

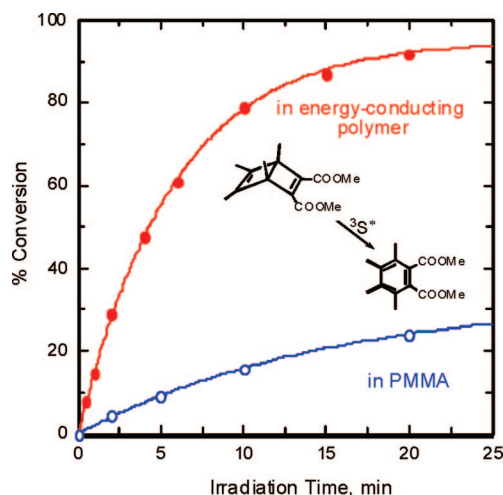
## Quantum Amplified Isomerization in Polymers Based on Triplet Chain Reactions

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Photoinitiated triplet quantum amplified isomerizations (QAI) of substituted Dewar benzene derivatives in polymeric media are reported. The quantum efficiencies and the ultimate extents of reactant-to-product conversions increase significantly with the incorporation of appropriate co-sensitizers; compounds whose triplet energies are similar to or lower than that of the sensitizer and close to that of the reactant. These co-sensitizers serve to promote chain-propagating energy transfer processes and thereby increase the action sphere of photosensitization. Isomerization quantum yields increase, as predicted, with increasing concentrations of the reactants and the co-sensitizers. Chain amplifications as large as  $\sim 16$  and extents of conversion that approach 100% have been achieved. Mechanistic schemes are proposed to account for the dynamics of the inherent energy transfer processes and provide a predictively useful model for the design of a new class of photoresponsive polymers based on changes in the refractive index of the materials.

### Introduction

We recently described a new class of photoresponsive polymeric materials based on a concept called quantum amplified isomerization (QAI).<sup>1</sup> These QAI materials were based on photoinitiated electron-transfer isomerizations that proceed via chain reactions. When appropriately designed, the isomerizations

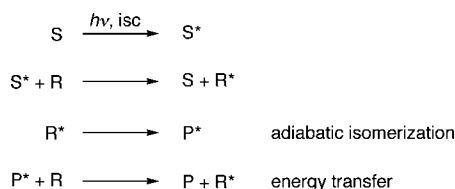
can lead to large changes in refractive index that can be exploited for optical recording applications.<sup>2</sup> For example, the isomerization of hexamethyl Dewar benzene (DB1) to the corresponding benzene product (B1) is accompanied by a large change in refractive index ( $\Delta n \sim 0.04$ ).<sup>2d</sup> Although this photoinduced electron-transfer reaction was known to proceed with high

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(1) Gillmore, J. G.; Neiser, J. D.; McManus, K. A.; Roh, Y.; Dombrowski, G. W.; Brown, T. G.; Dinnocenzo, J. P.; Farid, S.; Robello, D. R. *Macromolecules* **2005**, *38*, 7684.

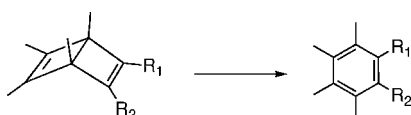
**SCHEME 1. Key Reactions in Quantum Amplified Isomerization of a Reactant, R, to a Product, P, via Triplet Energy Transfer Induced by a Triplet Sensitizer, S<sup>a</sup>**



<sup>a</sup> The asterisks here and throughout the paper denote triplet excited states.

quantum yield in polar solvents,<sup>3</sup> the reaction proceeded with only limited amplification in polymeric matrices. The lower quantum yield in polymers was attributed to the Coulombic barrier for charge separation of the radical ion pair intermediates that is required for efficient chain propagation.<sup>1</sup> Thus, in polymeric media, chain-terminating return electron transfer strongly competes with chain propagation.

To circumvent the Coulombic restrictions for chain amplification of electron-transfer QAI processes in polymers we considered the possibility of using QAI reactions based on energy transfer instead of electron transfer. Toward that goal we explored the triplet-sensitized, quantum chain isomerization of Dewar benzene derivatives in fluid solution and found Dewar benzene derivatives DB2 and DB3 to be excellent candidates.<sup>4</sup> Chain amplifications for DB2 and DB3 in excess of 100 were achieved via triplet, quantum chain reactions in solution. Importantly, adiabatic isomerizations of triplet reactants (R<sup>\*</sup>) to the triplet products (P<sup>\*</sup>) were found to occur with efficiencies near unity (Scheme 1). Furthermore, because the triplet energy of P is higher than that of R, the quantum chain is further propagated by energy transfer from P<sup>\*</sup> to another R. Extensive kinetic studies of the quantum chain isomerizations of DB2 and DB3 were conducted in fluid media to fully understand the energetic and kinetic requirements for efficient reaction.<sup>4</sup> The insight gained from these studies was used to address new challenges encountered when the reactions were carried out in polymeric media. The mechanistic and kinetic aspects used in the design of efficient systems are the subject of this paper.

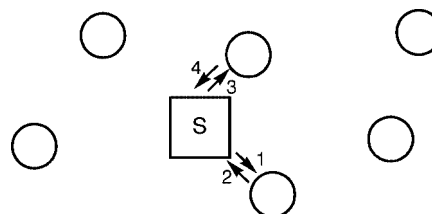


	R <sub>1</sub>	R <sub>2</sub>	
<b>DB1</b>	Me	Me	<b>B1</b>
<b>DB2</b>	CO <sub>2</sub> Me	Me	<b>B2</b>
<b>DB3</b>	CO <sub>2</sub> Me	CO <sub>2</sub> Me	<b>B3</b>

## Results and Discussion

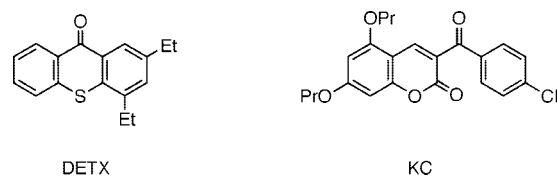
**Molecularly-Doped Polymers.** We began our investigation of the triplet-sensitized isomerization of Dewar benzenes DB2 and DB3 in polymeric matrices by molecularly doping the reactant, sensitizer, and other additives in a binder of poly-(methyl methacrylate), PMMA. Irradiation of a 20 μm film of DB2 (10 wt %) in PMMA sensitized with 2,4-diethylthioxanthone (DETX) showed an isomerization quantum yield of 2.2 at low conversion, in contrast to the quantum yield of ~100 for DB2 in ethyl acetate.<sup>4</sup> The markedly lower quantum yield in polymer solution was not entirely surprising given the restricted mobility in polymers and the greater susceptibility of

**SCHEME 2. Schematic Representation of Triplet-Sensitized Isomerization of Dewar Benzenes in Polymeric Matrices<sup>a</sup>**



<sup>a</sup> The square represents a sensitizer molecule. At various stages in the energy transfer/isomerization sequence the circles represent ground and triplet states: R, R<sup>\*</sup>, P<sup>\*</sup>, and P. See text for details.

the reaction to quenching by impurities. The magnitude of the drop in quantum yield, however, was dramatic. The detailed kinetics we reported for the reaction in ethyl acetate offered an explanation for the large difference in quantum yields and potential ways to increase the efficiencies in polymers.



We have shown that, following adiabatic isomerization of an excited reactant molecule R<sup>\*</sup> to an excited product molecule P<sup>\*</sup>, the rate for chain propagation involving energy transfer from P<sup>\*</sup> to another R is a slow process.<sup>4</sup> For example, in the case of DB2, the rate constant in ethyl acetate is only 2.3 × 10<sup>7</sup> M<sup>-1</sup> s<sup>-1</sup>; nearly 50 times less than the rate constant for energy transfer from P<sup>\*</sup> to DETX (1.2 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup>). The small rate constant for energy transfer from P<sup>\*</sup> to R is due to large differences in the nuclear configurations of R and R<sup>\*</sup>, as well as smaller differences between those of P and P<sup>\*</sup>. Whenever energy transfer between two molecules involves reorganization of both donor and acceptor the rate constant is considerably reduced, even with modest exothermicity.<sup>5</sup> We now consider the consequences of these kinetic processes in a polymeric matrix where diffusion is highly restricted (Scheme 2).

