

Novel Thin-Film Composite Membranes Containing Photoreactive Groups Part I: Choosing the Photoreactive Group

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Synopsis

Thin-film composite membranes containing photoreactive groups have been developed. The presence of these groups facilitates the subsequent photochemical conversion of the membrane to include a range of different chemical moieties. For example, a cationic or an anionic membrane can be made from the same initial composite membrane. In this paper the selection of an appropriate photolabile group is investigated.

INTRODUCTION

In recent years the separation processes, microfiltration, ultrafiltration, and reverse osmosis, have gained considerably in technical and economic significance. All of these processes depend on membranes with controlled surface porosity and chemical structure. The properties of the membrane surface and hence membrane performance are strongly influenced by both the chemical nature of the polymer and the method of membrane fabrication. However, this relationship is not well understood. In this project we propose to study the effect of the chemical nature of the membrane surface on membrane performance by modifying the surface of the membrane after the membrane has been made. The chemical nature of the membrane surface will be modified by using a novel photochemical method. The purpose of this paper, which is Part I in a series, is to develop a membrane with a photoreactive group attached to the membrane surface.

In order to achieve practical fluxes with reverse osmosis-type membranes, the relatively dense surface of the membrane must be made as thin as possible. To this end, thin-film composite membranes, fabricated by depositing a thin, dense layer of polymer onto a support membrane made from a different material have been developed.^{1,2} One method of making such membranes is interfacial polycondensation at the surface of the support membrane;^{3,4} an aqueous solution of one monomer is soaked into the support membrane whereupon the membrane is treated in a solution of the other monomer in an immiscible organic solvent. In the development of thin-film

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SURFACE MODIFICATION BY PHOTOCHEMISTRY

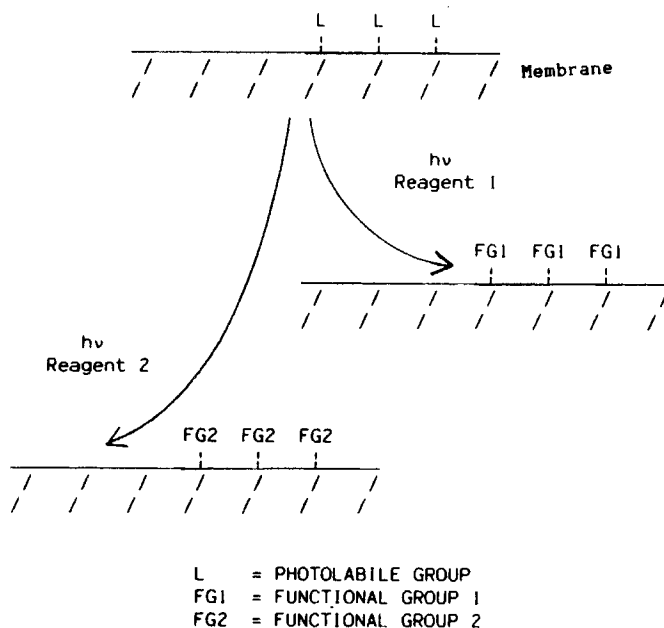


Fig. 1. Schematic of the photochemical process for modifying the surface of a synthetic membrane.

composite membranes the support material can be optimized for mechanical strength and chemical resistance while the surface layer can be optimized independently for high flux and good separation characteristics.

In this paper we describe the development of a unique thin-film composite membrane containing a photolabile group; this group is part of one of the monomers used in the interfacial polycondensation reaction. Irradiation of the surface of the composite membrane results in a photochemical reaction producing a chemically reactive species which can subsequently undergo nonphotochemical reactions with a broad range of reagents to afford new, stable derivatives. Depending on the choice of reagent (which may be the solvent), it is possible to convert the photolabile entity into a variety of different chemical groups within the thin-film composite membrane. This concept is illustrated in Figure 1. In this manner it should be possible to study systematically, for the first time, how the presence of different chemical groups on a single membrane surface affects the ultimate performance of the membrane.

Criteria for the Choice of the Photoreactive Group. The requirements for an acceptable, practical photoactive group are quite stringent:

1. The photochemistry should permit the introduction of a range of functional groups from a single precursor
2. The photochemical reactions should proceed efficiently to give single products in each reaction

3. The photolabile group should absorb light at wavelengths longer than the polymer support such that light-induced modification of these materials is avoided
4. The photolabile group should absorb light in the visible region to minimize the cost of the irradiation source.

With these criteria in mind we have developed and examined in detail two different photoreactive groups, both of which can be converted photochemically to afford carboxylic acid, ester, and amide groups at will from either photolabile precursor.

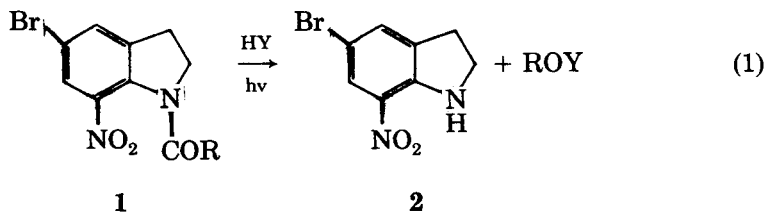
RESULTS AND DISCUSSION

In this section the results using two different photoreactive groups are presented. In both cases the photochemistry was first investigated and demonstrated to be viable in homogeneous solution with model compounds; only then was the photoreactive group incorporated into the surface of a thin-film composite membrane.

Polysulfone was chosen as the microporous support film because it offers a proven combination of compaction resistance, surface microporosity, and resistance to biological and chemical degradation. Thin films have been coated onto support membranes using a variety of methods, including dip coating and float casting.⁵ In the present work the thin-film was prepared by interfacial polymerization whereby a diamine and a diacid chloride containing the photolabile group were allowed to react using procedures similar to those reported earlier for the NS-100 and NS-300 membranes developed by the North Star Research Institute.⁴

The Substituted Nitroindoline Photolabile Group

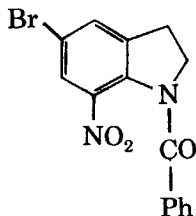
The first photolabile group examined in this work was the 5-bromo-7-nitroindoline system **1**. It has been shown previously that the photolysis of acylindolines such as **1** in the presence of nucleophilic agents produced the free bromonitroindoline **2** and an acyl derivative ROY [Eq. (1)].⁶ Thus irradiation of **1** in the presence of water or an alcohol produced a carboxylic acid or an ester, respectively. The indoline **2** could, in principle, be recovered and recycled.



