

Phototackification of Polymer Blends

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SYNOPSIS

A direct single-layer phototackification scheme is demonstrated making use of chemical amplification and photo-induced microphase separation in an initially nontacky miscible blend of acid-labile poly(2-tetrahydropyranyl methacrylate) and poly(2-tetrahydropyranyl acrylate), tacky poly(2-phenylethyl acrylate), and a photoacid generator. The mechanism involves four processes: photoacid generation, acid migration, acetal ester cleavage, and phase separation. Thin film *in situ* IR studies showed the rate of acid migration and acetal ester cleavage to be strongly dependent on the presence of ambient water and polymer matrix (T_g) effects. The rate of phase separation is affected by polymer molecular weight. A number of approaches to minimize humidity sensitivity are discussed. The system has been sensitized to both UV and near-IR radiation. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

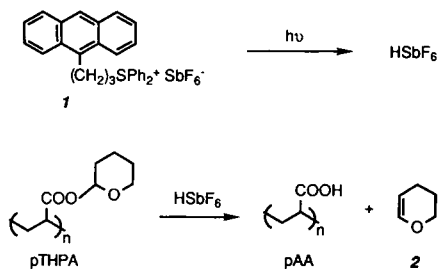
Creation of tackiness in thin films as the result of imagewise exposure to light (phototackification) has practical application in a number of areas. In the manufacture of TV tubes, RCA described the imagewise deposition of phosphor powders in irradiated areas of polyacetylene sulfone polymers followed by high temperature firing.¹ For the same application, Hitachi used a water-soluble aromatic diazonium salt in the presence of a polymeric binder. The composition became tacky upon exposure to light.² Grossa³ used substituted 4-(2'-nitrophenyl)-1,4-dihydropyridines in the manufacture of cathode ray tubes. The nitroso-pyridines produced upon UV irradiation imparted tackiness to a coating. Dudek and Pfeiffer described the preparation of conductive gold patterns on ceramic substrates using a toning process on irradiated thin amorphous layers of a mixture of nitrophenyl dihydropyridine derivatives.⁴ Kobayashi described the use of aromatic diazonium salts in the manufacture of solid electrolytic capacitors.⁵

Applications of phototackification for graphic arts proofing are probably the most studied, although, to our knowledge, no commercial system has yet

evolved. Examples of simple, single-layer compositions that exhibit an increase in tackiness upon exposure to light are rather rare. Reiser and Li used photogenerated acid to reduce the T_g of coatings by decross-linking microgels cross-linked with difunctional *tertiary*-alkyl methacrylates.⁶ Keuffel and Esser⁷ described a reprographic process using the photolysis of aromatic diazonium salts to generate tack. Abele and Grossa⁸ used lophine radicals to photooxidize suitably substituted dihydropyridines, and the products plasticized an accompanying binder. Hillenbrand⁹ described the use of colored phototackifiable microparticles and a transfer step to a receptor sheet to generate images. Lee used a photoacid generator and a main chain polyacetal whose decomposition products plasticized an accompanying binder.^{10,11}

Numerous indirect methods for proofing have been developed to introduce tackiness in exposed areas. DuPont's Negative Cromalin® is a well-known example. This commercial two-layer peel-apart color proofing product consists of a photopolymer layer and an adjacent adhesive layer. Increased adhesion occurs at the interface in exposed regions. Read out is accomplished by peel apart development and toning. Another indirect negative approach described by Grubb et al.¹² utilized a photopolymer film similar to Positive Cromalin®. After imagewise exposure, a colorless blocking toning material is applied to unexposed areas. The element is then heated to

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Scheme 1

make exposed areas tacky, and the desired colored toner is applied.

Recently, a new indirect two-layer negative-working composition was reported by Raymond and Hertler.¹³ It consists of a tacky elastomeric underlayer on top of which is coated a positive-working chemically amplified^{14,15} microlithographic resist.^{16,17} The resist is a polyacrylic acetal ester, such as poly(2-tetrahydropyranyl acrylate) (pTHPA) and a photoacid generator (PAG). A strong protic acid, generated imagewise upon irradiation, catalyzes cleavage of the acid-labile acetal ester side chains to give poly(acrylic acid) (pAA) and 3,4-dihydro-2H-pyran (DHP, **2**, see Scheme 1). Development with water or dilute aqueous base exposes the tacky underlayer which can then be toned. Most of the studies were carried out with 3-(9-anthracenyl)propyldiphenylsulfonium hexafluoroantimonate (**1**) as the PAG.^{18–20} In addition to acid-catalyzed cleavage, these poly(acetal esters) also undergo a purely thermal cleavage at modest temperatures (150–175°C) to give carboxylic acid and **2**.

