

PRESSURE-SENSITIVE ADHESIVE SHEET, PRODUCTION METHOD THEREFOR, AND DISPLAY DEVICE

TECHNICAL FIELD

5 [0001] The present invention relates to a pressure sensitive adhesive sheet and a production method therefor. The present invention further relates to an image display device using the pressure sensitive adhesive sheet.

BACKGROUND ART

10 [0002] Liquid crystal displays and organic light emitting diode (OLED) displays are widely used as various kinds of image display devices of mobile phones, car navigation devices, personal computer monitors, televisions and so on. On a viewing-side outermost surface of an image display panel, a front transparent plate (also referred to as a “cover window” etc.) such as a transparent resin plate or a glass plate may be provided, for the
15 purpose of, for example, preventing damage to the image display panel due to impact from the outer surface. In addition, display devices provided with a touch panel on front surface of an image display panel become common recently.

[0003] A colored layer (decorative printed layer) may be formed on the peripheral edge of a front transparent member for the purpose of decoration and light shielding. When a
20 pressure sensitive adhesive is bonded to a transparent member having a decorative printed layer, bubbles are easily generated on the periphery of a printing level difference portion. Accordingly, a pressure sensitive adhesive sheet having a large thickness is used to impart a level difference followability, so that a failure such as ingress of bubbles can be suppressed.

25 [0004] For impartation of level difference followability, it has been proposed to use a pressure sensitive adhesive sheet composed of a photocurable pressure sensitive adhesive composition for bonding a front transparent member. For example, Patent Document 1 shows an example in which a polyfunctional monomer and a photopolymerization initiator are added to a polymer solution prepared through solution polymerization to obtain a
30 composition, the composition is applied to a substrate, and the solvent is removed by heating to prepare a photocurable pressure sensitive adhesive sheet. Patent Document 2 shows an example in which a solvent-free composition containing a low molecular weight polymer, a monofunctional monomer, a polyfunctional monomer, and a

photopolymerization initiator is applied to a substrate and photocured to prepare a pressure sensitive adhesive sheet. A part of the monomer components in the composition is left unreacted during photocuring to form a pressure sensitive adhesive sheet having high fluidity and excellent level difference followability.

5 **[0005]** The photocurable pressure sensitive adhesive sheet contains a photopolymerizable monomer or oligomer in an unreacted state, and thus has high fluidity and is excellent in level difference followability. After being bonded to an adherend, the pressure sensitive adhesive sheet is irradiated with an active ray and thus is photocured, the fluidity of the pressure sensitive adhesive is reduced, so that the adhesion retaining
10 force is enhanced.

PRIOR ART DOCUMENTS

PATENT DOCUMENT

[0006] Patent Document 1: JP 2014-227453 A
15 Patent Document 2: WO2013/161666

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0007] In an image display device equipped with a front transparent member such as a
20 cover window with larger in size than a display panel, the front transparent member is bonded to a housing with an adhesive tape or the like at a region outside the outer peripheral edge of the display panel. That is, the front transparent member is fixed not only to a display panel surface with an interlayer filling pressure sensitive adhesive sheet but also to a housing with a pressure sensitive adhesive tape or the like.

25 **[0008]** In recent years, narrowing of the frames of display devices or popularization of bezel-less display devices has progressed mainly in mobile devices such as smartphones. Due to popularization of narrow frame display devices and bezel-less display devices, an image display device in which the size of a display panel 10 is comparable to or greater than the size of a front transparent member 7 has been developed. In such a
30 configuration, a housing 9 and the front transparent member 7 cannot be fixed to each other with an adhesive tape or the like, and it is necessary to fix the front transparent member 7 with a pressure sensitive adhesive sheet 5 alone (see FIG. 2). Accordingly, the pressure sensitive adhesive sheet is required to have higher adhesive strength, and also

required to prevent occurrence of peeling by impacts of falling and the like.

[0009] Further, in narrow frame display devices and bezel-less display devices, high dimensional stability is required in assembly of an image display device and conveyance of a product-in-process. In a photocurable pressure sensitive adhesive sheets described in Patent Document 1 and Patent Document 2, the pressure sensitive adhesive is made highly flexible for imparting a level difference followability, and thus, in a state before photocuring, the pressure sensitive adhesive sheet is easily deformed when an external force is applied in conveyance or processing, so that positional displacement may occur between bonded members. Further, since photocuring is to be performed after bonding to an adherend, the production process of an image display device tends to be complicated.

[0010] In view of the above, an object of the present invention is to provide a pressure sensitive adhesive sheet that is not to be photocured after bonding to an adherend, can achieve both level difference followability and dimensional stability, and has adhesion durability and impact resistance.

MEANS FOR SOLVING THE PROBLEMS

[0011] An embodiment of the present invention is a double-sided pressure sensitive adhesive sheet composed of a pressure sensitive adhesive that contains a base polymer having a crosslinked structure and is formed into a sheet. The pressure sensitive adhesive sheet preferably has a shear storage elastic modulus $G'_{25^{\circ}\text{C}}$ of 0.16 MPa or more at a temperature of 25°C, and a loss tangent $\tan \delta_{70^{\circ}\text{C}}$ of 0.25 or more at a temperature of 70°C. The pressure sensitive adhesive sheet preferably has a glass transition temperature of -3°C or lower.

[0012] The pressure sensitive adhesive sheet preferably has a gel fraction of 30 to 80%. The pressure sensitive adhesive constituting the pressure sensitive adhesive sheet preferably has a polymerization ratio of 95% or more. The sol component in the pressure sensitive adhesive has a weight average molecular weight of, for example, 150,000 to 400,000. The pressure sensitive adhesive sheet preferably has a haze of 1% or less.

[0013] The base polymer contained in the pressure sensitive adhesive sheet includes, for example, a polymer in which an acryl-based polymer chain is crosslinked by a urethane-based segment. In order to satisfy the above-described characteristics, the content of the urethane-based segment based on 100 parts by weight of the acryl-based polymer chain is preferably 0.3 to 10 parts by weight. The urethane-based segment has a weight average

molecular weight of, for example, 5,000 to 30,000.

[0014] The base polymer in the pressure sensitive adhesive is, for example, an acryl-based polymer having a crosslinked structure, and may be an acryl-based polymer in which a crosslinking by a polyfunctional (meth)acrylate or urethane (meth)acrylate is introduced into an acryl-based polymer chain. In the acryl-based polymer chain, the amount of (meth)acrylic acid alkyl ester is preferably 50% by weight or more of the amount of the total constituent monomer component. In the acryl-based polymer chain, the total of the amount of hydroxy group-containing monomer and the amount of nitrogen-containing monomer may be 15 to 45% by weight of the amount of the total constituent monomer component.

[0015] The base polymer may include a polymer in which a crosslinking by a urethane-based segment is introduced into an acryl-based polymer chain. For example, the acryl-based monomer included in the acryl-based polymer chain and a polyfunctional urethane (meth)acrylate having a (meth)acryloyl group at least two terminals are copolymerized to obtain an acryl-based polymer in which a crosslinking by a urethane-based segment is introduced into the acryl-based polymer chain.

[0016] The urethane (meth)acrylate is preferably urethane di(meth)acrylate having a (meth)acryloyl group at both terminals. The urethane (meth)acrylate preferably has a weight average molecular weight of 5,000 to 30,000. The urethane (meth)acrylate preferably has a glass transition temperature of 0°C or lower. The urethane (meth)acrylate may include a polyester urethane (meth)acrylate.

[0017] The pressure sensitive adhesive sheet including a base polymer in which an acryl-based polymer chain is crosslinked by a urethane-based segment is obtained by, for example, applying, in a layer form, a composition including an acryl-based monomer and/or a partially polymerized product thereof and a urethane (meth)acrylate to a substrate, and then irradiating the composition with an active ray to photocure the composition. The pressure sensitive adhesive composition preferably has a content of the urethane (meth)acrylate of 0.3 to 10 parts by weight based on 100 parts by weight of the total of the acryl-based monomer and the partially polymerized product thereof.

[0018] The pressure sensitive adhesive sheet of the present invention is used, for example, for bonding a transparent member in an image display device in which the transparent member is disposed on the viewing-side surface. For example, an image display device is formed by fixing a front transparent member to the viewing-side surface

of an image display panel via the pressure sensitive adhesive sheet. A substrate-equipped double-sided pressure sensitive adhesive sheet can also be formed by disposing a pressure sensitive adhesive sheet on a transparent film substrate.

5 EFFECTS OF THE INVENTION

[0019] The pressure sensitive adhesive sheet of the present invention has excellent level difference followability and excellent impact resistance due to a large shear storage elastic modulus at normal temperature, and has excellent bonding reliability and processability due to a large loss tangent at high temperature. An image display device in which a
10 cover window or the like is bonded to the viewing-side surface using the pressure sensitive adhesive sheet of the present invention has excellent bonding reliability, and can also cope with a narrower frame and a bezel-less frame.

BRIEF DESCRIPTION OF THE DRAWINGS

15 [0020] FIG. 1 is a sectional view showing an example of a configuration of a release film-equipped pressure sensitive adhesive sheet (substrate-less double-sided pressure sensitive adhesive sheet).

FIG. 2 is a sectional view showing an example of a configuration of an image display device.

20 FIG. 3 is a sectional view showing an example of a stacking configuration of a pressure sensitive adhesive sheet-equipped optical film.

FIG. 4 is a sectional view showing an example of a stacking configuration of a pressure sensitive adhesive sheet-equipped optical film.

25 FIG. 5 is a sectional view showing an example of a configuration of a release film-equipped pressure sensitive adhesive sheet (substrate-equipped double-sided pressure sensitive adhesive sheet).

FIG. 6 is a sectional view showing an example of a configuration of an image display device.

FIG. 7A is a photograph showing a state of an interlayer adhesiveness test.

30 FIG. 7B is a photograph for observing a sample in which streaky bubbles are generated in the interlayer adhesiveness test.

FIG. 8 is a schematic view showing an arrangement of a sample in an impact resistance test.

MODE FOR CARRYING OUT THE INVENTION

[0021] FIG. 1 shows a pressure sensitive adhesive sheet with a release film in which release films 21 and 22 are temporarily attached, respectively, to both surfaces of a pressure sensitive adhesive sheet 5. FIG. 2 is a sectional view showing an example of a configuration of an image display device in which a front transparent plate 7 is fixed using the pressure sensitive adhesive sheet.

[0022] [Properties of Pressure Sensitive Adhesive Sheet]

The pressure sensitive adhesive sheet 5 is a substrate-less double-sided pressure sensitive adhesive sheet in which a pressure sensitive adhesive is formed in a sheet shape. The pressure sensitive adhesive includes a base polymer having a crosslinked structure. The pressure sensitive adhesive sheet preferably has a high transparency. The total light transmittance of the pressure sensitive adhesive sheet is preferably 85% or more, more preferably 90% or more. The haze of the pressure sensitive adhesive sheet is preferably 1% or less.

[0023] From the viewpoint of enhancing adhesion retaining force in bonding of the pressure sensitive adhesive sheet to an adherend and securing processing dimensional stability, the shear storage elastic modulus at 25°C ($G'_{25^{\circ}\text{C}}$) of the pressure sensitive adhesive sheet is preferably 0.16 MPa or more, more preferably 0.18 MPa or more, further preferably 0.20 MPa or more, especially preferably 0.21 MPa or more.

[0024] On the other hand, from the viewpoint of imparting moderate viscosity to secure wettability, and imparting level difference followability and a cushion property against impacts from falling etc., the storage elastic modulus $G'_{25^{\circ}\text{C}}$ of the pressure sensitive adhesive sheet is preferably 0.5 MPa or less, more preferably 0.4 MPa or less, further preferably 0.3 MPa or less, especially preferably 0.28 MPa or less.

[0025] From the viewpoint of imparting level difference followability to the pressure sensitive adhesive sheet, the loss tangent at 70°C ($\tan \delta_{70^{\circ}\text{C}}$) of the pressure sensitive adhesive sheet is preferably 0.25 or more, more preferably 0.30 or more, further preferably 0.35 or more. The loss tangent $\tan \delta_{70^{\circ}\text{C}}$ may be 0.40 or more, 0.45 or more, 0.50 or more, or 0.55 or more. From the viewpoint of adhesion retaining force, the loss tangent $\tan \delta_{70^{\circ}\text{C}}$ is preferably 1.0 or less, more preferably 0.9 or less, further preferably 0.85 or less. The loss tangent $\tan \delta_{70^{\circ}\text{C}}$ may be 0.80 or less, 0.75 or less, or 0.70 or less.

[0026] The $\tan \delta$ peak-top value of the pressure sensitive adhesive sheet is preferably 1.5

or more, more preferably 1.6 or more, further preferably 1.7 or more. A pressure sensitive adhesive having a large $\tan \delta$ peak-top value tends to have a high viscous behavior, leading to excellent impact resistance. The upper limit of the $\tan \delta$ peak-top value of the pressure sensitive adhesive sheet is not particularly limited, and is typically 3.0 or less.

5 From the viewpoint of adhesion retaining force, the $\tan \delta$ peak-top value is preferably 2.7 or less, more preferably 2.5 or less.

[0027] The glass transition temperature of the pressure sensitive adhesive sheet is preferably -3°C or lower, more preferably -4°C or lower. The glass transition temperature of the pressure sensitive adhesive sheet is preferably -20°C or higher, more preferably -15°C or higher, further preferably -13°C or higher. When the glass transition temperature is within the above-described range, the pressure sensitive adhesive has an appropriate viscosity even in a low temperature region, and peeling of the adherend due to impacts from falling etc. tends to be suppressed.

