Photodegradation of Oligomeric Polyesters Containing Anthraquinone and 1,2-Diamine Units. Single Electron Transfer Induced Cation Radical Bond Cleavage in the Solid State

Jeffrey W. Leon and David G. Whitten*

Contribution from the Department of Chemistry, University of Rochester, Rochester, New York 14627

Received August 1, 1994[⊗]

Abstract: Oligomeric polyesters containing light-absorbing anthraquinone electron acceptor chromophores and fragmentable 1,2-diamine donors have been synthesized. Irradiation with $\lambda > 340$ nm in solution or as solid films results in photooxidative C−C bond cleavage of the 1,2-diamine units yielding essentially the same products in either case. The solid state photodegradation reaction was monitored using size exclusion chromatography and was found to be substantially less efficient than the corresponding solution reaction. This is attributed to an inefficient forward electron transfer step and the possibility of an induced reversibility of the fragmentation. The efficiency of photodegradation is suggested to be dependent on the donor/acceptor orientations in the solid state.

Introduction

There has been recent interest in the development of efficient solid state photoreactions, particularly due to their potential applications in such important areas as advanced lithographic techniques, photoreactive and photodegradable materials, and photoresist technology. Most reactions reported involve small molecule extrusions, radical abstractions, or homolytic bond cleavages. One rich and potentially useful area of chemistry which has received surprisingly little attention in terms of solid state applications is single electron transfer (SET) induced photoreactions.

Though few studies, if any, have focused on electron transfer initiated bond breaking and bond-forming reactions in the solid state, a significant amount of research has been done exploring the fundamentals of the solid state electron transfer process itself without regard to subsequent reactions of the photoproduced radical ion species. Theoretical models of solid state electron transfer have been developed by Miller,[1] Mataga,[2] and Marcus,[3] and several notable studies of electron transfer in frozen solvent matrices by Miller,[1,4–8] Wasielewski,[9,10] Meyer,[11] and Sanders[12] have greatly contributed to our understanding of electron transfer in the solid state as well as our understanding of electron transfer in general. Photoinduced electron transfer has also been studied in solid polymer matrices.[13] In addition, photoprocesses such as exciplex formation and luminescence quenching in polymer media have been well documented.[14–18] Despite the large amount of work done in the field of solid state electron transfer, almost all of this research has consisted of photophysical studies of reversible processes. Currently, little is known about the reactivity of photogenerated ion radical species in the solid state.

There are certain differences between solution and solid state media which could profoundly affect ion radical reactions. Photophysical and photochemical processes occurring within a solid matrix differ from similar reactions in solution on account of limitations of diffusional, translational, and rotational possibilities. A solid matrix is a sterically restrictive medium in which molecular motions can be expected to be hindered. This has additional implications for electron transfer reactions, as the photoproduced radical ions cannot diffuse apart, and hence the deactivating return electron transfer will always be competitive with any subsequent chemistry which the radical ions can undergo.

The electron transfer step by which the radical ions are generated can also be expected to show differences in going from solution to solid media. One common finding of several studies is that electron transfer processes in solid media are substantially slower than in solution,[10–12] a result which can be at least partially explained in terms of solvation effects. In the solution state, solvent dipoles are free to reorganize around the photogenerated radical ions, thereby decreasing the energy

---

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1995.

[1] Miller, J. R. *J. Am. Chem. Soc.* **1984**, *106*, 5057.

[2] Kakitani, T.; Mataga, N. *J. Phys. Chem.* **1988**, *92*, 5059.

[3] Marcus, R. A. *J. Phys. Chem.* **1990**, *94*, 4963.

[4] Miller, J. R.; Beitz, J. R. *J. Chem. Phys.* **1984**, *74*, 6746.

[5] Miller, J. R. *Science* **1974**, *189*, 221.

[6] Miller, J. R.; Hartman, K. W.; Abrash, S. *J. Am. Chem. Soc.* **1982**, *104*, 4296.

[7] Miller, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 6488.

[8] Closs, G. L.; Calcaterra, L. T.; Green, N. J.; Penfield, K. W.; Miller, J. R. *J. Phys. Chem.* **1986**, *90*, 3673.

[9] Wasielewski, M. R.; Johnson, D. G.; Svec, W. A.; Kersey, K. M.; Minsek, D. W. *J. Am. Chem. Soc.* **1988**, *110*, 7219.

[10] Gaines, G. L.; O'Neil, M. P.; Svec, W. A.; Niemczyk, M. P.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1991**, *113*, 719.

[11] Chen, P.; Danielson, E.; Meyer, T. J. *J. Phys. Chem.* **1988**, *92*, 3708.

[12] Harrison, R. J.; Pearce, B.; Beddard, G. S.; Cowan, J. A.; Sanders, J. A. *Chem. Phys.* **1987**, *116*, 429.

[13] Guarr, T.; McGuire, M. E.; McLendon, G. *J. Am. Chem. Soc.* **1985**, *107*, 5104.

[14] Farid, S.; Martic, P. A.; Daly, R. C.; Thompson, D. R.; Specht, D. P.; Hartman, S. E.; Williams, J. L. *Pure Appl. Chem.* **1979**, *51*, 241.

[15] Allen, N. S.; Schnabel, W. *Photochemistry and Photophysics in Polymers*; Elsevier: London, 1984.

[16] *New Trends in the Photochemistry of Polymers*; Allen, N. S., Rabek, J. F., Eds.; Elsevier: New York, 1985. Rabek, J. F. *Mechanisms of Photophysical Processes and Photochemical Reactions in Polymers*; John Wiley & Sons: Chichester, 1987.

[17] Guillet, J. E. *Polymer Photophysics and Photochemistry*; Cambridge University Press: Cambridge, 1985.

[18] Miller, R. D.; Baier, M.; Clecak, N.; Wallraf, G. M. *Abstracts of Papers*, 202nd National Meeting of the American Chemical Society; American Chemical Society: Washington, DC, 1991; POLY 188. Wallraf, G. M.; Miller, R. D.; Baier, M.; Ginsburg, E. J.; Kunz, R. R.; Horn, M. W.; Goodman, R. B. *Polym. Mater. Sci. Eng:* **1992**, *66*, 105–8. Miller, R. D.; Baier, M.; Diaz, A. F.; Ginsburg, E. J.; Wallraff, G. M. *Pure Appl. Chem.* **1992**, *64*, 1291–8.

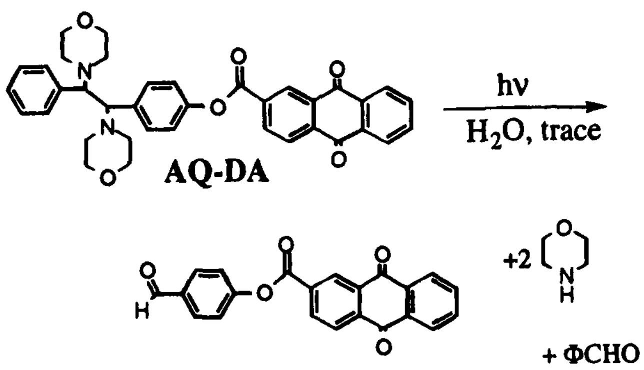
0002-7863/95/1517-2226$09.00/0

of the radical ion pair. In a frozen solvent matrix or in a polymer below the glass transition temperature, the medium can reorganize, but to a far lesser extent and on a time scale that is much slower than the electron transfer process itself. This lack of stabilization of the photoproduced radical ions manifests itself as a change both in the thermodynamic driving force and in the relationship between the thermodynamic driving force and the electron transfer rate.

In terms of Marcus theory,[19-22] the net result is that, on the fast time scale of electron transfer processes, λ_s is substantially lowered. This can also cause a further lowering of electron transfer rates. Another effect noticed (particularly in intermolecular solid state electron transfer) is a broadening of the distribution of electron transfer rates. This is caused by the donors and acceptors being "locked" in position and unable to approach each other to achieve an optimum distance and orientation, as they can in solution. As a result, the electron transfer takes place over a wide range of separations and donor/acceptor orientations and, hence, shows a broad distribution of rates.[2]

As radical ions can be efficiently generated in a solid matrix despite these considerations, it should then be possible to carry out basic bond-forming and bond-cleavage reactions of photogenerated ion radicals within the solid medium. Any reaction used for such a study will, of course, need to be specifically designed so as to take into account the short lifetimes of the photogenerated ion radical species and the restricted free volume of the solid matrix.

In a previous publication,[23] we reported the synthesis and study of a linked donor/acceptor dyad molecule (**AQ-DA**) which consisted of an anthraquinone electron acceptor chromophore covalently linked to a 1,2 diamine donor, which can fragment by a general mechanism reported in previous papers.[24-28] This compound undergoes a photooxidative carbon–carbon bond cleavage reaction upon photolysis. The reaction occurs cleanly and efficiently in a wide range of solvents with quantum yields varying from 0.33 in benzene to 0.78 in DMF. The efficiency of the reaction was attributed to a slow, spin-forbidden return electron transfer (due to efficient singlet–triplet intersystem crossing in the anthraquinone chromophore) and a fast bond fragmentation. It may be noted that this reaction in benzene is similar to the reaction in the solid state in two respects. First, the donor and acceptor are covalently bound and thus the photogenerated radical ions cannot diffuse apart. Secondly, the nonpolar solvent medium offers the radical ions little stabilization. The linked donor/acceptor molecule in benzene may, hence, be viewed as a model for the corresponding solid state reaction, and hence, it seemed logical to extend our studies to determine the feasibility of electron transfer induced bond cleavage reactions in the solid state.