In this article we describe a novel direct phototackification method that uses the Raymond–Hertler chemistry¹³ in a single-layer system. Through chemical amplification, microphase separation is photoinduced in an initially nontacky miscible blend of acid-labile and tacky polymers. The system can be sensitized in the UV with photoacid generators and in the near-IR with IR-absorbing dyes. A preliminary report on part of this work has recently appeared.²¹

EXPERIMENTAL

Materials

Poly(2-tetrahydropyranyl acrylate) and poly(2-tetrahydropyranyl methacrylate) were synthesized by group-transfer polymerization^{22,23} as previously described.¹³ 3-(9-Anthracenyl)propyl-

diphenylsulfonium hexafluoroantimonate (**1**) was synthesized by the literature procedure.^{18–20} Thio-pyrylium,4-[[3-[[2,6-bis(1,1-dimethylethyl)-4H-thiopyran-4-ylidene]methyl]-2-hydroxy-4-oxo-2-cyclobuten-1-ylidene]methyl]2,6-bis(1,1-dimethylethyl)-hydroxide, inner salt (SQS, **3**) was prepared as described by a literature method²⁴ and used at 2–4 wt %. 2-Phenylethyl acrylate was purchased from Polysciences, Inc. (Warrington, PA).

Poly(2-phenylethyl acrylate) by Group-Transfer Polymerization

2 Milliliters of tetrabutylammonium biacetate hexahydrate (0.04 M in tetrahydrofuran) was added to a stirred solution of 413 g (400 mL, 2.35 mol) of 2-phenylethyl acrylate (purified by passage through a column of basic alumina under argon), 10.35 g (37.5 mmol) of 1-trimethylsiloxy-1-(2-trimethylsiloxyethoxy)-2-methyl-1-propene, and 11 mL of bis-(dimethylamino)methylsilane in 1.2 L of tetrahydrofuran cooled to –19°C. After 15 min at –19°C, 1 mL of tetrabutylammonium fluoride (1 M in tetrahydrofuran) was added, and the temperature rose to 42°C during 35 min. After stirring at room temperature overnight, the reaction was quenched with methanol. ¹H NMR analysis showed that conversion was 98%. The poly(2-phenylethyl acrylate) was precipitated in methanol as a gum. The polymer was dried in a vacuum oven at 50°C. GPC: $\bar{M}_n = 11,000$; $\bar{M}_w = 16,500$; $\bar{M}_w/\bar{M}_n = 1.5$.

Poly(2-phenylethyl acrylate) by Free Radical Polymerization

A solution of 29.26 g (0.166 mol) of 2-phenylethyl acrylate in 100 mL of methyl acetate was purged with nitrogen. Then 0.10 g (1.11 mmol) of 1-butanethiol was added, and the reaction was brought to reflux. Just at reflux, 0.62 g of VAZO® 52 was added. The reaction was stirred at reflux for 6 h under nitrogen. After cooling, the reaction mixture was slowly added to 500 mL of methanol in a blender. Solvent was decanted from the white precipitated polymer, and the polymer was dried under vacuum overnight at 50°C. The polymer coalesced into a very viscous tacky semisolid. GPC: $\bar{M}_n = 9940$; $\bar{M}_w = 21,800$, $\bar{M}_w/\bar{M}_n = 2.19$.

3-Phenylpropyl Acrylate

To a stirred solution of 50.4 g (50 mL, 0.37 mol) of 3-phenyl-1-propanol and 40.9 g (57 mL, 0.404 mol)

of triethylamine in 350 mL of dichloromethane cooled in an ice-water bath was added 35.6 g (32 mL, 0.393 mol) of acrylyl chloride at a rate such that the temperature did not exceed 24°C. The mixture was stirred for 15 min at room temperature, and a small amount of phenothiazine was added. Then 5 mL of water was added, and the mixture was stirred for 30 min. The mixture was washed successively with 3% hydrochloric acid, water, 5% sodium bicarbonate solution, and water. The organic layer was dried over magnesium sulfate, and the solvent was removed under reduced pressure to give 58.64 g of 3-phenyl-1-propyl acrylate. ¹H NMR (CDCl₃): 1.95 (m, 2 H, CH₂); 2.70 (t, 2 H, PhCH₂); 4.15 (t, 2 H, OCH₂); 5.79 (d, 1 H, =CH); 6.10 (dd, 1 H, =CH); 6.40 (d, 1 H, =CH); 7.15–7.30 (m, 5 H, ArH).

