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(54) Title: UV-CURED HOT MELT PRESSURE-SENSITIVE ADHESIVES (57) Abstract <p>The present invention relates to a pressure-sensitive-adhesive copolymer comprising copolymerizable photoinitiator monomers such as benzoin compounds, acyloin compounds, and mixtures thereof; low-glass-transition-temperature monomers; and multifunctional monomers. The invention also provides a process for the preparation of such copolymers. The actinic radiation cure of the polymer is performed with light at about 240 to about 410 nm wavelength, a light intensity of about 6 to about 10 kWatts/m², and at a temperature of about 45 °C to about 125 °C, under aerobic conditions. The resultant pressure-sensitive adhesives exhibit cohesive strength and high-temperature shear strength which, in a static shear test, does not fail after several thousand minutes; a tack performance of about 300 to about 500 N/m; a peel adhesion performance of about 550 to about 650 N/m; a shelf-life at room temperature of more than about 10 months, with little or substantially no increase in the viscosity of the polymer; and a hot melt pot-life at 100 °C of at least 10 days, with little increase in the viscosity of the polymer.</p>		

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10 UV-CURED HOT MELT PRESSURE-SENSITIVE ADHESIVES

Field of the Invention

This invention is related to photo-curable, pressure-sensitive adhesives.

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Background of the Invention

High-performance pressure-sensitive adhesives (PSAs) are normally characterized by the ability of the adhesive to withstand creep or shear deformation at high loadings and/or high temperatures while exhibiting adequate tack and peel adhesion properties.

This balance of properties is derived from the polymer structure of the PSA. Such polymers are characterized by a high-molecular weight to provide the necessary resistance to shear deformation and by a low modulus of elasticity of the polymer backbone to allow the polymer to conform to a substrate surface upon contact. Certain surface energy and polarity requirements must also be satisfied for a good bond to form between the adhesive and the substrate.

The desired high molecular weights can be obtained either by primary polymerization of monomers to form long-chain-length backbones, or by crosslinking of pre-existing primary polymer chains.

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1 The PSA polymer backbone should consist of
material of low enough modulus or high enough compli-
ance to make a good contact with the adherent at the
application temperature. This condition is normally
5 satisfied by the use of material of low glass-transi-
tion temperatures (Tg's), such as polymers or copoly-
mers of 2-ethyl-hexylacrylate, iso-octylacrylate,
butylacrylate, ethylacrylate, methylacrylate, or the
like.

10 Frequently, small amounts of other types of
monomers are incorporated to modify the polarity, the
rheological and surface properties of the polymer,
such as acrylic acid, maleic acid, β -carboxyethylacr-
ylate, esters of methacrylic acid, laurylacrylate,
15 stearylacrylate, styrene, dibutylfumarate,
dioctylmaleate, dioctylfumarate, vinylacetate, or the
like.

Resistance to creep or shear deformation in a
high-performance PSA is normally the result of a high
20 internal cohesive strength. This condition can
usually be obtained from a high primary polymer
molecular weight. However, if the internal cohesive
strength imparted by the polymer is insufficient,
high internal cohesive strength can also be obtained
25 by incorporating, into the polymer body, a high
degree of interchain hydrogen bonding, ionic associa-
tion, or covalent crosslinking.

With hot melt PSAs, crosslinking the adhesive by
radiation after coating is one of the preferred
30 methods of incorporating high cohesive strength. The
conversion of a fluid which flows and coats out well,
into a non-flowing viscoelastic material can be done
with better control by radiation crosslinking than by
thermochemical means.

35 In order for a polymer to be crosslinkable by UV
radiation, the polymer needs to carry vinyl
unsaturation which, in the presence of small amounts

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1 of added multi-vinyl-functional monomers and a
photoinitiator, would respond to vinyl addition
polymerization upon UV radiation. The combination of
vinyl unsaturation on the polymer and multi-vinyl-
5 functional monomers leads to very poor melt pot
lives; polymer gelation in only an hour at the melt
temperature is not uncommon with hot melt PSA formu-
lations.

Crosslinking by UV radiation of a polymer
10 without vinyl unsaturation is also possible when a
peroxy compound is present in addition to the multi-
vinyl-functional monomer and photoinitiator. Peroxy
compounds which have been used are benzoylperoxide
and t-butylperbenzoate. However, once again, the pot
15 lives of the unfunctionalized hot melt polymer in the
presence of the peroxy compound and multi-vinyl-
functional monomers are very short, i.e., of the
order of an hour at the melt temperature.

U.S. Patent No. 4,181,752 discloses the manufac-
20 ture of PSAs in web polymerization of a polymer-
monomer syrup by UV irradiation. To form polymer
molecules of sufficiently high molecular weights, the
UV energy of 300 and 400 nm wavelength is supplied at
low intensities, 0.001 to 0.070 kWatts/m² while
25 maintaining the web temperature below 35°C. In an
on-web-syrup polymerization, the low UV intensity
requirement necessitates that cure takes place at
relatively low web speeds of about 2 inches per
minute to 2 feet per minute. However, this irradiation
30 is preferably carried out under anaerobic
conditions thus requiring an atmosphere control
system.

U.S. Patent No. 4,052,527, discloses a method of
production of UV crosslinkable hot melt pressure-
35 sensitive adhesives which contain photoinitiators of
the 3-(chlorinated aryloxy)-2-hydroxypropyl acrylates
or methacrylates. The photoinitiators were copoly-

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1 merized into acrylic polymers and which contained
other modifying monomers such as vinylics, and were
made in solution, emulsion, or in bulk. When not
made in bulk, the solvent medium is vacuum-stripped
5 so that the polymer can be coated as a melt between
120°C and 180°C. UV cure is obtained from commercial
medium-pressure lamps of 200 Watts per inch intensi-
ty. However, multiple passes under the UV lamp are
required to obtain moderate increases in shear
10 strengths, e.g., improvement of room-temperature
shears from 4 minutes before UV cure to only 0.5 hour
shear after passing 15 times under the UV lamp, 1.5
hour shear after 25 passes, and 3.5 hours shear after
35 passes under the UV lamp.

15 U.S. Patent No. 4,144,157 and DE 27-43-979
discloses the UV crosslinkability of acrylic pres-
sure-sensitive adhesives which were exemplified by
polymers which are made in and coated out of solu-
tion, or when made in bulk are to be coated out of
20 solution. The pressure-sensitive-adhesive materials
are UV-cross- linkable to high shear strengths,
because of copolymerizable photoinitiators in the
pressure-sensitive adhesive polymer which belong to
a class of (2-alkoxy,2-phenyl-2-benzoyl)ethyl 2-
25 acrylates or methacrylates and the acrylate or
methacrylate of benzoin or its derivative. The UV
cure is obtained by radiation from high-pressure
mercury lamps or burners, with very-high-intensity
outputs of from one lamp of 900 Watts to four lamps
30 of 2000 Watts each. Despite the use of high-intensi-
ty, high-pressure mercury lamps, the pressure-sensi-
tive-adhesive material needs relatively high UV
dosages of at least about 10 kJ/m² before high shear
strengths can be obtained in the adhesive. The
35 admixture of reactive crosslinking agents such as
multifunctional acrylic monomers to the pressure-
sensitive-adhesive material prior to coating and UV

- 1 cure is explicitly discouraged to prevent poor shelf stability of the coater-ready material.

U.S. Patent No. 4,281,152 describes the synthesis of benzophenone derivatives which are copolymerizable into a polymer backbone by way of acrylic functional groups. The benzophenone derivatives are useful as a component in UV-curable resin compositions and in anaerobic thermosetting adhesive compositions.

