(54) Title: ADHESIVES BASED ON ELASTOMERIC COPOLYMERS HAVING THERMOPLASTIC POLYMER GRAFTS

(57) Abstract

An adhesive is disclosed. The adhesive is a blend of a tackifier and a polymer, having an elastomeric main chain and incorporating thermoplastic macromonomer side chain grafts, which can exhibit enhanced shear thinning and allow spray application of the adhesive onto a substrate. In one embodiment, the polymer main chain comprises a polymer of an isoprene having about 4 to about 7 carbon atoms and a para-alkylstirene, and the side chains comprise a grafted macromonomer, such as a terminally functionalized poly(styryl) chain of very narrow molecular weight distribution, attached to the para-alkyl group of the para-alkyl-stirrene. In another embodiment, the polymer comprises a polyolefin main chain and a norbornene terminated macromolecule copolymerized to introduce the side chains.
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ADHESIVES BASED ON ELASTOMERIC COPOLYMERS HAVING THERMOPLASTIC POLYMER GRAFTS

Field Of The Invention

This invention relates to adhesives based on elastomeric copolymers having a thermoplastic graft structure used in hot melt, disposable tape and label applications. More particularly, this invention relates to adhesives exhibiting reduced melt viscosity with increasing shear rates.

Background of the Invention

The role of macromolecules is pervasive in the manufacture and fabrication of a wide variety of articles. Plastics, synthetic fibers, elastomers and innumerable other products are derived from polymers. A great deal of effort and attention has been funnelled into polymerization processes, i.e. the preparation of polymers. Much effort has also gone into the preparation of useful articles from polymers once they have been prepared. Such polymer processing techniques commonly involve molten processing of the polymers. Such molten processing technology includes molding, extrusion, compounding, spinning, spraying and other procedures.

A persistent problem remains in the fabrication of useful articles from polymers because of the unique rheological and mechanical properties of polymers. On the one hand, high molecular weights are generally desirable from the consideration of the mechanical properties of the article ultimately formed therefrom; on the other hand, however, higher molecular weights tend to make processing and fabrication from the melt more difficult. In the molten state, polymer chains can move freely, though often with enormous viscosity, past one another if a sufficient force is applied. The fabrication of most polymeric articles utilizes this principle, and this is the chief example of the plasticity from which the very name "plastics" is derived.
The melt viscosity of polymers in hot melt pressure sensitive adhesives (HMPSA's) applied by spraying is particularly troublesome. In order to be sprayable, the polymer must have a desirably low melt viscosity at high shear encountered during spraying the adhesive through a small orifice. On the other hand, the polymer desirably has a high melt viscosity at a low or non-shear condition in order to minimize spreading and creeping of the adhesive after it is applied to a substrate surface by spraying, but before it has cooled sufficiently to solidify. The adhesive must, of course, also have adhesive properties to serve as an adhesive, and cannot severely degrade at spraying conditions (i.e., under shear at high temperature).

Heretofore, multiblock copolymers have been used in a sprayable hot melt pressure-sensitive adhesive formulation with limited success. Such multiblock copolymers include, for example, poly(styrene-isoprene-styrene) ("SIS"), poly(styrene-butadiene-styrene) ("SBS"), poly(styrene-ethylene/butene-1-styrene) ("SEBS") and the like. Other two-phase polymers such as ethylene-vinyl acetate copolymer (EVA) have also been used. The multiblock copolymers (SIS, SBS and SEBS) are usually formulated with tackifiers and oils to form HMPSA's, whereas EVA's are generally formulated with tackifiers and wax for HMA's. The cohesive strength of these polymers depends strongly on the presence of a discrete, rigid reinforcing phase, e.g. polystyrene domains in the block copolymers and, in the case of EVA's, the crystallized phase of these semi-crystalline polymers.

The use of block copolymers in adhesive applications has grown rapidly in recent years. Their advantage over homopolymers or random copolymers such as natural rubber and styrene-butadiene rubber is shear performance and high temperature performance. This derives from the persistence of polystyrene phase structure in the tackified adhesive formulations. These high glass transition temperature (T_g) domains function as physical cross-links, or fillers, which enhance modulus at high
temperature and/or creep resistance over long periods of time. Therefore, an ideal tackifier would not intrude into the glassy polystyrene domains and should be either compatible, or at least partially compatible, with the elastomeric region of the two-phase polymers. Thus, different tackifiers are known to interact with block copolymers such as SIS, SBS and SEBS to affect viscoelasticity and adhesive performance.

A review on the melt rheology (i.e. at temperatures above Tg of polystyrene) of styrene-diene triblock copolymers appears in Lyngaae-Jørgensen, in Processing, Structure And Properties Of Block Copolymers, ed. by M. J. Folkes, Elsevier, London, (1985). The rheological properties of a block copolymer with a two-phase structure involve gradual structural changes as a function of time and deformation. The nature of flow mechanisms and flow units (breakdown of phase morphology and type of steady state flow structure) presents both experimental and theoretical difficulties.

In Arnold et. al., Journal of Applied Polymer Science, vol. 14, p. 427 (1970), the structural breakdown of an SBS polymer in simple flow was described. At low frequencies, the polymeric melt is an essentially intact, three-dimensional network. As the frequencies increase to some intermediate values, the three-dimensional network transforms to a system consisting of large star-shaped aggregates. Domains still occur, now as the linking points of the large star-shaped aggregates. At sufficiently high frequencies, this aggregate is further disrupted to form a system of individual, nonaggregated molecules which flow similarly to an ordinary thermoplastic of the same molecular weight (that is, in a monomolecular melt state).

From U. S. Patent 3,235,626 to Waack, it is known to use vinyl terminated macromonomers in forming graft copolymers. In this patent, a macromonomer is prepared by reacting a vinyl metal compound with an olefinic monomer to obtain a vinyl terminated macromonomer. After protonation and catalyst removal, the prepolymer is
dissolved in an inert solvent with a polymerization catalyst and is subsequently reacted with either a different polymer having a reactive end group, or a different vinyl monomer under free radical conditions. This technique suffers from two major limitations: (1) though the use of vinyl lithium ensures that each polymer chain has one vinyl end group, vinyl lithium is one of the slowest anionic polymerization initiators, and results in a very broad molecular weight distribution wherein the ratio $M_n/M_w$ is greater than 2, a consequence of the ratio of the overall rate of propagation of the styryl anion to that of the vinyl lithium initiation, with the result that graft copolymers prepared from these macromonomers cannot provide a uniform side chain molecular weight; and (2) substituted vinyl compounds do not generally polymerize to high conversions and the conversion decreases as the length of the side chain increases. Conversions of 50 percent, although relatively high for most substituted vinyls, means that the resulting graft copolymers contain 50 percent unreacted macromonomer which, for most applications, is unacceptable.

An alternative route, controlled termination of living polymers, is known from U. S. Patent 3,989,768 to Milkovich et al., and Milkovich et al., J. Appl. Polym. Sci., vol. 27, p. 4773 (1982). These references describe anionic polymerization of a number of monomers of 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 macromonomomers. Although this route clearly improves the resulting macromonomer polydispersity and allows for a broader range of end-functionalities, it nonetheless introduces an uncertainty into the "purity" or "cleanliness" of the end functional groups since one can no longer be assured that each and every chain has one functional group. Although each step in the preparation of such end-functionalized macromonomers can separately be about 95 percent in
yield, the steps together produce a polymer that is, at best, only 80 to 90 percent end-functionalized.

The most informative characterization of graft copolymers produced using the Milkovich-type macromonomers comes from an analysis of the graft copolymers produced thereby. In Huang et al., *J. Poly. Sci.: Part A: Polym. Chem. Ed.*, vol. 24, pp. 2853-2866 (1986), the vinyl terminated macromonomer described in Milkovich '768 was utilized to prepare graft copolymers of ethylene and propylene. The best conversions for vinyl terminated polystyrene macromonomers, with a moderate molecular weight and useful feed composition in the range of 10 to 30 weight percent, on ethylene-propylene copolymer was 40 percent.

In view of this prior art, it would be highly desirable to devise a means for preparing macromonomers wherein the guaranteed functionality introduced in the initiation step is combined with a more active polymerizable group.

The preparation and use of copolymers of styrene and isobutylene is known in the art. Thus, such copolymers ranging from tough, glassy high polystyrene content copolymers for use in plastic blends, to rubbery low styrene isobutylene copolymers for use as impact modifiers, etc., have become well known in this art. Styrene and isobutylene have been copolymerized rather readily in the past under cationic polymerization conditions to yield these copolymers covering the entire compositional range. It is also known that blocky or random homogeneous copolymers can be produced by altering the copolymerization conditions, such as shown in Powers, U. S. Patent No. 3,948,868. This patent thus describes the production of random homogeneous polymers comprising at least two cationically polymerizable monomers such as isobutylene and styrene. This disclosure also includes a lengthy list of various olefinic compounds including isobutylene, styrene, α-methylstyrene and other such compounds. Furthermore, these compounds have been used in a variety of applications, including use as adhesives.
in connection with other materials taking advantage of the surface characteristics of the polyisobutylene sequences, as coatings, as asphalt blends, and in various plastic blends. As is discussed in the '868 patent, it is also well known to produce terpolymers including isoprene, but doing so reduces the overall polymer molecular weight rendering the production of high molecular weight polymers therefrom difficult, and complicating the overall production sequence.

There have also been attempts to produce various functionalized polymers. For example, Hankey et al., U. S. Patent No. 3,145,187, discloses polymer blends which include a vinyl chloride polymer, a surfactant, and a chlorinated olefin polymer, and the latter is said by this patentee to include copolymers of various materials which can include isobutylene and styrene, as well as ring-alkyl styrenes, among a large number of other compounds, which olefin polymers can then be chlorinated by known methods.

The literature has also disclosed other routes for obtaining copolymers of isobutylene and styrene, such as that shown in Powers et al., U. S. Patent No. 4,074,034, which discloses the copolymerization of isobutylene with halomethylstyrene. This technique requires the use of vinylbenzyl chloride and the like as 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. See, "Isobutylene copolymers of vinylbenzyl chloride and isopropenylbenzyl chloride," Journal of Applied Polymer Science, vol. V, Issue No. 16, pp. 452-459 (1969) in which the aromatic
monomer is said to be a mixture of the para and meta isomers.

There has also been some interest in the halomethylation of isobutylene/styrene copolymers, such as discussed in a paper by Sadykhov, et al. entitled "Chloromethylation of an Isobutylene/styrene Copolymer and Some of Its Chemical Reactions," *Acerb. Neft. Khoz.*, 1979 (6) 37-9.

In an article by Harris, et al. entitled "Block and Graft Copolymers of Pivalolactone...", *Macromolecules*, 1986, vol. 19, pp. 2903-2908, the authors discuss the copolymerization of isobutylene with styrene and preferably a ring-methylated styrene. This article specifically discloses copolymerization with vinyl toluene, comprising a mixture of meta- and para-methylstyrene in approximately 65/35 amounts, and with para-methylstyrene, for the purpose of producing thermoplastic elastomer pivalolactone copolymer systems with no autooxidizable aliphatic unsaturation. The article fails to recognize any difference between the use of vinyl toluene and para-methylstyrene, and in any event, even when it employs the latter, it employs conditions which result in copolymers having the properties, including heterogeneous compositional distribution and very broad molecular weight distribution for the unfractonated copolymer, as set forth in Tables 4 and 5, which include an $M_n$ for the unfractonated copolymer of 16,000, and $M_w/M_n$ of 17.45, and a 4-methylstyrene content in the polymer which varies considerably from the monomer feed and varies significantly as a function of molecular weight.

Finally, there are also articles which discuss copolymers of isobutylene and para-methylstyrene without discussing any method for preparing them. These articles include Sadykhov, et al., "Studies of Oxidative Thermal Degradation of Copolymers of Isobutylene with m- and p-Methylstyrenes in a Solution of Mineral Oils," *Uch. Zap. Azerb. Un. t. Ser. Khim.*, 1975 (304), 87-92, and other such articles. Furthermore, in Toman, et al.,
"Isobutylene Polymers and Copolymers with Controlled Structure", Appl., 78/7, 339, (November 10, 1978), there is reference to the copolymerization of isobutylene with vinyl aromatic monomers. The search has thus continued for useful molecular weight copolymers of isobutylene and alkyl styrenes, and in particular for functionalized copolymers of this type which can be crosslinked, and otherwise used in a variety of applications.

Polymers with a saturated hydrocarbon backbone are well known to possess good environmental and aging resistance which makes them highly desirable in a variety of applications. Furthermore, rubbery copolymers containing major amounts of polyisobutylene are well known to possess low permeability, unique damping properties, and low surface energy which makes them particularly highly desired in many applications. However, the "inertness" of these saturated hydrocarbon polymers, their low reactivity and incompatibility with most other materials, and the difficulties in adhering them to, or using them in conjunction with most other materials has restricted their use in many areas.

In commonly assigned U. S. Serial No. 441,575, filed November 22, 1989, which is a Continuation-in-Part of copending U. S. Serial No. 416,503 filed October 3, 1989, which is a Continuation-in-Part of copending U. S. Serial No. 199,665 filed May 27, 1988; and copending U. S. Serial No. 416,713 filed October 3, 1989, which is a Continuation-in-Part of U. S. Serial No. 199,665 filed May 27, 1988; the disclosures of which are hereby incorporated by reference, it was theorized that the introduction of controlled amounts of the desired specific functionality as pendant groups on the saturated hydrocarbon backbone would greatly extend usefulness by permitting these polymers to be adhered to other surfaces and/or be co-reacted with or compatibilized with other functional polymers by "grafting" or crosslinking reactions. It was further theorized that the introduction of pendant functionality of the right type and amounts would permit these saturated hydrocarbon
polymers to be "painted" or coated with other materials or to be used as a coating on other materials and/or to be laminated with or dispersed in other materials to yield composite materials with a desired combination of properties.

As has been already pointed out, the fact that benzylic halogen functionality constitutes a very active electrophile that can be converted to many other functionalities via $S_N2$ nucleophilic substitution reactions has long been recognized, and the chemical literature is replete with examples of these reactions. "Clean" conversions in high yield to many functionalities, including the following have been reported: aldehyde, carboxy, amide, ether, ester, thioester, thioether, alkoxy, cyanomethyl, hydroxymethyl, thiomethyl, aminomethyl, cationic ionomers (quaternary ammonium or phosphonium, S-isothiouronium, or sulfonium salts), anionic ionomers (sulfonate and carboxylate salts), etc. In addition, the literature described many examples in which a benzylic halogen is replaced by a cluster of other functionalities by nucleophilic substitution with a multifunctional nucleophile such as: triethanol amine, ethylene polyamines, malonates, etc.

Nearly all of this previous work has been with simple, small (i.e. non-polymeric) molecules containing the aromatic halomethyl (or benzylic) functionality. However, a considerable amount of art also exists on nucleophilic substitution reactions involving chloromethyl styrene and polystyrenes containing aromatic chloromethyl groups to introduce other functionalities. Much of this work involves reactions with "styragels" or lightly crosslinked polystyrenes containing various amounts of benzylic chlorine, and while many of the same nucleophilic substitution reactions previously reported for small molecules containing benzylic chlorine have been achieved in "styragels," it has been necessary to modify reaction conditions and in particular to often employ phase transfer catalysts in order to promote the desired substitution reaction. Reactions involving the
benzylic chlorine in polystyrene have been more difficult to achieve than in simple small molecules because of the greater difficulty in achieving the intimate contact required between the reactants when one of the reactants (the aromatic chloromethyl moiety) is in a separate polymeric phase from the other reactant. Yields have also generally been lower and side reactions are more prevalent in the reactions involving the benzylic chlorine in polystyrene. However, since most of the work has been with "styrags," it has generally not been necessary to achieve high conversion in "clean" substitution reactions in order to preserve polymer solubility. Recent reviews of this work involving chloromethyl styrene and "styrags" containing benzylic chlorines are in the literature. See Marcel Camps et al., in "Chloromethylstyrene: Synthesis, Polymerization, Transformation, Applications" in Rev. Macromol. Chem. Physics, C22(3), 343-407 (1982-83) and JM Frechet in "Chemical Modification of Polymers via Phase Transfer Catalysts" in Crown Ethers and Phase Transfer Catalysts in Polymer Science, edited by Matthews and Canecher and Published by Plenum Press, NY, 1984, and Jean-Pierre Montheard, et al. in "Chemical Transformations of Chloromethylated Polystyrene" in JMS-Rev. Macromol. Chem. Phys., C-28 (3 & 4) pp. 503-592 (1988).

Previous workers have not applied nucleophilic substitution reactions to isobutylene/para-bromomethylstyrene/para-methylstyrene terpolymers to produce versatile, substantially saturated, macromonomer-grafted shear thinning copolymers.

Summary of the Invention

Applicants have discovered an adhesive composition having a polymer component incorporating polymer architecture to obtain a melt viscosity which decreases rapidly at high rates of shear. Such polymers, when utilized, for example, in a hot melt pressure-sensitive adhesive composition (HMPSA), exhibit viscosity drop under shear (shear thinning) wherein the HMPSA can
acquire sprayability at high shear rates. This is quite surprising because at low rates of shear the adhesives of the present invention exhibit a high viscosity. This enhanced, high viscosity property reduces spreading and creep on a substrate coated with the adhesive, for example, by spraying application, even while the HMPSA is still hot. Accordingly, the invention provides an ultra low melt viscosity adhesive system having advantages due to low melt viscosity of the polymer component under shear, and relatively high melt viscosity at low shear rates.

In one aspect, the invention broadly provides an adhesive composition comprising a shear thinning polymer having a rubbery main chain ("A") and a plurality of glassy side chains ("B") distributed along the main chain, admixed with a suitable tackifying resin. In accordance with a preferred embodiment of the present invention, the polymer has a rubbery main chain, preferably substantially saturated to enhance chemical stability, with a number average molecular weight (Mn^A) of at least about 25,000, preferably at least about 50,000, and more preferably from about 50,000 to about 100,000. In addition, the main chain desirably has a narrow molecular weight distribution as reflected in the ratio of weight average molecular weight (Mw^A) to number average molecular weight (Mn^A), or Mw^A/Mn^A, of less than about 6, more preferably less than about 4, even more preferably less than about 2.5, and most preferably less than about 2.