The arrows in Scheme 2 denote the direction of triplet energy transfer. Following energy transfer from an excited sensitizer, S<sup>\*</sup>, to an adjacent R (reaction 1) and adiabatic R<sup>\*</sup> → P<sup>\*</sup> isomerization, chain propagation through energy transfer from P<sup>\*</sup> to an adjacent R is expected to be much slower than the back energy transfer to the sensitizer (P<sup>\*</sup> + S → P + S<sup>\*</sup>,

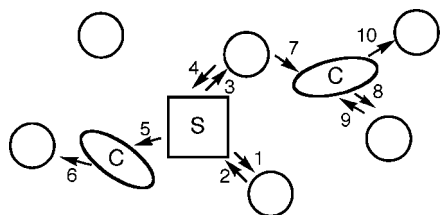
(2) (a) Robello, D. R.; Dinnocenzo, J. P.; Farid, S.; Gillmore, J. G.; Thomas, S. W., III *Polym. Prepr.* **2001**, *42*, 717. (b) Robello, D. R.; Farid, S.; Dinnocenzo, J. P.; Gillmore, J. G. *Polym. Prepr.* **2002**, *43*, 163. (c) Robello, D. R.; Dinnocenzo, J. P.; Farid, S.; Gillmore, J. G.; Thomas, S. W., III. Quantum Amplified Isomerization: A New Chemically Amplified Imaging System in Solid Polymers. In *Chromogenic Phenomena in Polymers*; Jenekhe, S. A., Kiserow, D. J., Eds.; American Chemical Society: Washington, DC; 2004; pp 135–146. (d) Robello, D. R.; Farid, S. Y.; Dinnocenzo, J. P.; Brown, T. G. *Proc. SPIE (Org. Photon. Mater. Dev. VIII)* **2006**, 61170F/1. (e) Robello, D. R.; Ferrar, L.; Mis, M.; Brown, T. G.; Li, Y. *Polym. Prepr.* **2007**, *48*, 155. (f) Dinnocenzo, J. P.; Farid, S. Y.; Robello, D. R.; Erdogan, T. *Optical Recording Material*. U.S. Patent 6,569,600, 2003. (g) Robello, D. R.; Farid, S. Y.; Dinnocenzo, J. P.; Gillmore, J. G. *Optical Recording Material*. US Patent 6,969,578, 2005.

(3) Evans, T. R.; Wake, R. W.; Sifain, M. M. *Tetrahedron Lett.* **1973**, 701.

(4) Merkel, P. B.; Roh, Y.; Dinnocenzo, J. P.; Robello, D. R.; Farid, S. J. *Phys. Chem. A* **2007**, *111*, 1188. For triplet sensitized isomerization of unsubstituted Dewar benzene, see: Turro, N. J.; Ramamurthy, V.; Katz, T. J. *Nouv. J. Chem.* **1977**, *1*, 363.

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**SCHEME 3. Schematic Representation of Triplet-Sensitized Isomerization of Dewar Benzenes in the Presence of a Co-sensitizer (C)<sup>a</sup>**



<sup>a</sup> As in Scheme 2, at various stages in the energy transfer/isomerization sequence the circles represent R, R\*, P\* and P. See text for explanation of the different reactions.

reaction 2), as mentioned above. In fluid solution this process is a relatively minor contributor due to rapid diffusional separation of S and P\*. Diffusion in the rigid polymer medium is highly restricted and, therefore, return energy transfer from P\* to S is expected to predominate. Thus, further chain propagation will proceed by subsequent energy transfer from S\* to another adjacent R, followed by similar steps as before (reactions 3 and 4). Importantly, after the R molecules in the immediate vicinity of the sensitizer have been converted to P molecules, the chain is likely to terminate because energy transfer from S\* to P is highly endothermic and energy transfer from S\* to more remote R molecules will be slow. Thus, in this situation, the excited sensitizer will simply undergo deactivation back to the ground state. We describe next a materials strategy that mitigates this limitation.

**Co-sensitization.** Promotion of energy transfer beyond the immediate vicinity of the sensitizer was achieved through use of a co-sensitizer (C). As shown in Scheme 3, the function of the co-sensitizer is to act as a chemically unreactive species that facilitates energy transfer from the sensitizer to reactants, first by energy transfer from S\* to C (reaction 5) and, subsequently, by energy transfer from C\* to an R that is further removed from S (reaction 6). This alternate route for energy transfer to R can extend the chain and expand the “action sphere” of the sensitizer. Similarly, energy transfer from P\* to C (reaction 7) can compete with return energy transfer to S (reaction 4) and extend the chain through energy transfer from C\* to a more remote R (reaction 8), followed by return energy transfer from P\* to C (reaction 9) and, potentially, additional energy transfer to another R (reaction 10). To function according to the design of Scheme 3, the co-sensitizer (C) must have a triplet energy similar to or lower than that of the sensitizer and close to that of the reactant to facilitate energy transfer from C\* to R. In addition, the co-sensitizer should be a fairly rigid molecule with minimal structural differences between its ground and triplet states; otherwise, its reorganization energy will slow the energy transfer rates to and from C (e.g., reactions 5–7). Finally, the co-sensitizer should have a long triplet lifetime to minimize chain-terminating deactivation to the ground state.

**Quantum Yields.** The effects of a variety of co-sensitizers with different triplet energies ( $E_T$ ) on the quantum yields for isomerization of DB2 and DB3 in PMMA were determined where the reactant concentration (10 wt %) and co-sensitizer concentration (5 wt %) were held constant. The results are listed in Table 1 and graphically illustrated in Figures 1–3.

As predicted based on the proposed co-sensitization mechanism in Scheme 3, the maximum enhancement on the isomerization quantum yield for DB2 with DETX as a sensitizer (Figure 1) was achieved with co-sensitizers that have triplet

energies similar to that of DB2 ( $E_T = 60$  kcal/mol).<sup>4</sup> These co-sensitizers led to an increase in quantum yield by a factor of ~2, to 5.3, at the modest level of 5 wt % of co-sensitizer. Similar behavior was observed in a limited set of data for DB3 with DETX as sensitizer (Figure 2). In both cases, quantum yield enhancement occurs only when the triplet energy of C is <60 kcal/mol, i.e., when the energy transfer from P\* ( $E_T \sim 69$  kcal/mol)<sup>4</sup> to C (reaction 7, Scheme 3) starts to compete favorably with the back energy transfer from P\* to S (reaction 4). As shown in Figure 1, the effect of the co-sensitizer decreased when its triplet energy became lower than that of the reactant, where it begins to act as a triplet quencher.