- 10 U.S. Patent No. 4,672,079 describes a method of manufacturing polystyrene derivatives with UV-activatable functional groups, and the use of these compounds in the photopolymerization of monomer or oligomer mixtures with ethylenic unsaturation for use
15 in wood paints, paper lacquers, printing inks, engraving printed and integrated circuits, fabric printing, and the like, but not for pressure-sensitive adhesives.

- European Patent Application No. 87-304396.2 and
20 U.S. Patent No. 4,737,559 describe the synthesis and the use of benzophenone and acetophenone photoinitiator derivatives, which are copolymerizable into a copolymer backbone by acrylic or acrylamide functional groups for use in adhesive compositions for
25 human skin contact application. A pressure-sensitive adhesive is described which is a copolymer of acrylic monomers and the ketone derivative, by means of which the copolymer can be UV-crosslinked. The amount of crosslinking ketone comonomer and the degree of
30 polymerization of the copolymer are controlled, to obtain the right creep compliance value for an enhanced level of initial adhesion when applied to the skin, but resist objectionable adhesion build-up over time.

- 35 DE 35-12-179 and DE 35-34-645 describe the conversion of phenyl(2-hydroxy-2-propyl)ketone (DAROCUR 1173), and similar acyloin compounds into

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1 copolymerizable acrylated or methacrylated deriva-
tives. The use of these copolymerizable
photoinitiators in coatings and ink compositions give
products, upon UV curing, which are free of odors and
5 other low molecular weight photoinitiation material.

Baeumer et al. from E. Merck, in a marketing
publication, described the usefulness of the above
functionalized photoinitiators in UV-cured hard
coating compositions which do not give off solvent
10 extractables or low-molecular-weight photochemical
products, which ooze to the surface of the cured
coatings. No application of these photoinitiators is
claimed in the UV cure of pressure-sensitive adhe-
sives.

15 J. P. Guarino and J. P. Ravijst, Journal of
Radiation Curing, July 1988, disclose the use of
copolymerizable photoinitiators in coating composi-
tions which emit very low levels of odor upon UV
curing. No application is mentioned for UV-curable
20 pressure-sensitive adhesives.

Therefore, there exists a need for a PSA which
is UV-curable and which has a long shelf-life and a
long hot melt pot life, even in the presence of
multifunctional monomers, but which retains cohesive
25 strength, high-temperature shear strength, and tack
and peel adhesion performance. It is also desirable
that the UV curing be performed using conventional
lamps and in an atmosphere of air.

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1 Summary of the Invention

 The present invention relates to a pressure-sensitive-adhesive copolymer comprising at least one copolymerizable photoinitiator monomer, at least one
5 low-glass-transition-temperature monomer, and at least one multifunctional monomer and to a process for preparing such polymers.

 The actinic radiation cure of the polymer is performed with light at about 240 to about 410 nm
10 wavelength, light intensity of about 6 to about 10 kWatts/m², and temperature of about 45°C to about 125°C, under aerobic conditions. The resultant pressure-sensitive adhesives exhibit cohesive strength and high-temperature shear strength which,
15 when put to a static shear test, do not fail after several thousand minutes; tack performance of about 300 to about 500 N/m; peel adhesion performance of about 550 to about 650 N/m; a shelf-life at room temperature of more than about 10 months, with no
20 increase in the viscosity of the polymer; and a hot-melt pot-life at 100°C of at least 10 days, with little or substantially no increase in the viscosity of the polymer.

 The copolymerizable photoinitiator monomers for
25 use in the present invention are selected from the group consisting of benzoin compounds, acyloin compounds, and mixtures thereof, and, in a preferred embodiment of the invention, are selected from the group consisting of DAROCUR ZLI 3331 and DAROCUR
30 2959.

 The multifunctional monomers for use in the present invention are selected from the group consisting of diethyleneglycoldiacrylate, triethyleneglycoldiacrylate, tripropyleneglycoldiacrylate,
35 diacrylate, 1,6-hexanedioldiacrylate, trimethylolpropanetriacrylate, trimethylolpropanetri-

1 methacrylate, pentaerythritoltriacylate, and mix-
tures thereof.

The low-glass-transition-temperature monomers
for use in the present invention are selected from
5 the group consisting of 2-ethylhexylacrylate, iso-
octylacrylate, butylacrylate, and mixtures thereof.

Other compounds such as acrylic acid, maleic
acid, β -carboxyethylacrylate, esters of methacrylic
acid, laurylacrylate, stearylacrylate, styrene,
10 dibutyl- fumarate, dioctylmaleate, dioctylfumarate,
and vinylacetate are added to the polymer to modify
the properties of the polymer.

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1 Brief Description of the Drawings

 These and other features and advantages of the
present invention will become better understood with
reference to the following description, appended
5 claims, and accompanying drawings, wherein:

 FIG. 1 is a graph of looptrack vs UV dosage for
polymer-2.

 FIG. 2 is a graph of peel adhesion vs. UV dosage
for polymer-2.

10 FIG. 3 is a graph of melt viscosity at 100°C vs
heating period at 100°C for polymer-4.

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1 Detailed Description

The present invention relates to high-performance, UV-cured, essentially acrylic-based, pressure-sensitive adhesives which can be in the form of hot
5 melts, solution adhesive compositions, or emulsion adhesives, and to methods for their manufacture.

The adhesive polymer compositions comprise low Tg monomers, such as 2-ethylhexylacrylate, iso-octylacrylate, butylacrylate, or the like. Preferably,
10 the low Tg monomer is present in an amount of from about 40% to about 60% by weight.

Other types of monomers are incorporated to modify the polarity and the rheological and surface properties of the polymer, such as acrylic acid,
15 methacrylic acid, maleic acid, β -carboxyethylacrylate, esters of methacrylic acid, laurylacrylate, stearylacrylate, styrene, vinyltoluene, dibutylfumarate, dioctylmaleate, dioctylfumarate, vinylacetate, or the like. These monomers are
20 present in an amount of from about 10% to about 40% by weight.

The adhesive polymer contains a copolymerizable photoinitiator sold under the trade name "DAROCUR ZLI 3331" by E. Merck of Darmstadt, Germany, and which is
25 4(2-acryloyloxyethoxy)phenyl-(2-hydroxy-2-propyl)ketone. The acryloyl group makes the molecule copolymerizable with other acrylic and vinylic monomers which make up the body of the adhesive polymer. The photoinitiator activity of DAROCUR ZLI
30 3331 resides in the phenyl(2-hydroxy-2-propyl)ketone moiety of the molecule. A compound with this latter structure is sold under the trade name "DAROCUR 1173" by E. Merck. An additional, related photoinitiator sold under the trade name "DAROCUR 2959" is also sold
35 by E. Merck. This compound is 4(2-hydroxyethoxy)phenyl-(2-hydroxy-2-propyl)ketone.

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1 DAROCUR 2959 can also be made copolymerizable
through the use of methacrylate ester and maleate
halfester compounds. The maleate halfester can be
formed in situ during the copolymerization of the
5 acrylic and vinylic monomers and maleic anhydride in
the presence of DAROCUR 2959. The halfester forma-
tion can be "pushed" to completion by the addition of
a tertiary amine such as N,N,-dimethylbenzylamine at
the termination of the polymerization reaction.

10 The copolymerizable photoinitiator monomer is
present in the range of from 0.1% to 10% by weight,
and preferably from 0.5% to 5% by weight, in the
adhesive copolymer composition.

