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PHOTOREVERSIBLE POLYMERIC MEMBRANES

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ABSTRACT

A variety of advances have been made in the use of environmental factors to control the separation characteristics of polymeric membranes in real time. These systems work by incorporating membrane materials which respond to external stimuli such as temperature or pH by making changes in conformation, solubility, or phase. In this review we focus on the use of light (photons) as the external control stimulus. Specifically, we examine the ability to control polymeric membrane properties by incorporating reversible photochromic moieties into the polymer structure. The first section is a brief review of the chemistry of photochromic compounds, the second section focuses on photocontrol of the separation properties of nonporous and hydrogel membranes, and the third section discusses the photocontrol of release rates from synthetic bilayer membranes.

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INTRODUCTION

The majority of studies involving photoreactions of polymers and macromolecules have centered on irreversible processes, such as photodegradation, photoinitiated crosslinking, or photopolymerization. A number of excellent reviews on this topic are available in the literature[1-4]. However, the use of reversible photochemical reactions to control polymer properties offers several unique advantages, including nondegradable modification of the system, and the potential to control the separation properties of a membrane in real time.

Among the earliest observations of photochroism was the photoregulation of visual pigments[5,6]. Vision occurs as a result of chromophores which regulate cell membrane transport properties. The visual pigment (rhodopsin) consists of a chromophore (retinal) which is bound to a protein (opsin). This molecule is incorporated into the cell membrane. When exposed to light, retinal undergoes a reversible cis/trans isomerization. This causes a configurational change in the protein, distorts the cell membrane, and increases the rate of Ca^{+2} permeation across the cell membrane. The net effect is vision[7]. The recognition of the role of photoisomerization in this process, and in similar processes, has stimulated interest in reversible photochromic reactions as an external control mechanism for membrane systems.

Photoisomerizable molecules, such as azobenzene, azobenzene derivatives, or spirobenzopyrans, exhibit photoinduced reversible isomerism. As suggested above, by rhodopsin, polymers which incorporate such photoresponsive molecules undergo conformational changes upon irradiation, reversibly modifying the physical and chemical properties of the polymers and their polymeric solutions. These property changes have been used to control viscosity, polymer conformation, and solubility in solutions, and contractile behavior and swelling in polymer films or fibers. Reviews by Irie and Smets[8-12] provide excellent overviews of photoresponsive polymers and their properties; however, we are aware of no previous reviews dealing with the use of photopolymers in separations.

The changes in physical properties of photoresponsive polymers have been used to photocontrol membrane properties. The majority of the effort in this area has been related to the photomodulation of membrane barrier properties (permeability, solubility, and diffusivity). The advantage of such a membrane is the ability to control the transport rate of materials through the membrane by controlling the conformation of a membrane component. Two primary methods of photocontrol have been used. The first emphasizes the direct control of membranes properties by incorporating the photoisomerizable moieties directly into non-porous polymeric membranes. The second method is the indirect control of liposomal (bilayer) membrane properties by photocontrolling the configuration of polymers which interact with the membrane. Both of these mechanisms will be discussed in detail in this review. The use of photoreactions to modify and model biological membrane properties has been reviewed by Valenzeno and Tarr[13]. The emphasis of the current review, however, is to consider the use of reversible photochromic chemistry to control polymeric membrane properties, and to examine totally synthetic models of the photocontrol of surfactant based membranes, such as liposomes. The consequences of the conformational transitions of spirobenzopyran, and leucohydroxide moieties on polymer membrane structure and property relationships will be evaluated. A comprehensive examination of the photocontrol of macromolecular separations (i.e. proteins), gas separations, and barrier properties of bilayer membranes is presented.