Interestingly, when photoisomerization of DB3 was sensitized with the ketocoumarin derivative, KC, a slight increase in quantum yield was observed even with co-sensitizers with triplet energies higher than that of the sensitizer (Figure 3). This behavior can be explained in terms of energy transfer from P\* to C (reaction 7 in Scheme 3) and the follow-up reactions 8–10, discussed above.<sup>7</sup>

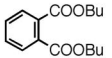
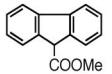
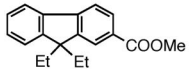
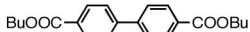
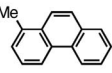
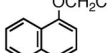
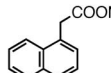
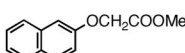
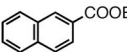


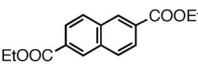


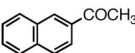
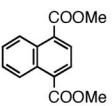
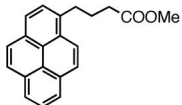
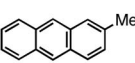
**Attainable Conversion.** In addition to increasing the isomerization quantum yields, the co-sensitizers can also increase the attainable levels of reactant-to-product conversion. This effect is illustrated in Figure 4 for the DETX- and KC-sensitized reactions of DB3 at 10 wt % of reactant and 5 wt % of co-sensitizer in PMMA (see also Table 1). Cosensitizers with  $E_T > 60$  kcal/mol have a relatively small effect on the extent of conversion. As noted above, co-sensitizers in this energy range also have only a small effect on the isomerization quantum yield for DB3. Thus, not surprisingly, the effect on attainable conversion is also limited in this range of co-sensitizer energies. As also noted earlier, with high-energy co-sensitizers energy transfer to C is only possible from P\* (reaction 7, Scheme 3) and, therefore, only partially promotes an increase in quantum yield and extent of conversion. As a result, the conversion of DB3 sensitized by KC only increases modestly from ~32% without co-sensitizer to ~55% for co-sensitizers with  $E_T > 60$  kcal/mol. With decreasing  $E_T$  of the co-sensitizer, however, the conversions increase significantly. In this energy range, energy transfer can also occur from S\* to C (reaction 5, Scheme 3), thus further increasing the quantum yield and the extent of conversion. We note that the higher attainable conversion with DETX vs KC is simply due to the higher concentration of the former (0.14 vs 0.013 mol/kg, respectively), which was necessitated by the lower extinction coefficient of DETX at the excitation wavelength.

**Concentration Effects.** The efficiencies of the quantum chain reactions described above are expected to increase with increasing concentration of both the reactants and the co-sensitizers. The effect of reactant concentration was tested using DB3 with KC as sensitizer. The concentration of DB3 was varied, while keeping the sum of DB3 plus di-*n*-butyl phthalate constant at 15 wt % to minimize potential effects of plasticization of the polymer and variations in the glass transition temperatures ( $T_g$ ) of the molecularly doped polymers. At DB3 concentrations of 5, 10, and 15 wt %, the quantum yields increased from 0.8 to 1.7 to 2.6, respectively.

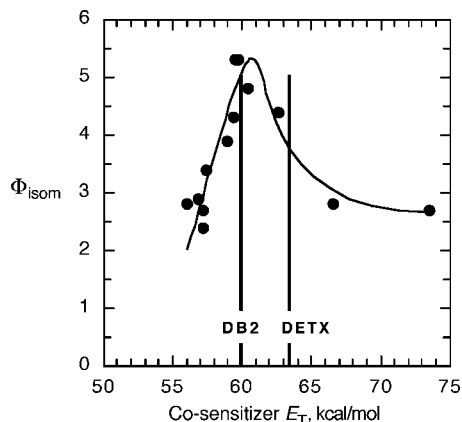
(6) Merkel, P. B.; Dinnocenzo, J. P. *J. Photochem. Photobiol. A: Chem.* **2008**, *193*, 110.

(7) The lack of this effect for the DETX-sensitized reactions is likely due to the higher concentration of DETX (~4 wt %) which will tend to favor energy transfer to nearby sensitizers ( $P^* + S \rightarrow P + S^*$ ) over energy transfer to nearby co-sensitizers ( $P^* + C \rightarrow P + C^*$ ) when  $E_T(C) > E_T(S)$  and  $[S] \approx [C]$ .

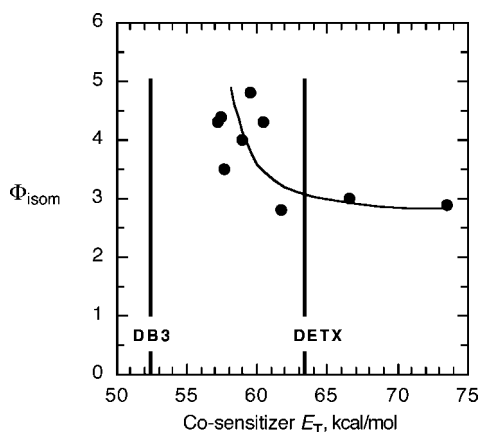
**TABLE 1.** Isomerization Quantum Yields ( $\Phi_{\text{isom}}$ ) and Maximum Attainable Conversions of Dewar Benzenes DB2 and DB3 Doped in PMMA at 10 wt % and Sensitized with DETX or KC as a Function Triplet Energies ( $E_T$ ) of Co-sensitizers, Added at 5 wt %

Co-sensitizer (C)	$E_T^a$ kcal/mol	DB2 DETX $\Phi_{\text{isom}}^b$	DB3 DETX		DB3 KC	
			$\Phi_{\text{isom}}^b$	% Conv <sup>c</sup>	$\Phi_{\text{isom}}^b$	% Conv <sup>c</sup>
None	--	2.2	--	--	1.5	32
	73.5	2.7	2.9	78	1.7	56
	66.6	2.8	3.0	80	2.6	56
	62.6	4.4	--	--	--	--
	61.7	--	2.8	80	2.6	53
	60.5	4.8	4.3	92	3.5	64
	59.7	5.3	--	--	--	--
	59.5	5.3	4.8	93	2.7	62
	59.4	4.3	--	--	--	--
	59.0	3.9	4.0	93	3.6	78
	57.7	--	3.5	90	3.2	80
	57.4	3.4	4.4	94	4.3	80
	57.2	2.7	--	--	3.6	73
	57.2	2.4	4.3	95	4.6	83
	56.9	2.9	--	--	--	--
	~56	2.8	--	--	--	--
	53.8	--	--	--	4.4	81
	47.7	--	--	--	2.9	80
	~42	--	--	--	0.6 <sup>d</sup>	--

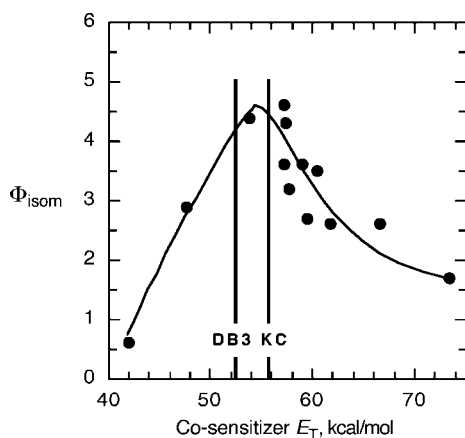
<sup>a</sup> Reference 6. <sup>b</sup> Measured at 10–15% conversion and corrected for incomplete light absorption, error limits <0.2. Excitation at 405 nm ( $6 \times 10^{-8}$  Einstein/min per  $\text{cm}^2$ ). <sup>c</sup> Attainable conversion upon prolonged exposure. Average values from several measurements ( $\pm 3\%$ ). <sup>d</sup> When the triplet energy of C is much lower than that of R, C acts as a quencher instead of a co-sensitizer.



**FIGURE 1.** Isomerization quantum yield of DB2 (10 wt %) in PMMA sensitized with DETX (0.14 mol/kg) as a function of the triplet energy ( $E_T$ , Table 1) of added co-sensitizer (5 wt %) measured at  $\sim 10\%$  conversion (data from Table 1).

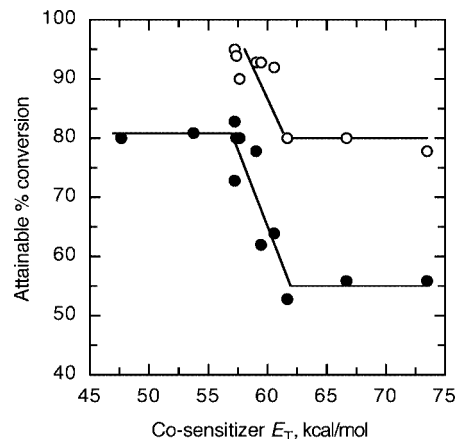


**FIGURE 2.** Isomerization quantum yield of DB3 (10 wt %) in PMMA sensitized with DETX (0.14 mol/kg) as a function of the triplet energy ( $E_T$ , Table 1) of added co-sensitizer (5 wt %) measured at  $\sim 10\%$  conversion.

