a polyethylene backbone containing grafted polystyrene side chains (Chemical Abstracts No. CA107 (20) 176624y, 1987).

Functionalized macromolecules are also disclosed by R. Milkovich et al., J. Appl. Polym. Sci., Vol. 27, 1982, pg. 4773. Milkovich et al. disclose anionic polymerization of a number of monomers with active initiators to form monodisperse living polymer chains. These living chains are then reacted with a wide-range of termination agents to introduce substantially end-functionalized macromonomers. This route clearly improves the resulting macromer polydispersity and allows for a broader range of end functionality.

Graft copolymers such as prepared above have a number of uses, including film applications and alloying (compatibilizing agents) for use in blends of rubbery polymers and thermoplastic vinyl aromatic polymers. Amorphous graft copolymers based, for example, on a polyisobutylene or ethylene/propylene backbone chain exhibit elastomeric properties are also useful for similar applications. However, these copolymers cannot be readily vulcanized or co-vulcanized with other elastomers due to the lack of unsaturation in the polymeric backbone. Another technique for rendering "essentially saturated" elastomeric polymers amenable to vulcanization and other reactions involves the inclusion of functional substituent groups, such as halogen, in the polymer chain. One such technique is disclosed in U.S. Patent No. 4,074,035, which discloses the polymerization of isobutylene with a halomethylstyrene using a Lewis Acid-type catalyst system. However, this method requires the use of vinylbenzyl chloride and the like as a starting material, and utilizes a specified continuous solution process with solvent or mixed solvent systems in which the monomers are soluble under specified conditions. Aside from the need to employ the expensive vinylbenzyl chloride starting material, these processes also have limitations in terms of the quantity of aromatic chloromethyl functionality which can be incorporated in this manner without encountering excessive chain branching and gel formation during polymerization and polymer recovery because of the reactivity of the benzylic chlorine under cationic polymerization conditions. In addition, halogen containing monomers used in anionic polymerization reactions involving Ziegler-Natta type coordination catalysts tend to poison the catalyst system rendering the process generally ineffective for the production of polymers of significant molecular weight.

An alternative process for preparing functionalized isobutylene/vinyl aromatic copolymers is disclosed in European Patent Application No. 0344021, published November 29, 1989. The process involves the preparation of random copolymers of isobutylene and a para-alkyl styrene such as para-methylstyrene using a Lewis acid-Friedel-Crafts catalyst, followed by selective halogenation of the benzylic sites. Sulfur curable quadripolymers containing halogen are disclosed in U.S. Patent No. 3,876,595. This patent discloses a process for preparing amorphous tetrapolymers via Ziegler-Natta catalysis from ethylene, an α-olefin, a non-conjugated diene hydrocarbon, and halogenated norbornene monomer represented by the formula I:



I

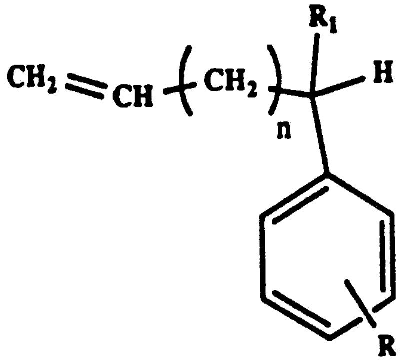
where R_1-R_4 are H1 (hydrogen) or a hydrocarbon fragment containing 1 to 20 carbon atoms, halogen, or halogenated hydrocarbon containing 1 to 20 carbon atoms, provided that at least one halogen is present in the monomer. The presence of a minor amount of a norbornene monomer in the polymerization recipe affords the preparation of high molecular weight polymers at other than extremely low temperatures using an organoaluminum catalyst component having a low Lewis acidity. U.S. Patent No. 4,039,491 teaches block and/or graft copolymers by the reaction of a norbornene derivative, having at least one polar group (optionally halogen), in the presence of a metatheses catalyst with at least one polymer containing olefinic unsaturation. The polymers are useful as flame retardants and for impact-resistance applications. The set of norbornene derivatives includes 5-halohydrocarbyl-2-norbornenes having 1 to 10 carbon atoms in the hydrocarbyl group.

European Patent No. 240,638 teaches a block copolymer useful for sheeting caulks, sealants, gaskets and lubricating oil additives comprising ethylene, and α-olefin, and an olefinic halide with the formula RR'X where R is a Ziegler copolymerizable olefin R' is a 10 to 20 carbon atom hydrocarbyl and X is halogen.

Ethylene-propylene-5-[p-(chloromethyl)phenyl]-2-norbornene block and graft copolymers are disclosed. In one example, the block copolymer is prepared by first polymerizing ethylene with propylene in hexane using VCl_4-$VCl_4Et_2Al_2Cl_2$ $Et_2Al_2Cl_2$ catalyst at 0-200 # psi (obtaining 49% conversion) and then adding 5-[(p-chloromethyl)phenyl]-2-norbornene to give the block copolymer with a polydispersity of 1.7.

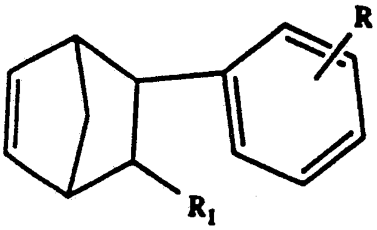
SUMMARY OF THE INVENTION

The present invention provides for halo-functionalized random copolymers prepared by halogenation of copolymers prepared by copolymerizing α-olefins particularly ethylene and one or more alkylaromatic comonomers selected from the group represented by formulae II, IIIa, IIIb or IV. The alkylaromatic comonomer can be monomeric having from 3 to about 28 carbon atoms with at least one ethylenically unsaturated aromatic monomer represented by the formula II, IIIa, IIIb:

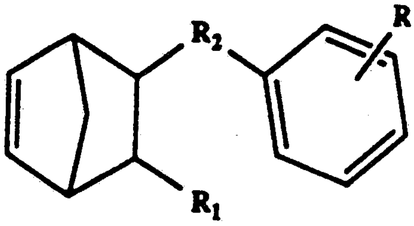


II

wherein n is an integer from 0 to 10, R and R_1 are independently selected from the group consisting of hydrogen and C_1 to C_4 alkyl; or



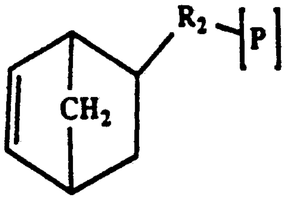
IIIa



IIIb

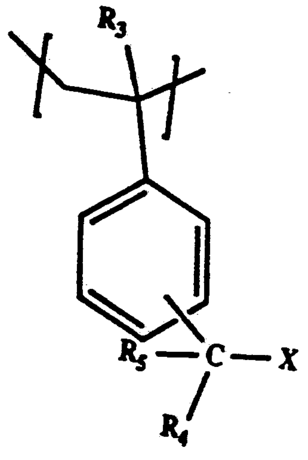
wherein R and R_1 are selected from the group consisting of hydrogen and C_1-C_4 alkyl, R_2 is a C_1 to C_{18} alkylene radical. Subsequent halogenation of the terpolymers to selectively halogenate one or more benzylic sites in R or R_1 or halogenate the aromatic ring when R is hydrogen and R2 is not present may be done.

The alkylaromatic monomer may also be a polymeric "macromonomer", formula IV, such as a norbornene-terminated macromonomer containing polymerized alkyl substituted styrene, and subsequent halogenation of the graft copolymer to selectively halogenate a portion of the benzylic sites present in the graft chain.



IV

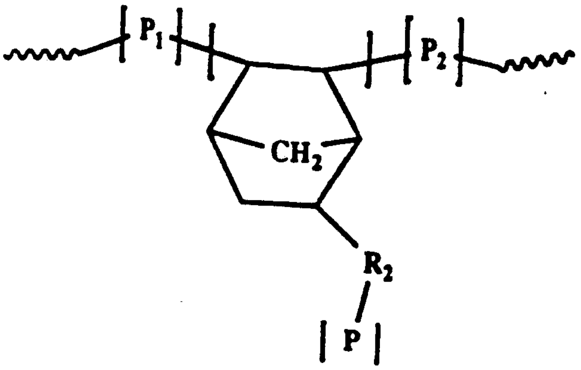
wherein R_2 is a straight or branched chain alkylene radical having from 1 to about 17 carbon atoms and P is a homopolymeric or copolymeric segment comprising an anionically polymerized vinyl alkylaromatic monomer or mixture of vinyl aromatic monomers or other anionically polymerizable vinyl monomers wherein upon halogenation the P repeating units and represented by the formula V:



V

wherein R_3, R_4 and R_5 are independently hydrogen or alkyl and X is hydrogen or halogen, or a mixture thereof.

A preferred polymer comprises a polyolefin elastomeric main-chain having copolymerized and randomly distributed therein a plurality of poly(alkylstyrene) thermoplastic sidechains as represented by formula VI



VI

wherein P_1 and P_2 independently represent a polymer or copolymer segment derived from an α-olefin monomer or mixture of α-olefin monomers copolymerizable with norbornene-type monomers, R_2 is a straight or branched chain alkylene radical having from 1 to about 17 carbon atoms and P is a homopolymeric or copolymeric segment comprising an anionically polymerized vinyl alkylaromatic monomer or mixture of vinyl aromatic monomers or other anionically polymerizable vinyl monomers wherein at least one of the P repeating units is represented by the formula V above.

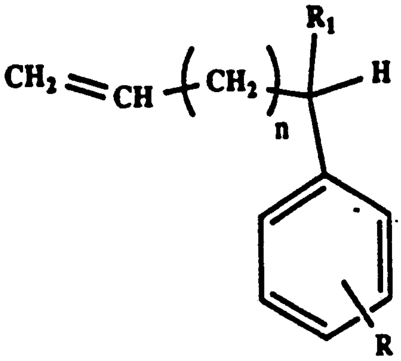
The polymer has discrete thermoplastic domains comprising from about 2 to about 50 percent by weight of the polymer and an elastomeric matrix comprising from about 50 to about 98 percent of the polymer. The side chain polymer preferably comprises alkylstyrene represented by formula V above. The alkylstyrene wherein X is hydrogen comprises from about 45 to about 99.9 percent by weight of the side chains, preferably from about 80 to about 99 percent by weight, more preferably from about 90 to about 98 percent by weight. The alkylstyrene wherein X is halogen comprises from 0.1 to 55 percent by weight of the side chains, preferably from about 0.1 to about 20 percent by weight.

These halogen containing polymers may be readily vulcanized under mild conditions using conventional vulcanization recipes for halogenated elastomers. The presence of the aromatic or benzylic halide functional group also permits easy transformation into a variety of other functionalities as desired for specific applications to enhance adhesion and compatibility as well as co-vulcanization and grafting with other copolymers.