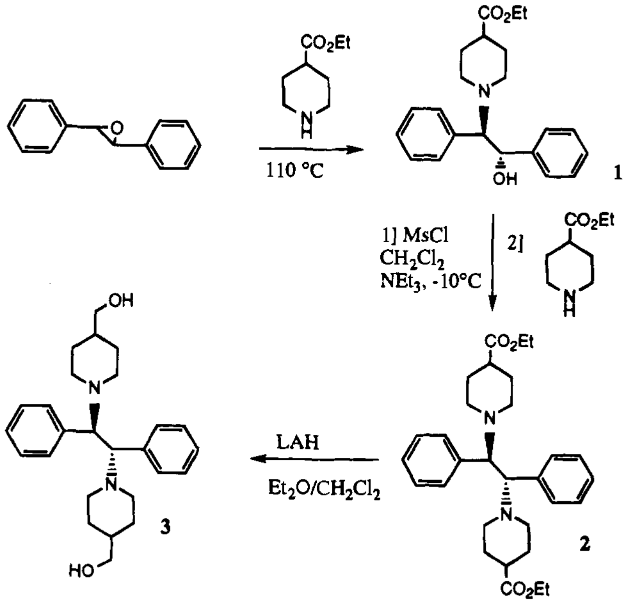


Figure 1. Synthesis of diamine donor segment.

Here we present the synthesis and study of two photodegradable oligomeric polyesters which consist of copolymerized anthraquinone acceptor and fragmentable diamine donor units. These polymers photodegrade in glassy films by a photo-SET induced bond cleavage mechanism yielding essentially the same products as the corresponding reaction in solution. The reaction is monitored by size exclusion chromatography and found to be notably less efficient in the solid state as compared to solution.

Results

Design and Synthesis of Polyesters. The polymers used in this study were designed to contain the same basic, reactive donor and acceptor groups as used in the previous studies of **AQ-DA** and to undergo the same fragmentation reaction. We proposed size exclusion chromatography (SEC) as our main analytical tool, but highly functionalized polymers will often adsorb to SEC columns. The design of the polymers used in this study was limited with respect to addressing these concerns. The synthetic plan involved the polyesterification of donor and acceptor units with one functionalized as a diacid and one functionalized as a diol. The diamine–diol monomer (see Figure 1) was made via a straightforward, convenient three-step synthesis with a total yield of 73%. It should be noted that in this compound the hydroxyl groups are primary and relatively unhindered, which should ensure a more efficient polymerization reaction. In addition, photocleavage of this diamine unit should release free benzaldehyde, which is an easily characterized product.

---

(19) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966.

(20) Marcus, R. A. *J. Chem. Phys.* **1957**, *24*, 979.

(21) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

(22) Duke, C. B.; Meyer, R. J. *Phys. Rev. B: Condens. Matter* **1981**, *23*, 2111.

(23) Leon, J. W.; Whitten, D. G. *J. Am. Chem. Soc.* **1993**, *115*, 8038.

(24) Whitten, D. G.; Kellett, M. A.; Leon, J. W.; Gan, H. In *Proceedings of the International Conference on Photochemical Conversion and Solar Energy*; International Academic Publishing: Beijing, 1992.

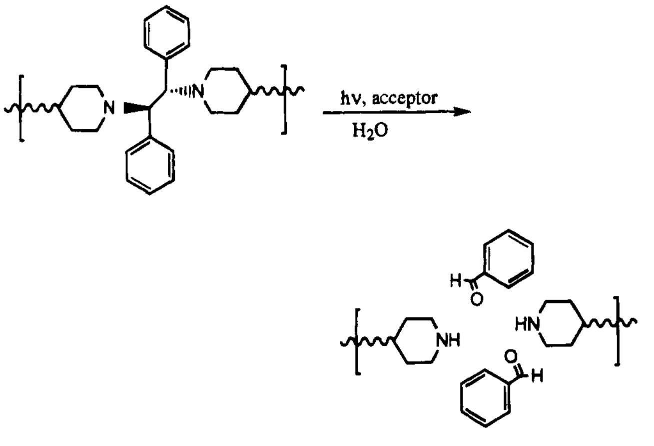
(25) Whitten, D. G.; Chesta, C.; Ci, X.; Kellett, M. A.; Yam, V. W. In *Photochemical Processes in Organized Molecular Systems*; Honda, Ed.; Elsevier: Amsterdam, 1991.

(26) Kellett, M. A.; Whitten, D. G. *J. Am. Chem. Soc.* **1989**, *111*, 2314.

(27) Kellett, M. A.; Whitten, D. G. *Mol. Cryst. Liq. Cryst.* **1991**, *194*, 275.

(28) Ci, X.; Kellett, M. A.; Whitten, D. G. *J. Am. Chem. Soc.* **1991**, *113*, 3893.

(29) Halfpenny, P. R.; Horwell, D. C.; Hughes, J.; Hunter, J. C.; Rees, D. C. *J. Med. Chem.* **1990**, *33*, 286.



The *meso* stereochemistry is another important feature of this molecule since we have found in previous studies that for 1,2-diheteroatom cation radical fragmentations, there exists an optimum reaction conformation in which the two heteroatoms (in this case, nitrogens) are in an antiperiplanar orientation.[24,28,30,31] The anthraquinone 1,3-diacid could be synthesized in large quantities by an adaptation of a process formerly used for the 2,3 isomer,[34] which proved to be efficient, though time consuming (see Figure 2). The use of the 1,3 isomer is also advantageous due to its asymmetry. One common strategy for solubilizing insoluble polymers is to add a degree of asymmetry or randomness to the basic repeating structure. Upon polycondensation, this diacid can add to the growing chain end at either its 1 position or 3 position. Each will result in a different "facing" of the anthraquinone unit. The random sequence of "facings" should add an element of irregularity to the macromolecular structure, resulting in decreased interchain interactions. Indeed, the alternating donor–acceptor polymer (**ADAP**) produced from the condensation of this diacid chloride with the diamine-diol (see Figure 4) has an absolute M_w of 3950 g/mol (about six repeating units) and is soluble in THF, DMF, and halocarbon solvents.

This polymer has lower molecular weight than we would have liked and can be better described as oligomeric than polymeric. This low degree of polymerization is not surprising considering the polymerization method used. High molecular weight polyesters are typically obtained by diacid/diol or diester/diol condensations driven by high temperatures and using extremely pure, structurally simple monomers. In this case, both monomers are structurally complex and the syntheses required several synthetic steps. The polymerization reaction uses water sensitive acid chlorides, and in this type of polycondensation, only a small fraction of hydrolyzed end groups can result in a sizable decrease in molecular weight. Higher molecular weight material could not be obtained despite rigorous exclusion of water and repeated purification of materials. Nevertheless, **ADAP** forms a smooth, yellow film when a concentrated chloroform solution is poured on glass and is sufficient for the purposes of this study.

Three other polymers were synthesized primarily for the purposes of structural comparison with **ADAP**. The first, and simplest, of the polymers synthesized was made by the pyridine-catalyzed condensation of the diamine diol with adipoyl chloride in refluxing dichloroethane. This donor polymer (**DP**) had an absolute $\bar{M}_w$ of 6830 g/mol and was soluble in halocarbon solvents and methanol (but no other alcohols).

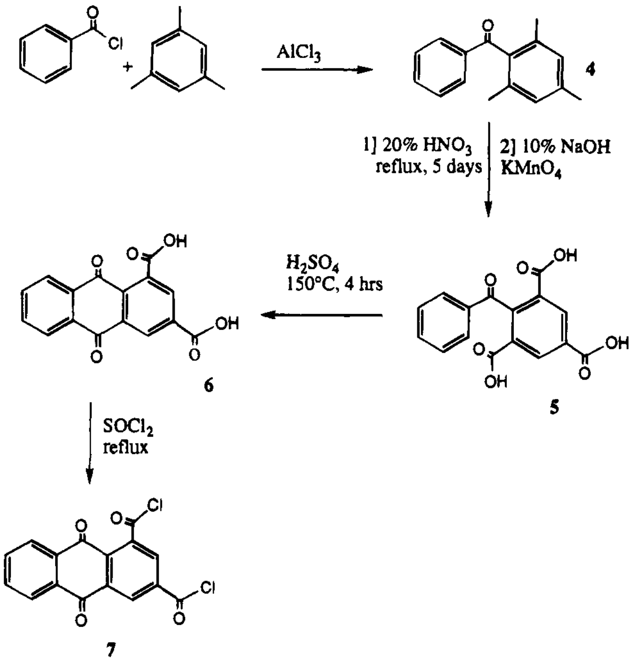


Figure 2. Synthesis of anthraquinone 1,3-diacid.

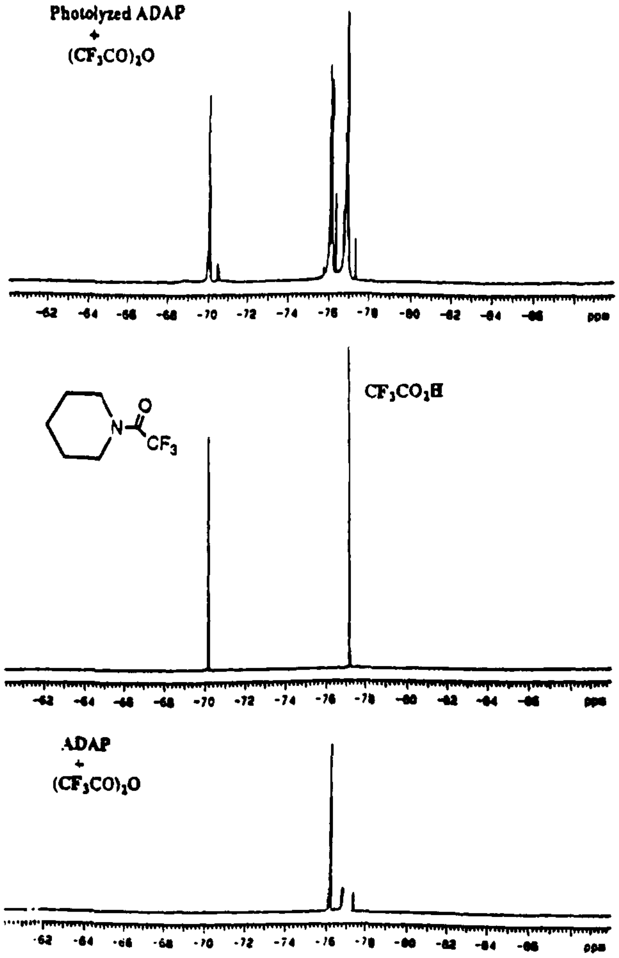


Figure 3. Trifluoroacetic anhydride end-capping experiment.