Poly(3-phenylpropyl acrylate)

A solution of 58.6 g (0.308 mol) of 3-phenylpropyl acrylate and 0.2 g of azobis(isobutyronitrile) in 450 mL of degassed ethyl acetate was heated at reflux for 5 h. Then 0.2 g of azobis(isobutyronitrile) was added, and refluxing was continued for another 5 h. After a final treatment with 0.2 g of azobis(isobutyronitrile) followed by 5 h of reflux, NMR analysis showed 14% residual monomer. The product was precipitated in methanol and reprecipitated four times from dichloromethane with methanol to give 29 g of poly(3-phenylpropyl acrylate) as a tacky gum. ¹H NMR (CDCl₃): 1.64 (br s, 2 H, backbone CH₂); 1.82 (br s, 2 H, CH₂); 2.33 (br s, 1 H, CH), 2.55 (br s, 2 H, PhCH₂); 3.95 (br s, 2 H, CH₂O); 7.05–7.2 (br m, 5 H, ArH). GPC: $\bar{M}_n = 8420$; $\bar{M}_w = 13,900$; $\bar{M}_w/\bar{M}_n = 1.65$. DSC: $T_g = -11.7^\circ\text{C}$.

2-Tetrahydrofuranyl Acrylate

To a stirred solution of 78.0 mL (72.3 g, 1.03 mol) of 2,3-dihydrofuran and 0.36 g (1.8 mmol) of phenothiazine was added 38 mL (0.55 mol) of acrylic acid dropwise at a rate that the reaction did not exotherm past 50–55°C. After 0.83 g (~ 6.5 mmol Cl/g resin, Fluka) of pyridine hydrochloride-polymer bound was added, the reaction was stirred overnight. The polymer catalyst was filtered off and ~ 2 g crushed calcium hydride and ~ 2 g potassium carbonate was added to the filtrate. Excess 2,3-dihydrofuran was removed in a rotary evaporator at reduced pressure. After ~ 10 mg phenothiazine and ~ 10 mg 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH) was added, the mixture was vacuum distilled (50°C, 1.5 mmHg) to give 41.6 g of 2-tetrahydrofuranyl acrylate. ¹H NMR (CDCl₃): 2.00 (m, 4 H, CH₂); 3.95

(m, 2 H, CH₂O); 5.80 (dd, 1 H, =CH); 6.04 (dd, 1 H, =CH); 6.35 (m, 2 H, =CH, OCHO).

Poly(2-tetrahydrofuranyl acrylate)

1 milliliter of tetrabutylammonium biacetate (0.04M in tetrahydrofuran) in 10 mL tetrahydrofuran was added dropwise to a solution of 35 mL of dry tetrahydrofuran, 0.65 mL (3.2 mmol) of 1-trimethylsiloxy-2-methyl-1-propene, and 26.41 g of 2-tetrahydrofuranyl acrylate (purified by passage through a column of basic alumina) in 35 mL of anhydrous tetrahydrofuran cooled to -20°C (dry ice/CCl₄). A slight (5°C) exotherm occurred. ¹H NMR analysis indicated that no reaction had occurred, so 3 mL of bis(dimethylamino)methylsilane scavenger was added, and the reaction was stirred for 15 min. After an additional 1 equiv. of initiator was added, the temperature rose to 52°C. The reaction was allowed to stir overnight, then quenched with methanol. After concentration in a rotary evaporator under reduced pressure, the reaction mixture was slowly added to 500 mL of ethyl ether in a blender to precipitate a white solid. The polymer was washed several times with ether and dried to give 17.1 g of poly(2-tetrahydrofuranyl acrylate). GPC: $\bar{M}_n = 630$; $\bar{M}_w = 2330$; $\bar{M}_w/\bar{M}_n = 3.7$.

2-Tetrahydrofuranyl Methacrylate

To a stirred mixture of 78 mL (72.3 g, 1.03 mol) of 2,3-dihydrofuran, 0.36 g of phenothiazine, and 1.87 g of pyridine hydrochloride-polymer bound was added 44 mL (44.7 g, 0.52 mol) of methacrylic acid by dropping funnel, not allowing the reaction to exotherm more than 5–10°C. The reaction was heated overnight at 40°C, cooled, and the catalyst removed by filtration. After addition of ~ 2 g of potassium carbonate and ~ 2 g crushed calcium hydride, the mixture was evaporated under reduced pressure to remove excess 2,3-dihydrofuran. After the addition of ~ 10 mg of phenothiazine and ~ 10 mg of 2,2-diphenyl-1-picrylhydrazyl hydrate, the crude product was distilled (55°C, 1.5 mmHg) to give 39.7 g of clear 2-tetrahydrofuranyl methacrylate. ¹H NMR (CDCl₃): 1.86 (m, 4 H, CH₂); 2.02 (d, 3 H, CH₃); 3.88, 4.02 (dt, 2 H, OCH₂); 5.50 (br s, 1 H, =CH); 6.02 (br s, 1 H, =CH); 6.29 (br s, 1 H, OCHO).