REVERSIBLE PHOTOCHROMIC BEHAVIOR

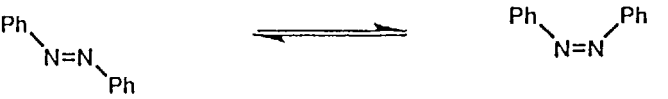
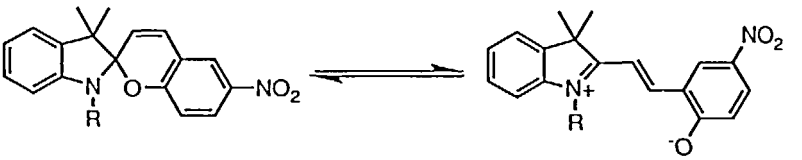
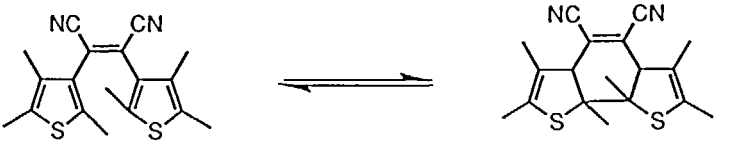
In this section, the mechanisms of reversible photochromic materials will be discussed. In particular, a brief overview of photochromic reactions and their expected impact on modifying polymer properties will be presented.

Classes of Photochromic Compounds

A number of compounds are known to undergo reversible, photoinduced transformations. These compounds can be classified by

TABLE I

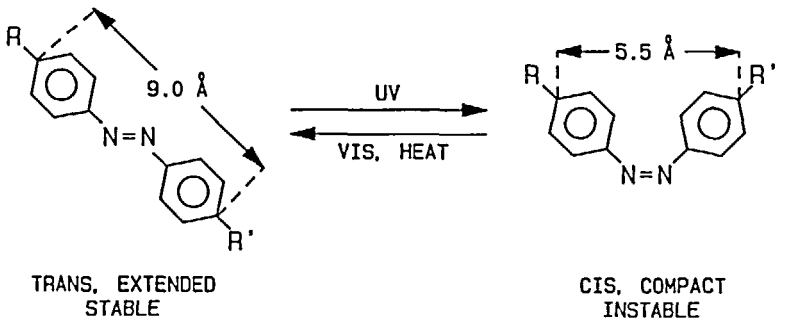
Photoisomerization Reactions[8]

Type of Reaction	Example
(a) Trans-Cis Isomerization	
(b) Zwitter Ion Formation	
(c) Radical Formation	
(d) Ionic Dissociation	
(e) Ring-Formation and Ring-Cleavage	

their photochemical reaction: cis/trans isomerization, zwitterion formation, radical formation, ionic dissociation, and ring-formation/cleavage[8]. Examples of such reactions are summarized in Table I. These reactions generally result in changes in the physical and chemical properties of the molecules (e.g. polarity, solubility, conformation, etc.). Attaching these molecules to polymers provides a method to reversibly modify the polymer properties. The majority of the reported studies have used azoaromatic and spirobenzopyran compounds. However, some interesting results have also been obtained using triphenylmethane leucoderivatives. The photochromic properties of each of these materials are discussed in more detail below.

Azoaromatic Compounds

In azoaromatic compounds, ultraviolet (UV) irradiation ($310 < \lambda < 400$ nm) induces a reversible, geometrical isomerization from the stable, planar trans to the non-planar cis conformation.



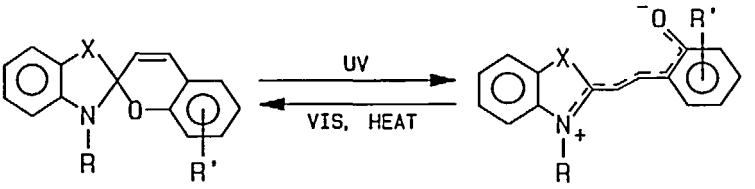
The mechanism for isomerization favors an inversion about one of the nitrogen atoms[14,15]. Isomerization is accompanied by significant changes in molecular size and dipole moment. For example, the distance between *para*-carbons is shortened from 9.0 Å to 5.5 Å by isomerization[16,17] and the dipole moment increases from 0.52 debye (trans) to 3.08 debye (cis)[18]. The cis-trans reverse isomerism occurs in darkness or is stimulated by visible light ($410 < \lambda < 440$ nm) or heat.

