



US 20060246296A1

(19) **United States**

(12) **Patent Application Publication** (10) **Pub. No.: US 2006/0246296 A1**

**Xia et al.** (43) **Pub. Date: Nov. 2, 2006**

(54) **MULTILAYER OPTICAL ARTICLE**

**Publication Classification**

(75) Inventors: **Jianhui Xia**, Woodbury, MN (US);  
**Ying-Yuh Lu**, Woodbury, MN (US);  
**Zhiming Zhou**, Woodbury, MN (US)

(51) **Int. Cl.**  
**B32B 27/36** (2006.01)  
(52) **U.S. Cl.** ..... **428/412**

Correspondence Address:

**3M INNOVATIVE PROPERTIES COMPANY**  
**PO BOX 33427**  
**ST. PAUL, MN 55133-3427 (US)**

(57) **ABSTRACT**

(73) Assignee: **3M Innovative Properties Company**

An optical article includes a rigid substrate, a reflective polarizer, and an adhesive composition disposed between the substrate and the polarizer. The adhesive composition includes a majority of a pressure sensitive adhesive component, a high Tg polymer, and a crosslinker. The pressure sensitive adhesive component includes at least one polymer having an acid or base functionality. The high Tg polymer has a weight average molecular weight greater than 100,000, a Tg greater than about 20° C., and an acid or base functionality. The functionality of the pressure sensitive adhesive component and the functionality of the high Tg polymer form an acid-base interaction when mixed. The adhesive composition is optically clear.

(21) Appl. No.: **11/457,235**

(22) Filed: **Jul. 13, 2006**

**Related U.S. Application Data**

(63) Continuation of application No. 10/411,933, filed on Apr. 11, 2003.

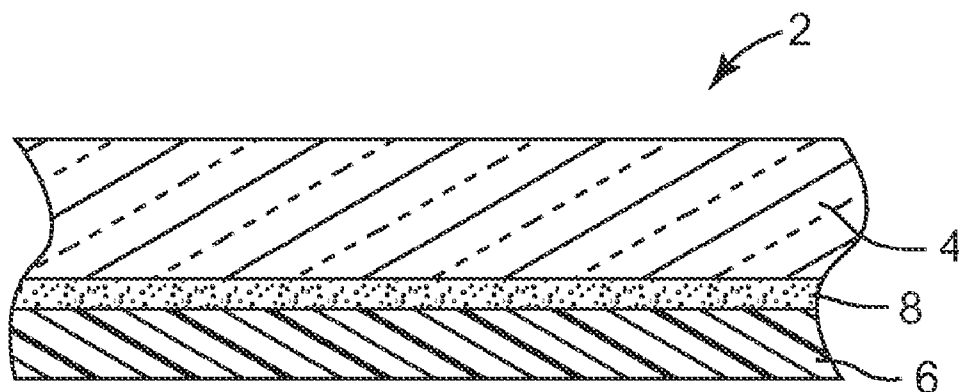


FIG. 1

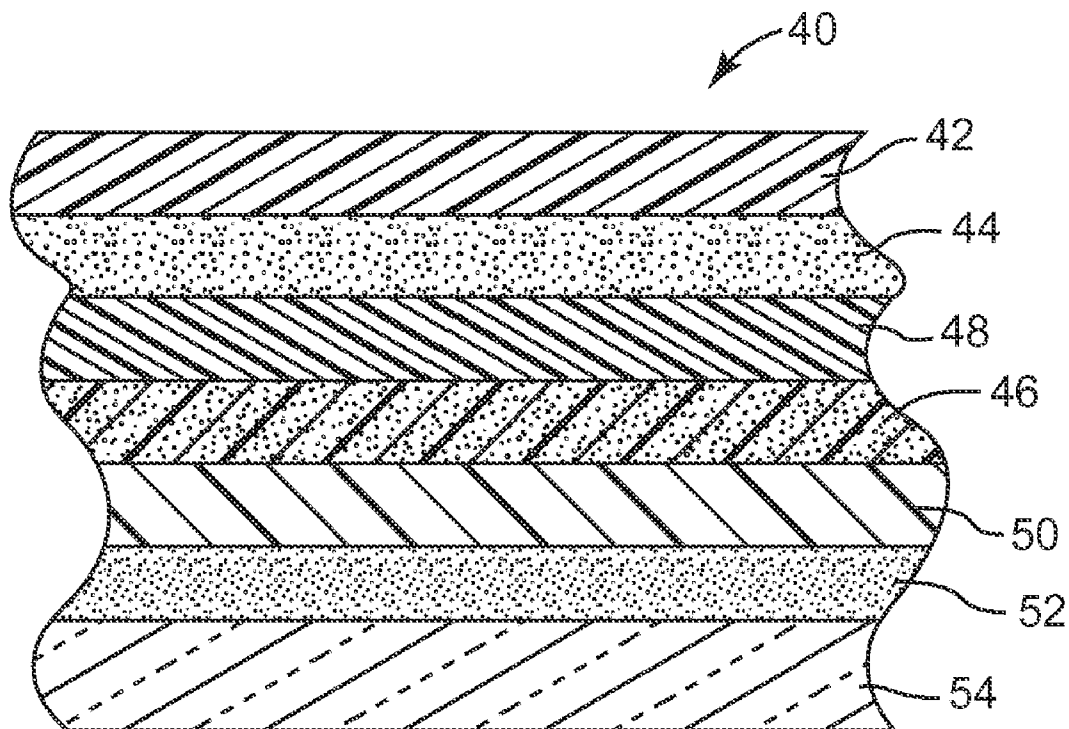
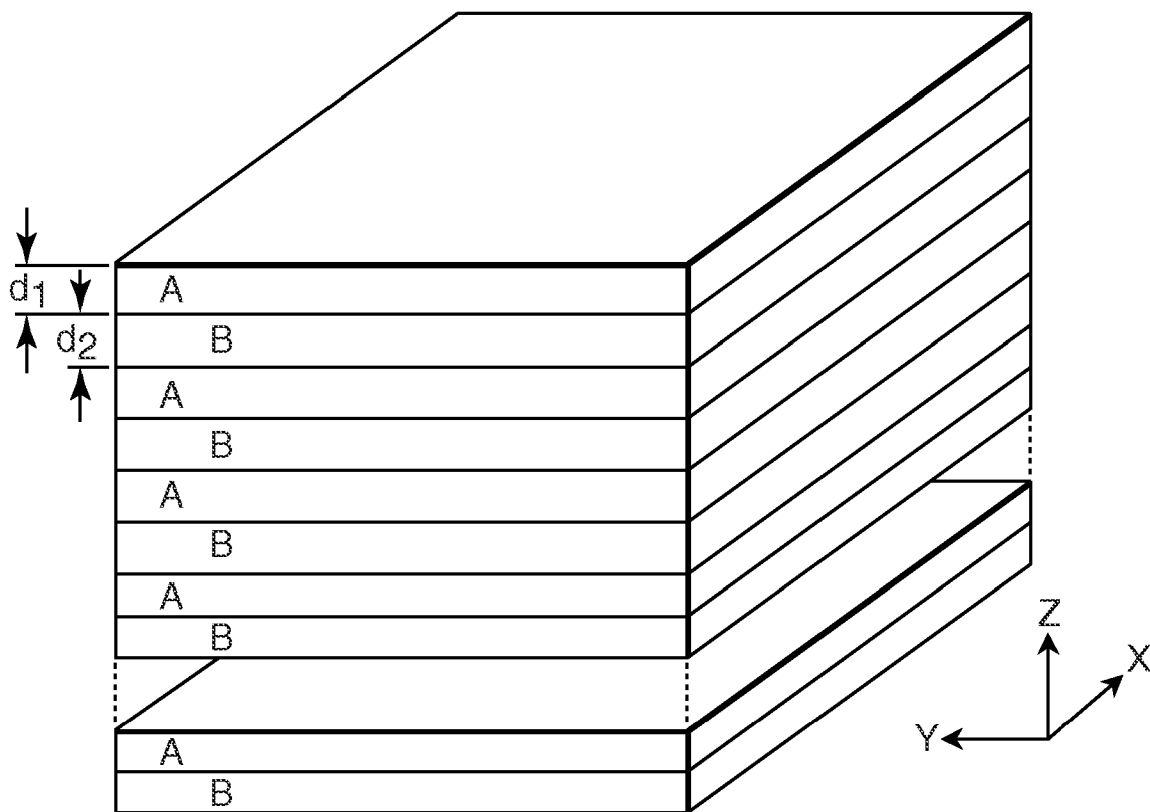


FIG. 2



*FIG. 3*

## MULTILAYER OPTICAL ARTICLE

### CROSS REFERENCE TO RELATED APPLICATION

[0001] This application is a continuation of U.S. patent application Ser. No. 10/411,933, filed Apr. 11, 2003, entitled "Adhesive Blends, Articles, and Methods," published as U.S. Patent Application Publication No. 2004/0202879.

### FIELD OF THE INVENTION

[0002] The invention relates to adhesive compositions. In particular, the invention relates to pressure sensitive adhesive compositions, methods of using such adhesives, and articles prepared using the adhesives, such as optical products.

### BACKGROUND

[0003] Pressure sensitive adhesives have significant commercial application. While a variety of adhesives have been prepared from countless combinations of ingredients including various polymers, e.g., acrylates, (meth)acrylates; epoxies; crosslinkers; heat and cationically curable polymers; and heat or radiation sensitive initiators; not all such compositions are suitable for use, especially in optical applications where clarity and stability are required. A useful adhesive for optical applications should be optically clear, and should also maintain that clarity over the life of the product in which it is used. The adhesive should withstand conditions present during manufacturing of optical elements and during use of such elements without losing a substantial amount of clarity. This property involves the adhesive being stable on its own, and also being stable and compatible when used with other elements in an optical element or optical product.

[0004] Optical elements include components bonded together by the adhesive. The adhesives are used, for example, to bond materials to polymeric materials such as polyesters; to bond materials to rigid materials such as rigid polycarbonate, polymethyl methacrylate, or glass; to bond materials to polarizer layers; etc.

[0005] Often, any of these components of an optical element can adversely affect the stability, clarity, bond strength, or other performance property of an adhesive in the same optical element. Polycarbonates, for example, are known to outgas in response to changing environmental conditions such as heat and humidity, producing bubbles or partial or full delamination at the adhesive bond between the polycarbonate and another layer of an optical element. Bubbling and delamination can be particularly common when the outgassing layer is bonded to another layer or laminate that exhibits low vapor transmissivity. Bubbles and delamination can affect clarity and integrity of the optical element, and should be avoided. It can be preferred, therefore, in these and other settings, that an adhesive be stable and not delaminate, bubble, or lose its clarity or integrity during use.

### SUMMARY OF THE INVENTION

[0006] An optical article includes a rigid substrate, a reflective polarizer, and an adhesive composition disposed between the substrate and the polarizer. The adhesive composition includes a majority of a pressure sensitive adhesive

component, a high T<sub>g</sub> polymer, and a crosslinker. The pressure sensitive adhesive component includes at least one polymer having an acid or base functionality. The high T<sub>g</sub> polymer has a weight average molecular weight greater than 100,000, a T<sub>g</sub> greater than about 20° C., and an acid or base functionality. The functionality of the pressure sensitive adhesive component and the functionality of the high T<sub>g</sub> polymer form an acid-base interaction when mixed. The adhesive composition is optically clear.

### BRIEF DESCRIPTION OF THE DRAWINGS

[0007] FIG. 1 illustrates an embodiment of an optical element according to the invention, comprising an outgassing layer and a low moisture vapor transfer layer.

[0008] FIG. 2 illustrates an embodiment of a polarizing optical element according to the present invention.

[0009] FIG. 3 is a perspective view of a multilayer film useful in the optical body of the present invention.

[0010] All figures are not drawn to scale.

### DETAILED DESCRIPTION

[0011] The present invention contemplates specific compatibilized compositions that comprise: a majority of a pressure sensitive adhesive component, a high T<sub>g</sub> polymer, and a crosslinker. As used herein the term "compatibilized" means that materials making up the adhesive composition form a stable multiphase morphology wherein the phases do not significantly coalesce and/or increase in size upon aging at temperatures at or above the glass transition temperature (T<sub>g</sub>) of the materials. As used herein, high T<sub>g</sub> polymer means a polymer with a glass transition temperature higher than polymers used to form a pressure sensitive adhesive, e.g., temperatures typically exceeding 20° C.

[0012] Pressure sensitive adhesives (PSAs) are well known to one of ordinary skill in the art to possess properties including the following: (1) aggressive and permanent tack, (2) adherence with no more than finger pressure, (3) sufficient ability to hold onto an adherend, and (4) sufficient cohesive strength to be removed cleanly from the adherend. Materials that have been found to function well as PSAs include polymers designed and formulated to exhibit the requisite viscoelastic properties resulting in a desired balance of tack, peel adhesion, and shear holding power. PSAs are one example of a preferred adhesive blend in accordance with the present invention. The compatibilized blend formed from the mixture of a PSA component and high T<sub>g</sub> polymer of the present invention is optionally also a pressure sensitive adhesive composition. Alternatively, the adhesive composition can be a laminating (heat-activated) adhesive.

[0013] "Polymer" refers to macromolecular materials having at least five repeating monomeric units, which may or may not be the same. The term polymer, as used herein, encompasses homopolymers and copolymers.