The glassy side chains may have a number average molecular weight of from about 1000 to about 30,000, preferably from about 2000 to about 15,000, and especially from about 3000 to about 10,000. The side chains also preferably have a narrow molecular weight distribution such that the ratio of weight average molecular weight to number average molecular weight (Mw^B/Mn^B) is less than about 6, more preferably less than about 2, even more preferably less than about 1.5, most preferably less than about 1.1 and especially in the
range of from 1.0 to about 1.05. In addition to the foregoing parameters, the average number of side chains attached to each main chain is preferably from about 2 to about 20, more preferably from about 3 to about 10, and most preferably from about 4 to about 8.

In one embodiment, the polymer component of the adhesive includes a main chain comprising a copolymer of an isoolefin having from about 4 to about 7 carbon atoms and a para-alkylstyrene wherein the main chain polymer has a substantially homogeneous compositional distribution. The side chains are distributed along the main chain and are attached to para-alkyl groups of the main chain para-alkylstyrerenes.

In a preferred embodiment, large molecule macromonomers with molecular weights >1000 are attached as the side chains to the isoolefin/para-alkyl styrene copolymer main chain. The macromonomers incorporate terminal nucleophilic groups which undergo a nucleophilic substitution reaction between the terminal nucleophiles and benzylic halide leaving groups attached to the main chain para-methylstyryl moieties. The product of this reaction is a macromolecule having a main chain comprising the isobutylene/para-methylstyrene/ para-bromomethylstyrene/ "base" terpolymer and a highly selected number of grafted large molecule side chains extending from several of the para-methylstyryl groups. The side chains comprise thermoplastic macromonomers selected from polymerizable monomers, such as, for example, polystyrene, poly(para-methylstyrene), poly(alpha-methylstyrene), poly(phenylene oxide), and the like. In a preferred embodiment, the isoolefin comprises isobutylene, the para-alkylstyrene comprises para-methylstyrene, and the macromonomer side chains comprise polystyrene or polyalphamethylstyrene.

In an alternate embodiment, the polymer component of the adhesive includes shear thinning architecture provided as the copolymerization reaction product of an \( \alpha \)-olefin and a monoolefinically terminated macromonomer. In this embodiment, the \( \alpha \)-olefin is preferably ethylene,
propylene or a combination thereof, producing an elastomeric main chain, and the monoolefinically
terminated macromonomer is preferably a norbornene
terminated, anionically polymerized monomer of high
purity, such as, for example, styrene, para-
methylstyrene, α-methylstyrene and the like, to introduce
glassy side chains into the main chain. The preferred
norbornene-terminated macromonomers can be employed in
very high purity, for example, at least 98 percent
norbornene terminated, preferably at least 99 percent,
more preferably at least about 99.5 percent, and most
preferably at least about 99.9 percent purity.
Furthermore, the molecular weight of the side chains can
be very tightly controlled through the preferred use of
macromonomers having a very narrow molecular weight
distribution, such as, for example, a ratio of $M_w/M_n$ less
than 2.0, preferably less than 1.5, more preferably less
than about 1.1, and especially in the range of from 1.0
to about 1.05. In a preferred embodiment, a norbornene-
terminated polystyrene, poly(para-methylstyrene) or
poly(styrene/para-methylstyrene) macromonomer is
polymerized together with ethylene and propylene monomers
in a continuous solution polymerization utilizing a
Ziegler-type coordination-complex initiator to obtain the
polymer component of the adhesive. Thus, there can be 90
percent or higher macromonomer conversion indicative of
the high reactivity of norbornene in most Ziegler-type
processes. The resulting polymer contains little
unreacted macromonomer, and therefore, the macromonomer
can be incorporated at widely varying concentrations.
Also, there are no loss of catalytic activity of the
Ziegler-type initiator, constant yield between about 30°C
and about 60°C and product recovery at conventional
ethylene/propylene copolymerization conditions.

In another aspect, the invention provides a method
of applying the adhesive described above. The method
includes the steps of: melting the polymer and the
tackifier to form a molten adhesive blend; spraying the
molten adhesive blend onto at least a portion of a
substrate surface; and cooling the adhesive blend to form an adhesive coating on the substrate surface. The spraying is preferably at a shear rate of at least about 100 sec⁻¹.

In yet another aspect, the invention provides an adhesive-coated article. The article includes a substrate having a layer of the shear thinning adhesive described above adhered to at least a portion of a surface thereof. The adhesive layer preferably has a domain structure substantially comprised of a spherical or a mixed cylindrical and lamellar morphology.

Brief Description of the Drawings

Fig. 1 is a semilog plot of storage modulus versus temperature for a macromonomer grafted isobutylene/para-methylstyrene/para-bromomethylstyrene copolymer ("BrXP-50-g-PS"; O-O-O) and several commercially available polymers, styrene-butadiene-tapered-styrene ("SBtS"; STEREON 840A; ∆-∆-∆), SIS (KRATON 1107; O-O-O), SBS (KRATON 1102; O-O-O) and EVA (ESCORENE 7750; V-V-V).

Fig. 2 is a semilog plot of log(storage modulus) versus temperature for a BrXP-50-g-PS (O-O-O) and a commercially available SEBS block copolymer (KRATON G 1657; x-x-x).

Fig. 3 is a semilog plot of loss tangent versus temperature for a BrXP-50-g-PS (O-O-O) and a comparison SIS block polymer (KRATON 1107; O-O-O) showing elastomeric transition temperature.

Fig. 4 is a log-log plot of complex viscosity at 180°C versus frequency for two BrXP-50-g-PS's(O-O-O) and the corresponding ungrafted XP-50 copolymer.

Fig. 5 is a log-log plot of complex viscosity at 180°C versus frequency for a BrXP-50-g-PS (O-O-O) and three commercially available polymers, SEBS (KRATON G 1657; x-x-x), SBtS (STEREON 840A; ∆-∆-∆) and SIS (KRATON 1107; O-O-O).

Fig. 6 is the plot of Fig. 5 at 160°C.

Fig. 7 is the plot of Fig. 5 at 140°C.
Fig. 8 is a log-log plot of complex viscosity at 180°C versus frequency for several adhesive compositions formulated with BrXP-50-g-PS copolymers (O-O-O) and two commercially available polymers, SIS (KRATON 1107; O-O-O) and SBS (STEREON 840A; Δ-Δ-Δ).

Fig. 9 is the plot of Fig. 8 with some of the same adhesive formulations at a temperature of 160°C.

Fig. 10 is the plot of Fig. 9 at 140°C.

Detailed Description of the Invention

I. Shear Thinning Adhesive Compositions

The adhesive composition, preferably as a sprayable hot melt adhesive, comprises a polymer component wherein the polymer has architecture including a rubbery or elastomeric main chain ("A") and a plurality of glassy or thermoplastic side chains ("B") distributed along the main chain, and a tackifying resin. For the polymer component, the main chain number average molecular weight will ordinarily be at least about 25,000, preferably at least about 50,000 and more preferably between about 50,000 and about 100,000. In addition, the main chain desirably has a narrow molecular weight distribution as reflected in the ratio of weight average molecular weight ($M_w^A$) to number average molecular weight ($M_n^A$), or $M_w^A/M_n^A$, of less than about 6, more preferably less than about 4, even more preferably less than about 2.5, and most preferably less than about 2.

The glassy side chains may have a number average molecular weight ($M_n^B$) from about 1000 to about 30,000, preferably from about 2000 to about 15,000, more preferably from about 3000 to about 10,000, and most preferably from about 5000 to about 8000. The side chains preferably have a narrow molecular weight distribution such that the ratio $M_w^B/M_n^B$ is less than about 6, more preferably less than about 2, even more preferably less than about 1.5, most preferably less than about 1.1 and especially in the range of from 1.0 to about 1.05. In addition to the foregoing parameters, the average number of side chains attached to each main chain...
is preferably from about 2 to about 20, more preferably from about 3 to about 10, and most preferably from about 4 to about 8.

As representative examples of monomers from which the rubbery main chains may be prepared, there may be mentioned some exemplary monomers known to form elastomeric polymers such as olefins and olefin mixtures, including, for example, isobutylene, para-alkylstyrene/C_4-C_7 isooolefin mixtures, ethylene/propylene, ethylene/1-butene, and ethylene/vinyl acetate mixtures; dienes and diene mixtures including, for example, butadiene, isoprene, 2-chloro-1,3-butadiene, styrene/butadiene, acrylonitrile/butadiene/styrene, and styrene/isoprene; and the like. Of these, C_4-C_7 isooolefin/para-alkylstyrene and rubbery ethylene/propylene mixtures are preferred embodiments and are described hereinafter in more illustrative detail as exemplary embodiments.

As representative examples of thermoplastic side chain polymers, there may be mentioned polystyrene, poly(para-methylstyrene), poly(alpha-methylstyrene), polyvinylnaphthalene, polyisopropenylstyrene, polynaphthalene, polyphenylstyrene, polycyclohexylstyrene, polyvinylxylene, polymethylvinylxylene, polymethylmethacrylate, poly(4-t-butylstyrene), poly(1,3-cyclohexadiene), poly(2,6-dimethyl-1,4-phenylene oxide) and the like, and also including combinations of these. Of these, polystyrene, poly(para-methylstyrene) and poly(styrene/para-methylstyrene) are preferred.

A particularly preferred polymer component comprises a main chain of a polymerized mixture of para-alkylstyrene (preferably para-methylstyrene) and isooolefin of from 4 to 7 carbon atoms (preferably isobutylene), and side chains of polystyrene, poly(para-methylstyrene) and/or poly(styrene/para-methylstyrene) grafted onto the para-alkyl groups of the para-alkylstyrene. Another particularly preferred polymer component comprises norbornene-terminated polystyrene and/or
polymethylstyrene copolymerized (as the glassy side chain) with ethylene and propylene (as the rubbery main chain). The invention is described herein below with reference to these two illustrative embodiments as representative examples of the invention, but it is understood that the invention is not limited thereto.

The second component of the present adhesive composition is a tackifier compatible with the polymer component. Tackifiers are chosen to impart substantial adhesive strength, promote substrate wetting and generally enhance adhesive performance, e.g., optimize tack performance versus temperature performance of the composition. The tackifier must generally not substantially interfere with the shear thinning property and the ability for spray application of the grafted polymer, nor should it substantially increase high temperature spread or creep.

Adhesion-promoting resins which are useful in the present adhesives include hydrogenated rosins, rosin esters, polyterpenes, terpenephenol resins, and polymerized mixed olefins. These tackifiers typically have a ring and ball softening point from about 10°C to about 180°C, preferably from about 15°C to about 105°C. Hydrocarbon tackifiers obtained from Exxon Chemical Co. under the trade designations ECR-111, and ECR-143H have been found to be preferred. ECR-143H resin, for example, is prepared by the cationic polymerization of a C5 olefin/diolen feed stream as described in U.S. Patent 4,916,192 which is hereby incorporated by reference herein.

Other tackifier components preferred in the present adhesive include aliphatic and aromatic hydrocarbon resins such as ESCOREZ or WINGTACK 95. WINGTACK 95 is the tradename for a diene-olefin copolymer of piperylene and 2-methyl-2-butene having a softening point of 95°C. The resin is prepared by the cationic polymerization of 60 weight percent piperylene, 10 weight percent isoprene, 5 weight percent cyclopentadiene, 15 weight percent 2-methylbutene and about 10 weight percent dimer. See U.
S. Patent 3,577,398. Other tackifying resins of the same general type which may be employed comprise the resinous copolymer of 20-80 weight percent piperylene and 80-20 weight percent 2-methyl-2-butene.

Adhesive properties are dependent on the proper selection of tackifier resin. Particularly important is the $T_g$ of the tackifier. Optimization studies show that tack-related properties which are nominally inversely proportional to crosslink density can be improved by optimizing the $T_g$ of the adhesive system. Selection of tackifier is an important variable in this regard. For example, when ECR-143H and ECR-111 tackifiers were blended together in equal proportions, several tack properties improved in adhesive systems incorporating the blended tackifier over adhesive systems incorporating each individual tackifier resin. General tackifier composition is also a strong variable in adhesive property optimization.

Adhesive systems of this invention may contain a tackifier resin in an amount of from about 5 to about 95 parts by weight and the shear thinning polymer or polymers in an amount of from about 5 to about 95 parts by weight. Preferred adhesive systems contain the tackifier in an amount of from about 30 to about 70 parts by weight, and shear thinning polymer or polymers in an amount of from about 30 to about 70 parts by weight.

The adhesive composition may further contain relatively minor amounts of ingredients, such as oils, fillers, coupling agents, colorants, antioxidants, and other stabilizing additives which do not substantially adversely affect the system, such as, for example, by adversely interfering with adhesion to a substrate surface or spray application techniques. The formulation is preferably a hot-melt essentially free of solvents and other vaporizable constituents which detract from the hot melt characteristics of the formulation, e.g., no need for drying or solvent removal.

The antioxidant or stabilizer can be added at from about 0.1 to about 3 percent by weight, preferably from
about 0.1 to about 1.5 percent by weight, more preferably from about 0.1 to about 1 percent by weight, and typically at about 0.5 weight percent.

The optional oils which may be mentioned include refined hydrocarbon oils typically present in adhesives, including paraffinic, aromatic, and naphthenic oils available under the trade designations KAYDOL (produced by WITCO), TUFFLO (produced by ARCO), and the like. The refined oils serve as a diluent for price reduction and improve surface tack properties.

Particulated fillers which may be used for thickening and price reduction include glass, silica, amorphous SiO₂, fumed alumina, calcium carbonate, fibers and the like. Suitable commercially available fillers are available under the trade designations CAB-O-SIL, ZEOSIL 35, AEROSIL R972, DUCRAL 10 and the like.

Suitable coupling agents include (but are not limited to) organometallic compounds such as, for example, silane-based compounds, organotitanates, organozirconates, organozircoaluminates, chrome complexes and the like. These are generally selected to promote adhesion based on the substrates and/or fillers involved in the particular application.

For hot melt application, the adhesive composition is generally prepared by blending in the melt under shear until a homogeneous blend is obtained. Various methods of blending hot melt pressure-sensitive adhesives are known to the art, and any method that produces a homogeneous blend is satisfactory. Typical blending equipment includes, for example, mixing extruders, roll mills, Banbury mixers, Brabenders and the like. In general, the blend components blend easily when subjected to high shear rates in the melt. The components are fed in no particular order, but generally the tackifying resin is added first and heated until molten. Thereafter, the grafted polymer is heated and mixed with the tackifier. Any other optional ingredients are generally added last.
The adhesive may be cooled and later reheated and reworked for use, or used directly, e.g. supplied under shear and/or pressure to a spray gun, extrusion die or other conventional hot melt applying equipment for application to a substrate. An important feature of the present invention is that the viscosity drop resulting from high shear enables the adhesive to be applied via a fine spray. Generally, the hot melt is heated sufficiently and worked at a frequency of from about 100 to about 1000 rad/sec to obtain a target viscosity of from about 1000 to about 10,000 poise at the feed to the spray gun. Spray application is typically a high shear application conducted at a shear rate from about 100 to about 200 sec⁻¹ or more. Spray equipment manufactured by MELTEX (MP300S) has been found to be suitable. Operating temperature typically ranges from about 140°C-200°C.

The adhesive may be applied to a wide variety of substrates, including both polar and nonpolar substrates. Examples include metal, glass, plastic, wood, etc. The adhesive may be applied as a hot melt coating to at least a portion of a surface of a substrate, or it may comprise an adhesive layer between opposed substrate surfaces in adhesive contact therewith. These latter laminate structures are generally formed by applying the adhesive to a first substrate surface, and then placing the second substrate surface in contact with the coating applied on the first substrate surface. Alternatively, the adhesive may be formed into a film or sheet which is applied to either or both surfaces of the laminate structure, and the adhesive can also be applied by other conventional adhesive application methods such as solution or emulsion techniques.

The present adhesive is particularly well-suited for both tape (generally requiring good shear properties) and label (generally requiring good tack properties) applications. Quite surprisingly, the present HMPSA has a sprayability comparable to an SBS-based PSA formulation, but with reduced high-temperature spread and creep resistance and chemical and oxidative resistance
due to the saturated backbone; however, it also has the adhesive and cohesive performance properties comparable to SBS formulations and in some instances SIS formulations.

II. Shear Thinning Polystyrene-Grafted Isoprene/Para-Alkylstyrene/Para-Bromoalkylstyrene Based Adhesives

A. Grafted Isoprene/Alkylstyrene Copolymers

A preferred polymer suited for use in the present shear thinning adhesive is an isoprene/para-alkylstyrene/para-bromoalkylstyrene main chain grafted with short glassy side chains of, for example, polystyrene, poly(para-methylstyrene) or poly(styrene/para-methylstyrene). The main chain comprises an isoprene/para-alkyl styrene copolymer halogenated in a post-polymerization reaction to incorporate an electrophilic leaving group. The side chains comprise a grafted macromonomer incorporating terminal nucleophilic functionality. The side chains are grafted onto the main chain terpolymer precursor in a nucleophilic substitution reaction.

The side chain grafted copolymers have shear thinning architecture, and when blended with a suitable tackifier, exhibit sprayability with enhanced adhesive properties. The copolymers can be characterized as a macromonomer grafted, nucleophilically substituted, halogenated copolymer of an isoprene and para-alkylstyrene copolymer which includes the para-alkylstyrene as:

\[
\text{H} \\
\sim\text{C-CH}_2\sim \\
\text{R}\sim\text{C-H} \\
\text{R'}
\]
or as:

(2) \[
\begin{align*}
5 & \quad H \\
10 & \quad \sim \text{C-CH}_2 \sim \\
15 & \quad \text{R-C-Y} \\
\end{align*}
\]

or as:

(3) \[
\begin{align*}
20 & \quad H \\
25 & \quad \sim \text{C-CH}_2 \sim \\
30 & \quad \text{R-C-X} \\
\end{align*}
\]

or as:

(4) \[
\begin{align*}
35 & \quad H \\
40 & \quad \sim \text{C-CH}_2 \sim \\
\end{align*}
\]

or as a mixture of (1), (2), and/or (3) and/or (4); wherein R and R' are independently selected from the group consisting of hydrogen, alkyl, preferably C₁ to C₅ alkyl, and primary or secondary alkyl halides, preferably primary or secondary C₁ to C₅ alkyl halides; X is selected from the group consisting of chlorine and bromine, preferably bromine; Y represents a glassy macromonomer side chain grafted to the para-alkylstyrene, preferably
attached to the main chain via nucleophilic substitution of one of the benzylic halogens; and Z represents an optional additional functional group or groups attached to the polymer via nucleophilic substitution of one of the benzylic halogens which may be vulcanizable or radiation-curable, for example.