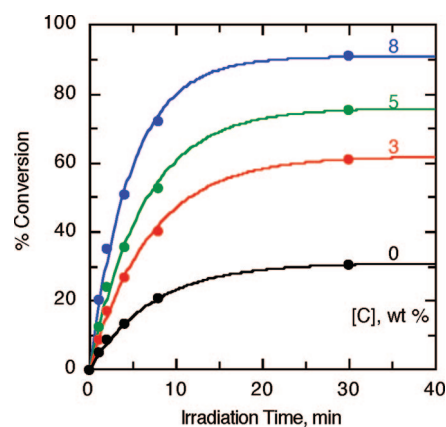


**FIGURE 3.** Isomerization quantum yield of DB3 (10 wt %) in PMMA sensitized with KC (0.013 mol/kg) as a function of the triplet energy of added co-sensitizers (Table 1, 5 wt %) measured at  $\sim 10\%$  conversion.

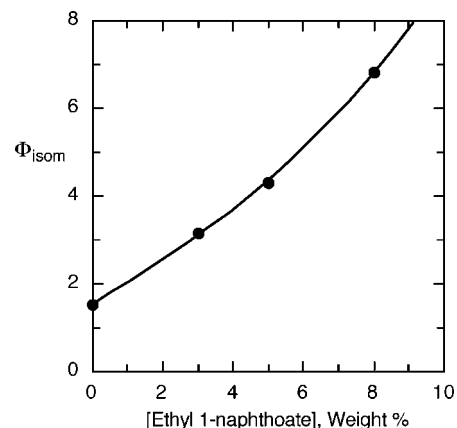
The effect of co-sensitizer concentration on the quantum yield was evaluated in the KC-sensitized reactions of DB3 in the presence of various amounts of ethyl 1-naphthoate. Figure 5 shows the dramatic effect of co-sensitizer concentration on the attainable conversion, which increased from  $\sim 32\%$  in the



**FIGURE 4.** Attainable conversion of DB3 (molecularly doped in PMMA at 10 wt %) as a function of the triplet energy of the co-sensitizer (5 wt %) using DETX (0.14 mol/kg), unfilled circles, or KC (0.013 mol/kg), filled circles.



**FIGURE 5.** Conversion of DB3 (molecularly doped in PMMA at 10 wt %), sensitized with KC, as a function of time at varying concentrations (0–8 wt %) of ethyl 1-naphthoate as co-sensitizer.



**FIGURE 6.** Isomerization quantum yield of DB3 (molecularly doped in PMMA at 10 wt %), sensitized with KC, as a function of co-sensitizer (ethyl 1-naphthoate) concentration.

absence of co-sensitizer to  $\sim 92\%$  in the presence of 8 wt % of ethyl 1-naphthoate. The significant effect of the co-sensitizer concentration on the initial quantum yield (at  $\sim 10\%$  conversion) is evident from the change in initial slope in Figure 5 and is plotted in Figure 6. The quantum yield increased more than 4 fold, from  $\sim 1.5$  without co-sensitizer to  $\sim 6.8$  with 8 wt % co-sensitizer.



**Effective Action Sphere.** The attainable conversion can be used to evaluate the “action sphere” of the sensitizer, i.e., the average, maximum distance from the center of a sensitizer molecule at which isomerization occurs. The size of the action sphere and the effect of co-sensitizers on increasing the attainable conversion will be discussed in terms of its mechanistic implications.

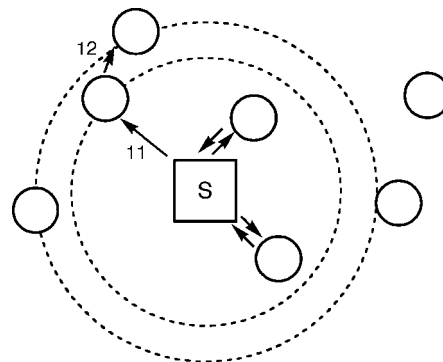
In the photoisomerization of DB3 in PMMA with KC as sensitizer, the average volume per sensitizer can be readily calculated from its concentration (0.013 mol/kg) to be  $\sim 106000 \text{ \AA}^3$ . Thus, a conversion level of  $\sim 32\%$  for KC in the absence of co-sensitizer corresponds to an action sphere of  $\sim 34000 \text{ \AA}^3$  with a radius  $\sim 20 \text{ \AA}$ . This large action sphere is partially reflective of the long lifetime of triplet KC\* in PMMA ( $\tau \sim 0.13 \text{ s}$ ). The Dexter model<sup>8</sup> can be used to estimate the KC/DB3 distance at which the rate constant for triplet energy transfer is equal to  $1/\tau$  of  $\sim 8 \text{ s}^{-1}$ . According to this model, the rate constant for triplet energy transfer,  $k(r)$ , as a function of donor/acceptor separation distance,  $r$ , may be expressed by eq 1, where  $k_0$  is the rate constant for triplet energy transfer from a donor to an acceptor in physical contact,  $r_0$  is the contact distance between donor and acceptor centers, and  $L$  is an orbital size factor.

$$k(r) = k_0 \exp[-2(r - r_0)/L] \quad (1)$$

From our solution energy transfer measurements  $k_0$  is estimated to be  $\sim 10^9 \text{ s}^{-1}$  for energy transfer from KC\* to DB3.<sup>9</sup> A value of  $7 \text{ \AA}$  may be used for  $r_0$  and  $L$  is typically  $\sim 1 \text{ \AA}$ .<sup>10</sup> Upon substitution of these values, a  $k(r)$  of  $8 \text{ s}^{-1}$  is obtained at radius of  $16.3 \text{ \AA}$ , which is less than the measured KC action sphere radius of  $\sim 20 \text{ \AA}$ . This difference is too large to be accounted for by Dexter energy transfer because a  $\sim 200 \text{ s}$  triplet lifetime for KC\* would be required to transfer energy directly to a DB3 molecule at  $\sim 20 \text{ \AA}$ , which is clearly unreasonable and inconsistent with the measured lifetime in PMMA ( $\sim 0.13 \text{ s}$ ). A reasonable explanation for the larger, effective action sphere is provided by Scheme 4. As explained earlier (cf. Scheme 2), the reactant molecules in close proximity to the sensitizer are the ones that would react first with a modest quantum amplification. Because of the long lifetime of KC\*, energy transfer from KC\* to a reactant molecule within  $\sim 16 \text{ \AA}$  (reaction 11) can take place (inner dashed circle in Scheme 4). However, unlike the situation at near contact distances, back energy transfer from P\* to S at such a long distance can be slower than energy transfer from P\* to another nearby R molecule that lies outside the  $16 \text{ \AA}$  radius (reaction 12), which would lead to the larger action sphere (outer circle in Scheme 4).<sup>11</sup>

As noted above, the attainable conversion with KC and DB3 increases from  $\sim 32\%$  in the absence of co-sensitizer to  $\sim 55\%$

**SCHEME 4. Schematic Representation of Triplet-Sensitized Isomerization of Dewar Benzenes from a Long-Lived Triplet Sensitizer (S) That Can Lead to Energy Transfer over a Long Distance (Reaction 11, at the Inner Dashed Circle), Followed by Further Energy Propagation to Reactants at Even Longer Distance from the Sensitizer (Reaction 12, at the Outer Dashed Circle)<sup>a</sup>**



<sup>a</sup> As in Scheme 1, at various stages in the energy transfer/isomerization sequence the circles represent R, R\*, P\*, and P. See text for detailed explanation.

in the presence of 5 wt % of co-sensitizers that have triplet energies  $>60 \text{ kcal/mol}$ . A 55% conversion corresponds to an action sphere radius of  $\sim 24 \text{ \AA}$ , i.e.  $\sim 4 \text{ \AA}$  longer than that in the absence of a co-sensitizer.<sup>12</sup> The increase in the action sphere for co-sensitizers in this energy range can be explained by a process similar to reaction 11 in Scheme 4, except where energy transfer occurs from P\* to a nearby co-sensitizer, which is followed by energy transfer from C\* to a nearby reactant molecule at further distance from the sensitizer.

