

Activatable and Patternable Acrylic Pressure Sensitive Adhesives

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Introduction

Smart adhesives have received considerable recent interest both in academic and industrial arenas as the performance criteria for adhesive materials becomes more specified and applications more complex.¹ Generally defined as adhesives that have the ability to activate or increase adhesion, or conversely, to deactivate or decrease adhesion in response to an external stimulus, smart or responsive adhesives have the potential to bring new functionality into the field of pressure sensitive adhesives (PSAs) and drive these materials toward new applications and market opportunities.² Towards this end, there have been numerous examples of smart adhesive concepts that utilize a host of mechanisms to elicit the desired change in properties of the underlying material. Stimuli often include heat^{3,4,5,6}, light irradiation^{7,8,9}, electrochemical¹⁰, ultrasonic vibrations¹¹, magnetic field¹², and others that are used to create chemical or physical changes¹³ within an adhesive in order to either activate the adhesive properties of the material, or more commonly, de-activate or debond the adhesive on demand.

We have recently developed a concept using crosslinkers containing cleavable hemi-acetal groups that allow for significant changes in the network structure of an acrylic PSA material to be facilitated on demand with either applied UV irradiation or heat. Cleavable crosslinkers of this type have seen abundant use in areas such as photo-lithography for integrated circuit assemblies^{14,15} while their use in adhesives have been much more limited. Utilizing this chemistry to trigger network changes within an adhesive, we demonstrate the capability to manipulate macroscopic properties within a PSA such as an increase in tack and increased bonding ability to name a few. Taking this concept one step further, the ability to “activate” and modify the adhesive performance of a PSA material on demand also unlocks the capability to pattern the adhesive properties within the adhesive. The ability to activate pressure sensitive adhesives through external stimuli could have tremendous potential in a number of applications including re-positional decorative, functional, or protective films, reworkable attachment adhesives for electronics, and dicing adhesives to name a few. Furthermore, the ability to pattern adhesives using this technology may allow for more advanced PSA function such as directional anisotropic peel, air-bleed, or highly engineered peel dynamics using specifically selected and tailorable illumination patterns.

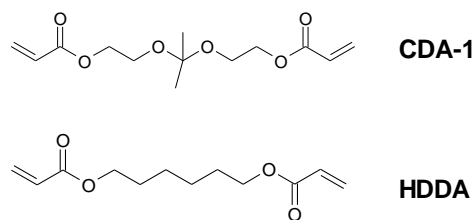


Fig. 1. Structure of the synthesized ketal containing cleavable crosslinker diacrylate (CDA-1) as well as the non cleavable crosslinker HDDA used in this study.

Results and Discussion

To evaluate the utility of cleavable crosslinkers and the scheme to use them to develop activatable and patternable PSAs, we sought to understand the behavior of this chemistry on multiple levels. This included: 1) conditions to trigger the cleavable event, 2) catalysts to increase the efficiency of this mechanism and direct this event with specific external stimuli, 3) the microscale effects on the network structure of the adhesive upon crosslink degradation, as well as 4) changes to the macroscale properties of the material such as bulk modulus, tack, and resistance to peel of the adhesive upon activation.

Acrylic PSA films were generally prepared using a formulation of 93 wt% isooctyl acrylate (IOA) and 7 wt% acrylic acid (AA). To this formulation, 0.2 parts per hundred (pph) relative to the acrylic monomers of either cleavable crosslinker (CDA-1) or non-cleavable crosslinker hexanediol diacrylate (HDDA) was added to crosslink the adhesive upon UV cure. Crosslinker structures are depicted above in Figure 1. Photoinitiator was added and each solution was coated with a set gap of 75 μm between two siliconized PET liners and UV cured into a PSA film using a black light array of UVA fluorescent bulbs.

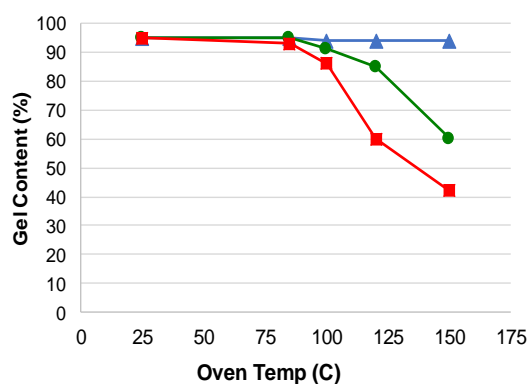


Fig. 2. Gel content of adhesive films treated at various temperatures for set periods of time. Films contain either non-degradable crosslinker HDDA treated for 30 minutes at each temperature (\blacktriangle), degradable crosslinker CDA-1 treated for 5 minutes at each temperature (\bullet), or CDA-1 treated for 30 minutes at each temperature (\blacksquare).