An acceptor polymer (**AP**), consisting of an aliphatic polyester backbone with pendant anthraquinone side chains, was made with the original intention of constructing a solid blend with a **DP** so as to study a system in which all electron transfers which occur would be interchain rather than intrachain processes. The

---

(30) Gan, H.; Kellett, M. A.; Leon, J. W.; Kloeppner, L.; Leinhos, U.; Gould, I. R.; Farid, S.; Whitten, D. G. *J. Photochem. Photobiol.*, in press.

(31) Ci, X.; Lester, Y. C.; Whitten, D. G. *J. Am. Chem. Soc.* **1987**, *109*, 2536.

(32) Fieser, L. F.; Martin, E. L. *J. Am. Chem. Soc.* **1936**, *58*, 1443.

(33) Gunderman, K. D.; Klockenbring, G.; Roker, C.; Brinkmeyer, H. *Liebigs Ann. Chem.* **1976**, 1873.

(34) Hallman, J. L.; Bartsch, R. A. *J. Org. Chem.* **1991**, *56*, 6243.

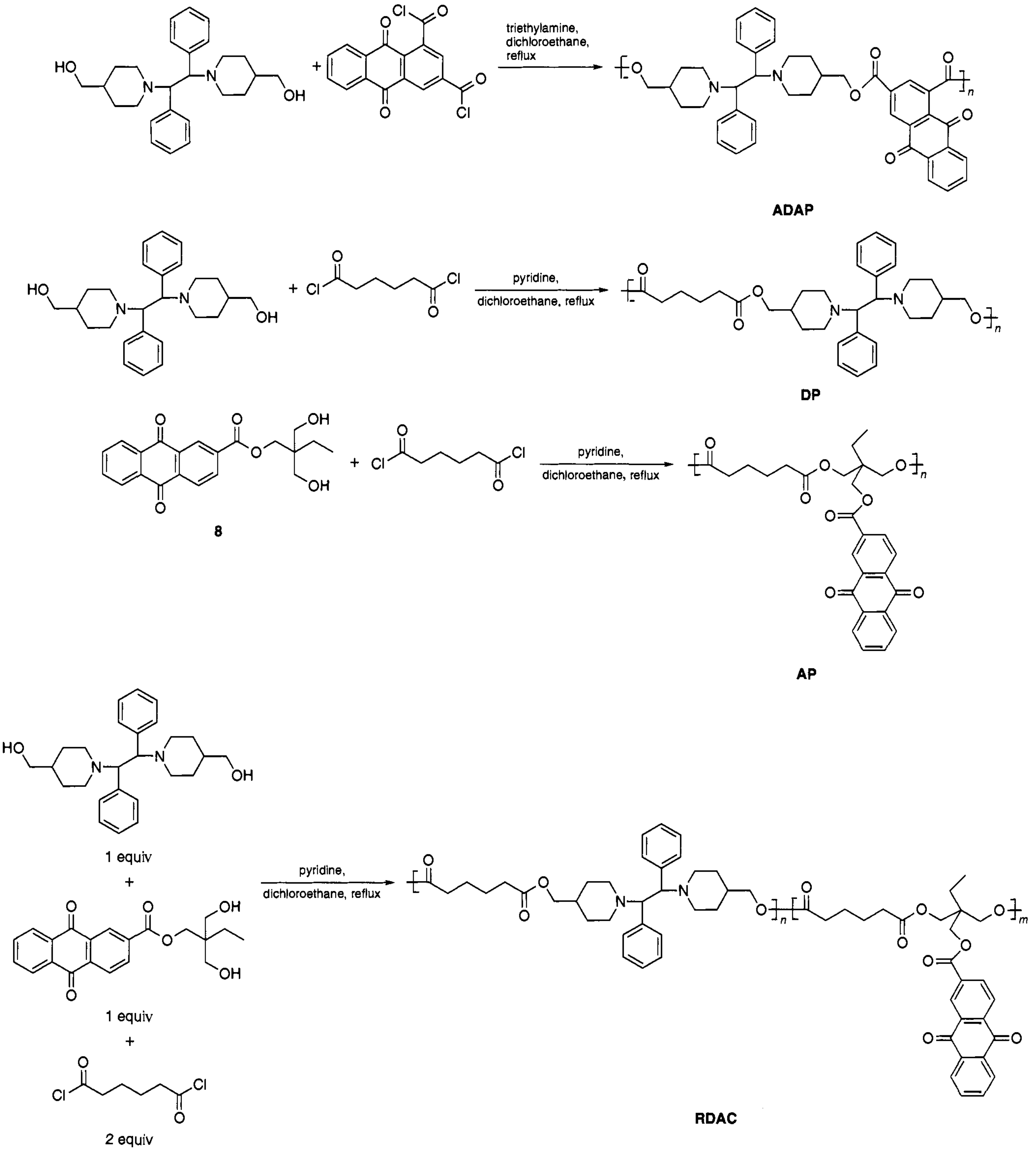


Figure 4. Synthesis of oligomers.

two polymers were found to be phase incompatible, and the blend could not be created. This polymer utilized a different anthraquinone monomer containing a diol functionality. The anthraquinone diol was made by the simple condensation of commercially available anthraquinone-2-carbonyl chloride with a large excess of 1,1,1-tris(hydroxymethyl)propane.

The anthraquinone diol was also used in the synthesis of a random donor/acceptor copolymer (**RDAC**). Equimolar amounts of the diamine diol **3** and the anthraquinone diol **8** were condensed with 2 equs of adipoyl chloride to give a yellow polymer with an absolute $\bar{M}_w$ of 4970 g/mol, suggesting an average of five donors, five acceptors, and ten adipate spacer groups per chain. Assuming a statistical distribution of monomers, the donor and acceptor units will be arrayed randomly along the chain. This contrasts to **ADAP**, in which the donors and acceptors alternate along the main chain and are separated only by a short distance. **RDAC** shows a single glass transition at 71 °C, which is midway between that of **DP** (92 °C) and **AP** (51 °C). This suggests that there is no microphase separation, and that the material is homogeneous.

Studies of Polymer Photolysis. The solution photochemistry of the donor/acceptor oligomers was found to be similar to that found in our previous solution studies of **AQ-DA**. Samples of **ADAP**, **RDAC**, and **AP/DP** (in a 1:1 ratio of donor/acceptor residues) were irradiated in degassed CH_2Cl_2 solution in sealed tubes, and the extent of reaction was monitored by measuring

Table 1. Quantum Yields of Polymer Solution Photoreaction

polymer	quantum yield
ADAP	0.66 ± 0.08
RDAC	0 .74 ± 0.10
DP + AP	0.12 ± 0.02

the appearance of the dihydroquinone reduction product by UV/vis spectrometry.[35] The quantum yields are shown in Table 1. The quantum yields of **ADAP** and **RDAC** are 0.66 and 0.74, respectively, both of which can be assumed to be to practically the same as the reported value for **AQ-DA** in methylene chloride of 0.75, within the limits of the experimental uncertainty. For the intrachain photoreaction of **AP** and **DP**, the quantum yield is significantly lower. This is most likely due to differential quenching, as the concentration of diamine quencher residues is 2×10^{-4} M, which is relatively dilute. In **ADAP** and **RDAC**, on the other hand, the donors and acceptors are contained on the same chain and the electron transfer can be assumed to be primarily intramolecular, and hence the quenching is more efficient.

When photolyzed in the solid state as films on glass ($\lambda >$ 340nm), **ADAP** shows a discoloration from a bright yellow to a dull brown. On prolonged photolysis the film degrades into a powder. As the NMR spectra of these compounds consists of broad, shapeless peaks, ^{1}H NMR analysis of the photolyzed polymer is of only limited value. Nonetheless, when photolyzed **ADAP** is dissolved in $CDCl_3$, a sharp singlet at δ 10.05 ppm can be observed, along with other peaks in the aromatic region pertaining to benzaldehyde. With prolonged photolysis, the broad, shapeless peaks appear to develop more fine structure, as the oligomers decompose into smaller oligomers with more defined structure. **RDAC** shows same trends when the photolysis is monitored by proton NMR.

The expected secondary amine end group photolysis product could not be observed using ^{1}H NMR monitoring, but this is hardly surprising. Amine proton resonances will typically only show up as slight rises in the base line, often over a range of several parts per million. The expected secondary amine oxidation product could, however, be indirectly observed by capping the ends of the photolyzed chains with trifluoroacetic anhydride and monitoring with ^{19}F NMR. **ADAP** was photolyzed as a solid film and dissolved in chloroform, and several drops of trifluoroacetic anhydride were added. The solution was stirred at room temperature overnight, and then the volatiles were stripped. ^{19}F spectra were taken of this sample and of identically treated but unphotolyzed **ADAP**. For purposes of comparison, a reference compound was made by combining piperidine and trifluoroacetic anhydride in an NMR tube. The results are shown in Figure 3. In the unirradiated **ADAP**, the alcohol and carboxylic acid end groups will be converted to trifluoroacetate ester and anhydride end groups. These species are typically observed in the region of δ −74 to −78 ppm, and indeed a cluster of peaks is evident in this region, along with residual trifluoroacetic acid and trifluoroacetic anhydride. In the case of photolyzed **ADAP**, any secondary amine end groups present will react to form a piperidine trifluoroacetamide moiety. The reference compound, piperidine trifluoroacetamide, shows a sharp singlet at δ −70 ppm. Similarly, the photolyzed **ADAP** shows a cluster of new peaks in this region, suggesting the initial presence of the secondary amine photolysis product.