As is shown in Figure 4, the attainable conversion increases substantially with decreasing co-sensitizer triplet energy from 60 to 58 kcal/mol and levels off at lower  $E_T$ . The increase in attainable conversion is also accompanied by a substantial increase in the initial quantum yield (Figure 3). As explained above (Scheme 3), the incremental increase in both conversion and quantum yield within this narrow range of co-sensitizer triplet energies is attributable to the added contribution of energy transfer from S\* to C, which can lead to further chain propagation.

Thus, overall, the net effect of co-sensitizers is to enhance the migration of energy away from the sensitizer, thereby, increasing the action sphere and the isomerization quantum yield. As shown in Figure 5, nearly complete conversion ( $\sim 92\%$ ) of DB3 can be achieved with 8 wt % co-sensitizer, which corresponds to an action sphere with a radius of  $\sim 29 \text{ \AA}$ . The effects of co-sensitization on the reaction efficiencies and conversion can also be observed when the co-sensitizer is covalently attached to the polymer backbone, as described below.

**Functionalized Polymers.** Attempts to continue increasing the quantum yields for QAI materials by further increases in co-sensitizer concentration have practical limits with molecularly doped polymers due to the effects of plasticization that lower the glass transition temperature and lead to tacky films. Several functionalized polymers were synthesized (see the Experimental

(8) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836.

(9) The measured rate constant for energy transfer,  $k_q$ , from KC\* to DB3 in ethyl acetate is  $2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . According to eq 9 in ref 4,  $k_q = k_d k_{et}/(k_{et} + k_{-d})$ , where  $k_{et}$  is the first-order rate constant for triplet energy transfer in an encounter of KC\* and DB3,  $k_d$  is the rate constant for diffusional formation of the encounter/cage complex, and  $k_{-d}$  is the rate constant for dissociation of the encounter/cage pair. Taking  $k_d$  as  $1.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  and  $k_{-d}$  as  $3 \times 10^{10} \text{ s}^{-1}$  in ethyl acetate<sup>4</sup> yields a value for  $k_{et}$  of  $4 \times 10^8 \text{ s}^{-1}$ . This value corresponds to the rate constant for triplet energy transfer within a solvent cage where KC\* and DB3 are nominally an average of  $\sim 0.5 \text{ \AA}$  apart. From the Dexter expression with  $L = 1 \text{ \AA}$ , the energy transfer rate constant,  $k_0$ , for KC\* and DB3 in physical contact (i.e.,  $\sim 0.5 \text{ \AA}$  closer) would be  $\sim 1 \times 10^9 \text{ s}^{-1}$ .

(10) (a) Strambini, G. B.; Galley, W. C. *J. Chem. Phys.* **1975**, *63*, 3467. (b) Strambini, G. B.; Galley, W. C. *Chem. Phys. Lett.* **1976**, *39*, 257.

(11) A small amount of long-range resonance energy transfer allowed by the long KC\* lifetime may also contribute to the larger action sphere: Anderson, R. W.; Hochstrasser, R. M.; Lutz, H.; Scott, G. W. *J. Chem. Phys.* **1974**, *61*, 2500.

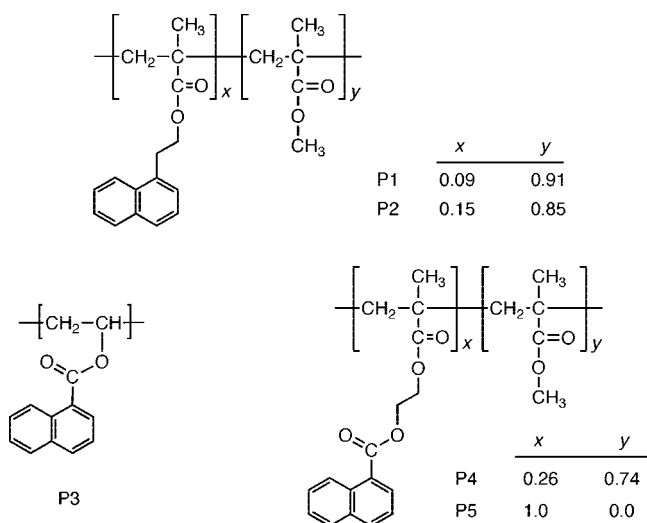
(12) In contrast, the 80% conversion of DB3 obtained with DETX and higher energy co-sensitizers leads to an apparent action sphere radius of only  $12.4 \text{ \AA}$ . This is largely reflective of the higher concentration of DETX. At 0.168 M, the average volume/molecule of DETX is  $9900 \text{ \AA}^3$ , which corresponds to a maximum action sphere radius of  $\sim 13 \text{ \AA}$ .

**TABLE 2.** Isomerization Quantum Yields ( $\Phi_{\text{isom}}$ ) and Percent of Attainable Conversions for 10 wt % DB2 and DB3, Sensitized with DETX and KC, Respectively, in Polymers with Covalently Attached Co-sensitizers

polymer	$T_g$ ( $^{\circ}\text{C}$ )	DB2/DETX		DB3/KC	
		$\Phi_{\text{isom}}^a$	% conversion <sup>b</sup>	$\Phi_{\text{isom}}^a$	% conversion <sup>b</sup>
P1	82	7.3	99		
P2	89	8.6	100		
P3	88			11.4	85
P4	85			~16	99
P5	54			~16	99

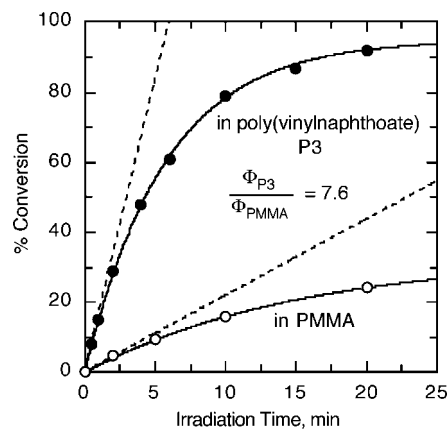
<sup>a</sup> Measured at 10–15% conversion and corrected for incomplete absorption; error limits <0.2. Excitation at 405 nm ( $6 \times 10^{-8}$  Einstein/min per  $\text{cm}^2$ ). <sup>b</sup> Attainable conversion with prolonged exposure (30 min).

Section) with covalently attached co-sensitizers (P1–P5) to explore higher levels of co-sensitizer concentration. These materials can be thought of as energy-conducting polymers. Polymers P1, P2, P4, and P5 were prepared by conventional free radical polymerization of the corresponding monomers, which were synthesized by esterification of the commercially available alcohols with methacryloyl chloride. P3 was prepared by esterification of poly(vinyl alcohol) with naphthoyl chloride.



The quantum yields and attainable conversions for 10 wt % DB2 and DB3 in P1–P5 are summarized in Table 2. The quantum yield for isomerization of DB2 sensitized with DETX in copolymer P2 containing a 1-alkyl-substituted naphthalene co-sensitizer (~25 wt % co-sensitizer) was 8.6. This compares with a lower quantum yield of 5.3 when the structurally similar co-sensitizer 1-naphthyl acetate was molecularly doped in PMMA at 5 wt % (Table 1). Similarly, the isomerization quantum yield of DB3 sensitized with KC was 11.4 in polyvinyl naphthoate (P3) and ~16 in copolymers P4 and P5. These compare to a quantum yield of only 4.3 when ethyl 1-naphthoate is molecularly doped in PMMA at 5 wt % (Table 1). The reason for the lower quantum yield in P3 than in P4 and P5 is, as yet, unclear. It may be due to the lower flexibility of the naphthoate moiety in P3, although trace impurities in P3 that terminate the triplet chain cannot be excluded.