DETAILED DESCRIPTION OF THE INVENTION

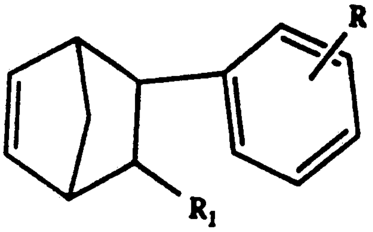
The present invention provides for copolymers of α-olefins and C_3 to C_{1000} ethylenically unsaturated alkylaromatic hydrocarbons which can be functionalized by halogenation by methods known in the art.

In particular, the present invention provides for functionalized copolymers prepared by halogenation of copolymers prepared by copolymerizing α-olefins particularly ethylene and one or more alkylaromatic comonomers selected from the group represented by formulae II, IIIa, IIIb or IV. The alkylaromatic comonomer can be monomeric having from 3 to about 28 carbon atoms with at least one ethylenically unsaturated aromatic monomer represented by the formula II, IIIa, or IIIb:

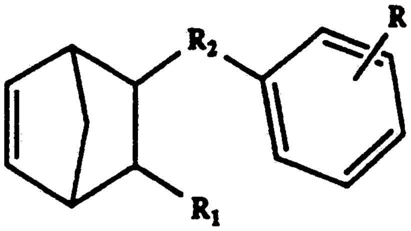


II

wherein n is an integer from 0 to 10, R and R_1 are independently selected from the group consisting of hydrogen and C_1 to C_4 alkyl; or



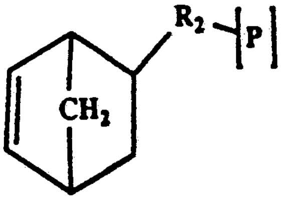
IIIa



IIIb

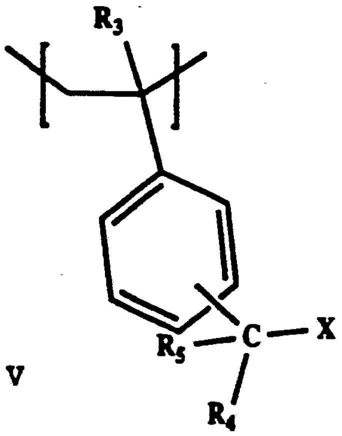
wherein R & R_1 are selected from the group consisting of hydrogen and C_1-C_4 alkyl, R_2 is a C_1 to C_{18} alkylene radical. Subsequent halogenation of the terpolymers to selectively halogenate one or more benzylic sites in R or R_1 or halogenate the aromatic ring when R is hydrogen and R_2 is not present may be done.

The alkylaromatic monomer may also be a polymeric "macromonomer", formula IV, such as a norbornene-terminated macromonomer containing polymerized alkyl substituted styrene. Subsequent halogenation of the graft copolymer to selectively halogenate a portion of the benzylic sites present in the graft chain may be done.



IV

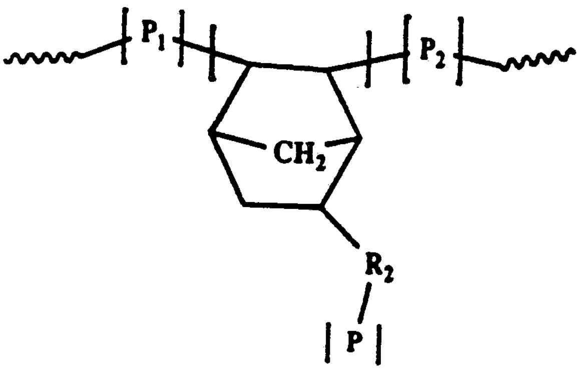
wherein R_2 is a straight or branched chain alkylene radical having from 1 to about 17 carbon atoms and P is a homopolymeric or copolymeric segment comprising an anionically polymerized vinyl alkylaromatic monomer or mixture of vinyl aromatic monomers or other anionically polymerizable vinyl monomers wherein upon halogenation the P repeating units is represented by formula V:



V

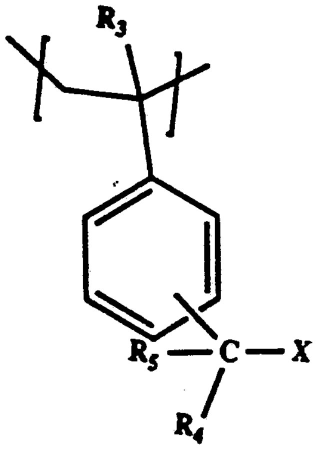
wherein R_3, R_4 and R_5 are independently hydrogen or alkyl and X is hydrogen, halogen or a mixture of hydrogen and halogen.

The present invention further provides polymers comprising a elastomeric main-chain having copolymerized and randomly distributed therein a plurality of poly(alkylstyrene) thermoplastic sidechains as represented by formula VI:



VI

wherein P_1 and P_2 independently represent a polymer or copolymer segment derived from an α-olefin monomer or mixture of α-olefin monomers copolymerizable with norbornene-type monomers, R_2 is a straight or branched chain alkylene radical having from 1 to about 17 carbon atoms and P is a homopolymeric or copolymeric segment comprising an anionically polymerized vinyl alkylaromatic monomer or mixture of vinyl aromatic monomers or other anionically polymerizable vinyl monomers wherein at least one of the P repeating units is represented by formula V:



V

wherein R_3, R_4 and R_5 are independently hydrogen or alkyl and X is hydrogen, halogen or a mixture of hydrogen and halogen. P may also comprise other anionically polymerizable monomer(s) which include, but are not limited to, vinyl alkylaromatic or mixtures thereof, or other vinyl monomers(s) or mixtures thereof.

Examples of.ethylenically unsaturated alkylaromatic hydrocarbon represented by the formula "monomer II", include but are not limited to, allyl benzenes or substituted allyl benzenes wherein R is located in the para position, such as allyl (4-methyl) benzene, allyl (4-ethyl) benzene and allyl (4-propyl) benzene. Allyl benzene and allyl (4-methyl) benzene are especially preferred because they are most readily copolymerizable with ethylene and other α-olefin monomers under coordination polymerization conditions to provide high molecular weight elastomeric copolymers wherein the aromatic monomer is randomly dispersed along the polymer chain. The polymers of formula II may then be selectively halogenated either at sites on the aromatic ring or through reactions with benzylic hydrogen wherein R is other than hydrogen.

The ethylinically unsaturated alkyl aromatic hydrocarbon represented by the formulas monomer IIIa and monomer IIIb are typically norbornene based with an aromatic substituted positioned at the 2-norbornenyl site. Preferred hydrocarbons represented by formula monomer IIIa include those where R_1 is hydrogen, and R is hydrogen or a C_1 to C_4 alkyl at the para position. Specific examples of monomer IIIa include, but are not limited, to 5-norbornene-2-phenyl; 5-norbornene-2-(4 methylphenyl). Preferred hydrocarbon represented by formula monomer IIIb include those where R_2 is a C_1 or C_2 alkylene and R_1 is hydrogen. Examples include but are not limited to 5-norbornene-2-(methylbenzyl)

The monomers of formulas monomer IIIa and monomer IIIb may be readily prepared by a conventional Diels-Alder addition reaction of an ethylenically unsaturated aromatic or substituted aromatic compound and cyclopentadiene. For example, styrene or alkyl styrenes when added to cylcopentadiene will yield monomer materials of formula monomer IIIa when R_1 is hydrogen and R is hydrogen or alkyl. Diels Alder addition of 4-methylstyrene and cyclopentadiene yields 5-norbornene-2-(4-methylphenyl). Allyl benzenes will add to cyclopentadiene to yield compounds of formula wherein is methylene and is hydrogen. Other phenyl substituted α-olefins or internal olefins having from 1 to 18 carbon atoms will add to cyclopentadiene to yield monomers with specific variations of the end substituent groups depending on the location of the double bond in the olefin compound. For example a reaction with p-phenyl-1-

butene will yield a compound of formula monomer IIIb wherein R_2 is ethylidene and R_1 and R are hydrogen.

The alkylaromatic comonomers of this invention particularly those represented by the formulae: monomer II, monomer IIIa and monomer IIIb, are copolymerized with any ethylenically unsaturated monomer which is copolymerizable with a norbornene-type monomer or an allyl-type monomer. These include α-olefins monomers containing from 2 to about 18 carbon atoms such as ethylene, propylene, 1-butene, isobutene, 1-pentene, 1-hexene, as well as mixtures of ethylene and one or more α-olefins. Especially preferred α-olefin monomer(s) is a mixture of ethylene and propylene present at a level such that the copolymer backbone contains from about 15 to about 80 mole percent polymerized ethylene, the balance being propylene and the interpolymerized alkylaromatic containing comonomer. Most preferred are copolymers containing from 30 to about 70 mole percent of polymerized ethylene.

When preparing copolymers having an olefin backbone of ethylene or propylene together with a alkylaromatic monomer, it is typical to employ a coordination catalyst known in the art as Ziegler Natta catalysts, the latter being commonly used for polypropylene. Some of these catalysts are disclosed in Belgian Patent No. 533,362, issued May 16, 1955, and U.S. Patent Nos. 3,113,115 and 3,257,332 to Ziegler et al, which are herein fully incorporated by reference. These catalysts are prepared by the interaction of a compound of transition metals of group IV-VII in the periodic table, including titanium, chromium, vanadium and zirconium, and a co-catalyst which is an organometal compound of a metal of Groups I-A, II-A, II-B or

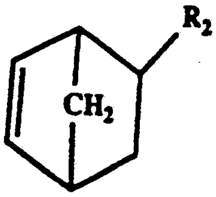
III-A of the Periodic Table. The preferred co-catalysts are organo aluminium compounds of the formulae:

AlR_3	$Al(OR')R_2$
AlR_2Cl	$R'_2Al-O-AlR'_2$ and
$AlR'RCl$	AlR_2I
$Al_2R'_3Cl_3$	
$AlR'Cl_2$	

where R and R′ represent C_1 to C_{10} aliphatic, alicyclic or aromatic hydrocarbon radicals which may be the same or different. The most preferred organo-aluminium compound is an aluminium alkylsesquichloride such as $Al_2Et_3Cl_3$ or $Al_2(iBu)_3Cl_3$.

Polymeric monomers, also called "macromonomers", are segments of "polymer" that function like monomers in a polymerization. The macromonomers represented by the formula "macromonomer IV" may be generally categorized as polymeric segments, P, attached to a norbornene type functionality at its end. Copolymerization occurs through the norbornene head group. P of macromonomer IV contain recurring units represented by formula V. Particularly those compounds represented by formula V, wherein X is H and R_3, R_4 and R_5 are independently selected from the group consisting of hydrogen and C_1 to C_4 alkyl. The graft copolymers of formula VI may be prepared by copolymerizing a norbornene "macromolecule" as hereafter described, with one or more α-olefin(s) containing 2 to 18 carbon atoms which form the backbone (P and P_2) segments of the graft copolymer. Examples of suitable α-olefin(s) include but are not limited to, ethylene, propylene, 1-butene, isobutene, 1-pentene, 1-hexene and the like as well as mixtures thereof . Mixtures of ethylene and one or more of said α-olefins are also suitable to form the backbone segments. Particularly preferred α-olefins are mixtures of ethylene and propylene which give rise to polymers having elastomeric properties when copolymerized in the presence of Ziegler-Natta coordination catalysts. The resulting graft copolymers are then halogenated such that the P in formula VI is modified to contain compounds represented by formula V, wherein X is either halogen or H.