The energy barrier separating the two isomers of azoaromatic compounds has been estimated at approximately 10 kcal/mole[19]. The isomerization is accompanied by a change in the absorption spectrum[20,21]. The trans isomer normally shows a strong maximum absorption band around 320 to 360 nm and corresponds to the $p \rightarrow p^*$ transition. The cis isomer shows a weak band around 410 to 440 nm, corresponding to the $n \rightarrow p^*$ transition. The apparent band positions, however, may be shifted depending on the type of substituent attached to the azoaromatic material. For example, azobenzene has a strong trans and a weak cis band at 319 nm and 432 nm, respectively. The addition of an ethoxy group (OC_2H_5) to a *para*-carbon results in a shift of the trans band to 349 nm. The addition of a N,N-dimethylamino group ($N(CH_3)_2$) to a *para*-carbon shifts the trans and cis bands to 410 nm and 460 nm, respectively.

Upon UV irradiation, conversion from the trans to the cis form results in a decrease of intensity in the trans band and an increase in the intensity of the corresponding cis band. The degree of photoconversion is commonly measured by following changes in the absorption maximum (trans band) using standard uv/vis spectroscopic methods. Recent unpublished studies in our laboratory indicate that infrared (IR) spectroscopy can also be used to characterize the cis/trans ratio in these systems. The light from the uv/vis spectrometer may disturb the equilibrium of the system being studied. Infrared spectroscopy is not expected to disturb the state of the system, and the sample can be irradiated by uv or visible light while undergoing IR examination. In addition, the extinction coefficients of the chromophores are considerably smaller for IR then uv/vis wavelengths. Therefore, samples which may be opaque to uv/vis wavelengths are transparent in the IR range.

Spirobenzopyrans

In spirobenzopyrans, UV irradiation induces cleavage of the carbon-oxygen bond and the subsequent rotation of part of the molecule, resulting in a change from a colorless, planar spiropyran to a colored, planar merocyanine[22].



SPIROBENZOPYRAN MEROCYANINE

The X in the 5-membered ring corresponds to S, O, or $C(CH_3)_2$. The resulting merocyanine is in the form of a zwitterion. The photo-transition is reversible in the dark, with heat, or with visible irradiation ($\lambda > 470$ nm).

The heat of transformation from the spiropyran to the colored merocyanine in solution has been estimated at 2-8 kcal/mole, depending on the solvent[22]. The absorption spectrum of spiropyrans exhibit bands at 300-375 nm and at 220-275 nm. The latter region absorbs two to five times more intensely. Upon UV irradiation, bands around 530 to 590 nm and 350 to 390 nm appear and are characteristic of the merocyanine form. The visible absorption maximum appears in this 530 to 590 nm region.

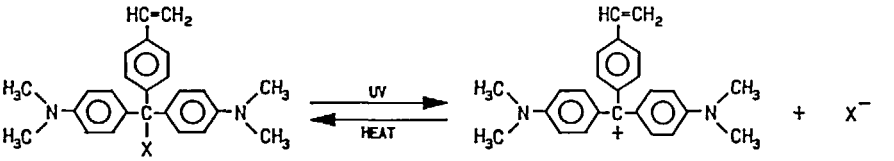
Absorption band positions are sensitive to temperature and solvent effects[22-25]. For example, as the temperature increases, the height and area of the visible absorption maximum increases; whereas, bands of shorter wavelength decrease. In general, as the polarity of the solvent increases, the equilibrium between the spiropyran and the merocyanine shifts toward the formation of the merocyanine. In addition, the visible absorption maximum shifts to shorter wavelengths, the extinction coefficient decreases, and the half-width of the band increases. Consequently, the merocyanine form is considered a dye of high intrinsic polarity. Because of rapid interconversion between the spiropyran and merocyanine forms of the molecule, flash spectroscopic techniques and rapid scanning spectrometers are common methods for recording spectra.

A few spiropyrans are known to change color when heated and return to the original color upon cooling. This reversible temperature

dependence of color is known as thermochroism[22,26,27]. The colored form which is produced thermally appears to be spectrally identical to the form produced photochemically. However, there is greater extent of conversion to the merocyanine photochemically (70-100%), than thermally (2-13%).