Another monomeric component which may be added
15 to the polymer composition is one or more vinyl
esters present in a total amount of 0 up to about 20%
by weight based on the total weight of the monomers.
Vinyl esters contain from 2 to about 16 carbon atoms
in the alkyl group of the acid. Representative of
20 the vinyl esters are vinyl acetate, vinyl butyrate,
vinyl propionate, vinyl isobutyrate, vinyl valerate,
vinyl versitate, and the like. Vinyl acetate is
preferred.

The monomer proportions are adjusted in such a
25 way that the adhesive has a glass-transition tempera-
ture of about -30°C or less and at least about 50°C
below the use temperature, giving a good balance of
adhesion and tack at room temperature and low temper-
atures.

30 The present invention is especially suitable for
making hot melt PSAs, which have low melt viscosi-
ties, allowing them to be easily coated out on a web
as a thin film, even by a printing process. Usually,
low melt viscosities are obtained by dilution of the
35 PSA polymer with relatively large quantities of
reactive diluents. However, in the present inven-

1 tion, low melt viscosities are achieved by relatively low initial polymer molecular weight.

The PSA polymers of the present invention are compounded with small amounts of multifunctional
5 acrylates or methacrylates, such as diethyleneglycol-diacrylate (DEGDA), triethyleneglycoldiacrylate (TEGDA), tripropyleneglycoldiacrylate (TPGDA), 1,6-hexanedioldiacrylate (HDODA), trimethylolpropanetriacrylate (TMPTA), trimethylolpropanetrimethacrylate
10 (TMPTMA), pentaerythritoltriacylate (PETA), or the like. The multifunctional acrylates or methacrylates are present in the range of from 0.1% to 10% by weight, preferably from 1% to 5% by weight.

After coating the compounded polymer as a thin
15 film, it can be UV-cured very rapidly with small UV dosages of as low as 3 kJ/m², to produce a PSA of very high cohesive strength and high-temperature shear strength, which retains a good balance of tack and peel performance.

20 The UV radiation in this invention is preferably by conventional, medium-pressure mercury lamps, with emission bands ranging from 240 nm to 410 nm, light intensities from 6 to 10 kWatts/m², and temperatures from 45°C to 125°C at the web surface. Unlike other
25 UV cures, the UV cures of the present invention are performed in an aerobic atmosphere.

Also unlike other PSAs, which contain multifunctional acrylic monomers, the PSAs of the present invention respond readily to UV crosslinking,
30 and the coater-ready hot melt PSA composition has an excellent shelf-life as well as an excellent melt pot-life. Storage of the polymer at room temperature of more than about 10 months results in no increase in the viscosity of the polymer. Similarly, exposing
35 the polymer to 100°C for 10 days results in only a slight increase in the viscosity of the polymer, from

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1 its initial viscosity of 16 Pascal seconds to only 28
Pascal seconds after 10 days at 100°C.

The tack and peel adhesion performance of the
PSAs of the present invention are relatively
5 insensitive to wide variations in the UV irradiation
dosage needed for cure, to variations in the
polymers' initial viscosity, and to levels of added
multifunctional acrylic monomers. The decrease in
tack and peel adhesion upon accelerated aging is also
10 smaller than in conventional UV-cured PSAs.

Polymer Synthesis

In a 1000-5000 ml jacketed resin kettle, which
is equipped with a strong mechanical stirrer,
thermocouple, water-cooled condenser, and nitrogen
15 blanketing, is polymerized a mixture of acrylic and
other vinylic monomers; copolymerizable
photoinitiator; polymerization initiator, which can
be a peroxide or other polymerization initiator such
as those sold under the trade name "VAZO" by DuPont
20 of Wilmington, Delaware; and chain transfer
modulators.

About 10% of the mixture is placed in the
reactor, and the polymerization is allowed to
initiate. Heating of the reacting mix is provided
25 through the jacket from a circulating oil bath.
After the reaction of the initial mixture has
subsided, the remainder of the mix is added to the
reactor, via a metering pump, over a period of 1 to
3 hours, while maintaining the reaction temperature
30 in the range of 80°C to 110°C. The reaction
temperature varies depending on the halflife
temperature of the initiators used.

The polymerization product is sampled for
percent conversion and for melt viscosity
35 measurements. The polymerization product is
immediately compounded with the multifunctional

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- 1 acrylic monomer, inside the reactor, before the product is discharged as coater-ready material.

Adhesive Coating and UV Cure

- 5 The compounded polymer is direct-coated on about 50 μm polyester film at a coating weight ranging from about 30 to about 40 g/m^2 , and is cured by UV radiation from two conventional medium-pressure mercury lamps which have spectral emissions from 240 nm to 410 nm, and light intensities from 6 to 10 kWatts/ m^2 . The coated polyester film is carried on a moving web under the UV radiation source, and the web temperature is from about 45°C to about 125°C. The UV dosage which the coated adhesive film receives is controlled by the UV lamp-intensity setting and web speed. All UV cure is performed in an aerobic atmosphere, and no special precautions to exclude air are required.

- After the adhesive film is cured, it is laminated with a sheet of release liner, for protection, until it is ready for application. When solution adhesives or emulsion adhesives are to be coated and cured, the major portion of the low volatiles are removed from the coated material, before UV cure. The volatiles are removed by placing the coated material in a forced-air oven at about 70°C for about 5 minutes before cure, and, to remove the last traces of low volatiles, for another 15 minutes after cure.

Adhesive Performance Testing

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Looptack

- Samples of the coated adhesive construction are cut in 2.54 cm x about 20 cm test strips. The strips are formed into a loop, which is brought, in an Instron tensile tester, into contact with a standard stainless steel test panel at a rate of about 30 cm/minute, with no other force than the weight of the strip itself. After a brief contact period, the loop

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1 is peeled from the test panel at about 30 cm/minute.
The force to remove the adhesive loop is measured, in
newtons (N)/m. Tests are performed in triplicate.
The possible adhesion failure modes are: panel (p)
5 = no visible stain on panel; panel staining (ps) =
visible stain on panel, but no sticky residue;
cohesive (c) = adhesive film splits during the test,
leaving residue films both on panel and on facestock;
facestock failure (f) = adhesive delaminates
10 completely from facestock; mixed (p/c or p/f) =
failure with mixed p/c or p/f.

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1 180° Peel Adhesion

 Samples were cut in 2.54 cm x about 20 cm test strips, which were rolled down on standard stainless steel test panels with about a 2 kg rubber-clad steel roller, back and forth once at a rate of about 30 cm/minute. After a dwell time of 20 minutes at standard testing laboratory conditions, the test strips were peeled away from the test panel in an Instron tensile tester at 180° to the test panel, i.e., folded back on itself and parallel to the surface of the panel, at a rate of about 30 cm/minute. The force to remove the adhesive test strip from the test panel was measured in N/m. Tests were performed in triplicate. Possible modes of adhesion failures are the same as above.

15 Static Shear

 Samples were cut in 1.27 cm x about 5 cm and 2.54 cm x about 6 cm test strips. When the shear test was performed at room temperature (RTS), the 1.27 cm x 5 cm test strips were applied on a standard stainless steel test panel, making a sample-overlap of 1.27 cm x 1.27 cm with the test panel. The sample portion on the test panel was rolled down with about a 2 kg rubber-clad steel roller, back and forth once at a rate of 30 cm/minute. The free end of the test strip was folded back on itself, and a small hole was made at the free end, where a load of 500 g could be attached during the test.

 The sample's free end can be reinforced with aluminum foil, cardboard, or the like, to prevent the sample from tearing when the load is applied. After a dwell time of at least 20 minutes at standard laboratory testing conditions, the test panels, with the test strips on it, were placed on a rack in a vertical position, and a load of 500 g was attached to the hole at the test strips' free end. The time, in minutes, for the sample to fail and fall off the

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1 panel was measured by means of a timing device. The modes of adhesive failure are recorded as above. Tests were performed in triplicate.