To investigate the cleavable behavior of these crosslinkers on the network properties of the bulk adhesive, strips of the adhesive films generated above using either CDA-1 or HDDA were treated at set temperatures for various periods of time as shown in Figure 2 before analyzing the gel content of each treated film through simple gravimetric analysis following an elution in toluene for 24 hours. Figure 2 shows the resulting gel content analysis as films of adhesive containing either cleavable CDA-1 or non-cleavable HDDA were exposed to elevated temperatures. While films with HDDA are stable up to significantly high temperatures, films with CDA-1 crosslinker exhibit a decrease in gel content at temperatures above 100°C that continues to decline as either temperature is increased or the treatment time is increased.

Catalyzed Cleavage

In some applications, it may be desirable to trigger the thermal degradation of cleavable crosslinks in an adhesive film more completely and at lower temperatures than demonstrated in Figure 2 above. It is known that the breakdown of hemi-acetal linkages may be accelerated with the use of acidic species and that a thermally latent effect can be attained through the use of thermal acid generators (TAGs) that are commonly offered as organic salts with a range of decomposition temperatures¹⁶. To investigate the effectiveness of this catalytic route with the current cleavable adhesive systems, similar compositions were generated as in the previous examples that further included the addition of the TAG, triethyl-ammonium para toluenesulfonic acid (TEA-pTSA).

Figure 3. below shows a differential scanning calorimetry profile for the particular TAG, TEA-pTSA in its pure form, exhibiting a strong thermal transition peak at approximately 82°C. The gel content experiment depicted in Figure 2 was repeated using the same base adhesive containing 0.2 pph CDA-1, with various low-level additions of the TAG, TEA-pTSA. The effect of the TAG was observed to cause both lower overall gel content as well as a lowered overall activation temperature for network breakdown.

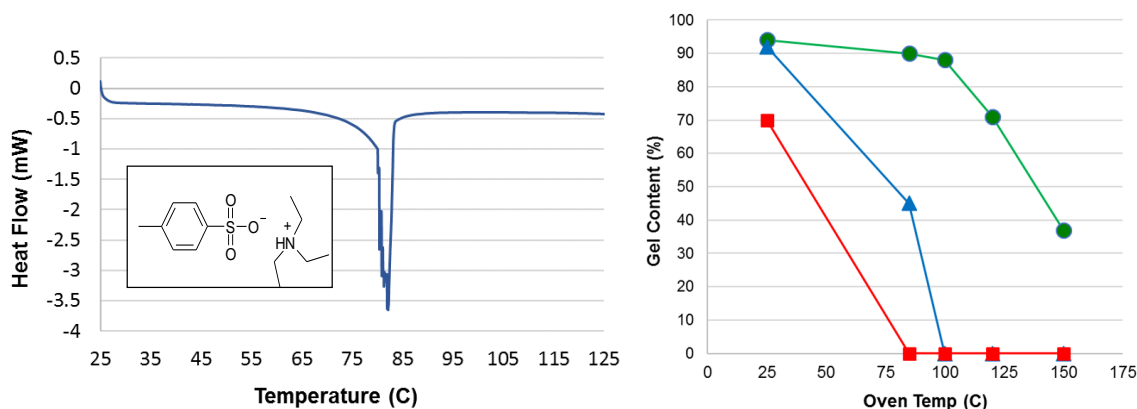


Fig. 3: Differential scanning calorimeter profile (top) of TAG catalyst TEA-pTSA (insert). Gel content of adhesive films treated for 10 minutes at indicated temperatures containing 0.2 pph CDA-1 cleavable crosslinker and 0 pph (●), 0.005 pph (▲), or 0.01 pph (■) of TEA-pTSA.

