

# Novel Pyridinium Photoinitiators and Their Applications for the Ultraviolet Crosslinking of Acrylic Pressure-Sensitive Adhesives

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**ABSTRACT:** The demand for ultraviolet (UV)-crosslinkable pressure-sensitive adhesives (PSAs) has rapidly been increasing. A variety of different PSAs containing new photoreactive pyridinium derivatives have been evaluated for their effectiveness in improving adhesion and cohesion in UV-crosslinkable PSAs. PSAs have been evaluated with

respect to the tack, peel adhesion, and shear strength. This article summarizes the breakthrough technology used to achieve better performances in UV-crosslinkable acrylic PSAs. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 558–561, 2007

**Key words:** adhesion; adhesives; crosslinking; shear; strength

## INTRODUCTION

Pressure-sensitive adhesives (PSAs) are nonmetallic materials used to bond other materials, mainly on their surfaces, through adhesion and cohesion.<sup>1</sup> Adhesion and cohesion are phenomena that can be described thermodynamically and chemically, but actually they cannot be measured precisely. The most important bonding processes are bonding by adhesion and bonding with PSAs.<sup>2</sup>

Industrial applications of ultraviolet (UV)-crosslinkable materials have grown tremendously over the past decade. An entire industry has evolved that is based on the existence of chemicals that respond to UV light. The growing success of UV-crosslinking technologies in a wide variety of industrial products and processes can be attributed to the productivity and environmental benefits that result from such technologies.

UV technology is well established in the market and allows the production of a wide range of UV-crosslinkable PSAs with interesting features. The balance between the adhesive strength and cohesive strength within crosslinked coatings is critical for the performance of UV PSAs. The combination of a pattern with UV-crosslinkable adhesives enables the manufacturing of films having zones with different adhesion/cohesion properties and offers novel opportunities to develop innovative tapes with new unique features.<sup>3,4</sup>

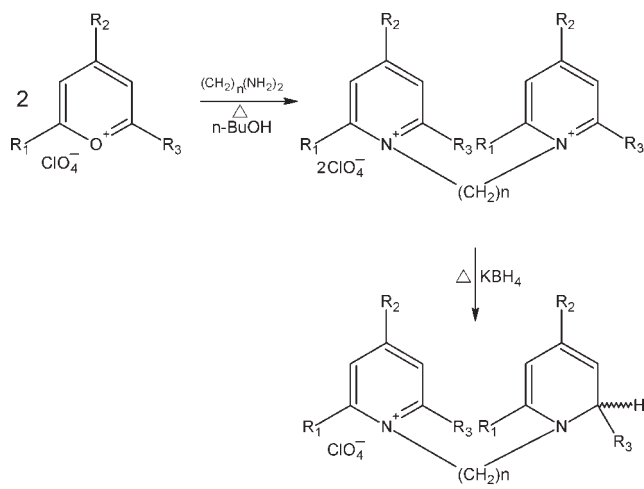
To improve further the performances of these UV-crosslinkable PSAs, pattern crosslinking is a new technology that makes it possible to introduce different levels of crosslinking within the same adhesive coating. The result is a combination of high cohesion and adhesion areas in a PSA film.<sup>5</sup> To get optimal pressure-sensitive performances with UV-crosslinkable adhesives, it is necessary to find process settings that lead to balanced values of the tack, peel, and shear resistance for the desired application.<sup>6,7</sup>

UV-radiation-crosslinkable PSAs are essentially room-temperature crosslinking systems and so lend themselves to the crosslinking of high-temperature coating systems, including calendaring and hot melt coating, for which the use of conventional thermal crosslinking technology is denied.<sup>8</sup>

The UV crosslinking of various coatings is based on the photoinitiation of radical and cationic crosslinking reactions. The UV-crosslinking technique calls for the use of a photoinitiator to be added to the PSA system. The photoinitiator is therefore one of the key components in UV crosslinking, and the outcome of such a polymerization is critically dependent on the choice of the photoinitiator, including its chemical nature and amount. As previously mentioned, a photoinitiator is one of the important and necessary constituents in the UV crosslinking of PSAs.<sup>9,10</sup> For this reason, the activity of a photoinitiator is one of the more important properties that must be considered when a photoinitiator is chosen because of the important advantages of these adhesives.