Shown in Figure 7 is a comparison of the quantum yield and the maximum attainable conversion for DB3 in P3 with that in PMMA without added co-sensitizer. The initial slopes are proportional to the quantum yields at low conversion (<10%).



**FIGURE 7.** Conversion as a function of time of DB3, molecularly doped at 10 wt % in P3 (filled circles) and in PMMA (unfilled circles) sensitized with KC. The dashed lines represent the initial slopes, which provide the quantum yields at low conversion. The solid lines are fittings to  $\% \text{ conversion} = \alpha\{1 - \exp(-\beta \times \text{time})\}$ . The parameter  $\alpha$  gives the maximum conversion, and the product  $\alpha \cdot \beta$  is proportional to the initial quantum yield.

The quantum yield ratio is 7.6, which shows that the quantum yield increased from 1.5 in PMMA to 11.4 in P3. The maximum conversion, derived from the fitting equations given in the caption of Figure 7, also shows an increase from PMMA to P3, from ~32% to ~95%.

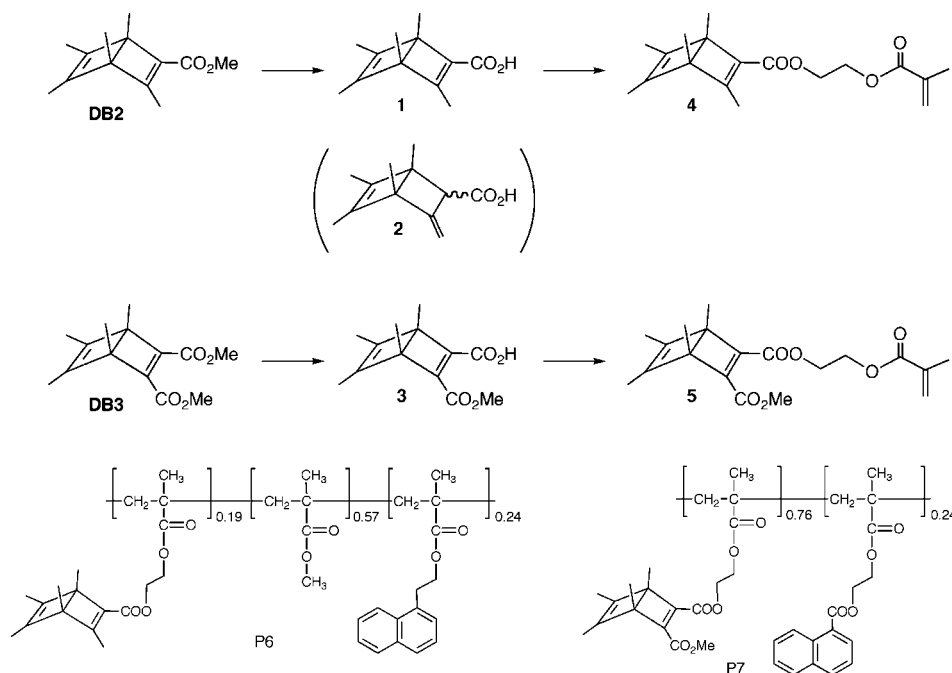
We next sought to prepare copolymers that were functionalized with both reactant and co-sensitizer to evaluate their performance. A polymerizable monomer (4) containing the Dewar benzene monoester reactant was synthesized from DB2 as shown in Scheme 5. Interestingly, initial attempts to hydrolyze DB2 under a variety of conventional conditions led to a mixture of conjugated (1) and deconjugated (2) acids that were difficult to separate. Control experiments showed that deconjugation occurs through ester DB2 not acid 1. Ultimately, clean conversion of DB2 to 1 was achieved under enzymatic hydrolysis conditions with pig liver esterase as the catalyst. Preparation of a diester Dewar benzene monomer (5) began with the selective monohydrolysis of DB3 under heterogeneous conditions using the method of Niwayama<sup>13</sup> to give monoacid 3 (Scheme 5). Esterification of acids 1 and 3 with hydroxyethyl methacrylate under dicyclohexylcarbodiimide coupling conditions proceeded uneventfully to give Dewar benzene monomers 4 and 5, which were successfully copolymerized to give polymers P6 and P7, respectively, under the standard free radical conditions described previously.<sup>1</sup>

The quantum yields for photoisomerization of P6 and P7 with DETX as sensitizer were found to be comparable, ~11 and  $10 \pm 1$ , respectively. The quantum yield for P6 is most appropriately compared to the isomerization quantum yield of 8.6 for 10 wt % DB2 in P2. P6 contains nearly the same co-sensitizer concentration as P2 (28 vs 25 wt %), however, P6 contains a greater loading of the reactant (22 vs 10 wt %).<sup>14</sup> Thus, the greater reactant concentration in P6 leads to a greater quantum yield, as found for molecularly doped polymers. The quantum yield with P7, which contains ~13 wt % co-sensitizer, is most appropriately compared to that for DB3 in PMMA containing a comparable amount of methyl 1-naphthyl acetate

(13) Niwayama, S. *J. Org. Chem.* **2000**, *65*, 5834.

(14) Calculations of the weight percentages of reactants and co-sensitizers in the functionalized polymers are based on the fractional weight equivalent of the corresponding molecularly doped materials.

SCHEME 5. Synthesis of Monomers 4 and 5



(10 wt %) as a co-sensitizer (Table 1). The greater quantum yield for P7 vs the molecularly doped polymer (4.8) reflects the greater concentration of reactant in the functionalized polymer (57 vs 10 wt %).

## Conclusions

A second, improved generation of QAI polymers has been successfully developed that is based on the triplet quantum chain isomerization of substituted Dewar benzene derivatives. Efficient chain propagation in polymeric media was achieved by incorporation of triplet energy co-sensitizers that facilitate long distance energy migration and, thereby, markedly increase the isomerization quantum yields and the extents of reactant-to-product conversion that can ultimately be achieved. In the best systems examined thus far, quantum amplifications of  $\sim 16$  and conversions approaching 100% have been achieved. The combined results, coupled with the large refractive index changes ( $\Delta n \sim 0.02$ ) for the materials,<sup>2d</sup> demonstrate that triplet QAI polymers may be promising optical materials for a variety of applications.<sup>15</sup> Experiments that demonstrate applications will be reported separately.

## Experimental Section

**Synthesis of Di-*n*-butyl 4,4'-Biphenyldicarboxylate.** A mixture of biphenyl-4,4'-dicarboxylic acid (15.2 g, 63 mmol), 100 mL of *n*-butanol, 200 mL of toluene, and a catalytic amount of *p*-toluenesulfonic acid was heated at reflux with continuous separation of evolved water for 7 d. The reaction mixture was cooled to room temperature, diluted with dichloromethane, filtered, washed with 10% aqueous NaHCO<sub>3</sub> and then with brine, dried (MgSO<sub>4</sub>), and concentrated. The crude product was purified by recrystallization from heptane to obtain 13.4 g (60%) of colorless crystals (mp 45–48 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.97 (t, 6 H), 1.5 (m, 4 H), 1.8 (m, 4 H), 4.35 (q, 4 H), 7.68 (d, 4 H), 8.13 (d, 4 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  13.77, 19.27, 30.76, 64.96, 127.18, 130.00, 130.13,

144.26, 166.35. Exact mass, C<sub>22</sub>H<sub>27</sub>O<sub>4</sub> (M + H): calcd 355.1909, found *m/z* 355.1915 (PIES-HRMS).

**Synthesis of Methyl 9,9-Diethylfluorene-2-carboxylate.** A mixture of 10.0 g (41 mmol) of 2-bromofluorene, 5.7 g (100 mmol) of potassium hydroxide, and 50 mL of dimethyl sulfoxide was stirred with slight cooling until a uniform solution was obtained. Ethyl iodide (19.1 g, 122 mmol) was added dropwise at room temperature, and the mixture was stirred for 1 h. An additional charge of ethyl iodide (6 g, 38 mmol) was added, and stirring was continued for 18 h. The reaction mixture was poured into 200 mL of water and extracted with ether (3  $\times$  100 mL). The combined ethereal extracts were dried (MgSO<sub>4</sub>) and concentrated to deposit a gold oil that partially crystallized after trituration with cold methanol. The intermediate product, 2-bromo-9,9-diethylfluorene, was recrystallized from methanol with decolorizing carbon, producing 5.64 g (46%) of a white solid in two crops.

