Polymers for Photothermography: Controlled Thermal Release of Color Photographic Developer from Substituted Polystyrene Derivatives

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ABSTRACT: A series of functionalized styrenic polymers were synthesized that were designed to release a low molar mass compound, a color photographic developer (a substituted phenylenediamine), when heated. The developer moieties were covalently bound via special protecting groups ("switches") that were stable at ambient temperature but decomposed to release the developer above 100 °C. In one series, the protecting group consisted of benzylic carbamates, designed to release via a cationic mechanism. In a second series, the protecting groups comprised ethylene linkages set up for 1,2-elimination, and release occurred via an anionic mechanism. Waterborne formulations of the title polymers suitable for coating were prepared via milling, evaporative dispersion, or emulsion polymerization. The polymers were incorporated into silver halide-based photothermographic media, which were capable of forming color images after appropriate exposure and heat treatment, indicating successful controlled release of the developer. This system may be applicable to other controlled-release applications in which a bound compound is to be released when the material is heated.

Introduction

Polymers for controlled release represent a major field of research and have found diverse applications in pharmaceuticals, food and fragrance chemistry, agricultural products, and other systems. In most cases, the active material to be released ("payload") is physically encapsulated within the polymer and gradually diffuses out, often promoted by erosion or biodegradation of the polymer under the conditions of use.[1−4] An alternative, but rarer, strategy is to attach the payload covalently to the polymer via a protecting group. The payload is then released under the influence of some external stimulus such as light, heat, a pH change, or moisture or by the action of a chemical reagent.[5,6] Indeed, the latter approach is related to photoresist chemistry[7−9] and to the linking groups used in solid-phase synthesis.[10−15] One of the advantages of the covalent-linker strategy for controlled release is that a potentially reactive functional group on the payload can be inactivated by the protecting group and its latent functionality released upon the appropriate stimulus. This paper describes application of the covalent-linker approach to photographic imaging chemistry, wherein the payload is a color developer, and the stimulus is heat. The chemistry described herein is not restricted to developer but might be generalized to include other applications in which a payload is to be released at elevated temperature.

Conventional silver halide photographic systems[16−18] are "wet-developed". That is, some of the chromogenic chemical reagents are supplied externally via developing baths. In the most widely used scheme for color photography, cyan, magenta, and yellow dyes are formed by oxidative coupling reactions between a color developer (a substituted *p*-phenylenediamine, present in the developing bath) and appropriate couplers (photographic dye precursors, embedded in the film or paper). An example of photographic dye formation with a class of commercially important magenta couplers relevant to this work is shown in Figure 1, where the equivalence of the coupler refers to the number of moles of silver ion needed to complete the oxidative coupling.

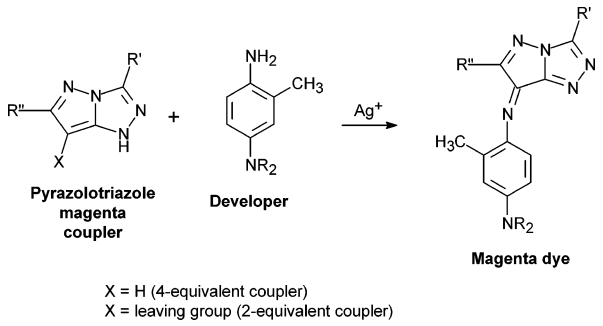

Figure 1. Photographic magenta dye formation from magenta couplers and developer.

Photothermography[19] is an alternative silver halide imaging system in which the image is formed by chemistry that is activated only at elevated temperatures. Like conceptually related "instant photography", photothermography does not utilize external developing baths; rather, all of the image-forming reagents are incorporated simultaneously within the medium. However, these reagents must be prevented from reacting with each other under ambient conditions; otherwise, premature and indiscriminate image formation ("fog") would occur. One way to inhibit these unwanted reactions is to confine the reagents to distinct phases, layers, or compartments, a scheme reminiscent of "wolf and lamb" polymeric reagents.[20] A more sophisticated approach applicable to photothermography involves inactivation of one of the chromogenic reagents using a thermally labile protecting group ("switch"). The active reagent might then be released during development at elevated temperature.[21]

For color photothermographic imaging, both developer and coupler must be present in the medium, and in principle, either might be protected to prevent premature reaction. However, couplers are relatively elaborate and expensive compounds, and

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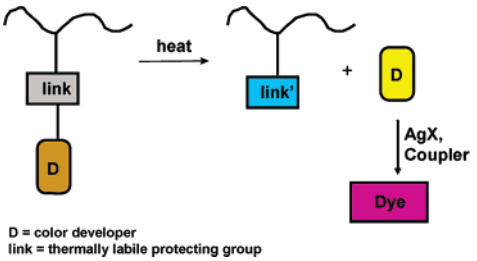


Figure 2. Schematic of action of polymeric blocked photographic developers.

it seemed impractical to introduce protecting groups into such already complicated compounds. On the other hand, developers are simpler molecules and more amenable to protecting group chemistry. Appropriate inactivation of the developer would impart the additional advantages of inhibiting oxidative degradation of the developer and preventing deleterious reactions of the developer with various components in the photographic emulsion. A large variety of such low molar mass "blocked developers" were synthesized and evaluated during the course of this research,[22−29] and we recognized that additional advantages might be imparted to the system if the protecting group were, in fact, a polymer.

(1) With its high molar mass, a polymer would not be prone to diffuse among layers or out of the film, even at elevated temperature.

(2) The T_g of the polymer might provide a discontinuity in the release rate vs temperature profile of the blocked developer (i.e., non-Arrhenius behavior). In particular, if the polymers could be prepared with a T_g of ~100 °C, the release reaction might be shut down near room temperature (necessary for long-term storage of the unexposed media) but still proceed at the anticipated thermal development temperatures above 100 °C, at which the polymer is a liquid.

(3) The thermally labile linking chemistry already developed and tested for low molar mass versions could guide polymer design.

(4) Polymer small-particle technology could be applied to the creation of aqueous dispersions (needed for photographic coating) of the polymers. For example, emulsion polymerization would combine polymer synthesis and dispersion making into one step.

The principal disadvantage of this approach is the cost associated with the more complex synthesis required.

We report herein aspects of a program directed toward a color photothermographic film[21] that contains a "polymeric blocked developer" as a key component. A schematic of the system is shown in Figure 2.

Polymeric blocked developers were prepared with two different release chemistries: benzylic carbamate switches and 1,2-elimination switches (Figures 3 and 4). In the former, release of the developer is triggered by ostensible formation of an α-cation; therefore, electron-donating groups on the adjacent aromatic moiety should increase reactivity, and release may be acid-catalyzed. In the latter, a β-anion may be involved; therefore, the activity of the blocked developer depends on the presence of a suitable electron-withdrawing group (EWG), and release may be base-catalyzed. The 1,2-elimination switches are closely related to the base-amplifying compounds prepared by Ichimura et al.[30,31]

Results and Discussion

Polymers designed for controlled release of color photographic developer were prepared by synthesis and free radical

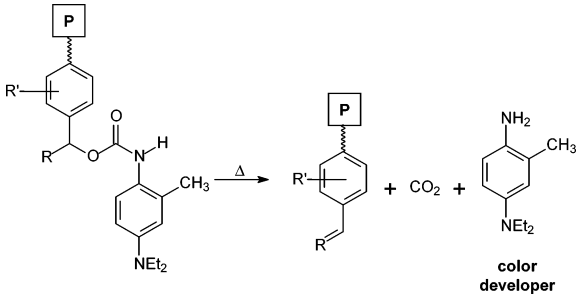


Figure 3. Release of color developer from functionalized polymers via a benzylic carbamate switch.