UV-crosslinkable acrylic PSAs are currently being used in tapes, labels, decorative banners, protective

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	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	n
<b>3b</b>	4-CH <sub>3</sub> Ph	3-ClPh	4-CH <sub>3</sub> Ph	5
<b>3c</b>	4-CH <sub>3</sub> Ph	3-ClPh	4-CH <sub>3</sub> Ph	6
<b>3d</b>	4-CH <sub>3</sub> Ph	3-ClPh	4-CH <sub>3</sub> Ph	8

**Figure 1** Synthesis of the novel pyridinium photoinitiators.

foils, and medicine. Typically, a PSA is applied to a clear film, crosslinked, and wound for tape. If labels are being made, then the labels are coated, a release liner is applied (usually clear if UV), and it is cross-linked.

## EXPERIMENTAL

The following experiments were conducted to study the influence of a new class of novel pyridinium photoinitiators on diverse parameters of the performance of acrylic PSAs: the tack, peel adhesion, and shear strength. The basic PSA was synthesized with 65 wt % 2-ethylhexyl acrylate (2-EHA), 30% methyl acrylate (MA), and 5% acrylic acid (AA). The investigated novel pyridinium photoinitiators were added after the polymerization. The polymerization process was performed in a typical organic solvent such as ethyl acetate. The solid content was about 50 wt %.

2-EHA, MA, AA, and ethyl acetate were purchased from Tokyo Chemical Industry Co. (Tokyo, Japan).

The novel pyridinium photoinitiators were synthesized according to the reaction described by Baeyer and Piccard<sup>11</sup> (Fig. 1) and classified by Van der Plas.<sup>12</sup>

The following pyridinium photoinitiators, synthesized by the authors, were evaluated to determine how they would influence the tack, peel adhesion, and shear strength of crosslinked acrylic PSAs (Table I).

## Standardization of the relevant parameters

Because PSA systems are sensitive to the temperature and pressure, these characteristics must be standardized in any given test method. The conditions favored by most laboratories are an environmental temperature of 23°C (room temperature) and a relative humidity of 50 ± 6%.

## Coating weight of the PSAs

The coating weight (thickness of the layer) of a dry PSA after the removal of the organic solvent essentially influences the tack, peel adhesion, and shear strength. The base weight of the adhesive layer covering the foil was 60 g/m<sup>2</sup>.

## Type of carrier

Tested adhesives have to be coated on the same type of carrier. For the tests, a 25-μm polyester film (Hostaphan RN, Degussa, Marl, Germany) was used.

## Drying terms in the drier

The PSA layer has to be dry and free from polymerization solvents and residual monomers. It was the aim of this study to examine the performance of the tested crosslinked adhesives at a constant temperature. The solvent-borne acrylic PSAs coated on polyester foil were dried for 10 min at 105°C.

**TABLE I**  
Pyridinium Photoinitiators

Pyridinium photoinitiator	Chemical formula	Chemical name
<b>3b</b>	C <sub>55</sub> H <sub>51</sub> Cl <sub>3</sub> N <sub>2</sub> O <sub>4</sub>	4-(3-Chlorophenyl)-1-[5-[4(3-chlorophenyl)-2,6-di-(4-methylphenyl)-2H-pyridin-1-yl]-pentyl]-2,6-di-(4-methylphenyl) pyridinium perchlorate
<b>3c</b>	C <sub>56</sub> H <sub>53</sub> Cl <sub>3</sub> N <sub>2</sub> O <sub>4</sub>	4-(3-Chlorophenyl)-1-[6-[4(3-chlorophenyl)-2,6-di-(4-methylphenyl)-2H-pyridin-1-yl]-hexyl]-2,6-di-(4-methylphenyl) pyridinium perchlorate
<b>3d</b>	C <sub>58</sub> H <sub>57</sub> Cl <sub>3</sub> N <sub>2</sub> O <sub>4</sub>	4-(3-Chlorophenyl)-1-[8-[4(3-chlorophenyl)-2,6-di-(4-methylphenyl)-2H-pyridin-1-yl]-octyl]-2,6-di-(4-methylphenyl) pyridinium perchlorate