Poly(2-tetrahydrofuranyl methacrylate)

To a solution of 0.65 mL (3.2 mmol) of 1-methoxy-1-trimethylsiloxy-2-methyl-1-propene and 0.3 mL

(0.02 mmol) of tetrabutylammonium biacetate in 35 mL of dry tetrahydrofuran, 24.09 g of 2-tetrahydrofuran-yl methacrylate (purified by passage through a column of basic alumina) was added dropwise resulting in an exotherm of 8°C. After stirring overnight, ¹H NMR indicated that no reaction had occurred, so 3 mL of bis(dimethylamino)methylsilane scavenger was added, and the mixture was stirred for 15 min. After cooling to -20°C (carbon tetrachloride/dry ice), 1 equiv. additional 1-methoxy-1-trimethylsiloxy-2-methyl-1-propene was added. The temperature of the reaction mixture rose to ~ 22°C. After stirring overnight at room temperature, the reaction was quenched with methanol, and the volume was reduced by evaporation in a rotary evaporator under reduced pressure. The concentrate was then added slowly to a blender containing 500 mL ethyl ether. The white precipitate was filtered off, washed with ether, and dried to give 17.5 g of poly(2-tetrahydrofuran-yl methacrylate). GPC: $\bar{M}_n = 2640$; $\bar{M}_w = 6160$; $\bar{M}_w/\bar{M}_n = 2.33$.

Methods

¹H NMR spectra were obtained with a General Electric QE 300 spectrometer. DSC measurements were performed with a DuPont differential scanning calorimeter (Model 910) with a heating rate of 20°C/min in a dry nitrogen atmosphere. Thermally Stimulated Current (TSC) measurements were performed with a TSC/RMA 41000 spectrometer (Solomat Instruments, Stamford, CT). For the standard TSC spectra the film was first polarized by a static electric field ($E = 1500$ kV/m) at the polarization temperature, T_p , for 2 min and then quenched down to the "freezing temperature," T_0 , with cooling during polarization at 30°C/min to freeze in dipolar orientation. With the field turned off and the sample short circuited, the depolarization current due to dipolar reorientation was measured as the temperature was increased from T_0 at 7°/min to the final temperature T_f ($\geq T_p$). T_f was chosen at least 10°C above T_g . Samples for TSC were dried extensively at T_g and melt pressed to ~ 0.2-mm thickness.

Film Preparation

DuPont Mylar® 200D polyester film (2 mil) was used as the coating substrate. In a typical preparation of the phototackifiable film composition, a 5–10 wt % solution of the active components in 2-butanone was coated onto the polyester support using a scalpel with a 2-mil (50 μm) gap. The coating

was allowed to air dry, then stored under nitrogen with protection from light before use. Dried clear coatings were typically 2–5 μm thick.

Irradiation Experiments

In a typical UV exposure, a UGRA Plate Control Wedge target (Graphic Arts Technical Foundation, Pittsburgh, PA) was placed on top of the composite film structure with the emulsion side in contact with the photosensitive layer. A strip of DuPont 92D Mylar® coversheet was sometimes placed between the target and film to protect the emulsion from volatile oils formed during the reaction but also to control ambient moisture effects on the "developing" film. The composite coating and target were placed in a vacuum frame, and a vacuum was drawn. The assembly was exposed to 50–200 mJ/cm² using a L1250 5 kW Photopolymer/Diazo halide lamp (355–365 nm/400–420 nm) mounted in an Olite® AL53 printing light (Olec Corp., Irvine, CA). The exposed composite was allowed to stand at room temperature and ambient humidity for 3–5 min or developed as described later. Tackification was then visualized by application of toner powder (DuPont Negative Cromalin® powder) to the film strip with a cotton ball or a Cromalin® hand-toning pad.

In a typical near-IR exposure, a 4 × 6 in coated piece of film sensitized with SQS dye (2–4 wt %, in place of the photoacid generator) was mounted on a Crosfield 646 scanner retrofitted with a CREO (Vancouver, BC) writehead²⁵ using an array of 36 infrared lasers emitting at 830 nm (Sanyo Semiconductor, SDL-7032-102, Allendale, NJ). Exposures were done air-incident in the case of samples to be directly toned with powder or toning foil and substrate-incident (through the polyester support) in the case of the peel-apart sandwich structure. A half-tone-dot step wedge test pattern was reproduced using 300–600 mJ/cm² of incident laser irradiation. Immediately after exposure a visible image was apparent. Further visualization of the image was accomplished by toning with conventional Cromalin® powders by hand or by lamination at 50–70°C using Europrint® toner transfer foils (registered in the United States as Colortrax®, available from DuPont).

A peel-apart laminate was also prepared by pre-laminating a comparably sized piece of the Europrint® toner-transfer foil to the phototack film using a roll temperature of 50–70°C. Upon cooling to room temperature the laminate had adequate adhesion to be handled in use and could be separated by peeling apart. When exposed substrate-incident on the

modified Crosfield scanner using 600 mJ/cm² of laser energy and then separated, toner selectively remained on the phototack film in imaged areas.