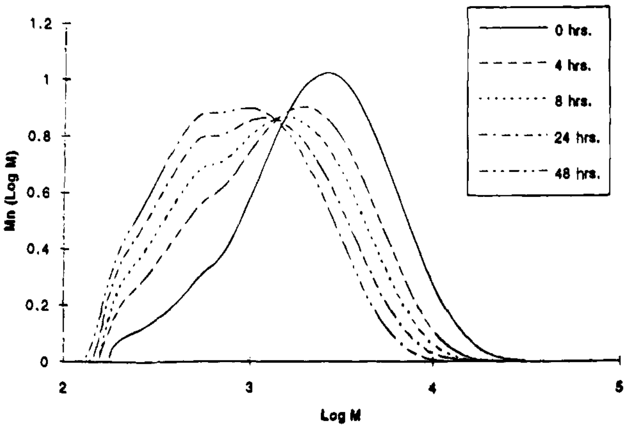


Figure 5. SEC monitoring of **ADAP** photodegradation.

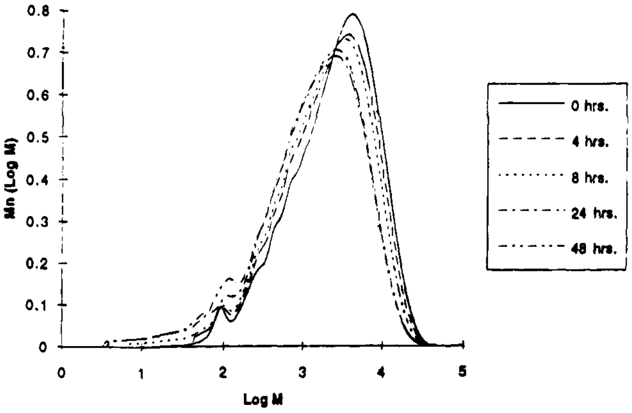


Figure 6. SEC monitoring of **RDAC** photodegradation.

Discussion

The findings of these product analysis studies indicate that the expected cation radical bond cleavage is, indeed, occurring in the solid film. In order to more directly quantify this process, a method was needed to monitor the change in molecular weight of the photolyzed sample as a function of irradiation time. Size exclusion chromatography (SEC) was found to be useful for this purpose. Solid films of the oligomers were prepared by pipetting aliquots of concentrated chloroform solutions of oligomer into identical, flat-bottomed dishes, allowing the solvent to evaporate, and drying the samples in a vacuum oven. The samples were irradiated in a centered four-cell holder in front of a tungsten lamp with a 340 nm cutoff filter, and the entire apparatus was secured on a track. Sample dishes were removed at various photolysis intervals, dissolved in DMF,[36] and subjected to SEC analysis.

ADAP (see Figure 5) shows clear evidence of photodegradation, as the SEC curve shifts toward lower molecular weight with irradiation time. **RDAC** (Figure 6) shows similar behavior, but the shift of the curve with time appears smaller, suggesting a slower photodegradation. Conversely, a sample of **DP**, which contains only diamine units without any acceptors present, showed no detectable change in the SEC plot after 48 h of photolysis.

The photoreaction quantum yield can be estimated from the SEC data using eq 1, derived by J. E. Guillet,[37,38] where w is the weight of the sample irradiated, $\bar{M}_w$ is the weight average molecular weight at time t, $(\bar{M}_w)_0$ is the original weight average molecular weight, and I is the ambient light intensity. The

---

[35] Alternately, the bleaching of the anthraquinone absorbance at 330 nm can be monitored, but in the case of **ADAP**, a shoulder grows in this region at high conversions.

[36] The oligomeric samples were found to adsorb strongly to the SEC column when THF or $CHCl_3$ was used as the eluent.

[37] Nemzek, T. L.; Guillet, J. E. *Macromolecules* **1977**, *10*, 94.

[38] Amerik, Y.; Guillet, J. E. *Macromolecules* **1971**, *4*, 375.

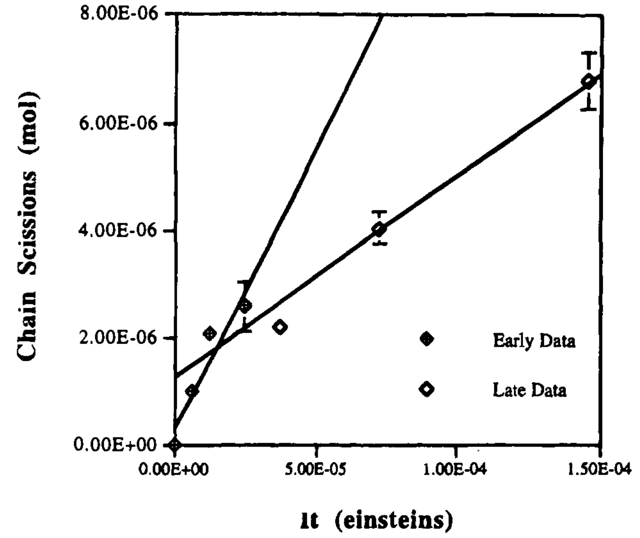


Figure 7. Plot of chain scissions versus light absorbed for **ADAP**.

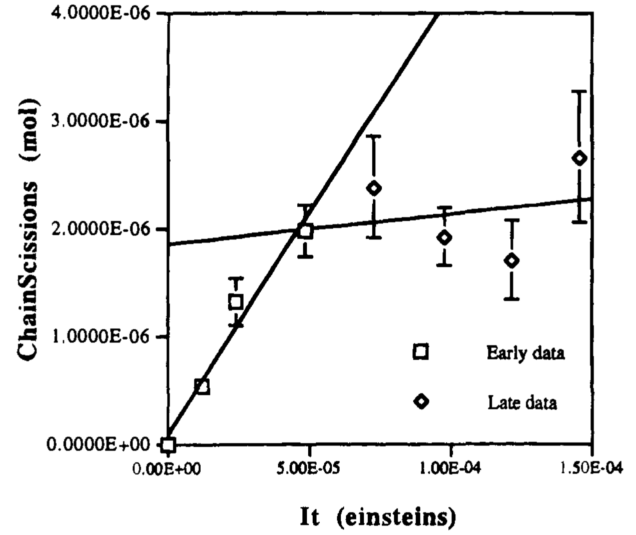


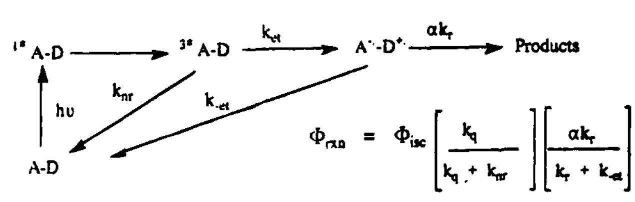
Figure 8. Plot of chain scissions versus light absorbed for **RDAC**.

numerator of this equation simply converts the change in weight average molecular weight, as determined by SEC, to the number of chain scissions. The number of chain scissions is then plotted against the number of einsteins of light absorbed, and the slope of this curve will equal the reaction quantum yield.

$$\Phi = \frac{\dfrac{2w}{(\bar{M}_w)_0}\, d\left\{\dfrac{(\bar{M}_w)_0}{\bar{M}_w} - 1\right\}}{d(It)} \qquad (1)$$

It must be noted here that, in using this method, there are several inherent sources of error which limit its accuracy. First, the molecular weights used are weight average molecular weights ($\bar{M}_w$); optimally, number average molecular weights ($\bar{M}_n$) would be used. The fact that both $\bar{M}_w$ and ($\bar{M}_n$) change proportionally with time allows quantum yield calculation using $\bar{M}_w$. Another source of error lies in the solid films themselves. Although they would theoretically absorb all of the incident light, there was no convenient way to determine the amount of light reflected or scattered. It is possible, thus, that the actual quantum yields tend to be higher.

Figures 7 and 8 show plots of chain scissions vs einsteins of incident light for the photolyses of solid **ADAP** and **RDAC**. The curve for **ADAP** shows a high initial rate of chain scission which appears to level off to a steady state, giving "early" and "late" quantum yields of ca. 10% and 4%, respectively. **RDAC** shows a similar trend, but the rate of chain scission appears to fall off completely after about 24 h of photolysis. The initial and final slopes (see Figure 8) give quantum yields of ~4% and ~0%, respectively. For **RDAC** samples which were photolyzed for more than 24 h, a small amount of material was formed which could not be dissolved in DMF. It is known that aromatic ketones can undergo efficient hydrogen atom abstraction reactions in the solid state. It is possible that, in addition to the electron transfer reaction, the polymer is undergoing a radical cross-linking process which contributes to the scatter in the plot at higher irradiation times.



$$\Phi_{rxn} = \Phi_{isc}\left[\frac{k_q}{k_q + k_{nr}}\right]\left[\frac{\alpha k_r}{k_r + k_{-et}}\right]$$

Figure 9. Kinetic scheme for polymer fragmentation.

These solid state quantum yield estimates are notably lower than the corresponding solution quantum yields (0.66 and 0.74 for **ADAP** and **RDAC**, respectively). The kinetic scheme for the photofragmentation of the donor/acceptor oligomers (see Figure 9) is similar to that of **AQ-DA**.[23] The initial step is photoexcitation of the anthraquinone chromophores to the short-lived singlet state, followed by intersystem crossing to the triplet. This is followed by an electron transfer to generate the radical ion pair, in competition with nonradiative decay of the triplet. From the radical ion pair, there exist two competing pathways, the deactivating return electron transfer and the cation radical fragmentation reaction followed by the subsequent product-forming steps. As in **AQ-DA**, radical ion pair separation cannot occur.