In one embodiment, the macromonomer grafted copolymer component is a nucleophilically-substituted halogenated copolymer of an isoolefin and para-alkylstyrene which includes the para-alkylstyrene as:

\[
\begin{align*}
\text{H} & \\
\sim & \\
\text{C-CH}_2 & \\
\sim & \\
\text{C-W} & \\
\end{align*}
\]

25 wherein W includes at least Y grafted onto the para-alkylstyrene, and may optionally include a mixture of Y and one or more of hydrogen, X and Z, wherein R, R', X, Y and Z are as defined above. The para-alkylstyrene (wherein W is hydrogen) may comprise from about 0.5 to about 90 weight percent of the precursor copolymer, i.e. prior to grafting, preferably from about 1 to about 20 weight percent and especially from about 2 to about 10 weight percent. The macromonomer grafted para-alkylstyrene side chains (wherein W is Y) may comprise from about 0.5 to about 55 mole percent of the para-methylstyrene, preferably from about 0.5 to about 20 mole percent, more preferably from about 0.5 to about 15 mole percent, and especially from about 1 to about 7 mole percent of the para-methylstyrene. The radically halogenated para-alkylstyrene (wherein W is X) may comprise up to about 55 mole percent of the para-methylstyrene, preferably less than about 20 mole percent, more preferably less than about 15 mole percent.
of the para-methylstyrene. In a preferred embodiment, the halogenated para-alkylstyrene is only partially converted, for example, by nucleophilic substitution thereof by Y and/or Z groups, so that the macromonomer grafted copolymer also includes ungrafted halogenated para-alkylstyrene, preferably comprising from about 50 to about 200 mole percent of the grafted para-alkylstyrene moiety. Functionalized para-alkylstyrene (wherein W is Z) may comprise from 0 to about 55 mole percent of the para-methylstyrene, preferably from 0 to about 20 mole percent, more preferably from 0 to about 15 mole percent of the para-methylstyrene. The remainder of the main chain copolymer generally comprises the isocyanin which usually ranges from about 10 to about 99.5 weight percent of the precursor main chain copolymer, i.e., prior to grafting, preferably from about 80 to about 99 percent by weight, more preferably from about 90 to about 98 weight percent.

The presence of other functionality is optional and may be either interdispersed on a single grafted base copolymer to which additional functional groups have been attached or two or more grafted and/or functionalized copolymers may be blended together. The presence of the additional functionality enables other desirable properties to be incorporated into an adhesive system. For example, the presence of radiation-reactive functionality can facilitate crosslinking of the shear-thinning polymer in radiation curable adhesives. As another example of additional functionality, certain silane functional groups grafted onto the shear-thinning polymer can act to enhance adhesion to certain substrates such as glass.

An advantage of HMPSA materials of this embodiment comprising a polyisobutylene polymer incorporating pendant phenyl rings, is a polymer backbone free of unsaturations which are typically highly reactive sites for ozone degradation. Such ozone degradation may be a problem in isoprene-containing elastomers. These sites also lead to polymer degradation during any optional
free-radical crosslinking cure process. In addition, the presence of the phenyl rings enhances the UV resistance to degradation of the polyisobutylene backbone. General aging and weathering properties are improved as compared to radiation crosslinked elastomers, such as natural rubber or Kraton 1320X.

B. Preparation of Nucleophilically Terminated Macromonomer Side Chains

To obtain the sprayable adhesives of the present invention, attached side chains are preferably of uniform length. It is highly desirable, therefore that macromonomers be prepared by polymerization methods whereby dispersity and chain length may be controlled. In addition, macromonomers should incorporate a single terminal nucleophilic functional group and are desirably essentially free of non-functionalized and non-terminally functionalized macromonomers. Anionic polymerization techniques are well suited to prepare such macromonomers.

Macromonomers generally have the form of a polymeric kernel including a terminal segment nucleophile however equally suitable are alkali or alkaline earth metal salts or ammonium and alkyl substituted ammonium salts of such nucleophilically terminated macromonomers.

Monomers suited for anionic polymerization are well known and the present invention contemplates the use of all such polymerizable compounds. Preferred anionically polymerizable monomers include vinyl aromatics such as styrene, para-methylstyrene, α-methylstyrene, α-vinylnaphthylene, 3-vinyl toluene, divinylbenzene, and the like; lower acrylate and methacrylate esters including methyl methacrylate, methyl acrylate and the like; acrylonitrile; α-olefin unsaturated carboxylic acids such as acrylic acid, methacrylic acid, and the like; α-olefin unsaturated dicarboxylic acids and anhydrides such as maleic acid, maleic anhydride, itaconic acid, citraconic acid, and the like; vinyl pyridines; vinyl unsaturated amides such as acrylamide, methacrylamide, N,N-dialkylacrylamide, and the like; acenaphthylene; 9-acrylcarbazole; organic isocyanates;
copolymers with monomers such as 1,1-diphenylethylene which do not homopolymerize; and random and block copolymers of the above thermoplastic forming monomers with minor concentrations of elastomeric forming monomers such as isoprene and butadiene. Other such anionically polymerizable monomers are disclosed in *Macromolecular Reviews*, vol. 2, pages 74-83, Interscience Publishers, Inc. (1967) and in *Anionic Polymerization*, ACS Symposium Series 166, page 60, American Chemical Society (1981) which is hereby incorporated herein by reference.

When conducting anionic polymerizations, initiator type, reaction medium and reaction conditions are strongly dependent upon the monomer polymerized. Initiator generally comprise organometallic compounds derived from alkali metals such as, for example n-butyllithium, sec-butyllithium, and the like. Other suitable initiator is describes is U. S. Patent 3,786,116 to Milkovich et al. which is hereby incorporated herein by reference.

The polymerization process is typically conducted in a polar or non-polar organic solvent. Suitable solvents do not contain active hydrogen and act primarily as diluents for diminishing solution viscosity as the polymerization progresses. Examples of these solvents include benzene, toluene, cyclohexane, tetrahydrofuran, carbon disulfide, ethylene dichloride, trichloroethane, ISOPAR solvents, naphtha, and the like. Selection of solvent should desirably be undertaken with regard to the grafting step which follows to avoid having to isolate the macromonomer prior to the grafting thereof onto the halogenated precursor copolymer.

A small amount of a polar activator may be utilized to increase the polymerization rate or propagation rate without increasing the rate of undesirable side reactions or broadening the molecular weight ratio. Examples of polar activators include ethers principally tetrahydrofuran and amines principally \( \text{N,N',N'-tetramethylethylenediamine} \).
The temperature of polymerization may be conducted over a wide range of temperatures, generally from about -80°C to about 100°C, depending on the rate of reaction, viscosity considerations, reaction heat, and the like. Polymerization of styrene may be conducted between about 25°C and about 70°C in cyclohexane, toluene or benzene utilizing n-butyllithium. However, anionic polymerizations of lower methacrylate esters, for example, are preferably carried out at a lower temperature, from about -80°C to about -50°C in a polar solvent like tetrahydrofuran.

Process conditions including temperature, solvent type and initiator quantity are well known. Common examples are given in Milkovich col. 8-9 mentioned above. "Living polymers" produced by anionic polymerizations will continue polymerizing until unreacted monomer is gone or termination causing reactants are added. One monomer may be replaced by another to produce copolymer blocks. While the polymer chain center remains active i.e. susceptible to polymerization, it may be useful unterminated as a macromonomer as the chain growth center is a very active carbanion nucleophile.

Termination of the "living" chain centers caps each polymer chain with other nucleophilic functionality e.g. carboxylate, alkoxide, thiolate, amide, etc. and their alkali metal salts which is more suitable for purposes of isolating the macromonomer.

Termination is effected by the addition of the terminating agent after allowing sufficient time for conclusion of the reaction to the desired extent. Preferably, essentially all monomer is reacted into macromonomer prior to termination to avoid the presence of ungraftable impurities in the grafting step.

Following termination with the desired nucleophilic functionality, grafting reactions with the isobutylene/para-alkylstyrene/para-bromoalkylstyrene or other base elastomer may be conducted in situ in the same solvent medium where possible. Alternatively, the
functionality-capped macromonomer can be isolated in an intermediate step.

Other monomers suited for polymerization into terminally functionalized thermoplastic macromonomers include 2,6-disubstituted phenols which undergo oxidative coupling reactions to form aromatic polyethers. Such polymerizations are conducted by passing oxygen through a solution of the monomer in an organic solvent containing a catalytic complex comprised of a cuprous salt and an amine. For phenol monomers containing small substituents, polymerization proceeds rapidly under mild conditions. Thus 2,6-dimethylphenol polymerizes at room temperature to produce a macromonomer comprising a substantially monofunctional phenoxide nucleophile.


Macromonomers may be polyolefins such as polyethylene, polypropylene and the like grafted with an anhydride functionality such as succinic or himic anhydride as set forth in U. S. Patent 3,862,265 which is hereby incorporated herein by reference. The resulting polyolefin is substantially monofunctional with most chains containing one anhydride group at or near the end. This functionality may be converted to a suitable nuleophile by subsequent reaction of the polymer with an alcohol-base mixture.

A metal coordination complex type initiator is generally preferred for olefin type thermoplastic-forming monomers such as propylene, ethylene, butene-1, and the like. These generally involve Group I-III alkyl metal compounds and a third complexing agent. A suitable transition metal component of the catalyst system is titanium trichloride in coordination with an aluminum trialkyl or aluminum alkylhalide. When the aluminum compound is the former, no complexing agent is required. When the aluminum compound is an aluminum alkylhalide or
sesquihalide a complexing compound capable of donating electrons to the aluminum alkyl dihalide is necessary. Complexing compounds include amines, ethers, nitriles and other compounds functioning as a Lewis base.

Other suitable macromonomers may be prepared from monomers which undergo ring opening polymerizations. Such reactions are cationic polymerizations in which a carbenium ion forms the basis of the chain center. Cationic polymerizations may be initiated by species such as Na, RO⁻, H⁺, and BF₃ and terminate upon the destruction of the cation center by either recombination with the counterion or reaction with some other species which does not propagate as is known in the art. While many aspects of cationic polymerization are similar to anionic polymerization including formation of "living chains," in cationic polymerizations, termination does not result in an end group nucleophile. Terminal nucleophilic functionalization depends upon the polymer structure i.e. the availability of -O- or -S-, for example, as in a poly(ethylene oxide) or poly(ethylene sulfide) wherein treatment of the polymer with sodium ethoxide yields a polymer with an active sodium alkoxide chain end. Such polymerizations are well known in the art and further details may be found, for example, in G. Odian, Principles of Polymerization, 2nd. Ed., J. Wiley & Sons, New York, pages 508-563, (1981).

C. Preparation of the Polymer Main Chain

As previously mentioned, a preferred rubbery main chain in the present invention comprises an isoolesfin/para-alkylstyrene/para-bromoalkylstyrene polymer. This embodiment is, in part, based on the discovery that the polymerization of isoolesfin and para-alkylstyrene under certain polymerization conditions now permits one to produce a backbone polymer having substantially homogeneous compositional distribution. This uniform polymer may be further uniformly halogenated to obtain a precursor polymer which is well suited for
grafting in a nucleophilic substitution reaction to obtain the polymer main chain.

Suitable halogen-containing copolymers of a C₄ to C₇ isomonooolefin and a para-alkylstyrene comprise at least 0.5 weight percent of the para-alkylstyrene moiety. For elastomeric copolymer products, the para-alkylstyrene moiety may range from about 0.5 weight percent to about 20 weight percent, preferably from about 1 to about 20 weight percent, more preferably from about 2 to about 20 weight percent of the copolymer. The halogen content of the copolymers may range from above zero to about 7.5 weight percent. The halogen may be bromine, chlorine, and mixtures thereof. Preferably, the halogen is bromine. The major portion of the halogen is chemically bound to the para-alkyl group, that is, the halogen-containing copolymer comprises para-haloalkyl groups.

The copolymers of the isomonooolefin and para-alkylstyrene useful to prepare the halogen-containing copolymer components include copolymers of isomonooolefin having from 4 to 7 carbon atoms and a para-alkylstyrene, such as those described in European patent application 89305395.9 filed May 26, 1989, (Publication No. 0344021 published November 29, 1989), which is hereby incorporated herein by reference. The preferred isomonooolefin comprises isobutylene. The preferred para-alkylstyrene comprises para-methylstyrene.

Suitable copolymers of an isomonooolefin and a para-alkylstyrene include copolymers having a number average molecular weight (Mₙ) of at least about 25,000, preferably at least about 30,000, more preferably from about 50,000 to about 100,000. The copolymers also, preferably, have a ratio of weight average molecular weight (Mₚ) to number average molecular weight (Mₙ), i.e., Mₚ/Mₙ of less than about 6, preferably less than about 4, more preferably less than about 2.5, most preferably less than about 2. These copolymers, as determined by gel permeation chromatography (GPC) demonstrate narrow molecular weight distributions and substantially homogeneous compositional distributions, or compositional
uniformity over the entire range of compositions thereof. At least about 95 weight percent of the copolymer product has a para-alkylstyrene content within about 10 weight percent, and preferably within about 7 weight percent, of the average para-alkylstyrene content for the overall composition, and preferably at least about 97 weight percent of the copolymer product has a para-alkylstyrene content within about 10 weight percent, and preferably within about 7 weight percent, of the average para-alkylstyrene content for the overall composition.

In addition, since the relative reactivity of para-alkylstyrene with isooolefin such as isobutylene is close to one, the intercompositional distribution of these copolymers will also be substantially homogeneous. That is, these copolymers are essentially random copolymers, and in any particular polymer chain the para-alkylstyrene and isooolefin units will be essentially randomly distributed throughout that chain.

The halogen-containing copolymers useful in the practice of the present invention have a substantially homogeneous compositional distribution and include the para-alkylstyrene moiety represented by the formula:

\[
\begin{align*}
\text{H} \\
\sim \text{C-CH}_2 \sim \\
\text{R} - \text{C-X} \\
\text{R}'
\end{align*}
\]

in which R and R' are independently selected from the group consisting of hydrogen, alkyl preferably having from 1 to 5 carbon atoms, primary alkyl halides, secondary alkyl halides preferably having from 1 to 5 carbon atoms, and mixtures thereof, and X is selected from the group consisting of bromine, chlorine and
mixtures thereof, such as those disclosed in European patent application 89305395.9.

Various methods may be used to produce the copolymers of isomonolefin and para-alkylstyrere, as described in said European publication. Preferably, the polymerization is carried out continuously in a typical continuous polymerization process using a baffled tank-type reactor fitted with an efficient agitation means, such as a turbo mixer or propeller, and draft tube, external cooling jacket and internal cooling coils or other means of removing the heat of polymerization, inlet pipes for monomers, catalysts and diluents, temperature sensing means and an effluent overflow to a holding drum or quench tank. The reactor is purged of air and moisture and charged with dry, purified solvent or a mixture of solvent prior to introducing monomers and catalysts.

Reactors which are typically used in butyl rubber polymerization are generally suitable for use in a polymerization reaction to produce the desired para-alkylstyrere copolymers. The polymerization temperature may range from about -100°C about -35°C, preferably from about -80°C to about -40°C.

The process for producing the copolymers can be carried out in the form of a slurry of polymer formed in the diluents employed, or as a homogeneous solution process. The use of a slurry process is, however, preferred, since in that case, lower viscosity mixtures are produced in the reactor and slurry concentration of up to 40 weight percent of polymer are possible.

The copolymers of isomonolefins and para-alkylstyrere may be produced by admixing the isomonolefin and the para-alkylstyrere in a copolymerization reactor under copolymerization conditions in the presence of a diluent and a Lewis acid catalyst.

Typical examples of the diluents which may be used alone or in a mixture include propane, butane, pentane, cyclopentane, hexane, toluene, heptane, isoctane, etc., and various halohydrocarbon solvents which are
particularly advantageous herein, including methylene, chloride, chloroform, carbon tetrachloride, methyl chloride, with methyl chloride being particularly preferred.

An important element in producing the copolymer is the exclusion of impurities from the polymerization reactor, namely, impurities which, if present, will result in catalyst poisoning or excessive molecular weight depression by complexing with the catalyst or copolymerization with the isomonoolefins or the para-alkylstyrene. Most particularly, these impurities include the catalyst poisoning material, moisture and other copolymerizable monomers, such as, for example, meta-alkylstyrenes and the like. These impurities should be kept out of the system. The para-alkylstyrene is preferably at least 95.0 weight percent pure, more preferably 97.5 weight percent pure, most preferably 99.5 weight percent pure. The isomonoolefin is preferably at least 99.5 weight percent pure, more preferably at least 99.8 weight percent pure. The diluents employed are preferably at least 99 weight percent pure, more preferably at least 99.8 weight percent pure.

The most preferred Lewis acid catalysts are ethyl aluminum dichloride and preferably mixtures of ethyl aluminum dichloride with diethyl aluminum chloride. The amount of such catalysts employed will depend on the desired molecular weight and the desired molecular weight distribution of the copolymer being produced, but will generally range from about 20 ppm to 1 weight percent and preferably from about 0.001 to 0.2 weight percent, based upon the total amount of monomer to be polymerized.

Halogenation of the polymer can be carried out in the bulk phase (e.g., melt phase) or 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. The details of such bulk halogenation
processes are set forth in U.S. Patent No. 4,548,995, which is hereby incorporated herein by reference.

Suitable solvents for solution halogenation include the low boiling hydrocarbons (C₄ to C₇) and halogenated hydrocarbons. Since the high boiling point of para-methylstyrene makes its removal by conventional distillation impractical, and since it is difficult to completely avoid solvent halogenation, it is very important where solution or slurry halogenation is to be used that the diluent and halogenation conditions be chosen to avoid diluent halogenation, and that residual para-methylstyrene has been reduced to an acceptable level.