RESULTS AND DISCUSSION

The same chemistry used in the Raymond and Hertler¹³ system (positive resist on a tacky sublayer) could be envisioned to be adaptable to a single-layer dry processible composition by first creating a miscible blend of both the acid-labile polymer and a low- T_g tacky resin and then relying on polarity-induced microphase separation after chemical reversion of the acetal ester polymer to poly(acrylic acid) and DHP **2** to "unmask" the tackiness of the low T_g component.

We have found that poly(2-phenylethyl acrylate) (pPEA, $T_g = -2^\circ\text{C}$ by DSC) forms optically clear nontacky blends with the polyacrylic acetal esters, pTHPA ($T_g = 49^\circ\text{C}$ by DSC), and pTHPMA ($T_g = 91^\circ\text{C}$ by DSC). If about 2% of **1** is included in a thin film of a blend (50% pPEA, 25% pTHPA, and 25% pTHPMA), imagewise exposure to near-UV light leads to conversion of pTHPA and pTHPMA to poly(acrylic acid) and poly(methacrylic acid), respectively, neither of which is miscible with pPEA (see Fig. 1). pPEA remains unchanged. As a result, microphase separation occurs, and pPEA, which would be expected to have a lower surface energy than the other components, migrates to the surface of the film. The tackiness that develops in the exposed regions permits these regions to be toned. Thus, the light-induced phase separation can readily be detected.

Blend Composition	Before Exposure	After Exposure
50% pPEA [$T_g -2^\circ\text{C}$] 25% pTHPA [$T_g 49^\circ\text{C}$] 25% pTHPMA [$T_g 91^\circ\text{C}$] 2% 1	$T_g 18^\circ\text{C}$ Optically Clear Non-tacky	$T_g 1^\circ, 198^\circ\text{C}$ Hazy Tacky

Figure 1 DSC Data for Polymer Blend and Components.

Table I Glass Transition Temperatures of Pure Polymers and Blends

Polymers and Blends	T_g by DSC ($^\circ\text{C}$)	T_g by TSC ($^\circ\text{C}$)
pPEA	-2	-9
pTHPA	49	37, 50 ^a
pTHPMA	91	83
50% pPEA, 50% pTHPA	—	14
50% pPEA, 50% pTHPMA	—	20, 44 ^b
50% pPEA, 25% pTHPA, 25% pTHPMA	13	18, 37 ^b

^a Two closely spaced glass transitions are observed in pure pTHPA for unknown reasons.

^b Two closely spaced glass transitions in blends indicate separate phases with similar compositions.

Blends of the acetal ester polymers, poly(tetrahydrofuran-2-yl acrylate) and poly(tetrahydrofuran-2-yl methacrylate) with tacky pPEA and **1** were also studied, and found to undergo phototackification. Poly(3-phenylpropyl acrylate), which has a T_g (DSC) of -11.7°C , could be used in place of pPEA ($T_g = -2^\circ\text{C}$) as the tack-producing component. However, our detailed studies were carried out with pPEA, pTHPMA, and pTHPA.

Phase Morphology Studies

Thermal analysis studies were undertaken to probe miscibility of the blends. DSC was inconclusive, so the TSC technique²⁶ was used. In the case of the T_g of the pure materials, a favorable comparison is seen (Table I) between DSC and TSC. The equivalent frequency of TSC is similar to that of DSC, and the spectra are similar to low frequency dielectric loss spectra.²⁶

Partial or complete miscibility is seen in all blends studied as is indicated by the intermediate T_g s of the two components. The TSC spectra for two blends and their respective pure components are shown in Figures 2 and 3 and the transitions summarized in Table I and Figures 4 and 5. In Figure 2, pure pPEA and pTHPMA exhibit single glass transitions, while the blend exhibits two glass transitions at ~ 20 and 44°C . These two glass transitions are not clearly resolved because of their close spacing and also because of ohmic conductivity at the higher temperatures that causes the sharp increase in current above the 44°C transition. The TSC thermal peak cleaning technique²⁷ verified that both transitions (shoulders) seen in the blend data in Figure 2, correspond to glass transitions. The high apparent

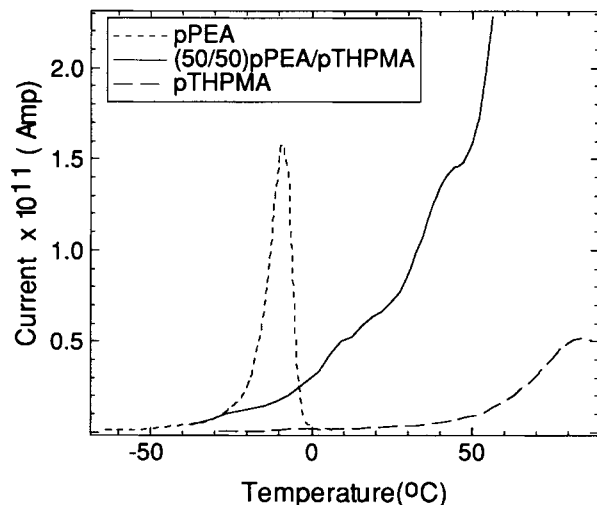


Figure 2 Thermally stimulated current spectra for pPEA, pTHPMA, and a 50/50 blend of the two.