Triphenylmethane Leucoderivatives

Triphenylmethane leucoderivatives are photochromic molecules which dissociate into ion pairs upon irradiation with ultraviolet light.



COLORLESS, NON-IONIZED HIGHLY COLORED, IONIZED

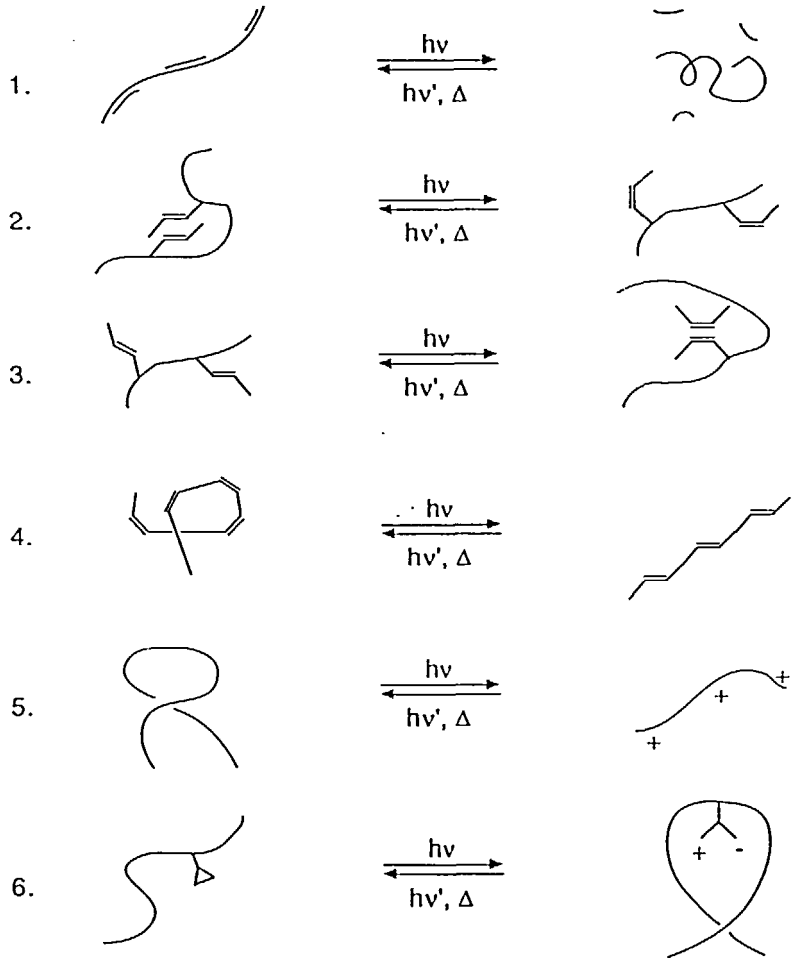
Such a dissociation results in a change from a colorless, non-ionized form to a highly colored, ionized, solvated form. Triphenylmethane leucohydroxide (X = OH) and leucocyanide (X = CN) have been the most widely used derivatives for photocontrolling polymeric materials. The photoionization is reversible: the cations can thermally recombine with counterions. Additional information on triarylmethane dyes and related compounds is available.

Polymer Photobehavior

A variety of mechanisms have been proposed to explain the effects of these photochromes on the observed polymer properties. important considerations include the location of the photochrome (backbone vs. sidechain) and the changes in the physical properties of the photochrome. Proposed mechanisms are summarized in Table II, and briefly reviewed below. The more interested reader is referred to Irie's recent review[8] as well as other reviews in this area[28].

TABLE II

Photostimulated conformational changes of polymer chains[8]



In the first mechanism, the polymer is in solution with a low molecular weight photoisomerizable compound. In the relaxed state, the photochrome interacts with the polymer, causing the polymer to adopt an extended configuration. This interaction is weakened by the photoisomerization of the low molecular weight compound. The polymer then relaxes to a more compact configuration[28]. While the initial reports of this mechanism have been discounted[29], this mechanism has been confirmed for certain systems[30,31].