[0014] The PSA component and the high T<sub>g</sub> polymer are compatibilized using a compatibilization scheme. As used herein the term "compatibilization scheme" refers to the method by which the PSA component and the high T<sub>g</sub> polymer are made to be compatible with one another due to a modification of their interfacial interactions. The compatibilization scheme comprises functionalizing at least one

polymer in the PSA and the high Tg polymer in such a way that an acid-base interaction is present between the two materials. The acid-base interaction that is present between the polymers described herein may be described as a Lewis acid-base type interaction. Lewis acid-base interactions require that one chemical component be an electron acceptor (acid) and the other an electron donor (base). The electron donor provides an unshared pair of electrons and the electron acceptor furnishes an orbital system that can accommodate the additional unshared pair of electrons. The following general equation describes the Lewis acid-base interaction:



The acid-base interactions between the polymer in the PSA and the high Tg polymer reduce their interfacial tension, leading to a reduction in the dispersed phase particle size and a stabilization of the multiphase morphology. The interfacial tension between the materials reduces the domain size of the high Tg polymer. In some embodiments, particularly those in optical applications, the domain size of the high Tg polymer dispersed within the pressure sensitive adhesive is less than the wavelength of light to produce optical clarity. In some embodiments, the domain size of the high Tg polymer is less than 100 nanometers. In other embodiments, the domain size of the high Tg polymer is less than 50 nanometers.

[0015] The compatibilization scheme is independent of the particular functionality on the respective polymer. That is, either the PSA component or the high Tg polymer can contain the acid or the base functionality. For example, an acid functionalized polymer in the PSA component can be paired with a base functionalized high Tg polymer. Alternatively, a base functionalized polymer of the PSA component can be paired with an acid functionalized high Tg polymer.

[0016] Acrylate and methacrylate monomers are referred to collectively herein as “(meth)acrylate” monomers. (Meth)acrylate polymers may be copolymers, optionally in combination with other, non-(meth)acrylate, e.g., vinyl-unsaturated, monomers. Such polymers and their monomers are well-known in the polymer and adhesive arts, as are methods of preparing the monomers and polymers. One of skill will understand and recognize that such polymers can be useful to impart adhesive properties, and will understand their use in providing an adhesive as described herein.

[0017] As used in the present invention, an “acidic copolymer” is a polymer that is derived from at least one acidic monomer and at least one non-acidic copolymerizable monomer (i.e., a monomer that can not be titrated with a base). In one embodiment, at least one copolymerizable monomer is a (meth)acrylate monomer such as an alkyl (meth)acrylate monomer. The acidic copolymer may optionally be derived from other copolymerizable monomers, such as vinyl monomers and basic monomers, as long as the resultant copolymer can still be titrated with a base. Thus, usually more acidic monomers are utilized to prepare the acidic copolymers than basic monomers.

[0018] A “basic copolymer” is a polymer that is derived from at least one basic monomer and at least one nonbasic copolymerizable monomer (i.e., a monomer that cannot be titrated with an acid). Other monomers can be copolymer-

ized with the basic monomers (e.g., acidic monomers, vinyl monomers, and (meth)acrylate monomers), as long as the basic copolymer retains its basicity (i.e., it can still be titrated with an acid). In one embodiment, at least one copolymerizable monomer is a (meth)acrylate monomer such as an alkyl (meth)acrylate monomer.

[0019] The adhesive compositions of the present invention, being optically clear, can be used to make a variety of useful products, especially products that benefit from an optically transmissive adhesive such as optical elements and optical products. Optical elements typically include a number of layers of different substrate materials, which can be any one or more of polymeric, glass, metallized polymer, or of the present adhesive or another adhesive, e.g., another pressure sensitive or structural adhesive. Any one or more of these materials may be flexible, rigid, reflective, antireflective, polarizing, and is typically sufficiently optically transmissive to function as a component of the optical element.

[0020] Some materials used in optical products may have particular physical or chemical properties that can create adverse effects within the optical product. As an example, some materials may outgas, compromising an adhesive bond if the outgassing affects the adhesive and adhesion. Some materials may be low in their ability to transmit moisture vapor, possibly exacerbating the effects of the outgassing layer on an intervening adhesive. The adhesives described herein can be useful, because the adhesives can be optically transmissive to resist combined effects such as outgassing and low moisture vapor transfer.

[0021] Thus, the invention includes the use of the described adhesive for any application, especially applications within optical products or optical elements, and especially to bond materials where an optically transmissive or clear adhesive is useful, required, or desired. The invention is particularly useful for bonding materials that tend to outgas, and where such outgassing tends to compromise integrity of an adhesive bond between the outgassing material and another material. Even more specifically, the invention contemplates bonding an outgassing material to a material that has a low moisture vapor transfer rate.

#### Pressure Sensitive Adhesive Component

[0022] The pressure sensitive adhesive component of the adhesive composition in the present invention comprises either an acidic or basic copolymer. When the PSA component comprises an acidic copolymer, the ratio of acidic monomers to non-acidic copolymerizable monomers utilized varies depending on desired properties of the resulting adhesive. The properties of the adhesive can also be adjusted by varying the amount of the acidic copolymer in the compatibilized blend of PSA component, high Tg polymer, and a crosslinker.

[0023] Generally, as the proportion of acidic monomers used in preparing the acidic copolymer increases, cohesive strength of the resulting adhesive increases. The proportion of acidic monomers is usually adjusted depending on the proportion of acidic copolymer present in the blends of the present invention.

[0024] To achieve pressure sensitive adhesive characteristics, the corresponding copolymer can be tailored to have a resultant glass transition temperature (Tg) of less than about 0° C. Particularly preferred pressure-sensitive adhe-

sive copolymers are (meth)acrylate copolymers. Such copolymers typically are derived from monomers comprising about 40% by weight to about 98% by weight, preferably at least 70% by weight, more preferably at least 85% by weight, most preferably about 90% by weight, of at least one alkyl (meth)acrylate monomer that, as a homopolymer, has a Tg of less than about 0° C.

[0025] Examples of such alkyl (meth)acrylate monomers are those in which the alkyl groups comprise from about 4 carbon atoms to about 12 carbon atoms and include, but are not limited to, n-butyl acrylate, 2-ethylhexyl acrylate, isooctyl acrylate, isononyl acrylate, isodecyl acrylate, and mixtures thereof. Optionally, other vinyl monomers and alkyl (meth)acrylate monomers which, as homopolymers, have a Tg greater than 0° C., such as methyl acrylate, methyl methacrylate, isobornyl acrylate, vinyl acetate, styrene, and the like, may be utilized in conjunction with one or more of the low Tg alkyl (meth)acrylate monomers and copolymerizable basic or acidic monomers, provided that the Tg of the resultant (meth)acrylate copolymer is less than about 0° C.

[0026] In some embodiments, it is desirable to use (meth)acrylate monomers that are free of alkoxy groups.

[0027] When used, basic (meth)acrylate copolymers useful as the pressure sensitive adhesive component typically are derived from basic monomers comprising about 2% by weight to about 50% by weight, preferably about 5% by weight to about 30% by weight, of a copolymerizable basic monomer.

[0028] When used to form the pressure sensitive adhesive component, acidic (meth)acrylate copolymers typically are derived from acidic monomers comprising about 2% by weight to about 30% by weight, preferably about 2% by weight to about 15% by weight, of a copolymerizable acidic monomer.

#### High Tg Polymer Additive

[0029] The high Tg polymer additive of the present invention comprises either an acidic or basic copolymer, depending on the functionality chosen for the pressure sensitive adhesive. For example, if the pressure sensitive adhesive comprises an acidic copolymer, then the high Tg polymer additive will be a basic copolymer to form a compatibilized blend.

[0030] To achieve the high Tg characteristics of the polymer additive, the corresponding copolymer is tailored to have a resultant glass transition temperature (Tg) of greater than about 20° C. In some embodiments, the Tg of the high Tg polymer additive is greater than 40° C., 50° C., or 60° C. In exemplary embodiments, the copolymers are (meth)acrylate copolymers. Such copolymers typically are derived from monomers comprising about 40% by weight to about 98% by weight, preferably at least 70% by weight, more preferably at least 85% by weight, most preferably about 90% by weight, of at least one alkyl (meth)acrylate monomer that, as a homopolymer, has a Tg of greater than about 20° C. Examples include vinyl monomers and alkyl (meth)acrylate monomers which, as homopolymers, have a Tg greater than 20° C., such as n-butyl methacrylate, methyl methacrylate, isobornyl acrylate, vinyl acetate, styrene, and the like.

[0031] Alkyl (meth)acrylate monomers with a Tg less than 0° C., such as monomers with alkyl groups comprising from

about 4 carbon atoms to about 12 carbon atoms, including n-butyl acrylate, 2-ethylhexyl acrylate, isooctyl acrylate, isononyl acrylate, isodecyl acrylate, and mixtures thereof, may be utilized in conjunction with one or more of the high Tg alkyl (meth)acrylate monomers and copolymerizable basic or acidic monomers, provided that the Tg of the resultant (meth)acrylate copolymer is greater than about 20° C.

[0032] When the high Tg polymer additive is a basic copolymer, it is typically a basic (meth)acrylate copolymer. Basic (meth)acrylate copolymers typically are derived from basic monomers comprising about 2% by weight to about 50% by weight, preferably about 5% by weight to about 30% by weight, of a copolymerizable basic monomer.

[0033] When the high Tg polymer additive is an acidic copolymer, it is typically an acidic (meth)acrylate copolymer. Acidic (meth)acrylate copolymers typically are derived from acidic monomers comprising about 2% by weight to about 30% by weight, preferably about 2% by weight to about 15% by weight, of a copolymerizable acidic monomer.

[0034] In some embodiments, the copolymer of the high Tg polymer additive typically has a weight average molecular weight greater than 100,000. Higher molecular weight, high Tg polymer is desirable because it enhances the thermal stability of the compatibilized blend, especially at elevated temperatures and extreme conditions. To utilize a high molecular weight, high Tg polymer additive, other attributes of the high Tg polymer additive (such as monomer selection) and of the compatibilized blend (such as acid-base interaction level) are varied to retain compatibility.

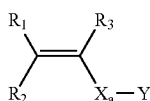
#### Acidic Monomers

[0035] Useful acidic monomers include, but are not limited to, those selected from ethylenically unsaturated carboxylic acids, ethylenically unsaturated sulfonic acids, ethylenically unsaturated phosphonic acids, and mixtures thereof. Examples of such compounds include those selected from acrylic acid, methacrylic acid, itaconic acid, fumaric acid, crotonic acid, citraconic acid, maleic acid, oleic acid, B-carboxyethyl acrylate, 2-sulfoethyl methacrylate, styrene sulfonic acid, 2-acrylamido-2-methylpropane sulfonic acid, vinyl phosphonic acid, and the like, and mixtures thereof.

[0036] Due to their availability, acidic monomers of the present invention are typically the ethylenically unsaturated carboxylic acids. When even stronger acids are desired, acidic monomers include the ethylenically unsaturated sulfonic acids and ethylenically unsaturated phosphonic acids. Sulfonic and phosphonic acids generally provide a stronger interaction with a basic polymer. This stronger interaction can lead to greater improvements in cohesive strength, as well as higher temperature resistance and solvent resistance of the adhesive.

#### Basic Monomers

[0037] A wide variety of basic monomers are useful in the present invention. In some embodiments, the basic monomer is a nitrogen-containing monomer, such as those of Formula (I):



Formula (I)

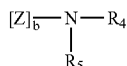
[0038] wherein

[0039] a is 0 or 1;

[0040] R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub> are independently selected from H— and CH<sub>3</sub>— or other alkyl group,

[0041] X is selected from an ester or amide group; and

[0042] Y is an alkyl group, a nitrogen-containing aromatic, nitrogen-containing group, such as the group:



[0043] wherein

[0044] Z is a divalent linking group (typically about 1 to 5 carbon atoms);

[0045] b is 0 or 1; and

[0046] R<sub>4</sub> and R<sub>5</sub> are selected from hydrogen, alkyl, aryl, cycloalkyl, and arenyl groups.

[0047] R<sub>4</sub> and R<sub>5</sub> in the above group may also form a heterocycle. In all embodiments, Y, R<sub>1</sub>, and R<sub>2</sub> may also comprise heteroatoms, such as O, S, N, etc. While Formula I summarizes the majority of basic monomers useful in the present invention, other nitrogen-containing monomers are possible if they meet the definition of a basic monomer (i.e., can be titrated with an acid).

[0048] Exemplary basic monomers include N,N-dimethylaminopropyl methacrylamide (DMAPMAm); N,N-diethylaminopropyl methacrylamide (DEAPMAm); N,N-diethylaminoethyl acrylate (DMAEA); N,N-diethylaminoethyl acrylate (DEAEA); N,N-dimethylaminopropyl acrylate (DMAPA); N,N-diethylaminopropyl acrylate (DEAPA); N,N-dimethylaminoethyl methacrylate (DMAEMA); N,N-diethylaminoethyl methacrylate (DEAEMA); N,N-dimethylaminoethyl acrylamide (DMAEAm); N,N-dimethylaminoethyl methacrylamide (DMAEMAm); N,N-diethylaminoethyl acrylamide (DEAEAm); N,N-diethylaminoethyl methacrylamide (DEAEMAm); N,N-dimethylaminoethyl vinyl ether (DMAEVE); N,N-diethylaminoethyl vinyl ether (DEAEVE); and mixtures thereof. Other useful basic monomers include vinylpyridine, vinylimidazole, tertiary amino-functionalized styrene (e.g., 4-(N,N-dimethylamino)-styrene (DMAS), 4-(N,N-diethylamino)-styrene (DEAS)), N-vinyl pyrrolidone, N-vinyl caprolactam, acrylonitrile, N-vinyl formamide, (meth)acrylamide, and mixtures thereof.