activation energies measured at 20 and 44°C are a signature of a cooperative glass transition-like relaxation as described previously.²⁷

In Figure 3, pure pTHPMA exhibits two closely spaced glass transitions that are not clearly resolved. The reasons for this are not known. On the other hand, the blend data exhibits a single strong glass transition at intermediate temperatures indicating a high degree of compatibility. No hint of glass transition-like relaxations were detected in the blend for a pure pPEA phase at -9°C.

A third blend was studied consisting of 25% pTHPMA, 25% pTHPA, and 50% pPEA. The glass transitions determined by TSC are reported in Table

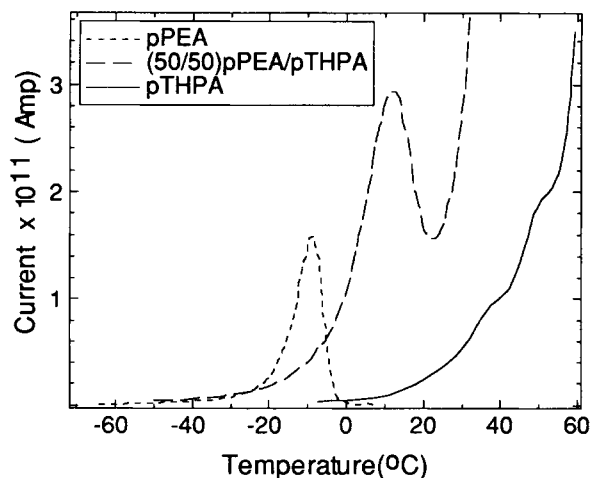


Figure 3 Thermally stimulated current spectra for pPEA, pTHPMA, and a 50/50 blend of the two.

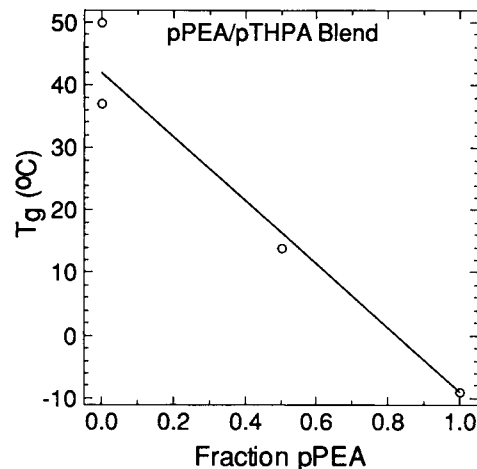


Figure 4 Glass-transition temperatures versus fraction pPEA for a blend of pPEA and pTHPMA and pure polymers. In cases where two values are plotted at the same temperature, two separate glass transitions were detected.

I, again indicating partial compatibility. It is possible that there is a pTHPMA rich phase and a pTHPA rich phase. As is the case with all the blends studied here, no pure pPEA phase relaxation is observed in the three component blend before exposure. Although the nature of the forces resulting in compatibility between the aromatic pPEA and the polymeric tetrahydropyranyl esters was not investigated, we note that Chong and Goh have reported on the miscibility of styrenic polymers with poly (tetrahydropyranyl-2-methyl methacrylate).²⁸⁻³⁰

After exposure, transmission electron microscopic

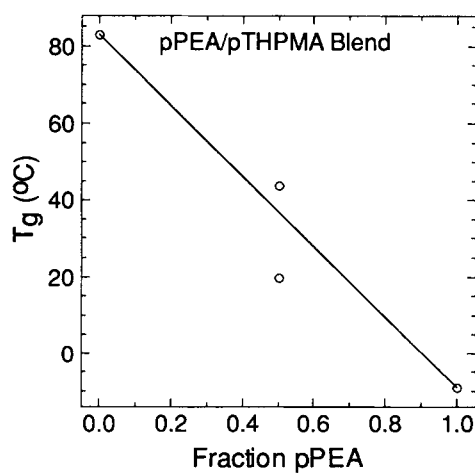


Figure 5 Glass-transition temperatures versus fraction pPEA for a blend of pPEA and pTHPMA and pure polymers. In cases where two values are plotted at the same temperature, two separate glass transitions were detected.

analysis of cross sections shows multiphase structure, with the dispersed phase containing carboxylic acid groups as indicated by staining techniques. Some thick (10–15 μm) exposed and toned films after aging for several months showed visible macroscopic phase separation with toner still adhering to discontinuous islands on the surface.