[0028] The shear storage elastic modulus G' , loss tangent $\tan \delta$ and glass transition temperature of the pressure sensitive adhesive sheet are determined by viscoelasticity measurement at 1 Hz. The $\tan \delta$ is a ratio G''/G' between the storage elastic modulus G' and the loss elastic modulus G'' , and the glass transition temperature is a temperature at which $\tan \delta$ is maximum (peak-top temperature). The storage elastic modulus G' corresponds to a part stored as elastic energy in deformation of a material, and is an index indicating a degree of hardness. As the storage elastic modulus of the pressure sensitive adhesive sheet increases, the adhesion retaining force tends to become higher, leading to suppression of peeling caused by strain. The loss elastic modulus G'' corresponds to a loss energy part scattered and lost by internal friction etc. in deformation of a material, and indicates the degree of viscosity. As the loss tangent ($\tan \delta$) increases, the pressure sensitive adhesive sheet tends to become more viscous, and exhibit a deformation behavior closer to that of liquid, leading to a decrease in rebound elastic energy.

[0029] From the viewpoint of imparting moderate flexibility for imparting a level difference followability while securing processing dimensional stability by setting the storage elastic modulus $G'_{25^{\circ}\text{C}}$ to 0.16 MPa or more, the gel fraction of the pressure sensitive adhesive sheet is preferably 30 to 80%, more preferably 35 to 70%. The gel fraction may be 40% or more, 45% or more and may be 65% or less, or 60% or less.

[0030] The gel fraction of the pressure sensitive adhesive sheet can be determined as a content of components insoluble in a solvent such as ethyl acetate, and specifically, the gel

fraction is determined as a weight fraction (unit: % by weight) of insoluble components after immersion of pressure sensitive adhesive that constitutes the pressure sensitive adhesive sheet in ethyl acetate at 23°C for 7 days to the sample before immersion. Generally, the gel fraction of the polymer is equal to a crosslinked degree, and the gel
5 fraction becomes higher as the number of crosslinked moieties in the polymer increases. The gel fraction (introduction amount of crosslinked structure) can be adjusted within a desired range by a method for introducing a crosslinked structure, the type and the amount of a crosslinker, and the like.

[0031] The adhesive strength of the pressure sensitive adhesive sheet is preferably 2
10 N/10 mm or more, more preferably 4 N/10 mm or more, further preferably 5 N/10 mm or more. When the adhesive strength of the photocured pressure sensitive adhesive sheet is within the above-mentioned range, peeling of the pressure sensitive adhesive sheet from the adherend can be prevented even in case of occurrence of stress by strain or an impact of falling or the like. The adhesive strength is determined by a peeling test conducted at
15 a tension speed of 300 mm/minute and a peeling angle of 180° with a glass plate used as an adherend. Unless otherwise specified, the adhesive strength is a value measured at 25°C.

[0032] The thickness of the pressure sensitive adhesive sheet is not particularly limited, and may be set according to the type, shape and the like of an adherend. When a
20 member having a printing level difference, such as a front transparent plate, is used as the adherend, the thickness of the pressure sensitive adhesive sheet is preferably greater than the thickness of the printing level difference. The thickness of the pressure sensitive adhesive sheet to be used for bonding a front transparent plate (cover window) is preferably 30 μm or more, more preferably 40 μm or more, further preferably 50 μm or
25 more. When the thickness of the pressure sensitive adhesive sheet is increased, level difference followability and impact resistance tend to be improved. The upper limit of the thickness of the pressure sensitive adhesive sheet is not particularly limited, but is preferably 500 μm or less, more preferably 300 μm or less, further preferably 250 μm or less from the viewpoint of, for example, productivity of the pressure sensitive adhesive
30 sheet.

[0033] [Compositions of Pressure Sensitive Adhesive]

Composition of the pressure sensitive adhesive is not particularly limited as long as the pressure sensitive adhesive sheet 5 satisfies the above-mentioned properties, and

pressure sensitive adhesives containing a base polymer such as an acryl-based polymer, a silicone-based polymer, a polyester, a polyurethane, a polyamide, a polyvinyl ether, a vinyl acetate/vinyl chloride copolymer, a modified polyolefin, an epoxy-based polymer, a fluorine-based polymer, or a polymer based on a rubber such as a natural rubber or a synthetic rubber can be appropriately selected. Particularly, an acryl-based pressure sensitive adhesive including an acryl-based polymer as a base polymer is preferably used because it is excellent in optical transparency, exhibits moderate wettability, cohesive strength and pressure sensitive adhesive properties such as adhesiveness, and is also excellent in weather resistance, heat resistance and the like.

[0034] <Acryl-based Polymer Chain>

In an acryl-based base polymer having a crosslinking structure, a crosslinked structure is introduced in an acryl-based polymer chain. The acryl-based polymer chain contains a (meth)acrylic acid alkyl ester as a main constituent monomer component. In this specification, the “(meth)acryl” means acryl and/or methacryl.

[0035] As the (meth)acrylic acid alkyl ester, a (meth)acrylic acid alkyl ester with the alkyl group having 1 to 20 carbon atoms is preferably used. The alkyl group of the (meth)acrylic acid alkyl ester may have a branch or may have a cyclic alkyl group.

[0036] Specific examples of the (meth)acrylic acid alkyl ester having a linear or branched alkyl group include methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, isobutyl (meth)acrylate, s-butyl (meth)acrylate, t-butyl (meth)acrylate, pentyl (meth)acrylate, isopentyl (meth)acrylate, neopentyl (meth)acrylate, hexyl (meth)acrylate, heptyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, octyl (meth)acrylate, isooctyl (meth)acrylate, nonyl (meth)acrylate, isononyl (meth)acrylate, decyl (meth)acrylate, isodecyl (meth)acrylate, undecyl (meth)acrylate, dodecyl (meth)acrylate, isotridodecyl (meth)acrylate, tetradecyl (meth)acrylate, isotetradecyl (meth)acrylate, pentadecyl (meth)acrylate, cetyl (meth)acrylate, heptadecyl (meth)acrylate, octadecyl (meth)acrylate, isooctadecyl (meth)acrylate, nonadecyl (meth)acrylate and aralkyl (meth)acrylate.

[0037] Specific examples of the (meth)acrylic acid alkyl ester having a cycloaliphatic alkyl group include (meth)acrylic acid cycloalkyl esters such as cyclopentyl (meth)acrylate, cyclohexyl (meth)acrylate, cycloheptyl (meth)acrylate and cyclooctyl (meth)acrylate; (meth)acrylic acid esters having a dicyclic aliphatic hydrocarbon ring, such as isobornyl (meth)acrylate; and (meth)acrylic acid esters having a tri-or-more-cyclic aliphatic hydrocarbon ring, such as dicyclopentanyl (meth)acrylate, dicyclopentanyloxyethyl

(meth)acrylate, tricyclopentanyl (meth)acrylate, 1-adamantyl (meth)acrylate, 2-methyl-2-adamantyl (meth)acrylate and 2-ethyl-2-adamantyl (meth)acrylate.

[0038] The amount of the (meth)acrylic acid alkyl ester based on the total amount of monomer components for forming an acryl-based polymer chain is preferably 50% by weight or more, more preferably 55% by weight or more, further preferably 60% by weight or more. From the viewpoint of ensuring that the glass transition temperature (T_g) of the polymer chain is within an appropriate range, the amount of the (meth)acrylic acid alkyl ester having a linear or branched alkyl group having 4 to 10 carbon atoms based on the total amount of constituent monomer components of the acryl-based polymer chain is preferably 40% by weight or more, more preferably 50% by weight or more, further preferably 55% by weight or more. The monomer components of the acryl-based base polymer are the monomer components of the polymer but crosslinker and monomers for forming a crosslinked structure (*e.g.*, polyfunctional (meth)acrylates and urethane (meth)acrylates as described later) are excluded.

[0039] The acryl-based base polymer may contain a hydroxy group-containing monomer and a carboxy group-containing monomer as constituent monomer components. When a crosslinked structure is introduced by an isocyanate crosslinker, the hydroxy group forms a reaction point with an isocyanate group, and when the crosslinked structure is introduced by an epoxy-based crosslinker, the carboxy group forms a reaction point with an epoxy group.

[0040] Examples of the hydroxy group-containing monomer include (meth)acrylic acid esters such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, 6-hydroxyhexyl (meth)acrylate, 8-hydroxyoctyl (meth)acrylate, 10-hydroxydecyl (meth)acrylate, 12-hydroxylauryl (meth)acrylate and (4-hydroxymethylcyclohexyl)-methyl (meth)acrylate. When a crosslinked structure is introduced into the acryl-based polymer chain by a urethane-based segment, it is preferable that the acryl-based base polymer contains as a constituent monomer component a (meth)acrylic acid ester having a hydroxyalkyl group having 4 to 8 carbon atoms, from the viewpoint of high compatibility with the urethane-based segment and improvement of the transparency of the pressure sensitive adhesive sheet.

[0041] When the acryl-based base polymer contains a hydroxyalkyl group containing monomer as a constituent monomer component, the transparency of the pressure sensitive adhesive sheet tends to be improved, and cloudiness under a high-temperature

and high-humidity environment tends to be suppressed. The hydroxy group of the hydroxy group-containing monomer can form a physical crosslinkage with an acryl-based polymer chain or a crosslinking segment (*e.g.*, urethane-based segment) which bridges acryl-based polymer chains by hydrogen bonding. Thus, by increasing the ratio of hydroxy group-containing monomers in monomer components of the acryl-based base polymer, cohesive force tends to be enhanced leading to an increase in $G'_{25^{\circ}\text{C}}$ even when the gel fraction is low. The amount of the hydroxy group-containing monomer based on the total amount of monomer components of the acryl-based polymer chain is preferably 5 to 30 wt%, more preferably 8 to 25 wt%, further preferably 10 to 20 wt%.

[0042] Examples of the carboxy group-containing monomer include acryl-based monomers such as (meth)acrylic acid, carboxyethyl (meth)acrylate and carboxypentyl (meth)acrylate, and unsaturated fatty acids such as itaconic acid, maleic acid, fumaric acid and crotonic acid.

[0043] When the pressure sensitive adhesive sheet is used for bonding a touch panel sensor, it is preferable that a pressure sensitive adhesive sheet has a low acid content for preventing corrosion of the electrode by acid components. In addition, when the pressure sensitive adhesive sheet is used for bonding a polarizing plate, it is preferable that a pressure sensitive adhesive sheet has a low acid content for suppressing generation of polyene structure in a polarizer. The content of organic acid monomers, *e.g.*, (meth)acrylic acid, in such an acid-free pressure sensitive adhesive sheet is preferably 100 ppm or less, more preferably 70 ppm or less, further preferably 50 ppm or less. The organic acid monomer content of the pressure sensitive adhesive sheet can be determined by immersing the pressure sensitive adhesive sheet in pure water, heating the pressure sensitive adhesive sheet at 100°C for 45 minutes, and determining the amount of acid monomers extracted in water by ion chromatography.

[0044] For reducing the content of acid monomers in the pressure sensitive adhesive sheet, the amount of organic acid monomer components such as (meth)acrylic acid in the monomer components that form the acryl-based base polymer is preferably small. Thus, for ensuring that the pressure sensitive adhesive sheet is free from acid, it is preferable that the base polymer does not substantially contain an organic acid monomer (carboxy group-containing monomer) as a monomer component. In the acid-free pressure sensitive adhesive sheet, the amount of the carboxy group-containing monomer is preferably 0.5 parts by weight or less, more preferably 0.1 parts by weight or less, further preferably 0.05

parts by weight or less, ideally 0 parts by weight based on 100 parts by weight of the total monomer components in the base polymer.

[0045] The acryl-based base polymer may contain a nitrogen-containing monomer as the constituent monomer component. Examples of the nitrogen-containing monomer include

5 vinyl-based monomer such as N-vinylpyrrolidone, methylvinylpyrrolidone, vinylpyridine, vinylpiperidone, vinylpyrimidine, vinylpiperazine, vinylpyrazine, vinylpyrrole, vinylimidazole, vinyloxazole, vinylmorpholine, (meth)acryloylmorpholine, N-vinylcarboxylic acid amides and N-vinylcaprolactam; and cyano group-containing acryl-based monomers such as acrylonitrile and methacrylonitrile. Among them, N-
10 vinylpyrrolidone is preferable because it considerably contribute to enhancement of adhesive strength by improvement of cohesive force.

[0046] When the acryl-based base polymer contains high-polarity monomers such as a hydroxy group-containing monomer, a carboxy group-containing monomer and a nitrogen-containing monomer as constituent monomer components, the cohesive force of the

15 pressure sensitive adhesive tends to be enhanced and $G'_{25^{\circ}\text{C}}$ is increased, leading to improvement of adhesion retainability. On the other hand, when the content of the high-polarity monomer is too large, glass transition temperature becomes high, leading to leading to deterioration of impact resistance. Therefore, the amount of high-polarity monomers (total of a hydroxy group-containing monomer, a carboxy group-containing
20 monomer and a nitrogen-containing monomer) based on the total amount of monomer components for forming the acryl-based polymer chain is preferably 15 to 45% by weight, more preferably 20 to 40% by weight, further preferably 25 to 37% by weight. Specifically, it is preferable the total of the hydroxy group-containing monomer and the nitrogen-containing monomer is within the above range. The amount of the nitrogen-containing
25 monomer based on the total amount of monomer components for forming the acryl-based base polymer is preferably 7 to 30% by weight, more preferably 10 to 25% by weight, further preferably 12 to 22% by weight.