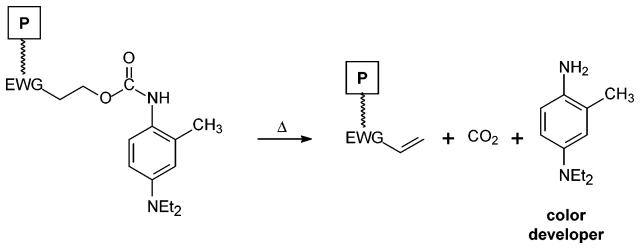
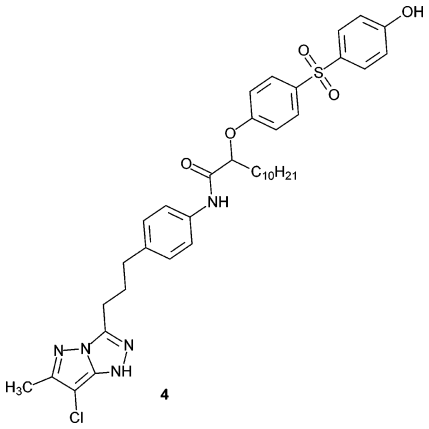


Figure 4. Release of color developer from functionalized polymers via a 1,2-elimination switch.

polymerization of the corresponding functionalized monomers, as described below. The polymerization reactions provided high molar mass polymers, despite the relatively complex functional groups present on the monomers. The polymers were soluble in ordinary organic solvents and could be made into the necessary waterborne formulations by homogenizing the solutions with water and an appropriate surfactant and stripping the solvent ("evaporative dispersion").[32] Alternatively, aqueous dispersions could be prepared by ball-milling the solid polymers, or, in a few cases, by emulsion polymerization of the monomers. The polymers were incorporated into photothermographic test coatings (see Experimental Section) containing a sensitized silver halide emulsion and magenta coupler **4**.[33] After exposure to a standardized light source, the coatings were heat-developed at a range of temperatures. Evidence of release of the payload was judged by the appearance of magenta color in the coating (formed by reaction between coupler **4** and developer **CD**), quantified as green absorption using a densitometer. Results are discussed in terms of color density at maximum exposure (D_{max}) or image discrimination, the difference between color density at maximum and minimum exposures ($D_{max} - D_{min}$).



A. Controlled Release from Polymers with Benzylic Carbamate Switches. Previous work[26] had shown that low molar mass benzylic carbamates analogous to the structure suggested by Figure 3 could be decomposed by heat to release

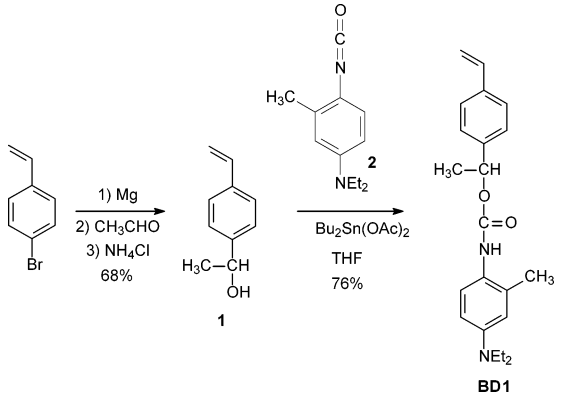


Figure 5. Synthesis of blocked developer monomer **BD1**.

phenylenediamine color developer. Therefore, we developed a series of polymeric blocked developers **PBD1**−**PBD4** along these lines, as follows.

A.1. Synthesis of Blocked Developer Monomers BD1−**BD4.** Monomer **BD1** was synthesized in two steps (Figure 5). First, 4-bromostyrene was converted to a Grignard reagent and then reacted with acetaldehyde to provide the known[34,35] benzylic alcohol (**1**). This compound could be acylated with isocyanate **2**[36] to provide **BD1**.

Two more highly activated monomers, **BD2** and **BD3**, were synthesized by corresponding methods as shown in Figure 6. For **DB2**, 4-hydroxyacetophenone was alkylated with 4-chloromethylstyrene to produce ketone **5**, which was then reduced to the benzylic alcohol **6**, and the monomer was obtained by reaction of **6** with isocyanate **2**. The synthesis of **BD3** followed an identical sequence, but starting from 2-hydroxy-4-methoxyacetophenone. Samples of the intermediate **7** were prepared under two different reaction conditions: NaH in DMF and Cs_2CO_3 in acetonitrile. The latter procedure gave slightly higher yields and was judged to be more expedient than the former.

The so-called "Rink resin" is a popular reaction support in solid-phase peptide and combinatorial syntheses.[37] It is based on the 4-(2,4-dimethoxyphenylhydroxymethyl)phenoxy group and is designed for rapid release of the bound compound upon treatment with mild acid. The monomer **BD4,** based on this structural motif, was synthesized as shown in Figure 7. First, the Grignard reagent derived from 4-bromostyrene was reacted with commercially available 2,4-dimethoxybenzaldehyde to produce the intermediate alcohol **9** in good yield. (This compound had been reported previously in the literature as part of a study directed toward UV-absorbing polymers.[38]) By treatment of **9** with the isocyanate **2**, the monomer **BD4** was obtained.

A.2. Synthesis of Polymeric Blocked Developers PBD1−**PBD4.** Solution free-radical vinyl polymerization of the above-mentioned functionalized monomers proceeded smoothly to provide polymers **PBD1**−**PBD4** with high molar mass and T_g values considered to be nearly ideal for the intended application. The isolation by precipitation for some of these polymers was complicated by their high solubility because it was difficult, in some cases, to find a nonsolvent for the polymer that was a solvent for the monomer. Nevertheless, fair to excellent yields of polymers were obtained. Relevant data are collected in Table 1.

With **BD3,** polymerization was carried out in two different organic solvents (DMF and chlorobenzene), and products with slightly different T_g values were obtained (83 and 89 °C). The reasons for this variation are unknown; the level of residual solvent in each sample was found to be very low by NMR. To test the influence of polarity on release rate, we also synthesized 50/50 (feed wt %) copolymers of **BD3** with styrene (**S**), methyl methacrylate (**MMA**), and 2-hydroxyethyl methacrylate (**HEM**). In this way, we covered the spectrum from nonpolar to polar comonomers. The composition of these copolymers was determined by ^{1}H NMR and found to be similar to the feed ratios.

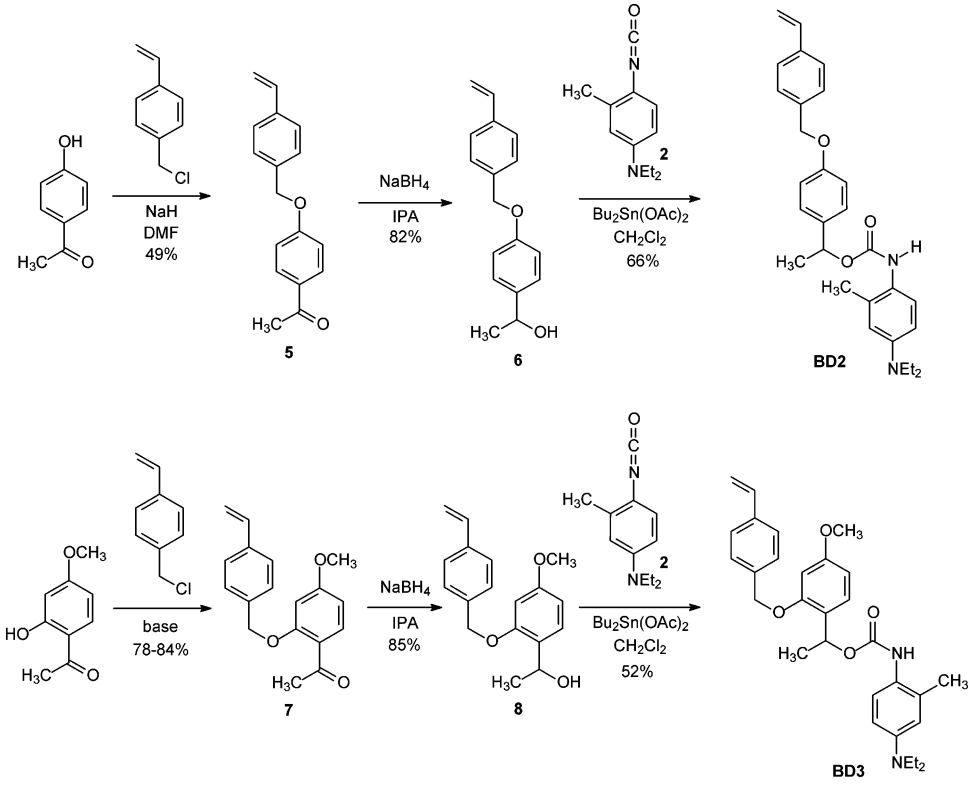


Figure 6. Synthesis of blocked developer monomers **BD2** and **BD3**.