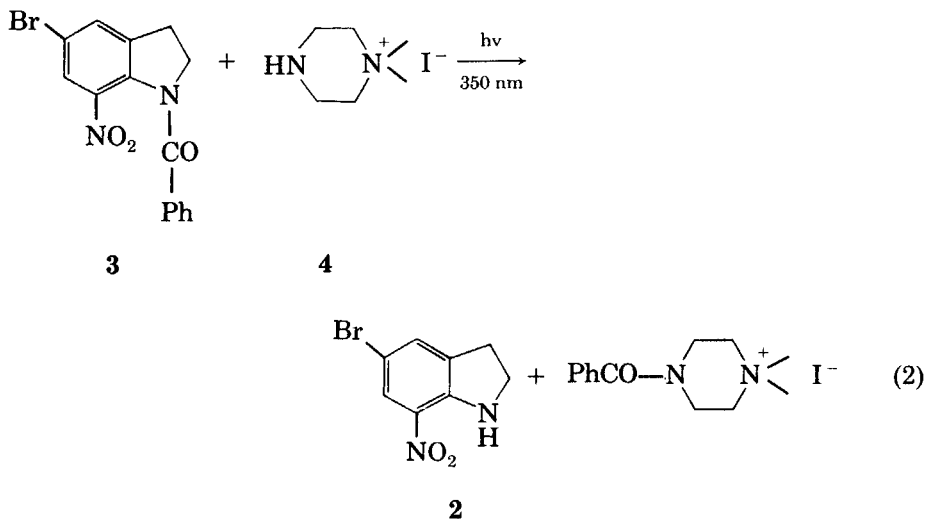
R = phenyl; *p*-MeOC₆H₄; *m*-NO₂C₆H₄; 3,4-Cl₂C₆H₃; 2-naphthyl; 2-furfuryl;
n-C₇H₁₅

Y = OH; OMe; OEt.

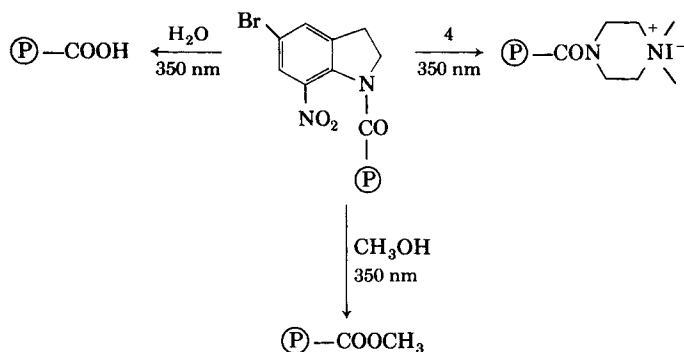
In this work, the photochemistry of a 1-acyl-5-bromo-7-nitroindoline in which the acyl group was a small molecular mass fragment, was reinvestigated to demonstrate that cationic, anionic, and neutral products could be produced in high yield. Irradiation of **3** in the presence of water

**3**

produced benzoic acid (cationic exchanger), in the presence of methanol, methyl benzoate (neutral), and in the presence of aniline, benzanilide (neutral). When *N,N*-dimethylpiperazinium iodide **4** was employed in place of aniline, an amide containing a quaternary ammonium salt was produced which could function as an anion exchanger [Eq. (2)]. In addition to these benzoyl derivatives, compound **2** and some related indoline derivatives were recovered.⁷ It should be stressed that these reactions proceeded efficiently using light of wavelengths greater than 310 nm; the polysulfone membrane does not absorb light in this region.



The acyl derivatives **3** underwent hydrolysis of the nitroindoline amide bond in the presence of base but were resistant to cleavage by strong acid. For example, these amides were found to be stable even after refluxing overnight in 4 *N* H₂SO₄ but were hydrolyzed after 10 minutes (room temperature) in a 1 *N* NaOH solution. Thus, the basicity of any solution in contact with a membrane *prior* to its irradiation must be carefully controlled so as to avoid hydrolytic degradation.

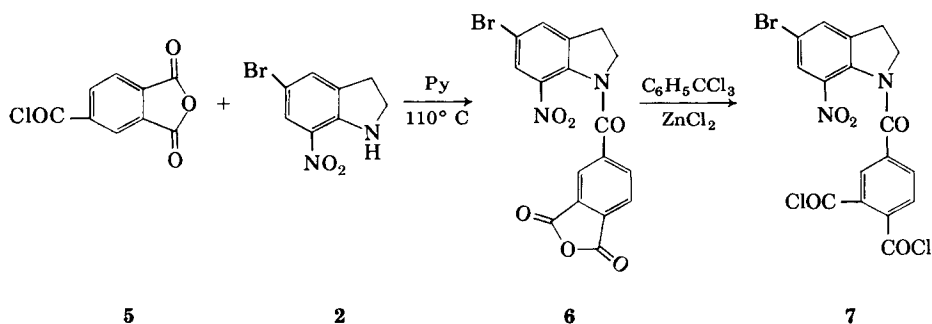


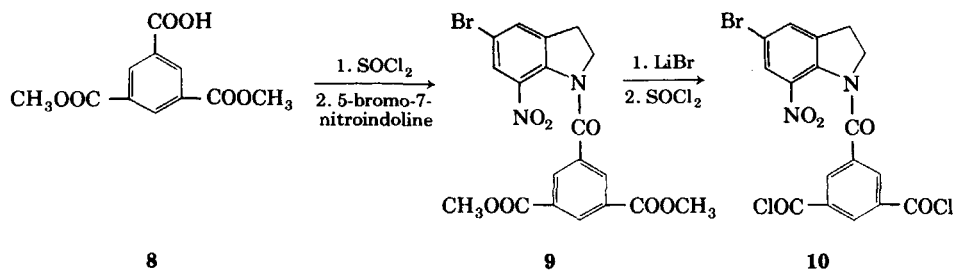
Incorporation of the Nitroindoline into a Polymer. Having prepared a polymer with an amide of 5-bromo-7-nitroindoline, it should be possible to produce a cationic, anionic, or neutral surface, depending on the medium in which the irradiation is done (Scheme 1).

The reaction of 1,6-hexanediamine with functionalized benzenedicarboxylic acid chlorides to afford polyamides is well known. In this work two diacyl chlorides (**7** and **10**) containing the photolabile 5-bromo-7-nitroindoline moiety were used. The acyl chloride **7** was prepared by the reaction of trimellitic anhydride acid chloride **5** with 5-bromo-7-nitroindoline; the anhydride was converted subsequently to the diacyl chloride using trichlorotoluene in the presence of zinc chloride (Scheme 2).

Various attempts to produce the acyl chloride **10** by the reaction of 5-bromo-7-nitroindoline with a large excess (up to 6-fold) of trimesoyl chloride resulted in mixtures of mono and diamides. Compound **10** was prepared from the diester acid **8** by conversion to the acid chloride then the 5-bromo-7-nitroindoline amide **9**; hydrolysis of the ester groups with lithium bromide was followed by formation of the diacyl chloride **10** (Scheme 3).