With halogenation of para-methylstyrene/isobutylene copolymers, it is possible to halogenate the ring carbons, but the products are rather inert and of little interest. However, it is possible to introduce the desired halogen functionality into the para-methylstyrene/isobutylene copolymers hereof in high yields and under practical conditions without obtaining excessive polymer breakdown, cross-linking or other undesirable side reactions.

It should be noted that radical bromination of the enchained para-methylstyryl moiety can be made highly specific, with almost exclusive substitution occurring on the para-methyl group, to yield the desired benzylic bromine functionality. The high specificity of the bromination reaction can thus be maintained over a broad range of reaction conditions, provided, however, that factors which would promote the ionic reaction route are avoided (i.e., polar diluents, Friedel-Crafts catalysts, etc.).

Thus, solutions of the suitable para-methylstyrene/isobutylene copolymers in hydrocarbon solvents such as pentane, hexane or heptane can be selectively brominated using light, heat, or selected radical initiators (according to conditions, i.e., a particular radical initiator must be selected which has an appropriate half-life for the particular temperature
conditions being utilized, with generally longer half-lives preferred at warmer halogenation temperatures) as promoters of radical halogenation, to yield almost exclusively the desired benzylic bromine functionality, via substitution on the para-methyl group, and without appreciable chain scission and/or cross-linking.

This reaction can be initiated by formation of a bromine atom, either photochemically or thermally (with or without the use of sensitizers), or the radical initiator used can be one which preferentially reacts with a bromine molecule rather than one which reacts indiscriminately with bromine atoms, or with the solvent or polymer (i.e., via hydrogen abstraction). The sensitizers referred to are those photochemical sensitizers which will themselves absorb lower energy photons and disassociate, thus causing, in turn, disassociation of the bromine, including materials such as iodine. It is, thus, preferred to utilize an initiator which has 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 percent by weight on the copolymer, preferably between about 0.02 and 0.3 percent. The preferred initiators are bis azo compounds, such as azobisisobutyronitrile (AIBN), azobis(2,4-dimethylvaleryl)nitrite, azobis(2-methylbutyryl)nitrite, and the like. Other radical initiators 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. In those cases, there would then tend to be resultant copolymer molecular weight loss, and promotion of undesirable side reactions, such as cross-linking.

The radical bromination reaction of the copolymers of para-methylstyrene and isobutylene can be highly selective, and almost exclusively produces the desired
benzylic bromine functionality. Indeed, the only major side reaction which appears to occur is dissubstitution at the para-methyl group, to yield the dibromo derivative, but even this does not occur until more than about 60 percent of the enchainened para-methylstyril moieties have been monosubstituted. Hence, any desired amount of benzylic bromine functionality in the monobromo form can be introduced into the above stated copolymers, up to about 60 mole percent of the para-methylstyrene content.

It is desirable that the 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 possible 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, turning off the light source, adding dilute caustic, the addition of a radical trap, or combinations thereof.

Since one mole of HBr is produced for each mole of bromine reacted with or substituted on the enchained para-methylstyril moiety, it is also desirable to neutralize or otherwise remove this HBr during the reaction, or at least during polymer recovery in order to prevent it from becoming involved in or catalyzing undesirable side reactions. Such neutralization and removal can be accomplished with a post-reaction caustic wash, generally using a molar excess of caustic on the HBr. Alternatively, neutralization can be accomplished by having a particulate base (which is relatively non-reactive with bromine) such as calcium carbonate powder present in dispersed form during the bromination reaction to absorb the HBr as it is produced. Removal of the HBr can also be accomplished by stripping with an inert gas (e.g., N₂) preferably at elevated temperatures.
The brominated, quenched, and neutralized para-methylstyrene/isobutylene copolymers can be recovered and finished using conventional means with appropriate stabilizers being added to yield highly desirable and versatile functional saturated copolymers.

In summary, halogenation is preferably accomplished by halogenating an isobutylene-para-methylstyrene copolymer using bromine in a normal alkane (e.g., hexane or heptane) solution utilizing a bisazo initiator, e.g., AIBN or VAZO 52 (2,2'-azobis(2,4-dimethylpentane nitrile)), at about 55 to 80°C, for a time period ranging from about 4.5 to about 30 minutes, followed by a caustic quench. The optionally recovered polymer can be washed in basic water wash and water/isopropanol washes, recovered, stabilized and dried.

D. Reaction of the Halogenated Base Terpolymer to Graft Glassy Side Chains and Other Functionality

The sprayable polymer component in this embodiment comprises the direct reaction product of the nucleophilic terminated macromonomer and the halogenated isooolefin/paraalkylstyrene polymeric main chain in a nucleophilic substitution reaction. The attachment of macromonomer grafts and, optionally, one or more different types of other functional groups allows preparation of polymers which can be radiation crosslinked, emulsified, and/or have improved adhesion to specific substrates, in addition to sprayability. Each of these attributes can be derived from the judicious choice of an appropriate functionality.

The benzylic bromine (halogen) functionality is uniquely suited, as the base from which the grafted copolymer components of this embodiment can be made, because it can be made to undergo selective nucleophilic substitution reactions with a great range of nucleophiles, so that almost any desired type and amount of functionality can be introduced without undesirable side reactions and under conditions which are mild enough to avoid degradation and/or crosslinking of the saturated
copolymer backbone containing the pendant benzylic halogen functionality. Furthermore, in many instances, it is possible to only partially graft or convert the pendant benzylic halogen to another desired functionality while retaining some, or to later graft or convert another portion, of the remaining benzylic halogen functionality to yet another new functionality, so that copolymers containing mixed grafts and/or other functionalities can be made. The mixed graft/functionality can advantageously provide unique combinations of properties, such as, for example, grafting with another functional polymer via one of the functionalities and/or crosslinking or adhering to some surface via another of the functionalities.

A benzylic halogen functionality constitutes a very active electrophile which will react under suitable conditions with any nucleophile capable of donating electrons to it. Suitable nucleophiles include those containing oxygen, sulfur, nitrogen, phosphorus, carbon, silicon, and various metals including especially magnesium, lithium, sodium, and potassium. Equally important to this versatility in types of nucleophiles which will react with the benzylic halogen functionality is the relatively mild conditions under which these nucleophilic substitution reactions proceed so that substitution reactions can be completed to introduce the desired new functionality without cleavage or crosslinking reactions involving the saturated hydrocarbon backbone of the isobutylene/para-methylstyrene copolymer.

Another of the attributes of the benzylic halogen functionality is the selectivity with which the desired substitution reactions can be made to proceed without undesirable side reactions such as complicating elimination reactions. This attribute is extremely important in reactions involving soluble high polymer components, since even a tiny amount of a side reaction which can lead to coupling may lead to gelation. In reactions involving simple molecules (which are usually
mono-functional) yields of only 70 percent of the desired product may be acceptable, since purification and separation of the undesired products is relatively simple. In reactions involving already crosslinked polymers (e.g. "Styrageks") lower yields to the desired product may also be acceptable, since the starting polymer is already insoluble. However, in reactions with the soluble high polymer components of this embodiment of the invention which contain many grafted and/or functional groups per molecule, it is necessary to achieve greater than 99 percent of the desired substitution reaction in order to maintain solubility during reaction and recovery. Tiny, almost insignificant (in other reactions) amounts of side reactions which produce gel may interfere with usefulness. Furthermore, purification of the substituted polymer to remove unwanted side products is usually very difficult or impossible. This is why the selective single route to high yield nucleophilic substitution reactions achievable with benzylic halogen functionality under controlled conditions is important.

In accordance with a preferred embodiment of the present invention, the nucleophilic reagents capable of donating electrons to benzyl halides and displacing a halide ion via a substitution nucleophilic displacement reaction may be Y or YM, and/or Z or ZM, wherein M is hydrogen, a metal ion, or an ammonium ion and Y is a macromonomer with mononucleophilic termination containing oxygen, sulfur, silicon, carbon, nitrogen, phosphorus, or various metals; and Z is a small molecule of <1000 molecular weight which may contain other functionality in addition to the simple nucleophile which becomes attached at the benzylic position.

Examples of suitable oxygen-containing nucleophiles which result in the attachment of -O- linkage to the benzylic position include, (but are not limited to):

"OR as in alkoxide or phenoxide;
as in carboxylates;

5 as in sodium salts.

Examples of suitable sulfur-containing nucleophiles which result in attachment of \(-S-\) linkage to the benzylic position include (but are not limited to):

10 \(-S-R\) as in thiolates and thiophenolates;

15 \(-SR_2\) as in thioethers;

\(\text{S} \equiv \text{C}-\text{R}\) as in thiocarboxylates;

20 \(\text{S} \equiv \text{C}-\text{R}\) as in dithiocarboxylates;

25 \(\text{S}=\text{C}-\text{NR}_2\) as in thioureas;

30 \(\text{S} \equiv \text{C}-\text{NR}_2\) as in dithiocarbamates;

35 \(\text{S} \equiv \text{C}-\text{OR}\) as in xanthates;

40 \(-\text{SCN}\) as in thiocyanates.

Examples of silicon-containing nucleophiles which result in the attachment of \(-\text{Si}-\) linkage to the benzylic position include (but are not limited to):

50 \(\text{H-SiR}_3\) as in silanes;

50 \(\text{H-SiX}_n\text{R}_{3-n}\) as in halosilanes.
Examples of nucleophiles which result in the attachment of -C- linkage to the benzylic position include (but are not limited to):

\[ -\text{CN} \quad \text{as in cyanides;} \]
\[ -\text{CR}_3 \quad \text{as in organolithium (or other alkali or alkaline earth metals) compounds;} \]
\[ \text{HC-}(\text{R})-(\text{CO}_2\text{R})_2 \quad \text{as in malonates and di- or trisubstituted methane derivatives in general in which the substituents activate the substituents methane carbon for carbon-alkylation reactions under basic conditions.} \]

Examples of nitrogen-containing nucleophiles which result in the attachment of -N- linkage to the benzylic position include (but are not limited to):

\[ \text{HN-C-R} \quad \text{as in amides;} \]
\[ \text{NH}_2\text{R}_3\cdot\text{n} \quad \text{as in various amines;} \]

\[ \text{as in carbazoles;} \]
\[ \text{as in phthalimides;} \]
Examples of phosphorus-containing nucleophiles which result in attachment of -P- linkage to the benzylic position (include but are not limited to):

$$\text{PH}_n\text{R}_{3-n}$$

as in various phosphines.

Examples of nucleophiles containing a metal (M) which result in the attachment of -M- linkage to the benzylic position include (but are not limited to):

$$\text{Mg-}$$ (anthracene complex in THF);

$$\text{Li-}$$ (appropriately complexed);

Examples in which Z is a small molecule of <1000 molecular weight containing other functionality in addition to the simple nucleophile which becomes attached at the benzylic position include (but are not limited to): triethanol amine, iminodiacetic acid, iminodiacetonitrile, iminodiethanol, vinyl pyridines, cinnamate, eleostearate, linoleate, acrylate, benzoyl benzoate, benzoyl phenolate, dihydroxybenzophenone, crown
ether derivatives, cryptand derivatives, cellulose derivatives, sugar derivatives, low molecular weight polyethylene oxide or polypropylene oxide chains with terminal nucleophilic groups, etc.

It should be noted that these reactions, in which Y and/or Z contain other functionalities in addition to the simple nucleophile which becomes attached at the benzylic position, greatly extend the type and range of functionalities which can be incorporated into the grafted/functionalized copolymers of the present adhesives.

However, it should also be noted that attachment of Y and/or Z groups containing other functionalities requires even greater care during the nucleophilic displacement reaction by means of which the Y and/or Z groups are attached to insure that the new functionalities are preserved and are not consumed by sequential reactions to produce unintended crosslinking or gelation. In some instances, it may be desirable to block the functionalities that need to be preserved until the nucleophilic substitution reaction is completed.

Most nucleophilic substitution reactions of this type also involve some degree of side reactions which can be extremely detrimental, since even minor amounts of side reactions in high polymers can lead to unintended gelation which can greatly diminish utility. It is known that nucleophilic substitution reactions can proceed by several different mechanisms, and with most electrophiles, these different mechanisms can lead to different products or to different amounts of side reactions. Those reactions which proceed by a concerted $S_N2$ mechanism usually yield more of the desired substitution product than those proceeding by an $S_N1$ mechanism. In the present invention, elimination reactions are entirely prevented so that even nucleophilic substitution reactions proceeding by an $S_N1$ mechanism still lead selectively to the desired substitution product without undesired side reactions.
The "key" requirements for producing sprayable copolymers via selective nucleophilic substitution reactions are:

1. Use of the isobutylene/para-halomethylstyrene/para-methylstyrene base terpolymers for nucleophilic substitutions under appropriate, controlled conditions. The composition of the terpolymer can be varied as desired to yield the desired combination of properties (i.e. $T_g$, hardness, flexibility, impact strength, functionality level, etc.).

2. Choosing the nucleophile and reaction medium so as to achieve the required intimate contact between the benzylic halogen attached to the base terpolymer and the nucleophile. It should be recognized that in some instances this can be accomplished by using a different solvent or reaction medium for the polymer and for the nucleophile and then employing an appropriate phase transfer catalyst to promote the reaction.

3. Achieving specific solvation at the reaction site so that the desired nucleophilic substitution reaction is facilitated at mild conditions.

4. Avoiding vigorous or harsh reactants or reaction conditions such as strong "hard" bases or high temperatures that would cause a loss in reaction selectivity and allow side reactions to become important and/or cause crosslinking or degradation reactions to occur.

5. Choosing the nucleophilic reagent and promoters appropriately so that the desired substitution reaction occurs quickly under mild conditions and potential undesired side reactions are avoided. For example, in using a carboxylic nucleophile in an esterification reaction to replace the benzylic bromines on an isobutylene/para-methylstyrene/para-bromo-
methylstyrene base terpolymer, one could choose the potassium salt of the acid as the nucleophilic reagent, along with 18 Crown-6 to solvate the potassium ion and promote the desired esterification substitution reaction, or one could choose the tetrabutyl ammonium counterion in an appropriate solvent as a nice weak acid to promote the reaction, rather than trying to use a hard ionic salt of the carboxylic acid as the nucleophilic reagent.

Choosing reaction conditions to minimize sequential reactions by recognizing that the nucleophilic substitution reaction being conducted can itself form attached pendant nucleophilic reagents on the base copolymer backbone and that these already attached nucleophilic reagents can nucleophilically "attack" other unreacted benzylic bromines on the base terpolymer in a sequential manner to consume the desired, already attached new functionality, and at the same time produce undesirable crosslinking and gelation.

Summarizing, reaction conditions must be chosen such that the unreacted nucleophilic reagent being used in the nucleophilic substitution reaction is either a much stronger, more reactive nucleophile, or is present in great excess over any attached nucleophilic functionality produced in the substitution reaction. For example, it must be recognized that attached basic groups will become available nucleophiles under basic conditions for further reaction with benzylic bromine. These intrapolymeric groups can react with other benzylic bromines to consume the already attached pendant functionality and produce undesired crosslinks. The result is gelled polymer instead of the desired pendant graft and/or functionalized copolymer component. Attempting to replace the remaining benzylic bromines of the base partially grafted terpolymer with mercaptan groups, it must be recognized that the attached SH (mercaptan)
groups will form incorporated mercaptide nucleophilic reagents under basic conditions and these incorporated mercaptide groups will react with other residual benzylic bromines to consume the already incorporated pendant mercaptan functionality and produce undesired thioether crosslinks resulting in gelled polymer instead of the desired pendant grafted and/or functionalized copolymer component.

Likewise, in producing additional pendant hydroxy groups on a partially grafted copolymer component of this invention embodiment, it must be recognized that the attached hydroxy groups will form alkoxide nucleophilic reagents under strongly basic conditions, and these attached alkoxide groups can react in a sequential manner with other residual unreacted benzylic bromines of the base terpolymer to consume the already attached pendant hydroxy functionality to produce ether crosslinks, resulting in gelled polymer rather than the desired pendant grafted and/or functionalized polymer component.

The key requirement of recognizing the potential for sequential reactions and choosing conditions to minimize them is especially important in cases where it is desired to produce the grafted polymer components of this embodiment of the invention with mixed pendant functionality. In these mixed functionality polymers, it is extremely important to choose functionalities and conditions such that the desired pendant functionalities are preserved and sequential reactions are avoided.

The exact conditions suitable for preparing the various grafted/functionalized copolymer components will vary depending upon the macromonomer and/or new functionality being introduced, as well as the base copolymer composition and other factors, and some experimentation may be necessary to define practical conditions in each case, but the same key factors as outlined herein must always be considered and observed. This will become clearer in the specific examples to follow, but some general reaction conditions can first be defined.
The nucleophilic substitution reactions can be run in solution using a solvent system in which both the base polymer and nucleophilic reagent (macromonomer) are soluble; can be run in a two-phase liquid run system with the base polymer dissolved in one phase and the nucleophilic macromonomer or other reagent in the other; can be run in a two-phase solid/liquid system (i.e. with the base polymer dispersed in a liquid phase containing the nucleophilic macromonomer or other reagent); or can be run in bulk with reactants dissolved or dispersed in the base polymer. The common solution situation is most controllable and generally the preferred case, but the bulk reaction may be economically advantageous in some cases where suitable reagents and reaction conditions can be found.

The intermediate two-phase systems may be advantageous under some circumstances and may be necessary in instances where the solubility parameters of the base polymer (containing the electrophile) and the nucleophilic macromonomer or other reagent are so different that no common solvents exist. In these two-phase cases, it is often or usually desirable to use phase transfer catalysts to promote the nucleophilic substitution reaction at the interface between the phases or to transport the nucleophilic macromonomer or other reagent to the electrophile site in the base polymer. A most preferred way of preparing the pendant grafted/functionalized polymers of this embodiment of the invention is to conduct the halogenation and the nucleophilic substitution in the same medium in sequential reactions (halogenate and then nucleophilically displace the halogen) without ever recovering the base halogenated polymer separately. As previously mentioned, the macromonomer can likewise be prepared using the same type of solvent, and the macromonomer grafting can be effected by admixing the respective solution intermediates, without the need of ever isolating the macromonomer or the base terpolymer to which the macromonomer is grafted.
Depending upon the reactivity of the nucleophilic macromonomer or other reagent used and the reaction conditions, the nucleophilic substitution reactions can be run at temperatures varying from about 0°C to about 200°C as limited by thermal stability of the nucleophilic macromonomer and/or reagent, the base polymer and the grafted/functionalized product polymer. Normally, temperatures between about 0°C and about 150°C are preferred. Reaction times are normally (but not necessarily) chosen to allow the nucleophilic displacement reaction to go to completion (i.e. exhaustion of either the electrophile or the nucleophilic reagent) and may range between several seconds and a few days. Normally, reaction times between a few minutes and several hours are preferred and reaction temperature and other conditions are set to make a convenient reaction time possible.