The norbornene macromolecules present in formula "macromonomer IV" can be represented by the following formula VII:

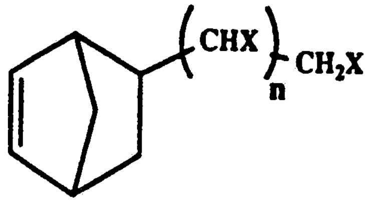


VII

wherein R_2 is a straight or branched chain C_1 to C_{18} alkylene radical. Preferred examples of compounds represented by Formula VII include, but are not limited to, 2-methylene-5-norbornene.

The norbornene forming the graft segments of the formula IV above can be prepared by any suitable technique. For example, they may be prepared by coupling a "living polymer" prepared using an alkyl lithium initiator which living polymer is then capped by a termination reaction with a norbornene alkyl halide as disclosed in U.S. Patent No. 3,862,077, incorporated herein by reference.

The more preferred process for preparing the norbornene macromolecules utilize a 2-metaloalkyl-5-norbornene initiator having the general formula VIII:



VIII

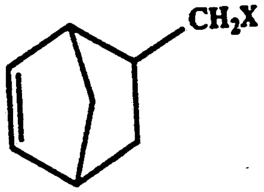
wherein n is 0 or an integer ranging from 1-17, X and X_1 are independently selected from the group consisting of H, Li, K, and Na, provided that where X_1 is Li, K or Na, then X is H, further provided that where X_1 is H, then n is an integer ranging from 1-17 and (n-1) of the X substituents are also H and X is Li, K or Na, and further provided that where n is 0, then X_1 is Li, K or Na.

These initiators may be generally prepared by contacting dicyclopentadiene with a mono-halogen containing olefinically unsaturated alkyl compound containing from 3 to 20 carbon atoms under Diels Alder reaction conditions to form the addition product which is an alkyl norbornene containing a halogen substituent group on the alkyl chain. This reaction product may then be reacted under conditions known in the art with an alkali metal such as lithium, sodium or potassium such that the halogen atom is displaced to form the alkali-metallated, alkyl substituted norbornene initiator.

Suitable halogen-substituted olefins which may be employed to form the Diels-Alder adduct include allyl bromide, 3-chloro-1-butene, 3-bromo-1-pentene, 1-chloro-2-butene, 5-chloro-1-pentene, 3-chloro-1-propene, 4-bromo-1-butene and 2-chloro-1-butene.

Suitable initiators are those of formula VIII above wherein n is 0 and X_1 is lithium. These are preferred because they are readily synthesized using a relatively inexpensive and available reactant (ally bromide) and the resulting intermediate alkyl norbornene halide is recovered in relatively high yields because of a minimization of side reactions including decomposition and unwanted cyclization reactions. Accordingly while the invention will be further described with a focus on these preferred initiators and their method of preparation, it should be understood that such description is equally applicable to the preparation of other initiators within the scope of formula VIII above.

Examples of preferred anionic initiators provided in accordance with this invention may be generally described as represented by the following formula IX:



IX

wherein X is an alkali metal selected from the group consisting of lithium, potassium and sodium. The preferred metal is lithium since the lithium-containing compound can be more readily prepared by simple lithiation of the corresponding 2-halomethyl-

5-norbornene compound and is quite soluble in solvents used for anionic polymerization reactions.

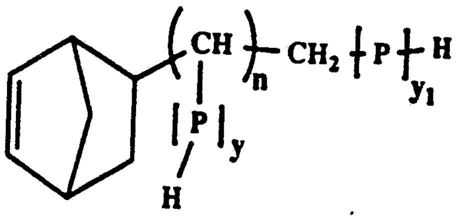
The initiators of formula IX may be typically prepared by a two stage process. In the first stage an allyl halide, preferably allyl bromide, may be reacted with cyclopentadiene to give the bicyloheptenyl-2 methyl halide derivative, i.e., 2-halomethyl-5-norbornene. The reaction may be carried out using cyclopentadiene as a solvent and at a temperature of from about to 100°C. A alternative first stage process involves refluxing the allyl halide with dicyclopentadiene whereby at high reflux temperatures (170-190°C) dicyclopentadiene dissociates to form cyclopentadiene, which then adds to the allyl halide. Reaction times under either process may vary between 2 and 8 hours. Although stoichiometric quantities or an excess of either reactant may be employed, it is preferred to use a slight excess of the allyl halide reactant.

The crude product of the first stage reaction is then purified using conventional distillation techniques to further separate the 2-halomethyl-5-norbornene from any unreacted reactants and isomers thereof.

The second stage of the preparation of the initiator involves the reaction of lithium, sodium or potassium metal with the 2-halomethyl-5-norbornene to form the 2-metalomethyl-5-norbornene having the structure of formula IX above. This reaction is conducted in a solvent which is inert under reaction conditions and which is free of materials which are detrimental to the reaction such as water, oxygen, carbon dioxide and/or alcohols. Suitable solvents which may be used are aromatic hydrocarbons such as benzene, toluene, xylene, ethyl benzene, t-butylbenzene and the like; saturated aliphatic and cycloaliphatic hydrocarbons such as n-hexane, n-heptane, n-octane, cyclohexane and the like; aliphatic and cyclic ethers such as dimethyl ether, diethyl either, dibutyl ether, tetrahydrofuran, dioxane, anisole, tetrahydropyran, diglyme and the like. Organic ethers are preferred solvents due to higher rates of reaction in ether medium.

The reaction is best conducted by gradual drop-wise addition of norbornene compound to a finely divided suspension of the metal present in excess and in solvent. The reaction is preferably conducted at temperatures below 0°C. preferably below -30°C, and reaction times may vary between about 3 to 8 hours. These reaction conditions are especially important to avoid thermally induced ring cleavage reactions and unwanted addition reactions which can lead to a low yield of the desired product as well as the formation of isomers which are difficult to separate. Under these preferred conditions, essentially all of the bromomethyl norbornene is reacted to give a mixture which is substantially the lithiomethyl norbornene containing less than 5% by weight of unidentified oligomeric products. The reaction product may then be recovered by filtering out residual metal particles and removal of the solvent by evaporation.

The macromonomers of this invention are preferably produced by living polymerization. In particular the anionically polymerizable monomer or mixture of monomers is contacted with the norbornene initiator prepared as above in the presence of an organic solvent which does not participate in or interfere with the polymerization reaction. The living polymers prepared in accordance with this invention using any of the above initiators may be generally characterized by the structure X:



X

wherein P represents a polymeric chain selected from the group consisting of homopolymers, random copolymers and block copolymers derived from an alkylstyrene monomer, preferably para allyl styrene, having the formula V above, wherein X is H, alone or in admixture with one or more other anionically polymerizable vinyl monomers; n is 0 or an integer ranging from 1-17, y and y1 are either 0 or 1, provided that where y1 is 1 then y is 0, further provided that where y1 is 0, then n is an integer ranging from 1-17 and (n-1) of the y substituents are also 0 the remaining y substituent is a 1, and further provided that where n is 0, then y1 is 1.

Suitable anionically polymerizable vinyl monomer, as mentioned in formula X, are well known in the art. These anionically polymerizable vinyl monomers include vinyl aromatic monomers such as styrene and α-methyl styrene; vinyl unsaturated amides such as acrylamide, methacrylamide, N,N-dialkyl acrylamides, e.g., N,n-dimethylacrylamide; acenaphtahlene; 9-acrylcarbazole; acrylonitrile and methacrylonitrile; organic diisocyanates including lower alkylene, phenylene and toluene diisocyanates; lower alkyl and allyl acrylates and methacrylates, including methyl, t-butyl acrylates and methacrylates; lower olefins, such as ethylene, propylene, butylene, isobutylene, pentene, hexene, etc; vinyl esters of aliphatic carboxylic acids such as vinyl acetate, vinyl propionate, vinyl octoate, vinyl oleate, vinyl stearate, vinyl benzoate; vinyl lower alkyl ethers; vinyl pyridines, vinyl pyrrolidones; and dienes including isoprene and butadiene. The term "lower" is used above to donate organic groups containing 8 or fewer carbon atoms.

Where the backbone polymer, P, is polymerized using a Zeigler-Natta catalyst as hereinafter discussed, it is preferred to avoid the use of monomer or macromolecules which contain functional groups which will deactivate or poison the catalyst system, i.e., halogen.

The preferred alkylstyrenes of P are methylstyrene, ethylstyrene and propyl styrene. Preferably, the back bone polymer P, in formula IV and X is a homopolymer of methylstyrene, ethylstyrene, or propylstyrene, or a copolymer containing at least about 5 mole percent of the alkylstyrene with up to about 95 mole percent of another vinyl aromatic comonomer such as styrene or $\underline{\alpha}$-methylstyrene.

The first step of the process to produce "P" is carried out by reacting a mono-functional lithium metal initiator system with the respective monomer or monomers to form the living polymer chain P-Li. This polymerization step can be carried out in one step or in sequence of steps. In the case where the polymer chain P is to be homopolymer or a random or tapered copolymer of two or more monomers, the monomers are simultaneously polymerized with the lithium metal initiator. In the case where the polymer chain P is to be a block copolymer comprising two or more homo-or copolymers blocks, these individual blocks can be generated by incremental or sequential monomer addition.

An inert solvent generally is used to facilitate heat transfer and adequate mixing of initiator and monomer. Hydrocarbons and ethers are the preferred solvents. Solvents useful in the anionic polymerization process include the aromatic hydrocarbons such as benzene, toluene xylene, ethylbenzene, t-butylbenzene etc.

Also suitable as solvents are the saturated aliphatic and cycloaliphatic hydrocarbons such as n-hexane, n-heptane, n-octane, cyclohexane and the like. In addition, aliphatic and cyclic ether solvents can be used, for example, dimethyl ether, diethyl ether, dibutyl ether, tetrahydrofuran, dioxane, anisole, tetrahydropyran, diglyme, glyme, etc. The rates of polymerization are faster in the ether solvents than in the hydrocarbon solvents.

As a general rule, the amount of initiator is an important factor in anionic polymerization because it determines the molecular weight of the living polymer. If a small proportion of initiator is used, with respect to the amount of monomer, the molecular weight of the living polymer will be larger than if a large proportion of initiator is used. Generally, it is advisable to add initiator dropwise to the monomer (when that is the selected order of addition) until the characteristic color of the organic anion persists, then add the calculated amount of the initiator for the molecular weight desired. The preliminary dropwise addition serves to destroy contaminants and thus permits better control of the polymerization.

Typically a polymer of narrow molecular weight distribution is generally prepared by introducing all of the reactive species into the system at the same time. By this technique, polymer growth by consecutive addition of monomer to an active terminal group, takes place at the same rate without chain transfer or termination reaction. When this is accomplished, the molecular weight of the polymer is controlled by the ratio of monomer to initiator. This may be represented by the molecular weight of living polymer = [(Moles of Monomer)/(Moles of Initiator)] x Molecular weight of Monomer.