When a sample does not fail after several
5 thousand minutes, without any creeping of the test strip down the test panel surface, it is recorded either as "infinite, NC" or, e.g., "4000+, NC" (NC = no creep).

When the shear test was performed at an elevated
10 temperature (ETS), either at 70°C, 100°C, or at any higher temperature, the 2.54 cm x 6 cm test strips were used, and were applied on the test panels to make a sample-overlap of 2.54 cm x 2.54 cm with the test panel. The rack with panels, test strips, 500
15 g load and timing device are placed in an oven, equipped with a constant-temperature-control mechanism.

Example 1

Polymer Synthesis

20 PSA polymer-1 (P-1) was a control and comprised 58% by weight 2-ethylhexylacrylate, 24% methylacrylate, 10% β -carboxyethylacrylate, and 8% dibutylfumarate. P-1 had a weight-averaged molecular weight (M_w) of 385,000 and a number-averaged molecular
25 weight (M_n) of 66,000, as determined by size exclusion chromatography (SEC). After compounding with 2% by weight of HDODA, P-1 had a 100°C Brookfield melt viscosity of 46.5 pascal seconds (Pa.s.), using the #29 spindle at 10 rpm. It was also compounded with
30 2% by weight of photoinitiator DAROCUR 1173.

PSA P-2 was the test material, made according to the present invention, and comprised 2% by weight of the copolymerizable photoinitiator DAROCUR ZLI 3331, 56% 2-ethylhexylacrylate, 24% methylacrylate, 10% β -
35 carboxyethylacrylate, and 8% dibutylfumarate. P-2 had a M_w 55,000, a M_n = 20,000 by SEC, and a 100°C Brookfield melt viscosity of 10 Pa.s. after

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1 compounding with 2% by weight of HDODA. The compositions of the P-1 and P-2 are summarized in Table I.

Table I

5		<u>P-1</u>	<u>P-2</u>
	2-ethylhexylacrylate	58	56
	methylacrylate	24	24
	β -carboxyethylacrylate	10	10
	dibutylfumarate	8	8
	DAROCUR ZLI 3331	-	2
10	HDODA, compounded after polymerization	2	2

P-2 developed infinite shear (4000+ minutes) after only 3 kJ/m² of UV exposure, whereas the control, P-1, with the conventional photoinitiator, did not form cohesive strength, even with 9 kJ/m² of UV. The results obtained with P-1 and P-2 are summarized in Table II.

Table II

20		<u>UV</u> <u>kJ/m²</u>	<u>Loop-</u> <u>tack</u>	<u>180°</u> <u>Peel</u> <u>(N/m)</u>	<u>RTS</u> <u>(Min.)</u>	<u>70°C</u> <u>ETS</u> <u>(Min.)</u>
	P-1					
	Control	9	540 p/c	1000 c	7 c	0 c
	P-2	0			4 c	0 c
25	P-2	3	500 p		560 p	4000+,NC
	4000+,NC					
	P-2	9	410 p		450 p	4000+,NC
	4000+,NC					

30 c = cohesive, adhesive film splits during the test, leaving residue films both on panel and facestock
 p = no visible stain on panel
 NC = no creep

35 P-2, which was UV crosslinkable by a mechanism using a copolymerizable photoinitiator, was not only unique in its rapid response to UV cure in developing high cohesive strength, but the adhesive performance

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1 in looptack and 180° peel adhesion remained
essentially the same over a wide range of UV
radiation dosage, from 3 to 9 kJ/m². This corresponds
to a web speed variation of about 50 to about 15
5 m/minute on a conventional UV printing press, and
indicates that UV overcure is improbable under these
conditions. FIGs. 1 and 2 illustrate a relatively
flat response of looptack and 180° peel adhesion of
P-2 to UV radiation dosage.

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Example 2Polymer synthesis

Adhesive performance of PSAs which are made
according to the present invention is characterized
by a low sensitivity to variations in the starting
15 polymer viscosity, its formulation, and the UV
irradiation dosage.

The synthesis of P-2 was repeated twice more (P-
2a and P-2b). Due to slightly different polymeriza-
tion conditions, the resultant products exhibited
20 different 100°C melt viscosities -- 35 Pa.s. for the
first repeat, and 65 Pa.s. for the second repeat --
indicating different polymer molecular weights in the
products. The polymers were subsequently compounded
with 1.0% by weight, 1.5% by weight, 2.0% by weight,
25 and 5.0% by weight of HDODA, coated and cured with 3
to 9 kJ/m² of UV. The compositions of the polymers
are summarized in Table III.

Table III

		<u>P-2</u>	<u>P-2</u>	<u>P-2</u>	<u>P-2</u>
30	2-ethylhexylacrylate	56	56	56	56
	methylacrylate	24	24	24	24
	β-carboxyethylacrylate	10	10	10	10
	dibutylfumarate	8	8	8	8
	DAROCUR ZLI 3331	2	2	2	2
	HDODA, compounded				
35	after polymerization	1	1.5	2	5

All samples gave infinite shears, and, despite
the differences in initial melt viscosities,

-20-

1 different levels of HDODA, and different UV dosages,
the looptack and peel adhesion performance were about
the same over the range of these differences. The
results are summarized in Table IV.

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Table IV

Low Dependence of Adhesive Performance
on Starting Polymer Viscosity, Formulation,
and UV Irradiation Dosage

5 (Adhesive coating weight 35-40 g/m² on 2 mil
 PET film; tack, peel, and shear tests
 on stainless steel panels)

		UV kJ/m ²	Loop- tack (N/m)	180° Peel (N/m)	<u>Static Shear</u>	
10	<u>P-2</u>					
	10 Pa.s. at 100°C, 2% HDODA					
	ETS	3	501 p	561 p	Infinite	70°C
	ETS	4.5	453 p	467 p	Infinite	70°C
15	ETS	6	429 p	456 p	Infinite	70°C
	ETS	9	414 p	452 p	Infinite	70°C
	1.5% HDODA					
		4.5	470 p	514 p	Infinite	RTS
20		6	445 p	467 p	Infinite	RTS
		9	396 p	436 p	Infinite	RTS
	1.0% HDODA					
		4.5	486 p	469 p	Infinite	RTS
		6	463 p	434 p	Infinite	RTS
		9	443 p	415 p	Infinite	RTS
25	5.0% HDODA					
		3	545 p	650 p	Infinite	RTS
		6	459 p	475 p	Infinite	RTS
	<u>P-2a</u>					
	35 Pa.s. at 100°C, 2.0% HDODA					
30	ETS	3	519 p	566 p	Infinite	70°C
	ETS	6	453 p	455 p	Infinite	70°C
	<u>P-2b</u>					
	65 Pa.s. at 100°C, 2.0% HDODA					
35	ETS	3	568 p	628 p	Infinite	70°C
	ETS	6	484 p	458 p	Infinite	70°C

-22-

1 ETS = Elevated Temperature Shear; RTS = Room
Temperature Shear; p = All sample failures were
panel failure

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1 Example 3 Post Cure

 Coated and UV-cured adhesives of the present
invention have better aging stability than adhesives
5 which are made by conventional UV curing methods.

 Drawdowns of the PSAs of the present invention
were subjected to an accelerated aging at 60°C over
a period of one week. Table V shows that the drop in
the adhesive's looptack and 180° peel is only about
10 10%-20% from the original values. In conventional
UV-cured PSAs, losses in excess of 50% in these
adhesion properties are very common.