A heavy-walled glass bottle was charged with 2-bromo-9,9-diethylfluorene (2.78 g, 9.2 mmol), methanol (7.4 g, 230 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (3.19 g, 23 mmol), triphenylphosphine (0.1 g, 0.4 mmol), dichlorobis(triphenylphosphine)palladium(II) (0.13 g, 0.2 mmol), and 40 mL of *N,N*-dimethylacetamide. The stirred mixture was deaerated by sparging with nitrogen, and then the bottle was closed and pressurized to 60 psi with carbon monoxide. The stirred reaction mixture was heated at 120 °C for 2 h, cooled to room temperature, filtered, and poured into 300 mL of water. The resulting milky suspension was extracted with ether (3  $\times$  100 mL), and the combined extracts were successively washed with 5% aq HCl, three times with water, and with brine. The solution was dried (MgSO<sub>4</sub>) and concentrated to deposit a gold oil. The product was purified by column chromatography (elution with a mixture of heptane and dichloromethane) and then distilled at reduced pressure to provide 1.91 g (74%) of a viscous colorless oil that gradually crystallized (mp 52–54 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.29 (t, 6 H), 2.07 (m, 4 H), 3.95 (s, 3 H), 7.36 (m, 3 H), 7.76 (d, 2 H), 8.01 (m, 2 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  8.40, 32.58, 52.05, 56.27, 119.34, 120.55, 123.05, 124.05, 127.03, 128.27, 128.52, 128.88, 140.30, 146.25, 149.92, 150.94, 167.54. Exact mass, C<sub>19</sub>H<sub>20</sub>O<sub>2</sub> (M): calcd 280.1463, found *m/z* 280.1458 (APPI-HRMS).

**Synthesis of 2-(1-Naphthyl)ethyl Methacrylate.** A solution of 2-(1-naphthyl)ethanol (30.0 g, 174 mmol), triethylamine (24.2 g,

(15) Farid, S. Y.; Robello, D. R.; Dinnocenzo, J. P.; Merkel, P. B.; Ferrari, L. S.; Roh, Y. U.S. Patent Application 2005136357 A1, June 23, 2005.



**TABLE 3.** Number Average ( $M_n$ ) and Weight Average ( $M_w$ ) Molecular Weights of Polymers P1–P7 and Their Glass Transition Temperatures ( $T_g$ )

polymer	$M_n^a$	$M_w^a$	$T_g^b$ (°C)
P1	13800	47000	82
P2	12200	41700	89
P3			88
P4	11300	23600	85
P5	14200	28000	54
P6	24300	57900	84
P7	37700	77300	77

<sup>a</sup> Absolute molar mass averages by SEC using viscometric detection and universal calibration. <sup>b</sup> Glass transition temperature measured by DSC.

239 mmol), 4-(dimethylamino)pyridine (1.1 g, 9.1 mmol), and dichloromethane (500 mL) was treated dropwise under nitrogen with methacryloyl chloride (18.9 g, 181 mmol) and then heated at reflux for 4 h. The reaction mixture was cooled to room temperature and diluted with diethyl ether. The solution was filtered and the filtrate washed twice with water, once with  $\text{NaHCO}_3$ , and once with brine. The solution was dried ( $\text{Na}_2\text{SO}_4$ ), concentrated to a yellow oil, and distilled at reduced pressure (bp 120–125 °C, 0.08 mm) to give 36.0 g (86%) of a colorless oil.  $^1\text{H}$  (CDCl<sub>3</sub>):  $\delta$  2.00 (s, 3 H), 3.50 (t, 2 H), 4.55 (t, 2 H), 5.60 (s, 1 H), 6.15 (s, 1 H), 7.50 (m, 4 H), 7.8 (d, 1 H), 7.9 (d, 1 H), 8.2 (d, 1 H).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>):  $\delta$  18.28, 32.18, 64.69, 123.61, 125.42, 125.54, 125.61, 126.13, 127.02, 127.39, 128.75, 132.02, 133.76, 133.82, 136.28, 167.39. Exact mass, C<sub>16</sub>H<sub>16</sub>O<sub>2</sub> (M + NH<sub>4</sub>): calcd 258.14940, found  $m/z$  258.14772 (ES-HRMS).

**Synthesis of 2-(1-Naphthoxy)ethyl Methacrylate.** A mixture of 1-naphthoic acid (8.0 g, 46 mmol), 2-hydroxyethyl methacrylate (18.1 g, 139 mmol), 4-(dimethylamino)pyridinium *p*-toluenesulfonate (5.5 g, 19 mmol), and anhydrous dichloromethane (45 mL) was cooled to 0 °C under nitrogen, and 1,3-dicyclohexylcarbodiimide (12.5 g, 60 mmol) was added. After 15 min, the reaction mixture was warmed to room temperature and stirred for 3 h. The precipitate that formed was filtered, and the filtrate was washed successively with 10% aqueous HCl, 10% aqueous  $\text{NaHCO}_3$ , water, and brine. The organic layer was dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated to a gold oil that was purified by column chromatography to provide 8.2 g (62%) of a pale yellow oil.  $^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta$  1.90 (s, 3 H), 1.55 (m, 2 H), 1.70 (m, 2 H), 5.60 (s, 1 H), 6.20 (s, 1 H), 7.55 (m, 3 H), 7.90 (d, 1 H), 8.05 (d, 1 H), 8.20 (d, 1 H), 8.90 (d, 1 H).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>):  $\delta$  18.29, 62.49, 62.67, 124.48, 125.70, 126.12, 126.22, 126.71, 127.79, 128.56, 130.41, 131.30, 133.58, 133.81, 135.92, 167.14, 167.23. Exact mass, C<sub>17</sub>H<sub>16</sub>O<sub>4</sub> (M + NH<sub>4</sub>): calcd 302.13923, found  $m/z$  302.13876 (ES-HRMS).

**Representative Polymer Synthesis Procedure: Synthesis of P2.** A solution of 2.50 g (10.4 mmol) of 2-(1-naphthyl)ethyl methacrylate, 10.1 g (101 mmol) of methyl methacrylate, and 0.28 g (1.11 mmoles) of 2,2'-azobis(2,4-dimethylvaleronitrile) in benzene was deaerated by sparging for 10 min with nitrogen. The reaction mixture was then heated to 52 °C for 24 h. The resulting polymer was precipitated into cold ligroin twice and dried in a vacuum oven at 60 °C (Table 3).

**Synthesis of Poly(vinyl 1-naphthoate), P3.** A suspension of 2.2 g of poly(vinyl alcohol) in 100 mL of dry pyridine was stirred overnight at 55–70 °C protected from air. 1-Naphthoyl chloride (9.5 g) was added, and the mixture was heated for 18 h at 60 °C. After being cooled to room temperature, the amber reaction mixture was filtered and the polymer precipitated in 1.5 L of cold water. The product was collected, washed with water, air-dried, and then dried in vacuo to give 7.6 g of a flaky white solid.  $T_g$  (DSC) = 88 °C.