In addition to thermal activated catalysts, it has been shown in previous publications that cleavage of acetal groups can also be facilitated using UV irradiation of photo acid generator (PAG) catalysts¹⁷. In a similar fashion to TAGs, a variety of PAGs are commercially offered, though specified by the particular wavelength of light absorption and activation for the latter as opposed to the temperature of activation for the former. In the studies below in which network breakdown is facilitated through the use of a PAG and a stimulus of UV irradiation, a commercially offered catalyst triphenylsulfonium-triflate (TPST) was utilized due to its expected low wavelength absorption profile. Importantly, the UV absorption of TPST is effectively 0% above 300 nm wavelength, allowing for the use of more common UVA wavelength radiation in the generation of the acrylic adhesive films while keeping the PAG dormant. Thus, cleavable crosslinks of the adhesive are theoretically in-tact until activated by a second irradiating source emitting sub-300 nm wavelengths of UV radiation.

Controlling PSA Performance

While the ability to manipulate the gel content of an adhesive with external stimuli is notable, the low levels of CDA investigated to this point do not elicit more significant changes in the bulk material or adhesive properties of these systems such as modulus, tack, and bonding ability. Thus, subsequent studies have explored higher levels of cleavable crosslinker incorporation in order to trigger larger, macro property changes of the material when cleavable groups are efficiently degraded with the aid of thermal or photo acid catalysts. Figure 4 below illustrates the scheme to use cleavable crosslinkers at high concentrations to elicit greater property changes as the PSA goes from an overly crosslinked state to a more typical level of network crosslinking upon activation. The expected material changes that may occur upon such an extreme change in crosslink density go beyond gel content and viscoelastic balances and may extend to properties such as the bulk modulus and overall compliance of the material.

The plateau modulus of a pressure sensitive adhesive, particularly when located in proximity to the application temperature and frequency, is inversely correlated with the compliance of the material which is critical to its ability to create a bond with a substrate or surface. This relationship was elucidated and developed into the formulation of the Dahlquist Criterion which, in simplified form, stipulates the minimal level of compliance, or conversely, the ceiling level of storage modulus, required of a material to be considered tacky and thus form an adhesive bond with only applied pressure¹⁸.

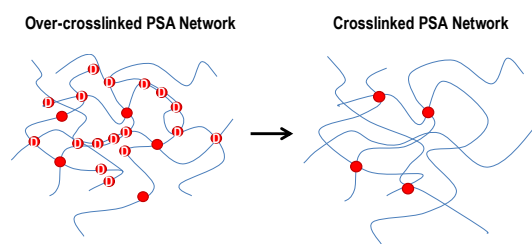


Fig. 4: Schematic of an overly crosslinked PSA network returning to a lesser crosslinked state that is more typical of a PSA through the cleavage of particular network crosslinking junctions (D) upon external stimuli.

The concept of significantly lowering modulus on demand was also demonstrated using systems that combined increased cleavable crosslinker, PAG catalyst, and UVC irradiation to elicit the immediate and significant modulus change in the adhesive film. Figure 5 below looks at the relationship between the amount of CDA-1 crosslinker and the resulting plateau modulus of the adhesive as measured by oscillatory rheology. In Figure 5, the storage modulus (G') measured at a set temperature and frequency that is expected to be representative of the plateau modulus, was shown to increase proportionally as the level of cleavable crosslinker is increased with a 93% IOA and 7 wt% AA PSA system. Additionally, it is observed that at levels of CDA-1 between 7 and 9 wt% in the PSA composition, the plateau modulus of the adhesive material at 50°C and 1 Hz crosses the Dahlquist Criterion (DC) in which the adhesive is no longer tacky, and thus its expected bond making ability would be significantly reduced.

Also, as shown in Figure 5, the adhesive containing 9 wt% CDA-1 was further exposed to 30 mJ/cm² of UVC radiation using a Fusion processor with D-bulb assembly. Even with a relatively short exposure period (approximately 1 second) the film upon exiting the Fusion processor was noticeably tacky and when re-measured using the DMA, exhibited a significantly lowered plateau modulus at 50°C. Furthermore, the approximate value of the plateau modulus of the “activated” system was similar to that of a traditional PSA containing a more typical loading of crosslinker (0.3 wt%) as shown in the first column of Figure 5. This suggests that the UVC dose and amount of PAG catalyst was sufficient to cleave