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-24-

Table V

Looptack and Peel Performance after
One Week's Aging at 60°C

(Adhesive coating weight 35-40 g/m² on 2 mil
 PET film; tack, peel, and shear tests
 on stainless steel panels)

	UV, kJ/m ²	<u>Looptack, N/m</u>			<u>180° Peel, N/m</u>		
		<u>Ini- tial</u>	<u>After Aging</u>	<u>%Δ</u>	<u>Ini- tial</u>	<u>After Aging</u>	<u>%Δ</u>
10	<u>P-2</u>						
	10 Pa.s. at 100°C						
	2.0% HDODA	4.5	453	403	11	467	426
	9	6	429	383	11	456	403
							12
15	5.0% HDODA	3	545	498	9	650	493
		6	459	383	17	475	432
	9						
	<u>P-2a</u>						
20	35 Pa.s. at 100°C						
	2.0% HDODA	3	556	488	12	572	540
	6	6	453	392	13	455	449
	1						
	<u>P-2b</u>						
25	65 Pa.s. at 100°C						
	2.0% HDODA	3	568	513	10	628	493
		6	484	459	5	458	408
							11

Example 4In situ Incorporation of Photoinitiator Function

30 Polymer-3 was made according to the present invention. The photoinitiator material used was the alcohol DAROCUR 2959 or 4(2-hydroxyethoxy)phenyl-(2-hydroxy-2-propyl)ketone, which was made copolymerizable through the maleate halfester
 35 compound. The maleate halfester, however, was not made in a separate synthesis step, but was made in

-25-

1 situ during the polymerization of the monomers which
 comprise the PSA material. The following monomers:
 57% by weight of butylacrylate, 4% acrylic acid, 35%
 dioctylfumarate, and 2% maleic anhydride, were
 5 copolymerized in the presence of 2% by weight DAROCUR
 2959, at 90°-95°C, using Vazo 52/64 as polymerization
 initiators. At the end of the polymerization step,
 the maleate halfester formation with the
 photoinitiator alcohol DAROCUR 2959 was completed by
 10 the addition of 0.25% of N,N-dimethylbenzylamine.
 The composition of P-3 is summarized in Table VI.

Table VI

	butylacrylate	57
	acrylic acid	4
	dioctylfumarate	35
15	maleic anhydride	2
	DAROCUR 2959	2
	N,N-dimethylbenzylamine	0.25
	Vazo 52/64 polymerization initiator	
	HDODA, compounded	
	after polymerization	4

20 The product has a 100°C melt viscosity of 30.4
 Pa.s. before compounding. It was subsequently
 compounded with 4% by weight of HDODA and after
 coating on 50 μ m poly-(ethylene terephthalate) (PET)
 at a coating weight of 30 g/m² and UV-cured. The
 25 adhesive performance of the PSA is summarized in
 Table VII.

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1 Table VII

		UV	Loop-	180°	70°C
		<u>kJ/m²</u>	<u>tack</u>	<u>Peel</u>	<u>ETS</u>
			<u>(N/m)</u>	<u>(N/m)</u>	<u>(Min.)</u>
5	P-3	4	407 p/ps	638 c	4000+,NC
		6	315 p	554 c/ps	4000+,NC
		8	402 p	546 p	4000+,NC

c = cohesive, adhesive film splits during the test,

leaving residue films both on panel and
facestock

10 p = no visible stain on panel

ps = visible stain on panel, but no sticky residue

NC = no creep

Example 5

Resistance to Liquid Immersion

15 Coated and UV-cured adhesives of the present
invention exhibit good immersion resistance to a
number of liquids, provided when the facestock
material is not affected by the liquids in the
immersion tests.

20 Polymer P-3 was evaluated for an under-the-hood
automotive labeling adhesive application, where the
labels might be exposed to a number of automotive
liquids. In this evaluation, 2.54 cm x about 20 cm
test samples from the previous illustration were
25 applied to standard stainless steel test panels.
After a dwell time of 24 hours, the panels and
applied test samples were immersed in the automotive
liquids. After the specified times of immersion, the
panels and samples were taken out. The adhering
30 liquids were carefully blotted with filter paper, and
after a 1-hour recovery at ambient, the test strips
were examined for liquid edge penetration and for any
changes to the facestocks. Maximum acceptable edge
penetration is normally no more than 5 mm. Finally,
35 the test strips were peeled away in a 180° peel angle

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- 1 from the test panels. The results are summarized in
Table VIII.

Table VIII

5 Changes to Facestock, Edge Penetration and
Peel Measurements after Exposure of Applied
Labels on Stainless Steel Panels

10	180°Peel N/m	Cure UV kJ/m ²	Change to face- stock and edge	
			<u>penetration</u>	
15	1 hour in gasoline c	4	No change to	764
	at ambient temp. c	6	facestock, 2 mm	741
	c	8	edge penetration	646
20	4 hours in 120°C c	4	No change in	767
	hot engine oil c	6	facestock or	738
	c	8	edge penetration	788
25	4 hours in brake c	4	No change in	785
	fluid at ambient c	6	facestock or	775
	temp. c	8	edge penetration	733

- 25 c = cohesive, adhesive film splits during the test,
leaving residue films both on panel and
facestock

Example 6

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Stable Pot-Lives of Compounded
Hot Melt PSA Formulations

- 35 Polymer-4 was a scale-up of P-3 from 800 g to
6000 g. It had a 100°C melt viscosity of 27.9 Pa.s.
before compounding. It was subsequently compounded
with 4% by weight of HDODA and after coating on 50 µm
PET at a coating weight of 30 g/m², was UV-cured. The

-28-

1 adhesive performance of P-4 is summarized in Table IX.

Table IX

5	UV kJ/m ²	Loop- tack (N/m)	180° Peel (N/m)	70°C ETS (Min.)
P-4	4	462 p	701 c	4000+,NC
	6	391 p	548 p	4000+,NC
	8	295 p	430 p	4000+,NC

c = cohesive, adhesive film splits during the test,
 10 leaving residue films both on panel and facestock.
 p = no visible stain on panel.
 NC = no creep.

Compounded polymers which are made according to
 15 the present invention have very good pot-lives, even when kept at elevated temperatures.

The coater-ready P-4 which contained 4% by weight of HDODA was heated continuously at 100°C in the Thermocell of a Brookfield viscometer, and the
 20 melt viscosity followed over several days. The melt viscosity rose from about 16 Pa.s. to only about 22 Pa.s. after 8 days of continuous heating, after which time it rose quicker to about 29 Pa.s. after 11 days of heating. The results are presented in FIG. 3.

Example 7

25 Polymer-5 was made according to the present invention. It contained 2% by weight of the copolymerizable photoinitiator DAROCUR ZLI 3331, and consisted further of 56% 2-ethylhexylacrylate, 24%
 30 methylacrylate, 3% acrylic acid, 7% β -carboxyethylacrylate, and 8% dioctylmaleate. It was subsequently scaled up to a 100 kilogram batch run, which, after compounding with 4% by weight of HDODA, had a 100°C melt viscosity of 12.0 Pa.s. The
 35 composition of P-5 is summarized in Table X.

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Table X

	2-ethylhexylacrylate	56
	methylacrylate	24
	β -carboxyethylacrylate	7
	acrylic acid	3
5	dioctylmaleate	8
	DAROCUR ZLI 3331	2
	HDODA, compounded after polymerization	4

The scaled-up batch had the following adhesive performance on 50 μ m PET facestock at a coating weight of 30 g/m² and after UV cure. The properties of P-5 are summarized in Table XI.