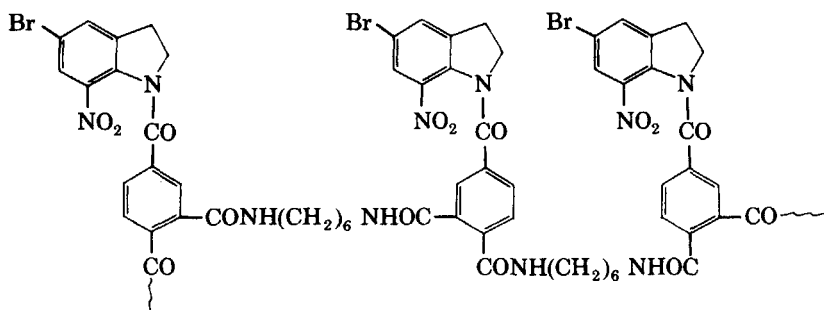
Homogeneous polymerizations of both diacyl chlorides (**7** and **10**) were carried out in pyridine using hexanediamine as the comonomer to give Polymers I and II, respectively. Polymer I was found to have a mass average molecular mass (M_m) of 9200 while Polymer II had an M_m of 40,000. These



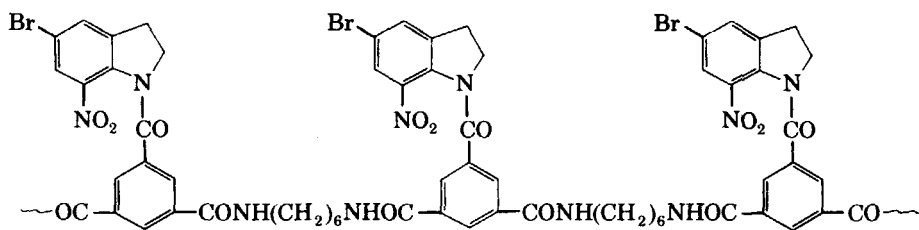


Scheme 3

mass values suggest that good membranes could be produced on top of the support film by an interfacial polymerization. The lower molecular mass of Polymer I may be due to the steric hindrance encountered by the amino group, since the acid chlorides are *ortho* to each other or due to chain termination by cyclization reactions.



Polymer I



Polymer II

Interfacial Polymerizations. Interfacial polymerizations of **7** and **10** with 1,6-hexanediamine were carried out using chloroform as a solvent for the acyl chlorides, and water for the diamine. Polymer formation occurred rapidly at the aqueous/organic interface; infrared and nuclear magnetic resonance spectra confirmed that amide formation had occurred.

Homogeneous solutions of polymers I and II in tetrahydrofuran (THF) were irradiated in the presence of various nucleophilic agents. Analysis of these reaction mixtures for the cleavage product, 5-bromo-7-nitroindoline, confirmed that the photolabile group was behaving in a manner similar to the low molecular mass model compounds previously studied.

Solubility Studies. For an interfacial polymerization reaction an appropriate solvent for the acyl chloride must be selected. In this particular case, the main criteria are that this solvent:

1. Should not dissolve or swell the polysulfone support membrane
2. Should dissolve the acyl chloride to a reasonable extent
3. Should be immiscible with water
4. Should not react with the acyl chloride

In this regard a number of solvents were tested for the solubility of acyl chloride **10**, as well as for compatibility with the polysulfone; the data are summarized in Table I. The solubilities of acyl chloride **10** in various solvents were determined from the ultraviolet absorptions of saturated solutions, while the effects of these solvents on polysulfone are based on the visible degradation of the membrane.

From the data in Table I, it is clear that the only solvents which have no harmful effect on polysulfone membrane are poor solvents for the acyl chloride **10**. These solvents include most of the nonpolar solvents (i.e., hexane, cyclohexane, esters, etc.). In order to prevent any deterioration of the polysulfone substrate, only these solvents were used for polymerization reactions. Although no harmful effect was visually noticeable, a number of these "inert" solvents were found to cause microscopic damage to the membrane, as judged by the reverse osmosis studies described below.

Interfacial Polymerization and Reverse Osmosis Data. Interfacial polymerizations of monomer **10** on polysulfone film surfaces were carried out using a number of solvents for the diacid chloride. Reverse osmosis experiments were then performed to evaluate the effect of the solvent on membrane performance. In each case, two membrane samples were cut from the same sheet of polysulfone membrane; one was used as a control, the other was coated by interfacial polymerization with Polymer II. In this way the effect of treatment could be assessed irrespective of sheet to sheet variations in the original polysulfone support. In some cases the untreated support membranes were exposed to the solvent only, in order to determine the effect of the solvent on the membrane performance.

Permeation characteristics for these membranes were evaluated for pure water, for a 1.0 mass% sodium chloride solution, and for 0.1 mass% dextran (molecular mass of 71,500) solution. The effect of tetrachloroethylene on polysulfone is illustrated in Table II. The membranes were soaked in tetra-

TABLE I
Solubility of the Acyl Chloride **10**^a and the Effect of Solvent
on the Polysulfone Support Membrane

Solvent	Solubility ^b of polysulfone	Solubility ^c of acyl chloride 10
Chloroform	s	sol
Acetone	s	sol
Dioxan	s	sl
Chlorobenzene	s	sl
Ethylbenzene	s	i
Nitropropane	s	sol
Nitrobenzene	s	sl
Nitrotoluene	s	sl
Chloropropane	s	sl
Trichloroethane	s	δ
Tetrachloroethane	s	δ
Dichloroethylene	s	—
Trichloroethylene	s	—
Dichloromethane	s	sl
Methylphenyl acetate	s	δ
Ethyl bromoacetate	s	δ
Ethyl acetate	sw	sl
Propyl acetate	sw	sl
Benzene	sw	sl
Toluene	sw	δ
Xylene	sw	sl
Acetophenone	sw	δ
Mesitylene	i	i
Tetrachloroethylene	i	sl
Carbon tetrachloride	i	i
Freon 113	i	i
Hexane	i	δ
Cyclohexane	i	δ
Ethyl hexanoate	i	δ
Ethyl octanoate	i	δ
Amyl acetate	i	δ

^a**10** = *N*-(3,5-di(chlorocarbonyl)benzoyl)-5-bromo-7-nitroindoline.

^bs = soluble; sw = swelling; i = insoluble.

^csol = > 1.0 mass%; sl = 0.003 – 1.0 mass%; δ = < 0.003 mass%; i = undetectable.

chloroethylene for 2.0 minutes. Although no visible external damage was apparent, both dextran separation and water flux decreased in all the treated membranes, indicating the solvent treatment resulted in some deterioration of the support film. In addition, for all membranes the pure water flux measured after exposure to the dextran was less than the pure water flux prior to this exposure. This effect is probably due to the dextran plugging some pores of the polysulfone film.

The interfacial polymerization of **10** in tetrachloroethylene with 1,6-hexanediamine provided thin-film composites which were evaluated for dextran and NaCl separation and flux (Table III). The dextran separation has not

TABLE II
Effect of Tetrachloroethylene on the Performance of the Polysulfone Support Membrane

Membrane	Treatment ^a	Dextran ^b separation, %	Pure water flux, ^b ×10 ³ , kg/m ² s	
			Initial	Final
Control 1	—	77.1	24.5	18.9
Membrane 1	Tetrachloroethylene	30.9	6.3	2.4
Control 2	—	94.5	24.0	14.6
Membrane 2	Tetrachloroethylene	50.9	9.5	3.7
Control 3	—	90.9	24.5	18.5
Membrane 3	Tetrachloroethylene	50.9	8.2	2.5

^aThe treatment consists of soaking the polysulfone membrane in tetrachloroethylene for 2 minutes.

^bSeparation is defined as: (feed conc - permeate conc)/feed conc × 100%. Initial and final pure water fluxes correspond to the pure water fluxes before and after the dextran separation was measured. Operating conditions: pressure, 420 kPa; feed concentration, pure water or 0.1 mass% dextran; temperature, 25 ± 2°C with fluxes corrected to 25°C.

been improved by the thin-film formation and the sodium chloride separation is very low and virtually unchanged. It seems that degradation of the support film by tetrachloroethylene and the formation of a polymer coating have compensating effects so that little net change in flux and separation were noted compared to the untreated support membrane. In principle, it should be possible to polymerize the surface coating fast enough so that the tetrachloroethylene will not have time to damage the support. However, we were not able to achieve this result and tetrachloroethylene was abandoned as a candidate solvent.