#### High Tg Monomers

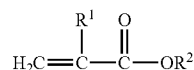
[0049] High Tg monomers are generally those monoethylenically unsaturated monomers which as homopolymers

have a glass transition temperature (Tg) greater than about 20° C. Preferably, the high Tg polymer is derived from monoethylenically unsaturated monomers, which as homopolymers have a Tg of greater than 20° C. Typically the high Tg polymer is independently derived from monoethylenically unsaturated monomers selected from the group consisting of (meth)acrylate esters of non-tertiary alkyl alcohols, the alkyl groups of which comprise from about 1 to about 20, preferably about 1 to about 18 carbon atoms as shown in Formula II (below); acidic or basic monomers as defined above; vinyl-terminated monomers; and combinations thereof.

[0050] In most embodiments, the high Tg polymers are independently derived from (meth)acrylate monomers, although, for certain formulations, vinyl-terminated monomers, such as styrene, may show comparable or superior results. Examples of suitable monomers useful in the present invention include, but are not limited to, t-butyl acrylate, methyl methacrylate, ethyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, s-butyl methacrylate, t-butyl methacrylate, stearyl methacrylate, phenyl methacrylate, cyclohexyl methacrylate, isobornyl acrylate, isobornyl methacrylate, benzyl methacrylate, bromoethyl methacrylate, 2-hydroxyethyl methacrylate, hydroxypropyl methacrylate, glycidyl methacrylate, alkyl methacrylate, styrene, vinyl acetate, vinyl chloride.

#### (Meth)acrylate Monomers

[0051] (Meth)acrylate copolymers useful in the invention contain at least one monofunctional unsaturated monomer selected from the group consisting of (meth)acrylate esters of non-tertiary alkyl alcohols, the alkyl groups of which comprise from about 1 to about 20, preferably about 1 to about 18 carbon atoms, such as those of Formula (II):



Formula (II)

wherein R<sup>1</sup> is H or CH<sub>3</sub>, the latter corresponding to where the (meth)acrylate monomer is a methacrylate monomer, and R<sup>2</sup> is a linear, branched, aromatic, or cyclic hydrocarbon group. When R<sup>2</sup> is a hydrocarbon group, it can also include heteroatoms (e.g., oxygen or sulfur). Criteria to consider when selecting R<sup>2</sup> include cost and the form in which the copolymer will be incorporated into the adhesive.

[0052] Examples of suitable (meth)acrylate monomers useful in the present invention include, but are not limited to, benzyl methacrylate, n-butyl acrylate, n-butyl methacrylate, cyclohexyl acrylate, cyclohexyl methacrylate, decyl acrylate, 2-ethoxy ethyl acrylate, 2-ethoxy ethyl methacrylate, ethyl acrylate, 2-ethylhexyl acrylate, ethyl methacrylate, n-hexadecyl acrylate, n-hexadecyl methacrylate, hexyl acrylate, hydroxy-ethyl methacrylate, hydroxy ethyl acrylate, isoamyl acrylate, isobornyl acrylate, isobornyl methacrylate, isobutyl acrylate, isodecyl acrylate, isodecyl methacrylate, isononyl acrylate, isooctyl acrylate, isooctyl methacrylate, isotridecyl acrylate, lauryl acrylate, lauryl methacrylate, 2-methoxy ethyl acrylate, methyl acrylate, methyl methacrylate, 2-methyl butyl acrylate, 4-methyl-2-pentyl acrylate, 1-methylcyclohexyl methacrylate, 2-methylcyclohexyl

methacrylate, 3-methylcyclohexyl methacrylate, 4-methylcyclohexyl methacrylate, octadecyl acrylate, octadecyl methacrylate, n-octyl acrylate, n-octyl methacrylate, 2-phenoxy ethyl methacrylate, 2-phenoxy ethyl acrylate, propyl acrylate, propyl methacrylate, n-tetradecyl acrylate, n-tetradecyl methacrylate, and mixtures thereof.

#### Vinyl Monomers

[0053] When used, vinyl monomers useful in the acidic and basic copolymers include vinyl esters (e.g., vinyl acetate), styrene, substituted styrene (e.g., *a*-methyl styrene), vinyl halide, vinyl propionate, and mixtures thereof. Other useful vinyl monomers include macromeric (meth)acrylates such as (meth)acrylate-terminated styrene oligomers and (meth)acrylate-terminated polyethers, such as are described in PCT Patent Application WO 84/03837 and European Patent Application EP 140941.

#### Polymerization Methods

[0054] The polymers herein can be prepared by any conventional free radical polymerization method, including solution, radiation, bulk, dispersion, emulsion, and suspension processes. In one solution polymerization method, the monomers, along with a suitable inert organic solvent, are charged into a four-neck reaction vessel that is equipped with a stirrer, a thermometer, a condenser, an addition funnel, and a thermowatch.

[0055] A concentrated thermal free radical initiator solution is added to the addition funnel. The whole reaction vessel, addition funnel, and their contents are then purged with nitrogen to create an inert atmosphere. Once purged, the solution within the vessel is heated to an appropriate temperature to activate the free radical initiator to be added, the initiator is added, and the mixture is stirred during the course of the reaction. A 98% to 99% conversion can typically be obtained in about 20 hours.

[0056] Bulk polymerization methods, such as the continuous free radical polymerization method described by Kotonour et al. in U.S. Pat. Nos. 4,619,979 and 4,843,134; the essentially adiabatic polymerization methods using a batch reactor described by Ellis in U.S. Pat. No. 5,637,646; suspension polymerization processes described by Young et al. in U.S. Pat. No. 4,833,179; and, the methods described for polymerizing packaged pre-adhesive compositions described by Hamer et al. in PCT Publication No. WO 97/33945 may also be utilized to prepare the polymers.

[0057] Suitable thermal free radical initiators which may be utilized include, but are not limited to, those selected from azo compounds, such as 2,2'-azobis(isobutyronitrile); hydroperoxides, such as tert-butyl hydroperoxide; and, peroxides, such as benzoyl peroxide and cyclohexanone peroxide. Photoinitiators which are useful according to the invention include, but are not limited to, those selected from benzoin ethers, such as benzoin methyl ether or benzoin isopropyl ether; substituted benzoin ethers, such as anisole methyl ether; substituted acetophenones, such as 2,2-diethoxyacetophenone and 2,2-dimethoxy-2-phenyl acetophenone; substituted alpha-ketols, such as 2-methyl-2-hydroxy propiophenone; aromatic sulfonyl chlorides, such as 2-naphthalene sulfonyl chloride; and, photoactive oximes, such as 1-phenyl-1,2-propanedione-2-(ethoxycarbonyl)oxime. For both thermal- and radiation-induced polymerizations, the

initiator is present in an amount of about 0.05% to about 5.0% by weight based upon the total weight of the monomers.

[0058] While solventless embodiments are visualized within the scope of this invention, it is preferred that solvents are used in preparing the adhesive compositions of the invention. Suitable solvent, if desired, may be any liquid which is sufficiently inert to the reactants and product such that it will not otherwise adversely affect the reaction. Such solvents include ethyl acetate, acetone, methyl ethyl ketones, and mixtures thereof. Representative solvents include acetone, methyl-ethyl-ketone, heptane, and toluene. If used, the amount of solvent is generally about 30-80% by weight based on the total weight of the reactants (monomer and initiator) and solvent. The solvent is optionally removed from the polymers prior to blending.

[0059] Chain transfer agents can also be utilized when polymerizing the polymers described herein to control the molecular weight of the polymers. Suitable chain transfer agents include halogenated hydrocarbons (e.g., carbon tetrabromide) and sulfur compounds (e.g., lauryl mercaptan, butyl mercaptan, ethanethiol, and 2-mercaptoether).

[0060] The amount of chain transfer agent that is useful depends upon the desired molecular weight and the type of chain transfer agent. Organic solvents (e.g., toluene, isopropanol, and ethyl acetate) can also be used as chain transfer agents, but they generally are not as active as, for example, sulfur compounds. The chain transfer agent is typically used in amounts from about 0.001 parts to about 10 parts; more often, 0.01 to about 0.5 parts; and specifically from about 0.02 parts to about 0.20 parts based on total weight of the monomers.

[0061] Crosslinkers. In order to increase cohesive strength of the coated adhesive composition, a crosslinking additive is incorporated into the blend. Two types of crosslinking additives are commonly used. The first crosslinking additive is a thermal crosslinking additive such as a multifunctional aziridine. One example is 1,1'-(1,3-phenylene dicarbonyl)-bis-(2-methylaziridine) (Bisamide). Such chemical crosslinkers can be added into the solvent-based PSA after polymerization and activated by heat during oven drying of the coated adhesive. Isocyanate and epoxy crosslinkers can also be used.

[0062] In another embodiment, chemical crosslinkers that rely upon free radicals to carry out the crosslinking reaction may be employed. Reagents such as, for example, peroxides serve as a source of free radicals. When heated sufficiently, these precursors will generate free radicals which bring about a crosslinking reaction of the polymer. A common free radical generating reagent is benzoyl peroxide. Free radical generators are required only in small quantities, but generally require higher temperatures to complete a crosslinking reaction than those required for the bisamide reagent.

[0063] The second type of chemical crosslinker is a photosensitive crosslinker which is activated by high intensity ultraviolet (UV) light. Two common photosensitive crosslinkers used are benzophenone and copolymerizable aromatic ketone monomers as described in U.S. Pat. No. 4,737,559. Another photocrosslinker, which can be post-added to the solution composition and activated by UV light is a triazine, for example, 2,4-bis(trichloromethyl)-6-(4-



methoxy-phenyl)-s-triazine. These crosslinkers are activated by UV light generated from artificial sources such as medium pressure mercury lamps or a UV blacklight.

[0064] Hydrolyzable, free-radically copolymerizable crosslinkers, such as monoethylenic ally unsaturated mono-, di-, and trialkoxy silane compounds including, but not limited to, methacryloxypropyltrimethoxysilane (available from Gelest, Inc., Tullytown, Pa.), vinyl dimethylethoxysilane, vinylmethyl diethoxysilane, vinyltriethoxysilane, vinyltrimethoxysilane, vinyltriphenoxysilane, and the like, are also useful crosslinking agents. Multi-functional acrylates are useful for bulk or emulsion polymerization. Examples of useful multi-functional acrylate crosslinking agents include, but are not limited to, diacrylates, triacrylates, and tetraacrylates, such as 1,6-hexanediol diacrylate, poly(ethylene glycol) diacrylates, polybutadiene diacrylate, polyurethane diacrylates, and propoxylated glycerin triacrylate, and mixtures thereof. Crosslinking may also be achieved using high energy electromagnetic radiation such as gamma or e-beam radiation.

[0065] The amount and identity of crosslinker is tailored depending upon application of the adhesive composition. Typically, the crosslinker is present in amounts less than 5 parts based on total dry weight of adhesive composition. More specifically, the crosslinker is present in amounts from 0.01 parts to 1 part based on total dry weight of the adhesive composition.

[0066] Additives. Following copolymerization, other additives may be added with the resultant adhesive blend composition, provided the additive causes no adverse affect to the desired properties, such as optical clarity and environmental stability, over time. For example, compatible tackifiers and/or plasticizers may be added to aid in optimizing the ultimate tack and peel properties of the PSA. The use of such tack-modifiers is common in the art, as is described in the Handbook of Pressure Sensitive Adhesive Technology, edited by Donatas Satas (1982). Examples of useful tackifiers include, but are not limited to, rosin, rosin derivatives, polyterpene resins, coumarone-indene resins, and the like. Plasticizers which may be added to the adhesive of the invention may be selected from a wide variety of commercially available materials. In each case, the added plasticizer must be compatible with the PSA. Representative plasticizers include polyoxyethylene aryl ether, dialkyl adipate, 2-ethylhexyl diphenyl phosphate, t-butylphenyl diphenyl phosphate, 2-ethylhexyl adipate, toluenesulfonamide, dipropylene glycol dibenzoate, polyethylene glycol dibenzoate, polyoxypropylene aryl ether, dibutoxyethoxyethyl formal, and dibutoxyethoxyethyl adipate. UV stabilizers as known in the art may also be added.

[0067] The adhesive composition can preferably be optically transmissive, e.g., optically clear. Optical clarity allows the adhesive to be used in preparing optical elements. The adhesive can also maintain optical clarity, e.g., transmissivity, for a useful period of time under normal use conditions and as shown by accelerated aging tests. A balance of desired clarity, stability, bond strength, integrity, etc., can be achieved in an adhesive by selection of the combination of ingredients of the adhesive. Additional ingredients can be selected to balance properties of clarity, bond strength, integrity, stability, etc., as will be appreciated.

#### Preparation of the Compatibilized Adhesive Blend

[0068] The composition of the present invention includes a PSA component and a high Tg polymer in an adhesive composition in any relative amounts that, in combination with the crosslinker and any other optional components, will result in a useful balance of properties of the adhesive, preferably meaning at least an optically clear, stable adhesive.

[0069] For the PSA component, an amount is included to provide the functional properties of a pressure sensitive adhesive, including a useful amount of tack or tackiness and other PSA properties. These and other properties of pressure sensitive adhesives, and the amounts necessary to achieve these properties, are well understood.

[0070] For the high Tg polymer, any amount can be included to provide sufficient stability and clarity, in a given application. Preferably, an amount of high Tg polymer can be included to maintain optical clarity of the adhesive during use and over time, under conditions that would be experienced by the adhesive or a product that incorporates the adhesive. In particular, the amount of high Tg polymer can provide a bond that does not delaminate or bubble over time, under a variety of environmental conditions. The required bond strength will depend on the materials being bonded, but preferred amounts of high Tg polymer can provide adhesives according to the invention that will not bubble or delaminate over time when used to bond an outgassing material to a low moisture vapor transfer material.