The second mechanism results from interactions between photomoieties attached as sidechains. In this case, the change in polymer configuration is proposed to result from the changes in sidechain-sidechain interactions which occur upon irradiation. Depending on the chromophore and the polymer system, irradiation has been proposed to either disrupt sidechain interactions (mechanism 2) or increase sidechain interactions (mechanism 3)[28,32].

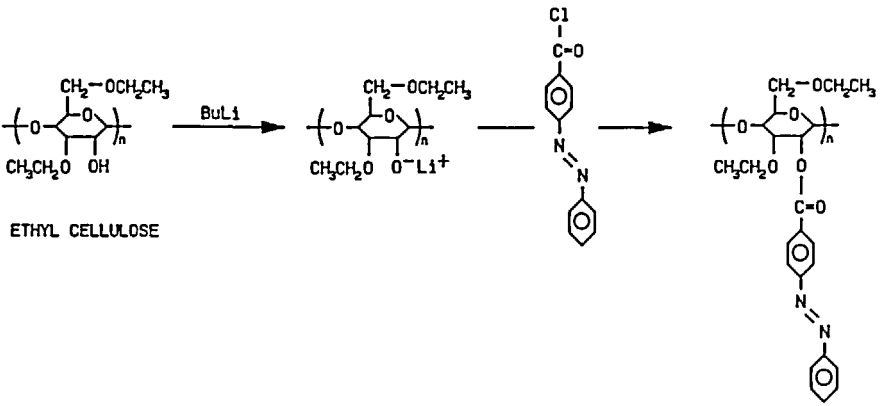
The third mechanism requires the incorporation of the photomoiety into the polymer backbone. In this case, the change in the photochrome configuration leads directly to changes in polymer configuration. Typically, a spirobenzopyran chemically contained in the backbone of a polymer has permitted greater changes in polymer characteristics upon ultraviolet irradiation than a comparable polymer containing an azoaromatic moiety. The extent of the photobehavior depends upon the rigidity of the polymeric system. A system which is too rigid or not rigid enough appears to reduce the photobehavior.

The fourth mechanism applies primarily to gels and solutions and provides the potential for perhaps the most dramatic photoresponse. In this case, the polymer contains photoionizable sidegroups. In the dark adapted state, these sidegroups are neutral, and the polymer chain will adapt a more or less random configuration. When irradiated, cations are formed along the polymer chain. The repulsive forces between these cations leads to a significant chain rearrangement and, consequently, to a more expanded configuration. Irie[33] has reported changes in swelling of as much as 1700% for polyacrylamide gels containing 1.9 mole% pendant triphenylmethane leucocyanide groups.

The final mechanism involves the formation of zwitterions. The formation of zwitterions is often accompanied by significant configurational changes in the photochrome. For example, spirobenzopyran undergoes a major change in both polarity and configuration upon irradiation. This is expected to affect the polymer configuration. The viscosity of poly(methyl methacrylate) containing 13 mole% spirobenzopyran groups was reported to decrease upon irradiation (zwitterion formation)[34]. This decrease was proposed to result from the solvation of the merocyanine by the ester groups in the polymer.

As suggested by the above mechanisms, the location of the photochrome in the polymer chain (direct incorporation in the backbone vs. attachment as a sidechain or crosslink) is important. Either approach has certain advantages. Intuition suggests that incorporation into the backbone should provide the largest change in polymer properties upon irradiation. However, the bonding to adjacent backbone groups can hinder the isomerization of the photomoiety[12,22]. In addition, the photochromic materials tend to be polar and rigid[21,22], therefore, the resulting photochromic polymers are often more glassy and brittle than the parent polymers.

A significant advantage of attaching the photomoieties as sidechains is the relative simplicity of the chemistry. Several photochromes are commercially available in a form which can be



ETHYL CELLULOSE

easily attached to the polymer. An example of this is the attachment of p-phenyl azobenzene (PAB) to a hydroxyl containing polymer, such as ethyl cellulose[35,36].

Thus, the majority of reported studies have been performed using polymers with chromophores as sidechains.