10

Table XI

	UV kJ/m ²	Loop- tack (N/m)	180° Peel (N/m)	70°C ETS (Min.)
15 Scaled-up				
P-5	4	507 p	663 c	1200+,NC
	6	520 p	677 p/c	1200+,NC
	8	575 p	603 p/c	1200+,NC

c = cohesive, adhesive film splits during the test,

leaving residue films both on panel and facestock

p = no visible stain on panel
NC = no creep

The scaled-up, P-5 coater-ready material was stored in closed, 19-liter metal pails, and was retrieved after 10 months of storage under uncontrolled warehouse conditions. The material had an excellent shelf-life. The 100°C melt viscosity rose only to 12.3 Pa.s. after the 10-month storage period. The material was still very UV-reactive; after coating on 50 μ m PET at 30 g/m² coating weight and UV cure with only 4 kJ/m², it gave infinite 70°C ETS, without any creep.

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Example 8Solution- and Emulsion-Based PSAs

The formation of high cohesive strength in PSAs by UV cure of the present invention is also

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- 1 applicable to solution-based as well as emulsion-based adhesives.

Polymer-6 was made in ethylacetate solution from 52.5% by weight of 2-ethylhexylacrylate, 18% methyl-
 5 acrylate, 18% vinylacetate, 8% dioctylmaleate, 3% acrylic acid, and 0.5% DAROCUR ZLI 3331, using Vazo 52 as the polymerization initiator. The composition of P-6 is summarized in Table XII.

Table XII

10	2-ethylhexylacrylate	52.5
	methylacrylate	18
	vinylacetate	18
	acrylic acid	3
	dioctylmaleate	8
	DAROCUR ZLI 3331	0.5
15	HDODA, compounded after polymerization	4

A portion of the product was evaporated to dryness; it had a 100°C melt viscosity of 136.0 Pa.s. The remainder of the product was subsequently compounded with 4% by weight of HDODA based on the
 20 polymer solids. UV cure developed high cohesive strength in the adhesive coating on 50 µm PET at a dry coating weight of 30 g/m². The properties of P-6 are summarized in Table XIII.

Table XIII

25	UV	Loop-	180°	70°C
	<u>kJ/m²</u>	<u>tack</u>	<u>Peel</u>	<u>ETS</u>
		<u>(N/m)</u>	<u>(N/m)</u>	<u>(Min.)</u>
	P-6	0	770 p	666 c
		4	424 p	710 ps
		6	358 p	501 p/c
30		8	380 p	381 p
				1200+, NC
				1200+, NC

c = cohesive, adhesive film splits during the test,

leaving residue films both on panel and facestock

p = no visible stain on panel

35 ps = visible stain on panel, but no sticky residue

NC = no creep

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1 Example 9

Polymer-7 was made in emulsion and consisted of 55% by weight of 2-ethylhexylacrylate, 20% methylacrylate, 8% dioctylmaleate, 5% acrylic acid, and 1% of DAROCUR ZLI 3331, using Alipal CO-436 (manufactured by Rhone Poulenc/Triton X-165 (manufactured by Union Carbide) as the surfactant, and t-butylhydroperoxide-FeEDTA as the redox initiator system. The product was compounded with 4% by weight of HDODA based on polymer solids. The composition of P-7 is summarized in Table XIV.

Table XIV

	2-ethylhexylacrylate	66
	methylacrylate	20
	acrylic acid	5
15	dioctylmaleate	8
	DAROCUR ZLI 3331	1
	HDODA, compounded after polymerization	4

UV cure developed high cohesive strength in the adhesive coating, on 50 μm PET at a coating weight of 30 g/m^2 . The properties of P-7 are summarized in Table XV.

Table XV

	UV	Loop-	180°	70°C
	kJ/m^2	tack	Peel	ETS
25		(N/m)	(N/m)	(Min.)
P-7	0	244 p	267 c/ps	0 c
	6	135 p	50 p	1200+, NC
	8	137 p	49 p	1200+, NC

c = cohesive, adhesive film splits during the test, leaving residue films both on panel and facestock

30 p = no visible stain on panel
 ps = visible stain on panel, but no sticky residue
 NC = no creep

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1 WHAT IS CLAIMED IS:

1. A pressure-sensitive-adhesive copolymer suitable for the preparation of hot melts, comprising:

5 a) at least one copolymerizable photoinitiator monomer selected from the group consisting of benzoin compounds, acyloin compounds, their derivatives and mixtures thereof;

10 b) at least one low-glass-transition-temperature monomer sufficient to provide a polymer having a T_g as low as about 50°C below the use temperature; and

c) at least one multifunctional monomer, wherein the actinic radiation cure is performed with light at about 240 to about 410 nm wavelength, a light intensity of about 6 to about 10 kWatts/m², and at a temperature of about 45°C to about 125°C, and wherein the resultant pressure-sensitive adhesive has a cohesive strength and high-temperature shear strength that does not fail after several thousand minutes; a tack performance of about 300 to about 500 N/m; a peel adhesion performance of about 550 to about 650 N/m; a shelf-life at room temperature of more than about 10 months, with no increase in the viscosity of the polymer; and a hot melt pot-life at 100°C of at least 10 days, with little or substantially no increase in the viscosity of the polymer.

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2. A pressure-sensitive-adhesive copolymer as recited in claim 1 wherein the low-glass-transition-temperature monomers are selected from the group consisting of 2-ethylhexyacrylate, iso-octylacrylate, butylacrylate, and mixtures thereof.

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1 3. A pressure-sensitive-adhesive copolymer as
recited in claim 1 wherein the copolymerizable
photoinitiator monomers are selected from the group
consisting of 4(2-acryloyloxyethoxy)phenyl-(2-
5 hydroxy-2-propyl)ketone and 4(2-hydroxyethoxy)phenyl-
(2-hydroxy-2-propyl)ketone.

 4. A pressure-sensitive-adhesive copolymer as
recited in claim 1 wherein the copolymerizable
10 photoinitiator monomers are present at a
concentration of about 0.1% to about 10% by weight.

 5. A pressure-sensitive-adhesive copolymer as
recited in claim 1 wherein the copolymerizable
15 photoinitiator monomers are present at a
concentration of about 0.5% to about 5% by weight.

 6. A pressure-sensitive-adhesive copolymer as
recited in claim 1 wherein the multifunctional
20 monomers are selected from the group consisting of
diethylene-glycoldiacrylate, triethyleneglycol-
diacrylate, tripropyleneglycoldiacrylate, 1,6-
hexanedioldiacrylate, trimethylolpropanetriacrylate,
trimethylolpropanetrimethacrylate, pentaeryth-
25 ritoltriacylate, and mixtures thereof.

 7. A pressure-sensitive-adhesive copolymer as
recited in claim 1 wherein the multifunctional
monomers are present at a concentration of about 0.1%
30 to about 10% by weight.

 8. A pressure-sensitive-adhesive copolymer as
recited in claim 1 wherein the multifunctional
monomers are present at a concentration of about 1%
35 to about 5% by weight.

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1 9. A pressure-sensitive-adhesive copolymer as
recited in claim 1 wherein the light is supplied by
medium-pressure mercury lamps.

5 10. A pressure-sensitive-adhesive copolymer as
recited in claim 1 wherein the cure is performed in
an aerobic environment.

10 11. A pressure-sensitive-adhesive copolymer
comprising:

a) at least one copolymerizable
photoinitiator monomer;

b) at least one low-glass-transition-
temperature monomer sufficient to provide a polymer
15 having a Tg as low as about 50°C below the use
temperature; and

c) at least one multifunctional monomer,
wherein the actinic radiation cure is performed under
aerobic conditions.