[0071] Overall, the PSA component and high Tg polymer can be included in the adhesive composition in relative amounts that will provide a desired combination of pressure sensitive adhesive properties, adhesive bond properties, and optical clarity, with stability of these properties and clarity over time during use. In general, depending on factors such as the chemical identities and molecular weights, amount of cross-linking, etc., among other variables, less than about 50 parts by weight high Tg polymer based on 100 parts by weight total PSA component and high Tg polymer can provide a compatibilized adhesive composition that will have acceptable optical clarity. Exemplary embodiments include amounts less than about 30 parts by weight high Tg polymer based on one hundred parts by weight total PSA component and high Tg polymer. At the low end, an amount of high Tg polymer useful to provide sufficient bond properties can depend on factors such as the type of high Tg polymer and PSA polymer, but in general, useful amounts can be from at least about 5 parts by weight high Tg polymer based on 100 parts by weight total high Tg polymer and PSA component. In most embodiments, the range of the two components can be from about 10 to about 30 parts by weight high Tg polymer based on a total of one hundred parts by weight high Tg polymer and PSA component.

[0072] The pressure sensitive adhesive component and high Tg polymer additive can be blended by traditional methods known to those skilled in the art. Such methods include mixing, mechanical rolling, hot melt blending, etc. Typically, the pressure sensitive adhesive component and the high Tg polymer additive are mixed in solution.

#### Application of the Compatibilized Adhesive Blend

[0073] The adhesive compositions may be applied by any conventional application method, including but not limited

to gravure coating, curtain coating, slot coating, spin coating, screen coating, transfer coating, brush or roller coating, and the like. The thickness of a coated adhesive layer, typically in the form of a liquid is in part dependent on the nature of the materials used and the specific properties desired, but those properties and the relationship of thickness to the properties is well understood in the art. Exemplary thicknesses of an adhesive layer may be in the range from about 0.05 to about 100 micrometers.

[0074] Exemplary embodiments involve coating the adhesive composition in a solvent. In alternative embodiments, copolymers are hot-melt coatable, followed by subsequent cross-linking.

[0075] The adhesive composition is preferably optically clear. Optical clarity can be measured in a number of different ways, as will be appreciated by the skilled artisan, but for the purposes of this disclosure optical clarity can be observed visually and optionally measured according to ASTM-D 1003-95. When so measured, adhesives according to the invention can exhibit a luminous transmission of at least about 90%, and haze of less than about 2%.

[0076] A preferred property of the adhesive composition is to avoid contributing to any loss of luminous transmission of a multi-layer article, e.g., a laminate, compared to the elements without the adhesive present. When the luminous transmission is measured for a laminate, the transmission can be recorded using the most transmissive substrate as a reference. For example for a glass/adhesive/film laminate, glass can be used as the reference (i.e., the transmission through the glass can be set as 100% transmission) and the percent transmission of the laminate can be relative to that of glass alone.

[0077] Exemplary adhesives can maintain useful optical transmissivity over a useful life of the adhesive, and can also maintain a secure bond strength and resist or avoid delamination or bubbling to maintain optical clarity between elements of a multilayer product, over a useful life. Such stability and retention of optical transmissivity can be measured by accelerated aging tests, whereby samples of adhesive optionally bonded to one or two other materials are exposed to elevated temperature, optionally with elevated humidity conditions, for a period of time. Adhesives of the invention can retain their optical clarity after such accelerated aging tests as follows: after aging an adhesive composition at 90° C. for approximately 500 hours in an oven for accelerated aging, the aged adhesive is translucent, e.g. optically clear and the luminous transmission of the aged adhesive can be greater than 90%, and the haze of the aged adhesive can be less than 2%. The humidity of the 90° C. oven is not controlled, and is ambient for an oven in an inside space; at 90° C. the relative humidity can generally be below 10 or 20%.

[0078] In exemplary embodiments, the adhesive compositions of the present invention can retain their optical clarity such that after aging an adhesive composition at 80° C. and 90% relative humidity in an oven with temperature and humidity control for approximately 500 hours, the aged adhesive is translucent, e.g., optically clear. In addition, the luminous transmission of the aged adhesive can be greater than 90%, and the haze less than 2%.

[0079] The adhesive, being optically clear, can be useful in bonding together components of a variety of optical com-

ponents, optical elements, and optical products. More generally, the adhesive can be useful in bonding together any type of product, and is particularly useful if the product requires or benefits from an optically transmissive, preferably optically clear, adhesive.

[0080] Optical elements include articles and products that have an optical effect or optical application, such as screens for computers or other displays; components of such screens such as polarizing layers, reflective layers, selectively reflective layers such as infrared reflecting optically clear layers; coatings for windows which may polarize or reflect; other partially or fully reflective optically transmissive products, etc.

[0081] Examples of optical elements include optical elements wherein an adhesive is used to bond together one or more different layers of optical materials, typically layers or films that are at least partially optically transmissive, reflective, polarizing, or optically clear. Optical elements typically include a number of different substrate layers, which can be any one or more of polymeric, glass, metal or metallized polymer, or of the present adhesive or another adhesive, e.g., another pressure sensitive or structural adhesive. Any one or more of these materials may also provide a desired physical property including flexibility, rigidity, strength, or support, or can be one or more of reflective, partially-reflective, antireflective, polarizing, selectively transmissive or reflective with respect to different wavelengths, and is typically sufficiently optically transmissive to function within an optical element. Such layers can be prepared from well known optical materials including materials that are polymeric, glass, or metallic, and also from layers of adhesives. Any one or more of these materials or layers may be a fragile layer, an outgassing layer, or a low moisture vapor transfer layer (see below).

[0082] Examples of rigid substrates that can be included to provide support for an optical element include glass or rigid polymeric materials such as polycarbonates, polyacrylates, polyesters, etc. Often, such rigid polymeric materials, especially when relatively thick (for example in the range of millimeters or centimeters, as opposed to smaller dimensions), can exhibit a property of outgassing. This is a well-known and frustrating problem in optical products and optical elements. This outgassing problem can be exacerbated if the outgassing layer is bonded to a layer that does not allow the gas to pass through, but acts as a barrier to the gas, resulting in the gas collecting at the adhesive interface and causing bubbling or delamination, reduced bond strength, or loss of clarity. Adhesives of the invention offer improved bond strength and stability and can therefore reduce or eliminate such bubbling or delamination even where the adhesive is used to bond an outgassing substrate to a low moisture vapor transfer layer.

[0083] Specific examples of outgassing substrate layers include polycarbonates, such as polycarbonates having a thickness in the range from about one or three millimeters up to any larger thickness; and polyacrylates such as polymethyl methacrylate, for example having a thickness of at least about one to three millimeters up to any larger thickness.

[0084] Materials considered to have low moisture vapor transmission rates are also known and understood and include certain chemistries and constructions of films,

including polymeric films that may or may not include certain coatings that can effectively act as barriers to moisture vapor. The threshold level of moisture vapor transmissivity that can cause delamination, bubbling, loss of bond strength, or loss of clarity in a specific optical product construction can depend on various factors such as the composition of an outgassing substrate layer and the amount of gas it produces, conditions of use, and the composition and overall strength, integrity, and stability of an adhesive.

[0085] Other polymers or polymeric materials may be used in an optical element to provide, e.g., mechanical properties, conductivity, and optical functionalities such as diffusion or color. Examples of polymeric materials include, but are not limited to plastic films such as polypropylene, polyethylene, polyvinyl chloride, polyester (polyethylene terephthalate (PET)), polyurethane, cellulose acetate, cellulose triacetate, ethyl cellulose, diffuse film, metallized polymeric film and ceramic sheet materials, and other optical film such as view angle compensation film. More specific examples include multilayer AR (antireflective) film such as described in U.S. Pat. No. 6,277,485 columns 13 and 14, the entire disclosure of the patent being incorporated herein by reference; and microlayer films such as those described in U.S. Pat. No. 6,049,419 (the entire disclosure of which is incorporated herein by reference), any of which can be reflective, partially reflective, or otherwise optically useful.

[0086] One embodiment of a film of the present invention comprises at least two layers and is a dielectric optical film having alternating layers of a material having a high index of refraction and a material having a low index of refraction. The film may be isotropic or birefringent. Preferably, the film is a birefringent polymeric film, and more preferably the film is designed to allow the construction of multilayer stacks for which the Brewster angle (the angle at which reflectance of p polarized light goes to zero) is very large or is nonexistent for the polymer layer interfaces. This feature allows for the construction of multilayer mirrors and polarizers whose reflectivity for p polarized light decreases slowly with angle of incidence, is independent of angle of incidence, or increases with angle of incidence away from the normal. As a result, the multilayered films of the present invention have high reflectivity (for both s and p polarized light for any incident direction in the case of mirrors, and for the selected direction in the case of polarizers) over a wide bandwidth.

[0087] Suitable films include those described in U.S. Ser. No. 08/402,401 filed Mar. 10, 1995, and U.S. Ser. No. 09/006,601 entitled "Modified Copolyesters and Improved Multilayer Reflective Film" filed on Jan. 13, 1998, both of which are hereby incorporated by reference.

[0088] Suitable films also include those which prevent higher order harmonics which prevent color in the visible region of the spectrum. Examples of such film include those described in U.S. Pat. No. RE 3,034,605, incorporated herein by reference, which describes a multilayer optical interference film comprising three diverse substantially transparent polymeric materials, A, B, and C and having a repeating unit of ABCB. The layers have an optical thickness of between about 0.09 and 0.45 micrometers, and each of the polymeric materials has a different index of refraction,  $n_i$ . The film includes polymeric layers of polymers A, B, and C. Each of the polymeric materials have its own different

refractive index,  $n_A$ ,  $n_B$ ,  $n_C$ , respectively. A preferred relationship of the optical thickness ratios of the polymers produces an optical interference film in which multiple successive higher order reflections are suppressed. In this embodiment, the optical thickness ratio of first material A,  $f_A$ , is 1/5, the optical thickness ratio of second material B,  $f_B$ , is 1/6, the optical thickness of third material C,  $f_C$  is 1/3, and  $n_B = \text{square root}(n_A n_C)$ .

[0089] For this embodiment, there will be an intense reflection at the first order wavelength, while the reflections at the second, third, and fourth order wavelengths will be suppressed. To produce a film which reflects a broad bandwidth of wavelengths in the solar infrared range (e.g., reflection at from about 0.7 to 2.0 micrometers), a layer thickness gradient may be introduced across the thickness of the film. Thus, the layer thicknesses may increase monotonically across the thickness of the film. Preferably, for the preferred three component system of the present invention, the first polymeric material (A) differs in refractive index from the second polymeric material (B) by at least about 0.03, the second polymeric material (B) differs in refractive index from the third polymeric material (C) by at least about 0.03, and the refractive index of the second polymeric material (B) is intermediate the respective refractive indices of the first (A) and third (C) polymeric materials. Any or all of the polymeric materials may be synthesized to have the desired index of refraction by utilizing a copolymer or miscible blend of polymers. For example, the second polymeric material may be a copolymer or miscible blend of the first and third polymeric materials. By varying the relative amounts of monomers in the copolymer or polymers in the blend, any of the first, second, or third materials can be adjusted so that there is a refractive index relationship where  $n_B = \text{square root}(n_A n_C)$ .

[0090] Another suitable film includes the film described in U.S. Pat. No. 5,360,659, incorporated herein by reference, which describes a two component film having a six layer alternating repeating unit suppresses the unwanted second, third, and fourth order reflections in the visible wavelength region of between about 380-770 nm while reflecting light in the infrared wavelength region of between about 770-2000 nm. Reflections higher than fourth order will generally be in the ultraviolet, not visible, region of the spectrum or will be of such a low intensity as to be unobjectionable. The film comprises alternating layers of first (A) and second (B) diverse polymeric materials with a six layer alternating repeat unit. The use of only six layers in the repeat unit results in more efficient use of material and simpler manufacture than previous designs.

[0091] A repeat unit gradient may be introduced across the thickness of the film. Thus, in one embodiment, the repeat unit thicknesses will increase linearly across the thickness of the film. By linearly, it is meant that the repeat unit thicknesses increase at a constant rate across the thickness of the film. In some embodiments, it may be desirable to force the repeat unit optical thickness to double from one surface of the film to another. The ratio of repeat unit optical thicknesses can be greater or less than two as long as the short wavelength range of the reflectance band is above 770 nm and the long wavelength edge is about 2000 nm. Other repeat unit gradients may be introduced by using logarithmic and/or quarter functions. A logarithmic distribution of repeat unit thicknesses will provide nearly constant reflectance

across the infrared band. In an alternative embodiment, the two component film may comprise a first portion of alternating layers comprising the six layer alternating layer repeating unit which reflects infrared light of wave lengths between about 1200-2000 nm and a second portion of alternating layers having an AB repeat unit and substantially equal optical thicknesses which reflect infrared light of wavelengths between about 770-1200 nm. Such a combination of alternating layers results in reflection of light across the infrared wavelength region through 2000 nm. Preferably, the first portion of the alternating layers has a repeat unit gradient of about 5/3:1, and the second portion of alternating layers have a layer thickness gradient of about 1.5:1.