TABLE III
Reverse Osmosis Performance for the Thin-Film Composite Membranes
Fabricated with the Acyl Chloride 10^a in Tetrachloroethylene

Membrane	Volume ^b mL	Pure water flux kg/m ² s, ×10 ³	Dextran-solution ^c		NaCl-solution ^d
			Separation %	Flux kg/m ² s, ×10 ³	separation %
Control 4	—	5.0	98.8	5.0	—
Membrane 4	30	17.8	97.6	16.4	—
Control 5	—	10.9	98.8	10.4	—
Membrane 5	50	8.4	92.9	7.2	—
Membrane 6	80	8.1	94.1	7.0	—
Control 7	—	21.5	99.7	13.9	3.8
Membrane 7	100	58.2	96.5	20.6	3.1

^a10 = *N*-(3,5-di(chlorocarbonyl)benzoyl)-5-bromo-7-nitroindoline.

^bVolume of tetrachloroethylene exposed to the membrane; concentration of acyl chloride 10 was 5.66 × 10⁻³ mass%.

^cExperimental conditions: 0.1 mass% Dextran, 420 kPa pressure, temperature, 25 ± 2°C with fluxes corrected to 25°C.

^dExperimental conditions: 1.0 mass% NaCl, 6000 kPa pressure, temperature, 25 ± 2°C with fluxes corrected to 25°C.

TABLE IV
Reverse Osmosis Performance for the Thin-Film Composite Membranes
Fabricated with the Acyl Chloride **10**^a in *n*-Hexane and Cyclohexane

Membrane	Solvent ^b	Pure water flux kg/m ² s, × 10 ³	Dextran-solution ^c Separation %	Flux kg/m ² s, × 10 ³	NaCl-solution ^d separation %	
Control	8	—	16.1	99.8	11.1	3.1
Membrane	8	<i>n</i> -Hexane	4.7	99.7	4.1	17.1
Control	9	—	65.7	94.5	29.7	—
Membrane	9	Cyclohexane	9.6	95.6	6.7	—
Control	10	—	30.3	90.1	21.9	—
Membrane	11	Cyclohexane	9.6	92.9	0.8	—

^a**10** = *N*-(3,5-di(chlorocarbonyl)benzoyl)-5-bromo-7-nitroindoline.

^bSolvent used for the interfacial polymerization; volume 100 mL; concentration of acyl chloride **10**: 2.0×10^{-3} mass% for *n*-hexane, 3.5×10^{-3} mass% for cyclohexane.

^cExperimental conditions: 0.1 mass% Dextran, 420 kPa pressure, temperature, $25 \pm 2^\circ\text{C}$ with fluxes corrected to 25°C .

^dExperimental conditions: 1.0 mass% NaCl, 6000 kPa pressure, temperature, $25 \pm 2^\circ\text{C}$ with fluxes corrected to 25°C .

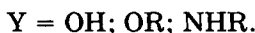
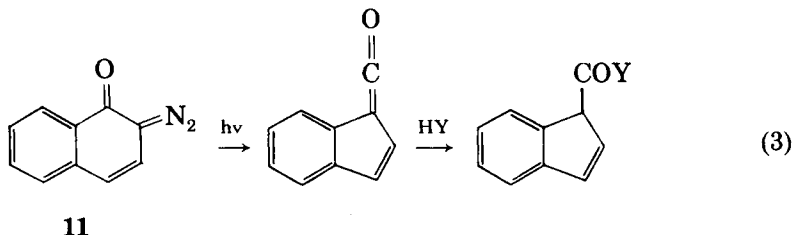
The performance data for composite membranes prepared in hexane and in cyclohexane are presented in Table IV. For the hexane-prepared membranes, the dextran separation is practically unchanged while the flux is decreased, indicating that the polysulfone membrane has been coated. The sodium chloride separation is significantly higher and the flux lower than the control membrane. This result also confirms that the polysulfone membrane has been coated, but the separation for sodium chloride is too low to be of any commercial interest. While hexane is known to be inert to the polysulfone,⁴ the solubility of the acyl chloride in hexane is so low that coherent coating is unlikely to occur. The acyl chloride **10** is marginally more soluble in cyclohexane but the results (Table IV) are similarly discouraging.

Several other solvents and cosolvent systems were investigated, and in all cases, it was found that the solvents which were compatible with the polysulfone would not dissolve the acyl chloride **7** or **10** to an extent sufficiently high enough to make a useful membrane. Several alternatives are possible to overcome this problem including changing the support membrane or trying additional solvent/cosolvent systems. Since the bromonitroindoline moiety tended to make all of its derivatives rather insoluble, it was decided to change the photolabile group to one which had a higher solubility in the nonpolar solvents compatible with polysulfone.

THE DIAZOKETONE PHOTOLABILE GROUP

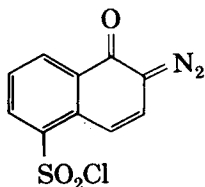
A second approach to incorporating a photoactive group into a polymer involved the use of derivatives of **11**. The diazoketone **11**, widely used commercially as a positive photoresist,⁸ on irradiation generates the reactive ketene, *via* a Wolff rearrangement.⁹ This ketene can in turn react with a

nucleophilic reagent¹⁰ as illustrated in Eq. (3).



In this case the photochemical reaction causes a ring contraction plus the incorporation of the Y group. Adaption of this chemistry requires that compound 11 be attached to a crosslinked membrane polymer in some manner. The subsequent reactions are similar to the nitroindoline case except that the compound 11 cannot be recovered and recycled.

Since 6-diazo-5-oxo-5,6-dihydro-1-naphthalenesulfonyl chloride 12 is commercially available, it was used as starting material. In order to incorporate compound 12 into a thin-film composite, a slightly different interfacial polymerization technique was employed. This method was similar to that used for the NS-100 type membrane published previously;⁴ water-soluble polyamine was crosslinked by an organic soluble diacid chloride. In the present work polyethylenimine (PEI) was first crosslinked with a naphthalenedisulfonyl chloride and then compound 12 was reacted with the remaining free amine sites to produce a sulfonamide. The diazoketone 12 has a much greater solubility than the nitroindolines in solvents which are inert toward polysulfone (Table 5). The resulting polysulfonamide reverse osmosis membranes should have greater chemical stabilities than polyamide membranes due to the lower reactivity of the sulfonamide linkage compared to the amide linkage.