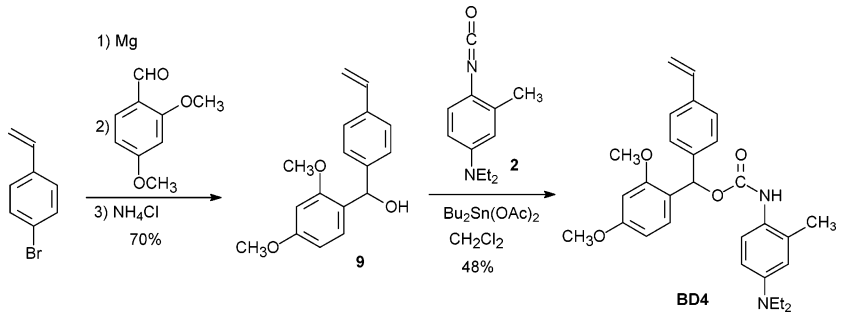


Figure 7. Synthesis of blocked developer monomer **BD4**.

Table 1. Solution Polymerization Results and Characterization of Polymeric Blocked Developers

monomer	comonomer[a]	solvent[b]	mol % initiator[c]	temp (°C)	time (h)	% yield	T_g[d] (°C)	$\bar{M}_n$[e]	$\bar{M}_w$[e]	relative activity[f]
BD1		PhCl	2.1	60	16	41	93	11 200	26 200	poor
BD2		PhCl	1.0	63	18	58	83	33 400	90 800	fair
BD3		PhCl	2.0	65	24	46	89	13 800	28 800	high
BD3		DMF	1.1	60	20	35	83	21 500	48 200	good
BD3	1:1 (wt) **S**	PhCl	2.0	65	24	30	97	5900	10 300	good
BD3	1:1 (wt) **MMA**	PhCl	2.0	65	24	53	95	13 000	28 700	good
BD3	1:1 (wt) **HEM**	DMF	2.0	65	24	100	102	20 600	59 900	good
BD4		PhCl	1.0	70	20	31	117	16 100	57 800	very high
BD5		PhCl	1.0	65	20	98	91	36 100	185 000	poor
BD6		PhCl	1.0	70	18	58	107	50 600	85 500	very high

[a] **S** = styrene, **MMA** = methyl methacrylate, **HEM** = 2-hydroxyethyl methacrylate. [b] Polymerization solvent; PhCl = chlorobenzene, DMF = *N*,*N*-dimethylformamide. [c] Initiator = 2,2′-azobis(2-methylbutanenitrile). [d] Glass transition temperature by DSC. [e] Molar mass averages by SEC in DMF, poly(ethylene oxide) calibration. [f] Comparison of effectiveness of controlled thermal release of developer from the polymer, determined by magenta dye formation in photothermographic test format.

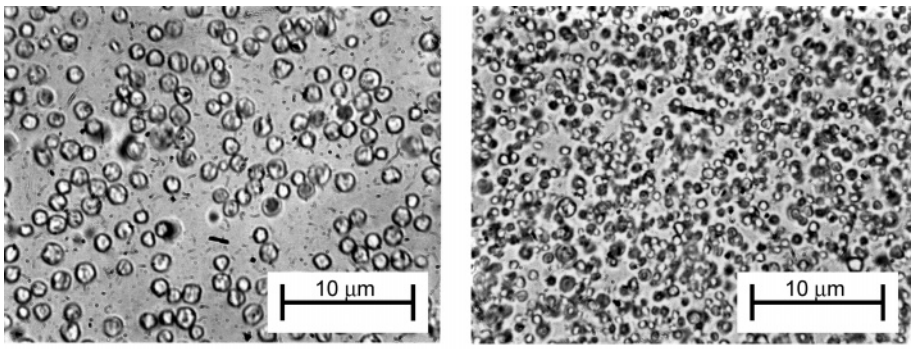


Figure 8. Photomicrographs of particles of **PBD3** prepared by evaporative dispersion (ED) with two different amounts of surfactant.

Emulsion copolymerization of **BD3** failed, despite numerous attempts in which temperature, comonomer, initiator, surfactant, pH, etc., were varied. An acceptable preemulsion could be obtained when the monomers were stirred in water; but in all cases, the polymerization mixture gradually discolored, and a substantial amount of coagulated material separated. Direct emulsion polymerization of a dispersion of solid **BD3** was also unsuccessful. Apparently, **BD3** or its polymer cannot withstand the contact with warm water that is present during attempted emulsion polymerization. The very small particle size of such emulsions may exacerbate the problem. Presumably, the carbamate linkage hydrolyzes under the reaction conditions, releasing free developer (a very reactive electron-rich aromatic compound) that subsequently reacts with the initiator or comonomer to produce highly colored species, eventually spoiling the emulsion.

Waterborne suspensions of polymeric blocked developer particles required for coating were prepared by ball-milling or by evaporative dispersion.[32] In the most convenient variation, the blocked developer monomer was polymerized in ethyl acetate to nearly complete conversion (>98% by ^{1}H NMR), and the resulting solution was used directly to make the dispersion, without isolation of the polymer. As is typical for this technique, very uniform spherical particles could be obtained (Figure 8). The particle size could be adjusted somewhat, with smaller particles forming when more surfactant was used.

A.3. Controlled Release from Polymeric Blocked Developers PBD1−PBD4. Waterborne dispersions of **PBD1**−**PBD4** were coated in a standard photothermographic test format, and the coatings were exposed and tested for production of magenta dye upon thermal development at various temperatures between 100 and 160 °C. **PBD1** was ineffective in releasing developer, as, even at the highest temperature studied, only a trace of magenta dye was detected. For **PBD2**, only a small amount of developer release could be detected when the pH of the coating was neutral. However, when the coating was adjusted to acidic pH, substantial magenta dye formation was observed at 160 °C, indicating that the release mechanism catalyzed by acid was successful at this temperature (Figure 9).

For **PBD3** and related copolymers, all were found to have acceptable release rates of developer, even at neutral pH (judging from the production of magenta dye in the thermally processed

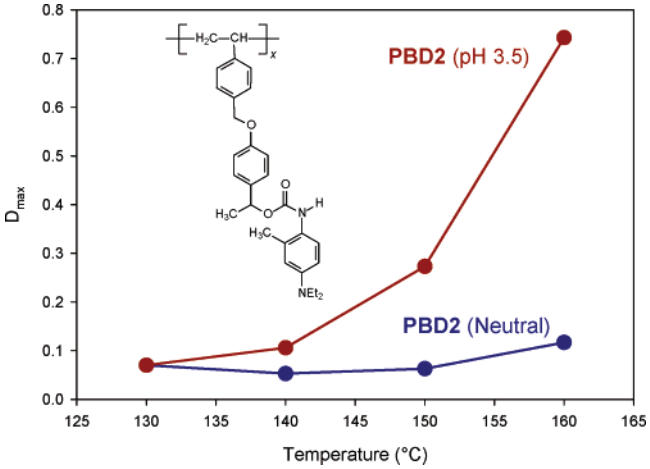


Figure 9. Photothermographic test results for **PBD2** for two coatings adjusted to different pH values, expressed as magenta density at maximum exposure (D_{max}) as a function of development temperature.

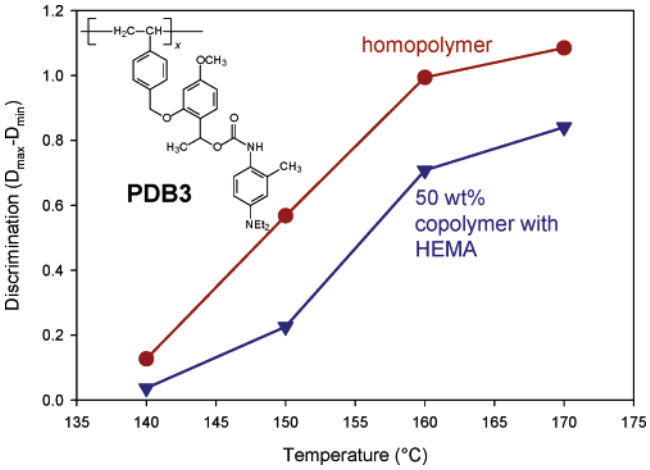


Figure 10. Photothermographic test results for **PBD3** homopolymer and related copolymer with 2-hydroxyethyl methacrylate (**HEMA**), expressed as image discrimination vs development temperature.