Studies of UV-Induced Tackification

Initial UV irradiation experiments with the 50:25:25 blend and PAG showed good photospeed (50 mJ/cm^2), dot tonal range, and resolution. However, a 2–5 min postexposure hold time necessary for good toning density, and a noticeable temperature/humidity sensitivity led us to explore the actual tackification mechanism in more detail.

After exposure and accompanying tackification, a strong, fragrant aroma emanated from the film. Olfactory comparison with DHP **2**, the expected cleavage product of the poly(acetal esters), proved this not to be the source of the odor. A GC–MS study of the off-gases implicated 5-hydroxypentanal and its hemi-acetal, tetrahydro-2*H*-pyran-2-ol **4**, the hydrate of dihydropyran (*vide infra*).

In situ real-time IR experiments were used to probe the humidity sensitivity. Thin phototack films were spin coated onto KBr wafers and dried. UV exposures were carried out in a temperature-/atmosphere-controlled IR cell using a high-intensity fiber optic source (Superlite UV, Lumatec, Munich). FTIR data acquisition was carried out before and after exposure under controlled conditions. Acetal esters show a number of characteristic bands in the fingerprint region assignable to C—O—C—O—C functionality. A decrease in absorbance of the band at 900 cm^{-1} was used to monitor the loss of acetal ester functionality in the film as a function of time. Two-minute exposures, corresponding to $\sim 500 \text{ mJ}/\text{cm}^2$ incident radiation, were used.

Data from three experiments, A–C, are shown in Figure 6. All experiments were run at room temperature. In A, the sample was preconditioned, exposed, and then held under a dry nitrogen purge. After approximately 2 h with little change in acetal ester functionality, the cell was opened and continuously purged with laboratory air (relative humidity $\sim 60\%$). An immediate, precipitous drop in acetal ester functionality was observed. In B, the sample was preconditioned in ambient air, then purged with nitrogen just before exposure. In C, the sample saw only an ambient air purge before and throughout the run. Control experiments ruled out oxygen as the differentiating factor. Water clearly plays a sig-

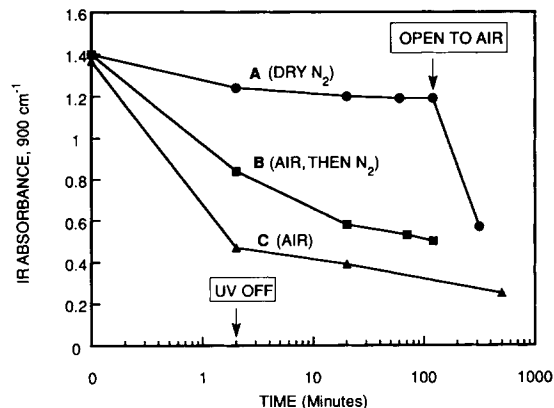


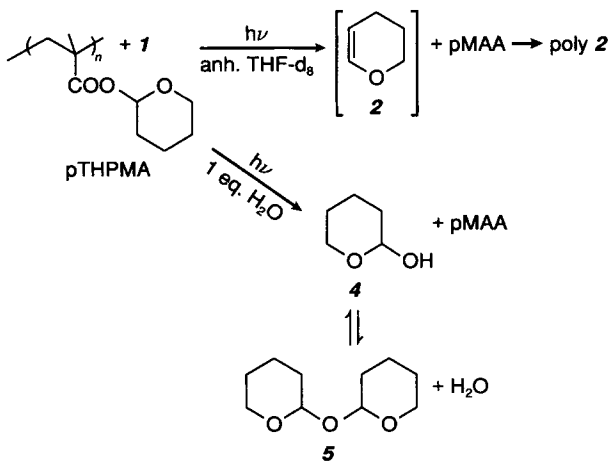
Figure 6 Real-time IR monitoring at 900 cm^{-1} of loss of acetal ester during and after UV exposure.

nificant role in the chemistry of this system. We attribute the intermediate rate of acetal ester loss in B to residual moisture in the thin film.

Complementary solution experiments in THF- d_8 containing 1 equiv. of water using ^1H NMR analysis confirm the formation of tetrahydro-2*H*-pyran-2-ol **4**, as well as its dehydrated dimer **5**³¹ after UV exposure (see Scheme 2). In contrast, under *anhydrous* conditions in solution the poly(acetal ester) cleaves almost instantaneously to give pMAA and product(s) that appear to be oligomeric or polymeric **2**. Photolysis of **2** in the presence of **1** under anhydrous conditions gives products with a similar ^1H NMR spectrum.

Postexposure hold time until tackification can be minimized by conditioning the exposed film in a solvent-vapor chamber such as dichloromethane, 2-butanone, or methanol.³² Studies in constant-humidity chambers with saturated aqueous salt solutions show that below relative humidities of $\sim 50\%$, postexposure hold times become very long (> 20 min). With increasing humidity above 50%, the time required after exposure for tack to develop decreases correspondingly. Even at low humidity, however, tack can be induced with a mild (50–70°C, 30–60 s) postexposure bake.