As can be seen from the above equation, high concentrations of initiator leads to the formation of low molecular weight polymers, whereas, low concentrations of initiator leads to the production of high molecular weight polymers.

The concentration of the monomer charged to the reaction vessel can vary widely, and is limited by the ability of the reaction equipment to dissipate the heat of polymerization and to properly mix the resulting viscous solutions of the living polymer. Concentrations of monomer as high as 50 percent by weight or higher based on the weight of the reaction mixture can be used. However, the preferred monomer concentration is from about 5 to about 25 percent in order to achieve adequate mixing.

As can be seen from the equation above and the foregoing limitations on the concentration of the monomer, the initiator concentration is determinative, but may be varied according to the desired molecular weight of the living polymer and the relative concentration of the monomer.

Generally, the initiator concentration can range from about 0.0001 to about 0.1 mole of active alkali metal per mole of monomer, or higher. Preferably, the concentration of the initiator will be from about 0.01 to about 0.004 mole of active alkali metal per mole of monomer.

The temperature of the polymerization will depend on the monomer. Generally, the reaction can be carried out at temperatures ranging from about -100°C up to about 100°C. When using aliphatic and hydrocarbon solvents, the preferred temperature range is from about -10°C to about 100°C. With ethers as the solvent, the preferred temperature range is from about -100°C to about 100°C. The polymerization of styrene monomer, for example is generally carried out at slightly above room temperature.

The preparation of the living polymer can be carried out by adding a solution of the alkali metal hydrocarbon initiator in an inert organic solvent to a mixture of a monomer and diluent at the desired polymerization temperature and allowing the mixture to stand with or without agitation until the polymerization is completed. A preferred alternative procedure is to add monomer to a solution of the catalyst in the diluent at the desired polymerization temperature at the same rate. In this method the monomer is converted quantitatively to a living polymer as long as the system remains free of impurities which inactivate the anionic species. As pointed out above, however, it is preferred to add all of the monomer ingredients together rapidly to insure the formation of a uniform molecular weight distribution of the polymer. The anionic polymerization must be carried out under carefully controlled conditions, so as to exclude substances which destroy the catalytic effect of the catalyst or initiator. For example such impurities as water, oxygen, carbon monoxide, carbon dioxide, and the like should be excluded from the system. Thus, the polymerizations are generally carried out in dry equipment, using anhydrous reactants, and under inert gas atmosphere, such as nitrogen, helium argon, methane, and the like.

The above-described living polymers are susceptible to further reactions including further polymerization. Thus, if additional monomer, such as para alkyl styrene, is added to the living paraalkylstyryl polymer, the polymerization is renewed and the chain grows until no more monomeric styrene remains.

As noted above, the living polymers employed in the present invention are characterized by relatively uniform molecular weight, i.e., the distribution of molecular weights of the mixture of living polymers produced is quite narrow. This is in marked contrast to the typical polymer, where the molecular weight distribution is quite broad. The difference in molecular weight distribution is particularly evident from analysis of the gel permeation chromatogram of commercial polystyrene (Dow '666) prepared by free-radical polymerization and polystyrene produced by the anionic polymerization process utilized in accordance with the practice of the present invention.

After the desired degree of polymerization is reached, the polymerization is terminated by contract of the ionic polymer with agents containing active hydrogen (proton donors) such as water, alcohols, aqueous acid solutions or mixtures thereof. An antioxidant such as butylated hydroxytoluene (BHT) may also be added to the reaction mixture before isolation of the final polymer.

The weight average molecular weight (Mw) of the living polymers produced in accordance with this invention may generally range from about 500 up to about 2,000,000 preferably from about 1000 up to about 500,000 and most preferably from about 1500 up to about 150,000. As stated above, 2-lithiomethyl-5-norbornene provides for rapid initiation of the anionic reaction mechanism thereby leading to polymers having a very narrow molecular weight distribution (Mw/Mn) of less than 1.25, generally in the order of 1.1 or less. As such, the polymers have enhanced mechanical and processing properties.

Norbornene is a very reactive monomer, in many cases as reactive as ethylene, and may therefore be readily copolymerized with other monomers in free radical, anionic and cationic polymerization systems, as well as in extruder graft reactions. This characteristic allows the utilization of the norbornene-capped macromonomers of this invention, represented by formulae IV and IX, in similar copolymerization reactions for the preparation of random graft copolymers containing the norbornene head monomer as part of the copolymeric backbone chain and the polymer associated therewith present as graft polymer segments of essentially uniform molecular weight pendant from the backbone chain, such as recurring polymer units represented by formula IX set forth above.

The preparation of such graft copolymers provides thermoplastic polymer composition(s) having balanced beneficial properties of both the backbone polymer and the macromonomer components alone and provides a technique for chemically linking these polymers which might otherwise be mutually incompatible when physically mixed or grafted by other techniques. The present graft copolymers differ structurally from conventional graft copolymers since the macromolecular monomer is interposed between polymeric segments of the backbone polymer rather than being arbitrarily attached to the backbone in a random manner. These characteristics contribute materially to the advantageous properties which inure in these novel graft copolymers.

The backbone component of the macromonomer copolymers of the present invention may be derived from any ethylenically unsaturated monomer which is copolymerizable with norbornene-type monomer materials. These include α-olefin monomers containing from 2 to about 18 carbon atoms such as ethylene, propylene, 1-butene, isobutene, 1-pentene, 1-hexene and the like as well as mixtures of ethylene and one or more of said olefins as described in connection with formula VI above. Especially preferred backbone monomer is a mixture of ethylene and propylene present at a level such that the copolymer backbone contains from about 15 to about 80 mole percent polymerized ethylene, the balance being propylene and the interpolymerized norbornene head monomer of the macromonomer. Most preferred are elastomeric copolymers containing from 30 to about 70 percent of polymerized ethylene.

The copolymerization of the polymerizable macromolecular monomers with the comonomers may be conducted in a wide range of proportions. Generally speaking, a sufficient amount of the macromolecular monomer should be present to provide the chemical joining of at least one of the uniform molecular weight side chain polymers to each backbone polymer, so that noticeable effect on the properties of the graft copolymeric properties can be obtained. The chemically joined, phase separated thermoplastic graft copolymers may be prepared by copolymerizing a mixture containing up to about 95 percent by weight, or more, of the polymerizable macromolecular monomers of this invention, although mixtures containing up to about 60 percent by weight of the polymerizable macromolecular monomer are preferred and mixtures containing up to 25 percent by weight of the polymerizable macromolecular monomer are most preferred. Stated, otherwise, the thermoplastic chemically joined, phase separated graft copolymer of the invention is comprised of: (1) from 1 to about 95 percent by weight of the polymerizable macromolecular monomer having a narrow molecular weight distribution (i.e., a Mw/Mn of less than 1.25), more preferably from about 1 to about 60 percent by weight, and most preferably from about 1 to about 25 percent by weight and; (2) from about 99 to about 5 percent by weight of a copolymerization α-olefin monomer or mixture of α-olefin monomers defined herein above, more preferably from about 99 to about 40 percent by weight of the latter, and most preferably from about 99 to about 75% by weight of the latter.

It will be understood by those skilled in the art that the solvent, reaction conditions and feed rate will be partially dependent upon the type of catalyst system utilized in the copolymerization process. One of the considerations is that the macromolecular monomer be dissolved in the solvent system utilized.

When preparing copolymers having an olefin backbone of ethylene or propylene together with a macromolecular monomer, it is preferred to employ a coordination catalyst known in the art as Ziegler and Natta catalysts, the latter being commonly used for polypropylene. Some of these catalysts are disclosed in Belgian Pat. No. 533,362, issued Mat 16, 1955, and U.S. Patent Nos. 3,113,115 and 3,257,332 to Ziegler et al. These catalyst are prepared by the interaction of a compound of transition metals of group IV-VII in the periodic table, including titanium, chromium, vanadium and zirconium, and a co-catalyst which is an organometallic compound of a metal of Groups I-A, II-A, II-B or III-A of the Periodic Table. The preferred oc- catalysts are organoaluminum compounds of the formula:

AlR_3
AlR_2Cl,
$AlR'RCl$
$Al_2R'_3Cl_3$
$Al_R'Cl_2$
$Al(OR')R_2$
$R'_2Al-O-AlR'_2$ and
AlR_2l

wherein R and R' represent C_1 to C_{10} aliphatic, alicylic or aromatic hydrocarbon radicals which may be the same or different. The most preferred organo-aluminium compound is an aluminum alkylsequichloride such as $Al_2Et_3Cl_3$ or $Al_2(iBu)_3Cl_3$.

As previously stated, the solvent system utilized will most conveniently be the solvent employed in the preparation of the marocmolecular monomer. Solvents useful for the polystyrene macromolecular monomers are those which dissolve polystyrene. Typical solvents for polystyrene include hexane, cyclohexane, benzene, toluene, xylene, decalin, tetralin and the like, as well as mixtures thereof. In some cases, however, the identity of the solvent system can have a marked effect on the percent of the macromolecular monomer converted to graft copolymer. For example, conversions of greater than 85% by weight of a macromolecule consisting of norbornene terminated poly(para-methylstyrene) can be achieved using hexane alone as a solvent or hexane mixed with a minor amount (about 5% by weight) of cyclohexane or toluene. On the other hand where the norbornene terminated macromolecule comprises para methylstyrene copolymerized with 50 mole percent or more of styrene monomer, then increasing amounts of cyclohexane or toluene, up to about 50% by weight, must be added to the hexane solvent to achieve greater than 85% by weight of macromonomer conversion. The amount of cyclohexane or toluene required above 5% by weight is a function of increasing styrene monomer content in the macromonomer above 50% by weight.

The copolymerization reaction may be conducted at any suitable temperature, depending on the particular catalyst, macromolecular monomer, monomer feed, resulting graft copolymer and solvent used. Generally, the graft copolymerization will be conducted at a temperature of from about 0°C to 100°C.

The graft copolymerization reaction is preferably conducted by placing a predetermined amount of the macromolecular monomer dissolved in the appropriate solvent in the reactor. The polymerization catalyst and monomer are thereafter fed into the solvent system to produce the graft copolymer.

The graft copolymers prepared in accordance with the invention generally may have a weight average molecular weight in the range of from about 10,000 up to 3,000,000 more preferably in the range of from about 25,000 to 250,000.

The copolymers prepared as described above provide an excellent substrate for further functionalization reactions such as halogenation. It is generally desirable to treat the polymerization product in an appropriate manner, prior to halogenation, in order to quench the catalyst and/or remove catalyst residues, remove residual unconverted monomers and place the polymer in a convenient form for the halogenation reaction.