The fragmentation of the diamine cation radical is an entirely intramolecular process consisting of the attack of a nitrogen lone pair on the oxidatively weakened central carbon−carbon bond[39] resulting in the formation of a benzylamine radical and an iminium cation. The intramolecular nature of the fragmentation would minimize reaction medium effects,[23−25] and as the diamine units have *meso* stereochemistry, they probably exist in the optimum conformation for fragmentation and, hence, require little or no bond reorientation in order to react. While the rigidity of the solid medium may not significantly affect the rate of cation radical fragmentation, it is conceivable that the two diamine fragments could recombine by a return electron transfer to the iminium cation (generating another benzylamine radical) followed by radical recombination. The constrained environment of the solid state, in which the diamine fragments will be unable to diffuse apart, might facilitate this process. Were this to occur, it would probably manifest itself as a "scrambling" of diamine diastereomers, which could be detected by proton NMR for simple diamines. This phenomenon has not been observed for any of the diheteroatom compounds studied in this lab, including two compounds in which the diamine fragments remain tethered together.[30] This phenomenon has, however, been observed on other studies using similar diamine compounds,[40] and thus the possibility of this reverse reaction cannot be ruled out.

The effects of the solid state environment on the rates of forward and return electron transfer could also lower the

---

(39) This fragmentation may alternately be viewed as an orbital rearrangement mechanism. This is discussed in the following: Gan, H.; Leon, J. W.; Kloeppner, L.; Leinhos, U. W.; Gould, I. R.; Farid, S.; Whitten, D. G. *J. Photochem. Photobiol.*, in press.

(40) Wang, Y.; Lucia, L. A.; Schanze, K. S. Submitted to *J. Am. Chem. Soc.*

quantum efficiency. An interesting study by Wasielewski[41] focused on comparison of the electron transfer rates of a series of linked porphyrin–quinoid dyads in 2-methlytetrahydrofuran both in solution and in the frozen solvent matrix. It was estimated that the radical ion pair states of the donor/acceptor molecules studied were destabilized by 0.8–0.9 eV in going from a moderately polar liquid ($\epsilon = 6.92$) to a rigid glass. For an electron transfer in the Marcus normal region, such a reduction in driving force could be expected to decrease the rate of electron transfer by up to 2 orders of magnitude.

For the anthraquinone–amine systems used in this study, the free energies of forward electron transfer (ΔG_{et}) in methylene chloride are ~−1 eV.[23] The dielectric constant of methylene chloride is $\epsilon = 9.08$, which is of a magnitude similar to that of methyltetrahydrofuran (used by Wasielewski). The donor/acceptor separation distances in **ADAP** are comparable to those of Wasielewski's compounds. A decrease of 0.8–0.9 eV in driving force would bring ΔG_{et} for the forward electron transfer close to 0 for the donor/acceptor polymers studied. It is reasonable to assume, thus, that the forward electron transfer step limits the overall reaction efficiency and, in effect, causes lowered quantum yields in the solid state reaction.

By the same reasoning, the return electron transfer, conversely, would be expected to become more exothermic due to the destabilization of the radical ions in the solid state. As the return electron transfer was hypothesized to occur at the top of the Marcus curve or very slightly into the normal region,[23] we can expect the rate of return electron transfer to decrease in going from the solution to the solid state, a change which could actually increase the quantum yield of the reaction.

Another possible source of lowered reaction efficiency is triplet energy migration. If energy migration can take place along the polymer chain, there is a finite chance that two triplets will arise on adjacent chromophores and subsequently react by triplet–triplet annihilation to give an excited state singlet and a ground state. The possibility of this occurring will depend primarily on the orientation of the triplet chromophores and the distances separating them. This phenomenon has been observed primarily in vinyl polymers such as poly(2-vinylnaphthalene),[42,43] which contain light-absorbing units as pendant side groups. In these systems, the chromophores are held at short separation distances and in a face to face arrangement in which energy transfer processes are facilitated. In an interesting study regarding the limits of this process,[44] it was found that triplet migration can occur with almost equal efficiency in an alternating 2-vinylnaphthalene/methyl methacrylate copolymer and in pure poly(2-vinylnaphthalene). In a random copolymer, however, there was substantially less migration, presumably because the triplet exciton cannot span the large distances between chromophores interposed by more than one spacer group. By similar reasoning, it is very unlikely, then, that triplet migration is a significant process in **RDAC**. Even in the case of **ADAP**, the distance between anthraquinone units will be upward of 15 Å, and the variable "facings" of the asymmetric anthraquinone diester units will prevent the formation of any stereoregular arrangement. It is thus doubtful that triplet migration is an important factor in the lowering of the reaction quantum yields in the solid state.

The shape of the polymer photolysis curves can be explained by what is known about the polymer microstructure and the donor/acceptor orientations. Figure 10 shows two donor/acceptor conformations of the **ADAP** repeating unit representing the extremes of donor/acceptor separation. Each is a local energy minimum as calculated by the MM2 calculation method with the electron transfer distance measured arbitrarily from the closest anthraquinone carbonyl to the amine nitrogen.[45] It is clear that the effective electron transfer distance can vary relatively little in **ADAP** (approximately 5–7 Å). Though the window of donor/acceptor orientations is narrow, it can be expected that those donor/acceptor pairs which occur in the most optimal distances/orientations will give the most efficient reaction, hence, the steep, initial slope, after which a steady state is reached.

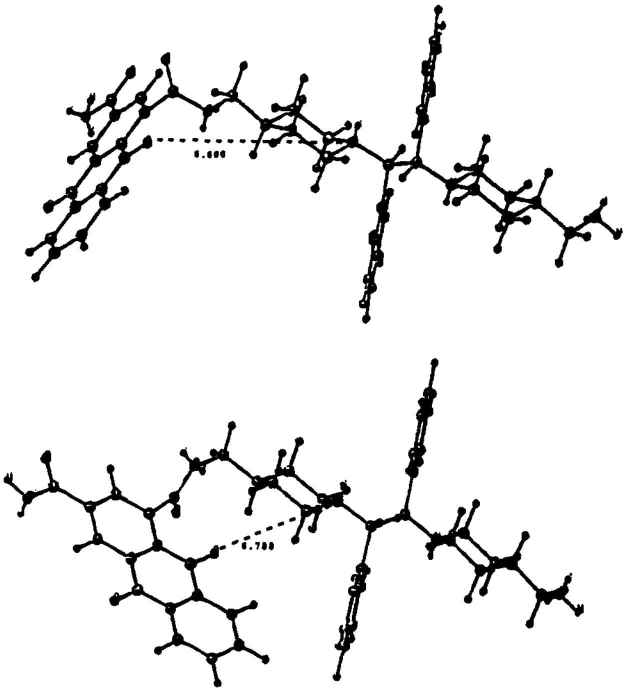


Figure 10. Donor/acceptor distances in **ADAP**.

The curvature is more pronounced in **RDAC**, as the distribution of electron transfer distances is much greater. As is shown in Figure 11, the donor/acceptor distance in one repeating unit can vary from ca. 4 to 17 Å, but as this is a random copolymer, the anthraquinone and diamine units will not necessarily alternate, and hence intrachain electron transfer distances will vary to much greater an extent than for **ADAP**. Unlike **ADAP**, in which there is always a donor in close proximity to an acceptor, in **RDAC**, it is entirely possible for diamine units to be located beyond the electron transfer "reach" of any acceptors, either by an interchain or intrachain electron transfer mode. It is probable that interchain electron transfer distances can be comparable, if not shorter than the intrachain processes. The leveling off of the curve can be attributed to all of the anthraquinone acceptors having oxidized all of the diamine linkages within "reach."

Experimental Section

(a) **Preparation of Materials.** All reagents were obtained from Aldrich, except for anthraquinone-2-carbonyl chloride (TCI America), and used without further purification except where noted. All solvents used were purified as follows. Methylene chloride, chloroform, and dichloroethane were distilled from P_2O_5. Diethyl ether and THF were

---

(41) Wasielewski, M. R.; Gaines, G. L.; O'Neill, M. P.; Svec, W. A.; Niemczyk, M. P. *J. Am. Chem. Soc.* **1990**, *112*, 4559.

(42) Cozzens, R. F.; Fox, R. B. *Macromolecules* **1969**, *2*, 181.

(43) Cozzens, R. F.; Fox, R. B. *J. Chem. Phys.* **1969**, *50*, 1532.

(44) Fox, R. B.; Price, T. R.; Cozzens, R. F.; Echols, W. H. *Macromolecules* **1974**, *7*, 937.

(45) For such complex oligomeric structures, it is difficult and somewhat risky to attempt to predict minimum energy conformations on the basis of molecular mechanics calculations. These representations are merely meant to show likely extremes in donor/acceptor separation.

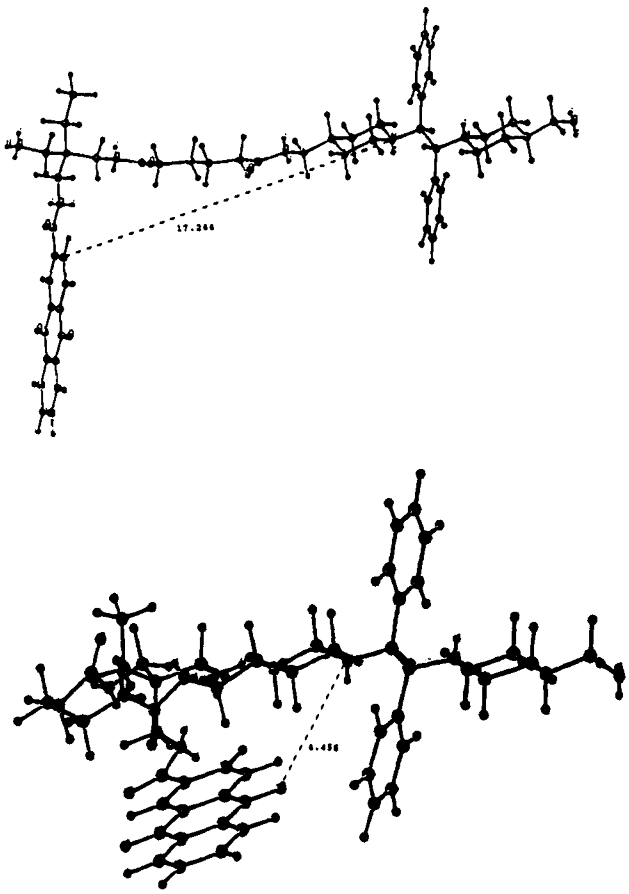


Figure 11. Donor/acceptor distances in **RDAC**.

distilled from CaH_2. Benzene was distilled from sodium/benzophenone. All other solvents were used without further purification.