A wide range of solvents and/or solvent blends may be used as the medium in which the nucleophilic displacement reaction is run and it is this factor which determines whether a solution, dispersion, or bulk reaction is conducted. A number of factors are important in selection of the solvents. They need to be inert under the reaction conditions, easily removed from the product, easily recycled for reuse in the process, of low toxicity under use conditions with minimum environmental health concerns, and economical to use. In addition, the solvents need to provide a reaction environment which is favorable for the reaction being run, that is, they must bring the reactants into the required intimate solution contact and should provide solvation stabilization for intermediate states along the desired reaction route. It is frequently necessary or desirable to use a blend of solvents to best achieve the various compromises required, with one solvent being an easily-handled good solvent for the base polymer and the other being a good solvent for the nucleophilic macromonomer or other reagent and/or providing solvation stabilization for the reaction intermediates. It is most preferred that the
chosen solvent system be one that is suitable for the three separate reaction processes including the radical halogenation reaction and the anionic polymerization of the macromonomer, so that a sequential reaction route is feasible without having to recover the halogenated base polymer or the nucleophilic terminated macromonomer.

Solvents which are particularly suited for this sequential reaction route vary somewhat depending upon composition of the base polymer and macromonomers. With the elastomeric base polymers high in isobutylene and with many glassy non-polar macromonomers, the low boiling saturated hydrocarbons (C₁-C₇) or halogenated hydrocarbons (C₁-C₇) are excellent. Often it is desirable to add a more polar co-solvent, such as a low boiling alcohol (C₁-C₄) during any optional nucleophilic displacement reaction in order to dissolve and carry-in any other simple nucleophilic reagent, as well as provide solvation stabilization for optional nucleophilic displacement reactions. Aromatic solvents such as benzene, toluene, and chlorobenzene are generally good solvents for the base polymer and nucleophilic macromonomer and provide a reaction medium favorable for many additional nucleophilic displacement reactions, but often present other problems (i.e. the toxicity of benzene or the high reactivity of toluene during radical halogenation which makes it unsuitable as the reaction medium during the halogenation stage of the sequential reaction route). Preferred solvent composition changes as composition of the base polymer is changed and depends upon whether it is desired to run the reactions in solution or dispersion.

Similar considerations apply when considering the nucleophilic displacement reaction(s) separately. In order to run this reaction(s) in solution, a good solvent for the base polymer and nucleophilic macromonomer (depending upon its composition) is required and a co-solvent for the other simple nucleophilic reagent(s) may also be desirable or required. Good solvents for the base polymer and nucleophilic macromonomers are similar
to those cited above as being suitable for the sequential reaction route, but a broader range of solvents can be considered since inertness during radical halogenation is not required. The low boiling saturated hydrocarbons (C₄-C₇) or halogenated hydrocarbons (C₁-C₇) and aromatic hydrocarbons or naphthenes are preferred. Where greater solvent polarity is desired, tetrahydrofuran can be employed or good solvating agents such as dimethyl formamide or dimethyl sulfide can be added. The latter solvents are also good solvents for many of the simple nucleophilic reagents and may be employed along with alcohols or ketones to dissolve the simple nucleophilic reagent for addition to the base polymer/macromonomer solution. This technique of adding a solution of the simple nucleophilic reagent (in a solvent miscible with that used for the base polymer/macromonomer) with rapid stirring of the base polymer solution often results in a fine dispersion of the nucleophilic reagent so that even in cases where the nucleophilic reagent is not completely soluble in the mixed solvent resulting after the addition, an essential solution nucleophilic displacement reaction can still be run because the simple nucleophilic reagent dissolves during reaction to replenish the nucleophilic solution concentration as the reaction progresses.

In more extreme cases, where the simple nucleophilic reagent is not soluble in co-solvents miscible with the base polymer/macromonomer solvent, or where the solubility of the simple nucleophilic reagent in mixed solvency (which will retain the base polymer/macromonomer in solution) is too low, then a two-phase reaction may be run with the base polymer/macromonomer dissolved in one phase and the nucleophilic reagent in the other. In such cases, good mixing is essential to provide lots of interfacial contact between the reactants, and a phase transfer catalyst is generally desirable to aid in transporting the nucleophilic reagent to the residual ungrafted benzylic halogen electrophile site(s) on the base polymer. An example might be highly polar water
soluble nucleophilic reagents such as potassium cyanide, sodium sulfite, or nitrilotriacetic acid. Examples of phase transfer catalysts useful in these two-phase reactors include (but are not limited to): tetrabutyl ammonium bromide, tetrabutyl ammonium bisulfate, tetrabutyl ammonium hydroxide, benzyl triethyl ammonium chloride, tetrabutyl phosphonium bromide, crown ethers, cryptands, Adogen 464, etc. These same types of materials are sometimes beneficial in speeding up the one-phase solution reaction by providing specific solvation at the reaction site.

The most convenient reaction condition is running a bulk reaction with the macromonomer and/or additional simple nucleophilic reagent dissolved or dispersed in the base polymer. Working with high solids eliminates the costs of solvent handling and recycle. However, the bulk reaction requires use of an expensive inefficient reactor such as an extruder which is capable of providing mixing in highly viscous systems and restricts the reaction medium so that only selected nucleophilic displacement reactions are possible, and even those are more prone to involve side reactions because of the more restrictive conditions and poorer mixing which prevails during reaction.

In addition to the general reaction considerations already discussed, the factors known to influence nucleophilic substitution reactions (by those skilled in the art) may be applied in making the pendant grafted/functionalized polymer components of this embodiment of the invention without materially affecting the invention. Thus, reaction routes and activation energy can be controlled by specific solvation, or catalysts, undesired reactions can be prevented by blocking, etc.
III. SHEAR THINNING OLEFIN-BASED ADHESIVES

A. Olefin Polymer Component Including a Main Chain with Polymeric Side Chains

An additional preferred embodiment of the sprayable polymer component suitable for use in the present adhesive is provided as a rubbery olefin polymer main chain including a main chain of one or more simple α-olefin monomer repeat units and a plurality of glassy polymeric side chains distributed along the main chain. In this embodiment, the rubbery main chain is preferably an ethylene-propylene copolymer. However, other monomer or monomer combinations producing elastomeric products having α,β-ethylenic unsaturation and capable of vinyl polymerization by any of the standard techniques including, cationic, anionic, coordination, radical polymerization, and the like may be used. Examples of olefin monomers or combinations thereof producing a rubbery olefin backbone include ethylene/propylene, ethylene/1-butene, ethylene/vinyl acetate, and the like. In addition, a relatively minor proportion of monomers introducing desired functionality into the main chain may also be utilized. Examples of olefin monomers suitable for introducing functionality into the rubbery backbone include monoolefinically unsaturated monocarboxylic acids such as acrylic acid, methacrylic acid, and the like; hydrocarbyl esters of monoolefinically unsaturated monocarboxylic acids including methyl acrylate, methyl methacrylate, t-butyl acrylate, ethyl acrylate, lauryl methacrylate, 2-ethylhexyl methacrylate, and the like; monoolefinically unsaturated dicarboxylic acids or anhydrides including maleic acid, maleic anhydride, citraconic acid, itaconic acid, and the like; vinyl esters of saturated carboxylic acids such as vinyl acetate, and the like; vinyl halides including vinyl chloride, vinylidene chloride, and the like; acrylonitrile, and the like; and carbon monoxide, sulfur dioxide, and the like. The main chain or backbone of such olefinic polymer may include one or more simple
monomers copolymerized together randomly and/or in blocks.

Ethylene-propylene rubber is a preferred main chain. The ethylene content of the rubbery ethylene/propylene copolymer main chain may vary from 0 to about 70 percent by weight, and preferably is from about 40 to about 60 percent by weight with the remainder being propylene.

In a preferred embodiment, the sprayable olefin polymer comprises an as-copolymerized product of one or more main chain α-olefin monomers with a monoolefinitely terminated macromonomer. The side chains comprise a plurality of macromonomer repeat units distributed in the polymer main chain.

In an alternate aspect, the sprayable olefin polymer in this embodiment may be a post-polymerized product comprising a main chain having grafted thereto a plurality of side chains wherein the main chain comprises the polymerized product of one or more olefin monomers and the macromonomers are grafted thereto. Examples of post-polymerization grafting reactions include transesterification, nucleophilic substitution, condensation, and the like. For example, in a main chain polymer comprising pendant carboxylic acid functionality such as an ethylene-propylene acrylic acid copolymer, the carboxylic acid groups may undergo a transesterification reaction with a macromonomer having terminal hydroxy functionality to incorporate the polymeric kernel as a 56 pendant ester side chain. Alternately, a nucleophilic substitution reaction may be utilized to graft the pendant side chains. Appropriate electrophile leaving groups such as halogens may be copolymerized into the main chain as a halide containing comonomer, or the polymer main chain may be functionalized in a post polymerization reaction, e.g. halogenation. Then the halide functionality containing main chain polymer can be reacted with a nucleophilic terminated macromonomer in a nucleophilic substitution reaction. Aspects of nucleophilic substitution reactions and nucleophilic terminated macromonomers have been mentioned previously.
Functionalization of polymers such as by halogenation and transesterification reactions are known in the art.

B. Preparation of Norbornene Terminated Macromonomers Suitable as Shear-Thinning Side Chains

The sprayable adhesive of this embodiment is based, in part, on uniformly functionalized norbornene terminated macromonomers. Norbornene terminated macromonomers having the desired molecular weight and compositional homogeneity are preferably prepared according to anionic polymerization techniques under conditions in which spontaneous termination or chain transfer does not occur. Since these anionic polymerizations lack termination or chain transfer reactions, the stable carbanion chain growth centers can be selectively tailored by molecular weight and functional end group.

Functionalization of these polymeric monomers may follow either of two routes: (i) initiation with an organolithium derivative containing a protected functional group; or (ii) controlled termination with one or more reagents to yield the desired functionality. Norbornene functionality cannot ordinarily be introduced with certainty as a termination step, so a post-termination nucleophilic reaction may be utilized. In this method, the nucleophilic termination step functionality is reacted with a norbornene containing electrophilic reagent. Alternatively, norbornene functionality may be introduced into a polymeric monomer at the chain initiation step by an appropriate norbornene functionality-containing organolithium initiator.

Whether norbornene functionality is introduced by either of these two methods, the resulting polymer is most useful if narrow molecular weight dispersity is preserved and the product is essentially completely norbornene terminated. Several problems are known in both of these methods. Initiation rates of organolithium initiators containing norbornene functionality ordinarily are too slow to maintain monodispersity, and the
introduction of norbornene functionality by a post termination nucleophilic reaction may not yield a polymeric monomer with the requisite yield of norbornene functionality. Furthermore, the incorporated norbornene functionality in the macromonomer must be sufficiently active compared to simple olefin monomers in the copolymerization reactions to obtain random distribution of copolymerized side chains.

A lithium norbornene anionic polymerization initiator has been found to meet these criteria. As a preferred specific example, 2-lithiomethyl-5-norbornene is a primary alkyl organolithium catalyst which initiates rapidly compared to chain propagation to give norbornene terminated polymers having narrow molecular weight distributions. Such macromonomers are essentially completely norbornene terminated. Norbornenes are known to be active monomers with reaction reactivities similar to the reactivity of α-olefins such as ethylene and propylene in various polymerization systems, including coordination catalyst, radical and olefin metathesis polymerizations.

As with all anionic polymerizations, preparation of lithionorbornene catalysts, of which 2-lithiomethyl-5-norbornene is especially preferred, proceeds under rigorous exclusion of water and oxygen. Reactants and solvents of top purity are utilized to exclude impurities capable of inhibiting reaction yield, such as water, oxygen, and other nucleophilic substances. Equipment is carefully dried and the reaction is carried out in a dry box under inert atmosphere.

Synthesis of the preferred 2-lithiomethyl-5-norbornene anionic initiator is a two-step reaction procedure. Initially, a 2-bromomethyl-5-norbornene precursor is prepared by the Diels-Alder reaction of dicyclopentadiene and allyl bromide. Then, a solution of the 2-bromomethyl-5-norbornene is lithiated with metallic lithium to produce the desired initiator.

Thermoplastic or glassy macromonomers terminated with norbornene functionality may be prepared from
monomers capable of anionic polymerization utilizing a lithium norbornene initiator. Among such monomers are vinyl aromatic compounds such as styrene, α-vinylstyrene, p-methylstyrene, α-methylstyrene, α-vinylnaphthene, and the like; acrylic and methacrylic esters including alkyl and branched alkyl esters; acrylonitrile; vinylidene chloride; polyisocyanate; and the like. Such polymerized macromolecules may be homopolymers or random or block multipolymers having two or more comonomers. Norbornene terminated macromolecules are preferably linear chains, but they may be star configured or any other block configuration utilizing a block linking compound of which dichlorodimethylsilane, trichloromethylsilane and tetrachlorosilane are representative examples. Reaction conditions required for anionic polymerizations have been previously described hereinabove.

These embodiments of the invention can be more fully understood with reference to the specific examples providing details on the introduction of shear thinning side chains in polymer systems, including olefinic and isobutylene/para-methylstyrene/para-bromomethylstyrene based polymers, suitable for use in hot melt pressure-sensitive adhesives, exhibiting a shear thinning property and sprayability.

Examples

These examples describe the specific preparations of several embodiments of macromonomer grafted polymer systems and their uses in several high shear applications.

Measurements of viscoelastic properties were performed using a RHEOMETRICS SYSTEM IV rheometer or a POLYMER LABORATORIES DMTA rheometer. Isothermal measurements were performed on the SYSTEM IV rheometer over a wide range of temperatures. Isochronal experiments were conducted at a frequency of 10 rad/s and 1 Hz on the SYSTEM IV and the DMTA rheometer, respectively.
Transmission electron microscopy (TEM) was conducted on a thin section of a sample prepared with a cryogenic microtome. The stains utilized RuO₄ vapor for the polystyrene-grafted isobutylene/para-methylstyrene co-polymer or OsO₄ for SIS and SBS block polymers. The microscopy was conducted on a PHILIPS EM-300 transmission electron microscope at an accelerating voltage of 100 keV.

To prepare a film sample for physical testing, the polymer sample or adhesive composition was dissolved in toluene and poured inside a hollow-glass cylinder over a piece of stretched cellophane. The cast films were formed by evaporating the solvent at room temperature. Further drying was conducted in a vacuum oven at 50°C or at room temperature.

Adhesive tests were performed on adhesive compositions dissolved in toluene and then knife-coated to a thickness of about 1.5 mil on a MYLAR substrate. Unless otherwise mentioned, the substrate for the adhesive test was a clean, smooth stainless steel.

The 180° peel adhesion test was conducted in accordance with the procedure of the Pressure Sensitive Tape Council (PSTC), No. 1 (PSTC-1). This test measures the force necessary to separate an adhesive tape prepared as described above from the substrate (stainless steel).

Briefly, a 1-inch wide tape was adhered to a clean substrate bar, the bar was mounted in an Instron tensile tester, and the free end of the tape was pulled away at a 180° angle at a rate of 12 in./min.

The 90° quick stick adhesion test was conducted in accordance with the PSTC, No. 5 (PSTC-5). This test measures the force required to peel an adhesive tape specimen at a 90° angle from the substrate surface to which it was applied under no pressure other than the weight of the tape itself.

The loop tack test was conducted in accordance with the PSTC, No. 6 (PSTC-6). Briefly, loop tack was measured by forming a loop from a 1" x 8" modified strip of adhesive tape, adhesive side out, inserted into the clamp of an Instron tensile tester, moving the loop at a
rate of 12 in./min onto a stainless steel panel, and then removing the strip at the rate of 2 in./min after 5 square inches of contact was made. The highest force required to remove the loop was reported as the loop tack.

The holding power (HP) was determined in accordance with PSTC, No. 7 (PSTC-7). HP is defined as the time required for either a 1" x 1" or a 1/2" x 1" adhesive-coated area of label adhered to steel to fail under a load of 1 kg applied in shear at a 2° antipeel. Unless otherwise noted, the HP reported herein was based on a bond area of 1" x 1".

The shear adhesion failure temperature (SAFT) was measured as the failure temperature of a tape, coated with a 1.5 mil thickness of the adhesive specimen and adhered on a 1" x 1" overlap onto a steel substrate, under a 1 kg vertical load. This test was conducted in an oven by increasing the oven temperature at the rate of 40°F per hour.

Sprayability was evaluated using a MELTEX MP-300S spray gun, at an application temperature varying from 140°C to 180°C. The gun had a spray nozzle of 9.21 cm in length and 0.13 cm inside diameter. The 180°C sprayability was evaluated as the flow rate measured in grams of adhesive material sprayed in 15 seconds. The shear rate (\( \gamma \)) and the viscosity (\( \eta \)) were calculated according to the following equations:

\[
\gamma = \frac{32V}{\pi t D^3} \quad (1); \text{ and}
\eta = \frac{DP}{4L \gamma} \quad (2);
\]

wherein \( V \) is the total volume of Newtonian fluid extruded under a pressure drop \( P \) along the nozzle in time \( t \), and \( L \) and \( D \) are the nozzle length and inside diameter, respectively.
Example A

Preparation of Brominated Base Polymer

A sample of isobutylene/para-methylstyrene/para-bromomethylstyrene base terpolymer was prepared as follows:

A 500 ml reaction flask, fitted with a thermometer, stirrer, and dropping funnel, was set up in a glove box having an oxygen-free and moisture-free nitrogen atmosphere, and the flask was cooled to -98°C by immersion in a controlled temperature, liquid nitrogen cooled, heat transfer bath. The reactor was charged with 386.6 g dry, purified methyl chloride (having a purity of 99.8%), 47.4 g purified, dried and distilled, polymerization grade isobutylene (having a purity of 99.9%), and 2.6 g purified, dried and vacuum-distilled para-methylstyrene (2.5 mole % of total monomers). Seventeen ml of a catalyst solution consisting of 0.19 weight percent ethyl aluminum dichloride (EADC) in methyl chloride was allowed to drip slowly into the feed blend from the dropping funnel over the course of 12 minutes while stirring and attempting to maintain temperature by immersion of the reactor in the heat transfer bath.