[0092] While the optical film of the present invention can be made with dielectric inorganic thin film stacks of materials such as indium tin oxide (ITO), silicon dioxide (SiO<sub>2</sub>), zirconium dioxide (ZrO<sub>2</sub>), or titanium dioxide (TiO<sub>2</sub>) as described, for example, in EP 0 080 182 and U.S. Pat. Nos. 4,705,356 and 5,179,468, the preferred optical film is a polymeric multilayer film having alternating layers of polymeric materials having high and low indices of refraction. The construction, materials, and optical properties of conventional multilayer polymeric films are generally known, and were first described in Alfrey et al., *Polymer Engineering and Science*, Vol. 9, No. 6, pp 400-404, November 1969; Radford et al., *Polymer Engineering and Science*, Vol. 13, No. 3, pp 216-221, May 1973; and U.S. Pat. No. 3,610,729 (Rogers). More recently patents and publications including PCT International Publication Number WO 95/17303 (Ouder Kirk et al.), PCT International Publication Number WO 96/19347 (Jonza et al.), U.S. Pat. No. 5,095,210 (Wheatley et al.), and U.S. Pat. No. 5,149,578 (Wheatley et al.) discuss useful optical effects which can be achieved with large numbers of alternating thin layers of different polymeric materials that exhibit differing optical properties, in particular different refractive indices in different directions. The contents of all of these references are incorporated by reference herein

[0093] Multilayer polymeric films can include hundreds or thousands of thin layers, and may contain as many materials as there are layers in the stack. For ease of manufacturing, preferred multilayer films have only a few different materials, and for simplicity those discussed herein typically include only two. The multilayer film includes alternating layers of a first polymeric material having a first index of refraction, and a second polymeric material having a second index of refraction that is different from that of the first material. The individual layers are typically on the order of 0.05 micrometers to 0.45 micrometers thick. As an example, the PCT Publication to Ouder Kirk et al. discloses a multilayered polymeric film having alternating layers of crystalline naphthalene dicarboxylic acid polyester and another selected polymer, such as copolyester or copolycarbonate, wherein the layers have a thickness of less than 0.5 micrometers, and wherein the refractive indices of one of the polymers can be as high as 1.9 in one direction and 1.64 in the other direction, thereby providing a birefringent effect which is useful in the polarization of light.

[0094] Adjacent pairs of layers (one having a high index of refraction, and the other a low index) preferably have a total optical thickness that is 1/2 of the wavelength of the light desired to be reflected, as shown in FIG. 3 For maximum

reflectivity the individual layers of a multilayer polymeric film have an optical thickness that is 1/4 of the wavelength of the light desired to be reflected, although other ratios of the optical thicknesses within the layer pairs may be chosen for other reasons. These preferred conditions are expressed in Equations 1 and 2, respectively. Note that optical thickness is defined as the refractive index of a material multiplied by the actual thickness of the material, and that unless stated otherwise, all actual thicknesses discussed herein are measured after any orientation or other processing. For biaxially oriented multilayer optical stacks at normal incidence, the following equation applies:

$$\lambda/2=t_1+t_2=n_1d_1+n_2d_2 \quad \text{Equation 1}$$

$$\lambda/4=t_1=t_2=n_1d_1=n_2d_2 \quad \text{Equation 2}$$

where  $\lambda$ =wavelength of maximum light reflection

[0095]  $t_1$ =optical thickness of the first layer of material

[0096]  $t_2$ =optical thickness of the second layer of material and

[0097]  $n_1$ =in-plane refractive index of the first material

[0098]  $n_2$ =in-plane refractive index of the second material

[0099]  $d_1$ =actual thickness of the first material

[0100]  $d_2$ =actual thickness of the second material

[0101] By creating a multilayer film with layers having different optical thicknesses (for example, in a film having a layer thickness gradient), the film will reflect light of different wavelengths. An important feature of the present invention is the selection of layers having desired optical thicknesses (by selecting the actual layer thicknesses and materials) sufficient to reflect light in the near infrared portion of the spectrum. Moreover, because pairs of layers will reflect a predictable band width of light, as described below, individual layer pairs may be designed and made to reflect a given band width of light. Thus, if a large number of properly selected layer pairs are combined, superior reflectance of a desired portion of the near infrared spectrum can be achieved.

[0102] The bandwidth of light desired to be blocked, i.e., not transmitted, at a zero degree observation angle in accordance with an optical body of the present invention is from approximately 700 to 1200 nm. Thus, the layer pairs preferably have optical thicknesses ranging from 350 to 600 nm (1/2 the wavelength of the light desired to be reflected) in order to reflect the near infrared light. More preferably, the multilayer film would have individual layers each having an optical thickness ranging from 175 to 300 nm (1/4 the wavelength of the light desired to be reflected), in order to reflect the near infrared light. Assuming for purposes of illustration that the first layer material has a refractive index of 1.66 (as does biaxially oriented PET), and the second layer material has a refractive index of 1.52 (as does the biaxially oriented thermoplastic polyester commercially available from Eastman Chemical Co., Knoxville, Tenn., under the trade designation "Ecdel"), and assuming that both layers have the same optical thickness (1/4 wavelength), then the actual thicknesses of the first material layers would range from approximately 105 to 180 nm, and the actual thicknesses of the second layers would range from approximately 115 to 197 nm. The optical properties of multilayer films such as this are discussed in detail below.

[0103] The various layers in the film preferably have different thicknesses. This is commonly referred to as the layer thickness gradient. A layer thickness gradient is selected to achieve the desired band width of reflection. One common layer thickness gradient is a linear one, in which the thickness of the thickest layer pairs is a certain percent thicker than the thickness of the thinnest layer pairs. For example, a 1.055:1 layer thickness gradient means that the thickest layer pair (adjacent to one major surface) is 5.5% thicker than the thinnest layer pair (adjacent to the opposite surface of the film). In another embodiment, the layer thickness could decrease, then increase, then decrease again from one major surface of the film to the other. This is believed to provide sharper bandedges, and thus a sharper or more abrupt transition from clear to colored in the case of the present invention. This preferred method for achieving sharpened bandedges is described more fully in U.S. Ser. No. 09/006,085 entitled "Optical Film with Sharpened Bandedge" filed on Jan. 13, 1998.

[0104] Suitable polymeric materials for use in the optical films of the present invention may be amorphous, semicrystalline, or crystalline polymeric materials. The films consist of at least two distinguishable polymers having different indices of refraction. The number is not limited, and three or more materials may be advantageously used in applications wherein it is desirable to eliminate higher order harmonics that would otherwise reflect light in the visible region of the spectrum and give a film with a colored appearance. For simplicity, the films will be described further considering an optical stack made from only two materials.

[0105] A variety of polymer materials suitable for use in the present invention have been taught for use in making coextruded multilayer optical films. For example, in U.S. Pat. Nos. 4,937,134, 5,103,337, 5,122,448,404, 5,540,978, and 5,568,316 to Schrenk et al., and in U.S. Pat. Nos. 5,122,905, 5,122,906, and 5,126,880 to Wheatley and Schrenk. Of special interest are birefringent polymers such as those described in U.S. Pat. Nos. 5,486,949 and 5,612,820 to Schrenk et al., U.S. Pat. No. 5,882,774 to Jonza et al., and U.S. Ser. No. entitled "Modified Copolyesters and Improved Multilayer Reflective Films" filed on Jan. 13, 1998 all of which are herein incorporated by reference. Regarding the preferred materials from which the films are to be made, there are several conditions which should be met to make the multilayer optical films of this invention. First, these films should consist of at least two distinguishable polymers; the number is not limited, and three or more polymers may be advantageously used in particular films. Second, at least one of the two required polymers, referred to as the "first polymer", should have a stress optical coefficient having a large absolute value. In other words, it must be capable of developing a large birefringence when stretched. Depending on the application, the birefringence may be developed between two orthogonal directions in the plane of the film, between one or more in-plane directions and the direction perpendicular to the film plane, or a combination of these. Third, the first polymer should be capable of maintaining birefringence after stretching, so that the desired optical properties are imparted to the finished film. Fourth, the other required polymer, referred to as the "second polymer," should be chosen so that in the finished film, its refractive index, in at least one direction, differs significantly from the index of refraction of the first polymer in the same direction.

Because polymeric materials are typically dispersive, that is, the refractive indices vary with wavelength, these conditions must be considered in terms of a particular spectral bandwidth of interest.

[0106] Other aspects of polymer selection depend on specific applications. For polarizing films, it is advantageous for the difference in the index of refraction of the first and second polymers in one film-plane direction to differ significantly in the finished film, while the difference in the orthogonal film-plane index is minimized. If the first polymer has a large refractive index when isotropic, and is positively birefringent (that is, its refractive index increases in the direction of stretching), the second polymer will be chosen to have a matching refractive index, after processing, in the planar direction orthogonal to the stretching direction, and a refractive index in the direction of stretching which is as low as possible. Conversely, if the first polymer has a small refractive index when isotropic, and is negatively birefringent, the second polymer will be chosen to have a matching refractive index, after processing, in the planar direction orthogonal to the stretching direction, and a refractive index in the direction of stretching which is as high as possible.

[0107] Alternatively, it is possible to select a first polymer which is positively birefringent and has an intermediate or low refractive index when isotropic, or one which is negatively birefringent and has an intermediate or high refractive index when isotropic. In these cases, the second polymer may be chosen so that, after processing, its refractive index will match that of the first polymer in either the stretching direction or the planar direction orthogonal to stretching. Further, the second polymer will be chosen such that the difference in index of refraction in the remaining planar direction is maximized, regardless of whether this is best accomplished by a very low or very high index of refraction in that direction.

[0108] One means of achieving this combination of planar index matching in one direction and mismatching in the orthogonal direction is to select a first polymer which develops significant birefringence when stretched, and a second polymer which develops little or no birefringence when stretched, and to stretch the resulting film in only one planar direction. Alternatively, the second polymer may be selected from among those which develop birefringent in the sense opposite to that of the first polymer (negative-positive or positive-negative). Another alternative method is to select both first and second polymers which are capable of developing birefringence when stretched, but to stretch in two orthogonal planar directions, selecting process conditions, such as temperatures, stretch rates, post-stretch relaxation, and the like, which result in development of unequal levels of orientation in the two stretching directions for the first polymer, and levels of orientation for the second polymer such that one in-plane index is approximately matched to that of the first polymer, and the orthogonal in-plane index is significantly mismatched to that of the first polymer. For example, conditions may be chosen such that the first polymer has a biaxially oriented character in the finished film, while the second polymer has a predominantly uniaxially oriented character in the finished film.

[0109] The foregoing is meant to be exemplary, and it will be understood that combinations of these and other tech-

niques may be employed to achieve the polarizing film goal of index mismatch in one in-plane direction and relative index matching in the orthogonal planar direction.

[0110] Absorbance is another consideration. For most applications, it is advantageous for neither the first polymer nor the second polymer to have any absorbance bands within the bandwidth of interest for the film in question. Thus, all incident light within the bandwidth is either reflected or transmitted. However, for some applications, it may be useful for one or both of the first and second polymer to absorb specific wavelengths, either totally or in part.

[0111] Polyethylene 2,6-naphthalate (PEN) is frequently chosen as a first polymer for films of the present invention. It has a large positive stress optical coefficient, retains birefringence effectively after stretching, and has little or no absorbance within the visible range. It also has a large index of refraction in the isotropic state. Its refractive index for polarized incident light of 550 nm wavelength increases when the plane of polarization is parallel to the stretch direction from about 1.64 to as high as about 1.9. Its birefringence can be increased by increasing its molecular orientation which, in turn, may be increased by stretching to greater stretch ratios with other stretching conditions held fixed.

[0112] Other semicrystalline naphthalene dicarboxylic polyesters are also suitable as first polymers. Polybutylene 2,6-Naphthalate (PBN) is an example. These polymers may be homopolymers or copolymers, provided that the use of comonomers does not substantially impair the stress optical coefficient or retention of birefringence after stretching. The term "PEN" herein will be understood to include copolymers of PEN meeting these restrictions. In practice, these restrictions impose an upper limit on the comonomer content, the exact value of which will vary with the choice of comonomer(s) employed. Some compromise in these properties may be accepted, however, if comonomer incorporation results in improvement of other properties. Such properties include but are not limited to improved interlayer adhesion, lower melting point (resulting in lower extrusion temperature), better rheological matching to other polymers in the film, and advantageous shifts in the process window for stretching due to change in the glass transition temperature.

[0113] Suitable comonomers for use in PEN, PBN or the like may be of the diol or dicarboxylic acid or ester type. Dicarboxylic acid comonomers include but are not limited to terephthalic acid, isophthalic acid, phthalic acid, all isomeric naphthalenedicarboxylic acids (2,6-, 1,2-, 1,3-, 1,4-, 1,5-, 1,6-, 1,7-, 1,8-, 2,3-, 2,4-, 2,5-, 2,7-, and 2,8-), bibenzoic acids such as 4,4'-biphenyl dicarboxylic acid and its isomers, trans-4,4'-stilbene dicarboxylic acid and its isomers, 4,4'-diphenyl ether dicarboxylic acid and its isomers, 4,4'-diphenylsulfone dicarboxylic acid and its isomers, 4,4'-benzophenone dicarboxylic acid and its isomers, halogenated aromatic dicarboxylic acids such as 2-chloroterephthalic acid and 2,5-dichloroterephthalic acid, other substituted aromatic dicarboxylic acids such as tertiary butyl isophthalic acid and sodium sulfonated isophthalic acid, cycloalkane dicarboxylic acids such as 1,4-cyclohexanedicarboxylic acid and its isomers and 2,6-decahydronaphthalene dicarboxylic acid and its isomers, bi- or multi-cyclic dicarboxylic acids (such as the various isomeric norbornane and norbornene

dicarboxylic acids, adamantane dicarboxylic acids, and bicyclo-octane dicarboxylic acids), alkane dicarboxylic acids (such as sebacic acid, adipic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, azelaic acid, and dodecane dicarboxylic acid), and any of the isomeric dicarboxylic acids of the fused-ring aromatic hydrocarbons (such as indene, anthracene, phenanthrene, benzonaphthene, fluorene and the like). Alternatively, alkyl esters of these monomers, such as dimethyl terephthalate, may be used.