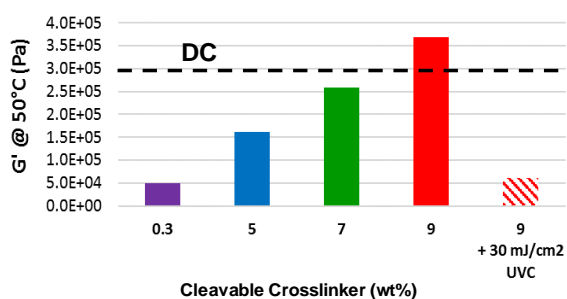


Fig. 5. Effect of increasing amounts of cleavable crosslinker on the plateau modulus of the formed PSA material relative to the Dahlquist Criterion (DC) at 1 Hz and room temperature. Also shown is the effect of the activated crosslinker degradation on one of the materials upon exposure to a 30 mJ/cm² dose of UVC irradiation.

a significant portion of the cleavable crosslinker within this network. To ensure that a portion of the network crosslinks remain upon activation and degradation of the cleavable linkages, a mixture of non-degradable HDDA and cleavable CDA-1 could be utilized in combination. Using this strategy, the activated adhesive should retain sufficient cohesive strength and have a permanent degree of crosslinking locked into the formulation.

The significant shift in the plateau modulus of the adhesive as demonstrated in Figure 5 is expected to have a strong influence over the tack and the material’s ability to conform to a surface, and therefore, the adhesive performance of these systems. To demonstrate this relationship, the adhesive described

above and represented in Figure 5 as the green bar (7 wt% cleavable crosslinker) was re-made and evaluated for peel adhesion to stainless steel.

In Figure 6 on the right, the 180 degree peel adhesion to stainless steel was measured as a function of the dose of UV irradiation used to activate the adhesive before it was applied to the substrate. It is theorized that at this set level of cleavable crosslinker in each system (7 wt%), the degree of modulus shift resulting from the breakdown of this crosslinker will directly depend on the amount of PAG that is activated. By controlling this factor as a function of UV dose, a direct relationship between the amount of UV irradiation and ultimately the peel performance of adhesive system was established.

Patterned Pressure Sensitive Adhesives

With the ability to utilize UV irradiation to activate or increase the adhesive properties of a PSA system on demand, the next step was to demonstrate the spatial control of this effect through the use of aperture masks to structure the activating UV irradiation. Again, a PSA composition of 93 wt% IOA and 7 wt% of acrylic acid was compounded with 8 pph of the cleavable crosslinker CDA-1, 0.2 pph of a non-cleavable crosslinker hexanediol diacrylate, 0.2 parts of a UVA photoinitiator (Irgacure 651) and 0.05 parts of a UVC photoacid generator (TPST). This adhesive formulation was coated between release liner and PET backing and polymerized using the array of black light fluorescent bulbs with a UVA centered output. Subsequently, the release liner was removed and an aperture mask with vertical line spacing of approximately 4 mm was placed between the acrylic film and a Fusion UV light source with D-bulb assembly. After an exposure dose of approximately 30 mJ/cm² of UVC, the mask was removed.

One-inch wide strips were cut from the activated adhesive film in varying directions that were either parallel or perpendicular relative to the line directionality of the aperture mask used above. The peel adhesion performance of these strips to stainless steel was quantified using an IMass peel tester that records the peel force as a function of time. Taking into account the rate of the IMass head, the peel force as a function of time could also be represented as a relative function of location on the adhesive material or distance as shown on the right in Figure 7.

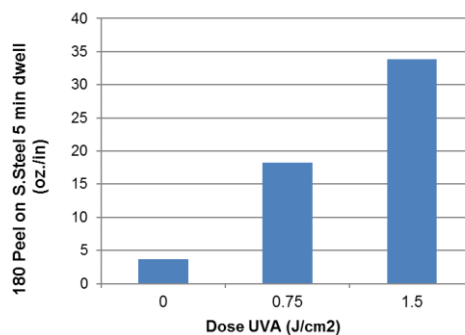


Fig. 6: Effect of activation dose on the 180 degree peel adhesion to Stainless Steel of a PSA containing 7 wt% cleavable crosslinker CDA-1 and 0.03 wt% of a photoacid generator (TPST) as a function of UVA dose applied to PSA prior to bonding.