Despite the efforts at cooling, reactor temperature rose from -98°C to -80°C due to the exothermic polymerization reaction, and a slurry of polymer in a slightly tannish-colored liquid was formed. Some of the polymer agglomeration on the stirrer and reactor walls. The reactor was quenched by adding 25 ml of cold methanol to yield an agglomerated mass of white polymer in a clear, colorless liquid. The polymer was recovered by allowing the methyl chloride to flash off and kneading and washing the polymer in methanol; 0.2 weight percent butylated hydroxytoluene (BHT) was added as an antioxidant and the polymer was dried in a vacuum oven at 80°C. Fifty grams of dried white, opaque, tough, rubbery polymer were recovered. Conversion was 100% with a quantitative recovery of the polymer. Catalyst efficiency was about 1550 grams of polymer/gram of EADC. The recovered
polymer had a viscosity average molecular weight (M_v) of 458,000, and contained 5.2 weight percent (2.5 mole percent) para-methylstyrene. Gel permeation chromatography (GPC) analysis using ultraviolet (UV) and refractive index (RI) detectors showed the para-methylstyrene to be uniformly distributed over the entire molecular weight range, indicating that a compositionally homogeneous copolymer had been formed.

The GPC was performed using a Waters 150-C ALC/GPC (Millipore Corporation) with a Waters Lambda-Max Model 481 LC UV Spectrophotometer on line. Data were collected and analyzed using customized software developed with Computer Inquiry Systems, a division of Beckman Inc. Tetrahydrofuran was used as the mobile phase at various flow rates, but generally 1.0 ml/min. The instruments operated at 30°C at a wavelength of about 254 nm for the UV. The polyisobutylene backbone had negligible absorbance compared to the aromatic ring at this wavelength. Columns used were μ Styrage (Waters) or Shodex (Showa Denko). Sets of columns of wide porosity range were calibrated with narrow molecular weight distribution polystyrene standards with molecular weights from 10^3 to 4 X 10^6. Molecular weights were reported in terms of the polyisobutylene backbone using a universal calibration. The output from the UV and RI detectors were compared quantitatively to calculate deviations in composition from the mean. Generally, viscosity average molecular weights were based on separate measurements in diisobutene at 20°C.

The high molecular weight, random, uniform copolymer of para-methylstyrene and isobutylene prepared as above was dissolved in dried normal hexane in a two-liter baffled and jacketed resin flask set up for bromination with a four-neck resin flask top. An air-driven turbine mixer was used to provide efficient mixing, and a thermometer and thermocouple were used to measure and control the temperature, which was adjusted as noted hereinbelow by circulating a controlled temperature heat transfer fluid through the jacket. One of the necks was
used for mounting a dropping funnel containing the bromine solution, which was added dropwise into the reactor. The funnel and reactor were foil-wrapped to exclude light. A nitrogen bubbler tube with a sintered glass frit at its end was mounted in one of the necks, with the frit immersed in the reactor solution to provide nitrogen sparging at a rate which was set and controlled by a rotometer. The fourth neck was connected by plastic tubing to a knock-out trap and caustic scrubber in order to maintain several inches of water positive pressure during reaction, and to absorb and neutralize any HBr and bromine vapors given off during the reaction.

The bromine solution was prepared by adding a weighed amount of bromine to pure mole-sieve dried n-hexane (essentially olefin-free) in the dropping funnel, and mixing to form less than a 30% solution. The bromine dropping funnel was then mounted on the stirred, temperature-controlled, nitrogen-purged reactor, and a 500 watt tungsten light bulb was mounted immediately next to the reactor. The reactor was heated to 40°C and the bromine solution added dropwise. The bromine charge was 5 percent by weight of the copolymer, and the reaction occurred rapidly as the bromine was added, as evidenced by rapid HBr evolution and rapid fading of the color of the solution. Bromine was added over the course of two minutes, and the reaction was quenched with excess caustic ten minutes after bromine addition had been initiated. The quenched solution then was washed with water, and the brominated copolymer was recovered by alcohol precipitation and vacuum oven drying as previously described. BHT and tetramethylthiuram disulfide were mixed into the copolymer at 0.1% by weight as stabilizers prior to drying. The recovered brominated copolymer was soluble in diisobutylene, had an M_n of 254,000, and included 1.26 wt. % bromine as measured by Dietert analysis. Analysis using 400 MHz NMR showed the presence of 0.9 mole % benzylic bromide group, with no other brominated structures detectable. GPC analysis using UV and RI detectors showed the brominated copolymer
to be a uniform, homogeneous compositional distribution, narrow molecular weight distribution ($M_w/M_n$ about 2) functional copolymer.

5 Example B

Preparation of Nucleophilically Terminated Polystyrene Macromonomers

10 In the following examples, macromonomers of nucleophilically terminated polystyrene were prepared for subsequent nucleophilic reaction with the isobutylene/para-methylstyrene/para-bromomethylstyrene copolymers (BrXP-50).

15 Example B(1)

A monofunctional polymeric nucleophile based upon polystyrene was prepared by neutralization of carbon dioxide terminated polystyryllithium or polystyrene carboxylic acid. The apparatus was oven dried, placed into a vacuum chamber to cool and stored in a dry box prior to use. The polystyrene carboxylic acid was prepared by "living" anionic polymerization of styrene (10 wt. % solution) in tetrahydrofuran (THF) or cyclohexane at 40°C with sec-butyllithium initiator. The polymerization was terminated at -78°C by addition of the "living" polymer solution to the saturated solution of carbon dioxide in THF. The polymer was precipitated in isopropanol containing 1 ml HCl and 0.2 wt. % BHT. The polymer was dried for 24 hrs at 45°C in vacuum. The molecular weight of the polystyrene carboxylic acid was readily varied by altering the monomer to initiator ratios and typical molecular weights were 10,000 and 25,000. The polystyrene carboxylic acid was neutralized in THF solution with either the potassium or tetrabutylammonium salt of BHT (prepared by reacting an excess of BHT with potassium tert-butoxide or tetrabutylammonium hydroxide), and the polystyrene carboxylate was precipitated in isopropanol/BHT (0.2 wt. %). The polymeric salt was dried for 24 hrs in vacuum.
Example B(2)
Poly(styryl)lithium was prepared by addition of 25 ml sec-butyllithium (1 M, in hexane) and carbon dioxide. A 3 liter round bottom flask was fitted with a reflux-takeoff head and an adapter containing a stopcock and serum stopper. The flask was charged with 2.75 l of cyclohexane. The cyclohexane was distilled until 2 liters remained. After cooling to 40°C, 200 g (300 ml) styrene was added. The flask was placed in a hexane bath to control temperature. Polymerization was initiated by addition of 0.05 g/ml solution. A bright orange-red color immediately appeared. The flask was then cooled to -10°C and reagent grade carbon dioxide was bubbled into the flask. The color was discharged instantaneously with mixing. The resulting polymer was neutralized with dilute HCl (3 ml of conc. HCl, 7 ml of water, and 50 ml of THF) and precipitated in isopropanol.

Example B(3)
Poly(styryl)lithium was prepared in this example by addition of 25 ml sec-butyllithium in cyclohexane using N,N,N',N'-tetramethylethylenediamine and carbon dioxide. A three liter round bottom flask was fitted with a reflux-takeoff head and an adapter containing a stopcock and serum stopper. The flask was charged with 2.75 liters of cyclohexane. The cyclohexane was distilled until 2 liters remained, then the flask was allowed to cool to 40°C before styrene (100 grams, 100 ml) was added. The flask was placed in a hexane bath to aid in the regulation of the temperature. Polymerization was initiated by addition of 18.9 ml s-butyllithium (1 M in hexane). The temperature of the bath rose to 50°C and viscosity increased rapidly. After four hours, a
solution of the N,N,N',N'-tetramethylethylenediamine in cyclohexane was added (25 ml of 0.25 g/ml solution). The flask was then cooled to -10°C and reagent grade carbon dioxide was bubbled into the flask. Color discharged instantaneously with mixing.

**Examples 1-5 and Comparative Examples 1-5**

In the following examples, base terpolymers of isobutylene/para-methylstyr/ene/para-bromomethylstyrene (BrXP-50) prepared similarly to Example A were grafted with polystyrene (PS) chains of varying length described in Example B to produce PS-grafted BrXP-50 (BrXP-50-g-PS). The composition of the XP-50 starting material of each of the five example BrXP-50-g-PS polymers was about 3 mole percent para-methylstyr/ene. The BrXP-50 obtained from brominating the XP-50 starting material contained about 1 mole percent para-bromomethylstyr/ene. Generally about half of the para-bromomethylstyr/ene was PS-grafted in the BrXP-50-g-PS so that the main chains in the example BrXP-50-g-PS polymers contained about 97 mole percent isobutylene, 2 mole percent para-methylstyr/ene, 0.5 mole percent para-bromomethylstyr/ene and about 0.5 mole percent PS-grafted-para-methylstyr/ene.

For the preparation of Example 1, THF 10 wt. % solutions of BrXP-50 prepared as in Example A and macromonomer potassium salt prepared in Example B(1) were mixed in a 250 ml flask equipped with stir bar condenser and nitrogen purge. The flask was heated to reflux and aliquots were periodically taken to monitor the reaction progress. The reaction was complete after 48 hrs (as determined by GPC). The polymer was precipitated in isopropanol containing 0.5 ml HCl and 0.2 wt. % BHT. The polymer was dried for 24 hrs at 45°C and 0.1 mm Hg pressure. Evidence of grafting included changes in the GPC integrated areas, morphology and solubility of the resulting polymer.

For the preparation of Examples 2-3, a cyclohexane solution 7.5 g of poly(styryl)carboxylic acid from Example B(2) was treated with tetrabutylammonium
hydroxide (10 ml, 1M in methanol) and BHT (2 g). This solution was added to a cyclohexane solution of the BrXP-50 polymer (22.5 g in 500 ml). The flask was heated to 70°C and allowed to react for four hrs. The solution was then placed in a TEFLOK tray and the solvent was removed in vacuum. FT-infrared analysis of thin films indicated that all the carboxylate groups present in the sample were converted into the ester form. GPC analysis (3 mg/ml THF solutions) of the graft copolymer conducted on a Waters 150 GPC at 0.5 cc/min indicated that less than 5 % ungrafted polystyrene remained.

For the preparation of Examples 4-5, polystyrene lithium carboxylate (50 g) prepared as in Example B(3) was reacted with tetrabutylammonium fluoride (15 ml, 1 M in THF). The resulting solution was added to a solution of BrXP-50 (150 g in 1.5 l cyclohexane). The mixture was then stirred and heated slowly to 70°C and allowed to react for 2 hrs. The polymer was isolated by precipitation in isopropanol (0.1 g BHT). The resulting graft copolymer was transparent and tough. GPC indicated that more than 90 % of the polystyrene was grafted.

The BrXP-50-g-PS polymers were then compared to commercial grade adhesive polymers, including poly(styrene/isoprene/styrene) ("SIS"; KRATON 1107), poly(styrene/butadiene/tapered-styrene) ("SButS"; STEREON 840A), poly(styrene/butadiene/styrene) ("SBS"; KRATON 1102), poly(styrene/ethylene-butene-1/styrene) ("SEBS"; KRATON G 1657) and a 28 weight percent vinyl acetate ethylene/vinyl acetate random copolymer ("EVA"; MT 32; ESCORENE UL7750). Polymer morphology, viscoelastic behavior, adhesive performance and melt rheology were evaluated. Tackifier compatibility with the BrXP-50-g-PS was also investigated. Further characterization of the BrXP-50-g-PS polymers and comparative polymers are shown in Table I.
# TABLE I

<table>
<thead>
<tr>
<th>EXAMPLE</th>
<th>STYRENE CONTENT (WT. %)</th>
<th>GRAFTS PER MAIN CHAIN</th>
<th>MOLECULAR WEIGHT (Mw X 10^-3)</th>
</tr>
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<tbody>
<tr>
<td></td>
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<td>Side Chain</td>
</tr>
<tr>
<td>1</td>
<td>38</td>
<td>1.5</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>3.6</td>
<td>10</td>
</tr>
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<td>3</td>
</tr>
<tr>
<td>5</td>
<td>19</td>
<td>4.0</td>
<td>4</td>
</tr>
<tr>
<td>Comp. 1</td>
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<td>0</td>
<td>--</td>
</tr>
<tr>
<td>Comp. 2</td>
<td>43</td>
<td>0</td>
<td>--</td>
</tr>
<tr>
<td>Comp. 3</td>
<td>14</td>
<td>0</td>
<td>--</td>
</tr>
<tr>
<td>Comp. 4</td>
<td>28</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Comp. 5</td>
<td>--</td>
<td>--</td>
<td>(Mw=32)</td>
</tr>
</tbody>
</table>

a - KRATON 1107 SIS  
b - STEREO 840A SBS  
c - KRATON G 1657 SEBS  
d - KRATON 1102 SBS  
e - ESCORENE U7750 EVA

Storage modulus \((G')\) was measured against temperature for several of the polymers in Table I. In Figs. 1 and 2, the Example 1 BrXP-50-g-PS \((\text{O}-\text{O}-\text{O})\) was compared to the polymers of Comparative Examples 1 \((\text{O}-\text{O}-\text{O})\), 2 \((\text{A}-\text{A}-\text{A})\), 3 \((\text{x}-\text{x}-\text{x})\), 4 \((\text{c}-\text{c}-\text{c})\) and 5 \((\text{V}-\text{V}-\text{V})\). Each polymer had a high storage modulus at very low temperatures. The storage modulus decreased rapidly at a glassy-to-rubbery transition temperature to a "plateau modulus" taken as an average value of the storage modulus in the plateau region. The Example 1 BrXP-50-g-PS had a higher and broader glassy-to-rubbery transition temperature than the block copolymers. SIS (Comparative Example 1) and the BrXP-50-g-PS (Example 1) had a comparable plateau modulus which was lower than the other polymers tested. The storage modulus decreased relatively rapidly again when the polystyrene phase began to soften, i.e. at the polystyrene domain glass transition temperature \((T_g)\), about 100°C for the SIS, SBS and BrXP-50-g-PS polymers.

It is hypothesized that the reason for the higher and broader glassy-to-rubbery transition temperature for the Example 1 BrXP-50-g-PS polymer was attributable to a
unique phase structure of the BrXP-50-g-PS polymer. Examination of the damping behavior, such as, for example, the loss tangent (ratio of loss to storage modulus), of the BrXP-50-g-PS (O-O-O) showed a loss tangent peak at -54°C associated with the glass transition temperature and an extra damping peak at -33°C, compared to SIS (□-□-□) which exhibited a single loss tangent peak at about -52°C.

Results of rheological tests performed indicated that, at temperatures above the Tg of the polystyrene phase, the BrXP-50-g-PS polymers were more viscous than the triblock SBS and SIS copolymers. Melt viscosity is preferably significantly below a Brookfield viscosity of 1000 poise at 180°C for formulated adhesives. However, since Brookfield viscosity only represents the viscosity at a single shear rate, the adhesive materials may experience other shear rates in other processing equipment and various processing stages thereof. Therefore, the dependence of viscosity on shear rate at a given processing temperature is important.

In Fig. 4, complex viscosity versus frequency (or shear rate) for the BrXP-50-g-PS polymers of Examples 2 and 5 was compared to the ungrafted BrXP-50 polymer at 180°C. These polymers showed similar viscosities at high shear rates which can be explained by the BrXP-50-g-PS polymers being unable to form a distinct polystyrene phase or domain at the higher shear rates and therefore behaving similarly to the ungrafted BrXP-50 polymer. In contrast, the BrXP-50 polymer seemed to exhibit Newtonian behavior (viscosity independent of shear rate) at low shear rates, but both BrXP-50-g-PS polymers showed significantly increasingly higher viscosities at low shear rates.

An explanation for the increased low-shear viscosity of the BrXP-50-g-PS polymers is due to persistence of a two-phase network in the melt state at lower shear rates. It is also apparent from Fig. 4 that the complex viscosity of the BrXP-50-g-PS polymers at low rates of deformation was higher for the longer PS-grafted side
chains, higher PS content polymer of Example 2 than for the shorter side chains, lower PS content polymer of Example 5.

In Figs. 5-7 the relationship of complex viscosity with frequency for the Example 2 BrXP-50-g-PS is compared with that for the polymers of Comparative Examples 1, 2 and 3. It can be seen from Fig. 5, for example, that the Example 2 BrXP-50-g-PS was more viscous than all the linear triblock copolymers at low frequencies; however, the BrXP-50-g-PS had the lowest viscosity at high frequencies. At low frequency, the steady flow of the linear block copolymers involved disruption of PS domains through the thermodynamically incompatible rubbery matrix. In general, the larger the solubility parameter difference between the elastomeric midblocks and the PS end blocks, the higher is the melt viscosity.

The rubbery main chains of the BrXP-50-g-PS polymers and the midblocks of SEBS have similar solubility parameter values. However, the BrXP-50-g-PS polymer was more viscous at low frequency because of its greater PS side chain length and the resulting cylindrical/lamellar phase morphology determined by TEM. In other words, it was easier to get the spherical morphology in the SEBS to flow than the cylindrical/lamellar morphology in the BrXP-50-g-PS.

Similarly, SBS was more viscous than SIS at low frequencies. This was probably because of lamellar SBS morphology and polystyrene blocks having greater molecular weight in the SBS. For polymers of similar morphology, the greater the incompatibility between the glassy and rubbery phases, the more viscous the polymer generally is. The solubility parameter difference of the two phases, the morphology of the two phases and the molecular weight of the hard (glassy) PS phase, all contribute to the viscosity of the linear block copolymers and BrXP-50-g-PS polymers at low frequencies.