For the polyesterification reactions, specific precautions were taken to exclude adventitious water. The polymerization solvent, 1,2-dichloroethane, was freshly distilled from P_2O_5 after at least 2 h reflux time and used immediately. Adipoyl chloride (Aldrich, 99%) was freshly distilled before each use. All solid polymerization reagents (compounds **3**, **7**, and **8**) were stored in a desiccator and dried for at least several hours in a vacuum oven just prior to use. Triethylamine and pyridine catalysts were distilled twice over CaH_2 and stored under nitrogen and over molecular sieves. Glassware used for polymerizations was kept in an oven at 60 °C and removed just before use. All polymerization reactions were protected with calcium chloride or Drierite drying tubes. All polymerization reagents were weighed on an analytical balance to the fourth decimal place to ensure stoichiometry. For the synthesis of light sensitive polymers **ADAP** and **RDAC**, the reactions were carried out under very dim room light and the reaction vessels were wrapped in aluminum foil. Silica gel used for column chromatography was 70−230 mesh. Monitoring of reactions by thin layer chromatography was performed using Kodak chromatogram silica gel TLC sheets. All differential scanning calorimetry measurements were performed using a DuPont Series 2100 instrument.

All ^1H and ^{13}C NMR analyses were conducted at room temperature using a General Electric/Nicolet QE-300 MHz spectrometer. Proton chemical shifts[46] are relative to tetramethylsilane and were referenced to the residual deuterium lock solvents: i.e., $CDCl_3$, 7.27; (DMSO-d_6, 2.50. All IR spectra were recorded on a Matheson Galaxy 6020 spectrometer. Melting points were taken on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Galbraith Labs. FAB mass spectra were obtained at the Midwest Center for Mass Spectrometry.

***erythro*-1,2-Diphenyl-2-(4-carbethoxypiperidyl)ethanol (1).** Ethyl isonipecotate (100 mL, 0.65 mol) and *trans*-stilbene oxide (20.00 g, 0.10 mol) were combined in a 300 mL Schlenck flask with a slow, positive nitrogen flow and a reflux condenser protected with a drying tube and placed in a pre-equilibrated oil bath at 110 °C. The clear solution was stirred at 110 °C (caution must be taken, as the reaction solution will rapidly gel at temperatures above 115 °C) for 2 h at which point the reactant spot on silica TLC (2:1 hexanes/EtOAc eluent) had completely disappeared. The condenser was then replaced by a standard distillation apparatus, and most of the amine (~60 mL) was recovered by vacuum distillation. The remaining yellowish solution was poured into 300 mL of H_2O and extracted twice with 200 mL of ether. The combined ether extracts were concentrated to 200 mL on a rotary evaporator, washed three times with 300 mL of H_2O, and dried over $MgSO_4$, and the solvent was stripped off by rotary evaporation to yield a yellow-white powder. The product was recrystallized twice from 95% ethanol to yield 31.08 g of white crystals (87.9%, mp 81−82 °C): IR (KBr) ν 1733 (s, C=O), 3471 (br, OH); ^1H NMR (300 MHz) in $CDCl_3$ δ 1.27 (t, J = 6.84 Hz, 3H), 1.81 (m, 3H), 2.00 (d, J = 13.23 Hz, 2H), 2.30 (q, J = 11.16 Hz, 2H), 2.89 (d, J = 11.27, 1H), 3.30 (d, J = 10.91 Hz, 2H), 3.43 (d, J = 4.74 Hz, 1H), 4.15 (q, J = 7.10 Hz, 2H), 5.37 (d, J = 4.51 Hz, 1H), 7.01−7.28 (m, 10H).

***meso*-1,2-Bis(4-carbethoxypiperidyl)-1,2-diphenylethane (2).** Compound **1** (29.00g, 0.082 mol) was combined with 450 mL of freshly distilled CH_2Cl_2 and triethylamine (20 mL, 0.142 mol) in a 1000 mL three-neck round bottom flask (RBF) equipped with an N_2 inlet, reflux condenser, drying tube, addition funnel, and low-temperature thermometer. The reaction solution was placed on an ice−salt bath until a temperature of −12 °C was reached, at which point methanesulfonyl chloride (8.50 mL, 0.110 mol) was slowly added via addition funnel over 20 min such that the temperature was never allowed to exceed −7 °C. The reaction was stirred at −12 °C for 1 h, at which point the reactant TLC spot (2:1 hexanes/EtOAc eluent) had completely disappeared. Ethyl isonipecotate (45 g, 0.287 mol) was then added all at once, the ice bath was replaced by a hot water bath (~75 °C), and the reaction solution was stirred for 1 h. Next, the flask was outfitted with a standard vacuum distillation apparatus, and the solvent and excess amines were distilled off to leave a damp, yellow-white powder. The crude product was purified by twice boiling in absolute EtOH (600 mL the first time, 500 mL the second) for $^1/_2$ h, cooling over ice, and filtering. The white, crystalline powder was dried overnight in a vacuum oven at 70 °C to give 37.54 g of product (93.4%, mp 180−182 °C) IR (KBr) ν 1719 (s, C=O); ^1H NMR (300 MHz) in $CDCl_3$ δ 1.08 (m, 8H), 1.34 (m, 2H), 1.55−1.72 (m, 6H), 1.85 (dd, J = 8.05, 9.22 Hz, 2H), 2.05 (t, J = 11.09, 2H), 2.70 (dd, J = 12.31, 14.97 Hz, 4H), 3.98 (q, J = 7 Hz, 4H), 4.14 (s, J = 2H), 7.17−7.33 (m, 10H).

***meso*-1,2-Bis(4-(hydroxymethyl)piperidyl)-1,2-diphenylethane (3).** Lithium aluminum hydride (11.0 g, 0.074 mol) was added to 200 mL of freshly distilled Et_2O in a three-neck RBF equipped with an N_2 inlet, addition funnel, reflux condenser, and drying tube. Vigorous stirring was initiated (a mechanical stirrer is recommended, but a strong magnetic stirrer may be adequate), and the flask was placed on an ice bath. Diamine **2** (36.10 g, 0.074 mol) in 200 mL of dry CH_2Cl_2 was then added dropwise over $^1/_2$ h, producing a white precipitate. A heating mantle was then applied, and the reaction mixture was heated at reflux for 3 h. The ice bath was then reapplied and 11 mL of H_2O was added, followed by 11 mL of 15% NaOH and 33 mL of H_2O, with 20 min intervals between additions. The mixture was stirred for 1 h, and ~5 g of $MgSO_4$ was then added to absorb the excess water. The white mixture was filtered and the solvent was removed by rotary evaporation to give 16.72 g of white, crystalline powder. An additional 13 g of crude product was recovered by twice boiling the filter cake in CH_2Cl_2, filtering, and removing the solvent on a rotary evaporator. The crude product was recrystallized once from 600 mL of toluene and once from 450 mL of acetonitrile and dried in a vacuum oven to yield 26.79 g of coarse crystals (88.6%, mp 211−212 °C) IR (KBr) ν 3333 (br, OH); ^1H NMR (300 MHz) in $CDCl_3$ δ 0.59 (m, 2H), 0.91 (m, 2H), 1.13 (m, 4H), 1.44 (t, J = 12.13 Hz, 4H), 1.69 (t, J = 8.13 Hz, 2H), 2.07 (t, J = 9.69 Hz, 2H), 2.75 (t, J = 9.72 Hz, 4H), 3.23 (s, 4H), 4.19 (s, 2H), 7.25−7.35 (m, 10H). Anal. Calcd for $C_{26}H_{36}N_2O_2$: C, 76.42; H, 8.88; N 6.86. Found: C, 76.69; H, 8.97 N, 7.19.

---

[46] The ^1H NMR spectral data reported for polymers (**ADAP**, **RDAC**, **DP**, **AP**) describes spectra in which most of the peaks are broad and structureless, at times appearing as merely a rise in the base line over >1 ppm. Many of the peaks reported describe overlapping, structureless resonances corresponding to several different protons. Regions which consist of a "cluster" of small peaks pertaining to one or more assignable protons will be designated as "cl."

2,4,6-Trimethylbenzophenone (4). Benzoyl chloride (39 mL, 0.34 mol) was added via addition funnel over $^1/_2$ h to a mixture of mesitylene (100 mL, 0.72 mol) and aluminum trichloride (50 g, 0.37 mol) in a 500 mL RBF cooled with an ice bath. After the addition was complete, the ice bath was replaced by a heating mantle and the red reaction mixture was heated at 60 °C for 1 h, at which point the reaction mixture solidified. Then 100 mL of CH_2Cl_2 was added, and the reaction mixture was heated at reflux overnight. The black, viscous reaction solution was poured into a mixture of 100 mL of HCl/500 cm^3 of ice and stirred for $^1/_2$ h. The resulting emulsion was extracted with 200 mL of Et_2O, the organic layer was removed and washed three times with 500 mL of 10% K_2CO_3 and once with 100 mL of brine, and the solvent was stripped on a rotary evaporator to afford 120 mL of a thick, green oil. The excess mesitylene was distilled off in vacuo. The remaining ~90 mL of oil was purified by vacuum fractional distillation through a Vigreux column to afford 62.32 g of clear oil (81.8%, bp 162 °C/1.5 mmHg): IR (neat) ν 1672 cm^{-1} (s, C═O); ^1H NMR (300 MHz) in $CDCl_3$: δ 2.10 (s, 6H), 2.35 (s, 3H), 6.92 (s, 2H), 7.46 (t, J = 7.69 Hz, 2H), 7.60 (d J = 7.33, 1H), 7.83 (d, J = 7.46, 2H).