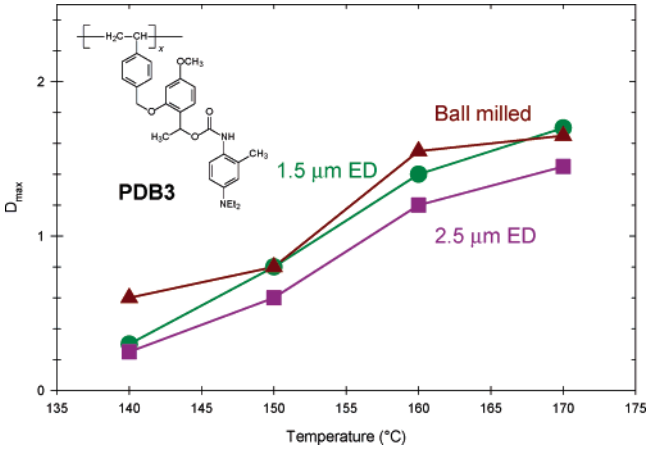


Figure 11. Photothermographic test results for **PBD3** formulations prepared by ball-milling or evaporative dispersion (ED, two different particle sizes), expressed as magenta density at maximum exposure (D_{max}) vs development temperature.

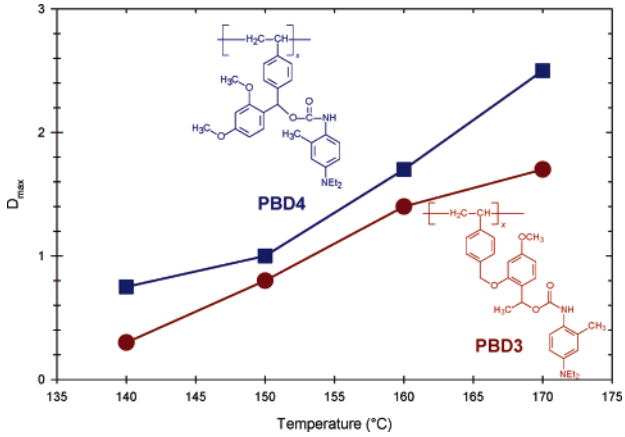


Figure 12. Photothermographic test comparison for **PBD3** and **PBD4** polymeric blocked developers, expressed as color density at maximum exposure (D_{max}) vs development temperature.

film). For example, Figure 10 shows the image discrimination for **PBD3** and **PBD3**-*co*-**HEM** for various processing temperatures. The copolymers of **BD3** with styrene **S** and with methyl methacrylate **MMA** were approximately equally active to the **HEM** copolymer, but all three copolymers were significantly less active than the homopolymer. (Note: The copolymers were coated at twice the concentration as the homopolymer to account for the dilution by comonomer.) There were no major differences in release rate from samples of **PBD3** that had been ball-milled or evaporatively dispersed (Figure 11), although smaller particle size appeared to impart slightly enhanced release. The activity and discrimination observed for the polymers based on **BD3** were significantly greater than that of **PBD2**, consistent with the presumption that increased electron density adjacent to the benzylic carbamate would facilitate release.

PBD4 was dispersed by ball-milling and incorporated into a photothermographic system. Test results (Figure 12) showed that **PBD4** was the most active polymeric blocked developer in this class, producing substantial magenta color indicative of successful thermal release of the developer.

B. Controlled Release from Polymers with 1,2-Elimination Switches. As was the case with the benzylic carbamate polymers (section A), low molar mass compounds had been prepared[23,28] that released color developer in photothermographic formulations via 1,2-elimination from activated ethylenic linkages. Two examples of analogous polymeric blocked developers with the general structure of Figure 4 were synthesized and tested, as follows.

B.1. Synthesis of Blocked Developer Monomers BD5−BD6. Monomer **BD5**, designed according to Figure 4 and activated by a sulfonyl electron-withdrawing group, was synthesized as shown in Figure 13. (Very similar chemistry had been reported as part of a solid support for combinatorial synthesis.[14,39]) The required starting material, hydroxyethyl sulfone (**10**), was synthesized according to the literature[40] but was inevitably contaminated with significant amounts of the sulfoxide, **11**. Simple recrystallization of the mixture from various solvent systems either failed to remove all of the **11** or resulted in a low recovery of **10**. However, treatment with Oxone and crystallization directly from the reaction mixture provided pure **10** with good recovery. The monomer **BD5** was obtained in excellent yield by reaction of alcohol **10** with isocyanate **2**.

An alternative blocked developer monomer, **BD6**, activated by an electron-deficient heterocycle was synthesized as shown in Figure 14. 2-Methylbenzimidazole was alkylated with 4-chloromethylstyrene to provide **12**. The active methyl group on **12** reacted with formaldehyde in a kind of Mannich reaction to yield alcohol **13**. Unfortunately, this reaction gave rise to several unidentified byproducts, so pure **13** was obtained only after flash chromatography. Acylation of **13** with isocyanate **2** gave a nearly quantitative yield of **BD6**.

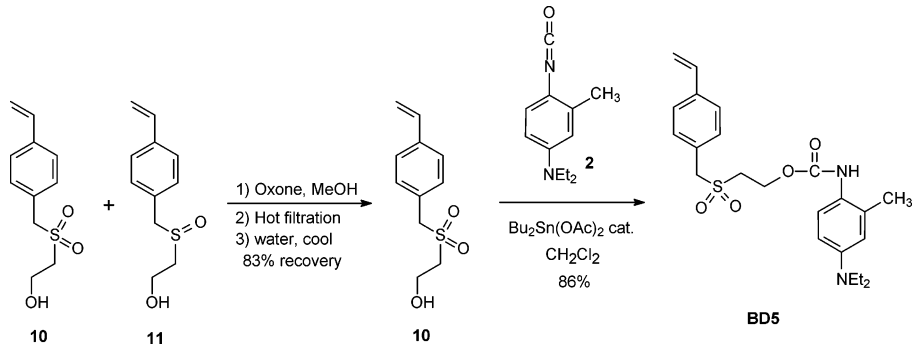


Figure 13. Synthesis of blocked developer monomer **BD5**.

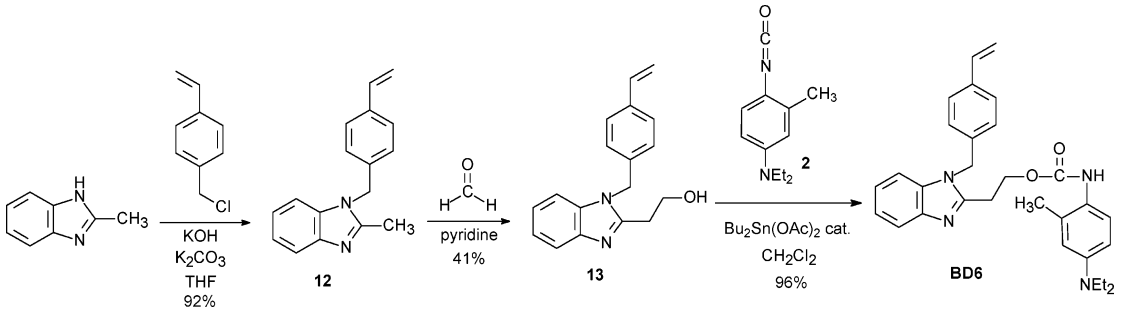


Figure 14. Synthesis of blocked developer monomer **BD6**.

B.2. Synthesis of Polymeric Blocked Developers PDB5−PBD6. Simple solution free-radical polymerization of **BD5** or **BD6** produced the respective homopolymers with high molar mass, although, inexplicably, the distribution of **PBD5** was broad, while that of **PDB6** was narrow (Table 1). **BD5** was also copolymerized in an emulsion with butyl methacrylate, methyl methacrylate, or butyl acrylate to produce stable latexes. Emulsion polymerization was especially convenient because the latex could be used directly in photothermographic coatings. In addition, the particle sizes were much smaller than those obtainable by ball-milling the solid polymer (e.g., ca. 65 nm vs 500 nm).