Halogenation of the copolymers of this invention using a source of halogen and in the presence of a free radical initiator is highly selective towards halogenation of benzylic sites, i.e., sites present in the alkylstyrene sidechains, than sites present in the backbone chain. In fact almost exclusive halogen substitution occurs on one or more of the alkylaromatic groups present in the pendent chain as consequence of hydrogen atom extraction from these groups. This is significant because halogenation of the backbone polymer chain is undesirable due to the possibility of facile dehydrohalogenation reactions leading to backbone unsaturation and resulting environmental instability, i.e., decreased ozone resistance and thermal instability. In addition, the presence of halogen (bromine) on the ring alkyl groups leads to several additional significant advantages, such as facile functionalization by substitution of other functional groups at that site. More particularly, the highly reactive nature of the halogen in the haloalkyl group attached to an aromatic ring makes it a particularly desirable functionality to enhance and extend the usefulness of these copolymers in a range of applications. The presence of aromatic haloalkyl groups in the copolymer permits cross linking in a variety of ways under mild conditions.

A second advantage offered by the copolymerized macromonomers with respect to the halogenation is that the terpolymers of the invention contain relatively little residual unreacted volatile monomer content. Residual unreacted monomer, such as para-methylstyrene, left in the copolymer will react curing halogenation to both consume halogen and produce generally undesirable toxic by-products, and their presence thus renders it difficult to control and measure the amount of desired functionality introduced into the copolymer. Unreacted olefin monomers in the backbone polymer ar volatile enough to be easily removed in any of a variety of stripping operations, but para-methylstyrene, with its high boiling point of 170°C, is much more difficult to remove.

However, the graft copolymers prepared in accordance with this invention are relatively free of such difficult to remove unreacted monomers due to the fact that essentially all of the aromatic monomer used to prepare the norbornene-terminated macromolecules is consumed in the anionic polymerization process and also as a consequence of the very high (90% or greater) conversion of the macromolecule when copolymerized with the olefin monomers forming the backbone.

The halogenation reaction itself can be carried out in the bulk phase or on the graft copolymer either in solution or in a finely dispersed slurry. Bulk halogenation can be effected in an extruder, or other internal mixer, suitably modified to provide adequate mixing and for handling the halogen and corrosive by-products of the reaction. It has the advantages of permitting complete removal of residual unreacted para-methylstyrene by conventional finishing operations prior to halogenation, and of avoiding possible diluent halogenation as an undesirable side reaction.

Solution halogenation is advantageous in that it permits good mixing and control of halogenation conditions to be achieved, easier removal of undesired halogenation by-products, and a wider range of initiators of halogenation to be employed.

Suitable solvents for such halogenation include the low boiling hydrocarbons (C_4 to C_7) and halogenated hydrocarbons. The halogenation can also be conducted with the copolymer as a fine slurry or cement suspension in a suitable diluent which is a poor solvent for the copolymer. This is advantageous from a viscosity viewpoint and allows high solids content during halogenation.

As indicated above, the halogenation is preferably conducted in solvent in the presence of a free radical initiator and a source of halogen. Suitable indicators include heat, light or initiators which have a half life of between about 0.5 and 2500 minutes under the desired reaction conditions, more preferably about 10 to 300 minutes. The amount of initiator employed will usually vary between 0.02 and 1% by weight on the copolymer, preferably between about 0.02 and 0.3%. The preferred initiators are bis azo compounds, such as:

(1) azo bis isobutyronitrile;

(2) azo bis (2,4-dimethylvalero)nitrile;

(3) azo bis(2-methylbutyro)nitrile, and the like.

Other radical indicators such as peroxides can also be used, but it is preferred to use a radical initiator which is relatively poor at hydrogen abstraction, so that it reacts preferentially with the bromine molecules to form bromine atoms rather than with the copolymer or solvent to form alkyl radicals.

The halogenating agent can be gaseous, liquid or solid and may be added either in a pure state or diluted with a suitable inert solvent. Suitable halogenating agents include chlorine, sulfuryl chloride, N-chloro-succinimide, 1,3-dichloro-5, 5-dimethylhydantoin, bromine, bromine chloride, sodium hypochlorite, sulfur bromide and N-bromosuccinimide. Where gaseous chlorine, bromine or bromine chloride is used, gaseous diluents, e.g., nitrogen, argon, air, CO_2 etc., can be used when a diluent is desired. Mixtures of any of these halogenation agents may also be used. The most preferred halogenating agent is liquid bromine.

Halogenation in solution may be conducted at any temperature between about 40°C and the reflux temperature of a solution of the polymer. It is preferred to conduct the halogenation at relatively low temperatures, i.e., 45 to 80°C, since selectively towards hydrogen displacement on the alkylaromatic groups on the chain is further enhanced at a lower temperatures.

Since one mole of HX, wherein X is chlorine or bromine, is produced for each mole of halogen reacted or substituted on the enchained alkylstyrene moiety, it is desirable to neutralize or otherwise remove this HX during the reaction or at least during polymer recovery in order to prevent it from causing undesirable side reaction or corrosion of equipment. Such neutralization and/or removal can be accomplished by having a base (which is relatively non-reactive with the halogen) such as, for example, calcium carbonate powder present in dispersed form during the halogenation reaction to absorb the HX as it is produced. Removal of HX can also be accomplished by stripping with an inert gas, e.g. N_2, preferably at elevated temperatures. Final traces of HX may be neutralized by incorporation of a suitable base, e.g. calcium stearate into the stripped halogenated copolymer.

The degree of halogenation of the polymers is largely a function of the quantity of reactants used in the halogenation process and the structure and molecular weight of the graft polymer substrate. Generally speaking the halogen content of the graft polymers may range from about 0.05 up to about 7.5 weight percent based on the total weight of copolymer, more preferably from about 0.1 up to about 5.0 weight percent.

In the case of copolymers having the repeating units shown in formula VI above, it is believed that at least one of the side graft chains represented by "P" contain at least one repeating unit shown by the structure of formula V, wherein X is a halogen atom such as chlorine or bromine. It is possible that plurality of the formula VI repeating units in a given "P" side chain contain halogen. On the other hand, it is possible that other pendant "p" chains repeating along the P1 polymer backbone contain no halogen.

In addition, although the radical bromination is highly selective producing desired benzylic functionality almost exclusively, a possible side reaction involving disubstitution at the para-alkyl group may occur, yielding the dihalo derivative. However, it is believed that this does not occur until more than about 60% of the enchained para-alkylstyryl moieties have been monosubstituted. Hence, any desired amount of benzylic bromine functionality in the monobromo form can be introduced into the copolymers of this invention, up to about 60 mole % of the para-alkylstyrene content. Furthermore, since the para-alkylstyrene content can be varied over a wide range as described herein, it is possible to therefore introduce a significant functionality range. The halogenated copolymers of this invention are thus highly useful in subsequent reactions, for example cross-linking reactions.

It is desirable that termination reactions be minimized during bromination, so that long, rapid radical chain reactions occur, and so that many benzylic bromines are introduced for each initiation, with a minimum of the side reactions resulting from termination. Hence, system purity is important, and steady-state radical concentrations must be kept low enough to avoid extensive recombination and cross-linking. The reaction must also be quenched once the bromine is consumed, so that continued radical production with resultant secondary reactions (in the absence of bromine) do not then occur. Quenching may be accomplished by cooling, adding dilute caustic, the addition of a radical trap, or combination thereof.

The halogenated neutralized copolymers of the present invention can be recovered and finished using conventional means with appropriate stabilizers being added to yield highly desirable and functional saturated halogenated copolymers suitable for many uses.

The aromatic halomethyl group permits facile cross-linking to be accomplished in a variety of ways, for example, either directly through the halomethyl group or by conversion to other conversion to other functional groups to permit the desired cross-linking reactions be employed. Direct cross-linking can be effected with a variety of polyfunctional nucleophilic reagents such as ammonia, amines, or polyamines; organosulfides; metal dicarboxylates; metal dithiolates; promoted metal oxides (i.e., ZnO + dithiocarbamates), etc. Cross-linking can also be effected via polyalkylation reactions. The aromatic halomethyl groups thus provide a wide choice of cross-linking reactions to be used. Vulcanization is usually accomplished at a temperature ranging from about 120°C to about 250°C, preferably from about 140°C to 200°C, and usually takes from 1 to about 150 minutes.

The halogenated copolymers of the present invention may be processed in standard equipment used for rubber such as internal mixers. These halogenated copolymers are amendable to conventional compounding practice and various fillers and extenders can be incorporated, e.g., carbon blacks, clays, silicas, carbonates, oils, resins, waxes, etc., to produce a composition. The halogenated copolymers of the present invention can be cured alone or a composition comprising a halogenated copolymer of the present invention may be blended with other co-vulcanizable elastomers and thermoplastics.

EXAMPLES

The following examples are illustrative of the invention:

Example 1

Synthesis of Terpolymer of Ethylene-Propylene-(5-(4-methylphenyl))-2-norbornene

Reactor: 1l Continuous Flow Stirred Tank Reactor

Temperature: 30°C

Pressure: 500kpa

Agitation: 1200 kpa

Residence: 9 min

Feeds:

Hexane	4.11 kg/hr
Ethylene	95g/hr
Propylene	138g/hr
(5-(4-methylphenyl)-2-norbornene	
Condition A	0g/hr
Condition B	5.63g/hr
Condition C	11.26g/hr
Condition D	16.89g/hr
Hydrogen	50 wppm on Ethylene
VC14	0.493g/hr
Ethyl aluminum sesquichloride	3.162g/hr

Polymer Characterization:

Condition	A	B	C	D
Polym. Rate (gms/hr)	210	207	202	208
Ethylene wt%(1)	42	43	45	47
MPN wt%(2)	0	3	5.7	8
Mn by GPC	55k	52k	56k	51k
Mw by GPC	111k	117k	119k	117k

Notes: (1) Ethylene content using ASTM 1246.

(2) MPN content is the weight percent of the incorporated 5-(4-methylphenyll)-2-norbornene as determined by Hnmr.

Monomer conversion for this monomer is uniformly above 90% under these polymerization conditions.

This distribution of the styrenic residues in the polymer was determined by analyzing an alliquot of the polymer by gel permeation chromatography. The eluant of the chromatograph column was analyzed sequentially by a differential refractometer (which responds to all polymers) and a detector at 254nm which reveals the presence of aromatic residues. In all cases the responses of these two detectors were coincident indicating that the aromatic residues are incorporated in the polymer.

Example 2

Preparation of Ethylene-propylene-Allylbenzene Terpolymer

Reactor: 11 Continuous Flow Stirred Tank Reactor
Temperature: 30°C
Pressure: 500 kpa
Agitation: 1200 kpa
Residence: 9 min

Feeds:

Hexane	4.11 kg/hr
Ethylene	95 gm/hr
Propylene	138 gm/hr
Vanadium tetrachloride	0.493 gm/hr
Ethyl aluminum sesquichloride	3.16 gm/hr
Hydrogen	100 wppm on Ethylene
Allyl benzene:	
Condition A	0 gm/hr
Condition B	14 gm/hr
Condition C	42 gm/hr

Results:

Condition Rates	gms/hr	Ethylene wt%	wt% Allyl benzene
A	206	41.4	0
B	178	49.7	0.9
C	177	55.1	1.9

This monomer incorporation was statistical since the distribution as determined using a differential refractometer was identical to that obtained using an ultraviolet detector.