Benzophenone-2,4,6-tricarboxylic Acid (5). 2,4,6-Trimethylbenzophenone (4) (62.0 g, 0.28 mol) was added to 350 mL of 20% HNO_3 in a 1000 mL three-neck RBF with a reflux condenser, and the two-phase mixture was heated at reflux for 5 days, at which point a waxy, yellowish semisolid had accumulated at the bottom of the flask. The acid was decanted, and the viscous product (presumably a mixture of isomeric monoacids) was washed twice with 500 mL of H_2O.

The flask was next outfitted with a thermometer and mechanical stirrer and 500 mL of 10% NaOH was poured into the flask, resulting in an opaque, brown solution. A heating mantle was applied until a solution temperature of 90 °C was reached, and *then the heating mantle was turned off.* $KMnO_4$ (173.10 g, 1.10 mol) was then added in very small portions over 2 h. Each addition resulted in formation of a brown precipitate (MnO_2), violent foaming (care must be taken to avoid boiling over), and a vigorous exotherm which was sufficient to keep the reaction mixture at reflux. After the addition was complete, the heating mantle was reapplied, and the mixture was heated at reflux for 3 h, cooled to room temperature, and filtered once through a standard paper filter and once through a Millipore nylon filter to remove fine particles. The clear solution was then concentrated by distillation to a final volume of 250 mL and placed on an ice bath. Concentrated HCl was then slowly added over $^1/_2$ h until pH 2 was reached, at which point a white precipitate fell out of solution. The powder was collected by vacuum filtration and dissolved in 500 mL of boiling acetone. Then 500 mL of hot water was added, and the solution was heated under a stream of nitrogen until half of the volume had evaporated. The supersaturated solution was allowed to cool to room temperature. Fine, white crystals were collected by vacuum filtration and dried in a vacuum oven overnight at 60 °C to afford 72 g of product (81.9%, mp > 350 °C): IR (KBr) ν 3228 (br, CO_2H), 1728 (s, C═O), 1710 (s, C=O), 1674 cm^{-1} (s, C═O); ^1H NMR (300 MHz) in acetone-d_6 δ 7.42 (t, J = 7.23 Hz, 2H), 7.51 (d, J = 7.27 Hz, 1H), 7.71 (d, J = 7.20 Hz, 2H), 8.89 (s, 2H).

Anthraquinone-1,3-dicarboxylic Acid (6). Triacid **5** (52.35 g, 0.167 mol) was dissolved in 350 mL of concentrated H_2SO_4 in a 500 mL RBF and heated in an oil bath at 120 °C for 3 h. The dark brown solution was poured onto 1000 cm^3 of crushed ice, filtered, washed with water, and air dried to give a pale yellow solid product, which NMR analysis showed to contain ~50% starting material. The solids were again dissolved in 350 mL of H_2SO_4 and heated for an additional 4 h at 150 °C,[47] precipitated, filtered, washed with water, and air dried. The crude product was recrystallized three times from glacial acetic acid and dried overnight in a vacuum oven at 70 °C to afford 8.32 g of a fine, orange-brown powder. An additional 10.05 g of product was recovered by slow evaporation of the recrystallization solvents (37.1%, mp 322−340 °C dec): IR (KBr) ν 2863 (br, CO_2H), 1703 (s, C═O), 1678 cm^{-1} (s, C═O); ^1H NMR (300 MHz) in DMSO-d_6 δ 7.94 (2 overlapping doublets, J = 3.31, 2.81 Hz, 2H), 8.18 (m, 3H), 8.68 (s, 1H), 13.30−14.15 (br, 2H); mass spectrum (FAB, positive ion, nitrobenzyl alcohol matrix) calcd for $C_{16}H_8O_8$ m/z 297.0321 (M + H), found m/z 297.03390 (M + H). Anal. Calcd for $C_{16}H_8O_6$: C, 64.87; H, 2.72. Found: C, 64.53; H, 2.82.

Anthraquinone-1,3-dicarbonylchloride (7). Anthraquinone-1,3-dicarboxylic acid (**6**) (2.00 g, 6.75 × 10^{-3} mol) and $SOCl_2$ (15 mL, excess) were combined in a 25 mL RBF and heated at reflux for 1.5 h. The mixture was then filtered hot to remove a small amount of brown solids and heated at reflux for 2 h more. The reflux condenser was replaced by a microdistiller, and the $SOCl_2$ was distilled off, first at atmospheric pressure and then in vacuo. The yellow-brown solids were recrystallized three times from ~5 mL of freshly distilled benzene and dried overnight in a vacuum oven at 60 °C. Fine yellow-orange crystals (1.22 g) were collected (54.2%, mp 120−122 °C): IR (KBr) ν 1782 (s, C═O), 1765 (s, C═O), 1678 (s, C═O), 1669 cm^{-1} (s, C═O); ^1H NMR (300 MHz) in $CDCl_3$ δ 7.94 (2 overlapping doublets, J = 4.00, 3.78 Hz, 2H), 8.34 (m, 3H), 9.17 (s, 1H); mass spectrum (FAB, positive ion, nitrobenzyl alcohol matrix/Na_2CO_3) calcd for $C_{16}H_6Cl_2O_4Na$ m/z 354.9541 (M + Na). Found: m/z 354.9538 (M + H).

Anthraquinone Diol 8. 1,1,1-Tris(hydroxymethyl)propane (20.71 g, 0.154 mol), pyridine (6.0 mL, 7.20 × 10^{-2} mol) and 100 mL of freshly distilled THF were combined in a 250 mL RBF. Anthraquinone-2-carbonyl chloride (8.21 g, 3.03 × 10^{-2} mol) in 100 mL of THF was added over 10 min by dropping funnel, and the solution was stirred at room temperature overnight. The solution was filtered, and a fine yellow powder was collected, purified twice by recrystallization from THF, and dried overnight in a vacuum oven at 60°C (7.20 g collected) (64.50%, mp 170−172 °C): IR (KBr) ν 3400 (br, OH), 1706 (s, C═O), 1679 cm^{-1} (s, C═O); ^1H NMR (300 MHz) in $CDCl_3$ δ 0.86 (t, J = 7.51, 3H), 1.39 (q, J = 7.61, 2H), 3.37 (d, J = 11.1, 4H), 4.19 (s, 2H), 7.95 (2 overlapping doublets, J = 3.37, 3.12 Hz, 2H), 8.20 (m, 2H), 8.31 (d, J = 8.15 Hz, 1H), 8.39 (d, J = 10.07 Hz, 1H), 8.64 (s, 1H). Anal. Calcd for $C_{21}H_{20}O_6$: C, 68.47; H, 5.47. Found: C, 68.45; H, 5.49.

Alternating Donor/Acceptor Polymer (ADAP). Anthraquinone dicarbonylchloride **7** (1.0400 g, 3.1220 × 10^{-3} mol) and diamine diol **3** (1.2756 g, 3.1221 × 10^{-3} mol) were combined in 30 mL of dichloroethane in a 50 mL RBF outfitted with a reflux condenser (protected with a drying tube), N_2 inlet, and addition funnel. Triethylamine (1.30 mL, 9.33 × 10^{-3} mol) was added slowly over 10 min via addition funnel. After the addition was complete, the flask was placed on an oil bath and the reaction mixture was heated at reflux for 3 h and then cooled to room temperature. The thick, orange mixture was filtered to remove precipitated triethylamine hydrochloride and then precipitated three times into absolute ethanol. The bright orange solids were dried overnight in a vacuum oven to afford 1.74 g of material (83.4%): IR (KBr) ν 2933 (m, aliph C−H), 1798 (m, ester C═O), 1729 (s, ester C═O), 1679 (s, anthraquinone C═O), 1595 cm^{-1} (w, anthraquinone ring stretch); ^1H NMR[46] (300 MHz) in $CDCl_3$ δ 0.3−0.9 (Br, 2H), 0.9−1.3 (br, 2H), 1.3−1.7 (br, 6H), 1.7−2.0 (br, 2H), 2.0−2.4 (br, 2H), 2.5−3.4 (cl, 6H), 3.9−4.2 (br, 4H), 4.2−4.4 (br, 2H), 6.8−7.5 (br, 10H), 7.5−8 (cl, 2H), 8.0−8.5 (cl, 2H), 8.5−8.8 (cl, 1H), 8.8−9.1 (cl, 1H); no T_g is seen below 175 °C (onset of decomposition exotherm); $\bar{M}_w$ (absolute) = 3950, $\bar{M}_w/\bar{M}_n$ = 3.26.

Donor Polymer (DP). Diamine diol **3**, pyridine (1.10 mL, 1.42 × 10^{-2} mol), and 25 mL of dichloroethane were combined in a 50 mL three-neck RBF outfitted as described above. Vigorous stirring was initiated and adipoyl chloride (0.9530 g, 5.2067 × 10^{-3} mol) in 10 mL of dichloroethane was added via addition funnel over 10 min, after which an additional 5 mL of dichloroethane was used to flush through any residual acid chloride. The mixture was then brought to a steady reflux in an oil bath. After about 20 min at reflux, all of the reactants had dissolved and the reaction solution was yellowish and slightly viscous. The solution was stirred at reflux for 4 h, then cooled to room temperature, and precipitated twice into 700 mL of diethyl ether. The white solids were then stirred overnight in 250 mL 10% K_2CO_3, filtered, washed several times with water, and dried in a vacuum oven. White material (2.48 g, 91.8%) was collected: IR (KBr) ν 2938 (m, aliph C−H), 1735 cm^{-1} (s, ester C═O); ^1H NMR (300 MHz) in $CDCl_3$ δ 0.5−2.0 (br, 14H), 2.0−2.5 (br, 8H), 2.6−2.9 (br, 2H), 2.9−3.3 (br, 2H), 3.6−3.9 (br, 4H), 4.7−5.1 (br, 2H), 7.1−8.0 (br, 10H); T_g = 92.24 °C; T_m = 138.07 °C, $\bar{M}_w$ = 6380, $\bar{M}_w/\bar{M}_n$ = 8.41.