[0114] Suitable diol comonomers include but are not limited to linear or branched alkane diols or glycols (such as ethylene glycol, propanediols such as trimethylene glycol, butanediols such as tetramethylene glycol, pentanediols such as neopentyl glycol, hexanediols, 2,2,4-trimethyl-1,3-pentanediol and higher diols), ether glycols (such as diethylene glycol, triethylene glycol, and polyethylene glycol), chain-ester diols such as 3-hydroxy-2,2-dimethylpropyl-3-hydroxy-2,2-dimethyl propanoate, cycloalkane glycols such as 1,4-cyclohexanedimethanol and its isomers and 1,4-cyclohexanediol and its isomers, bi- or multicyclic diols (such as the various isomeric tricyclodecane dimethanols, norbornane dimethanols, norbornene dimethanols, and bicyclo-octane dimethanols), aromatic glycols (such as 1,4-benzenedimethanol and its isomers, 1,4-benzenediol and its isomers, bisphenols such as bisphenol A, 2,2'-dihydroxy biphenyl and its isomers, 4,4'-dihydroxymethyl biphenyl and its isomers, and 1,3-bis(2-hydroxyethoxy)benzene and its isomers), and lower alkyl ethers or diethers of these diols, such as dimethyl or diethyl diols.

[0115] Tri- or polyfunctional comonomers, which can serve to impart a branched structure to the polyester molecules, can also be used. They may be of either the carboxylic acid, ester, hydroxy or ether types. Examples include, but are not limited to, trimellitic acid and its esters, trimethylol propane, and pentaerythritol.

[0116] Also suitable as comonomers are monomers of mixed functionality, including hydroxycarboxylic acids such as parahydroxybenzoic acid and 6-hydroxy-2-naphthalenecarboxylic acid, and their isomers, and tri- or polyfunctional comonomers of mixed functionality such as 5-hydroxyisophthalic acid and the like.

[0117] Polyethylene terephthalate (PET) is another material that exhibits a significant positive stress optical coefficient, retains birefringence effectively after stretching, and has little or no absorbance within the visible range. Thus, it and its high PET-content copolymers employing comonomers listed above may also be used as first polymers in some applications of the current invention.

[0118] When a naphthalene dicarboxylic polyester such as PEN or PBN is chosen as first polymer, there are several approaches which may be taken to the selection of a second polymer. One preferred approach for some applications is to select a naphthalene dicarboxylic copolyester (coPEN) formulated so as to develop significantly less or no birefringence when stretched. This can be accomplished by choosing comonomers and their concentrations in the copolymer such that crystallizability of the coPEN is eliminated or greatly reduced. One typical formulation employs as the dicarboxylic acid or ester components dimethyl naphthalate at from about 20 mole percent to about 80 mole percent and dimethyl terephthalate or dimethyl isophthalate at from about 20 mole percent to about 80 mole percent, and

employs ethylene glycol as diol component. Of course, the corresponding dicarboxylic acids may be used instead of the esters. The number of comonomers which can be employed in the formulation of a coPEN second polymer is not limited. Suitable comonomers for a coPEN second polymer include but are not limited to all of the comonomers listed above as suitable PEN comonomers, including the acid, ester, hydroxy, ether, tri- or polyfunctional, and mixed functionality types.

[0119] Often it is useful to predict the isotropic refractive index of a coPEN second polymer. A volume average of the refractive indices of the monomers to be employed has been found to be a suitable guide. Similar techniques well-known in the art can be used to estimate glass transition temperatures for coPEN second polymers from the glass transitions of the homopolymers of the monomers to be employed.

[0120] In addition, polycarbonates having a glass transition temperature compatible with that of PEN and having a refractive index similar to the isotropic refractive index of PEN are also useful as second polymers. Polyesters, copolyesters, polycarbonates, and copolycarbonates may also be fed together to an extruder and transesterified into new suitable copolymeric second polymers.

[0121] It is not required that the second polymer be a copolyester or copolycarbonate. Vinyl polymers and copolymers made from monomers such as vinyl naphthalenes, styrenes, ethylene, maleic anhydride, acrylates, acetates, and methacrylates may be employed. Condensation polymers other than polyesters and polycarbonates may also be used. Examples include: polysulfones, polyamides, polyurethanes, polyamic acids, and polyimides. Naphthalene groups and halogens such as chlorine, bromine and iodine are useful for increasing the refractive index of the second polymer to a desired level. Acrylate groups and fluorine are particularly useful in decreasing refractive index when this is desired.

[0122] It will be understood from the foregoing discussion that the choice of a second polymer is dependent not only on the intended application of the multilayer optical film in question, but also on the choice made for the first polymer, and the processing conditions employed in stretching. Suitable second polymer materials include but are not limited to polyethylene naphthalate (PEN) and isomers thereof (such as 2,6-, 1,4-, 1,5-, 2,7-, and 2,3-PEN), polyalkylene terephthalates (such as polyethylene terephthalate, polybutylene terephthalate, and poly-1,4-cyclohexanedimethylene terephthalate), other polyesters, polycarbonates, polyarylates, polyamides (such as nylon 6, nylon 11, nylon 12, nylon 4/6, nylon 6/6, nylon 6/9, nylon 6/10, nylon 6/12, and nylon 61/T), polyimides (including thermoplastic polyimides and polyacrylic imides), polyamide-imides, polyether-amides, polyetherimides, polyaryl ethers (such as polyphenylene ether and the ring-substituted polyphenylene oxides), polyarylether ketones such as polyetheretherketone ("PEEK"), aliphatic polyketones (such as copolymers and terpolymers of ethylene and/or propylene with carbon dioxide), polyphenylene sulfide, polysulfones (including polyethersulfones and polyaryl sulfones), atactic polystyrene, syndiotactic polystyrene ("sPS") and its derivatives (such as syndiotactic poly-alpha-methyl styrene and syndiotactic polydichlorostyrene), blends of any of these polystyrenes (with each other or with other polymers, such as polyphenylene oxides), copolymers of any of these polystyrenes (such as styrene-

butadiene copolymers, styrene-acrylonitrile copolymers, and acrylonitrile-butadiene-styrene terpolymers), polyacrylates (such as polymethyl acrylate, polyethyl acrylate, and polybutyl acrylate), polymethacrylates (such as polymethyl methacrylate, polyethyl methacrylate, polypropyl methacrylate, and polyisobutyl methacrylate), cellulose derivatives (such as ethyl cellulose, cellulose acetate, cellulose propionate, cellulose acetate butyrate, and cellulose nitrate), polyalkylene polymers (such as polyethylene, polypropylene, polybutylene, polyisobutylene, and poly(4-methyl)pentene), fluorinated polymers and copolymers (such as polytetrafluoroethylene, polytrifluoroethylene, polyvinylidene fluoride, polyvinyl fluoride, fluorinated ethylene-propylene copolymers, perfluoroalkoxy resins, polychlorotrifluoroethylene, polyethylene-co-trifluoroethylene, polyethylene-co-chlorotrifluoroethylene), chlorinated polymers (such as polyvinylidene chloride and polyvinyl chloride), polyacrylonitrile, polyvinylacetate, polyethers (such as polyoxymethylene and polyethylene oxide), ionic resins, elastomers (such as polybutadiene, polyisoprene, and neoprene), silicone resins, epoxy resins, and polyurethanes.

[0123] Also suitable are copolymers, such as the copolymers of PEN discussed above as well as any other non-naphthalene group-containing copolyesters which may be formulated from the above lists of suitable polyester comonomers for PEN. In some applications, especially when PET serves as the first polymer, copolyesters based on PET and comonomers from said lists above (coPETs) are especially suitable. In addition, either first or second polymers may consist of miscible or immiscible blends of two or more of the above-described polymers or copolymers (such as blends of sPS and atactic polystyrene, or of PEN and sPS). The coPENs and coPETs described may be synthesized directly, or may be formulated as a blend of pellets where at least one component is a polymer based on naphthalene dicarboxylic acid or terephthalic acid and other components are polycarbonates or other polyesters, such as a PET, a PEN, a coPET, or a co-PEN.

[0124] Another preferred family of materials for the second polymer for some applications are the syndiotactic vinyl aromatic polymers, such as syndiotactic polystyrene. Syndiotactic vinyl aromatic polymers useful in the current invention include poly(styrene), poly(allyl styrene)s, poly(aryl styrene)s, poly(styrene halide)s, poly(alkoxy styrene)s, poly(vinyl ester benzoate), poly(vinyl naphthalene), poly(vinylstyrene), and poly(acenaphthalene), as well as the hydrogenated polymers and mixtures or copolymers containing these structural units. Examples of poly(alkyl styrene)s include the isomers of the following: poly(methyl styrene), poly(ethyl styrene), poly(propyl styrene), and poly(butyl styrene). Examples of poly(aryl styrene)s include the isomers of poly(phenyl styrene). As for the poly(styrene halide)s, examples include the isomers of the following: poly(chlorostyrene), poly(bromostyrene), and poly(fluorostyrene). Examples of poly(alkoxy styrene)s include the isomers of the following: poly(methoxy styrene) and poly(ethoxy styrene). Among these examples, particularly preferable styrene group polymers, are: polystyrene, poly(p-methyl styrene), poly(m-methyl styrene), poly(p-tertiary butyl styrene), poly(p-chlorostyrene), poly(m-chloro styrene), poly(p-fluoro styrene), and copolymers of styrene and p-methyl styrene.

[0125] Furthermore, comonomers may be used to make syndiotactic vinyl aromatic group copolymers. In addition to the monomers for the homopolymers listed above in defining the syndiotactic vinyl aromatic polymers group, suitable comonomers include olefin monomers (such as ethylene, propylene, butenes, pentenes, hexenes, octenes or decenes), diene monomers (such as butadiene and isoprene), and polar vinyl monomers (such as cyclic diene monomers, methyl methacrylate, maleic acid anhydride, or acrylonitrile).

[0126] The syndiotactic vinyl aromatic copolymers of the present invention may be block copolymers, random copolymers, or alternating copolymers.

[0127] The syndiotactic vinyl aromatic polymers and copolymers referred to in this invention generally have syndiotacticity of higher than 75% or more, as determined by carbon-13 nuclear magnetic resonance. Preferably, the degree of syndiotacticity is higher than 85% racemic diad, or higher than 30%, or more preferably, higher than 50%, racemic pentad.

[0128] In addition, although there are no particular restrictions regarding the molecular weight of these syndiotactic vinyl aromatic polymers and copolymers, preferably, the weight average molecular weight is greater than 10,000 and less than 1,000,000, and more preferably, greater than 50,000 and less than 800,000.

[0129] The syndiotactic vinyl aromatic polymers and copolymers may also be used in the form of polymer blends with, for instance, vinyl aromatic group polymers with atactic structures, vinyl aromatic group polymers with isotactic structures, and any other polymers that are miscible with the vinyl aromatic polymers. For example, polyphenylene ethers show good miscibility with many of the previous described vinyl aromatic group polymers.

[0130] When a polarizing film is made using a process with predominantly uniaxial stretching, particularly preferred combinations of polymers for optical layers include PEN/coPEN, PET/coPET, PEN/sPS, PET/sPS, PEN/Eastar,<sup>TM</sup> and PET/Eastar,<sup>TM</sup> where “coPEN” refers to a copolymer or blend based upon naphthalene dicarboxylic acid (as described above) and Eastar<sup>TM</sup> is a polyester or copolyester (believed to comprise cyclohexanedimethylene diol units and terephthalate units) commercially available from Eastman Chemical Co. When a polarizing film is to be made by manipulating the process conditions of a biaxial stretching process, particularly preferred combinations of polymers for optical layers include PEN/coPEN, PEN/PET, PEN/PBT, PEN/PETG and PEN/PETcoPBT, where “PBT” refers to polybutylene terephthalate, “PETG” refers to a copolymer of PET employing a second glycol (usually cyclohexanedimethanol), and “PETcoPBT” refers to a copolyester of terephthalic acid or an ester thereof with a mixture of ethylene glycol and 1,4-butanediol.

[0131] Particularly preferred combinations of polymers for optical layers in the case of mirrors or colored films include PEN/PMMA, PET/PMMA, PEN/“Ecdel”, PET/“Ecdel”, PEN/sPS, PET/sPS, PEN/coPET, PEN/PETG, and PEN/a fluoropolymer commercially available from Minnesota Mining and Manufacturing Company (3M), St. Paul, Minn. under the trade designation “THV”, where “PMMA” refers to polymethyl methacrylate, “coPET” refers to a copolymer or blend based upon terephthalic acid (as

described above), and “PETG” refers to a copolymer of PET employing a second glycol (usually cyclohexanedimethanol).

[0132] As described previously, it is sometimes preferred for the multilayer optical films of the current invention to consist of more than two distinguishable polymers. A third or subsequent polymer might be fruitfully employed as an adhesion-promoting layer between the first polymer and the second polymer within an optical stack, as an additional component in a stack for optical purposes, as a protective boundary layer between optical stacks, as a skin layer, as a functional coating, or for any other purpose. As such, the composition of a third or subsequent polymer, if any, is not limited. Preferred multicomponent films include those described in U.S. Pat. No. 6,207,260 filed on Jan. 13, 1998, entitled “Multicomponent Optical Body”, hereby incorporated by reference.

[0133] The reflectance characteristics of multilayer films are determined by several factors, the most important of which for purposes of this discussion are the indices of refraction for each layer of the film stack. In particular, reflectivity depends upon the relationship between the indices of refraction of each material in the x, y, and z directions ( $n_x$ ,  $n_y$ ,  $n_z$ ). Different relationships between the three indices lead to three general categories of materials: isotropic, uniaxially birefringent, and biaxially birefringent. The latter two are important to the optical performance of the present invention.