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12. A pressure-sensitive-adhesive copolymer as
recited in claim 11 wherein the low-glass-transition-
temperature monomers are selected from the group
consisting of 2-ethylhexyacrylate, iso-octylacrylate,
25 butylacrylate, and mixtures thereof.

13. A pressure-sensitive-adhesive copolymer as
recited in claim 11 wherein the copolymerizable
photoinitiator monomers are selected from the group
30 consisting of benzoin compounds, acyloin compounds,
and mixtures thereof.

14. A pressure-sensitive-adhesive copolymer as
recited in claim 13 wherein the copolymerizable
35 photoinitiator monomers are selected from the group
consisting of 4(2-acryloyloxyethoxy)phenyl-(2-

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1 14. A pressure-sensitive-adhesive copolymer as
recited in claim 13 wherein the copolymerizable
photoinitiator monomers are selected from the group
consisting of 4(2-acryloyloxyethoxy)phenyl-(2-
5 hydroxy-2-propyl)ketone and 4(2-hydroxyethoxy)phenyl-
(2-hydroxy-2-propyl)ketone.

 15. A pressure-sensitive-adhesive copolymer as
recited in claim 11 wherein the copolymerizable
photoinitiator monomers are present at a
10 concentration of about 0.1% to about 10% by weight.

 16. A pressure-sensitive-adhesive copolymer as
recited in claim 11 wherein the copolymerizable
photoinitiator monomers are present at a
15 concentration of about 0.5% to about 5% by weight.

 17. A pressure-sensitive-adhesive copolymer as
recited in claim 11 wherein the multifunctional
monomers are selected from the group consisting of
20 diethyleneglycoldiacrylate, triethyleneglycoldi-
acrylate, tripropyleneglycoldiacrylate, 1,6-
hexanedioldiacrylate, trimethylolpropanetriacrylate,
trimethylolpropanetrimethacrylate, pentaeryth-
ritoltriacylate and mixtures thereof.

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 18. A pressure-sensitive-adhesive copolymer as
recited in claim 11 wherein the multifunctional
monomers are present at a concentration of about 0.1%
to about 10% by weight.

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 19. A pressure-sensitive-adhesive copolymer as
recited in claim 11 wherein the multifunctional
monomers are present at a concentration of about 1%
to about 5% by weight.

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1 20. A pressure-sensitive-adhesive copolymer as
recited in claim 11 wherein the light is supplied by
medium-pressure mercury lamps.

5 21. A pressure-sensitive-adhesive copolymer as
recited in claim 11 wherein the copolymer is suitable
for use as a hot melt.

22. A process for preparing a pressure-
10 sensitive-adhesive copolymer suitable for the
preparation of hot melts comprising:

a) copolymerizing at least one low-glass-
transition-temperature monomer in an amount
sufficient to provide a polymer having a Tg as low as
15 about 50°C below the use temperature, at least one
copolymerizable photoinitiator monomer, and a
polymerization initiator;

b) heating the polymerization mixture to
maintain the polymerization reaction;

20 c) adding at least one multifunctional
monomer to the copolymer;

d) coating the copolymer onto a suitable
surface; and

e) curing the coated copolymer with light
25 at about 240 to about 410 nm wavelength, a light
intensity of about 6 to about 10 kWatts/m², and at a
temperature of about 45°C to about 125°C under
aerobic conditions.

30 23. The process as recited in claim 22 wherein
the low-glass-transition-temperature monomers are
selected from the group consisting of 2-
ethylhexyacrylate, iso-octyl- acrylate,
butylacrylate, and mixtures thereof.

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24. The process as recited in claim 22 wherein
the copolymerizable photoinitiator monomers are

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1 selected from the group consisting of benzoin
compounds, acyloin compounds, and mixtures thereof.

25. The process as recited in claim 24 wherein
5 the copolymerizable photoinitiator monomers are
selected from the group consisting of 4(2-
acryloyloxyethoxy)phenyl-(2-hydroxy-2-propyl)ketone
and 4(2-hydroxyethoxy)phenyl-(2-hydroxy-2-
propyl)ketone.

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26. The process as recited in claim 22 wherein
the copolymerizable photoinitiator monomers are
present at a concentration of about 0.1% to about 10%
by weight.

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27. The process as recited in claim 22 wherein
the copolymerizable photoinitiator monomers are
present at a concentration of about 0.5% to about 5%
by weight.

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28. The process as recited in claim 22 wherein
the multifunctional monomers are selected from the
group consisting of diethyleneglycoldiacrylate,
triethylene-glycoldiacrylate, tripropyleneglycol-
25 diacrylate, 1,6-hexanedioldiacrylate,
trimethylolpropanetriacrylate, trimethylolpro-
panetrimethacrylate, pentaerythritoltriacylate, and
mixtures thereof.

30 29. The process as recited in claim 22 wherein
the multifunctional monomers are present at a
concentration of about 0.1% to about 10% by weight.

30. The process as recited in claim 22 wherein
35 the multifunctional monomers are present at a
concentration of about 1% to about 5% by weight.

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1 31. The process as recited in claim 22 wherein
the light is supplied by medium-pressure mercury
lamps.

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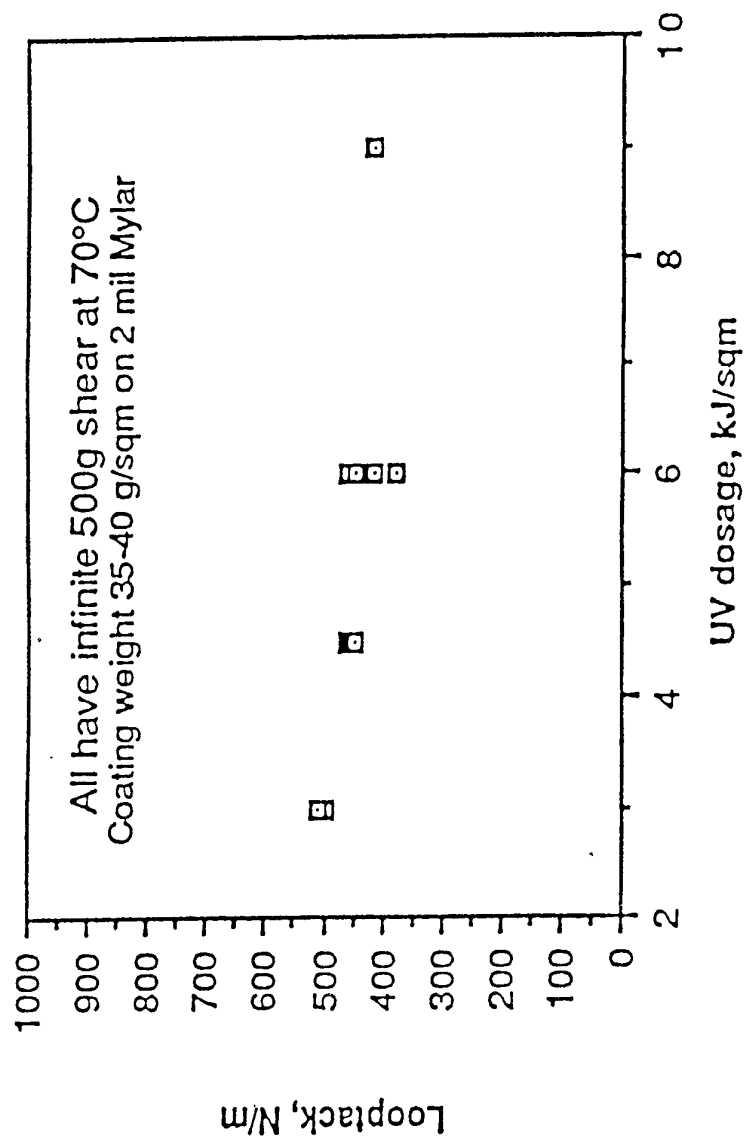
Fig. 1