At high frequencies, however, the restraining effect of entanglements of the elastomeric phase chains may become significant. Therefore, the highly entangled SEBS
copolymers had higher viscosity at high frequencies.

5 Examples 6-10 and Comparative Examples 6-9

Adhesive formulations were prepared using various commercially available tackifiers. The tackifier properties are summarized in Table III:

<table>
<thead>
<tr>
<th></th>
<th>TACKIFIER</th>
<th>DESCRIPTION</th>
<th>$T_g (^\circ C)$</th>
<th>$M_w$</th>
<th>$M_w/M_n$</th>
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<tbody>
<tr>
<td>15</td>
<td>ESC-1310LC</td>
<td>Aliphatic</td>
<td>40</td>
<td>1500</td>
<td>1.3</td>
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<tr>
<td>20</td>
<td>ECR-111</td>
<td>Hydrogenated aliphatic</td>
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<td>1400</td>
<td>1.5</td>
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<td></td>
<td>ECR-143H</td>
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<td>-26</td>
<td>460</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>ECR-318</td>
<td>Hydrogenated cyclic</td>
<td>8</td>
<td>400</td>
<td>3.3</td>
</tr>
<tr>
<td>25</td>
<td>ECR-327</td>
<td>Hydrogenated cyclic</td>
<td>-13</td>
<td>340</td>
<td>3.3</td>
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<tr>
<td></td>
<td>ESC-5380</td>
<td>Hydrogenated cyclic</td>
<td>36</td>
<td>590</td>
<td>1.5</td>
</tr>
<tr>
<td>30</td>
<td>ZONTAC 105 Lite</td>
<td>Styrenated terpene</td>
<td>57</td>
<td>850</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>KRISTALEX F120</td>
<td>Aromatic</td>
<td>70</td>
<td>1600</td>
<td>1.5</td>
</tr>
</tbody>
</table>

The adhesive was prepared by solvent blending the polymer and tackifier with a BHT or IRGANOX 1010 stabilizer (1 wt. % based on total adhesive weight) in toluene. Test samples were made by coating 1.5 mil MYLAR film with a 1.5 mil thickness layer of the formulation from toluene. The adhesive compositions and properties are summarized in Table IV:
The SIS-based adhesive (Comparative Example 6) had the best tack and shear properties, but no melt sprayability. Performance of the BrXP-50-g-PS adhesives was comparable to the SBS block copolymer adhesive (Comparative Example 7) with the exception of Example 10 which had slightly inferior tack properties.

The melt processability of adhesives formulated with the BrXP-50-g-PS polymers and block copolymers was compared in Fig. 8 which shows the 180°C viscosity of Examples 7, 8 and 10 and Comparative Examples 6 and 7 at
various frequencies where the range of shear rates is representative of different processing techniques. Results indicated that the block copolymer adhesives exhibited Newtonian behavior while the graft polymer adhesives were non-Newtonian. Generally speaking, the BrXP-50-g-PS formulations had decreasing viscosity with increasing shear rates, that is, shear thinning.

Fig. 8 suggests that viscosity may be reduced by utilizing BrXP-50-g-PS having shorter PS side chain grafts. For example, the Example 10 adhesive based on BrXP-50-g-PS with 4000 M₉ PS grafts has a viscosity even lower than the SIS formulation (Comparative Example 6) and the SBTS formulation (Comparative Example 7). Similar viscosity behavior was observed at lower temperatures such as 160°C and 140°C, as seen in Figs. 9 and 10. The BrXP-50-g-PS adhesives surpassed the block copolymers for melt processability (i.e. less viscous at lower shear rates) at these lower temperatures.

Comparison of BrXP-50-g-PS adhesive formulations to SIS and SBS adhesive formulations for hot melt sprayability at 180°C indicated that the SIS formulation as mentioned previously was not sprayable. Flow rate in terms of weight of the extruded adhesive in 15 seconds and the appearance of the sprayed filaments were used as the measures of sprayability. Both the SBTS block copolymer adhesive (Comparative Example 7) and the Example 8 BrXP-50-g-PS adhesive exhibited similar flow rates and fine structure of sprayed filaments. The SIS adhesive (Comparative Example 6) showed no fine spray and dripped from the spray gun nozzle.

Example C
Preparation of Norbornene Terminated Polystyrene Macromonomers

A Diels-Alder reaction was conducted in a 1 liter steel reaction vessel fitted with a 2000 kPa pressure relief valve and a steel plug to prepare 2-bromomethyl-5-norbornene. The reaction vessel was charged with 264.4 g (4 moles) of dicyclopentadiene, 532.4 g (4.4 moles) of
allylbromide (purified by passing first through a column containing sodium bicarbonates, then magnesium sulfate), 3.9 g of hexadecane (the GC internal standard) and 0.5 g BHT. The reaction mixture was allowed to react for 6 hours at 180°C and the resulting mixture contained about 75 weight percent 2-bromomethyl-5-norbornene, 9 weight percent dicyclopentadiene, 3 weight percent allylbromide and unidentified isomers of each. Analysis was conducted by GLC.

The above reaction was repeated except that 580.8 g (4.8 moles) of allylbromide was utilized. The resulting reaction mixture contained 78 weight percent 2-bromomethyl-5-norbornene, 2 weight percent dicyclopentadiene, 7 weight percent allylbromide, and unidentified isomers. Next, the reaction mixtures from above were combined and purified by distillation. The first distillation was conducted in a 3 liter, 3 neck flask fitted with a nitrogen purge, a thermocouple and an efficient column. The system pressure was maintained at 700 mm Hg pressure and the temperature was slowly raised to 175°C. At these conditions, the dicyclopentadiene decomposed and cyclopentadiene and allylbromide were distilled. When no additional volatile products were produced, the pressure was reduced and the contents of the flask were flashed into a receiver vessel. This distillate contained 2 weight percent dicyclopentadiene, 95 weight percent 2-bromomethyl-5-norbornene and unidentified higher boiling isomers. This mixture was then fractionally distilled at 13 mm Hg to produce several fractions ranging from 96 to 99.8 weight percent of the product. The overall purified yield was 60 percent.

In the reaction steps that followed to produce the norbornene terminated polystyrene macromonomers, all reactions and reagents were handled under nitrogen with great care taken to prevent contamination by oxygen and water. The monomers were purified by distillation from dibutylmagnesium within 24 hours of polymerization. The solvents (heptane, cyclohexane, ether or tetrahydrofuran)
were purified prior to polymerization by vacuum distillation from butyllithium. All glassware and equipment were oven dried at 150°C for 3 hours then cooled and assembled under inert atmosphere in a dry box. The monomer was added to the solvent just prior to use.

The 2-bromomethyl-5-norbornene prepared above was lithiated in a 2 liter 2 neck flask, fitted with a stirrer and septum inlet and assembled in a dry box. A quantity of 700 ml ether, previously distilled from dibutylmagnesium, and 4 g lithium (from Lithco, containing 0.8 percent by weight sodium) was placed in the reaction vessel. The flask was closed and 38 g of a 5 weight percent solution of 2-bromomethyl-5-norbornene was added dropwise over a period of 6 hours. As the reaction began, the reaction flask was cooled to -50°C. At the end of the reaction period, an aliquot was removed and analyzed by GLC. The bromide reactant was quantitatively converted to 2-lithiomethyl-5-norbornene at about a 90 percent conversion factor. Excess lithium was removed by passing the reaction effluent through a frit and the ether solvent was rotary evaporated under vacuum at -50°C. The 2-lithiomethyl-5-norbornene reaction product was redissolved in cyclohexane to produce approximately 1 molar solution of the organolithium reactant.

Styrene was polymerized in an anionic polymerization process using the 2-lithiomethyl-5-norbornene prepared as a catalyst. In a 3 liter flask fitted with a magnetic stirring bar, 2800 ml cyclohexane was added. The flask was heated to distill 600 ml cyclohexane and then was cooled. To the solvent, 250 g freshly distilled styrene monomer (from dibutylmagnesium) was added together with 80 ml of the 2-lithiomethyl-5-norbornene solution. The polymerization began immediately and the flask temperature increased from 35°C to 55°C. The reaction was held at 55°C for 3 hours and the polymerization was terminated by adding methanol. The resulting polymer was precipitated in isopropanol and 0.1 weight percent BHT was added as stabilizer. Analysis showed that the
resulting norbornene terminated polystyrene had a $M_w$ of 6600, a $M_n$ of 5700 and $M_w/M_n = 1.1$. Approximately 240 g of the polystyrene product was recovered.

Example C1

An additional quantity of styrene was polymerized as in Example C except that 90 g of styrene was reacted with 3 ml of the 1-molar 2-lithiomethyl-5-norbornene. The reaction temperature was 35-55°C and the reaction was conducted for 3 hours. The resulting polymer product had a $M_w = 73,000$, $M_n = 69,000$ and $M_w/M_n = 1.06$. The polystyrene yield was approximately 95 percent.

Examples 11-14 and Comparative Example 10

In the following examples, 2-polystyryl-5-norbornene macromonomers prepared similarly to Examples C and C1 above were copolymerized by Ziegler mechanism with ethylene and propylene to prepare an ethylene-propylene copolymer main chain with polystyryl side chains incorporated along the main chain (EP-g-PS). The polymerization was conducted in a one liter reactor in a lab scale continuous polymerization process. Reactor temperature was 30°C, reaction pressure was 500 kPa, agitation speed was 1200 rpm and residence time in the reactor was 9 minutes. Toluene was fed as a solvent at a rate of 4.11 g/hr, ethylene at 95 g/hr and the propylene at 138 g/hr. The catalyst was VCl₄, fed at a rate of 0.493 g/hr and ethylaluminum sesquichloride at 3.162 g/hr. The feed rate of 2-polystyryl-5-norbornene macromonomer was 5.63 g/hr in Example 11, 11.26 g/hr in Examples 12 and 13 and 16.89 g/hr in Example 14. In Comparative Example 10, the ethylene-propylene polymer was prepared without copolymerized side chains. Conversion rate was about 85 percent for all polymerizations at a polymerization rate ranging from 202 to 210 g/hr. Results and selected polymer properties are shown in Table V.
The distribution of polystyrene grafts in the polymer was determined by analyzing an aliquot from the reactor by gel permeation chromatography. The eluent of the chromatographic column was analyzed sequentially first by a differential refractometer which revealed the presence of polymer and a UV detector operating at 254 nm which revealed the presence of styrenic residue. The responses of these analyzers indicated that styrenic residues were incorporated in the polymer.

The side chain copolymerized polymers were tough transparent thermoplastic elastomers. The polymers were examined by transmission electron microscopy revealing multiphase morphology having spherical polystyrene domains interspersed and separated by an average of 30 nm. The viscosity was relatively constant between a temperature range of 100-200°C indicating continuation of 2-phase morphology in the melt. Under shear, the polymer exhibited non-Newtonian behavior with the melt viscosity
falling four orders of magnitude as the shear increased from $10^{-2}$ to $10^2$ rad/sec. The mechanical properties of the grafted copolymers increased with increasing polystyrene content. Ungrafted, the EP polymer had very little cohesive strength, however, the Example 14 polymer containing 19 percent grafted polystyrene had a tensile strength of about 900 psi with an elongation break at 870 percent.

**Examples 15-18**

Polystyrene (PS) or poly(para-methylstyrene) (P(pms)) grafted EP copolymers were prepared similarly to the procedure outlined in Examples 11-14 and Comparative Example 10. The grafted polymers had a molecular composition as detailed in Table VI.

<table>
<thead>
<tr>
<th>TABLE VI</th>
<th>EXAMPLE</th>
<th>15</th>
<th>16</th>
<th>17</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>MAIN CHAIN &quot;A&quot;</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composition (wt. %)</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Ethylene</td>
<td></td>
<td>41</td>
<td>41</td>
<td>40</td>
</tr>
<tr>
<td>Propylene</td>
<td></td>
<td>41</td>
<td>41</td>
<td>40</td>
</tr>
<tr>
<td><strong>MOLECULAR WEIGHT</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$M_w$ ($10^3$)</td>
<td></td>
<td>148</td>
<td>113</td>
<td>101</td>
</tr>
<tr>
<td>$M_n$ ($10^3$)</td>
<td></td>
<td>70</td>
<td>77</td>
<td>52</td>
</tr>
<tr>
<td><strong>SIDE CHAIN &quot;B&quot;</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composition (wt. %)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Styrene (grafted)</td>
<td></td>
<td>18</td>
<td>--</td>
<td>20</td>
</tr>
<tr>
<td>Para-methylstyrene (grafted)</td>
<td></td>
<td>--</td>
<td>18</td>
<td>--</td>
</tr>
<tr>
<td><strong>MOLECULAR STRUCTURE</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No. Grafts</td>
<td></td>
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<td>3.2</td>
<td>3.2</td>
</tr>
<tr>
<td>$M_n$ ($10^3$)</td>
<td></td>
<td>4.8</td>
<td>5.3</td>
<td>4.0</td>
</tr>
<tr>
<td>$M_w/M_n$</td>
<td></td>
<td>1.1</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td><strong>GRAFT POLYMER</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Residue (wt. %)</td>
<td></td>
<td>2</td>
<td>--</td>
<td>2</td>
</tr>
<tr>
<td>Poly(para-methyl/styrene)</td>
<td></td>
<td>--</td>
<td>2</td>
<td>--</td>
</tr>
</tbody>
</table>
Examples 19-24 and Comparative Examples 11-13

The grafted polymers of Examples 15-17 were formulated into HMPSA's and the resulting properties were compared to adhesive formulations prepared using KRATON 1107 (Comparative Example 11) and KRATON G 1657 (Comparative Examples 12 and 13). Adhesive formulations and the resulting PSA properties are shown in Table VII.

<table>
<thead>
<tr>
<th>TABLE VII</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
</tr>
<tr>
<td>19 20 21 22 23 24</td>
</tr>
<tr>
<td>POLYMER COMPONENTS</td>
</tr>
<tr>
<td>Example 15</td>
</tr>
<tr>
<td>Example 16</td>
</tr>
<tr>
<td>Example 17</td>
</tr>
<tr>
<td>KRATON 1107</td>
</tr>
<tr>
<td>KRATON G1657</td>
</tr>
<tr>
<td>25 TACKIFIER COMPONENTS</td>
</tr>
<tr>
<td>ESC-5360</td>
</tr>
<tr>
<td>ESC-1310LC</td>
</tr>
<tr>
<td>ECR-111</td>
</tr>
<tr>
<td>TUFFLO-6056</td>
</tr>
<tr>
<td>IRGANOX-1010</td>
</tr>
<tr>
<td>30 PROPERTIES</td>
</tr>
<tr>
<td>Viscosity (150°C) (poise)</td>
</tr>
<tr>
<td>35 Viscosity (170°C) (poise)</td>
</tr>
<tr>
<td>Rolling Ball (cm)</td>
</tr>
<tr>
<td>Quick Stick (lb/in.)</td>
</tr>
<tr>
<td>Peel SS (lb/in.)</td>
</tr>
<tr>
<td>Peel PE (lb/in.)</td>
</tr>
<tr>
<td>SAFT (°C)</td>
</tr>
<tr>
<td>HP SS</td>
</tr>
<tr>
<td>(1/2 x 1/2 x 2kg; 10 hr)</td>
</tr>
</tbody>
</table>

Of the different formulations shown in Table VII, the SIS-based formulation (Comparative Example 11) still had the best tack properties but the EP-g-PS-based
adhesive (Example 21) had superior holding power with an equivalent SAFT.

5 **Examples 25-28**

An additional BrXP-50-g-PS graft polymer based on isobutylene/p-methylstyrene/p-bromomethylstyrene terpolymer main chain and polystyrene side chains was prepared as outlined in Examples A and B(3). Molecular structure of both main and side chains and composition are described in Table VIII.

Additional ethylene-propylene graft polymers were copolymerized with norbornene terminated macromonomers prepared as outlined in Examples 11-14 and Comparative Example 10 and Examples C and C1 except that the macromonomer was copolymer of styrene and p-methylstyrene. Molecular structure and composition of the EP-g-P(S/pmS) graft polymer main and side chains are also described in Table VIII.

<table>
<thead>
<tr>
<th>TABLE VIII</th>
<th>EXAMPLE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25</td>
</tr>
<tr>
<td><strong>MAINTAIN</strong></td>
<td><strong>COMPOSITION (Wt.)</strong></td>
</tr>
<tr>
<td>Ethylene</td>
<td>--</td>
</tr>
<tr>
<td>Propylene</td>
<td>--</td>
</tr>
<tr>
<td>Isobutylene</td>
<td>72.4</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>1.8</td>
</tr>
<tr>
<td>Bromine</td>
<td>0.8</td>
</tr>
<tr>
<td><strong>MOLECULAR WEIGHT</strong></td>
<td><strong>Mw (10^3)</strong></td>
</tr>
<tr>
<td></td>
<td><strong>Mn (10^3)</strong></td>
</tr>
<tr>
<td>**SIDE CHAIN **</td>
<td><strong>B</strong></td>
</tr>
<tr>
<td>Styrene</td>
<td>25</td>
</tr>
<tr>
<td>Paramethyln</td>
<td>7.5</td>
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<tr>
<td><strong>MOLECULAR STRUCTURE</strong></td>
<td><strong>Wx Grafts</strong></td>
</tr>
<tr>
<td></td>
<td><strong>Mw (10^3)</strong></td>
</tr>
<tr>
<td></td>
<td><strong>Mw/Mn</strong></td>
</tr>
</tbody>
</table>
Examples 29-40 and Comparative Examples 14-19

The above graft polymers were formulated into adhesives and performance tests were conducted for comparison to similarly formulated SIS and SBS block polymers-based adhesives. Results in Tables IX and IXa show that tack properties of the comparative block polymer adhesives were matched by several of the present invention adhesives while holding power was generally superior to the comparative adhesives. See Example 33 versus Comparative Example 14, Example 35 versus Comparative Example 16 and Example 37 versus Comparative Example 17.