**TABLE II**  
Main Properties of Acrylic PSAs Containing the Pyridinium Photoinitiators

UV dose (mJ/cm <sup>2</sup> )	Tack (N/2.5 cm)			Peel adhesion (N/2.5 cm)			Shear strength (N/6.25 cm <sup>2</sup> )		
	3d	3c	3b	3d	3c	3b	3d	3b	3c
200	3.3	3.3	3.3	6.2	6.2	6.2	5	5	5
400	3.3	3.3	3.3	6.2	6.2	6.3	5	5	5
600	3.3	3.4	3.7	6.6	6.6	6.7	5	5	5
800	3.4	3.6	4.0	6.8	6.9	7.0	5	5	6
1000	3.6	3.8	4.1	7.1	7.3	7.5	6	8	10
1200	3.8	4.1	4.3	7.2	7.4	7.7	6	8	10
1400	4.1	4.3	4.6	7.2	7.5	7.9	8	10	12

### Kind of cover material

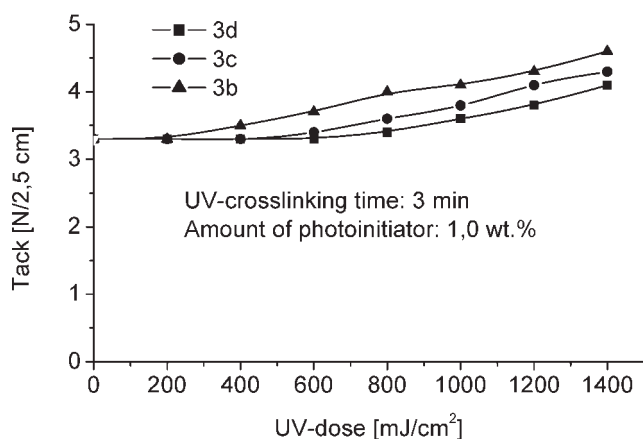
The kind of covering adhesive material has an important influence on the performance of coated adhesive surfaces. The dried layer of the acrylic PSAs was covered with adhesive brown silicone paper (95 g/m<sup>2</sup>) from Laufenberg (Neuss, Germany).

### Conditioning

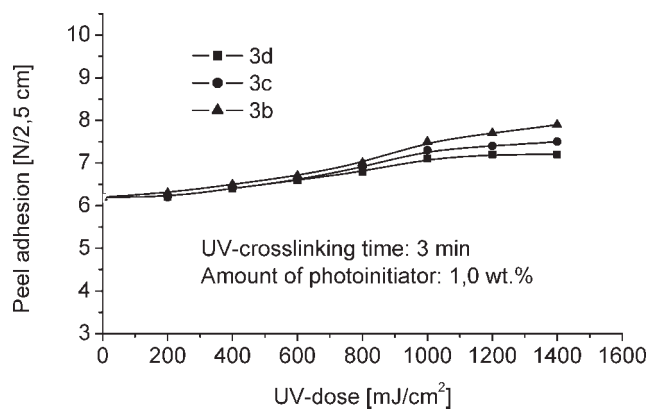
Before the test, the adhesive-coated strips were stored for 7 days at room temperature and 50% relative humidity. Three samples were tested, and the given values of the tack, peel adhesion, and shear strength were the arithmetic means of the results.

The UV-crosslinkable acrylic PSAs were coated directly onto polyester foil and were crosslinked after being dried with a UV lamp (type U 350-M-I-DL, IST Co.) with a UV-A wavelength between 315 and 380 nm. The UV exposure was measured with a Dynachem model 500 integrating radiometer available from Dynachem Corp. (Georgetown, IL).