[0047] Besides the above-described monomer components, the acryl-based base polymer may contain other monomer components. Examples of the monomer components
30 include: vinyl-based monomers such as acid anhydride group-containing monomers, caprolactone adducts of acrylic acids, sulfonic acid group-containing monomers, phosphoric acid group-containing monomers, styrene and α -methylstyrene; cyano group-containing acryl-based monomers such as acrylonitrile and methacrylonitrile; epoxy group-containing

monomers such as glycidyl (meth)acrylate; glycol-based acryl ester monomers such as polyethylene glycol (meth)acrylate, polypropylene glycol (meth)acrylate, methoxyethylene glycol (meth)acrylate and methoxypolypropylene glycol (meth)acrylate; and acrylic acid ester-based monomers such as tetrahydrofurfuryl (meth)acrylate, fluorine (meth)acrylate, 5 silicone (meth)acrylate and 2-methoxyethyl (meth)acrylate.

[0048] Preferably, the acryl-based base polymer contains a (meth)acrylic acid alkyl ester in the largest amount among the above-mentioned monomer components. The properties of the pressure sensitive adhesive sheet are apt to depend on the type of a monomer contained in the largest amount among the constituent monomers of the acryl-based polymer chain (main monomer). For example, when the main monomer of the acryl-based polymer chain is a (meth)acrylic acid alkyl ester having a linear or branched alkyl group having 6 or less carbon atoms, the $\tan \delta_{70^{\circ}\text{C}}$ tends to increase, leading to improvement of level difference followability. Particularly, when the main monomer is an acrylic acid C₄-alkyl ester such as butyl acrylate, the $\tan \delta_{70^{\circ}\text{C}}$ tends to increase. The amount of the (meth)acrylic acid alkyl ester having a linear or branched alkyl group having 6 or less carbon atoms is preferably 40 to 85% by weight, more preferably 45 to 80% by weight, further preferably 50 to 75% by weight based on the total amount of monomer components for forming the acryl-based polymer chain. Particularly, the content of butyl acrylate as a constituent monomer component is preferably within the above-mentioned range.

[0049] The theoretical T_g of the acryl-based polymer chain is preferably -50°C or higher. The theoretical T_g of the acryl-based polymer chain is preferably -10°C or lower, more preferably -20°C or lower, further preferably -25°C or lower. The theoretical T_g is calculated from the glass transition temperature T_{g_i} of a homopolymer of a constituent monomer component of the acryl-based polymer chain and the weight fraction (W_i) of each monomer component of accordance with the following Fox equation:

$$1/T_g = \Sigma(W_i/T_{g_i}).$$

[0050] T_g represents a glass transition temperature (unit: K) of the polymer, W_i represents a weight fraction (copolymerization ratio on a weight basis) of a monomer component i forming the polymer chain, and T_{g_i} represents a glass transition temperature (unit: K) of a homopolymer of the monomer component i. As the glass transition temperature of the homopolymer, the value described in Polymer Handbook, 3rd edition (John Wiley & Sons, Inc., 1989) can be referred. As the T_g of a homopolymer of a

monomer which is not described in the document, a loss tangent ($\tan \delta$) peak-top temperature obtained by dynamic viscoelasticity measurement may be employed.

[0051] <Crosslinked Structure>

A polymer in which crosslinked structure is introduced in an acryl-based polymer chain may be obtained by, for example, (1) a method in which a acryl-based polymer having a functional group capable of reacting with a crosslinker is prepared, and the crosslinker is then added to react the acryl-based polymer with the crosslinker; and (2) a method in which a photopolymerizable polyfunctional compound is incorporated in polymerization components of a polymer to introduce a branched structure (crosslinked structure) into the polymer chain. These methods may be adopted in combination to introduce multiple kinds of crosslinked structure into the base polymer.

[0052] Specific examples of the crosslinker in the method (1) above in which base polymer and crosslinker are reacted include isocyanate-based crosslinkers, epoxy-based crosslinkers, oxazoline-based crosslinkers, aziridine-based crosslinkers, carbodiimide-based crosslinkers and metal chelate-based crosslinkers. In particular, isocyanate-based crosslinkers and epoxy-based crosslinkers are preferable because they have high reactivity with the hydroxy group and the carboxy group of the base polymer, so that introduction of a crosslinked structure is facilitated. Such a crosslinker forms a crosslinking by reacting with functional groups such as a hydroxy group and a carboxy group which are introduced into the base polymer. In an acid-free pressure sensitive adhesive in which the base polymer does not contain a carboxy group, it is preferable to form a crosslinking by use of an isocyanate-based crosslinker, *i.e.*, by reaction of a hydroxy group in the base polymer with the isocyanate crosslinker.

[0053] As an isocyanate-based crosslinker, a polyisocyanate having two or more isocyanate groups per molecule is used. Examples of the isocyanate-based crosslinker include lower aliphatic polyisocyanates such as butylene diisocyanate and hexamethylene diisocyanate; cycloaliphatic isocyanates such as cyclopentylene diisocyanate, cyclohexylene diisocyanate and isophorone diisocyanate; aromatic isocyanates such as 2,4-tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate and xylylene diisocyanate; isocyanate adducts such as trimethylolpropane/tolylene diisocyanate trimer adducts (*e.g.* "CORONATE L" manufactured by Tosoh Corporation), trimethylolpropane/hexamethylene diisocyanate trimer adducts (*e.g.* "CORONATE HL" manufactured by Tosoh Corporation), trimethylolpropane adducts of xylylene diisocyanate

(*e.g.* “TAKENATE D110N” manufactured by Mitsui Chemicals, Incorporated) and isocyanurate forms of hexamethylene diisocyanate (*e.g.* “CORONATE HX” manufactured by Tosoh Corporation). By using a urethane prepolymer having an isocyanate group at the terminal as the isocyanate-based crosslinker, crosslinking by urethane-based segment
5 can be introduced.

[0054] In the method (2) in which a polyfunctional monomer is added to the polymerization component for the base polymer, the total amount of a monomer component for forming the acryl-based base polymer and the polyfunctional compound for introducing a crosslinked structure may be reacted at once, or polymerization may be
10 performed in a multiple stages. For performing polymerization in multiple stages, a method is preferable in which a monofunctional monomer for forming a base polymer are polymerized (prepolymerization) to form a partially polymerized product (prepolymer composition), and a polyfunctional compound such as a polyfunctional (meth)acrylate is added in the prepolymer composition to polymerize the prepolymer composition and the
15 polyfunctional monomer (main polymerization). The prepolymer composition is a partially polymerized product containing a polymerized product with a low polymerization ratio and an unreacted monomer.

[0055] By performing prepolymerization of a constituent component of the acryl-based base polymer, branch points (crosslinked points) with a polyfunctional compound can be
20 uniformly introduced into the base polymer. In addition, the pressure sensitive adhesive sheet can also be formed by applying a mixture of a low-molecular-weight polymer or a partially polymerized product and an unpolymerized monomer component (pressure sensitive adhesive composition) onto a substrate, and then performing main polymerization on the substrate. A low-polymerization composition such as a prepolymer
25 composition has a low viscosity, and is thus excellent in application property, and therefore by using a method in which a pressure sensitive adhesive composition that is a mixture of a prepolymer composition and a polyfunctional compound is applied, and then main polymerization is performed on a substrate, productivity of the pressure sensitive adhesive sheet can be improved, and the thickness of the pressure sensitive adhesive sheet can be
30 made uniform.

[0056] Examples of the polyfunctional compound to be used for introducing a crosslinked structure include compounds having two or more polymerizable functional groups having an unsaturated double bond (ethylenically unsaturated group) in one molecule. The

polyfunctional compound is preferably a polyfunctional (meth)acrylate because it is easily copolymerized with the monomer component of the acryl-based base polymer. When a branched (crosslinked) structure is introduced by active energy ray polymerization (photopolymerization), a polyfunctional acrylate is preferable as the polyfunctional
5 compound.

[0057] Examples of the polyfunctional (meth)acrylate include polyethylene glycol di(meth)acrylate, polypropylene glycol di(meth)acrylate, polytetramethylene glycol di(meth)acrylate, bisphenol A ethylene oxide-modified di(meth)acrylate, bisphenol A propylene oxide-modified (meth)acrylate, alkanediol di(meth)acrylate, tricyclodecane
10 dimethanol di(meth)acrylate, ethoxylated isocyanuric acid triacrylate, pentaerythritol tri(meth)acrylate, pentaerythritol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, ditrimethylolpropane tetra(meth)acrylate, ethoxylated pentaerythritol tetra(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol poly(meth)acrylate, dipentaerythritol hexa(meth)acrylate, neopentyl glycol di(meth)acrylate, glycerin
15 di(meth)acrylate, epoxy (meth)acrylate, butadiene (meth)acrylate and isoprene (meth)acrylate. A crosslinking by a urethane-based segment can be introduced by using a urethane (meth)acrylate having a (meth)acryloyl group at a terminal of a polyurethane chain as the poly functional (meth)acrylate.

[0058] <Introduction of Crosslinking Structure by Urethane-based Segment>

20 When the acryl-based polymer chain is crosslinked with a urethane-based segment, a pressure sensitive adhesive in which low glass transition temperature and high adhesion retaining force are compatible can be attained easily. The urethane-based segment is a molecular chain having a urethane bond, and both terminals of the urethane-based segment are covalently bonded to the acryl-based polymer chain, so that a
25 crosslinked structure is introduced into the acryl-based polymer chain. The urethane-based segment typically includes a polyurethane chain obtained by reacting diol and diisocyanate.

[0059] The molecular weight of the polyurethane chain in the urethane-based segment is preferably 5,000 to 30,000, more preferably 6,000 to 23,000, further preferably 7,000 to
30 20,000. The larger the molecular weight of the polyurethane chain in the urethane-based segment increases, the longer the distance between crosslinked points of the acryl-based polymer chain. When the molecular weight of the polyurethane chain is within the above-described range, the polymer having crosslinked structure has appropriate

cohesiveness and fluidity, so that it is possible to achieve all of adhesive strength, level difference followability and impact resistance.

[0060] When the molecular weight of the polyurethane chain is excessively small, and thus the distance between the crosslinked points is short, an increase in cohesive force tends to decrease $\tan \delta$, leading to deterioration of level difference followability and impact resistance. On the other hand, when the molecular weight of the polyurethane chain is excessively large, and thus the distance between crosslinked points is long, the storage elastic modulus may be low, leading to an insufficient adhesion retaining force. Even if the polyurethane chain has a large molecular weight, the storage elastic modulus can be increased by increasing the amount of urethane-based segments to enhance the gel fraction. However, a polyurethane chain having a large molecular weight has low compatibility with an acryl-based polymer chain, and an increase in the amount of urethane-based segments may increase the haze of a pressure sensitive adhesive, leading to deterioration of transparency.

[0061] When the amount of the urethane-based segment is excessively large, the viscosity of the pressure sensitive adhesive may be reduced due to an increase in gel fraction, leading to deterioration of level difference followability and impact resistance. In addition, when the amount of the urethane-based segment is excessively large, the transparency of the pressure sensitive adhesive sheet may be deteriorated, leading to an increase in haze. Thus, the amount of the urethane-based segment in the base polymer is preferably 10 parts by weight or less, more preferably 7 parts by weight or less, further preferably 5 parts by weight or less, based on 100 parts by weight of the acryl-based polymer chain. On the other hand, from the viewpoint of the gel fraction and imparting adhesion retaining force, the amount of the urethane-based segment in the base polymer is preferably 0.3 parts by weight or more, more preferably 0.4 parts by weight or more, further preferably 0.5 parts by weight or more, based on 100 parts by weight of the acryl-based polymer chain. The amount of urethane-based segments in the base polymer may be 4 parts by weight or less, or 3 parts by weight or less, and may be 0.7 parts by weight or more, or 1 part by weight or more, based on 100 parts by weight of the acryl-based polymer chain.

[0062] Examples of the diol to be used for formation of the polyurethane chain include low-molecular-weight diols such as ethylene glycol, diethylene glycol, propylene glycol, butylene glycol and hexamethylene glycol; and high-molecular-weight polyols such as

polyester polyol, polyether polyol, polycarbonate polyol, acryl polyol, epoxy polyol and caprolactone polyol.

[0063] The polyether polyol is obtained by ring-opening and addition polymerization of an alkylene oxide with a polyhydric alcohol. Examples of the alkylene oxide include
5 ethylene oxide, propylene oxide, butylene oxide, styrene oxide and tetrahydrofuran. Examples of the polyhydric alcohol include the above-described diols, glycerin and trimethylolpropane.

[0064] The polyester polyol is polyester having a hydroxy group at the terminal, and is obtained by reacting a polybasic acid with a polyhydric alcohol in such a manner that the
10 alcohol equivalent is in surplus over the carboxylic acid equivalent. As a polybasic acid component and a polyhydric alcohol component which form the polyester polyol, a combination of a dibasic acid a diol is preferable.

[0065] Examples of the dibasic acid component include aromatic dicarboxylic acids such as orthophthalic acid, isophthalic acid and terephthalic acid; cycloaliphatic dicarboxylic
15 acids such as hexahydrophthalic acid, tetrahydrophthalic acid, 1,3-cyclohexanedicarboxylic acid and 1,4-cyclohexanedicarboxylic acid; aliphatic dicarboxylic acids such as oxalic acid, succinic acid, malonic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, decanedicarboxylic acid, dodecanedicarboxylic acid and octadecanedicarboxylic acid; and acid anhydrides and lower alcohol esters of these
20 dicarboxylic acids.

[0066] Examples of the diol component include ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, neopentyl glycol, pentanediol, 1,6-hexanediol, 1,8-octanediol, 1,10-decanediol, diethylene glycol, triethylene glycol, polyethylene glycol, dipropylene glycol, polypropylene glycol, 1,4-cyclohexanedimethanol, 1,4-cyclohexanediol,
25 bisphenol A, bisphenol F, hydrogenated bisphenol A and hydrogenated bisphenol F.