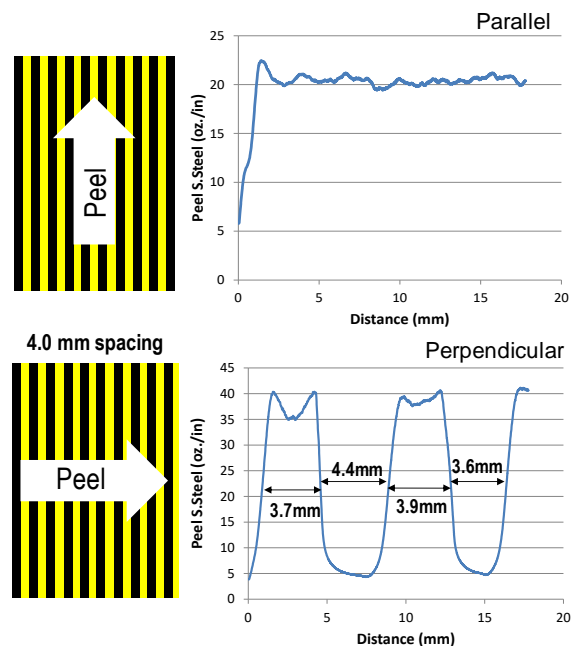


Fig. 7: Peel performance profiles of a patterned PSA material where peel is either in a parallel (top) or perpendicular (bottom) direction relative to the line spacing of the aperture mask used to structure irradiate the sample and create the pattern.

Figure 7 illustrates the directionality of the peel relative to the lines of the aperture mask as well as the profile of the peel adhesion while peeling in each direction. Here the effect of the aperture mask and thus spatial UV exposure is evident in an apparent pattern of high and low peel adhesion when peeling across or perpendicular to this pattern. Furthermore, the line spacing of the areas of high and low adhesion match well to the line spacing of the aperture mask demonstrating good registration between the areas of UV exposure and “activated” adhesive.

Conclusions

We have developed and demonstrated a concept that utilizes cleavable crosslinkers within a pressure sensitive adhesive material to control the level of network crosslinking, plateau modulus, tackiness, and the ability of the material to bond to substrates. Through this control, we have also demonstrated the capability to “activate” the adhesive on demand through external stimuli such as UV and thermal exposure, and subsequently increase the peel adhesive performance of the PSA with these triggers. Finally, by spatially manipulating the activating UV exposure through the use of aperture masks, it was demonstrated that we could induce patterned areas of high and low tackiness or peel performance within the PSA.

Literature References

1. Matsumoto A. et al. (2014) *J. Adhes. Soc. Jpn.* (50):72-81
2. Ye, Z. et al. (2016) *Adv. Mater.* 28 (25) 5088-5092
3. Schenzel A.M., et al. (2016) *Adv. Sci.*, 3:1500361
4. Zhang, X. et al (2009) *J. Poly. Sci., Part A: Poly. Chem.*, 47 (4) 1073-1084
5. Bovaldinova, K.A. et al. (2017) *Polymer*, 125 (8) 10-20
6. Everaerts et al. (2003) US 6,652,970
7. Heinzmann C., et al. (2014) *ACS Appl. Mater. Interfaces*, 6 (7), 4713-4719
8. Sato E. et al, (2010) *ACS Applied Mater. & Interf.*, 2(9) 2594-2601
9. Kian et al. (2015) US 9,181,462
10. Leijonmarck S. et al. (2011) *J. Electrochem Soc.* 158(10): 109-114
11. Tachi, H. et al. (2017) *J. Photopolymer Sci and Tech*, (30): 253-257
12. Krahn, J. et al. (2015) *ACS Appl. Mater. & Int.*, 7 (4), 2214-2222
13. Gorsche, C. et al, (2018) *Macromolecules*, 51 (3) 660-669
14. Kuczynski, J.P. (1999) US Patent 5,872,158
15. Wilson, C.G. et al. (2007) *ACSNano*, 1 (4) 307-312
16. Oberlander, J.E. et al. (2000) *Proc. SPIE 3999 Advances in Resist Technology and Processing XVII*
17. Lawson, R.A., *Overview of Materials and Processes for Lithography*, Vol 11, (2017) Elsevier B.V.
18. Dahlquist, C.A., *Adhesion Fundamentals and Practice* (1966), McLaren and Sons, Ltd., London

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Appendix A. Experimental and Methods

Dynamic Mechanical Analysis of PSA Films

Dynamic mechanical analysis (“DMA”) was used to characterize the physical properties of sample PSA films as a function of temperature out using a DHR-3 rheometer (TA Instruments) with an 8 mm parallel plate assembly and environmental chamber. For each sample, 50 micrometer thick sheets of the polymerized adhesive sample were laminated together to achieve a 1 mm thick slab. A circular punch with a diameter of 8 mm was used to cut a sample from this slab which was then centered between the 8 mm diameter parallel plates of the rheometer. The temperature was then scanned from 5°C to 140°C at a rate of 3°C/min. while the parallel plates were oscillated at a frequency of 1 Hz and a constant strain of 0.4%. Physical parameters of the material were recorded during the temperature ramp, including shear storage modulus (G'), shear loss modulus (G''), and Tan Delta (i.e., G'' / G').

