

SHORT COMMUNICATIONS

Photodegradable Toners for Electrophotography I. Photodegradability of Matrix Resin

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In highly modernized present society, the larger part of information is communicated and recorded by hard-copy. A huge volume of paper is consumed for this purpose, and development of effective methods for recycling paper is important to conserve natural resources. At present, used paper is unraveled into slurry, and paper is made from it. This paper is more expensive than paper made from virgin pulp, which means the present paper-recycling requires much more natural resources including fossil energy, though it may be friendly to wooden resource. Consequently, it is urgently needed to develop a truly effective method of paper-recycling.

Recently toner images containing fadable colorants¹ and detachment of toner images with a roller after swelling with an organic solvent² are proposed as reusing methods of copying paper, but they are still under development. Here we propose to detach the image of photodegradable toners from the paper substrate by brushing, crumpling and/or blowing after ultraviolet (UV) light irradiation. In a previous study³ we found phenyl isopropenyl ketone (PIPK) copolymers 1200 times as sensitive as poly(methyl methacrylate). Therefore, they are more than 240 times as sensitive as aliphatic ketone polymers, developed for disposable containers and packaging foamed materials photodegradable by sunlight in a few days to several months.⁴

In this study we copolymerized PIPK into the known toner resin for electrophotography and measured spectral and molecular weight changes as well as photodegradability by mid/near or deep UV irradiation.

EXPERIMENTAL

Materials

PIPK was prepared as described in a previous paper,⁵ and copolymerized with styrene(St) and methyl methacrylate(MMA)/*n*-butyl acrylate (BuA) in emulsion or suspension. The product was reprecipitated from benzene/methanol system. The copolymerization molar ratio, molecular weight, glass transition temperature (T_g), and softening point (T_s) were determined by NMR,⁶ GPC, DSC, and Shimadzu Flow Tester, respectively. Polymer data are summarized in Table I.

Specimen Preparation and UV Irradiation

Terpolymer layers of *ca.* 400 nm thick were spincoated from tetrahydrofuran solutions onto glass or quartz plates, and prebaked at 90°C for 20 min. The layer was irradiated with a super-high pressure mercury lamp (SHPL) of 75 W, Toshiba SHL-100-UV-2, or a low pressure mercury lamp (LPL) of 8 W, Toshiba GL-8, from a distance of 10 cm. The distribution of radiation energy of SHPL is 33% at 366 nm and 19% at 313 nm. The emission from LPL can be regarded as a monochromatic radiation at 254 nm. Light intensity was measured with a thermopile as 23 mW cm⁻² and 0.65 mW cm⁻².

RESULTS AND DISCUSSION

Photodegradability was estimated by brushing off the polymer layer after UV irradiation, as indicated in Table II. The layers of Terpolymers A and C were removed completely by brushing after 5 min-exposure to SHPL

Table I. Summary of polymer data

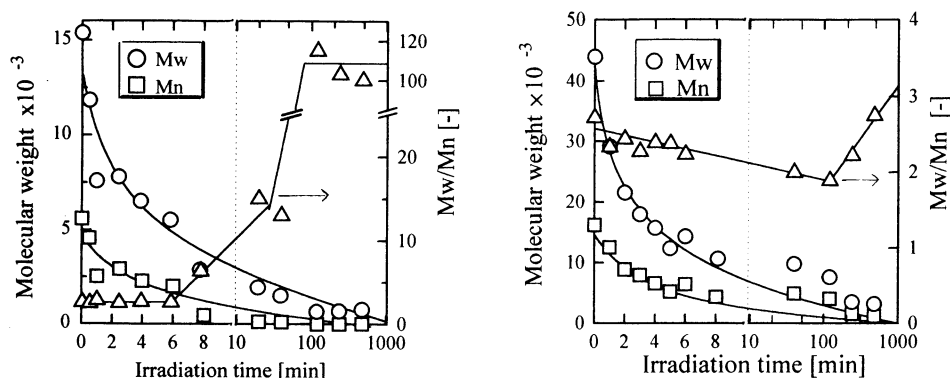
Terpolymer	Polymn. initiator	composition	M_w	M_n	M_w/M_n	T_g °C	T_s °C
		PIPK : St : BuA					
A	(NH ₄) ₂ S ₂ O ₈	19 : 28 : 53 (MMA)	53000	16000	3.3	110	111
B	(NH ₄) ₂ S ₂ O ₈	30 : 45 : 25	16000	5000	3.2	73	112
C	(NH ₄) ₂ S ₂ O ₈	12 : 69 : 19	44000	17000	2.6	75	102
D	AIBN ^b	35 : 41 : 24	22000	9200	2.4	62	95

^a MMA, methyl methacrylate. ^b AIBN α,α' -azobisisobutyronitrile.

Table II. Polymer layers irradiated with a mercury lamp^a

Irradiation time in min	Super high pressure						Low pressure					
	1	2	3	4	5	6	1	2	3	4	5	6
Terpolymer A	△	○	○	○	⊙	⊙	△	○	⊙	⊙	⊙	⊙
B	×	×	×	○	●	●	○	○	●	●	●	●
C	△	△	○	○	⊙	⊙	△	○	⊙	⊙	⊙	⊙
D	×	×	○	○	●	●	○	△	●	●	●	●

^a ×, no change observed; △, layer was slightly damaged by brushing; ○, layer was partly removed; ⊙, layer was completely removed; ●, most of the layer was removed, leaving a thin residual layer.

**Figure 1.** Molecular weight changes in Terpolymer B (left) and C (right) by mid/near UV irradiation.

or 3 min-exposure to LPL, while those of Terpolymers B and D were not. Since BuA content was large in Terpolymers B and D, it is assumed that BuA is cross-linked by UV irradiation to form the residual layer.

UV spectra of Terpolymers B and C layers were scanned before and after UV exposure to SHPL and LPL. As discussed previously,³ absorbance of the band at 242 nm due to benzoyl group decreased and that at 250–400 nm due to conjugated double bond increased gradually as the irradiation dose increased. Absorbance decrease of the band at 220 nm was accompanied with thinning of polymer films in the case of UV irradiation with SHPL.

Molecular weight changes were measured on Terpolymers B and C scratched from the layers exposed to SHPL and LPL, and the results with SHPL are shown in Figure 1. Change in $\bar{M}_w/\bar{M}_n$ clearly demonstrates that cross-linking is not negligible with Terpolymer B, while Terpolymer C degrades predominantly by random scission

of main chains.

In conclusion, the PIPK-St-BuA terpolymer with smaller BuA content is degraded predominantly by random scission and is photosensitive enough for the polymer layer to be removed easily by brushing-off after UV exposure for several minutes.

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