[0067] Examples of the polycarbonate polyol include polycarbonate polyols obtained by subjecting a diol component and phosgene to polycondensation reaction; polycarbonate polyols obtained by subjecting a diol component and a carbonic acid diester such as dimethyl carbonate, diethyl carbonate, dipropyl carbonate, diisopropyl carbonate, dibutyl
30 carbonate, ethylbutyl carbonate, ethylene carbonate, propylene carbonate, diphenyl carbonate or dibenzyl carbonate to transesterification condensation; copolymerized polycarbonate polyols obtained using two or more polyol components; polycarbonate polyols obtained by subjecting the above-mentioned various polycarbonate polyols and a

carboxy group-containing compound to esterification reaction; polycarbonate polyols obtained by subjecting the above-mentioned various polycarbonate polyols and a hydroxy group-containing compound to etherification reaction; polycarbonate polyols obtained by subjecting the above-mentioned various polycarbonate polyols and an ester compound to transesterification reaction; polycarbonate polyols obtained by subjecting the above-mentioned various polycarbonate polyols and a hydroxy group containing compound to transesterification reaction; polyester-based polycarbonate polyols obtained by polycondensation of the above-mentioned various polycarbonate polyols and a dicarboxylic acid compound; and copolymerized polyether-based polycarbonate polyols obtained by copolymerizing the above-mentioned various polycarbonate polyols and an alkylene oxide.

[0068] The polyacryl polyol is obtained by copolymerizing a (meth)acrylic acid ester and a monomer component having a hydroxy group. Examples of the monomer having a hydroxy group include (meth)acrylic acid hydroxyalkyl esters such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate and 2-hydroxypentyl (meth)acrylate; polyhydric alcohol (meth)acrylic acid monoesters such as glycerin and trimethylolpropane; and N-methylol (meth)acrylamide. Examples of the (meth)acrylic acid ester include methyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate and cyclohexyl (meth)acrylate.

[0069] The polyacryl polyol may contain as a copolymerizable component a monomer component other than the components described above. Examples of the copolymerizable monomer component other than the components described above include unsaturated monocarboxylic acids such as (meth)acrylic acid; unsaturated dicarboxylic acids such as maleic acid, and anhydrides and mono- or diesters thereof; unsaturated nitriles such as (meth)acrylonitrile; unsaturated amides such as (meth)acrylamide and N-methylol (meth)acrylamide; vinyl esters such as vinyl acetate and vinyl propionate; vinyl ethers such as methylvinyl ether; α -olefins such as ethylene and propylene; halogenated α,β -unsaturated aliphatic monomers such as vinyl chloride and vinylidene chloride; and α,β -unsaturated aromatic monomers such as styrene and α -methylstyrene.

[0070] The diisocyanate to be used for formation of the polyurethane chain may be either an aromatic or aliphatic diisocyanate. Examples of the aromatic diisocyanate include 1,5-naphthalene diisocyanate, 4,4'-diphenylmethane diisocyanate (MDI), 4,4'-diphenyldimethylmethane diisocyanate, tetramethyldiphenylmethane diisocyanate, 1,3-

phenylene diisocyanate, 1,4-phenylene diisocyanate, 2-chloro-1,4-phenyl diisocyanate, 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, xylylene diisocyanate, 4,4'-diphenyl ether diisocyanate, 4,4'-diphenylsulfoxide diisocyanate, 4,4'-diphenylsulfone diisocyanate and 4,4'-biphenyl diisocyanate. Examples of the aliphatic diisocyanate include butane-1,4-
5 diisocyanate, hexamethylene diisocyanate, 2,2,4-trimethylhexamethylene diisocyanate, 2,4,4-trimethylhexamethylene diisocyanate, cyclohexane-1,4-diisocyanate, isophorone diisocyanate, dicyclohexylmethane-4,4'-diisocyanate, 1,3-bis(isocyanatemethyl)cyclohexane and methylcyclohexane diisocyanate.

[0071] A derivative of an isocyanate compound may also be used as the diisocyanate.

10 Examples of the derivative of an isocyanate compound include dimers of polyisocyanate, trimers of isocyanate (isocyanurates), polymeric MDI, adducts with trimethylolpropane, biuret modified products, allophanate modified products and urea modified products. As the diisocyanate component, a urethane prepolymer having an isocyanate group at the terminal may be used.

15 **[0072]** Among the exemplified polyurethane chains, those including a polyether urethane having a polyether polyol as a diol component and/or a polyester urethane having polyester polyol as a diol component are preferable because these components have high compatibility with an acryl-based polymer chain. In particular, when a crosslinked structure is introduced with polyester urethane, the storage elastic modulus at room
20 temperature tends to increase, leading to improvement of adhesion retaining force and processability. One reason is that polyester has a more rigid molecular structure as compared to polyether etc. It is considered that when the crosslinked structure is introduced with rigid segments, the storage elastic modulus is increased because movement of the acryl-based polymer chain is restricted, while impact resistance and level
25 difference followability are exhibited because the distance between crosslinked points in the polymer chain is retained.

[0073] When a compound having at the terminal of a polyurethane chain a polyfunctional group copolymerizable with a monomer component for forming an acryl-based polymer chain, or a compound having at the terminal of a polyurethane chain a
30 functional group capable of reacting with a carboxy group, a hydroxy group or the like contained in an acryl-based polymer chain is used, a crosslinked structure can be introduced into the acryl-based polymer chain by a urethane-based segment. It is preferable that a crosslinked structure is introduced by a urethane-based segment using a

urethane di(meth)acrylate having a (meth)acryloyl group at both terminals of a polyurethane chain because crosslinked points are easily introduced uniformly into the acryl-based polymer chain, and excellent compatibility between the acryl-based polymer chain and the urethane-based segment is exhibited. For example, when a monomer component for forming an acryl-based polymer chain is copolymerized with a urethane di(meth)acrylate, a crosslinked structure can be introduced into the acryl-based polymer chain by a urethane-based segment.

[0074] The urethane di(meth)acrylate having a (meth)acryloyl group at both terminals is obtained by, for example, using a (meth)acrylic compound having a hydroxy group, in addition to a diol component, in polymerization of polyurethane. From the viewpoint of controlling the chain length (molecular weight) of the urethane-based segment, it is preferable that an isocyanate-terminated polyurethane is synthesized by reacting a diol with a diisocyanate in such a manner that the isocyanate is in surplus, and a (meth)acrylic compound having a hydroxy group is then added to react the isocyanate group at the terminal of the polyurethane with a hydroxy group of the (meth)acrylic compound.

[0075] By reacting a polyhydric alcohol with a polyisocyanate compound in such a manner that the polyisocyanate compound is in surplus, a polyurethane chain having an isocyanate group at the terminal is obtained. For obtaining an isocyanate-terminated polyurethane, a diol component and a diisocyanate component may be used in such a manner that the NCO/OH ratio (equivalent ratio) is preferably 1.1 to 2.0, more preferably 1.15 to 1.5. A diol component and a diisocyanate component may be mixed in substantially equal amounts and reacted, followed by adding a diisocyanate component.

[0076] Examples of the (meth)acrylic compound having a hydroxy group include hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, hydroxybutyl (meth)acrylate, hydroxyhexyl (meth)acrylate, hydroxymethyl acrylamide and hydroxyethyl acrylamide.

[0077] As the urethane (meth)acrylate, a commercially available product from a company such as Arakawa Chemical Industries, Ltd., Shin-Nakamura Chemical Co., Ltd., Toagosei Co., Ltd., Kyoisha Chemical Co., Ltd., Nippon Kayaku Co., Ltd., The Nippon Synthetic Chemical Industry Co., Ltd., Negami Chemical Industrial Co., Ltd., Daicel-Allnex Ltd may be used. The weight average molecular weight of the urethane (meth)acrylate is preferably 5,000 to 30,000, more preferably 6,000 to 23,000, further preferably 7,000 to 20,000.

[0078] The glass transition temperature of the urethane (meth)acrylate is preferably 0°C

or lower, more preferably -10°C or lower, further preferably -20°C or lower. By using a urethane (meth)acrylate having a low glass transition temperature (T_g), a pressure sensitive adhesive excellent in adhesive strength at a low temperature even when a crosslinked structure is introduced by a urethane-based segment to enhance the cohesive force of the base polymer. The lower limit of the glass transition temperature of the urethane (meth)acrylate is not particularly limited, but is preferably -100°C or higher, more preferably -90°C or higher, further preferably -80°C or higher from the viewpoint of obtaining a pressure sensitive adhesive excellent in retaining force at a high temperature.

[0079] When a crosslinked structure is introduced into the acryl-based polymer chain by a urethane-based segment using a urethane (meth)acrylate, the glass transition temperature of the urethane-based segment of the base polymer is substantially equal to the glass transition temperature of the urethane (meth)acrylate.

[0080] <Preparation of Base Polymer>

A polymer with a crosslinked structure introduced into an acryl-based polymer chain by a urethane-based segment can be polymerized by various known methods. When a urethane (meth)acrylate is used as a constituent component of the urethane-based segment, a monomer component for forming the acryl-based polymer chain may be copolymerized with the urethane (meth)acrylate.

[0081] The amount of the urethane (meth)acrylate is preferably 0.3 to 10 parts by weight, more preferably 0.5 to 7 parts by weight, further preferably 0.7 to 5 parts by weight based on 100 parts by weight of the monomer component for forming the acryl-based polymer chain. When the amount of the urethane (meth)acrylate is adjusted, it is possible to prepare a base polymer in which the content of a urethane-based segment is within the above-mentioned range. When the content of the urethane-based segment is excessively low, the adhesion retaining force of the pressure sensitive adhesive sheet tends to be reduced due to reduction of cohesiveness of the base polymer. When the content of the urethane-based segment is excessively high, the viscosity of the pressure sensitive adhesive sheet tends to be reduced due to an increase in cohesiveness of the base polymer, leading to deterioration of impact resistance and level difference followability.

[0082] It is also possible to introduce, into the acryl-based polymer chain, a crosslinking by a polyfunctional (meth)acrylic compound, other than a urethane (meth)acrylate, in addition to or instead of a urethane (meth)acrylate. If the introduction amount of the crosslinking by a polyfunctional compound other than a urethane (meth)acrylate is

increased, impact resistance and level difference followability of the pressure sensitive adhesive sometimes deteriorate. Therefore, the amount of the polyfunctional compound other than a urethane (meth)acrylate is preferably 0.2 parts by weight or less, more preferably 0.1 parts by weight or less, further preferably 0.05 parts by weight or less based on 100 parts by weight of the monomer component for constitution of the acryl-based polymer chain.

[0083] Photopolymerization is preferable as a method for polymerization of the base polymer. In photopolymerization, a polymer can be prepared without use of a solvent, so that it is not necessary to dry and remove the solvent during formation of the pressure sensitive adhesive sheet, and a pressure sensitive adhesive sheet having a large thickness can be uniformly formed.

[0084] In preparation of the base polymer, the total amount of a monomer component for forming the acryl-based polymer chain and the urethane (meth)acrylate for introducing a crosslinked structure may be reacted at once, or polymerization may be performed in multiple stages. For performing polymerization in multiple stages, a method is preferable in which a monofunctional monomer for forming an acryl-based polymer chain are polymerized to form a prepolymer composition (prepolymerization), and a polyfunctional compound such as a urethane di(meth)acrylate is added in a syrup of the prepolymer composition to polymerize the prepolymer composition and the polyfunctional monomer (main polymerization). The prepolymer composition is a partially polymerized product containing a polymerized product with a low polymerization ratio and an unreacted monomer.

[0085] By performing prepolymerization of a constituent component of the acryl-based polymer, branch points (crosslinking points) with a polyfunctional compound such as a urethane di(meth)acrylate can be uniformly introduced into the acryl-based polymer chain. In addition, the pressure sensitive adhesive sheet can also be formed by applying a mixture of a low-molecular-weight polymer or a partially polymerized product and an unpolymerized monomer component (pressure sensitive adhesive composition) onto a substrate, and then performing main polymerization on the substrate.

[0086] A low-polymerization composition such as a prepolymer composition has a low viscosity, and is thus excellent in application property, and therefore by using a method in which a pressure sensitive adhesive composition that is a mixture of a prepolymer composition and a polyfunctional compound is applied, and then main polymerization is

performed on a substrate, productivity of the pressure sensitive adhesive sheet can be improved, and the thickness of the pressure sensitive adhesive sheet can be made uniform.

[0087] [Pressure Sensitive Adhesive Sheet]

As described above, a prepolymer composition with a low polymerization ratio is prepared by prepolymerization, a pressure sensitive adhesive composition obtained by adding a polyfunctional compound etc. to the prepolymer composition is applied in the form of a layer onto a substrate, and the pressure sensitive adhesive composition on the substrate is polymerized (main polymerization) to obtain a semi-cured pressure sensitive adhesive sheet.

[0088] <Prepolymerization>

The prepolymer composition can be prepared by, for example, polymerizing a composition obtained by mixing a monomer component for forming the acryl-based polymer chain and a polymerization initiator. The prepolymer forming composition may contain a polyfunctional compound (polyfunctional monomer or polyfunctional oligomer). For example, a part of the polyfunctional compound as a raw material for the polymer is included in the prepolymer forming composition, and after polymerization of the prepolymer, the remainder of the polyfunctional compound is added, and subjected to main polymerization.