**Synthesis of 1.** Crude porcine liver esterase (25 g) was dissolved in 500 mL of pH 7.8 buffer and warmed to 40 °C. To this solution was added 53.0 g (257 mmol) of DB2. NaOH solution (0.1 M)

was added via a FMI laboratory pump at a rate to maintain the pH at  $7.8 \pm 0.1$ . After 8 h, the reaction mixture was filtered, insoluble material was washed with pH 7.8 buffer, and the filtrate was acidified with 10% HCl. The resulting tan precipitate was collected and dissolved in warm (60 °C) ethyl acetate. The solution was filtered to remove residual enzyme, dried ( $\text{MgSO}_4$ ), and concentrated to give 38 g (76%) of **1**.  $^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta$  1.15 (s, 3H), 1.25 (s, 3H) 1.58 (s, 3H), 1.64 (s, 3H), 2.05 (s, 3H).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>):  $\delta$  9.3, 10.6, 11.0, 11.3, 14.4, 54.6, 57.1, 137.7, 141.5, 145.5, 169.8, 172.6. Exact mass, C<sub>12</sub>H<sub>15</sub>O<sub>2</sub> (M – H): calcd 191.1072, found  $m/z$  191.1052 (NIES-HRMS).

**Synthesis of 3.** DB3 (5.0 g, 20 mmol) was dissolved in 80 mL of tetrahydrofuran, cooled to 0 °C, and treated with 80 mL of 0.375 M aqueous NaOH (30 mmol). The resulting mixture was stirred at 0 °C for 2 h and then warmed to room temperature. The mixture was washed three times with diethyl ether, and the aqueous phase was separated and acidified. The resulting precipitate was extracted into ethyl acetate and dried over sodium sulfate. The solvent was removed at reduced pressure to deposit a yellow solid which was purified by column chromatography to give 3.2 g (68%) of **3** (mp 108–110 °C).  $^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta$  1.30 (s, 3 H), 1.35 (s, 3 H), 1.60 (s, 3 H), 1.64 (s, 3 H), 3.90 (s, 3 H), 12.10 (s, 1 H).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>):  $\delta$  9.51, 9.91, 11.09, 11.20, 53.17, 55.45, 57.09, 142.52, 143.67, 150.42, 159.43, 161.07, 166.52. Exact mass, C<sub>13</sub>H<sub>15</sub>O<sub>2</sub> (M – H): calcd 235.0970, found  $m/z$  235.0970 (NIES-HRMS).

**Syntheses of 4 and 5.** A mixture of **1** (3.8 g, 19.8 mmol), 2-hydroxyethyl methacrylate (7.7 g, 59.3 mmol), 4-(dimethylamino)pyridinium *p*-toluenesulfonate (2.3 g, 7.8 mmol), and anhydrous dichloromethane (31 mL) was cooled to 0 °C under nitrogen, and 1,3-dicyclohexylcarbodiimide (5.3 g, 25.7 mmol) was added. After 15 min, the reaction mixture was warmed to room temperature and stirred for 12 h. The precipitate that formed was filtered, and the filtrate was washed successively with 10% aqueous HCl, 10% aqueous  $\text{NaHCO}_3$ , water, and brine. The organic layer was dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated to give a yellow oil. The product (**4**) was vacuum distilled (bp 85–90 °C, 0.05 mm) to give 3.0 g (50%) of a colorless oil.  $^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta$  1.15 (s, 3 H), 1.23 (s, 3 H), 1.57 (s, 3H), 1.60 (s, 3 H), 1.95 (s, 3 H), 2.00 (s, 3 H), 4.35 (m, 4 H), 5.6 (s, 1 H), 6.25 (s, 1 H).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>):  $\delta$  9.30, 10.62, 10.98, 11.19, 14.24, 18.23, 54.61, 56.98, 61.01, 62.62, 125.88, 135.99, 137.64, 141.73, 145.32, 163.88, 167.08, 169.98. Exact mass, C<sub>18</sub>H<sub>24</sub>O<sub>4</sub> (M + Na): calcd 327.15722, found  $m/z$  327.15702 (ES-HRMS). The synthesis of **5** was analogous to **4** except that the product was purified by column chromatography (60% yield).  $^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta$  1.20 (s, 3 H), 1.23 (s, 3 H), 1.55 (s, 3 H), 1.58 (s, 3 H), 1.90 (s, 3 H), 3.72 (s, 3 H), 4.35 (m, 4 H), 5.5 (s, 1 H), 6.1 (s, 1 H).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>):  $\delta$  9.90(2C), 10.91, 10.99, 18.20, 51.65, 56.12, 56.33, 62.15, 62.32, 126.03, 135.86, 143.17, 143.26, 150.70, 152.28, 161.73, 162.69, 166.99. Exact mass, C<sub>19</sub>H<sub>24</sub>O<sub>6</sub> (M + H): calcd 349.16511, found  $m/z$  349.16417 (ES-HRMS).

**Preparation of Polymer Films.** Solutions were prepared with DB2 or DB3 (100 mg), co-sensitizer (50 mg), sensitizer (40 mg of DETX or 5 mg of KC), and PMMA (810 or 845 mg, so that the total weight of solids was 1 g) in 4 mL of dichloromethane and filtered by using a Whatman syringeless PTFE membrane (0.45  $\mu\text{m}$ ).

The solutions were hand coated using a 10 cm  $\times$  127  $\mu\text{m}$  knife on a 100  $\mu\text{m}$  transparent poly(ethylene terephthalate) support with a thin (<0.5  $\mu\text{m}$ ) adhesion layer (15/79/6 copolymer of acrylonitrile, vinylidene chloride, and acrylic acid), maintained at 23–25 °C, and the samples were air-dried for 15 min. The films were cut into  $\sim 4 \times 4$  cm square pieces and mounted between two black-anodized aluminum plates with a 25 mm circular aperture, clamped, and dried in a vacuum oven at 40 °C for 16–17 h. The thickness of the dried films was  $\sim 22 \pm 2$   $\mu\text{m}$ , and the optical densities at 405 nm were  $0.4 \pm 0.05$ .

**Quantum Yield Measurements and Conversion Experiments.** The samples were irradiated (usually in duplicates for 0.5, 1, 2, 4, and 30 min) using the strongly defocused output of a high-pressure

Hg lamp (200 W), filtered through Corning 5–58 broadband filter, a 3–75 cutoff filter, and a 404.7 nm interference filter. The photon flux of the lamp at 405 nm ( $\sim 5\text{--}6 \times 10^{-8}$  Einstein/min/cm<sup>2</sup>) was measured using the reaction of 9,10-phenanthrenequinone (0.001 M) with *trans*-stilbene (0.1 M) in benzene as an actinometer.<sup>16</sup>

In the case of DB2 as reactant, the center of the exposed films was cut out using a 12.3 × 12.3 mm arch punch and extracted with 0.4 mL dichloromethane to which was added 50 μL of a cyclohexane solution containing tetradecane (6.04 mg/mL,  $1.53 \times 10^{-6}$  M) as an internal standard. The samples were sonicated for 15 min, cyclohexane (1.8 mL) was added to precipitate the polymer, and the solutions were filtered through a cotton-plugged pipet. The solutions were analyzed by GC using an RTX-5 Crossbond 5% diphenyl-95% dimethyl polysiloxane column (15 m × 0.32 mm × 0.25 μm) with an oven temperature that was ramped from 45 to 235 °C over 17 min. In an independent experiment, a GC calibration was performed to determine the ratio of area counts/mol for several concentrations (from  $6 \times 10^{-8}$  to  $1.5 \times 10^{-6}$  M) of the product (P2) and the reactant (DB2) to that of  $1.5 \times 10^{-6}$  M of tetradecane. In general, the mass balance of product plus reactant of the irradiated samples against the amount of reactant from unirradiated samples was quantitative within experimental error ( $\pm 3\%$ ).

In the case of DB3, the polymer films were prepared as for DB2 but were analyzed by HPLC (see Instrumentation, Supporting Information). Peak areas were standardized vs those of unirradiated samples and were response factor corrected.

For polymers P6 and P7, the isomerization quantum yields were obtained by comparing the diffraction efficiency response after holographic exposure of the irradiated film relative to that of a sample in which DB2 was molecularly doped in PMMA.<sup>17,18</sup> Details of this experiment will be described in a separate paper.

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**Supporting Information Available:** Experimental methods, materials, and <sup>1</sup>H NMR spectra of Dewar benzene derivatives, co-sensitizers, monomers, and functionalized polymers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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