Gel Content Measurements

To determine the fraction of crosslinked polymer or gel within each material, adhesive formulations were coated at approximately 0.05 mm and UV cured between silicone coated release liners T10 and T50. Squares of 1 inch by 1 inch were cut from each adhesive film, the release liners were removed, and the adhesive square was then transferred to a steel mesh cage of dimensions 1.5 inch by 1.5 inch by 0.5 and of known mass. The mass of the cage and sample was recorded, and the cage was submersed in toluene for a period of 24 hours. After this time, the cage was removed from the toluene and dried in an oven for 2 hours at 120 °C. The mass of the cage and dried sample was recorded and the gel fraction was calculated using the following formula:

$$\text{Gel Fraction \%} = ((M_{\text{FP}} - M_{\text{C}}) / (M_{\text{IP}} - M_{\text{C}})) \times 100$$

where M_{C} was the mass of the cage, M_{FP} was the mass of the cage and final dried polymer film, and M_{IP} was the mass of the cage and initial polymer film. Two samples for each adhesive film were tested and the gel fraction averaged.

Peel Adhesion

Peel adhesion was the force required to remove a coated flexible sheet material from a clean stainless steel test panel, measured at a specific angle and rate of removal. The stainless steel panel was cleaned by wiping with 2-isopropanol before testing. In the examples, the force was expressed in ounces of force per width of coated sheet (i.e., oz./in.) For each test, a 0.5 in width of the adhesive coated sheet material approximately 6 inches long was cut and the release layer was peeled away from the coated adhesive. The adhesive strip was then applied to the clean face of a stainless steel test panel. A 2 kg rubber roller was used to apply the strip. The free end of the coated strip was doubled back so that the angle of removal was 180 degrees. The free end was attached to the horizontal arm of the adhesion tester scale. The stainless steel plate was then affixed to the platform of the instrument which was mechanized to move at a controlled rate (12"/min. (30 cm/min.)) away from the scale. The peel test was initiated 5 minutes after the adhesive was applied to the substrate. The scale reading was read during the test as an average of both the peak and minimum forces during the peel. Three peel tests were run for each sample and averaged to yield the peel adhesion value.

Preparation of Cleavable Crosslinker Diacrylate (CDA-1)

To a mixture of 785 g (6.76 moles, 3 eq) of 2-hydroxyethyl acrylate and 0.429 g (2.25 mmol, 0.001 eq) of p-toluenesulfonic acid (monohydrate) was added 235 g (2.25 moles, 1 eq) of 2,2-dimethoxypropane, 0.236 g of MEHQ and 1.12 L of cyclohexane. A steady stream of air was passed through the flask and the mixture was heated to 80°C. Methanol was collected by azeotropic distillation (approximately 160 mL was collected). The mixture was heated at 80°C for a total of 10 hours. Air was passed through the solution for several days to remove the solvent. The reaction mixture was diluted with approximately 400 mL of ethyl acetate and extracted with 200 mL of saturated aqueous sodium bicarbonate solution followed by several water/brine washes. After approximately 7 L of aqueous wash a sample was concentrated and ¹H NMR analysis indicated less than 1% residual 2-hydroxyethylacrylate remaining. This mixture was concentrated under reduced pressure and then air was passed through this mixture for several hours until ¹H NMR analysis showed less than 0.05% ethyl acetate remaining. A total of 429 grams (64% yield) of product (DCDA-1) was obtained.

Preparation of Thermal Acid Generator TEA-pTSA

To a solution of 10.0 g (52.6 mmol, 1 eq) of p-toluenesulfonic acid (monohydrate) in 30.0 mL of THF was added 6.38 g (63.1 mmol, 1.2 eq) of triethylamine. The reaction mixture exothermed to 40°C and was allowed to stir for three hours and then concentrated under reduced pressure (40°C, 20 torr (~2700 Pa), 2 hours). The product was a viscous liquid that was soluble in THF, methyl ethyl ketone, or isopropyl alcohol, and was insoluble in ethyl acetate.