[0089] It is preferable the prepolymer forming composition contains a photopolymerization initiator. Examples of the photopolymerization initiator include benzoin ether-based photopolymerization initiators, acetophenone-based photopolymerization initiators, α -ketol-based photopolymerization initiators, aromatic sulfonyl chloride-based photopolymerization initiators, photoactive oxime-based photopolymerization initiators, benzoin-based photopolymerization initiators, benzyl-based photopolymerization initiators, benzophenone-based photopolymerization initiators, ketal-based photopolymerization initiators, thioxanthone-based photopolymerization initiators and acylphosphine oxide-based photopolymerization initiators.

[0090] In polymerization, a chain-transfer agent, a polymerization inhibitor (polymerization-delaying agent) or the like may be used for the purpose of, for example, adjusting the molecular weight. Examples of the chain-transfer agent include thiols such as α -thioglycerol, lauryl mercaptan, glycidyl mercaptan, mercaptoacetic acid, 2-mercaptoethanol, thioglycolic acid, 2-ethylhexyl thioglycolate and 2,3-dimercapto-1-propanol, and α -methylstyrene dimers.

[0091] Although the polymerization ratio of the prepolymer is not particularly limited, it is preferably 3 to 50% by weight, more preferably 5 to 40% by weight for adjusting a viscosity of the prepolymer syrup suitable for application onto a base member. The polymerization ratio of the prepolymer can be adjusted to fall within a desired range by adjusting the type and used amount of a photopolymerization initiator, the irradiation intensity/irradiation time of an active ray such as UV light, and so on. The polymerization ratio of the prepolymer is calculated in accordance with the following expression from weights before and after heating at 130°C for 3 hours. The polymerization ratio of the pressure sensitive adhesive sheet is calculated by the same method.

$$\text{Polymerization ratio (\%)} = \text{weight after drying} / \text{weight before drying} \times 100$$

[0092] <Preparation of Pressure Sensitive Adhesive Composition>

The urethane di(meth)acrylate, and the remainder of a monomer component for forming the acryl-based polymer chain, a polymerization initiator and a chain-transfer agent, and other additives as necessary are mixed with the prepolymer composition to prepare a pressure sensitive adhesive composition. Preferably, the pressure sensitive adhesive composition has a viscosity (*e.g.*, about 0.5 to 20 Pa·s) suitable for application of the composition onto a substrate. The viscosity of the pressure sensitive adhesive composition can be set within an appropriate range by adjusting the polymerization ratio of the prepolymer, the amount of the urethane (meth)acrylate, the compositions, molecular weights and amounts of other components (*e.g.*, oligomer), and so on. Additives such as thickener may be used for the purpose of, for example, adjusting the viscosity.

[0093] The polymerization initiator to be used for main polymerization are not particularly limited, and for example, the above-mentioned photopolymerization initiators may be used. When the polymerization initiator used in prepolymerization is not deactivated and remains in the prepolymer composition, addition of the polymerization initiator for main polymerization may be omitted.

[0094] (Chain Transfer Agent)

In main polymerization, it is preferable to adjust the molecular weight by incorporating a chain-transfer agent in a pressure sensitive adhesive composition. The chain-transfer agent used in main polymerization is not particularly limited, and for example, the above-described chain-transfer agents can be used. The amount of the chain-transfer agent in the pressure sensitive adhesive composition is preferably 0.001 to

2 parts by weight, more preferably 0.005 to 1 part by weight, further preferably 0.01 to 0.5 parts by weight, based on 100 parts by weight of the constituent components of the base polymer. When the chain-transfer agent used in the prepolymerization is not deactivated and remains in the prepolymer composition, addition of the chain-transfer agent in the pressure sensitive adhesive composition may be omitted.

[0095] The chain-transfer agent receives radicals from a growing polymer chain to stop extension of the polymer, and the chain-transfer agent having received the radicals attacks the monomer to start polymerization again. By using a chain-transfer agent, an increase in molecular weight of the polymer is suppressed without reducing the concentration of radicals in the reaction system.

[0096] When the ratio between the monofunctional monomer and the polyfunctional monomer is constant, an increase in molecular weight tends to raise the probability that one polymer chain contains a crosslinked point (branching point) from a polyfunctional monomer, resulting in an increase in gel fraction. By suppressing elongation of the polymer using a chain-transfer agent, the molecular weight of the polymer tends to decrease, leading to suppression of increase in gel fraction. Thus, when the pressure sensitive adhesive composition contains a chain-transfer agent, a pressure sensitive adhesive sheet having a large $\tan \delta$ and excellent level difference followability is easily formed.

[0097] (Oligomer)

The pressure sensitive adhesive composition may contain oligomers for the purpose of, for example, adjusting the adhesive strength and the viscosity of the pressure sensitive adhesive sheet. As the oligomer, one having a weight average molecular weight of, for example, about 1,000 to 30,000 is used. The oligomer is preferably an acryl-based oligomer because it is excellent in compatibility with the acryl-based base polymer.

[0098] The acryl-based oligomer contains a (meth)acrylic acid alkyl ester as a main constituent monomer component. In particular, the acryl-based oligomer is preferably one containing as a constituent monomer component a (meth)acrylic acid alkyl ester having a linear or branched alkyl group (linear or branched alkyl (meth)acrylate) and a (meth)acrylic acid alkyl ester having a cycloaliphatic alkyl group (cycloaliphatic alkyl (meth)acrylate). Specific examples of the linear or branched alkyl (meth)acrylate and the cycloaliphatic alkyl (meth)acrylate are as shown above as constituent monomers of the acryl-based polymer chain.

[0099] The glass transition temperature of the acryl-based oligomer is preferably 20°C or higher, more preferably 40°C or higher. The glass transition temperature of the acryl-based oligomer may be 60°C or higher, 80°C or higher, 100°C or higher, or 110°C or higher. When an acryl-based base polymer which has a low glass transition temperature (T_g) and in which a crosslinked structure is introduced by a urethane-based segment, and an acryl-based oligomer having a high glass transition temperature (T_g) are used in combination, the adhesion retaining force of the pressure sensitive adhesive sheet tends to be improved. The upper limit of the glass transition temperature of the acryl-based oligomer is not particularly limited, but is generally 200°C or lower, preferably 180°C or lower, more preferably 160°C or lower. The glass transition temperature of the acryl-based oligomer is calculated in accordance with the Fox equation.

[0100] Among the shown (meth)acrylic acid alkyl esters, the linear or branched alkyl (meth)acrylate is preferably methyl methacrylate because it has a high glass transition temperature, and is excellent in compatibility with the base polymer. As the cycloaliphatic alkyl (meth)acrylate, dicyclopentanyl acrylate, dicyclopentanyl methacrylate, cyclohexyl acrylate and cyclohexyl methacrylate are preferable. That is, the acryl-based oligomer is preferably one containing as constituent monomer components at least one selected from the group consisting of dicyclopentanyl acrylate, dicyclopentanyl methacrylate, cyclohexyl acrylate and cyclohexyl methacrylate, and methyl methacrylate.

[0101] The amount of the cycloaliphatic alkyl (meth)acrylate based on the total amount of monomer components for forming the acryl-based oligomer is preferably 10 to 90% by weight, more preferably 20 to 80% by weight, further preferably 30 to 70% by weight. The amount of the linear or branched alkyl (meth)acrylate based on the total amount of monomer components for forming the acryl-based oligomer is preferably 10 to 90% by weight, more preferably 20 to 80% by weight, further preferably 30 to 70% by weight.

[0102] The weight average molecular weight of the acryl-based oligomer is preferably 1,000 to 30,000, more preferably 1,500 to 10,000, further preferably 2,000 to 8,000. When an acryl-based oligomer having a molecular weight falling within the above-mentioned range is used, the adhesive strength and the adhesion retaining force of the pressure sensitive adhesive tend to be improved.

[0103] The acryl-based oligomer is obtained by polymerizing the above-mentioned monomer components by various polymerization methods. In polymerization of the acryl-based oligomer, various polymerization initiators may be used. In addition, a chain-

transfer agent may be used for the purpose of adjusting the molecular weight.

[0104] When the pressure sensitive adhesive composition contains an oligomer component such as an acryl-based oligomer, the content of the oligomer component is preferably 0.5 to 20 parts by weight, more preferably 1 to 15 parts by weight, further preferably 2 to 10 parts by weight, based on 100 part by weight of the above base polymer. When the content of the oligomer in the pressure sensitive adhesive composition is within the above-described range, adhesiveness and retention strength at high temperature tend to be enhanced.

[0105] (Silane Coupling Agent)

A silane coupling agent can also be added in the pressure sensitive adhesive composition for the purpose of adjusting the adhesive strength. When the pressure sensitive adhesive composition includes a silane coupling agent, the content thereof is normally about 0.01 to 5.0 parts by weight, preferably 0.03 to 2.0 parts by weight based on 100 parts by weight of the base polymer.

[0106] (Ultraviolet Absorber)

The pressure sensitive adhesive composition may contain an ultraviolet absorber. When the pressure sensitive adhesive composition contain an ultraviolet absorber, ultraviolet absorption property is impart to the pressure sensitive adhesive sheet, so that deterioration of the polarizing plate 3 and image display cell 6 can be prevented.

[0107] Examples of the ultraviolet absorber include benzotriazole-based ultraviolet absorbers, benzophenone-based ultraviolet absorbers, salicylate-based ultraviolet absorbers, triazine ultraviolet absorbers and cyanoacrylate-based ultraviolet absorbers. Triazine-based ultraviolet absorbers and benzotriazole-based ultraviolet absorbers are preferable because they have high ultraviolet absorbability and have excellent compatibility with acryl-based polymers so that highly transparent acryl-based pressure sensitive adhesive sheet can be easily obtained. Among them, triazine-based ultraviolet absorbers containing a hydroxy group is preferable, and hydroxyphenyl triazine-based ultraviolet is especially preferable.

[0108] As the ultraviolet absorber, a commercially available product may be used.

Examples of the commercially available triazine-based ultraviolet absorber include reaction products of 2-(4,6-bis (2,4-dimethylphenyl)-1,3,5-triazin-2-yl)-5-hydroxyphenyl with [(alkyloxy)methyl]oxirane ("TINUVIN 400" manufactured by BASF SE), reaction products of 2-(2,4-dihydroxyphenyl)-4,6-bis-(2,4-dimethylphenyl)-1,3,5-triazine with (2-

ethylhexyl)-glycidic acid ester ("TINUVIN 405" manufactured by BASF SE), (2,4-bis[2-hydroxy-4-butoxyphenyl]-6-(2,4-dibutoxyphenyl)-1,3,5-triazine ("TINUVIN 460" manufactured by BASF SE), 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-[(hexyl)oxy]-phenol ("TINUVIN 577" manufactured by BASF SE), 2-(2-hydroxy-4-[1-octyloxycarbonylethoxy]phenyl)-4,6-bis(4-phenylphenyl)-1,3,5-triazine ("TINUVIN 479" manufactured by BASF SE), bis(ethylhexyl) oxyphenolmethoxyphenyl triazine ("Tinosorb S" manufactured by BASF SE), and 2-(4,6-diphenyl-1,3,5-triazine-2-yl)-5-[2-(2-ethyhexanoyloxy)ethoxy]-phenol ("ADK STAB LA-46" manufactured by ADEKA Corporation).

[0109] When the ultraviolet absorber is added in the pressure sensitive adhesive composition, the content thereof is generally about 0.1 to 10 parts by weight, preferably 0.3 to 5 parts by weight, based on 100 parts by weight of the base polymer. When the content of the ultraviolet absorber is within the above range, ultraviolet shielding property of the pressure sensitive adhesive sheet can be improved, while deterioration of the transparency due to bleed out, etc. can be suppressed.

[0110] (Other Additives)

In addition to the components exemplified above, additives such as a tackifier, a plasticizer, a softener, a degradation inhibitor, a filler, a colorant, an antioxidant, a surfactant and an antistatic agent maybe contained in the pressure sensitive adhesive composition.

[0111] <Application and Main Polymerization of Pressure Sensitive Adhesive Composition>

The pressure sensitive adhesive composition is applied in the form of a layer onto a substrate, and irradiated with an active ray to perform photocuring. At the time of performing photocuring, it is preferable that a cover sheet is disposed over the surface of the coating layer, and the pressure sensitive adhesive composition is irradiated with an active ray while being held between two sheets, so that hindrance of polymerization by oxygen is prevented.

[0112] For each of the substrate and cover sheet to be used for formation of the pressure sensitive adhesive sheet, any suitable material is used. Each of the substrate and the cover sheet may be a release film having a release layer on a contact surface with the pressure sensitive adhesive sheet.

[0113] As the base film of the release film, films composed of various resin materials are

used. Examples of the resin material include polyester-based resins such as polyethylene terephthalate and polyethylene naphthalate, acetate-based resins, polyether sulfone-based resins, polycarbonate-based resins, polyamide-based resins, polyimide-based resins, polyolefin-based resins, (meth)acryl-based resins, polyvinyl chloride-based resins, polyvinylidene chloride-based resins, polystyrene-based resins, polyvinyl alcohol-based resins, polyacrylate-based resins and polyphenylene sulfide-based resins. Among them, polyester-based resins such as polyethylene terephthalate are especially preferable. The thickness of the base film is preferably 10 to 200 μm , more preferably 25 to 150 μm . Examples of the material of the release layer include silicone-based release agents, fluorine-based release agents, long-chain alkyl-based release agents and aliphatic amide-based release agents. The thickness of the release layer is generally about 10 to 2000 nm.

[0114] For applying the pressure sensitive adhesive composition on the substrate, various kinds of methods such as roll coating, kiss roll coating, gravure coating, reverse coating, roll brushing, spray coating, dip roll coating, bar coating, knife coating, air knife coating, curtain coating, lip coating, and extrusion coating may be employed.