#### Biaxially Birefringent Materials (Polarizers)

[0134] In a biaxially birefringent material, all three indices are different. Biaxially birefringent materials are important to the film of the present invention. A biaxially birefringent system can be made by uniaxially orienting (stretching along one axis) the multilayer polymeric film, such as along the x direction in FIG. 3. A biaxially birefringent multilayer film can be designed to provide high reflectivity for light with its plane of polarization parallel to one axis, for all angles of incidence, and simultaneously have low reflectivity (high transmissivity) for light with its plane of polarization parallel to the other axis at all angles of incidence. As a result, the biaxially birefringent system acts as a polarizer, reflecting light of one polarization and transmitting light of the other polarization. Stated differently, a polarizing film is one that receives incident light of random polarity (light vibrating in planes at random angles), and allows incident light rays of one polarity (vibrating in one plane) to pass through the film, while reflecting incident light rays of the other polarity (vibrating in a plane perpendicular to the first plane). By controlling the three indices of refraction— $n_x$ ,  $n_y$  and  $n_z$ —the desired polarizing effects can be obtained. If the layers were appropriately designed to reflect light in the near infrared, and the reflective band positioned within the infrared region such that even at grazing angles of incidence the reflectance band does not shift into the visible region of the spectrum, an infrared polarizer can be made that is transparent in the visible region of the spectrum, even at high angles of incidence.

[0135] Alternatively, if some color is acceptable or desirable, the reflective band may be positioned so that even at grazing angles of incidence, the reflectance band does not shift past the colored portion of the visible spectrum, thereby maintaining the same visible color at grazing angles as at



normal angle of incidence. Two crossed sheets of biaxially birefringent film would yield a highly efficient mirror, and the films would perform similar to a single uniaxially birefringent film.

[0136] A novel way of making multilayer polymeric polarizers using biaxial orientation is described U.S. Pat. No. 6,179,948, filed on Jan. 13, 1998 entitled "An Optical Film and Process for Manufacture Thereof," hereby incorporated by reference. In this approach, two polymers capable of permanent birefringence are drawn sequentially such that in the first draw, the conditions are chosen to produce little birefringence in one of the materials, and considerable birefringence in the other. In the second draw, the second material develops considerable birefringence, sufficient to match the final refractive index of the first material in that direction. Often the first material assumes an in-plane biaxial character after the second draw. An example of a system that produces a good polarizer from biaxial orientation is PEN/PET. In that case, the indices of refraction can be adjusted over a range of values. The following set of values demonstrates the principle: for PEN,  $n_{1x}=1.68$ ,  $n_{1y}=1.82$ ,  $n_{1z}=1.49$ ; for PET  $n_{1x}=1.67$ ,  $n_{1y}=1.56$  and  $n_{1z}=1.56$ , all at 632.8 nm. Copolymers of PEN and PET may also be used. For example, a copolymer comprising approximately 10% PEN subunits and 90% PET subunits by weight may replace the PET homopolymer in the construction. Indices for the copolymer under similar processing are about  $n_{1x}=1.67$ ,  $n_{1y}=1.62$ ,  $n_{1z}=1.52$ , at 632.8 nm. There is a good match of refractive indices in the x direction, a large difference (for strong reflection) in the y direction, and a small difference in the z direction. This small z index difference minimizes unwanted color leaks at shallow observation angles. The film formed by biaxial orientation is strong in all planar directions, while uniaxially oriented polarizer is prone to splitting. Depending on the application, either approach has merit.

#### Additional Layers and Features

[0137] In addition to the skin layer described above, which add physical strength to the film and reduce problems during processing, other layers and features of the inventive film may include slip agents, low adhesion backsize materials, conductive coatings, antistatic, antireflective or antifogging coatings or films, barrier layers, flame retardants, UV stabilizers or protective layers, abrasion resistant materials, optical coatings, or substrates to improve the mechanical integrity or strength of the film. Non-continuous layers may also be incorporated into the film to prevent tampering.

[0138] It may be desirable to add to one or more of the layers, one or more inorganic or organic adjuvants such as an antioxidant, extrusion aid, heat stabilizer, ultraviolet ray absorber, nucleator, surface projection forming agent, and the like in normal quantities so long as the addition does not substantially interfere with the performance of the present invention.

[0139] Lamination of two or more sheets together may be advantageous, to improve reflectivity or to broaden the bandwidth, or to form a mirror from two polarizers. Amorphous copolyesters are useful as laminating materials. Exemplary amorphous copolyesters include those commercially available from Goodyear Tire and Rubber Co. of Akron, Ohio, under the trade designations "VITEL Brand 3000" and "VITEL Brand 3300". The choice of laminating

material is broad, with adhesion to the sheets 10, optical clarity and exclusion of air being the primary guiding principles.

[0140] The invention contemplates the use of the described adhesive to bond any of the above-described or other outgassing substrate materials to any of the above-described or other substrate materials, including low moisture vapor transfer materials, preferably to create an optically clear and environmentally stable bond within an optically transmissive multilayer article. Below are described, as illustrated in FIGS. 1 and 2, exemplary embodiments of multi-layer, optical products prepared according to the present invention. These embodiments are illustrative of the larger invention described herein of using the described adhesive for any application, but especially where optical clarity is desired.

[0141] FIG. 1 illustrates an embodiment of an optical element according to the invention, comprising a low moisture vapor transmissive film bonded using the adhesive to an outgassing layer. Referring to the drawing, optical element 2 includes outgassing layer 4 bonded to low moisture vapor transmissive film 6 using optically transmissive adhesive 8 comprising as described herein. The outgassing layer 4 can be any outgassing substrate, as described above or otherwise, such as a rigid polycarbonate or polyacrylate, and the low moisture vapor transmissive film can be any such film as described above or otherwise. Outgassing layer 4 may be 4.4 millimeter thick polycarbonate or 3.0 mm thick acrylic, and low moisture vapor transmissive film 6 can be an AR Film. Alternatively, low moisture vapor transmissive film 6 may be an IR film (i.e., an infrared reflecting film such as solar reflecting film), such as a microlayer film having selective transmissivity such as an optically clear but infrared reflecting film as described in U.S. Pat. No. 5,360,659, the entire disclosure of which is incorporated herein by reference.

[0142] FIG. 2 illustrates another embodiment of a polarizing optical element according to the invention. FIG. 2 shows polarizing optical element 40 that includes PET layer 42, adhesive layers 44, 46 and 52, polarizing layer 48, PC retarder layer 50, and LCD glass layer 54. At least one of, and optionally all of adhesive layers 44, 46, and 52 is the adhesive composition as described herein, or may be a different pressure sensitive or structural adhesive.

[0143] The invention further relates to methods of using the adhesive compositions, for example by dispensing the adhesive onto a substrate layer, and optionally contacting the adhesive with another material, such as a different layer of a multi-layer article. Exemplary steps of inventive methods may include placement of the adhesive onto a substrate such as a release liner or optical film; and optional drying of an optional solvent in the adhesive or polymerization of (meth)acrylate components; or other steps, techniques, or methods known to be used in the preparation of multi-layer articles using an adhesive.

[0144] Adhesives as described herein can, in an important embodiment of the invention, be used in methods typically understood to be useful for preparing optically clear components and optical elements. Exemplary methods of preparing optical elements include, among others, those identified in U.S. Pat. No. 5,897,727; 5,858,624; and 6,180,200, each of which is incorporated herein by reference. The

adhesive composition is typically in the form of a liquid that can be coated or applied by methods generally useful with liquid pressure sensitive adhesives, e.g., coated onto a release liner. If solvent is used, solvent can later be removed from the coated adhesive. An example of a useful next step would be to transfer the coated adhesive onto a substrate, typically with lamination.

[0145] Exemplary release liners are well known and commercially available, and include paper and film liners coated with release agents such as silicones, fluorocarbons, etc. such as the T-30 liner available from CP Film, Martinsville, Va.

[0146] In some embodiments of the invention, the adhesive-bearing substrate can then be contacted with another material for bonding. This step can be accomplished by lamination or otherwise.

### EXAMPLES

[0147] These examples are merely for illustrative purposes only and are not meant to be limiting on the scope of the appended claims. All parts, percentages, ratios, etc. in the examples and the rest of the specification are by weight unless indicated otherwise. Unless otherwise noted, materials were obtained from Aldrich Chemicals, Milwaukee, Wis.

Table of Abbreviations

Trade Designation or Other Abbreviation	Description
AA	Acrylic Acid
BA	n-butyl acrylate
Bisamide	1,1'-(1,3-phenylene dicarbonyl)-bis-(2-methylaziridine)
Crosslinker	
BMA	n-butyl methacrylate
DMAEMA	(N,N-dimethylamino)ethyl methacrylate
Glass	75 millimeter × 50 millimeter × 1 millimeter Corning No. 2947 MicroSlides commercially available from Corning
Microscope Slide	Glass Works; Corning, NY
IOA	Iso-octyl acrylate
MA	Methyl acrylate
MMA	Methyl methacrylate
NNDMA	N,N-dimethyl acrylamide
HEA	Hydroxy ethyl acrylate
BOSCODUR 16 crosslinker	An isocyanate crosslinker commercially available from Bostik Co.
PC plate	4.4 millimeter thick LEXAN polycarbonate plate commercially available from General Electric, Schenectady, NY
PMMA plate	Optix acrylic plate of 3.0 millimeter thick polymethyl methacrylate commercially available from Plaskolite, Inc, Columbus, OH
SRF	Solar Reflecting Film, multilayer IR reflecting film, which comprises alternating layers of Polyethylene terephthalate (A-layer) and co-Polymethylmethacrylate (B-layer). These layers are arranged in 6 layer optical repeat units 7A, 1B, 1A, 7B, 1A, 1B with 96 such optical repeat units for a total of 576 layers. This film reflects light in the infrared wavelength region between about 900–1300 nm while allowing light transmission in the visible between 380–770 nm.
VAZO-67 Initiator	2,2'-azobis-(2-methylbutyronitrile), an initiator commercially available from E.I. duPont de Nemours & Co.; Wilmington, DE.

#### Preparation of Polymer Additive 1

[0148] In a glass reaction vessel were placed VAZO-67 Initiator (0.3 g), MMA (70 g), BMA (25 g), DMAEMA (5 g), and ethyl acetate (150 g). The resulting solution was degassed with nitrogen for 15 minutes, and the vessel was sealed and spun in a 65° C. water bath for 24 hours to yield a viscous solution (40 wt % solids). The polymer thus obtained had a weight average molecular weight of 210,000 and the calculated T<sub>g</sub> shown in Table 1.

#### Preparation of Polymer Additive 2

[0149] The same procedure and conditions as in the Preparation of Polymer Additive 1 were used except VAZO-67 Initiator (1 g) and was used and the reaction was carried out at 60° C. with 30 wt % solids. The polymer thus obtained had a weight average molecular weight of 115,000 and the calculated T<sub>g</sub> shown in Table 1.

#### Preparation of Polymer Additive 3

[0150] The same procedure and conditions as in the Preparation of Polymer Additive 2 were used except additionally isooctyl thioglycolate (1 g) was added. The polymer thus obtained had a weight average molecular weight of 27,400 and the calculated T<sub>g</sub> shown in Table 1.

#### Preparation of Polymer Additive 4

[0151] The same procedure and conditions as in the Preparation of Polymer Additive 2 were used except monomers were IOA (5 g), MMA (90 g), and DMAEMA (5 g). The polymer thus obtained had a weight average molecular weight of 104,000 and the calculated T<sub>g</sub> shown in Table 1.

#### Preparation of Polymer Additive 5

[0152] The same procedure and conditions as in the Preparation of Polymer Additive 2 were used except monomers were IOA (25 g), MMA (70 g), and DMAEMA (5 g). The polymer thus obtained had a weight average molecular weight of 104,000 and the calculated T<sub>g</sub> shown in Table 1.

#### Preparation of Polymer Additive 6

[0153] The same procedure and conditions as in the Preparation of Polymer Additive 2 were used except monomers were IOA (45 g), MMA (50 g), and DMAEMA (5 g). The polymer thus obtained had a weight average molecular weight of 107,000 and the calculated T<sub>g</sub> shown in Table 1.

#### Preparation of Polymer Additive 7

[0154] The same procedure and conditions as in the Preparation of Polymer Additive 2 were used except monomers were IOA (95 g) and DMAEMA (5 g). The polymer thus obtained had a weight average molecular weight of 130,000 and the calculated T<sub>g</sub> shown in Table 1.

#### Preparation of Polymer Additive 8

[0155] The same procedure and conditions as in the Preparation of Polymer Additive 2 were used except monomers were MMA (80 g) and NNDMA (20 g). The polymer thus obtained had a weight average molecular weight of 85,600 and the calculated T<sub>g</sub> shown in Table 1.

#### Preparation of Polymer Additive 9

[0156] The same procedure and conditions as in the Preparation of Polymer Additive 2 were used except monomers were MMA (85 g) and NNDMA (15 g). The polymer thus obtained had a weight average molecular weight of 74,700 and the calculated T<sub>g</sub> shown in Table 1.

## Preparation of Polymer Additive 10

[0157] The same procedure and conditions as in the Preparation of Polymer Additive 2 were used except monomers were MMA (90 g) and NNDMA (10 g). The polymer thus obtained had a weight average molecular weight of 85,700 and the calculated  $T_g$  shown in Table 1.

## Preparation of Polymer Additive 11

[0158] In a glass reaction vessel were placed VAZO-67 Initiator (0.3 g), MMA (42 g), BMA (15 g), AA (3 g), and ethyl acetate (140 g). The resulting solution was degassed with nitrogen for 15 minutes, and the vessel was sealed and spun in a 58° C. water bath for 24 hours to yield a viscous solution (30 wt % solids). The polymer thus obtained had a weight average molecular weight of 164,000 and the calculated  $T_g$  shown in Table 1.