The following examples illustrate the preparation and purification of 2-bromethyl-5-norbornene, and the lithiation thereof to produce 2-lithiomethyl-5-norbornene.

Example 3

Synthesis of 2-Bromomethyl-5-norbornene

A 1 liter steel reaction vessel, fitted with a 2000 kpa pressure release safety and a steel plug was used for the Diels Alder reaction. 264.4g. (4 moles) dicyclopentadiene (Aldrich), 532.4g (4.4 moles) allyl bromide (Aldrich Gold Label which was purified by passing it through a column containing sodium bicarbonate, then magnesium sulfate), 3.9g hexadecane (GC internal standard) and 0.5g BHT (butylated hydroxytoluene - antioxidant) were placed into the reactor and reacted 6 hours at 180°C. The resulting crude mixture contained 75% 2-bromomethyl-5-norbornene, 9% dicyclopentadiene, 3% allylbromide and unidentified isomers of each.

Example 4

Synthesis of 2-bromomethyl-5-norbornene

A liter steel reaction vessel, fitted with a 2000 kpa pressure release safety and a steel plug was used for the Diels-Alder reaction. 264.4g (4 moles) dicyclopentadiene (Aldrich), 580.8g (4.8 moles) allyl bromide (Aldrich Gold) Label which was purified by passing it through a column containing sodium bicarbonate, then magnesium sulfate), 3.9g hexadecane (GC internal standard) and 0.5g BHT were placed into the reactor and reacted 6 hours at 180°C. The resulting crude mixture contained 78% 2-bromomethyl-5-norbornene, 2% dicyclopentadiene, 7% allylbromide and unidentified isomers of each.

Example 5

Purification of 2-bromomethyl-5-norbornene

The crude reaction mixtures from Examples 1 and 2 were combined and purified by two distillation steps. The first distillation was conducted in a 3 liter, 3 neck flask fitted with a nitrogen sweep, a thermocouple, and an efficient column. The system pressure was kept at 700 mm Hg pressure and the pot temperature was slowly raised to 175°C. Under these conditions the dicyclopentadiene cracked and cyclopentadiene co-distilled with the allyl bromide. When it appeared that no more volatile products were distilling, the pressure was dropped and the contents of the flask were flashed into a receiver. This distillate contained 2% dicyclopentadiene, 95% 2-bromomethyl-5-norbornene and higher boiling unidentified isomers. This receiver was then fractionally distilled at 13 mm. Several fractions were obtained ranging from 99.8 to 96% 2-bromomethyl-5-norbornene (by GLC) giving an overall purified yield of 60%.

Example 6

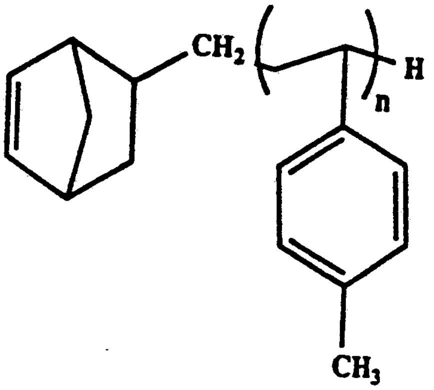
Lithiation of 2-bromomethyl-5-norbornene

A 2 liter 2 neck flask, fitted with a stirrer and a septum inlet was assembled in a dry box. 700ml of diethyl ether (distilled from dibutylmagnesium) was placed in the flask along with 4g lithium (Lithco, 0.8% sodium, slivered from rod). The flask was stoppered and 5% of a solution of 38g 2-bromomethyl-5-norbornene was added. As soon as the reaction begins (lithium is very bright) the flask was cooled to -50°C or below. The addition was continued dropwise at -50°C over 6 hour period. An alliquot was removed and analyzed by GLC; the bromide was quantitatively converted to 2-

lithiomethyl-5-norbornene (90% 2-methyl-5-norbornene was found after reaction was methanol). The excess lithium was removed by passing the mixture through a frit and the ether was removed under vacuum via rotary evaporation at -50°C. The 2-lithiomethyl-5-norbornene (LMNB) was redissolved in cyclohexane to give a solution that was approximately 1 molar in organolithium.

Example 7

The following example illustrates the preparation of a 2-poly(4-methylstyrene)-5-norbornene polymer having the structure of formula XI:



XI

wherein n is an integer sufficient to provide a polymer molecular weight (Mw) of about 2000. Generally n may range from about 5 to about 600.

All reactions and reagents were handled under an inert atmosphere of nitrogen with careful exclusion of both oxygen and water. The monomers were purified by distillation within a day of polymerization from dibutylmagnesium. The solvent (heptane, cyclohexane, ether or tetrahydrofuran) was purified the day of the polymerization by distillation under nitrogen of 25% of the total volume or alternatively by vacuum distillation from butyl lithium. The monomer was added to the solvent just prior to use. All glassware, syringes and needles were oven dried at 150° for 3 hours. The hot glassware, syringes and needles were oven dried at 150°C for 3 hours. The hot glassware was cooled and assembled under inert atmosphere usually in a dry box.

Example 8

Synthesis of Poly(4-methylstyrene) Macromonomer Using 2-lithiomethyl-5-norbornene Initiation of 4-methylstyrene Monomer

A two liter two neck flask, fitted with a stirrer and septum inlet is assembled in a dry box, nitrogen atmosphere. 700ml ether (distilled from dibutylmagnesium) is placed in the flask along with 4g lithium (Lithco, 0.8% sodium, cut from a rod). The flask is stoppered and 5% of a solution of 38g 2-bromomethyl-5-norbornene is added. As soon as the reaction begins (lithium brightens) the flask is cooled to -30°C or below. The addition is continued dropwise over a 6 hour period. An alliquot was removed and analyzed by GLC (hydrolyzed with methanol); the bromide was quantitatively converted to 2-lithiomethyl-5-norbornene (90% 2-methyl-5-norbornene was found and no remaining bromide). The excess lithium is removed by passing the mixture through a frit. The ether is removed under vacuum via rotary evaporation at -30°C. The 2-lithiomethyl-5-norbornene was redissolved in cyclohexane and filtered to give a solution that is approximately 1 molar in organolithium. A 3 liter flask is fitted with a stirrer and filled with 2.8 liters cyclohexane. The flask is heated and 600ml cyclohexane was distilled (this distillation is adequate to remove the oxygen and water from the cyclohexane). 236g freshly distilled 4-

methylstyrene (vacuum distilled from dibutylmagnesium) was added along with 100ml of the 2-lithiomethyl-5-norbornene solution. The polymerization began instantaneously and the flask temperature rose from 35°C to 55°C at which temperature it was maintained for three hours. The polymerization was terminated with methanol vapor and 0.1g BHT was added before the polymer was isolated by precipitation. The resulting poly(4-methylstyrene) (235g) macromonomer had a Mw = 2080 and Mn = 2050.

The following example illustrates the synthesis of an ethylene/propylene copolymer and an ethylene/propylene/graft 2-poly (4-methylstyrene)-5-norbornene copolymer by a continuous process employing a continuous flow stirred tank reactor and a Ziegler catalyst system.

Example 9

Synthesis of Terpolymer of Ethylene-Propylene-(2-poly(4-methylstyrene))

200g of the macromonomer prepared as in Example 8 is dissolved under an inert nitrogen atmosphere in Two liters of cyclohexane. This macromonomer solution is then used to prepare a terpolymer under the following conditions:

Reactor: One liter CFSTR (Continuous Flow Stirred Tank Reactor)

Temperature: 30°C

Pressure: 500 kpa

Agitation: 1200 kpa

Residence: 9 min

Feeds:

Hexane	3.16 kg/hr
Ethylene	95g/hr
Propylene	138g/hr
Macromer	

Condition A	0g/hr
Condition B	11.26g/hr
Hydrogen	0 wppm on Ethylene
VC14	.493g/hr
Ethyl aluminum sesquichloride	3.162g/hr

Polymerization Characterization:

Condition	A	B
Polymerization Rate (g/hr)	210	230
Ethylene wt%	48	50
P(4-MeS) wt%	0	10
Mn by GPC	112k	116k
Mw by GPC	182k	189k
Tensile (PSI)	14	170
% Elongation	410	690

Notes: (1) Ethylene content using ASTM 1246
(2) Poly(4-methylstyrene), (P(4-MeS)) is the weight percent of the incorporated (2-(poly(4-methylstyrene))-5-norbornene as determined by GPC.

Macromonomer conversion for this macromer is uniformly above 85% under these polymerization conditions. The distribution of the grafts in the polymer was determined by analyzing an alliquot of the polymer by gel permeation chromatography. The eluant of the chromatograph column was analyzed sequentially by a differential refractometer (which responds to all polymers) and a UV detector at 254 nanometers which responds to the aromatic branches.

In all cases the responses of these two detectors were coincident indicating that the branches are uniformly incorporated in the polymer.

The graft copolymers prepared in Example 9 above are clear, tough thermoplastic elastomers. Transmission electron micrographs of the grafts indicate that they are microphase separated with spherical polystyrene domains averaging 30 nanometers. The rheology of the graft copolymers is typical for multiphase materials. A temperature sweep from 20 to 100°C did not show a large change in viscosity, which indicates that the system likely remains biphasic in the melt. This corresponds to the non-newtonian shear behavior. The polymer undergoes a 4 order of magnitude drop in viscosity upon increasing the shear-rate from 10-2 to 10-2 rad/sec. The mechanical properties of the graft copolymers increase with increasing poly(4-methylstyrene) content, i.e, the ungrafted EP has no strength. However, the sample containing 10% grafted poly 4-methyl styrene had a tensile of 170 psi with an elongation at break of 690%.

The following examples illustrate preferred processes for preparing halogenated copolymers in accordance with this invention.

Example 10

Halogenation of Ethylene-(5-(4-methylphenyl))-2-norbornene)-Propylene Terpolymer

Free radical catalyzed bromination of the terpolymer was conducted on stabilizer free terpolymer. 100 grams of the terpolymer of Example 9 (Condition D) was dissolved in 1600ml carbon tetrachloride and refluxed under nitrogen for 30 minutes. 7.0 grams of N-bromosuccinimide was added to the stirred polymer solution. A solution of azoisobutyronitrile (0.1g in 10ml CC14) was added to the refluxing solution. A dark red color quickly formed and was dissipated over the next hour. The polymer solution was filtered to remove the succimide salt and the polymer was coagulated in methanol. The resulting polymer contained 2 wt% bromine which NMR results confirmed to be largely in the form of benzylbromide. GPC (DRI and UV) - as above) indicated the halogenation was uniform over the polymer composition.