[0115] The pressure sensitive adhesive composition applied in a layer-form onto the substrate is irradiated with an active ray to perform main polymerization. In main polymerization, unreacted monomers and polyfunctional compounds such as urethane di(meth)acrylate in the prepolymer composition react to give a polymer having a crosslinked structure in the acryl-based polymer chain.

[0116] The active ray may be selected according to the type of a polymerizable component such as monomer and urethane (meth)acrylate, the type of a photopolymerization initiator or the like, and in general, an ultraviolet ray and/or visible light having a short wavelength are used. The accumulated amount of irradiation light is preferably about 100 to 5000 mJ/cm^2 . The light source for photoirradiation is not particularly limited as long as it can emit light in a wavelength range over which the photopolymerization initiator contained in the pressure sensitive adhesive composition is sensitive to light, and a LED light source, a high-pressure mercury lamp, an ultra-high mercury lamp, a metal halide lamp, a xenon lamp or the like is preferably used. If the residual amount of unreacted monomers is large, $G'_{25^\circ\text{C}}$ of the pressure sensitive adhesive sheet may decrease, leading to deterioration of adhesion retaining force. Therefore, the polymerization ratio of the pressure sensitive adhesive sheet after the main polymerization is preferably 95% or more, more preferably 97% or more, further preferably 98% or more, especially preferably

99% or more. For increasing the polymerization ratio, the photocured pressure sensitive adhesive sheet may be heated to volatilize residual monomers, unreacted polymerization initiator and so on.

[0117] As described above, the gel fraction of the pressure sensitive adhesive sheet is preferably 30 to 80%, more preferably 35 to 70%. When the gel fraction is 30% or more, the adhesion retaining force of the pressure sensitive adhesive is enhanced, glue missing during processing and positional deviation between members are unlikely to occur, and excellent processability and processing dimensional stability are exhibited. When the gel fraction is 80% or less, excellent level difference followability can be exhibited.

[0118] The weight average molecular weight of the sol component in the pressure sensitive adhesive sheet is preferably 150,000 to 450,000, more preferably 180,000 to 420,000. The sol component is a soluble component obtained by extracting the base polymer with tetrahydrofuran (hereinafter, referred to as THF). Since it is difficult to measure the molecular weight of individual polymer chains of a crosslinked polymer (gel component), the molecular weight of the sol component (non-crosslinked polymer) is an index of the degree of elongation of the polymer chain. If the molecular weight of the sol component is excessively large, the glass transition temperature may increase, leading to decrease in impact resistance. On the other hand, if the molecular weight of the sol component is excessively small, the adhesion retaining force may decrease.

[0119] Release films 21 and 22 are bonded, respectively, to surfaces of the pressure sensitive adhesive sheet 5 to obtain a pressure sensitive adhesive sheet in which a release film is temporarily attached to each of both surfaces as shown in FIG. 1. The substrate and the cover sheet used for formation of the pressure sensitive adhesive sheet may be remain attached to the pressure sensitive adhesive to be used as release films 21 and 22.

[0120] When release films 21 and 22 are disposed on both surfaces of the pressure sensitive adhesive sheet 5, the thickness of one release film 21 and the thickness of the other release film 22 may be the same, or different. The peeling strength in peeling of the release film temporarily attached to one surface from the pressure sensitive adhesive sheet 5 and the peeling strength in peeling of the release film temporarily attached to the other surface from the pressure sensitive adhesive sheet 5 may be the same or different. When the peeling strength of the release film on one surface is different from the peeling strength of the release film on the other surface, excellent processability can be attained by performing the bonding of adherends in the following procedure: the release film 22

with relatively small peeling strength (lightly peelable film) is first peeled from the pressure sensitive adhesive sheet 5, and bonded to a first adherend, and the release film 21 with relatively large peeling strength (heavily peelable film) is peeled, and bonded to a second adherend.

5 **[0121]** [Image Display Device]

The pressure sensitive adhesive sheet 5 can be used for bonding various transparent members and opaque members. The type of the adherend is not particularly limited, and examples thereof include various resin materials, glass and metals. The pressure sensitive adhesive sheet 5 has high transparency, and is therefore suitable for
10 bonding optical members of an image display device etc. In particular, the pressure sensitive adhesive sheet of the present invention can impart level difference followability and impact resistance, and is therefore suitably used for bonding a transparent member such as a front transparent plate or a touch panel onto a viewing-side surface of an image display device.

15 **[0122]** FIG. 2 is a sectional view showing an example of a stacking configuration of an image display device in which the front transparent plate 7 is bonded to a viewing-side surface of an image display panel 10 with the pressure sensitive adhesive sheet 5 interposed therebetween. The image display panel 10 includes an image display cell 6 such as a liquid crystal cell or an OLED cell, and a polarizing plate 3 bonded to the
20 viewing-side surface of the image display cell 6 with a pressure sensitive adhesive sheet 4 interposed therebetween. The front transparent plate 7 includes a transparent flat plate 71 and a printed layer 76 disposed on the peripheral edge of one principal surface of the transparent flat plate 71. As the transparent plate 71, for example, a transparent resin plate such as that of an acryl-based resin or a polycarbonate-based resin, or a glass plate is
25 used. The transparent plate 71 may have a touch panel function. As the touch panel, a touch panel of any type such as resistive film type, capacitance type, optical type or ultrasonic type is used.

[0123] The polarizing plate 3 disposed on a surface of the image display panel 10 and the printed layer 76-formed surface of the front transparent plate 7 are bonded to each other
30 with the pressure sensitive adhesive sheet 5. The order of bonding is not particularly limited, bonding of the image display panel 10 to the pressure sensitive adhesive sheet 5 may precede, or bonding of the front transparent plate 7 to the pressure sensitive adhesive sheet 5 may precede. The former bonding and the latter bonding may be performed

simultaneously. For improving processability in bonding, it is preferred that one release film (lightly peelable film) 22 is first peeled off to expose the first principal surface of the pressure sensitive adhesive sheet followed by bonding the image display panel 10, and then the other release film (heavily peelable film) 21 is peeled off to expose the second principal surface of the pressure sensitive adhesive sheet 5 followed by bonding the front transparent plate 7.

[0124] It is preferred to perform degassing for removing bubbles at the interface between the pressure sensitive adhesive sheet 5 and the flat plate 71 of the front transparent plate 7, and in the vicinity of a non-flat portion such as the printed layer 76 after pressure sensitive adhesive sheet 5 and the front transparent plate 7 are bonded to each other. As a degassing method, an appropriate method such as heating, pressurization or pressure reduction can be employed. For example, it is preferred that bonding is performed while ingress of bubbles is suppressed under reduced pressure and heating, and pressurization is then performed in parallel with heating through autoclave or the like for the purpose of, for example, suppressing delay bubbles. When degassing is performed by heating, the heating temperature is generally in a range of 40°C to 150°C. When pressurization is performed, the pressure is generally in a range of generally about 0.05 MPa to 2 MPa.

[0125] When the gap 90 exists between the housing 9 and the front transparent plate 7, it is preferable that the gap 90 is filled with a resin material or the like to perform sealing.

As described above, the pressure sensitive adhesive sheet 5 has a high shear storage elastic modulus, and is therefore excellent in bonding reliability over a wide temperature range. Thus, even when stress strain occurs at a bonding interface of the pressure sensitive adhesive sheet due to a temperature change in sealing with the resin material or the like, peeling at the bonding interface can be suppressed. In addition, the pressure sensitive adhesive sheet 5 has a low glass transition temperature and a large $\tan \delta$ peak-top value, and is therefore excellent in impact resistance over a wide temperature range, so that peeling by impacts of falling and the like hardly occurs.

[0126] [Pressure Sensitive Adhesive-equipped Optical Film]

The pressure sensitive adhesive sheet 5 can be used not only in a form in which a release film is temporarily attached to each of both surfaces as shown in FIG. 1, but also as a pressure sensitive adhesive-equipped optical film in which a pressure sensitive adhesive sheet is bonded to an optical film or the like. For example, in the form shown in FIG. 3, the release film 21 is temporarily attached to one surface of the pressure sensitive

adhesive sheet 5, and a polarizing plate 3 is bonded to the other surface of the pressure sensitive adhesive sheet 5. In the form shown in FIG. 4, a pressure sensitive adhesive sheet 4 is further provided on the polarizing plate 3, and the release film 24 is temporarily attached on the pressure sensitive adhesive sheet 4.

[0127] In a form in which an optical film such as a polarizing plate is bonded to a pressure sensitive adhesive sheet beforehand as described above, the release film 21 temporarily attached to a surface of the pressure sensitive adhesive sheet 5 may be peeled and then the pressure sensitive adhesive sheet 5 may be bonded to a front transparent member.

[0128] [Modified Example of Stacking Embodiment]

Although FIGs. 1 to 4 mainly illustrate an embodiment in which the image display panel 10 (polarizing plate 3) and the front transparent plate 7 (cover window) are bonded to each other by the substrate-less double-sided pressure sensitive adhesive sheet 5, the kind and the combination of adherends are not limited to these embodiments. For example, a cover window and a touch panel sensor may be bonded to each other via the pressure sensitive adhesive sheet 5. In this embodiment, another pressure sensitive adhesive sheet is used for bonding the touch panel sensor and the image display panel.

[0129] The pressure sensitive adhesive sheet 5 can also be used as one or both pressure sensitive adhesive layers of a substrate-equipped double-sided pressure sensitive adhesive sheet. In the substrate-equipped double-sided pressure sensitive adhesive sheet 15 shown in FIG. 5, one surface of a transparent film substrate 59 is laminated with a first pressure sensitive adhesive layer 51 and the other surface of the transparent film substrate 59 is laminated with a second pressure sensitive adhesive layer 53. The pressure sensitive adhesive layers 51 and 53 have a surface to which release films 21 and 23 are temporarily attached, respectively.

[0130] FIG. 6 is a sectional view illustrating a configuration example of an image display device 206 in which the front transparent plate 7 is fixed to the viewing-side surface of the image display panel 10 using the substrate-equipped double-sided pressure sensitive adhesive sheet 15. In the image display device 206, the first pressure sensitive adhesive layer 51 is bonded to the front transparent plate 7, and the second pressure sensitive adhesive layer 53 is bonded to the polarizing plate 3 of the image display panel 10.

[0131] A transparent resin film is used for the transparent film substrate 59 of the substrate-equipped double-sided pressure sensitive adhesive sheet 15. The total light

transmittance of the transparent film substrate 59 is preferably 85% or more, more preferably 90% or more. The resin material constituting the film substrate is not particularly limited as long as it has transparency. Examples of the resin include polyesters such as polyethylene terephthalate and polyethylene naphthalate; polyolefins
5 such as polyethylene and polypropylene; cyclic polyolefins such as norbornene-based polymers; cellulose-based polymers such as diacetyl cellulose and triacetyl cellulose; acryl-based polymers; styrene-based polymers; polycarbonate, polyamide, polyimide, and polyether ether ketone.

[0132] The thickness of the transparent film substrate 59 is preferably 15 to 150 μm ,
10 more preferably 25 to 120 μm , further preferably 35 to 100 μm . From the viewpoint of suppressing rainbow-like coloring (iris phenomenon) at the time of viewing the screen of the image display device, it is preferable that the transparent film substrate 59 has optical isotropy. The in-plane retardation of the transparent film substrate 59 at a wavelength of 590 nm is preferably 50 nm or less, more preferably 30 nm or less, further preferably 10
15 nm or less, especially preferably 5 nm or less.

[0133] When bonded to the front transparent plate, the substrate-equipped double-sided pressure sensitive adhesive sheet 15 preferably has level difference followability in addition to adhesion retaining force, dimensional stability, and impact resistance. Therefore, the pressure sensitive adhesive sheet 5 having the above-described
20 characteristics is preferably used as the first pressure sensitive adhesive layer 51. From the viewpoint of ensuring level difference followability and impact resistance, the first pressure sensitive adhesive layer 51 preferably has a thickness of 30 μm or more, more preferably 40 μm or more, further preferably 50 μm or more. From the viewpoint of productivity, the first pressure sensitive adhesive layer 51 preferably has a thickness of
25 500 μm or less, more preferably 300 μm or less, further preferably 250 μm or less.

[0134] The pressure sensitive adhesive included in the second pressure sensitive adhesive layer 53 disposed on the image display panel 10-side of the transparent film substrate 59 is not particularly limited as long as the pressure sensitive adhesive is transparent. The pressure sensitive adhesive of the first pressure sensitive adhesive
30 layer 51 and the pressure sensitive adhesive of the second pressure sensitive adhesive layer 53 may be the same or different. From the viewpoint of enhancing the adhesion retaining force, the dimensional stability, and impact resistance, the pressure sensitive adhesive sheet 5 having the above-described characteristics may be used as the second

pressure sensitive adhesive layer 53 in the same manner as in the first pressure sensitive adhesive layer 51.

[0135] The thickness of the second pressure sensitive adhesive layer 53 is not particularly limited. From the viewpoint of imparting impact resistance, the thickness of the second pressure sensitive adhesive layer 53 is preferably 30 μm or more, more preferably 50 μm or more. The second pressure sensitive adhesive layer 53 is not required to have level difference followability. Therefore, from the viewpoint of dimensional stability and productivity, the thickness of the second pressure sensitive adhesive layer 53 is preferably 200 μm or less, more preferably 150 μm or less, further preferably 120 μm or less. The thickness of the second pressure sensitive adhesive layer 53 may be 100 μm or less or 80 μm or less.