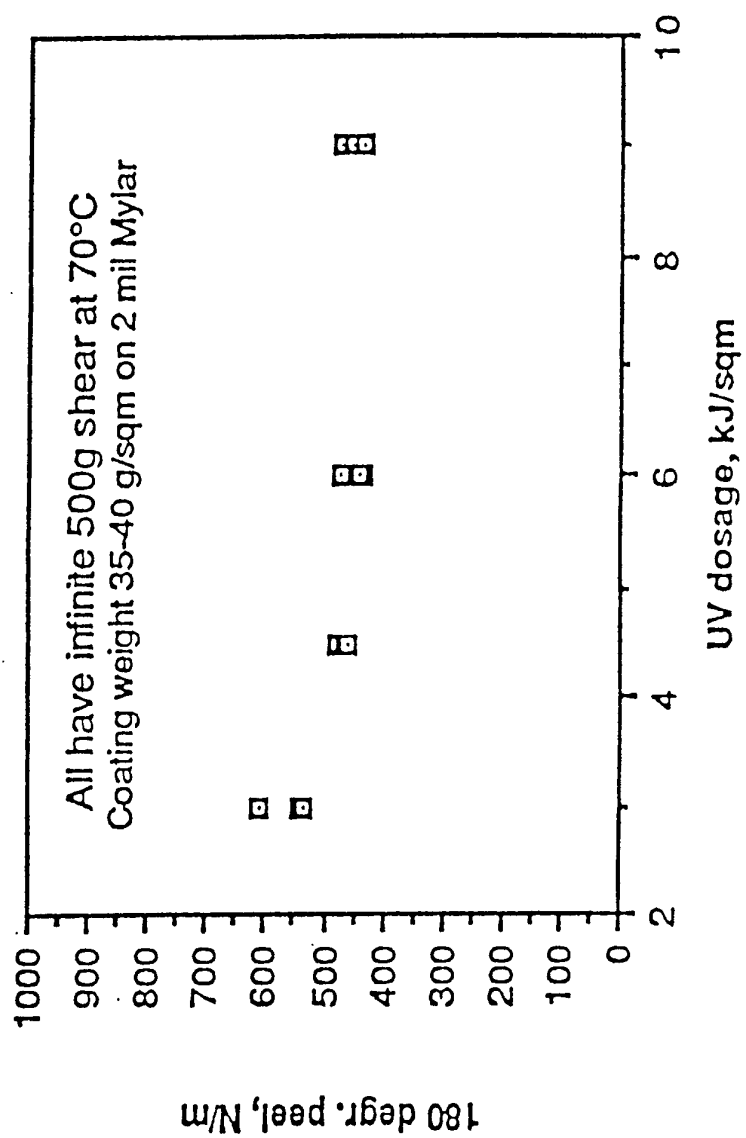
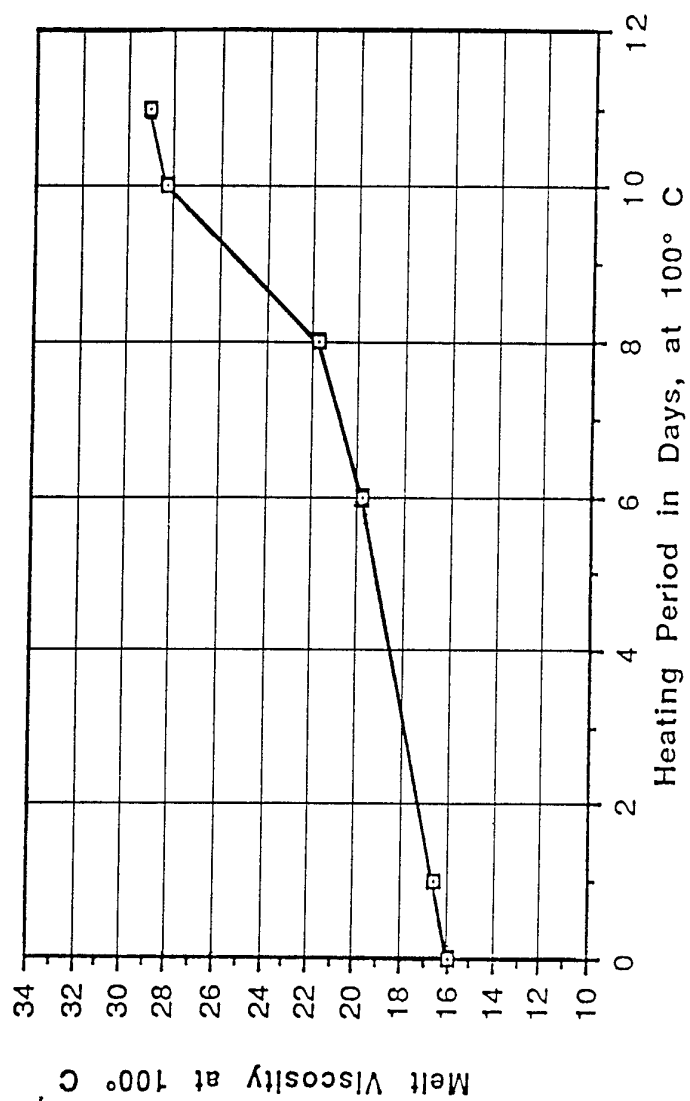
Fig. 2

Fig. 3

INTERNATIONAL SEARCH REPORT

 Int. application No.
PCT/US92/09493
A. CLASSIFICATION OF SUBJECT MATTERIPC(5) : ~~Please See Extra Sheet.~~US CL : ~~522/34,35,42,182,905~~; 526/328,328.5,329.7,935; 528/271.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : ~~522/34,35,42,182,905~~; 526/328,328.5,329.7,935; 528/271.

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
<u>X</u> Y	EP, A, 0,373,662 (SEKISUI KAGAKU KOGYO KABUSHIKI KAISHA) 20 JUNE 1990. See pages 3-4 and page 5, lines 18-27.	<u>1-6,9-17,20,21</u> 7,8,1819,22-31
<u>X</u> Y	US, A, 3,926,639 (ROSEN ET AL) 16 DECEMBER 1975. See columns 2-3, column 4, lines 35-47; column 5, lines 6-32; column 9, lines 13-16, and Example 1.	<u>22,24,25,28,31</u> 1 - 2 1 , 2 3 , 26,27,29,30
<u>X</u> Y	US, A, 4,737,559 (KELLEN ET AL) 12 APRIL 1988. See columns 4-6 and column 7, line 35, to column 8, line 7.	<u>11-13,20,21</u> 1,2,4,5,7- 10,15,16,18,19,2 2-31
<u>X</u> Y	US, A, 4,144,157 (GUSE ET AL) 13 MARCH 1979. See column 2, line 44, to column 3, line 42.	<u>11-13,20-31</u> 1,2,4,5,7-

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be part of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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Date of the actual completion of the international search

14 JANUARY 1993

Date of mailing of the international search report

 Name and mailing address of the ISA/US
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/09493

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Location of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4,914,004 (KOHLER ET AL) 03 APRIL 1990.	2,3,13,14,24,25

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US92/09493

A. CLASSIFICATION OF SUBJECT MATTER:

IPC (5):

C08F 20/18, ~~20/20~~, 2/50, 220/18, 220/20, 216/36; C09J 133/06, 133/08, 133/10.