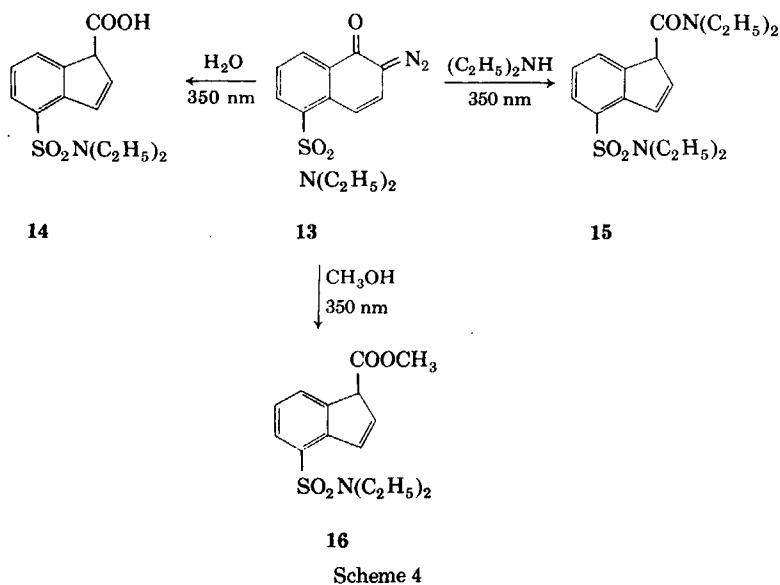
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In order to demonstrate the feasibility of the diazoketone group to produce cationic, anionic, or neutral groups upon irradiation, a model compound was prepared. The diazoketone 12 was reacted with a secondary amine (diethylamine) at room temperature to produce the sulfonamide 13.

TABLE V
Solubility of Diazoketone 12^a, in Solvents Compatible with the
Polysulfone Support Membrane

Solvent	Solubility, mass% × 10 ²
Carbon tetrachloride	42
Dibutyl ether	23
Diethyl ether	66
Freon 113	7
<i>n</i> -Hexane	4
Cyclohexane	7

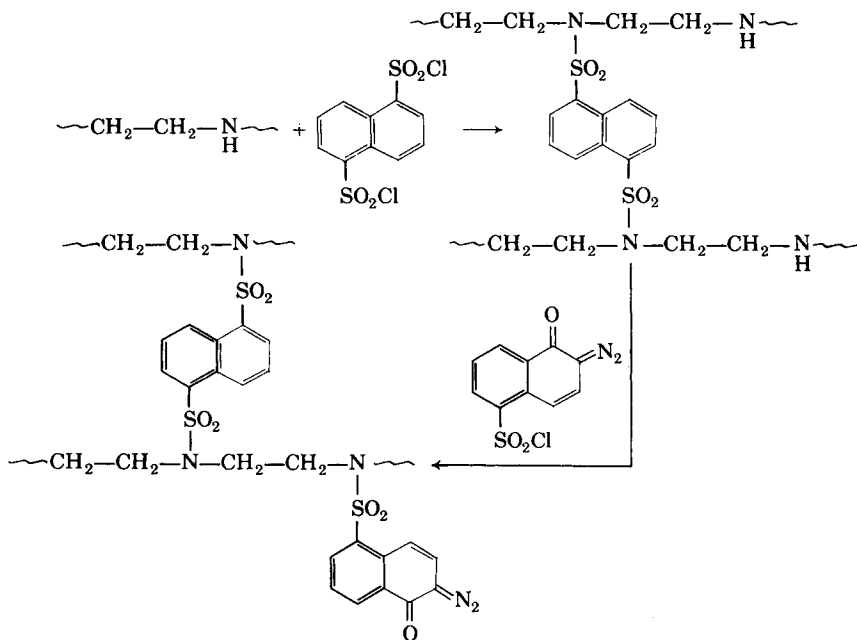
^a12 = 6-diazo-5-oxo-5,6-dihydro-1-naphthalenesulfonyl chloride.



Irradiation of 13 using light with a wavelength of 350 nm produced: the carboxylic acid 14, in the presence of water; the amide 15, in the presence of diethylamine; and the ester 16, in the presence of methanol (Scheme 4). Once more the wavelength of the light used to cause these reactions was such that polysulfone would not absorb.

Interfacial Polymerizations. The photolabile diazoketone group was coupled with PEI on the surface of the polysulfone support in a *two-step* interfacial polymerization. Since the flux and separation of the hand-cast polysulfone support membranes showed considerable variations from film to film, a machine cast polysulfone membrane was used in this part of the project.

In the first step, the PEI was dissolved in water and soaked into the support membrane. The PEI was crosslinked by exposing the membrane to 1,5-naphthalenedisulfonyl chloride dissolved in hexane. In the second step,



compound **12** was dissolved in hexane and exposed to the membrane in order to add the photolabile group to the membrane surface, as in Scheme 5.

The presence of diazoketone group in the surface of the membrane prepared by these methods was confirmed by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR)¹¹ in which the characteristic absorptions of the C-N₂ group at 2113 and 2163 cm⁻¹ were clearly visible [Fig. 2(a)]. On irradiation of the membrane in the presence of methanol, with light of wavelength > 310 nm, the C-N₂ absorptions disappeared and a band, due to the C=O stretching of a carboxylic ester, formed at 1713 cm⁻¹ (Fig. 2). The absorptions below 1600 cm⁻¹ are due to the polysulfone support material. These results confirm that the photolabile group was incorporated into the thin-film composite membrane surface and that irradiation in methanol can completely convert the photolabile group into carboxylic ester. Similar changes in the IR spectra of the thin-film composite membrane occurred upon irradiation in the presence of water.

Reverse Osmosis Data. Using the methods discussed above, a series of membranes were fabricated and photochemically modified to carboxylic acid, quarternary amine (using *N,N*-dimethylpiperazinium iodide), or ethyl ester form. Some membranes were also tested in the diazoketone form for comparison. The reverse osmosis pure water flux and the separation for sodium chloride-water solutions for these membranes are presented in Table VI. These results are quite encouraging. For the diazoketone membrane, separations greater than 90% and fluxes that are of commercial interest have been obtained. When the diazoketone membrane is photochemically converted to acid, quaternary amine, and ester, the separation for sodium chloride is approximately constant. However, the flux is significantly increased by con-

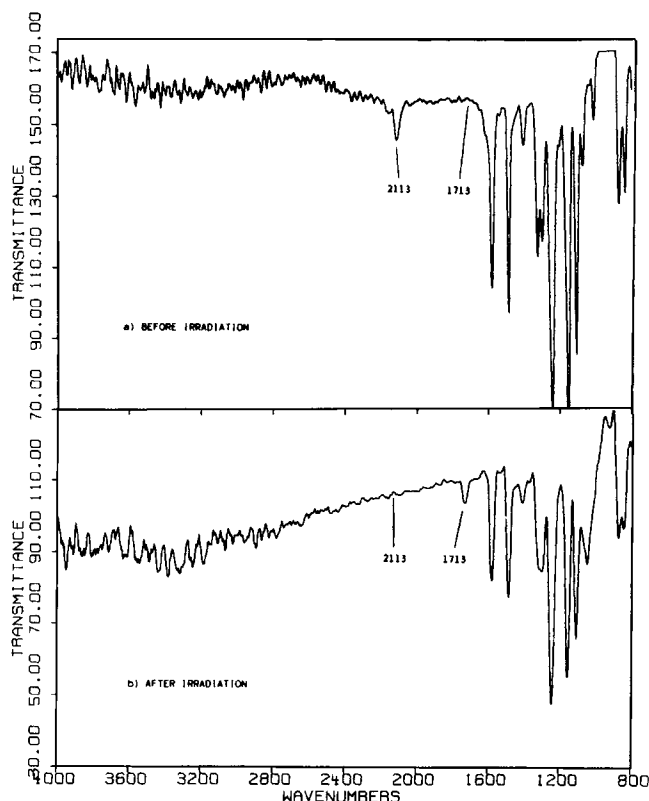


Fig. 2. Attenuated total reflectance FTIR spectra for two thin-film composite membranes: (a) the membrane containing the photoreactive diazoketone group before irradiation, and (b) a similar membrane after conversion to methyl ester in methanol.