The influence of crosslinking agents or crosslinking methods is usually determined in relation to the reac-



**Figure 2** Tack of UV-crosslinked acrylic PSAs containing the pyridinium photoinitiators versus the UV dose.



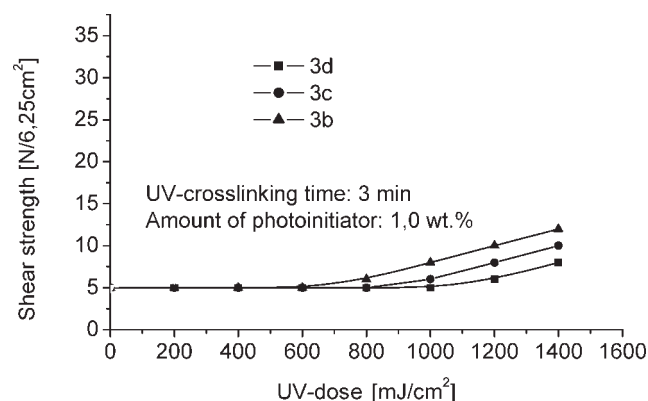
**Figure 3** Peel adhesion of UV-crosslinked acrylic PSAs containing the pyridinium photoinitiators versus the UV dose.

tion time and the concentration versus the adhesion properties with respect to the following properties: the tack, adhesion, cohesion, and shrinkage. The first three properties were determined by standard Association des Fabricants Europeens de Rubans Auto-Adhesifs (AFERA) procedures. The exact details can be found in AFERA 4015 (tack), AFERA 4001 (peel adhesion), and AFERA 4012 (shear strength).

## RESULTS AND DISCUSSION

The UV-crosslinking effect for the examined novel pyridinium photoinitiators (1.0 wt %) on the tack, peel adhesion, and shear strength of acrylic PSAs, dependent on UV doses between 200 and 1400 mJ/cm<sup>2</sup> after 3 min of UV crosslinking, is presented in Table II and shown in Figures 2–4.

The tack behavior of UV-crosslinked acrylic PSAs containing pyridinium photoinitiators will increase with an increasing UV dose. Studies have shown that the UV dose for the tack level is also an important parameter.



**Figure 4** Shear strength of UV-crosslinked acrylic PSAs containing the pyridinium photoinitiators versus the UV dose.

The uncrosslinked solvent-borne acrylic PSA shows low values of the tack and peel adhesion along with cohesive failure. After the addition of a small amount of a pyridinium photoinitiator and UV exposure, the acrylic PSA begins to crosslink. The PSA structure is now compact, and by light crosslinking of the structure, the tack and peel adhesion increase.

The cohesion of UV-crosslinked acrylic PSAs is directly proportional to the UV exposure time, and the value of the shear strength after UV crosslinking depends on the length of the alkylene chain in the molecules of the investigated pyridinium photoinitiators (Fig. 4). During the UV-curing reaction, the elastomeric acrylic PSA chains react with one another to form radical pyridinium photoinitiators as internal chemical crosslinkers, and a very strong chemical three-dimensional network is created. In the first phase of the UV-initiated crosslinking process to UV exposure of about 600 mJ/cm<sup>2</sup>, all evaluated pyridinium photoinitiators yielded the same cohesion values.

### CONCLUSIONS

Summarizing the results of this study, we can conclude that these photosensitive compounds are very effective for the photocrosslinking of acrylic PSAs

and ameliorate the adhesive properties (tack and peel adhesion) and cohesion. The shorter alkylene chain yielded the best result for all measured performances.

Pyridinium photoinitiators are preferred as photo-reactive crosslinking agents for UV-crosslinked coatings of adhesives with improved tack and peel adhesion and with moderate cohesion at room temperature. These photoreactive solvent-borne PSAs based on acrylics are used for the manufacturing of novel kinds of protective foils.

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