B.3. Controlled Release from Polymeric Blocked Developers PBD5 and PBD6. A ball-milled dispersion of **PBD5** homopolymer and various latexes of related copolymers were incorporated into photothermographic test packages. Unfortunately, all of the polymers based on **BD5** exhibited very low activity in photothermographic systems (i.e., apparently released very little developer), even though samples with substantial variations in particle size and glass transition temperature were examined. Judging from the reports of similar linking groups used in combinatorial chemistry, a strong base such as methoxide or fluoride may be required to effect release.[14,39] On the contrary, **PBD6** (applied via a ball-milled dispersion) was much more active and very effectively released developer under the thermal processing conditions, as evidenced by a substantial amount of magenta color produced (Figure 15).

C. Conformational Equilibria in Carbamate Blocked Developer Monomers. During the course of synthesis of monomers for polymeric blocked developers, we discovered an unusual occurrence of what appears to be restricted conformational isomerization in certain *N*-arylcarbamates. It is notable that this phenomenon did not occur with every compound we synthesized containing this substructure.

The ^{1}H NMR spectrum of **BD5** was unexpectedly complicated under ordinary conditions. Even though the compound has been carefully purified, anomalous signals appeared, including several broad peaks. An explanation for this phenomenon

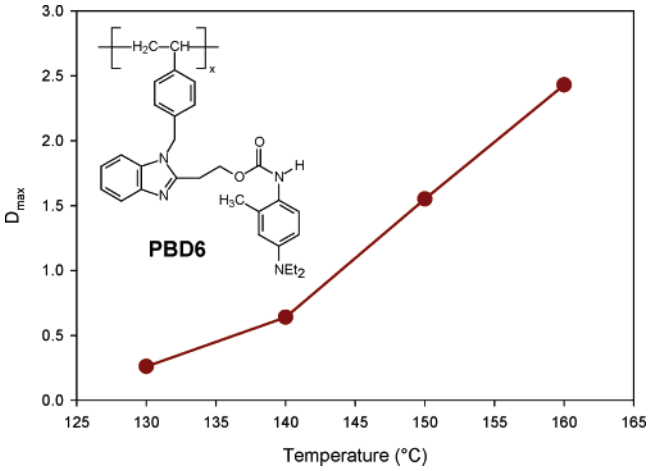


Figure 15. Photothermographic test results for **PBD6** polymeric blocked developer, expressed as magenta density (D_{max}) as a function of development temperature.

became apparent when the spectrum was reexamined at high and low temperatures (Figure 16).

At low temperatures, two distinct sets of sharp signals are observed, each consistent with the structure of **BD5**. At elevated temperature, these signals coalesce into a new, single set of sharp signals, again consistent with the assigned structure. These observations appear to be a textbook case[41] of restricted rotation around the amide bond. At low temperature, the rotation is slow on the NMR time scale, and the two conformational isomers are detected. It is interesting to note that the integration ratio between the two sets of signals is approximately 55:45; therefore, one isomer appears to be slightly lower in free energy than the other. At elevated temperature, the rotation becomes rapid, and only a single average spectrum is observed.

It is quite surprising that the greatest chemical shift difference between conformers was observed for the benzylic methylene protons (highlighted with green arrows in Figure 16), which lie far from the hindered rotation site. It may be that this compound tends to adopt a folded structure in which the

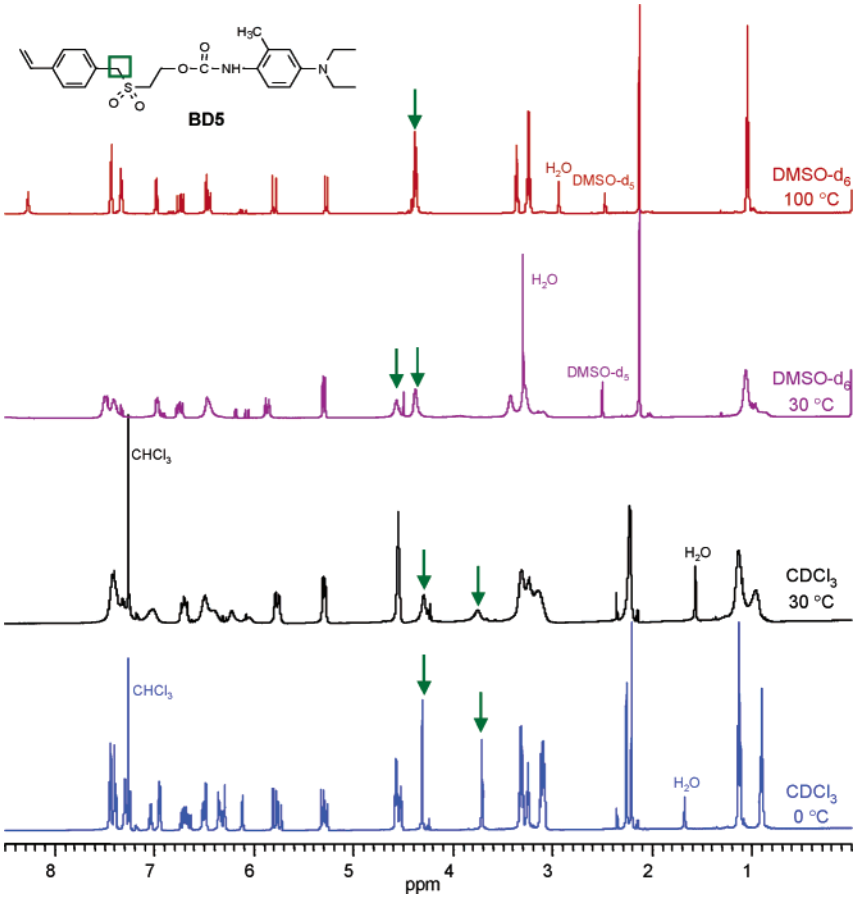
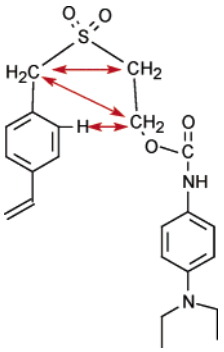


Figure 16. Comparison of 500 MHz ^{1}H NMR spectrum of **BD5** at various temperatures. The arrows designate signals assigned to the benzylic methylene protons.

benzylic protons are, in fact, near in space to the amide. Examination of **BD5** by NOESY NMR spectroscopy revealed interactions among the benzylic, *ortho*-aromatic, and ethylene protons, consistent with this hypothesis.



The red arrows above indicate protons between which interactions were detected, and therefore, these are likely to be in proximity.

A similar observation, consistent with conformational isomerism, was made with **BD6**, which contains a benzimidazole ring system in place of the sulfonyl group in **BD5**. In contrast, none of the benzylic carbamates (section A) showed evidence for restricted rotation by NMR. The difference may be attributable to polar intramolecular interactions that favor or disfavor a folded conformation that reinforces restricted rotation about the carbamate. That is, the relatively electron-rich latent developer moiety may interact more strongly with the electron-poor groups that are present in **BD5** and **BD6**, but less strongly with electron-rich benzylic groups in **BD1**−**BD4**.

Conclusions

A series of polymeric blocked developers containing benzylic carbamate switches were synthesized and evaluated for controlled thermal release in a photothermographic application. Results indicated that developer could be released from these materials at temperatures above about 150 °C, and the more active polymers possessed relatively electron-rich aromatic rings in the switches.

Two examples of polymeric blocked developers designed for a 1,2-elimination release mechanism were successfully synthesized. The low activity of **PBD5** suggests that a simple sulfone provides insufficient activation to promote thermal release of developer. However, the presence of a benzimidazole group in **PBD6** appears to confer high activity. Heterocycles of this kind are known to interact with silver halide surfaces. Indeed, many sensitizing dyes contain benzimidazole moieties. It is possible such interactions serve to increase the activity of **PBD6**.

The strategy of using a protecting group to deactivate latent functionality was successful, in that premature oxidation and other undesirable reactions of the developer moiety were not observed in any of the examples. The facility for producing aqueous small-particle dispersions and latexes (in some cases) of the polymeric blocked developers is particularly advantageous.

The experiments described in this paper possibly point to a generally useful approach to controlled release for broader applications in solid-phase (combinatorial) synthesis or for "smart polymer" systems in which a compound is to be released when the material is thermally stressed.