Random Donor/Acceptor Copolymer (RDAC). Anthraquinone diol **8** (0.5137 g, 1.3944 × 10^{-3} mol), diamine diol **3** (0.5690 g, 1.3927

---

(47) Heating of the triacid in sulfuric acid for 4 h at 150 °C was found to be sufficient to give complete conversion.

$\times 10^{-3}$ mol) and pyridine (0.60 mL, 7.41×10^{-3} mol), were combined in a 100 mL three-neck RBF outfitted as described earlier. Dichloroethane (40 mL) was added, and the mixture was brought to reflux, at which point a clear, yellow solution was achieved. Adipoyl chloride (0.5102 g, 2.7852×10^{-3} mol) in 20 mL of dichloroethane was added over 20 min via addition funnel, and the reaction mixture was stirred at reflux for 3 h and at room temperature overnight. The bright yellow copolymer was isolated and purified as in the **DP** procedure to yield 1.20 g of bright, yellow powder (86%): IR (KBr) ν 2939 (m, aliph C—H), 1734 cm^{-1}(s, ester C═O), 1678 (m, anthraquinone C═O), 1594 (w, anthraquinone ring stretch); ^{1}H NMR (300 MHz) in CDCl$_3$ δ 0.5−0.8 (Br, 2H), δ 0.8−1.1 (br, 3H), 1.1−1.9 (br, 18H), 2.0−2.2 (br, 8H), 2.2−2.4 (br, 2H), 2.5−2.9 (br, 4H), 4.12 (br, 4H), 4.35 (br, 2H), 7−7.7 (br, 10H), 7.82 (s, 2H), 8.2−8.5 (br, 4H), 8.9−9 (br, 1H); $T_g = 70.51$ °C; $T_m = 149.93$ °C, $\bar{M}_w$ (absolute) = 4970, $\bar{M}_w/\bar{M}_n = 4.32$.

Acceptor Polymer (AP). To a mixture of anthraquinone diol **8** (0.8050 g, 2.1854×10^{-3} mol) and pyridine (0.53 mL, 6.56×10^{-3} mol) in 10 mL of dichloroethane was added adipoyl chloride (0.4000 g, 2.1854×10^{-3} mol) in 5 mL of dichloroethane via addition funnel over 5 min. The reaction mixture was brought to reflux on an oil bath for 3 h, at which time the yellow reaction solution became viscous. The reaction solution was precipitated into 500 mL of ice cold *n*-pentane. The bright yellow solids were dissolved in 50 mL of CH_2Cl_2, extracted three times with 100 mL of H_2O, and then dried over $MgSO_4$. The solution was concentrated to a volume of 10 mL on a rotary evaporator and again precipitated into ice cold *n*-pentane. The product was dried overnight in a vacuum oven at 60 xb0°C to afford 0.80 g (79.0%): IR (KBr) ν 2966 (m, aliph C—H), 1734 cm^{-1} (s, ester C═O), 1678 (m, anthraquinone C═O), 1594 (w, anthraquinone ring stretch); ^{1}H NMR (300 MHz) in CDCl$_3$ δ 0.9−1.1 (Br, 3H), 1.5−2.0 (br, 6H), 2.3−2.6 (br, 4H), 4.1−4.3 (br, 4H), 4.3−4.5 (br, 2H), 7.8−8.0 (br, 2H), 8.3−8.4 (br, 2H), 8.4−8.5 (br, 2H), 8.7−9.0 (br, 1H); $T_g = 50.92$ °C; $T_m = 189.21$ °C, $\bar{M}_w = 7300$, $\bar{M}_w/\bar{M}_n = 7.35$.

(b) **Solution Quantum Yields.** Solution quantum yields for the polymer photodegradation reactions in solution were determined using a procedure similar to that described previously.[23] Three different polymer solutions in CH_2Cl_2 ("dampened" by shaking in a separatory funnel with H_2O) were prepared, each containing equimolar ratios of acceptor (anthraquinone) and donor (diamine) residues: 2×10^{-4} M **ADAP**; 2×10^{-4} M **RDAC**; 2×10^{-4} M **DP** + 2×10^{-4} M **AP** (it must be noted here that the molarities expressed are in terms of *mol-repeating units* per liter). Aliquots of 4 mL of the polymer solutions were pipetted into degassible Kimax sample tubes, vacuum degassed through six to eight freeze/pump/thaw cycles until a pressure of 3×10^{-6} Torr was reached, and sealed under vacuum with a torch. The solutions were then simultaneously irradiated to 5−20% conversion along with vacuum-degassed solutions of anthraquinone/ethanol (1×10^{-4} M) as a secondary actinometer[48] in a merry-go-round equipped with a 450 W medium-pressure Hanovia mercury lamp and a Corning 0−52 filter. The solutions were withdrawn at 3 min intervals, and UV/vis spectra were taken. The quantum yields were calculated by monitoring the appearance of the dihydroquinone absorbances.[35]

(c) **Preparation and Photolysis of Solid Samples.** Two polymer stock solutions in $CHCl_3$ (**ADAP**, **RDAC**) were prepared, each containing 0.1 mol-repeating units of donor and acceptor residues per liter. Aliquots of 0.1 mL of stock solution were transferred to custom-made flat-bottomed sample dishes (13 mm diameter × 21 mm height) via delivery pipet, resulting in the deposit of approximately 1×10^{-5} mol-repeating units in each dish. The dishes were allowed to sit at room temperature in the dark for 24 h, after which yellow films coated the bottoms. The residual solvent was removed by heating the dishes in an oven at 50 °C for 24 h and then in a vacuum oven at 50 °C for 24 h. The solid samples were then placed in a centered, four-cell holder (consisting simply of a plastic block with four holes to hold sample dishes) in front of a 250 W tungsten−halogen lamp mounted on a metal track, so as to ensure that the position of the light source remains stationary with regard to the photolyzed samples between different runs. The light passes through a water chamber (to filter out infrared radiation) and then through a Corning 0-52 filter. The lamp flux was determined by anthraquinone/ethanol actinometry. Sample dishes were removed after the appropriate photolysis times and prepared for SEC analysis. LiBr/DMF (1 mL, 0.01 M) was added to each dish by delivery pipet, and magnetic stirring was initiated until all of the solid polymer was dissolved. The samples were then sealed in brown glass septum capped vials and loaded into the SEC system's autoinjector.

(d) **Size Exclusion Chromatography Analysis of Samples.** A multidetector SEC system at the Eastman Kodak Company (Analytical Technology Division) was used for all size exclusion chromatography. The system, similar to that described previously,[49] employs UV−visible (UV), differential refractive index (DRI), and differential viscometry detection (DV). Two 10 mm i,d. × 250 mm mixed-bed linear columns from Jordi Associates (Bellingham, MA) are connected in series and thermostated to 30.0 °C. The eluent was DMF (HPLC grade, used without further purification) containing 0.01M LiBr to minimize anomalous effects due to polar polymers. The eluent is pumped by a Waters Model 590 pump at a nominal flow rate of 1 mL/min through a Spectroflow Model 757 UV−vis detector and is then split equally to a Model 100 (Viscotek Corp., Houston, TX) DV detector and a Waters Model 410 DRI detector, both of which are thermostated to 30.0 °C. The samples were injected (in a volume of 100 mL) by a Hewlett-Packard 7985 autoinjector with a 100 mL injection volume. Flow rates were corrected by monitoring the retention time of 1-chloro-2,4-dinitrobenzene (Kodak Laboratory Chemicals), which was added at a concentration of 0.10% to all sample solutions.

Equivalent molecular weight distributions are calculated from a Log *M*−retention volume curve made from narrow poly(ethylene oxide) standards obtained from Polymer Laboratories (Amherst, MA). Absolute molecular weight distributions are calculated from the DV response and universal calibration as described previously.[49]

(e) **End Group Study Using Fluorine NMR.** Several films were made (as described earlier) of approximately 50 mg weight of **ADAP** in flat-bottomed Petri dishes (of approximately 25 mm diameter). The films were photolyzed in front of a 250 W tungsten lamp for 48 h and dissolved in 1 mL of chloroform. Ten drops of trifluoroacetic anhydride was added, and the samples were stirred overnight at room temperature in stoppered vials. Next, the vials were placed in a water bath at 50 °C, and the solvent was evaporated under a stream of dry nitrogen. The vials were then placed in a vacuum oven at 50 °C overnight to remove all remaining volatiles. The solid samples were dissolved in 1 mL of $CDCl_3$ with hexafluorobenzene added as an internal reference. For purposes of comparison, samples of unphotolyzed **ADAP** were processed in parallel in an identical manner.

^{19}F NMR measurements were performed on a Varian VXR 500S 500 MHz NMR spectrometer operating on a ^{19}F frequency of 470.268 MHz. All fluorine chemical shifts were referenced to a C_6F_6 standard and reported relative to $CFCl_3$.

Acknowledgment. This work was supported by the Department of Energy (Grant No. DE-FG02-86ER13504). The authors would like to express their appreciation to Dr. Tom Mourey and Trevor Bryan of the Eastman Kodak Co. for their help in the SEC analysis of these compound and for their many helpful discussions. We would also like to thank Dr. S. Richard Turner of the Tennessee Eastman Company for his useful synthetic advice in the beginning stages of this project.

JA9425389

---

(48) *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1121. Quantum yield was independently confirmed using ferrioxalate actinometry.

(49) Mourey, T. H.; Bryan, T. G. *J. Liq. Chromatogr.* **1991**, *14*, 719.