<table>
<thead>
<tr>
<th>POLYMER COMPONENTS</th>
<th>EXAMAPLE</th>
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<tbody>
<tr>
<td></td>
<td>29</td>
</tr>
<tr>
<td>Example 25</td>
<td>100</td>
</tr>
<tr>
<td>Example 26</td>
<td>...</td>
</tr>
<tr>
<td>Example 27</td>
<td>...</td>
</tr>
<tr>
<td>Example 28</td>
<td>...</td>
</tr>
<tr>
<td>KRAFON 1107</td>
<td>...</td>
</tr>
<tr>
<td>KRAFON G 1657</td>
<td>...</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TACKIFIER COMPONENTS</th>
<th>EXAMAPLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>ESC-5380</td>
<td>...</td>
</tr>
<tr>
<td>ESC-1310LC</td>
<td>...</td>
</tr>
<tr>
<td>ECR-111</td>
<td>125</td>
</tr>
<tr>
<td>TUFFLO-6056</td>
<td>20</td>
</tr>
<tr>
<td>IRGAMOX-1010</td>
<td>2.45</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PROPERTIES</th>
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</thead>
<tbody>
<tr>
<td>Viscosity (150°C) (poise)</td>
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<tr>
<td>Viscosity (170°C) (poise)</td>
</tr>
<tr>
<td>Rolling Ball (cm)</td>
</tr>
<tr>
<td>Quick Stick (lb/in.)</td>
</tr>
<tr>
<td>Peel SS (lb/in.)</td>
</tr>
<tr>
<td>Peel PE (lb/in.)</td>
</tr>
<tr>
<td>SAFT (°C)</td>
</tr>
<tr>
<td>MP SS (1/2 in. x 1/2 in. x 2kg; hr)</td>
</tr>
</tbody>
</table>
### TABLE IXa

<table>
<thead>
<tr>
<th>POLYMER COMPONENTS</th>
<th>30</th>
<th>40</th>
<th>14</th>
<th>15</th>
<th>16</th>
<th>17</th>
<th>18</th>
<th>19</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 25</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
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<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Example 26</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Example 27</td>
<td>100</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Example 28</td>
<td>---</td>
<td>100</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>KRATON 1107</td>
<td>---</td>
<td>100</td>
<td>100</td>
<td>---</td>
<td>100</td>
<td>---</td>
<td>100</td>
<td>---</td>
</tr>
<tr>
<td>KRATON G 1657</td>
<td>---</td>
<td>100</td>
<td>100</td>
<td>---</td>
<td>100</td>
<td>---</td>
<td>100</td>
<td>---</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TACKIFIER COMPONENTS</th>
<th>(PARTS BY WT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ESC-5380</td>
<td>---</td>
</tr>
<tr>
<td>ESC-1310LC</td>
<td>---</td>
</tr>
<tr>
<td>ECR-111</td>
<td>125</td>
</tr>
<tr>
<td>TUFFLO-6056</td>
<td>20</td>
</tr>
<tr>
<td>IRGANOL-1010</td>
<td>2.45</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PROPERTIES</th>
<th>(POLYMER)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity (150°C)</td>
<td>279.5</td>
</tr>
<tr>
<td>Viscosity (170°C)</td>
<td>1375</td>
</tr>
<tr>
<td>Rolling Ball (cm)</td>
<td>2.9</td>
</tr>
<tr>
<td>Quick Stick</td>
<td>2.4</td>
</tr>
<tr>
<td>Peel SS (lb/in.)</td>
<td>3.6</td>
</tr>
<tr>
<td>Peel PE (lb/in.)</td>
<td>2.4</td>
</tr>
<tr>
<td>SAFT (°C)</td>
<td>80.8</td>
</tr>
<tr>
<td>HP SS (1/2&quot; x 1/2&quot; x 2kg; hr)</td>
<td>0.7</td>
</tr>
</tbody>
</table>

### Examples 41-42 and Comparative Example 20

An adhesive was prepared from a poly(2,6-dimethyl-1,4-phenylene oxide) macromonomer grafted isobutylene/para-methylstyrene/para-bromomethylstyrene (BrXP-50) by blending the graft polymer with the tackifier ESC-5380 and adhesion properties were compared to a EUROLON 2140 high performance polyamide hot melt adhesive.

The BrXP-50 was similarly prepared as in Example A. The poly(2,6-dimethyl-1,4-phenylene oxide) macromonomer was prepared from the phase transfer polymerization of 4-
bromo-2,6-dimethylphenol. The macromonomer had a $M_w$ of 7,000 and a $M_n$ of 3,000.

In one flask a 30 g sample of the BrXP-50 was dissolved in 300 ml of toluene. In another, 10 g of the poly(2,6-dimethyl-1,4-phenylene oxide) macromonomer was dissolved in 500 ml of toluene at 70°C. Two ml of 1 M tetrabutylammonium hydroxide in methanol and 5 g BHT were then added to the second flask. After 15 minutes, the BrXP-50 solution was added. The solutions were mixed together and allowed to react for 4 hrs at 70°C under constant stirring. At the end of this time, the reaction effluent was poured through a 150 mesh screen to remove any portion which had become gel as occurs when the macromonomer has more than a single terminal nucleophile.

No gel was observed and the screen contained less than 0.1 g polymer indicating the system was largely free of a gel fraction. The graft polymer Example 41 was isolated in isopropanol/BHT and oven dried at 50°C under vacuum for 24 hrs. The isolated graft polymer (39.0 g, 95 % yield) was a clear tough yellow elastomer. DSC indicated the presence of the isobutylene/p-methylstyrene polymer backbone ($T_g = -61°C$) and the poly(2,6-dimethyl-1,4-phenylene oxide) ($T_g = 90-140°C$) with a peak at 110°C. The quantity of poly(2,6-dimethyl-1,4-phenylene oxide) in the graft polymer was 22 wt. % as determined by NMR. The polymer contained approximately 8.4 side chains per main chain. TEM analysis of the graft polymer indicated a microphase morphology with spherical poly(phenylene oxide) domains of 5 to 10 nm.

Adhesive coatings on MYLAR (1.5 mil thick) were prepared from the graft polymer, a tackified adhesive formulation and the EUROLON 2140. Several performance properties are shown in Table X. Examples 41 and 42 had greater SAFT adhesion to aluminum than Comparative Example 20.
### TABLE X

<table>
<thead>
<tr>
<th></th>
<th>EXAMPLE</th>
<th>COMPARATIVE EXAMPLE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>41</td>
<td>42</td>
</tr>
<tr>
<td><strong>POLYMER COMPONENTS</strong> (PARTS BY Wt)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Example 41</td>
<td>100</td>
<td>60</td>
</tr>
<tr>
<td>EUROLON 2140</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td><strong>TACKIFIER COMPONENTS</strong> (PARTS BY Wt)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ESC-5380</td>
<td>---</td>
<td>40</td>
</tr>
</tbody>
</table>

|               |         |                     |                     |
| **PROPERTIES** |         |                     |                     |
| T- Peel Al (lb/in.) | 3.9     | 5.1                 | 10.2                |
| S.A.F.T. (°C) Al  |         |                     |                     |
| (1" x 1" x 0.5kg) | 149+    | 149+                | ---                 |
| (1" x 1" x 1kg)  | 149+    | 131                 | 128                 |
| P.A.F.T. (°C) Al  |         |                     |                     |
| (1" x 3" x 0.5kg) | 61      | 53                  | 93                  |

The foregoing description of the invention is illustrative and explanatory thereof. Various changes in the materials, apparatus, and particular parts employed will occur to those skilled in the art. It is intended that all such variations within the scope and spirit of the appended claims be embraced thereby.
Claims:

1. An adhesive, comprising:
   (a) a polymer having an elastomeric main chain and a plurality of thermoplastic side chains distributed along said main chain, said main chain having a number average molecular weight ($M_n^{\text{A}}$) of at least about 25,000, said side chains having a number average molecular weight ($M_n^{\text{S}}$) in a range of from about 1000 to about 30,000;
   (b) a tackifier admixed therewith; and
   (c) an optional oil or plasticizer admixed therewith.

2. The adhesive of claim 1, wherein said main chain molecular weight ($M_n^{\text{A}}$) is at least about 50,000.

3. The adhesive of claim 1, wherein said main chain molecular weight ($M_n^{\text{A}}$) is from about 50,000 to about 100,000.

4. The adhesive of claim 1, wherein said main chain has a ratio of $M_n^{\text{A}}$ to number average molecular weight ($M_n^{\text{A}}$) less than about 6.

5. The adhesive of claim 4, wherein said ratio of $M_n^{\text{A}}$/M$_n^{\text{A}}$ is less than about 4.

6. The adhesive of claim 4, wherein said ratio of $M_n^{\text{A}}$/M$_n^{\text{A}}$ is less than about 2.5.

7. The adhesive of claim 4, wherein said ratio of $M_n^{\text{A}}$/M$_n^{\text{A}}$ is less than about 2.

8. The adhesive of claim 1, wherein $M_n^{\text{S}}$ is from about 2000 to about 15,000.

9. The adhesive of claim 1, wherein $M_n^{\text{S}}$ is from about 3000 to about 10,000.

10. The adhesive of claim 1, wherein $M_n^{\text{S}}$ is from about 5000 to about 8000.

11. The adhesive of claim 1, wherein said side chain has a ratio of $M_n^{\text{S}}$ to number average molecular weight ($M_n^{\text{S}}$) less than about 6.

12. The adhesive of claim 11, wherein said ratio of $M_n^{\text{S}}$/M$_n^{\text{S}}$ is less than about 2.
13. The adhesive of claim 11, wherein said ratio of \( M_n^p/M_n^s \) is less than about 1.5.

14. The adhesive of claim 11, wherein said ratio of \( M_n^p/M_n^s \) is less than about 1.1.

15. The adhesive of claim 11, wherein said ratio of \( M_n^p/M_n^s \) is from 1.0 to about 1.05.

16. The adhesive of claim 1, comprising an average of from about 2 to about 20 of said side chains per said main chain.

17. The adhesive of claim 1, comprising an average of from about 3 to about 10 of said side chains per said main chain.

18. The adhesive of claim 1, comprising an average of from about 4 to about 8 of said side chains per said main chain.

19. The adhesive of claim 1, wherein said main chain comprises a copolymer of an isooolefin having about 4 to about 7 carbon atoms and a para-alkylstyrene, wherein said main chain copolymer has a substantially homogeneous compositional distribution.

20. The adhesive of claim 1, wherein said main chain comprises polyolefin rubber.

21. The adhesive of claim 1, wherein said side chains comprise polymerized monomer selected from styrene, para-methylstyrene, alpha-methylstyrene, vinylnaphthalene, isopropenylstyrene, naphthalene, phenylstyrene, cyclohexylstyrene, vinylxylene, methylvinylxylene, methyl methacrylate, 4-t-butylnystrene, 1,3-cyclohexadiene, phenylene oxide and combinations thereof.

22. The adhesive of claim 1, wherein said side chains comprise polymerized monomer selected from styrene and para-methylstyrene.

23. The adhesive of claim 1, wherein said tackifier comprises from about 5 to about 95 parts by weight of said polymer and from about 5 to about 95 parts by weight of said tackifier.
24. The adhesive of claim 1, wherein said tackifier comprises from about 30 to about 70 parts by weight of said polymer and from about 30 to about 70 parts by weight of said tackifier.

25. The adhesive of claim 1, wherein said tackifier is selected from the group consisting of rosin, hydrogenated rosins, rosin esters, polyterpenes, terpene phenol resins, polymerized mixed olefin resins and combinations thereof.

26. A shear thinning adhesive, comprising:

(a) from about 5 to about 95 parts by weight of a polymer having a shear thinning architecture including: (i) an elastomeric main chain having a number average molecular weight ($M_n^{el}$) of at least about 25,000, a ratio of $M_n^{el}$ to number average molecular weight ($M_n^{th}$) less than about 4, and comprising copolymerized isoolefin having about 4 to about 7 carbon atoms and para-alkylstyrene, wherein said main chains have a substantially homogeneous compositional distribution; and (ii) an average of from about 2 to about 20 thermoplastic side chains distributed along said main chains, said side chains having a number average molecular weight ($M_n^{s}$) in a range of from about 2000 to about 15,000 and a ratio of $M_n^{s}$ to number average molecular weight ($M_n^{th}$) less than about 6; and

(b) from about 5 to about 95 parts by weight of a tackifier admixed therewith.

27. The adhesive of claim 26, wherein at least about 95 weight percent of said polymer main chains has a para-alkyl styrene content within about 10 weight percent of the average para-alkyl styrene content thereof.
28. The adhesive of claim 26, wherein said isoolesfin comprises isobutylene and said para-alkylstyrene comprises para-methylstyrene.

29. The adhesive of claim 26, wherein said isoolesfin comprises from about 10 to about 99.5 percent by weight of said polymer main chain and said para-alkylstyrene comprises from about 0.5 to about 90 percent by weight of said polymer main chain.

30. The adhesive of claim 26, wherein the para-alkylstyrene is included in the main chain as:

\[
\begin{align*}
\text{H} \\
\sim \text{C} \sim \text{CH}_2 \sim \\
\sim \text{C} \sim \text{Y} \\
\sim \text{R} \sim \text{R}'
\end{align*}
\]

wherein R and R' are independently selected from the group consisting of hydrogen, alkyl and primary and secondary alkyl halides, and Y is a side chain attached to said para-alkylstyrene by nucleophilic substitution.

31. The adhesive of claim 30, wherein said side chains comprise polymerized monomer selected from styrene, para-methylstyrene, alpha-methylstyrene, vinylnaphthalene, isopropenylstyrene, naphthalene, phenylstyrene, cyclohexylstyrene, vinylxylene, methylvinylxylene, methyl methacrylate, 4-t-butylstyrene, 1,3-cyclohexadiene, phenylene oxide and combinations thereof.

32. The adhesive of claim 30, wherein said side chains comprise polymerized styrene or para-methylstyrene.
33. The adhesive of claim 30, wherein said para-alkylstyrene is further included in said main chains as:

\[
\begin{align*}
\text{H} \\
\sim \text{C-CH}_2 \sim \\
\text{R-C-H} \\
\text{R}'
\end{align*}
\]

34. The adhesive of claim 33, wherein said para-alkylstyrene is further included in said main chains as:

\[
\begin{align*}
\text{H} \\
\sim \text{C-CH}_2 \sim \\
\text{R-C-X} \\
\text{R}'
\end{align*}
\]

wherein X is halogen.
35. The adhesive of claim 33, wherein said para-alkylstyrene is further included in said main chains as:

\[ \begin{align*}
& \text{H} \\
& \overset{\sim}{\text{C-CH}_2\text{C}} \\
& \overset{\sim}{\text{C}} \\
& \text{R-C-Z} \\
& \text{R'}
\end{align*} \]

wherein Z is a functional group containing oxygen, sulfur, silicon, nitrogen, carbon, phosphorus or a metal selected from sodium, potassium, lithium, and magnesium.

36. A shear thinning adhesive, comprising:

(a) from about 5 to about 95 parts by weight of a polymer having a shear thinning architecture including: (i) an elastomeric, polyolefin main chain having a number average molecular weight \( (M_n^A) \) of at least about 25,000 and a ratio of \( M_n^A \) to number average molecular weight \( (M_n^A) \) less than about 6; and (ii) an average of from about 2 to about 20 thermoplastic side chains distributed along said main chains, said side chains having a number average molecular weight \( (M_n^B) \) in a range of from about 2000 to about 15,000 and a ratio of \( M_n^B \) to number average molecular weight \( (M_n^B) \) less than about 6; and

(b) from about 5 to about 95 parts by weight of a compatible tackifier admixed therewith.
37. The adhesive of claim 36, wherein said main chain monomers are copolymerized with a terminally, mono-olefinically unsaturated macromonomer incorporated as the side chains.

38. The adhesive of claim 37, wherein said macromonomer is norbornene terminated.

39. The adhesive of claim 38, wherein said norbornene termination comprises 2-methyl-5-norbornene.

40. The adhesive of claim 37, wherein said macromonomer comprises polymerized monomer selected from styrene, para-methylstyrene, alpha-methylstyrene, vinylnaphthalene, isopropenylstyrene, naphthalene, phenylstyrene, cyclohexylstyrene, vinylxylene, methylvinylxylene, methyl methacrylate, 4-t-butylstyrene, 1,3-cyclohexadiene, phenylene oxide and combinations thereof.

41. The adhesive of claim 37, wherein said macromonomer comprises polymerized styrene or para-methylstyrene.

42. The adhesive of claim 36, wherein said main chain comprises polymerized monomers selected from the group consisting of ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene and combinations thereof.

43. The adhesive of claim 36, wherein said main chain comprises ethylene-propylene rubber.

44. A method for applying the adhesive of claim 1 to a substrate surface, comprising the steps of:
   (a) melting the polymer and the tackifier to form a molten adhesive blend;
   (b) spraying the molten adhesive blend onto at least a portion of the substrate surface; and
   (c) cooling the adhesive blend to form an adhesive coating on said surface.

45. The method of claim 44, wherein said spraying is at a shear rate of at least about 100 sec⁻¹.
46. An adhesive-coated article, comprising:
   a substrate surface having a layer of the
   adhesive of claim 1 adhered to at least a
   portion thereof.

47. The article of claim 46, wherein said adhesive layer
   has a crystalline domain substantially comprised of
   a spherical or a mixed cylindrical and lamellar
   morphology.
Fig-1

Fig-2

SUBSTITUTE SHEET
Fig-5

Fig-6

Substitute Sheet
Fig 10

140°C

SUBSTITUTE SHEET

LOG (COMPLEX VISCOSITY) (POISE)

EXEMPLARY 8

COMPARATIVE
EXAMPLE 6

COMPARATIVE
EXAMPLE 7

COMPRESSION
MOLDING
CALENDERING
EXTRUSION
INJECTION
MOLDING

LOG (FREQUENCY) (RAD/S)
### Fields Searched

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### Certification

Date of the Actual Completion of the International Search: 20 MARCH 1992

Date of Mailing of this International Search Report: 09.04.92

International Searching Authority: EUROPEAN PATENT OFFICE

Signature of Authorized Officer: MEULEMANS R.A.M.
**ANNEX TO THE INTERNATIONAL SEARCH REPORT**

**ON INTERNATIONAL PATENT APPLICATION NO. US 9109701 SA 55539**

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