We propose the following sequential four-step mechanism for tackification: photoacid generation, acid diffusion, acetal ester cleavage, and microphase separation. Acid diffusion and acetal ester cleavage appear to be dominated by film matrix effects (primarily T_g), because the T_g (18°C) of the polymer blend is near room temperature. Moisture plasticizes the matrix, aiding acid migration and effecting hydrolysis of the ester. Consistent with this, pMAA and particularly pAA are hygroscopic. In the absence of water, tackification is very slow unless some other



Scheme 2

plasticizing agent or heat is used. An alternate mechanistic pathway may occur here through formation of **2**. In both cases, DSC studies show that the small molecule products formed also plasticize the matrix. As acetal ester cleavage proceeds, an autocatalytic effect would be expected as more plasticizer and hygroscopic species are formed.

For commercial applications, minimization of the hold time and humidity sensitivity would be desirable. This was approached in several ways. Numerous plasticizing additives were investigated including water, alcohols, glycols, phthalates, and high-boiling solvents. Most showed minimal impact, or at an effective level lowered the T_g of the blend so much that background stain (toning) in unimaged areas was a problem. Pentaethylene glycol worked particularly well. At 5% loading in the composition, this high-boiling plasticizer markedly lowered time-to-tack even at low relative humidity. During stress aging studies of the films at high humidity, this material bloomed to the surface of the film. Oligomeric or polymeric glycols acted as compatibilizers and hindered phase separation. Numerous hydrates, both organic and inorganic, and humectant polymer additives were investigated, but were found to be either ineffective or not compatible with the polymer blend. Also evaluated as additives were several small-molecule acetals and ketals as well as silanols that dehydrate under strongly acidic conditions to provide alcohols or water. These were found to have little or no effect on postexposure hold time.

Poly(tetrahydrofuranyl acrylate) and poly(tetrahydrofuranyl methacrylate) with pPEA gave phototackifiable compositions that were less moisture sensitive than the corresponding pTHPA and pTHPMA compositions. Acrylate backbones were

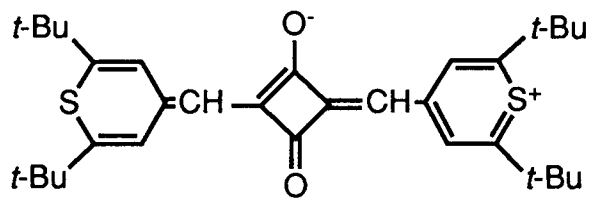
more active than methacrylate backbones, presumably due to the more hygroscopic nature of the corresponding carboxylic acids.

Detailed studies of molecular weight effects were not carried out, but, in general, low molecular weight polymers ($< 20,000$ Da) gave faster tackification. One formulation using pPEA with \bar{M}_w of $\sim 300,000$ did not develop tack at all.

Studies of Thermally Induced Tackification

The intensity of new semiconductor diode lasers operating in the near-IR (700–850 nm) is sufficient to generate intense thermal heating in thin imaging layers with high resolution and reasonable scanning rates. This allows the development of new types of imaging media based on thermal rather than photolytic processes. Benefits include daylight handling of the film and elimination of wet processing or other polluting effluent. Electronic or digital offpress color proofing systems are reviewed elsewhere.³³

Digital proofing capability has been demonstrated by taking advantage of the thermal lability of the poly(acetal esters). Thermal gravimetric analysis (TGA) of pTHPMA and pTHPA shows they cleanly lose **2** at modest temperatures (T_{dec} 174 and 154°C, respectively). Conversion of the UV system to a photothermal mode of imaging was accomplished using a near-IR dye in place of the PAG. The dye SQS **3** was chosen due to its intense absorption ($\lambda_{max} > 450,000$ at 830 nm) and near lack of color in the visible region.



SQS 3

Imaging was done on a near-IR-diode-laser (830 nm) modified Crosfield 646 scanner.²⁵ Visible images were obtained with write energies of ~ 600 mJ/cm² and a 10.4 μ m raster width (spot size). These were tonable either with powders or by toner transfer during lamination at ~ 50 –70°C using Europrint® toner transfer foils. In the case of powder toning, 2–98% dots (150 lpi screen) were reproduced. The transfer foil and peel-apart experiments gave crude images but demonstrated feasibility. The full scope of this system in terms of photospeed, resolution,

tonal range, dot gain, and shape, and preferred proofing configuration is yet to be determined.

CONCLUSION

A new direct single-layer phototackification system with application to four-color half-tone proofing has been invented. It makes use of chemical amplification and is based on photoinduced microphase separation in an initially nontacky miscible blend of acid-labile and tacky polymers. The system can be sensitized to either UV or near-IR wavelengths.

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