Example 11

Halogenation of Ethylene-Propylene-Allylbenzene Terpolymer

Free radical catalyzed bromination of the EP terpolymer was conducted on stabilizer free terpolymer. 30 grams of the terpolymer (Condition C) was dissolved in 450ml hexane and refluxed under nitrogen for 30 minutes. 3.0 grams of N-bromosuccinimide was added to the stirred polymer solution. A solution of Vazo 52 (0.1g in 10ml hexane) was added to the refluxing solution. A dark red color quickly formed and was dissipated over the next 30 minutes. The polymer solution was filtered to remove the succimide salt and the polymer was coagulated in methanol. The resulting polymer contained 0.7 wt% bromine which NMR results confirmed to be largely in the form of benzylbromide. GPC (DRI and UV) indicated the halogenation was uniform over the polymer composition.

Example 12

Bromination of Ethylene-Propylene-g-Poly(p-methylstyrene) Terpolymer

Free radical catalyzed bromination of the EP graft terpolymer was conducted on stabilizer free terpolymer prepared as in Example 9. 50 grams of the terpolymer was dissolved in 1 liter of heptane and refluxed under nitrogen for 30 minutes. The solution was cooled to 70°C and a solution of AIBN (azoisobutyronitrile) in heptane (0.2g in 20ml) was added. A solution of bromine (8g in 100ml heptane) was added over 45 minutes. After the addition, the polymer was washed with 10% aqueous sodium bicarbonate solution followed by two washes with 10% aqueous isopropanol. The polymer cement was then precipitated into acetone and vacuum dried at 40°C overnight. Analysis by NMR indicated that there is 2.6st% benzylbromide which is the same value observed by X-ray florescence.

Example 13

Bromination of Ethylene-Propylene-g-Poly(p-methylstyrene

Free radical catalyzed bromination of the EP graft terpolymer was conducted on stabilizer free terpolymer prepared as in Example 9. 80 grams of terpolymer was dissolved in 1.5 liter of heptane and refluxed under nitrogen for 30 minutes. The solution was cooled to 70°C and a solution of AIBN (azoisobutyronitrile) in heptane (0.25g in 20ml) was added. A solution of bromine (17g in 100ml heptane) was added over 45 minutes. After the addition, the polymer was washed with 10% aqueous sodium bicarbonate solution followed by two washes with 10% aqueous isopropanol. The polymer cement was then precipitated into acetone and vacuum dried at 40°C overnight. Analysis by NMR indicated that there is 4.4 wt% benzylbromide which is too high to be accurately determined by X-ray.

Example 14

Curing Brominated Ethylene-Propylene-g-Poly(p-methylstyrene)

A mixture was prepared on a cold mill containing Tetrone A (1 pph), Zinc oxide (1pph), stearic acid (2 pph), carbon black (60 pph) and graft polymer (100 pph). The mixture was then placed in a Monsanto rheometer and a cure curve (Document 1) at 160°C was obtained. The torque increase as a function of time provides an indication of cure-state and cure time.

The bromo(EP-g-Poly(p-methylstyrene)) has cure characteristics which are the same as a good halobutyl cure: rapid torque rise, no reversion and a high cure state MH-ML = 43.8

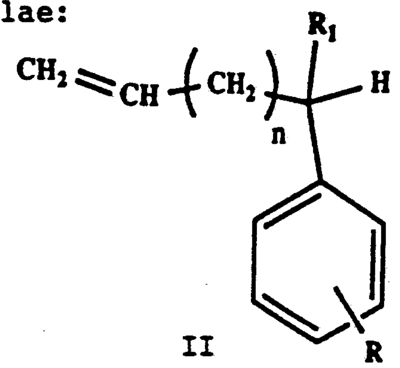
As is apparent from the foregoing description, the materials prepared and the procedures followed relate to specific embodiments of the broad invention. It is apparent from the foregoing general description and the specific embodiments that, while forms of the invention have been illustrated and described, various modifications can be made without departing from the spirit and scope of this invention. Accordingly, it is not intended that the invention be limited thereby.

CLAIMS:

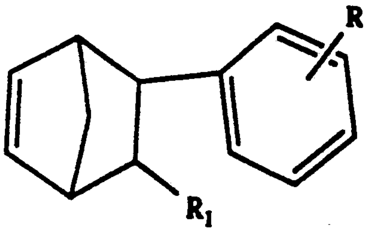
1. A copolymer comprising:

(1) one or more α-olefin(s), and

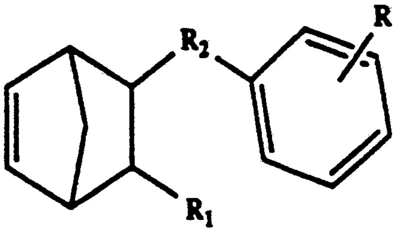
(2) an ethylenically unsaturated aromatic hydrocarbon selected from the group consisting of the monomers or macromonomers represented by the following formulae:



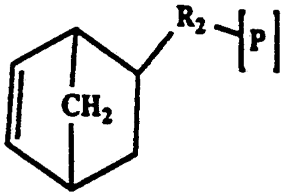
II



IIIa

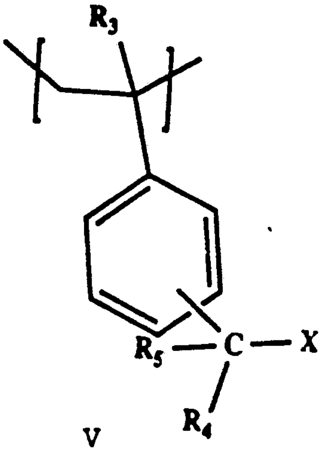


IIIb



IV

wherein n is zero or an integer from 1 to 10; R and R_1 are independently hydrogen or a C_1 to C_4 alkyl; R_2 is a straight or branched chain C_1 to C_{18} allylene radical; P is a homopolymeric or copolymeric segment comprising at least one monomer represented by the formula V:

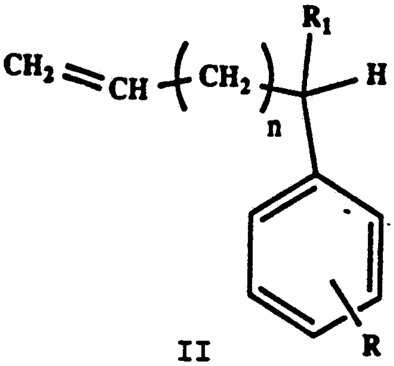


V

wherein R_3, R_4 and R_5 are independently H or a C_1 to C_4 alkyl and X is hydrogen or a halogen. P may also comprise other anionically polymerizable monomer(s) which include, but are not limited to, vinyl alkyl aromatic monomer or mixtures thereof, or other vinyl monomer or mixtures thereof.

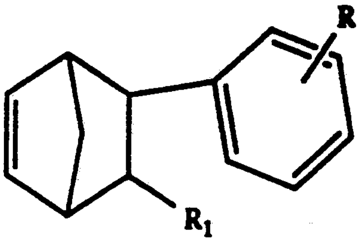
2. A copolymer of claim 1, wherein the α-olefin(s) is ethylene, propylene, 1-butene, isobutene,1-pentene, 1-hexane or a mixture of thereof.

3. The copolymer of claim 1, wherein the allyl aromatic hydrocarbon is represented by the formula:



II

4. The copolymer of claim 1, wherein the allyl aromatic hydrocarbon is represented by the formula:

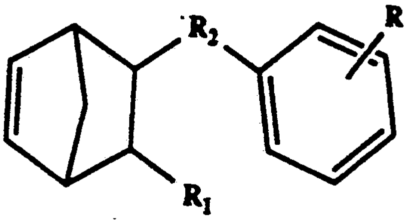


IIIa

5. The copolymer of claim 4, wherein R_1 is H and R is H or a C_1 to C_4 alkyl.

6. The copolymer of claim 4, wherein the hydrocarbon is 5-norbornene-2-phenyl or 5-norbornene-2-(methylphenyl).

7. The copolymer of claim 1, wherein the allyl aromatic hydrocarbon is represented by the formula:

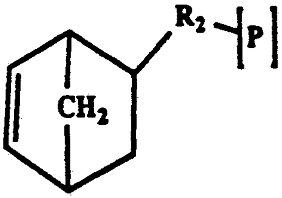


IIIb

8. The copolymer of claim 7, wherein R_2 is a C_1 or C_2 alkylene and R_1 is H.

9. The copolymer of claim 7, wherein the hydrocarbon is 4-methylstyrene.

10. The copolymer of claim 1, wherein the allyl aromatic hydrocarbon is represented by the formula:



IV

11. The copolymer of claim 3, wherein monomer II is an allyl benzene or substituted allyl benzene.

12. The copolymer claim 3, wherein the hydrocarbon is allyl(4-methyl) benzene, allyl (4-ethyl) benzene or allyl (4-propyl) benzene.

13. The copolymer of claim 3, wherein the copolymer is further halogenated at sites on the aromatic ring or through reactions with benzolic hydrogen, wherein R is other than H.

14. The copolymer of claim 1, wherein the copolymer contains 15 to 55 mole % ethylene.

15. The copolymer of claim 7, wherein in "monomer V" is characterized by X being hydrogen, and R_3 R_4 and R_5 are independently hydrogen or a C_1 to C_4 allyl.

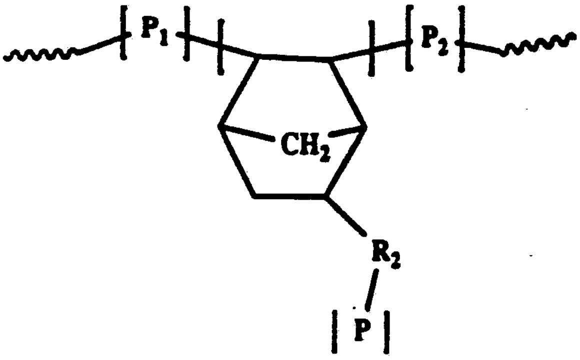
16. The copolymer claim 5, wherein alkyl styrene comprises 45 to 99.9 percent by weight of the side chains.

17. The copolymer of claim 9, wherein X of formula monomer V is a halogen and monomer V comprises 0.1 to 55 percent by weight of the side chains.

18. A copolymer of claim 1, comprising an elastomeric matrix comprising about 50 to about 98 weight percent of the copolymer.

19. The copolymer of claim 1, comprising discrete thermoplastic domains of from 2 to 50 weight percent of the polymer.

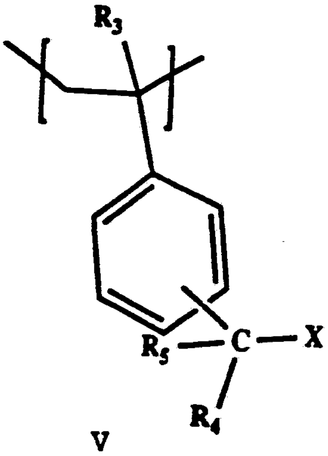
20. A copolymer represented by the formula:



VI

wherein P_1 and P_2 independently represent an elastomeric main chain comprising one or more C_2 to C_{18} α-olefins, particularly ethylene; R represents a straight or branched chain alkylene radical having 1 to 17 carbon atoms; and P is

a homopolymeric or copolymeric segment comprising at least one monomer represented by the formula V:



V

wherein R_3, R_4 and R_5 are independently H or a C_1 to C_4 alkyl and X is hydrogen or a halogen. P may also comprise other anionically polymerizable monomer(s) which include, but are not limited to, vinyl alkyl aromatic monomer or mixtures thereof, or other vinyl monomer or mixtures thereof.