TABLE VI
Reverse Osmosis Performance Characteristics of the Thin-Film
Composite Membranes Fabricated with Diazoketone **12** in *n*-Hexane^a

Membrane	Pure water flux kg/m ² s, × 10 ³	NaCl	Separation % ^b		
			Na ₂ SO ₄	MgCl ₂	MgSO ₄
Diazoketone	8.1	90.1	93.2	97.3	98.0
Acid	12.5	91.3	89.2	98.0	96.9
Quaternary amine	11.2	90.4	92.1	97.0	98.9
Ethyl ester	6.0	92.9	94.8	98.3	98.6

^aMembranes fabricated by the two step procedure, **12** = 6-diazo-5-oxo-5,6-dihydro-1-naphthalenesulfonyl chloride.

^bExperimental conditions: 0.17 mol% salt, 6000 kPa pressure, temperature, 25 ± 2°C with fluxes corrected to 25°C. Values shown are the average of results for 4 membranes for the Diazoketone and 2 membranes for the others. The variation in separation is about ± 1% and the variation in average flux is about ± 10%.

version to an ionic form and the flux is slightly decreased upon conversion to the ester form. These results suggest that the membrane may be swelling in either of the ionic forms leading to an increase in water flux. The ester form and diazoketone form are both neutral and it is noteworthy that the flux is approximately the same for these membranes.

Reverse osmosis experiments were also conducted on a series of inorganic salts: NaCl, Na₂SO₄, MgCl₂, and MgSO₄. The separations obtained are summarized in Table VI. For the diazoketone membrane the separation increased in the order NaCl < Na₂SO₄ < MgCl₂ < MgSO₄. Similar trends are observed for the quaternary amine and the ester membranes. However, for the acid form the separation is less for the Na₂SO₄ salt than for NaCl salt. Also the separation for the Na⁺ salts is marginally higher for the ester membrane than for the other membranes. It is notable that the separation for the divalent Mg²⁺ salts is always higher than for the monovalent Na⁺ salts independent of the two anions examined.

The reasons for the above results are not well understood at this point. However, it is clear that we have successfully affected the performance characteristics of a series of membranes by photochemically modifying the membrane surface. A more detailed investigation of the properties of these polysulfonamide membranes will be presented in Part II of this paper.

CONCLUSIONS

In this paper the concept of utilizing photochemistry to produce at will different cationic, neutral, or anionic groups on the surface of a thin-film composite membrane is introduced. The criteria for the choice of a photolabile group are defined. A detailed investigation of photolabile 1-acyl-5-bromo-7-nitroindolines demonstrated the feasibility of the photochemistry in this series. In the end, the nitroindoline approach was abandoned because of the low solubilities of the requisite nitroindoline acyl chlorides in solvents that would not attack the polysulfone support membrane. An alternate photolabile molecule, a diazoketone, was prepared. Investigations with model compounds showed that the proposed photochemistry was feasible. Thin-film composite reverse osmosis membranes containing the latter photolabile group were synthesized and subsequently converted photochemically to acid, base, and neutral forms. ATR-FTIR spectroscopy was used to confirm that the diazoketone had been incorporated into the membrane and was subsequently lost following irradiation. The diazoketone and irradiated membranes proved to have high separation and reasonable fluxes for sodium chloride-water solutions. The reverse osmosis performance of these membranes depended on the chemical modification of the membrane surface. The exact effect of changing the membrane surface photochemically on the membrane performance is not well understood and investigations on these membranes are continuing.

EXPERIMENTAL

Materials. Polysulfone used was PS-3500 from Union Carbide Corporation. 6-Diazo-5-oxo-5,6-dihydro-1-naphthalenesulfonyl chloride was obtained from Fluka and the polyethylenimine from Eastman Kodak Company. 1,6-

hexanediamine was obtained from BDH. All the work with photolabile group 12 was done on a proprietary machine-cast polysulfone support membrane. Water was purified by distillation, carbon filtration, and passage through ion exchange resins.

General Equipment. The ^1H nuclear magnetic resonance (NMR) spectra were recorded on a Varian EM 390 spectrometer. The UV spectra were recorded on Pye Unicam SP8-100 spectrometer. Infrared spectra were obtained using a Perkin-Elmer Model 283 Spectrometer. Attenuated total reflection Fourier transform infrared (ATR-FTIR) were obtained on a Nicolet 7199 using twin parallel mirror reflection attachment. The determination of mass average molecular mass (M_m) was done using laser low-angle light scattering in a Chromatix KMX-6. Irradiations were carried out using a Rayonet photoreactor (Southern New England Ultraviolet Company) with ten Model PRP 3500 Å lamps. In a different apparatus, the membranes were irradiated while immersed in solvent in a Petri dish with a Pyrex cover. This irradiation apparatus consisted of four Model PRP 3500 Å lamps fixed horizontally 3 cm apart and 14 cm from the membrane. Pyrex tubes of 1.5 cm diameter were used for preparative work. The NMR samples were prepared in 5 mm NMR tubes sealed with plastic caps.

Membrane Fabrication. The polyamide thin-film composite membranes were made by interfacial copolymerization on the surface of an inert polysulfone support layer. To prepare the polysulfone substrate, a 15 mass% solution of PS-3500 in 1-methyl-2-pyrrolidinone was cast on a flat glass plate, using a Gardner Knife with a gap of 0.005 inches. The casting solution was evaporated at room temperature for 1 minute and then immersed in ice water to gel the membrane. Interfacial membrane synthesis was done on the surface of polysulfone support without stirring.

To prepare Polymers I and II, the polysulfone support was immersed in a solution of 1.0 mass% of 1,6-hexanediamine in water for 5 minutes. The membrane was drained for 2 minutes and then soaked in acid chloride solution for 5.0 minutes.

Thin-film membranes containing the diazoketone were prepared as follows. The machine-cast polysulfone support was immersed in 0.67 mass% of polyethylenimine in water for 30 minutes. The membrane was drained for 10 minutes and then immersed in 0.05 mass% 1,5-naphthalenedisulfonyl chloride dissolved in hexane for 1.5 h. This was followed by a second immersion in 0.0107 mass% of 12 in hexane for 1.5 h. After removal from the bath the membranes were heat cured at 110°C for 5.0 minutes.

Reverse Osmosis Experiments. The flat thin-film composite membranes were tested in a reverse osmosis radial flow test cell system similar to a system reported earlier.¹² Briefly, this consisted of a pump, six test cells, a pressure gauge, and a pressure regulator. A feed solution was pressurized and circulated over the surface of the membranes. Samples of the feed and permeate were collected, weighed, and analyzed to determine flux and separation. The membrane area was 1.508×10^{-3} m and the feed flow rate was 1.0 L/min.

The concentration of inorganic salt solutions were determined using a YSI Model 31 Conductivity Meter. The concentration of dextran solutions were determined using a Beckman Model 915B Total Carbon Analyzer.