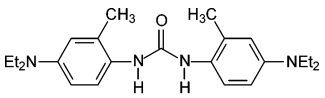
Experimental Section

Analyses. NMR measurements were carried out at 300 MHz on a Varian VXR-300S spectrometer or at 500 MHz on a Varian Unity 500 spectrometer. Field desorption mass spectrometry (FD-MS) was performed with a Varian MAT model 731 instrument. Electrospray mass spectrometry (ES-MS) was performed on a Micromass Platform II instrument. Sample injections were made from solutions into a flowing stream of 45% methanol, 45% acetonitrile, and 10% 0.05 M ammonium acetate solution, buffered to pH 4.65. The mass-to-charge (*m*/*e*) ratio of the ions was then determined utilizing a quadrupole mass spectrometer that was scanned from 65 to 2000 amu, alternately scanning in positive and negative modes once per second. Polymer molar mass distributions were determined by size exclusion chromatography (SEC) in *N*,*N*-dimethylformamide (DMF) containing 0.01 M lithium nitrate, using two Jordi Gel mixed-bed columns. The system was calibrated using narrow molar mass distribution poly(ethylene oxide) standards between 645 and 865 000 Da. Glass transition temperatures (T_g) were measured by differential scanning calorimetry (DSC) under nitrogen at 10 °C/min heating rate. The reported values are the midpoint of the change in heat capacity.

Materials. Isocyanate **2**,[36] magenta coupler **4**,[33] and compound **10**[40] were prepared according to the literature. Evaporative dispersions of polymers were prepared using published methods.[32]

4-(1-Hydroxyethyl)styrene (1).[34,35] A suspension of 4.82 g (0.198 mol) of magnesium in 200 mL of dry THF was treated under nitrogen with 36.3 g (0.198 mmol) of 4-bromostyrene plus a trace of iodine. The reaction mixture was heated at reflux for 4 h and cooled in an ice bath. Acetaldehyde (9.6 g, 0.218 mol) was added, and the mixture was stirred overnight. The reaction mixture was poured onto 300 g of ice plus 25 g of ammonium chloride and was extracted with ether (3 × 200 mL). The combined ethereal extracts were concentrated, and the residue was vacuum-distilled. The product (17.3 g, 59%) was obtained as a slightly yellow oil; bp 67−99 °C/0.10 mm. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.50 (d, J = 6.4, 3H), 1.8 (br s, 1H), 4.89 (q, J = 6.4, 1H), 5.24 (d, J = 11.0, 1H), 5.74 (d, J = 17.7, 1H), 6.7 (m, 1H), 7.34 (d, J = 8.2, 2H), 7.40 (d, J = 8.2, 2H).

BD1 Monomer. A mixture of 17.3 g (0.117 mol) of 4-(1-hydroxyethyl)styrene (**1**), 23.84 g (0.117 mol) of *N*,*N*-diethyl-4-isocyanato-*m*-toluidine (**2**), and four drops of dibutyl tin diacetate in 150 mL of dry THF under nitrogen was refluxed for 16 h. After cooling to room temperature, the reaction mixture was filtered to remove a small amount of white solid byproduct (identified as the symmetrical urea **3**) and concentrated to deposit a tan oil that gradually crystallized. The product was recrystallized from heptane, utilizing a small amount of silica gel as decolorant, to produce 26.9 g (65%) of a cream-colored powder; mp 74−6 °C. An additional 4.6 g (11%) of product was recovered as a second crop by partial concentration of the mother liquor, filtration, and then repeated recrystallization from heptane. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.14 (t, J = 7.0, 6H), 1.58 (d, J = 6.9, 3H), 2.20 (s, 3H), 3.32 (q, J = 7.0, 4H), 5.24 (d, J = 10.8, 1H), 5.74 (d, J = 17.6, 1H), 5.88 (q, J = 6.6, 1H), 6.13 (br s, 1H), 6.5 (m, 2H), 6.7 (m, 1H), 7.4 (m, 5H).



3

Byproduct Urea 3. ^{1}H NMR (DMSO-d_6, 300 MHz): δ 1.07 (t, J = 6.9, 12H), 2.17 (s, 6H), 3.27 (q, J = 7.0, 8H), 6.5 (m, 4H), 7.24 (d, J = 8.6, 2H), 7.40 (br s, 2H). FD-MS *m*/*e* 382 (M^+).

4-(4-Acetylphenoxy)methyl)styrene (5). Sodium hydride (3.7 g of 60% dispersion in mineral oil, 92 mmol) under nitrogen was washed with ligroin (3 × 25 mL) and then treated dropwise with a solution of 10.0 g (73 mmol) of 4-hydroxyacetophenone dissolved in 50 mL of DMF with mechanical stirring. *CAUTION: hydrogen gas evolution!* 4-Vinylbenzyl chloride (11.2 g, 73 mmol) was added slowly, and the resulting mixture was stirred at 110 °C for 17 h. Upon cooling the reaction mixture to room temperature, some of the product crystallized. This material was collected, washed with cold methanol, and recrystallized from 2-propanol to produce 3.6 g (19%) of product. Additional product (5.5 g, 30%) was obtained by concentrating the combined filtrates and recrystallizing successively from 2-propanol and then from heptane. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.55 (s, 3H), 5.12 (s, 2H), 5.28 (d, J = 10.9, 1H), 5.77 (d, J = 17.6, 1H), 6.75 (m, 1H), 7.01 (d, J = 8.8, 2H), 7.41 (AB q, J = 8.2, $\Delta\nu$ = 24.0, 4H), 7.94 (d, J = 8.8, 2H). ES-MS: *m*/*e* 253 ($M^+ + 1$).

4-(4-(1-Hydroxyethyl)phenoxy)methylstyrene (6). A mixture of 8.00 g (32 mmol) of 4-(4-acetylphenoxy)methyl)styrene (**5**), 1.20 g (32 mmol) of sodium borohydride, and 75 mL of 2-propanol was stirred magnetically at reflux for 30 min. The reaction mixture was cooled to room temperature and poured slowly into 500 mL of water. The resulting suspension was acidified by the dropwise addition of 10% HCl. *CAUTION: vigorous hydrogen gas evolution!* The precipitated product was collected, washed with water, and air-dried. The product was recrystallized from heptane to deposit 6.6 g (82%) of white crystals. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.48 (d, J = 6.4, 3H), 1.73 (s, 1H), 4.86 (q, J = 6.4, 1H), 5.06 (s, 2H), 5.26 (d, J = 10.9, 1H), 5.76 (d, J = 17.6, 1H), 6.73 (m, 1H), 6.96 (d, J = 8.6, 2H), 7.30 (d, J = 8.8, 2H), 7.41 (AB q, J = 8.3, $\Delta\nu$ = 19.2, 4H). ES-MS: *m*/*e* 237 ($M^+ - H_2O + 1$).

BD3 Monomer. A mixture of 6.60 g (26 mmol) of 4-(4-(1-hydroxyethyl)phenoxy)methylstyrene (**6**), 5.30 g (26 mmol) of *N*,*N*-diethyl-4-isocyanato-*m*-toluidine (**2**), and three drops of dibutyl tin diacetate in 50 mL of dry dichloromethane under nitrogen was held at room temperature for 24 h. The reaction mixture was filtered and concentrated to deposit a tan oil that gradually crystallized. The product was recrystallized from heptane (200 mL), utilizing a little alumina as decolorant, and then from methanol (125 mL) to produce 7.8 g (66%) of a cream-colored powder. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.13 (t, J = 7.0, 6H), 1.57 (d, J = 8.0, 3H), 2.18 (s, 3H), 3.31 (q, J = 7.0, 4H), 5.05 (s, 2H), 5.26 (d, J = 10.9, 1H), 5.76 (d, J = d, J = 17.6, 1H), 5.85 (q, J = 6.5, 1H), 6.09 (br s, 1H), 6.5 (m, 2H), 6.7 (m, 1H), 6.95 (d, J = 8.6, 2H), 7.32 (br m, 3H), 7.41 (AB q, J = 8.3, $\Delta\nu$ = 19.7, 4H). ES-MS: *m*/*e* 459 ($M^+ + 1$).