21. The copolymer of claim 20, wherein P_1 or P_2 or both comprise ethylene.

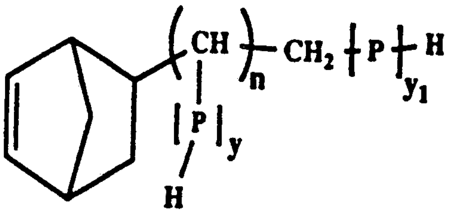
22. The copolymer of claim 20, wherein P_1 or P_2 or both comprise ethylene and propylene.

23. The copolymer of claim 20, wherein P, P_1 or P_2 independently comprise one or more α-olefins selected from the group consisting of ethylene, propylene, 1-butene, isobutene, 1-pentene, 1-hexene.

24. The copolymer of claim 10, wherein in R_2 is a straight or branched chain C_2 to C_{18} alkylene radical.

25. The copolymer of claim 10, wherein R_2 is methylene.

26. A copolymer represented by the formula:



X

wherein P represents a polymeric chain selected from the group consisting of homopolymers, random copolymers and block copolymers derived from an alkylstyrene monomer, preferably para allyl styrene, having the formula V above, alone or in admixture with one or more other anionically polymerizable vinyl monomers; n is 0 or an integer ranging from 1-17, y and y1 are either 0 or 1, provided that where y1 is 1 then y is 0, further provided that where y1 is 0, then n is an integer ranging from 1-17 and (n-1) of the y substituents are also 0 the remaining y substituent is a 1, and further provided that where n is 0, then y1 is 1.

27. The copolymer of claim 26, wherein the vinyl monomer is an aromatic monomer, a vinyl unsaturated

amide, an organic diisocyanate, a C_2 to C_8 alkyl allyl, a allyl acrylate, a methacrylate, a lower olefin, a vinyl ester of an aliphatic carboxylic acid, a C_2 to C_8 alkyl ether, a vinyl pyridines, a vinyl pyrrolidones, or a diene.

28. The copolymer of claim 26, wherein P is a homo polymer of an alkyl styrene or a copolymer of alkylstyrene and a vinyl aromatic hydrocarbon.

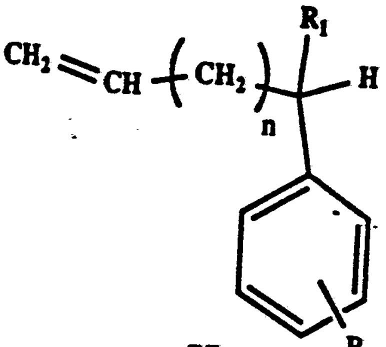
29. The copolymer of claim 28, wherein the alkyl of the alkylstyrene is methyl, ethyl or propyl.

30. The copolymer of claim 26, wherein P is a homopolymer, a block copolymer, a tapered block copolymer or a random copolymer.

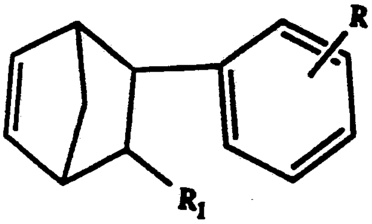
31. A process for producing a copolymer comprising:

(1) contacting one or more α-olefins; and

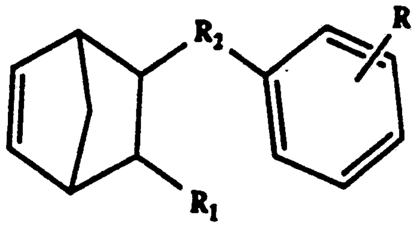
(2) one or more ethylenically unsaturated aromatic hydrocarbons selected from the group consisting of the monomers or macromonomers represented by the following formulae:



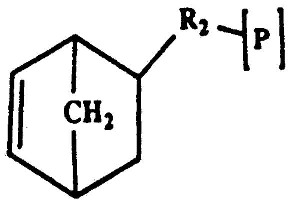
II



IIIa

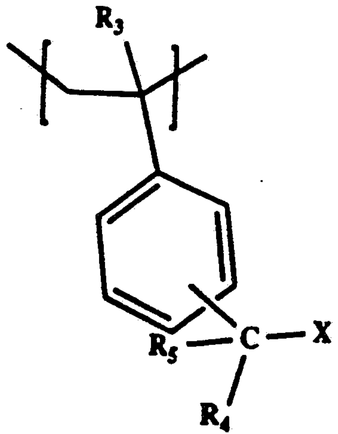


IIIb



IV

wherein n is zero or an integer from 1 to 10; R and R_1 are independently hydrogen or a C_1 to C_4 alkyl; R_2 is a straight or branched chain C_1 to C_{18} allylene radical; y = an integer and P is a homopolymeric or copolymeric segment comprising at least one monomer represented by the formula V:



V

wherein R_3, R_4 and R_5 are independently H or a C_1 to C_4 alkyl and X is hydrogen or a halogen, P may also comprise other anionically polymerizable monomer(s) which include, but are not limited to, vinyl alkyl aromatic monomer or mixtures thereof, or other vinyl monomer or mixtures thereof;

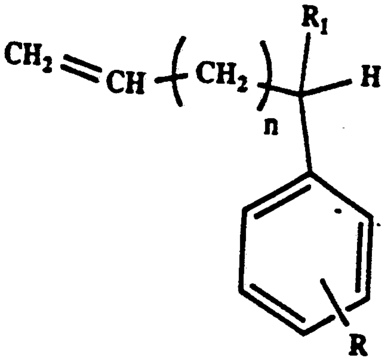
(3) with an initiator under polymerization conditions.

32. The process of claim 31, wherein the initiator is 2-lithiomethyl-5-norbornene.

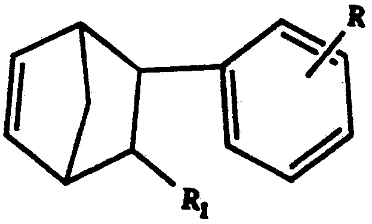
33. A process for producing a copolymer comprising:

(1) containing one or more α-olefins; and

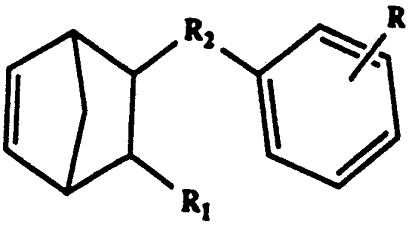
(2) one or more ethylenically unsaturated aromatic hydrocarbons selected from the group consisting of the monomers or macromonomers represented by the following formulae:



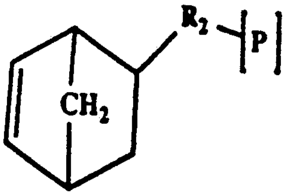
II



IIIa

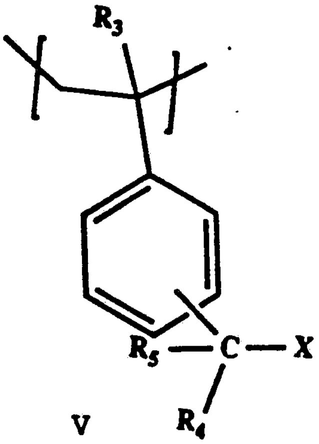


IIIb



IV

wherein n is zero or an integer from 1 to 10; R and R_1 are independently hydrogen or a C_1 to C_4 alkyl; R_2 is a straight or branched chain C_1 to C_{18} allylene radical; y = an integer and P is a homopolymeric or copolymeric segment comprising at least one monomer represented by the formula V:



V

wherein R_3, R_4 and R_5 are independently H or a C_1 to C_4 alkyl and X is hydrogen or a halogen, P may also comprise other anionically polymerizable monomer(s) which include, but are not limited to, vinyl alkyl aromatic monomer or mixtures thereof, or other vinyl monomer or mixtures thereof; (3) with an initiator under polymerization conditions,

(3) with a coordination catalyst and an aluminum alkyl cocatalyst under polymerization conditions.

34. The copolymer of claim 1 wherein the copolymer has an Mw of 500 to 2,000,000.

35. The copolymer of claim 1, wherein the Mw/Mn is less than 1.25.

36. The copolymer of claim 1, wherein the monomer or macromonomer comprises 1 to 95 wt% of the copolymer, and the α-olefin(s) comprise 99 to 5 wt% of the copolymer.

37. The copolymer of claim 1, which has been functionalized, halogenated, or crosslinked.

38. The copolymer of claim 26 which has been functionalized, halogenated, or crosslinked.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 93/03200

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C08F210/00

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C08F ; C08C

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
X	EP,A,0 325 260 (NIPPON OIL CO., LTD.) 26 July 1989 see the whole document ---	1,2,4-6, 31,33-38
X	EP,A,0 181 482 (NIPPON PETROCHEMICALS CO., LTD.) 21 May 1986 see the whole document ---	1-3,31, 33-38
A	EP,A,0 180 771 (NIPPON PETROCHEMICALS CO., LTD.) 14 May 1986 see claims 1-6 ---	1
A	US,A,3 494 897 (F. P. REDING) 10 February 1970 see claim 1 --- -/--	1

° Special categories of cited documents : [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

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1

IV. CERTIFICATION

Date of the Actual Completion of the International Search 12 AUGUST 1993	Date of Mailing of this International Search Report 23. 08. 93
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer PERMENTIER W.A.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	US,A,4 599 384 (M. F. FARONA) 8 July 1986 see the whole document ---	1
A	EP,A,0 095 787 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ) 7 December 1983 see claims 1-8 -----	1

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. US 9303200 SA 73275

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0325260	26-07-89	JP-A-	1185307	24-07-89
		US-A-	4931520	05-06-90
EP-A-0181482	21-05-86	JP-B-	4081603	24-12-92
		JP-A-	61085416	01-05-86
		EP-A,B	0180771	14-05-86
		US-A-	4994539	19-02-91
		US-A-	4717759	05-01-88
		US-A-	4736007	05-04-88
EP-A-0180771	14-05-86	JP-B-	4081603	24-12-92
		JP-A-	61085416	01-05-86
		JP-A-	61096604	15-05-86
		JP-A-	61110907	29-05-86
		EP-A,B	0181482	21-05-86
		US-A-	4994539	19-02-91
		US-A-	4717759	05-01-88
		US-A-	4736007	05-04-88
US-A-3494897	10-02-70	None		
US-A-4599384	08-07-86	None		
EP-A-0095787	07-12-83	US-A-	4408017	04-10-83
		CA-A-	1194641	01-10-85
		JP-B-	4047682	04-08-92
		JP-A-	58215407	14-12-83

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82