CHEMICAL SYNTHESIS

5-Bromo-7-nitroindoline. 2 1-Acetyl-5-bromo-7-nitroindoline 1 ($R = CH_3$) was obtained from indoline by acetylation, bromination, and nitration as described by Gall et al.¹³ A mixture of 1-acetyl-5-bromo-7-nitroindoline (25 g, 88 mmol) in 40 mL ethanol and 104 mL 6 *N* hydrochloric acid was refluxed for 6 h, cooled, and poured into cold dilute ammonium hydroxide. The brown precipitate obtained was filtered, washed thoroughly with dilute sodium hydroxide solution and then with water. Recrystallization from methanol yielded 18.2 g (85.4%) of product 2, mp 130–132°C (Lit¹⁴ 131–132°C), UV (CH_2Cl_2) λ_{max} 246 nm (log ϵ 4.08), 434 (3.78), ¹H NMR ($CDCl_3$) δ 3.17 (t, 2, H-3), 3.89 (t, 2, H-2), 6.8 (br, 1, N-H), 7.27 (s, 1, H-6), 7.90 (s, 1, H-4).

1-Benzoyl-5-bromo-7-nitroindoline. 3 5-Bromo-7-nitroindoline (10 g, 41 mmol) was added to benzoyl chloride (8 g, 57 mmol) in 100 mL of pyridine and heated at 110°C for 3 h under nitrogen atmosphere. The reaction mixture was poured into 500 mL of water and the yellow precipitate was washed with 5 mass% sodium hydroxide solution, then water until the washings were neutral to litmus. The precipitate was dried and crystallized from ethanol to give 12.1 g (84.1 %) of 3 mp 208–211°C, UV (CH_2Cl_2) λ_{max} 242 nm (log ϵ 4.27), 352 (3.57), ¹H NMR ($CDCl_3$) δ 3.17 (t, 2, H-3), 4.34 (t, 2, H-2), 7.6 (s, 1, H-6), 7.5–7.88 (m, 5, C_6H_5), 8.0 (s, 1, H-4).

Photoirradiation of 1-benzoyl-5-bromo-7-nitroindoline. Photoirradiation of 1-benzoyl-5-bromo-7-nitroindoline to produce (i) benzoic acid (ii) methyl benzoate ester, and (iii) benzanilide were performed as follows:

Irradiation in water. 1-benzoyl-5-bromo-7-nitroindoline (1 g, 2.9 mmol) was dissolved in 5 mL of methylene chloride-dioxane-water (5 : 10 : 0.5) in a Pyrex tube. This mixture was irradiated at 350 nm with stirring for 6 h. Pure benzoic acid in 75.2% yield was obtained by column chromatography with silica gel on the reaction mixture using diethyl ether: petroleum ether 35–60°C (1 : 1) as eluting solvent. mp 121–123°C (Lit¹⁵ 122.4°C), ¹H NMR ($CDCl_3$) δ 7.55 (m, 3, H-3, 4, 5), 8.20 (m, 2, H-2, 6), 11.9 (s, 1, COOH).

Irradiation in methanol. 1-benzoyl-5-bromo-7-nitroindoline (1 g, 2.9 mmol) was dissolved in 5 mL of methylene chloride-methanol (5 : 1) in a Pyrex tube. This mixture was irradiated at 350 nm while stirring for 6 h. Pure methyl benzoate in 68% yield was obtained by column chromatography on silica gel using ether: petroleum ether 35–60°C (1 : 4) as eluting solvent. bp 192–196°C (Lit¹⁵ 199.6°C), ¹H NMR ($CDCl_3$) δ 3.8 (s, 3, CH_3), 7.42 (m, 3, H-3, 4, 5), 8.1 (m, 2, H-2, 6).

Irradiation with aniline. 1-benzoyl-5-bromo-7-nitroindoline (1 g, 2.9 mmol) and aniline (0.4 g, 4.2 mmol) were dissolved in 5 mL solution of methylene chloride in a Pyrex tube. This mixture was irradiated at 350 nm while stirring for 6 h. Benzanilide in 81.2 % yield was obtained by column chromatography on silica gel using diethyl ether: petroleum ether 35–60°C (1 : 1) as eluting solvent. mp 161–164°C (Lit¹⁵ 163°C), ¹H NMR ($DMSO-d_6$) δ 6.8–7.8 (m, 6, H-3, 4, 5, 3', 4', 5'), 7.8 (m, 2, H-2', 6'), 8.2 (m, 2, H-2, 6).

***N,N*-Dimethylpiperazinium iodide. 4** *N*-Carbethoxypiperazine (10 g, 63.3 mmol), prepared in 45% yield by the method used by Baltzly et al.,¹⁶ and sodium carbonate (10 g) were dissolved in 100 mL acetone. After the addition

of 20 g methyl iodide, the reaction mixture was stirred overnight. Then the solvent was removed and the residue mixed with 20 mL of 50% hydrochloric acid and the mixture refluxed for 48 h. The reaction mixture was made basic with sodium carbonate and the salt precipitated with ethanol. The product was collected by filtration and crystallized from ethanol/water; yield 12.2 g (80%). $^1\text{H NMR}$ (d_6 -DMSO) δ 3.14 (d, 6, CH_3), 3.4 (t, 4, H-3, 5), 3.76 (m, 4, H-2, 6).

***N*-(3,4-Dicarboxyanhydrobenzoyl)-5-bromo-7-nitroindoline. 6** A mixture of trimellitic anhydride (4 g, 20.8 mmol) and 20 mL thionyl chloride containing 2 drops of pyridine was refluxed for 2 h. After the removal of excess thionyl chloride, the crude acid chloride **5** was treated with a solution of 4 g (16.5 mmol) 5-bromo-7-nitroindoline in 20 mL pyridine and the mixture refluxed for 2 h. The solvent was removed at reduced pressure and the residue washed with hot water to afford 6.1 g of crude product. After washing with ether, recrystallization from acetone gave a pure product 4.8 g (70.6%). Mass spectrum m/e (relative intensity) 416,418 (M^+), 175 (100). $^1\text{H NMR}$ (d_6 -DMSO) δ 3.2 (t, 2, H-3), 4.25 (t, 2, H-2), 7.98 (m, 5, H-4, 6, 2', 5', 6'). IR 3000 cm^{-1} (OH), 1720 cm^{-1} (C=O).

***N*-(3,4-Di(chlorocarbonyl)benzoyl)-5-bromo-7-nitroindoline. 7** A mixture of 3 g (6.4 mmol) of **6** with 15 g α,α,α -trichlorotoluene and 0.3 g zinc chloride was heated at 120°C for 20 h. The solvent was removed under reduced pressure and the residue washed with dry ether to remove the residual trichlorotoluene and the zinc chloride. The residue was used directly for polymerization reactions. Mass spectrum m/e (relative intensity) 470,472 (M^+), 229 (100), 175 (15). $^1\text{H NMR}$ (d_6 -DMSO) δ 3.2 (t, 2, H-3), 4.25 (t, 2, H-2), 7.98 (s, 1, H-6), 8.0 (s, 1, H-4), 8.28 (m, 3, H-2', 5', 6').