TABLE 1

Sample	Composition	$M_{w,SEC}$	$T_{g,Cal}$ (° C.)
Polymer Additive 1	MMA/BMA/DMAEMA (70/20/5)	210,000	76
Polymer Additive 2	MMA/BMA/DMAEMA (70/20/5)	115,000	76
Polymer Additive 3	MMA/BMA/DMAEMA (70/20/5)	27,400	76
Polymer Additive 4	MMA/IOA/DMAEMA (90/5/5)	104,000	87
Polymer Additive 5	MMA/IOA/DMAEMA (70/25/5)	104,000	43
Polymer Additive 6	MMA/IOA/DMAEMA (45/50/5)	107,000	8
Polymer Additive 7	IOA/DMAEMA (95/5)	130,000	-52
Polymer Additive 8	MMA/NNDMA (80/20)	85,600	101
Preparation Additive 9	MMA/NNDMA (85/15)	74,700	102
Polymer Additive 10	MMA/NNDMA (90/10)	85,700	103
Polymer Additive 11	MMA/BMA/AA (70/25/5)	164,000	79

$M_{w,SEC}$  = Weight average molecular weight as measured by size exclusion chromatography (SEC). SEC measurement was carried out using a Waters 712 WISP autosampler, 1515 HPLC pump, 2410 differential detector, and the following Waters columns: Styragel HR 5E and Styragel HR 1. All samples were run in THF at 35° C. with a flow rate of 1.0 mL/min. Linear polystyrene standards were used for calibration.

$T_{g,Cal}$  = Calculated  $T_g$  based on the Fox equation, assuming  $T_{g,MMA}$  = 378° K,  $T_{g,BMA}$  = 293° K,  $T_{g,DMAEMA}$  = 298° K, and  $T_{g,NNDMA}$  = 362° K, and  $T_{g,AA}$  = 378° K.

## Preparation of PSA 1

[0159] In a glass reaction vessel were placed VAZO-67 Initiator (0.15 g), IOA (93 g), AA (7 g), and ethyl acetate (186 g). The resulting solution was degassed with nitrogen for 30 minutes, and the vessel was sealed and spun in a 60° C. water bath for 24 hours to yield a viscous solution (35 wt % solids). The viscous solution was further diluted with toluene to 25 wt % solids. The polymer thus obtained had a weight average molecular weight of 491,000.

## Preparation of PSA 2

[0160] The same procedure and conditions as in the Preparation of PSA 1 were used except monomers were IOA (57.5 g), MA (35 g), and AA (7.5 g). The polymer thus obtained had a weight average molecular weight of 557,000.

## Preparation of PSA 3

[0161] In a glass reaction vessel were placed VAZO-67 Initiator (0.12 g), BA (49.8 g), NNDMA (9.0 g), HEA (1.2

g) and ethyl acetate (140 g). The resulting solution was degassed with nitrogen for 30 minutes, and the vessel was sealed and spun in a 58° C. water bath for 24 hours to yield a viscous solution (30 wt % solids). The polymer thus obtained had a weight average molecular weight of 694,300.

TABLE 2

Sample	Composition	$M_{w,SEC}$
PSA 1	IOA/AA (93/7)	491,000
PSA 2	IOA/MA/AA (57.5/35/7.5)	557,000
PSA 3	BA/NNDMA/HEA (83/15/2)	694,300

## Example 1

[0162] An adhesive film was prepared by adding 15 parts of solids Polymer Additive 1 to 85 parts of solids PSA 1, and further adding 0.10 part by solids of bisamide as a crosslinking agent, coating the mixture onto a SRF film having a thickness of 50  $\mu$ m so that the adhesive layer had a thickness of 25  $\mu$ m. After heat drying in a 70° C. oven for 10 minutes, the adhesive film was covered with a silicone-coated release liner. Samples of the coated film were then laminated to PMMA and PC plates. Additionally a sample of the mixture of PSA 1, Polymer Additive 1, and bisamide crosslinker was coated onto a silicone-coated release liner, heat dried in a 70° C. oven for 10 minutes to give an adhesive layer thickness of 25  $\mu$ m. This adhesive film was laminated to a Glass Microscope Slide, the release liner was removed and the optical transmission and haze were measured using a TCS Plus Spectrophotometer model 8870 commercially available from BYK Gardner, Inc.; Silver Springs, Md. according to the ASTM Test Method D 1003-95 ("Standard Test for Haze and Luminous Transmittance of Transparent Plastic"). The Luminous Transmittance was 92.8% and the Haze was 0.7%.

## Example 2

[0163] Samples were prepared in the same manner as in Example 1, except 0.05 part of bisamide as a crosslinking agent was added.

## Example 3

[0164] Samples were prepared in the same manner as in Example 1, except 15 parts of Polymer Additive 2 were added to 85 parts of PSA 1.

## Example 4

[0165] Samples were prepared in the same manner as in Example 1, except 15 parts of Polymer Additive 4 were added to 85 parts of PSA 2.

## Example 5

[0166] Samples were prepared in the same manner as in Example 1, except 15 parts of Polymer Additive 5 were added to 85 parts of PSA 2.

## Example 6

[0167] Samples were prepared in the same manner as in Example 1, except 15 parts of Polymer Additive 8 were added to 85 parts of PSA 2.

## Example 7

[0168] Samples were prepared in the same manner as in Example 1, except 15 parts of Polymer Additive 9 were added to 85 parts of PSA 2.

## Example 8

[0169] Samples were prepared in the same manner as in Example 1, except 15 parts of Polymer Additive 10 were added to 85 parts of PSA 2.

## Example 9

[0170] Samples were prepared in the same manner as in Example 1, except 15 parts of Polymer Additive 11 was added to 85 parts of PSA 3, and 0.4 parts of a crosslinker Boscodur 16 were used instead of Bisamide crosslinker.

## Comparative Example 1

[0171] Samples were prepared in the same manner as in Example 1, except no bisamide as a crosslinking agent was added.

## Comparative Example 2

[0172] Samples were prepared in the same manner as in Example 1, except 15 parts of Polymer Additive 3 were added to 85 parts of PSA 1.

## Comparative Example 3

[0173] Samples were prepared in the same manner as in Example 1, except 15 parts of Polymer Additive 6 were added to 85 parts of PSA 2.

## Comparative Example 4

[0174] Samples were prepared in the same manner as in Example 1, except 15 parts of Polymer Additive 7 were added to 85 parts of PSA 2.

## Testing Example 1

[0175] Several different accelerated aging protocols have been used for testing the aging properties of laminate structures. One protocol is carried out by placing the laminate in a 90° C. oven for a week and is called the "90° C.". Another is carried out by placing the laminate in an oven with controlled humidity at 80° C. and 90% relative humidity for a week and is called the "80° C., 90% RH". The results of all testing protocols are determined by visual observation to determine whether the optical properties of the sample are maintained. The data are reported as either "Pass" if the sample retains its optical clarity, "Bubbles" if bubbles (0.2 mm -5 mm in size) are present, and "Blisters" for the presence of large bubbles (>5 mm in size) upon post aging examination. The test results are summarized in Table 4 below.

TABLE 4

Sample	PMMA Laminate		PC Laminate	
	90° C.	80° C., 90% RH	90° C.	80° C., 90% RH
Example 1	Pass	Pass	Pass	Pass
Example 2	Pass	Pass	Pass	Pass
Comp.	Blisters	Blisters	Blisters	Blisters
Example 1				
Example 3	Pass	Pass	Pass	Pass
Comp.	Blisters	Blisters	Blisters	Blisters
Example 2				
Example 4	Pass	Pass	Pass	Pass
Example 5	Pass	Pass	Pass	Pass
Comp.	Bubbles	Bubbles	Bubbles	Bubbles
Example 3				

TABLE 3

Sample	Additive	Additive M <sub>w,SEC</sub>	Additive T <sub>g,Cal</sub> (° C.)	PSA	Crosslinker Amount
Example 1	MMA/BMA/DMAEMA (70/25/5)	210,000	76	IOA/AA (93/7)	0.10%
Example 2	MMA/BMA/DMAEMA (70/25/5)	210,000	76	IOA/AA (93/7)	0.05%
Example 3	MMA/BMA/DMAEMA (70/25/5)	115,000	76	IOA/AA (93/7)	0.10%
Example 4	MMA/IOA/DMAEMA (90/5/5)	104,000	87	IOA/MA/AA (57.5/35/7.5)	0.10%
Example 5	MMA/IOA/DMAEMA (70/25/5)	104,000	43	IOA/MA/AA (57.5/35/7.5)	0.10%
Example 6	MMA/NNDMA (80/20)	85,600	101	IOA/MA/AA (57.5/35/7.5)	0.10%
Example 7	MMA/NNDMA (85/15)	74,700	102	IOA/MA/AA (57.5/35/7.5)	0.10%
Example 8	MMA/NNDMA (90/10)	85,700	103	IOA/MA/AA (57.5/35/7.5)	0.10%
Example 9	MA/BMA/AA (70/25/5)	164,000	79	BA/NNDMA/ HEA (83/15/2)	0.40%
Comp.	MMA/BMA/DMAEMA (70/25/5)	210,000	76	IOA/AA (93/7)	0.00%
Example 1	MMA/BMA/DMAEMA (70/25/5)	27,400	76	IOA/AA (93/7)	0.10%
Comp.	MMA/IOA/DMAEMA	107,000	8	IOA/MA/AA (57.5/35/7.5)	0.10%
Example 3	(45/50/5)				
Comp.	IOA/DMAEMA	130,000	-52	IOA/MA/AA (57.5/35/7.5)	0.10%
Example 4	(95/5)				

TABLE 4-continued

Sample	PMMA Laminate		PC Laminate	
	90° C.	80° C., 90% RH	90° C.	80° C., 90% RH
Comp.	Blisters	Blisters	Blisters	Blisters
Example 4				
Example 6	Pass	Pass	Pass	Pass
Example 7	Pass	Pass	Pass	Pass
Example 8	Pass	Pass	Pass	Pass
Example 9	Pass	Pass	NT	NT

NT = not tested

[0176] Other modifications and variations of the present invention are possible in light of the above teachings. It is to be understood, however, that changes may be made in the particular embodiments described above which are within the full intended scope of the invention as defined in the appended claims.

What is claimed is:

1. An optical article comprising:

a rigid substrate;

a reflective polarizer; and

an adhesive composition disposed between the substrate and the polarizer,

wherein the adhesive composition comprises:

a majority of a pressure sensitive adhesive component comprising at least one polymer with an acid or base functionality;

a high Tg polymer with a weight average molecular weight greater than 100,000, a Tg greater than about 20° C., and comprising an acid or base functionality; and

a crosslinker;

wherein the functionality of the pressure sensitive adhesive component and the functionality of the high Tg polymer form an acid-base interaction when mixed; and

wherein the adhesive composition is optically clear.

2. The optical article of claim 1 wherein after aging at 80° C. and 90% relative humidity for 500 hours, a bond between the rigid substrate and the polarizer formed by the adhesive composition does not delaminate or bubble, and the optical article remains optically clear.

3. The optical article of claim 1 wherein after aging at 80° C. and 90% relative humidity for 500 hours, the adhesive composition has a luminous transmission greater than 90%, and a haze less than 2%.

4. The optical article of claim 1 wherein the high Tg polymer has a Tg greater than about 50° C.

5. The optical article of claim 1 wherein the high Tg polymer comprises a monomer selected from the group consisting of vinyl esters, (meth)acrylamide, styrenes, (meth)acrylonitriles, substituted styrenes, vinyl halides, vinyl propionate, (meth)acrylates, and mixtures thereof.

6. The optical article of claim 1 wherein the high Tg polymer is a basic copolymer.

7. The optical article of claim 1 wherein the pressure sensitive adhesive component comprises a copolymer with an weight average molecular weight less than 800,000.

8. The optical article of claim 1 wherein the pressure sensitive adhesive component is formed from free-radically polymerizable monomers selected from the group consisting of (meth)acrylates, vinyl monomers, and mixtures thereof.

9. The optical article of claim 1 wherein the crosslinker is selected from the group consisting of multifunctional aziridine, peroxides, benzophenones, triazines, monoethylenically unsaturated mono-, di-, and trialkoxy silane compounds, diacrylates, triacrylates, and tetraacrylates, isocyanates, epoxies, and mixtures thereof.

10. The optical article of claim 1 wherein the reflective polarizer comprises a dielectric multilayer film.

11. The optical article of claim 10 wherein the dielectric multilayer film comprises alternating layers of a material having a high index of refraction and a material having a low index of refraction.

12. The optical article of claim 10 further comprising at least one of: an adhesion promoting layer, a protective boundary layer, a skin layer and a functional coating.

13. The optical article of claim 10 wherein the dielectric multilayer film comprises at least three diverse substantially transparent polymeric materials.

14. The optical article of claim 10 wherein the dielectric multilayer film comprises alternating layers of PEN and coPEN.

15. The optical article of claim 10 wherein the dielectric multilayer film comprises alternating layers of PET and coPET.

16. The optical article of claim 1 wherein the rigid substrate is more than about 1 mm thick.

17. The optical article of claim 1 wherein the rigid substrate is more than about 3 mm thick.

18. The optical article of claim 1 wherein the rigid substrate comprises a low moisture vapor transfer material.

19. The optical article of claim 1 wherein the rigid substrate comprises an outgassing material.

20. The optical article of claim 1 wherein the rigid substrate comprises a material selected from the group consisting of polycarbonate, polyacrylate, and polyester.

\* \* \* \* \*