[0136] The second pressure sensitive adhesive layer 53 preferably has a smaller thickness than the first pressure sensitive adhesive layer 51. The second pressure sensitive adhesive layer 53 preferably has a thickness of 0.2 to 0.85 times, more preferably 0.3 to 0.8 times, further preferably 0.4 to 0.75 times of the thickness of the first pressure sensitive adhesive layer 51.

[0137] In addition to an embodiment in which the release films 21 and 23 are temporarily attached to the pressure sensitive adhesive layers 51 and 53 respectively as shown in FIG. 5, an embodiment is possible in which the substrate-equipped double-sided pressure sensitive adhesive sheet 15 is used as a pressure sensitive adhesive-equipped film in which an optical film or the like is fixed to the second pressure sensitive adhesive layer 53. Furthermore, the substrate-equipped double-sided pressure sensitive adhesive sheet 15 can also be used as a pressure sensitive adhesive-equipped optical film in which an optical film (polarizing plate) bonded to the second pressure sensitive adhesive layer is further provided with a pressure sensitive adhesive sheet in the same manner as in an embodiment shown in FIG. 4.

EXAMPLES

[0138] The present invention will be described more specifically below by showing examples and comparative examples, but the present invention is not limited to these examples.

[0139] [Preparation of Acrylic Oligomer]

60 parts by weight of dicyclopentanyl methacrylate (DCPMA), 40 parts by weight

of methyl methacrylate (MMA), 3.5 parts by weight of α -thioglycerol as a chain-transfer agent, and 100 parts by weight of toluene as a polymerization solvent were mixed, and stirred in a nitrogen atmosphere at 70°C for 1 hour. 0.2 parts by weight of 2,2'-azobisisobutyronitrile (AIBN) is added as a thermopolymerization initiator, and the mixture was reacted at 70°C for 2 hours, then heated to 80°C, and reacted for 2 hours. Thereafter, the reaction liquid was heated to 130°C, and toluene, the chain-transfer agent and unreacted monomers were removed by drying to obtain a solid acrylic oligomer. The weight average molecular weight of the acrylic oligomer was 5100.

[0140] [Example 1]

(Polymerization of Prepolymer)

78 parts by weight of butyl acrylate (BA), 16 parts by weight of N-vinyl-2-pyrrolidone (NVP), and 6 parts by weight of 4-hydroxybutyl acrylate (4HBA) as prepolymer forming monomer components, and photopolymerization initiators (0.05 parts by weight of "IRGACURE 184" manufactured by BASF SE and 0.05 parts by weight of "IRGACURE 651" manufactured by BASF SE) were blended. The mixture was irradiated with an ultraviolet ray to perform polymerization until the viscosity of the composition reaches about 20 Pa·s (BH viscometer No. 5 Rotor, 10 rpm, measurement temperature: 30°C), thereby obtaining prepolymer composition (polymerization ratio: about 9%).

[0141] (Preparation of Photocurable Pressure Sensitive Adhesive Composition)

The followings were added to the prepolymer composition: 3 part by weight of NVP and 8 parts by weight of 4HBA as monofunctional monomers; 2 parts by weight of polyester urethane diacrylate having a weight average molecular weight of 12500 ("Art Resin UN-350" manufactured by Negami Chemical Industrial Co., Ltd.) as a urethane urethane (meth)acrylate; 5 parts by weight of the acrylic oligomer; 0.05 parts by weight of "IRGACURE 184" and 0.55 parts by weight of "IRGACURE 651" as photopolymerization initiators; 0.2 parts by weight of an α -methylstyrene dimer ("NOFMER MSD" manufactured by NOF CORPORATION) as a chain-transfer agent; and 0.3 parts by weight of "KBM 403" manufactured by Shin-Etsu Chemical Co., Ltd. as a silane coupling agent. The mixture was then homogeneously mixed to prepare a pressure sensitive adhesive composition.

[0142] (Preparation of Pressure Sensitive Adhesive Sheet)

A 75 μ m-thick polyethylene terephthalate (PET) film having a surface provided

with a silicone-based release layer ("DIAFOIL MRF 75" manufactured by Mitsubishi Chemical Corporation) was used as a substrate (also serving as a heavily peelable film). The the photocurable pressure sensitive adhesive composition was applied to have a thickness of 150 μm on the substrate to form a coating layer. To the coating layer, a 75 μm -thick PET film having one surface subjected to silicone release treatment ("DIAFOIL MRE 75" manufactured by Mitsubishi Chemical Corporation) was bonded as a cover sheet (also serving as a lightly peelable film). By a black light, which was position-adjusted so that the irradiation intensity at an irradiation surface just below the lamp was 5 mW/cm², the laminate was irradiated with an ultraviolet ray from the cover sheet-side to be photocured, the laminate was irradiated with an ultraviolet thereby obtaining a pressure sensitive adhesive sheet having a thickness of 150 μm and a polymerization ratio of 99%.

[0143] [Examples 2 to 16 and Comparative Examples 1 to 6]

The monomer composition in polymerization of the prepolymer, the kinds and the amounts of the monofunctional monomer and the polyfunctional compound (urethane acrylate and/or polyfunctional acrylate) added to the pressure sensitive adhesive composition, and the amount of the chain-transfer agent were changed as shown in Tables 1 and 2. A photocurable pressure sensitive adhesive composition was prepared in the same manner as in Example 1 except for the above, and was applied to a substrate and photocured to obtain a pressure sensitive adhesive sheet. In the post addition composition, the photopolymerization initiator ("IRGACURE 184": 0.05 parts by weight, and "IRGACURE 651": 0.55 parts by weight) and the silane coupling agent ("KBM-403": 0.3 parts by weight) are the same in all Examples and Comparative Examples, and therefore, Tables 1 and 2 omit description of these components.

[0144] [Evaluation]

<Gel Fraction>

About 0.2 g of the pressure sensitive adhesive was scraped off from the pressure sensitive adhesive sheet. The sample was wrapped in a porous polytetrafluoroethylene film having pore diameter of 0.2 μm (manufactured by Nitto Denko Corporation; trade name: "NTF-1122") cut to a size of 100 mm $\times$ 100 mm, and the wrapped opening was tied with a kite string. The total weight (A) of the porous polytetrafluoroethylene film and the kite string measured beforehand was subtracted from the weight of this sample to calculate the weight (B) of the pressure sensitive adhesive sample. The pressure sensitive adhesive sample wrapped in the porous polytetrafluoroethylene film was

immersed in approximately 50 mL of ethyl acetate at 23°C for 7 days to elute sol components of the pressure sensitive adhesive to the outside of the polytetrafluoroethylene film. After immersion, the pressure sensitive adhesive wrapped in the porous polytetrafluoroethylene film was taken out, dried at 130°C for 2 hours, and allowed to cool for about 20 minutes, and the dry weight (C) was measured. The gel fraction of the pressure sensitive adhesive was calculated from the following formula.

$$\text{Gel fraction (\%)} = 100 \times (C - A) / B$$

[0145] <Weight Average Molecular Weight of Sol Component>

About 0.2 g of the pressure sensitive adhesive was scraped off from the pressure sensitive adhesive sheet, and immersed in a 10 mM tetrahydrofuran phosphate solution for 12 hours to extract a sol component. With consideration given to the gel fraction of the pressure sensitive adhesive, the amount of the tetrahydrofuran phosphate solution was adjusted so that the sol component content of the solution after extraction was 0.1 wt%. A filtrate obtained by filtering solution after extraction with a 0.45 µm membrane filter was provided as a sample. Gel permeation chromatography (GPC) analysis was performed under the following conditions with a GPC apparatus (product name “HLC-8120GPC”) manufactured by TOSOH CORPORATION, and the weight average molecular weight Mw of the sol component was calculated.

(Measurement conditions)

Column: G7000HXL + GMHXL + GMHXL manufactured by TOSOH CORPORATION

Column size: 7.8 mm φ x 30 cm each (total column length: 90 cm)

Column temperature: 40°C and flow rate: 0.8 mL/min

Injection volume: 100 µL

Eluent: tetrahydrofuran

Detector: Differential Refractometer (RI)

Standard sample: polystyrene

[0146] <Storage Elastic Modulus, Loss Tangent and Glass Transition Temperature of Pressure Sensitive Adhesive Sheet>

Ten pressure sensitive adhesive sheets were laminated to a thickness of about 1.5 mm, and the laminate thus obtained was used as a sample for measurement. The dynamic viscoelasticity was measured under the following conditions using “Advanced Rheometric Expansion System (ARES)” manufactured by Rheometric Scientific, Inc.

(Measurement Conditions)

Deformation mode: torsion

Measurement Frequency: 1 Hz

Temperature elevation rate: 5°C/minute

5 Shape: parallel plate (7.9 mmφ)

[0147] The shear storage elastic modulus $G'_{25^{\circ}\text{C}}$ at 25°C and the loss tangent $\tan \delta_{70^{\circ}\text{C}}$ at 70 °C were read from the measurement result. The temperature at which the loss tangent ($\tan \delta$) was maximum (peak-top temperature) was defined as the glass transition temperature of the pressure sensitive adhesive sheet.

10 [0148] <Adhesive Strength>

The lightly peelable film was peeled from the pressure sensitive adhesive sheet, the pressure sensitive adhesive sheet was bonded to a 50 μm-thick PET film, and cut to a width of 10 mm and a length of 100 mm. Thereafter, the heavily peelable film was peeled off, and the pressure sensitive adhesive sheet was press-bonded to a glass plate with a 5 kg roller to prepare an adhesive strength measuring sample. The adhesive strength measuring sample was held under an environment at 25°C or 65°C for 30 minutes, and thereafter, using a tensile tester, a test piece was peeled from the glass plate under the condition of a tension speed of 300 mm/minute and a peeling angle of 180° to measure the peeling strength.

20 [0149] <Haze>

The pressure sensitive adhesive sheet was bonded to an alkali-free glass (total light transmittance: 92% and haze: 0.4%) with a thickness of 800 μm to prepare a test piece, and the haze of the test piece was measured with a haze meter (“HM-150” manufactured by MURAKAMI COLOR RESEARCH LABORATORY). A value obtained by subtracting the haze (0.4%) of the alkali-free glass from the measured value was defined as the haze of the pressure sensitive adhesive sheet.

[0150] <Level Difference Followability>

The pressure sensitive adhesive sheet was cut to a size of 75 mm × 45 mm, the lightly peelable film was peeled from the pressure sensitive adhesive sheet. Using a roll laminator (inter-roll pressure: 0.2 MPa and feeding speed: 100 mm/minute), the pressure sensitive adhesive sheet was bonded to the center of a 125 μm-thick PET film cut to a size of 100 mm × 50 mm. Thereafter, the heavily peelable film was peeled from the pressure sensitive adhesive sheet, and a 500 μm-thick glass plate (100 mm × 50 mm) printed with a

black ink (print thickness: 25 μm or 40 μm) in a frame pattern on the peripheral edge portion was bonded to the pressure sensitive adhesive sheet by a roll laminator (inter-roll pressure: 0.2 MPa and feeding speed: 100 mm/minute). The ink-printed region of the glass plate extended over 5 mm from both ends in the short-side direction and 15 mm from the both ends in the long-side direction, and the black ink layer was in contact with the region of 5 mm from the ends of the four sides of the pressure sensitive adhesive sheet. The sample was treated in an autoclave (50°C, 0.5 MPa) for 30 minutes. The vicinity of the boundary of the black ink printed-region was observed with a digital microscope at a magnification of 20 times to examine presence or absence of bubbles. For each of samples with a black ink print thickness of 25 μm and 40 μm , level difference followability was evaluated in accordance with the following criteria.

Excellent: There were no bubbles at any position on the entire circumference.

Good: There were bubbles at one of the four corners, and there were no bubbles on any of the four sides.

Fair: There were bubbles at two of four corners, or on one or more of the four sides.

[0151] <Processability>

The lightly peelable film was peeled from the pressure sensitive adhesive sheet, the pressure sensitive adhesive sheet was bonded to a 100 μm -thick PET film ("COSMOSHINE A4100" manufactured by Toyobo Co., Ltd.), and the resulting product was punched from the PET film-side using a press machine to prepare a sample for evaluation of the processability. The sample was left standing in an atmosphere at a temperature of 23°C and a relative humidity of 50% for 1 week, the heavily peelable film was then peeled, and whether or not glue missing occurred was visually checked. A sample in which no glue missing was observed was evaluated as "Good", and a sample in which glue missing was observed was evaluated as "Fair".

[0152] <Interlayer Adhesiveness>

(Preparation of Test Sample)

The pressure sensitive adhesive sheet was cut to a size of 75 mm $\times$ 45 mm, the lightly peelable film was peeled from the pressure sensitive adhesive sheet, and the pressure sensitive adhesive sheet was bonded to the center of an ink-printed layer-free 500 μm -thick flat glass plate (100 mm $\times$ 50 mm) by a roll laminator (inter-roll pressure: 0.2 MPa and feeding speed: 100 mm/minute). The heavily peelable film was peeled from the pressure sensitive adhesive sheet, and a 500 μm -thick glass plate printed with a 30 μm -

thick black ink in a frame pattern on the peripheral edge portion (50 mm × 100 mm, the ink-printed region is identical to that used in the level difference absorbency test) was bonded to the pressure sensitive adhesive sheet by vacuum pressure-bonding (surface pressure: 0.3 MPa, pressure: 100 Pa). The ink-printed region of the glass plate extended over 5 mm from both ends in the short-side direction and 15 mm from the both ends in the long-side direction, and the black ink layer was in contact with the region of 5 mm from the ends of the four sides of the pressure sensitive adhesive sheet. The sample was treated in an autoclave (50°C, 0.5 MPa) for 30 minutes.