4-(2-Acetyl-5-methoxyphenoxy)methyl)styrene (7). *Procedure A.* Sodium hydride (60% mineral oil dispersion, 4.52 g, 0.113 mol) was washed with ligroin (3 × 25 mL) under nitrogen. A solution of 15.0 g (0.090 mol) of 2-hydroxy-4-methoxyacetophenone dissolved in 100 mL of DMF was added dropwise with magnetic stirring. *CAUTION: hydrogen gas evolution!* The resulting mixture was stirred for 30 min, and a solution of 15.2 g (99 mmol) of 4-chloromethylstyrene in 15 mL of DMF was added. The resulting mixture was stirred under nitrogen and warmed with a 100 °C oil bath for 3 days. The reaction mixture was cooled to room temperature, poured into 700 mL of water, and extracted with ether (3 × 300 mL). The combined ethereal extracts were washed successively with 300 mL of 5% HCl and 300 mL of brine, dried, and concentrated to deposit a tan oil that solidified upon standing. The product was recrystallized from 100 mL of methanol to provide 17.6 g (69%) of off-white crystals. A second crop of product (2.2 g, 9%) was obtained after concentrating the mother liquor and repeating the recrystallization from methanol.

Procedure B. A mixture of 5.07 g (31 mmol) of 2-hydroxy-4-methoxyacetophenone, 5.01 g (33 mmol) of 4-chloromethylstyrene, 10.1 g (31 mmol) of cesium carbonate, and 200 mL of acetonitrile was heated at reflux for 18 h. The reaction mixture was cooled to room temperature and filtered. The solvent was stripped to deposit 7.80 g (84%) of product.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.56 (s, 3H), 3.83 (s, 3H), 5.12 (s, 2H), 5.28 (d, J = 10.9, 1H), 5.78 (d, J = 17.6, 1H), 6.52 (s, 1H), 6.54 (d, J = 8.9, 1H), 6.75 (m, 1H), 7.42 (AB q, J = 8.3, $\Delta\nu$ = 20.5, 4H). ES-MS: *m*/*e* 283 ($M^+ + 1$).

4-(2-(1-Hydroxyethyl)-5-methoxyphenoxy)methylstyrene (8). A mixture of 17.5 g (62 mmol) of 4-(2-acetyl-5-methoxyphenoxy)-methyl)styrene (**7**), 2.58 g (68 mmol) of sodium borohydride, and

100 mL of 2-propanol was stirred magnetically and heated at reflux for 30 min. The reaction mixture was cooled to room temperature and poured slowly onto a mixture of 500 g of ice and 25 mL of acetic acid. *CAUTION: vigorous hydrogen evolution!* The resulting white precipitate was collected, washed with water, and dried. The product was recrystallized from a mixture of toluene and heptane (20/80 v/v). An off-white solid was obtained, 15.0 g (85%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.50 (d, J = 6.5, 3H), 2.45 (br s, 1H), 3.79 (s, 3H), 5.07 (s, 2H), 5.10 (q, 6.5, 1H), 5.27 (d, J = 10.8, 1H), 5.77 (d, J = 17.6, 1H), 6.55 (m, 2H), 6.73 (m, 1H), 7.27 (d, J = 8.6, 1H), 7.41 (AB q, J = 8.2, $\Delta\nu$ = 26.4, 4H). FD-MS: *m/e* 284 (M^+).

BD3 Monomer. A mixture of 15.0 g (53 mmol) of 4-(2-(1-hydroxyethyl)-5-methoxyphenoxy)methylstyrene (**8**), 10.8 g (53 mmol) of *N*,*N*-diethyl-4-isocyanato-*m*-toluidine (**2**), 100 mL of dichloromethane, and four drops of dibutyl tin diacetate was stirred magnetically at room temperature for 3 days. The reaction mixture was concentrated to deposit a brown oil that gradually solidified. The product was twice recrystallized from 100 mL of 70/30 (v/v) toluene/heptane to provide 9.5 g (37%) of a light yellow powder. An additional 3.9 g (15%) of product was obtained by concentrating the mother liquors and repeating the two recrystallizations. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.14 (t, J = 7.0, 6H), 1.57 (d, J = 6.4, 3H), 2.19 (s, 3H), 3.30 (q, J = 7.0, 4H), 3.78 (s, 3H), 5.09 (s, 2H), 5.25 (d, J = 10.9, 1H), 5,75 (d, J = 17.6, 1H), 6.1 (br s, 1H), 6.26 (q, J = 6.5, 1H), 6.5 (m, 4H), 6.7 (br m, 2H), 7.41 (s, 4H). ES-MS: *m/e* 489 ($M^+ + 1$).

α-(4-Ethenylphenyl)-2,4-dimethoxybenzenemethanol (9). The literature procedure[38] was adapted. In a thoroughly dry flask, magnesium metal (1.33 g, 55 mmol) was treated with a catalytic amount of iodine under nitrogen with slight warming. Dry tetrahydrofuran (THF) was added (25 mL), and the mixture stirred magnetically. A solution of 4-bromostyrene (10.0 g, 55 mmol) in 25 mL of dry THF was added dropwise, and once the initial exotherm had subsided, the reaction mixture was heated at reflux for 15 min. The mixture was cooled in an ice bath, and a solution of 9.08 g (55 mmol) of 2,4-dimethoxybenzaldehyde in 50 mL of dry THF was added slowly. To this yellow, heterogeneous mixture was added 100 mL of saturated aqueous ammonium chloride, and the mixture was extracted with ether (3 × 75 mL). The combined ethereal extracts were dried (Na_2SO_4) and concentrated at reduced pressure to deposit a yellow oil. The oil was triturated with ligroin and stored overnight at −15 °C to crystallize. The ligroin was decanted, and the solid residue was recrystallized from 80% heptane/20% toluene to produce, after drying in vacuo, 10.4 g (70%) of white crystals. ^{1}H NMR ($CDCl_3$): δ 2.88 (d, J = 5.2, 1H), 3.80 (s, 6H), 5.22 (d, J = 11.0, 1H), 5.73 (d, J = 17.5, 1H), 6.0 (d, J = 5.1, 1H), 7.35 (AB q, J = 8.5, $\Delta\nu$ = 17.4, 4H). ES-MS: *m/e* 253^+ ($M + 1 - H_2O$). FD-MS: *m/e* 270^+ (M).

BD4 Monomer. A solution of 10.4 g (38 mmol) of **9**, 7.86 g (38 mmol) of isocyanate **2**, and 5 drops of dibutyl tin diacetate in 100 mL of dry dichloromethane was stirred at 25 °C for 48 h and concentrated at reduced pressure. The resulting solid was twice recrystallized from 60% toluene/40% heptane to produce 8.7 g (48%) of a yellow powder. ^{1}H NMR ($CDCl_3$): δ 1.13 (t, J = 7.0, 6H), 2.19 (s, 3H), 3.31 (q, J = 6.9, 4H), 3.80 (s, 6H), 5.22 (d, J = 10.9, 1H), 5.71 (d, J = 17.6, 1H), 6.2 (br s, 1H), 6.6 (m, 4H), 6.7 (m, 1H), 7.15 (s, 1H), 7.2 (m, 1H), 7.35 (m, 4H). ES-MS: *m/e* 475^+ ($M + 1$).

Purification Procedure for 2-(((4-Ethenylphenyl)methyl)-sulfonyl)ethanol (10). Samples of **10** prepared by adapting the literature procedure[14,39] appeared to contain varying amounts of the sulfoxide **11**, as detected by ^{1}H NMR and by ES-MS (*m/e* = 211^+ $M + 1$). Simultaneous conversion of residual **11** to **10** and purification was effected as follows. A 19.5 g sample of a mixture containing 10 mol % **11** and 90 mol % **10** was mixed with 200 mL of methanol and 10.5 g of Oxone. This suspension was stirred and heated at reflux for 10 min and hot-filtered. Water (100 mL) was added to the filtrate, which was cooled to −15 °C and held at that temperature for several hours. The resulting white plates were collected, washed with cold 50% aqueous methanol, and dried in vacuo over $CaSO_4$. The recovery of pure **10** was 16.2 g (83%). ^{1}H NMR ($CDCl_3$): δ 2.40 (br s, 1H), 3.08 (t, J = 5.2, 2H), 4.08 (t, J = 5.3, 2H), 4.33 (s, 2H), 5.30 (d, J = 10.9, 1H), 5.78 (d, J = 17.6, 1H), 6.7 (m, 1H), 7.42 (AB, J = 8.3, $\Delta\nu$ = 19.9, 4H). ES-MS: *m/e* 225^- ($M - 1$), 195 ($M - 31$).