3,5-Dicarbomethoxy benzoic acid. 8 Benzene-1,3,5-tricarboxylic acid trimethyl ester was prepared from trimesic acid in 71% yield by the Pechmann method.¹⁷ The above ester (12 g, 47.6 mmol) in 200 mL of methanol was added to 20 mL 2 *N* sodium hydroxide in 30 minutes and stirred at room temperature for 16 h. The reaction mixture was acidified with hydrochloric acid and concentrated *in vacuo*. The resulting precipitate was filtered, washed with water, and recrystallized from methanol/water to obtain 8.4 g (74.2%) yield of crystalline product, mp 142–144°C. $^1\text{H NMR}$ (CDCl_3) δ 4.0 (s, 6, CH_3), 8.89 (s, 2, H-2, 6), 8.97 (s, 1, H-6).

***N*-(3,5-Dicarbomethoxybenzoyl)-5-bromo-7-nitroindoline. 9** A mixture of 3,5-*bis*-carbomethoxy benzoic acid (8 g, 33.6 mmol), and 40 mL thionyl chloride containing two drops of pyridine was refluxed for 2 h. Excess thionyl chloride was removed under reduced pressure. Final traces of thionyl chloride were removed by azeotroping with benzene. 40 mL Pyridine were added to the acid chloride followed by 8 g (33 mmol) of 5-bromo-7-nitroindoline. The reaction mixture was heated at 110°C for 3 h. The solvent was removed and the precipitate washed with water, ether and the crystallized from acetone to yield 11.6 g (74.5%) of product. Mass spectrum m/e (relative intensity) 462,464 (M^+), 221 (100). $^1\text{H NMR}$ (d_6 -DMSO) δ 3.2 (t, 2, H-3), 3.98 (s, 6, CH_3), 4.25 (t, 2, H-2), 7.96 (s, 1, H-6), 8.02 (s, 1, H-4), 8.48 (d, 2, H-2', 6'), 8.7 (m, 1, H-4').

***N*-(3,5-Dicarboxybenzoyl)-5-bromo-7-nitroindoline.** A solution of 1-(3', 5'-carbomethoxy)benzoyl-5-bromo-7-nitroindoline (6 g, 13 mmol), 40 g

lithium bromide (previously dried at 100°C/0.5 mm) in 100 mL dimethylformamide was refluxed for 24 h. The mixture was cooled, poured into 100 mL water, and acidified with dilute hydrochloric acid. The resulting precipitate was filtered, washed with water, and recrystallized from acetone to yield 4.8 g (85.1%) of product. $^1\text{H NMR}$ (d_6 -DMSO) δ 3.2 (t, 2, H-3), 4.28 (t, 2, H-2), 8.0 (s, 1, H-6), 8.1 (s, 1, H-4), 8.42 (d, 2, H-2', 6'), 8.66 (m, 1, H-4'). IR 3000 cm^{-1} (OH), 1752 cm^{-1} (C=O).

***N*-(3,5-Di(chlorocarbonyl)benzoyl)-5-bromo-7-nitroindoline 10** A mixture of the above acid (2 g) in 10 mL thionyl chloride containing 1 drop of pyridine was refluxed for 3 h. After removal of excess thionyl chloride, the residue was washed with benzene to afford 1.8 g of 10. Mass spectrum *m/e* relative intensity 470,472 (M^+), 229 (52). $^1\text{H NMR}$ (d_6 -DMSO) δ 3.2 (t, 2, H-3), 4.28 (t, 2, H-2), 7.9 (s, 1, H-6), 8.0 (s, 1, H-4), 8.45 (d, 2, H-2', 6'), 8.7 (m, 1, H-4').

Polymer I. A solution of 1,6-hexanediamine (0.3 g) and acyl chloride 7 (1 g) in 10 mL pyridine was stirred at room temperature for 2 h before the reaction mixture was poured into water; the polymer was filtered, washed with water, dissolved in THF then precipitated by methanol. The M_m was determined by light scattering to be 9200.

Polymer II. A solution of 1,6-hexanediamine (0.3 g) and acyl chloride 10 (1 g) in 10 mL pyridine was stirred at room temperature for 2 h before the reaction mixture was poured into water; the polymer was filtered, washed with water, dissolved in THF the precipitated by methanol. M_m was determined by light scattering to be 40,000.

6-Oxo-5,6-dihydro-1-naphthalene diethylsulfonamide. 13 To a solution of the diazoketone 12 (2 g, 7.4 mmol) in 30 mL of benzene was added diethylamine (1.2 g, 16.4 mmol). This mixture was stirred at room temperature for 2 h. After removal of solvent, the residue was dissolved in chloroform and washed with water. The chloroform solution was evaporated and the residue crystallized from diethyl ether to obtain 2.1 g (92.5%) of 13. Mass spectrum *m/e* (relative intensity) 305 (M^+), 277 (21), 205 (62), 141 (84), 84 (100). $^1\text{H NMR}$ (CDCl_3) δ 1.14 (t, 6, CH_3), 3.34 (q, 4, CH_2), 7.22 (d, 1, H-8), 7.51 (m, 2, H-3, 7), 8.28 (d, 1, H-4), 8.6 (d, 1, H-2). IR KBr 2115, 2158 (C-N₂) 1630 cm^{-1} (C=O).

Irradiation of 13. The irradiations of 13 to produce acid, amide, and ester products were performed as follows:

4-Diethylsulfonamido-1-indenecarboxylic acid. 14 A sample of 13 (0.5 g) dissolved in a mixture of 10 mL methylene chloride and 0.5 mL water was irradiated in a Pyrex tube at 350 nm for 2 h. After the removal of solvent, the product was chromatographed on silica with diethyl ether. Crystallization from chloroform/hexane afforded 0.36 g (74.4%) of the carboxylic acid 14. Mass spectrum *m/e* (relative intensity) 295 (M^+), 159 (62), 115 (100). $^1\text{H NMR}$ (CDCl_3) δ 1.1 (t, 6, CH_3), 3.34 (q, 4, CH_2), 3.95 (d, 1, H-1), 7.53 (d, 1, H-3), 7.77 (m, 3, H-2, 6, 7), 8.63 (d, 1, H-5), 10.4 (br, 1, COOH).

4-Diethylsulfonamido-1-indenecarboxylic acid diethylamide. 15 A solution of 13 (0.5 g) in diethylamine (0.2 g) and 10 mL of dichloromethane was irradiated for 2 h. The product was purified by chromatography on silica gel with diethyl ether and crystallized from ether to give 0.48 g (84%) of 15.

Mass spectrum m/e (relative intensity) 350 (M^+), 214 (30), 115 (32), 72 (100). 1H NMR ($CDCl_3$) δ 1.15 (t, 12, CH_3), 3.34 (q, 8, CH_2), 3.8 (s, 1, H-1), 7.1 (d, 1, H-3), 7.41 (m, 3, H-2, 6, 7), 8.67 (d, 1, H-5).

4-Diethylsulfonamido-1-indenecarboxylic acid methyl ester. 16 A solution of **13** (0.5 g) in 0.2 g methanol and 10 mL methylene chloride was irradiated for 2 h. After crystallization from diethyl ether 0.37 g (73%) of **16** was obtained. 1H NMR ($CDCl_3$) δ 1.09 (t, 6, CH_3), 3.27 (q, 4, CH_2), 3.9 (s, 1, H-1), 7.48 (d, 1, H-3), 7.6 (m, 3, H-2, 6, 7), 8.61 (d, 1, H-5).

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