[0153] The sample was held under an environment at 60°C for 30 minutes, and a 200 µm-thick polystyrene sheet was then inserted between two glass plates to a distance of 1 mm from the end portion of the pressure sensitive adhesive sheet as shown in FIG. 7A, and was held for 10 seconds. The end portion of the pressure sensitive adhesive sheet was observed with a digital microscope at a magnification of 20 times. A sample suffering from generation of streaky bubbles (see FIG. 7B) or delamination between the glass plate and the pressure sensitive adhesive sheet was rated “Fair”, and a sample which did not suffer from either generation of bubbles or delamination was rated “Good”.

[0154] <Impact Resistance>

A test sample was prepared in the same manner as in the above-described preparation of an interlayer adhesiveness test sample except that the size of the ink-printed layer-free flat glass plate was changed to 100 mm × 70 mm. The glass plate was bonded to both surfaces of the pressure sensitive adhesive sheet, treatment was performed in an autoclave, and the pressure sensitive adhesive was cured. As shown in FIG. 8, both ends of the test sample 95 in the short side direction were placed on tables 93 disposed with a distance of 60 mm therebetween in such a manner that the ink-printed layer-free glass plate 7 was situated on the lower side, and the upper surface of the end portion of the ink-printed layer-free glass plate 8 was fixed on a table 80 with a pressure sensitive adhesive tape (not shown). The test sample 95 fixed on the tables 93 with the pressure sensitive adhesive tape was held under an environment at -5°C for 24 hours, and then taken out into an environment at room temperature, and after 40 seconds or less, a metal ball 97 having a mass of 11 g was dropped from a height of 300 mm to the glass plate 7 to conduct an impact resistance test.

[0155] In the impact resistance test, a cylindrical guide 99 was used for maintaining consistency of the drop position of the metal ball, and the metal ball 97 was dropped to a

position at a distance of 10 mm in each of the short side direction and the long side direction from the inner edge corners of the frame of the printed region of the printed layer 76. Two tests were conducted. A sample in which the glass plate was not peeled in any of the tests was rated “Good”, and a sample in which the glass plate was peeled in one or both of the two tests was rated “Fair”.

[0156] [Evaluation Results]

The composition of pressure sensitive adhesive compositions used for preparation of each pressure sensitive adhesive sheet and evaluation results of the pressure sensitive adhesive sheet are shown in Tables 1 and 2. In Table 1 and 2, the components are represented by the following abbreviations.

<Acryl-based Monomer>

2HEA: 2-ethylhexyl acrylate

BA: butyl acrylate

CHA: cyclohexyl acrylate

NVP : N-vinyl-2-pyrrolidone

4HBA : 4-hydroxybutyl acrylate

[0157] <Urethane Diacrylate>

UN-350: “ART RESIN UN-350” manufactured by Negami Chemical Industrial Co., Ltd. (polyester urethane diacrylate having a weight average molecular weight of about 12500)

UN-350ND: “ART RESIN UN-350NDTN011” manufactured by Negami Chemical Industrial Co., Ltd. (polyester urethane diacrylate having a weight average molecular weight of about 7,600)

UN-350MU: “ART RESIN UN-350MU” manufactured by Negami Chemical Industrial Co., Ltd. (polyester urethane diacrylate having a weight average molecular weight of about 25,000)

UV-3305B: “SHIKO UV-3305B” manufactured by The Nippon Synthetic Chemical Industry Co., Ltd. (polyether urethane diacrylate having a weight average molecular weight of about 12,000)

UT-6957: “SHIKO UT-6957” manufactured by The Nippon Synthetic Chemical Industry Co., Ltd. (polyether urethane diacrylate having a weight average molecular weight of about 15,000)

UV-3010B: “SHIKO UV-3010B” manufactured by The Nippon Synthetic Chemical

Industry Co., Ltd. (polyester urethane diacrylate having a weight average molecular weight of about 11,000)

<Urethane Monoacrylate>

5 UA-2334: “NK-Oligo UA-2334PHB” manufactured by Shin-Nakamura Chemical Co., Ltd. (polyether urethane monoacrylate having a weight average molecular weight of about 20,000)

<Polyfunctional Acrylate>

 HDDA: hexanediol diacrylate

Table 1

[illegible]

[0159] Table 2

Composition		Example 14	Example 15	Example 16	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6
Prepolymer Composition	2EHA	-	-	-	-	-	-	-	-	-
	BA	78	78	67	78	78	78	78	78	67
	CHA	-	-	14	-	-	-	-	-	14
	NVP	16	16	-	16	16	16	16	16	-
	4HBA	6	6	9	6	6	6	6	6	9
	2EHA	10	10	-	-	-	-	-	-	-
	NVP	3	3	12	3	3	3	3	3	12
	4HBA	-	-	-	8	8	8	8	8	-
	UN-350	5	3	4	2	0.5	-	-	-	5
	UN-350ND	-	-	-	-	-	-	-	-	-
Urethane Diacrylate	UN-350MU	-	-	-	-	-	-	2	-	-
	UV-3305B	-	-	1	-	-	-	-	-	5
	UT-6957	-	-	-	-	-	-	-	-	-
	UA-2234	-	-	-	-	-	-	-	15	-
Polyfunctional Acrylate	HDDA	-	-	-	-	-	0.1	-	-	-
Acryl Oligomer		5	5	5	5	5	5	5	5	5
Chain Transfer Agent	NOFMER MSD	0.20	0.20	0.20	-	0.20	0.10	0.10	0.10	0.20
Tg (°C)		-6	-5	-4.7	-2.1	-3.5	-4.2	-4.4	-4.7	-5
G'25°C (kPa)		200	200	160	200	210	210	220	130	200
tan $\delta_{70^\circ\text{C}}$		0.48	0.69	0.31	0.20	0.71	0.30	0.56	0.90	0.10
Adhesive Strength (N/10mm)		10.5	14.8	14.4	6.4	11.2	5.2	11.7	24.8	10.0
Gel Fraction (%)		62	40	65	82	13	83	26	20	81
Mw of Sol Component ($\times 10^4$)		18	20	17	43	21	34	36	38	17
Haze (%)		0.4	0.3	0.3	0.2	0.2	0.2	1.8	0.2	0.4
Level Difference Followability	40 μm	Excellent	Excellent	Good	Fair	Excellent	Fair	Excellent	Excellent	Fair
	25 μm	Excellent	Excellent	Good	Good	Excellent	Good	Excellent	Excellent	Fair
Interlayer Adhesiveness		Good	Good	Good	Good	Good	Good	Fair	Fair	Good
Processability		Good	Good	Good	Good	Fair	Good	Fair	Fair	Good
Drop Impact Resistance		Good	Good	Good	Fair	Good	Good	Good	Good	Good
Evaluation										

[0160] As shown in Tables 1 and 2, all the pressure sensitive adhesives in Examples were excellent in adhesiveness and processability, and had excellent level difference followability and excellent drop impact resistance.

[0161] In Examples 1 to 4, as the amount of the chain-transfer agent in the post-addition was reduced, the gel fraction and the molecular weight of the sol component increased, and the $\tan \delta_{70^{\circ}\text{C}}$ decreased. In Example 4 in which the amount of the chain-transfer agent was 0.03 parts by weight, level difference followability was lower than in other Examples. In Comparative Example 1 in which no chain-transfer agent was added, the gel fraction was more than 80%, the glass transition temperature was high, and level difference followability and drop impact resistance were low.

[0162] In Examples 5 and 6 in which the amount of the urethane diacrylate was larger than in Example 1, the gel fraction was increased, and the $\tan \delta_{70^{\circ}\text{C}}$ was decreased. In Examples 12 and 13, the kind of the urethane diacrylate was changed, and comparison between Examples 12 and 13 also showed that the gel fraction tended to increase and the $\tan \delta_{70^{\circ}\text{C}}$ tended to decrease as the amount of the urethane diacrylate was increased. In Example 16 and Comparative Example 6, the composition of the polymer was changed, and comparison between Example 16 and Comparative Example 6 also showed a similar tendency. In Comparative Example 6 in which the amount of the urethane diacrylate was large, level difference followability was poor.

[0163] In Example 7 in which the amount of the urethane diacrylate was small, the gel fraction was lower than in Example 1, and the $\tan \delta_{70^{\circ}\text{C}}$ was larger than in Example 1. In Comparative Example 2 in which the amount of the urethane diacrylate was further small, the gel fraction was reduced to 13%, and the processability was insufficient.

[0164] In Example 8 in which a polyfunctional acrylate was used as a polyfunctional monomer in combination with the urethane diacrylate, excellent characteristics similar to those in other Examples were exhibited. In Comparative Example 3 in which no urethane diacrylate was used and only the polyfunctional acrylate was used as a polyfunctional monomer, the gel fraction was significantly increased, the $\tan \delta_{70^{\circ}\text{C}}$ was small, and level difference followability was poor. In Comparative Example 5 in which the urethane monoacrylate was used as a component added later, although the amount of the urethane acrylate used was large, an appropriate crosslinked structure was not formed, and therefore the gel fraction and the storage elastic modulus were low, and the interlayer adhesiveness and the processability were poor.

[0165] In comparing Examples 9, 10, and 11 in which a urethane diacrylate having a relatively low molecular weight was used with Examples 6, 1, and 7 in which a urethane diacrylate having a relatively high molecular weight was used, the smaller the molecular weight of the urethane diacrylate was, the smaller the $\tan \delta_{70^\circ\text{C}}$ tended to be. In Comparative Example 4 in which a urethane diacrylate having a further large molecular weight was used, the interlayer adhesiveness and the processability deteriorated. In Comparative Example 4, the haze of the pressure sensitive adhesive sheet was increased, and the transparency was poor. It is considered that the deterioration of the transparency is caused by decrease in the compatibility between the main skeleton structure of the base polymer and the urethane segment forming a crosslinked structure.

[0166] From the results of Examples and Comparative Examples described above, it is found that a pressure sensitive adhesive sheet having characteristics such as level difference followability and impact resistance is obtained by adjusting the composition and the crosslinked structure of the base polymer and setting the gel fraction, the shear storage elastic modulus $G'_{25^\circ\text{C}}$ at normal temperature, and the loss tangent $\tan \delta_{70^\circ\text{C}}$ at high temperature within specific ranges.

DESCRIPTION OF REFERENCE CHARACTERS

[0167]	5, 51, 53	pressure sensitive adhesive sheet
20	21, 22, 23, 24	release film
	59	transparent film substrate
	3	polarizing plate
	4	pressure sensitive adhesive sheet
	6	image display cell
25	10	image display panel
	7	front transparent plate
	9	housing
	202, 206	image display device

CLAIMS

1. A pressure sensitive adhesive sheet in which a pressure sensitive adhesive comprising a based base polymer having a crosslinked structure, wherein
5 the pressure sensitive adhesive sheet has the following properties:
 - a shear storage elastic modulus of 0.16 MPa or more at a temperature of 25°C;
 - a loss tangent of 0.25 or more at a temperature of 70°C;
 - a glass transition temperature of -3°C or lower; and
 - a gel fraction of 30 to 80%.
- 10 2. The pressure sensitive adhesive sheet according to claim 1, having a haze of 1% or less.
3. The pressure sensitive adhesive sheet according to claim 1 or 2, having a
15 polymerization ratio of 95% or more.
4. The pressure sensitive adhesive sheet according to any one of claims 1 to 3, wherein a weight average molecular weight of sol component is 150,000 to 450,000.
- 20 5. The pressure sensitive adhesive sheet according to any one of claims 1 to 4, wherein the base polymer is an acryl-based polymer containing an acryl-based polymer chain having a crosslinked structure.
6. The pressure sensitive adhesive sheet according to claim 5, wherein
25 in the acryl-based polymer chain, based on an amount of total constituent monomer component, an amount of (meth)acrylic acid alkyl ester is 50% by weight or more, and a total of an amount of hydroxy group-containing monomer and an amount of nitrogen-containing monomer is 15 to 45% by weight.
- 30 7. The pressure sensitive adhesive sheet according to claim 5 or 6, wherein the base polymer includes an acryl-based polymer in which a crosslinking by a urethane-based segment is introduced into an acryl-based polymer chain.

8. The pressure sensitive adhesive sheet according to claim 7, wherein the urethane-based segment has a weight average molecular weight of 5,000 to 30,000.

9. The pressure sensitive adhesive sheet according to claim 7 or 8, wherein the
5 urethane-based segment is polyester urethane.

10. The pressure sensitive adhesive sheet according to any one of claims 7 to 9, wherein in the acryl-based polymer, a content of the urethane-based segment based on 100 parts by weight of the acryl-based polymer chain is 0.3 to 10 parts by weight.

10

11. The pressure sensitive adhesive sheet according to any one of claims 7 to 10, wherein the acryl-based polymer includes a copolymer of an (meth)acrylic acid alkyl ester and a urethane (meth)acrylate having a (meth)acryloyl group at a terminal.

15 12. A method for manufacturing the pressure sensitive adhesive sheet set forth in any one of claims 5 to 11,
the method comprising:

applying a composition onto a substrate in a layer shape; and

thereafter irradiating the composition with an active ray to photocure the

20 composition,
wherein

the composition contains: an acryl-based monomer and/or a partially polymerized product thereof; and a polyfunctional monomer having two or more (meth)acryloyl groups in one molecule.

25

13. The method for manufacturing the pressure sensitive adhesive sheet according to claim 12, wherein the polyfunctional monomer is a urethane di(meth)acrylate having a (meth)acryloyl group at both terminals.

30 14. An image display device comprising: an image display panel; and a front transparent member arranged on a viewing-side surface of the image display panel,
wherein

the front transparent member is fixed on the image display panel with the pressure

sensitive adhesive sheet according to any one of claims 1 to 11 being interposed therebetween.