BD5 Monomer. A solution of **10** (16.2 g, 72 mmol), isocyanate **2** (14.6 g, 72 mmol), and five drops of dibutyltin diacetate (catalyst) in 200 mL of dry dichloromethane was stirred magnetically under nitrogen for 24 h at reflux. The reaction mixture was cooled to ambient, and a small amount of insoluble precipitate was removed by filtration through a pad of Celite. The filtrate was concentrated by rotary evaporation to deposit a brown solid. The product was purified by recrystallization from 200 mL of 60% toluene/40% heptane to produce 26.5 g (86%) of a yellow powder. ^{1}H NMR (100 °C, DMSO-d_6): δ 1.04 (t, J = 7.0, 6H), 2.13 (s, 3H), 3.24 (q, J = 7.0, 4H), 3.36 (t, J = 5.9, 2H), 4.4 (m, 4H), 5.28 (d, J = 11.0, 1H), 5.80 (d, J = 17.6, 1H), 6.45 (m, 2H), 6.75 (m, 1H), 6.98 (d, J = 8.6, 1H), 7.33 (d, J = 7.9, 2H), 7.43 (d, J = 8.1, 2H), 8.27 (s, 1H).

1-(4-Vinylbenzyl)-2-ethylbenzimidazole (12). A suspension of 2-methylbenzimidazole (25.0 g, 0.19 mol), 4-chloromethylstyrene (31.8 g, 0.21 mol), powdered potassium hydroxide (10.6 g, 0.19 mol), and potassium carbonate (13.1 g, 0.1 mol) in 200 mL of dry THF was stirred at 25 °C for 5 days. The reaction mixture was filtered, and the solid residue was extracted with additional THF. The combined liquids were concentrated at reduced pressure, and the resulting brown oil was triturated with ligroin 950 and held at −15 °C for a few hours to induce crystallization. The ligroin was decanted from the product, which was then purified by recrystallization from 70% methanol/30% water. A cream-colored solid (43.2 g, 92%) was obtained after drying. ^{1}H NMR ($CDCl_3$): δ 2.61 (s, 3H), 5.28 (d, J = 11.0, 1H), 5.33 (s, 2H), 5.75 (d, J = 17.6, 1H), 6.7 (m, 1H), 7.05 (d, J = 8.1, 2H), 7.25 (m, 2H), 7.37 (d, J = 8.2, 2H), 7.78 (d, J = 7.3, 1H). ES-MS: *m/e* 249^+ ($M + 1$).

1-(4-Vinylbenzyl)-2-(2-hydroxyethyl)benzimidazole (13). A mixture of **12** (20.0 g, 81 mmol), formaldehyde (320 mmol as 26.1 g of the 37% aqueous solution), and 25 g of pyridine was stirred magnetically and heated to 95 °C. The mixture became homogeneous within minutes. After 24 h, the mixture was cooled to ambient and concentrated at reduced pressure to deposit a tan oil. The product was purified by flash chromatography (silica gel, 75% dichloromethane/25% ether), followed by recrystallization from a mixture of 100 mL of methanol plus 40 mL of water. The product was obtained as 9.1 g (41%) of an off-white solid. ^{1}H NMR ($CDCl_3$): δ 2.97 (t, J = 5.5, 2H), 4.12 (t, J = 5.5, 2H), 4.1 (br s, 1H), 5.24 (d, J = 10.8, 1H), 5.30 (s, 2H), 5.71 (d, J = 17.6, 1H), 6.7 (m, 1H), 7.00 (d, J = 8.1, 2H), 7.2 (m, 3H), 7.34 (d, J = 8.2, 2H), 7.73 (m, 1H). ES-MS: *m/e* 279^+ ($M + 1$).

BD6 Monomer. A mixture of 9.00 g (32 mmol) of **13**, 6.93 g (34 mmol) of isocyanate **2**, and five drops of dibutyltin diacetate in 75 mL of dry dichloromethane was stirred at 25 °C for 4 days. The solvent was removed at reduced pressure to deposit a tan solid. The product was purified by recrystallization from 100 mL of toluene to obtain 15.0 g (96%) of an off-white solid. ^{1}H NMR (100 °C, $(CD_3)_2SO$): δ 1.07 (t, 6H), 2.07 (s, 3H), 3.18 (t, 2H), 3.25 (q, 4H), 4.48 (t, 2H), 5.21 (d, 1H), 5.42 (s, 2H), 5.72 (d, 1H), 6.41 (d, 1H), 6.48 (s, 1H), 6.68 (m, 1H), 6.94 (d, 1H), 7.17 (d, 2H), 7.24 (d, 2H), 7.37 (m, 3H), 7.58 (m, 1H), 8.05 (br s, 1H). ES-MS: *m/e* 483^+ ($M + 1$).

Solution Polymerization Procedure. The synthesis of the polymers is typified by the following description of the polymerization of **BD3**: Chlorobenzene was passed through a short column of alumina prior to use to remove any acidic impurities. A flask was charged with 5.00 g (10 mmol) of **BD3**, 0.039 g (0.2 mmol) of 2,2′-azobis(2-methylbutyronitrile) (Vazo67, DuPont), and 35 mL of chlorobenzene. The resulting solution was degassed by sparging with nitrogen for 10 min, and the flask was sealed with a septum. The reaction mixture was heated in a 65 °C water bath for 24 h and cooled to room temperature. The polymer was precipitated into 700 mL of methanol, depositing a solid mass. The supernatant was decanted, and the solid was dried in vacuo. The polymer was

reprecipitated from dichloromethane (50 mL) into ligroin (700 mL), producing 2.3 g (46%) of a white powder.

Emulsion Polymerization. The following procedure typifies the procedure used for emulsion polymerization: A mixture of 5.0 g (12 mmol) of **BD5** and 20 g (200 mmol) of methyl methacrylate (**MMA**) was warmed gently to achieve a homogeneous solution. This solution was added to 100 mL of methanol, 1.25 g of OMT surfactant, and 0.2 g of sodium bicarbonate, and the resulting suspension was stirred for 1 h to achieve a uniform preemulsion. The mixture was purged with nitrogen for 30 min and heated to 60 °C, and purging was continued for 15 min. The initiator 2,2′-azobis-(2-methylpropionamidine) dihydrochloride (0.1 g) was added, and reaction proceeded for 2 h. The resulting emulsion was cooled to ambient and filtered to remove a small amount of coagulated material. Analysis indicated an average particle size of 76 nm and 19% solids.

Photothermographic Coating and Evaluation. In one format, the polymeric developer was included as a component of a gelatin layer (0.4 g/ft^2) coated on a transparent polyester film base. Other components were a blue-light-sensitized silver bromoiodide emulsion (0.6 × 0.09 μm, 0.05 g/ft^2), magenta photographic coupler **4**^{33} (0.05 g/ft^2, as a 1:0.5 by weight dispersion in tricresyl phosphate), the silver salt of benzotriazole (0.05 g/ft^2 as silver), 1-phenyl-5-mercaptotetrazole (0.03 g/ft^2, as a ball-milled dispersion), salicylanilide (0.08 g/ft^2, as a ball-milled dispersion), and surfactant (TX-200, 1%). The polymeric blocked developers were dispersed by ball-milling, solution dispersion, evaporative limited coalescence dispersion, or emulsion polymerization. Coating formulations were pH adjusted using 1 N nitric acid. The coatings were air-dried, and no overcoat or hardener was used.

Strips of each coating were exposed (1 s, 3.04 log lux light source at 3000 K) through a neutral optical density filter (0−4 stepwedge, Wratten 2B filter, Daylight Va filter) and processed at a variety of temperatures using a 20 s residence time using a platen heating element. The strips were then fixed using KODAK FLEXICOLOR Fixer with low agitation for 4 min at about 10 °C. After washing (4 min at 10 °C) the strips were air-dried, and the sensitometric responses at each temperature of development were read and recorded. The green density as a function of exposure was recorded for each strip using a densitometer.

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