Photothermal vs. Photochemical Effects

When evaluating results of the effect of photoirradiation on sample properties, great care must be taken to ensure that the results are due to photochemical reactions and not the simple result of photothermal heating. This is particularly important when small changes (< 10%) in observable properties are reported. Irie has proposed rules which can be used to help determine whether an observation is a true photochemical effect or simply a result of heating by absorption of light[8]. These rules are briefly stated below.

1. For a true photochemical effect, the recovery rate of deformation when irradiation is discontinued should always be less than or equal to the rate of deformation observed upon photoisomerization. This is true whether recovery results from thermal or photochemical processes. If the recovery rate is greater than the deformation rate, the property change may result from photoheating.

2. At elongations (l) smaller than the inversion elongation (l_{inv}), the temperature increase causes the force to decrease. Whereas, at l larger than l_{inv}, an increase in the modulus with temperature causes the contraction force to increase. Therefore, photoheating should give rise to reverse effects, depending on l. The photochemical effect is independent of l. If the photostimulated contraction depends on l, the contraction is due to photoheating.

3. If the observed photodeformation is larger than 20%, the result is due to a photochemical effect.

These rules can be applied in a modified form to membrane studies. For example, the diffusion coefficient of a gas in a polymer is a strong

function of temperature, and increases with increasing temperature. In previous studies, the diffusion coefficient of gases in a ethyl cellulose sample containing 40 mole% PAB decreased by 18% upon irradiation[35,36]. Photoheating would have increased the diffusion coefficient. This provides strong evidence that the observed effect was caused by a photochemical process.

CONTROL OF MEMBRANE FUNCTIONS

In this section, some of the basic mechanisms which have been used to control membrane properties will be introduced. The simplest technique is stretching the membrane[37-39]. For example, the diffusion of acidic organic dyes in nylon 66 decreased by 76% when the draw ratio was increased from 1.0 to 5.2. The permeability of helium in linear polyethylene decreased by 4% when the membrane was elongated by 43% at 25°C. Under the same conditions, the permeability of argon decreased by 5%. Similarly, a 490% elongation of a dibutyl maleate-ethylene copolymer film resulted in a 20% decrease in helium permeability and a 40% decrease in argon permeability at 29°C. Although this technique can be used to modify membrane properties, enhancement is relatively small and temporary, and irreversible changes in the membrane result if the elastic limit of the polymer is exceeded. Therefore, this technique is of limited use as a control mechanism.

Several methods have been reported for controlling membrane properties in real time. Most of these methods involve porous membranes using a polymer with a "chemical valve" function. In these membranes, a mechanico-chemical contractive force is used to enlarge and contract membrane pores reversibly resulting in controlled permeability and improved performance in separating macromolecular solutes. This valving action is controlled by use of temperature[40], magnetic fields[41], electrical fields[42], changes in pH or ionic concentration of the medium[43,44], and chemical complexing agents[45]. These techniques have been shown to increase the performance in protein separations by up to three orders of magnitude compared to un-

treated membranes[46]. The expansion and contraction of the micropores has also been used to control the diffusional velocity of substrates to regulate an enzyme reaction and for the controlled release of drugs[47,48]. While these control mechanisms are readily implemented in liquid systems, they are difficult to use for gas separation membranes. For example, pH, ionic concentration, and chemical complexing agents require the presence of liquids as solvents or electrolytes.

More recently the photocontrol of membrane activity has gained popularity as a method of mimicking biological processes. Biological photoresponsive systems contain photochromic molecules embedded in biopolymeric matrices. Control of the conformation and assembly of biopolymers by photoisomerization causes stimulation of biochemical reactions. These processes have been applied to the design of synthetic photoresponsive polymeric membranes. In the following sections, we will review the use of photoresponsive polymeric membranes for the separations of macromolecules and gases, and examine the developments in the field of photocontrolled synthetic bilayer membranes.

Photocontrol of Membrane Separations

The earliest studies of photoresponsive alteration of membrane properties involved determination of changes in the membrane potential caused by photoirradiation of membranes containing photoisomerizable chromophores[49-54]. These studies clearly indicated that reversible changes were induced by irradiation. The reader is referred to a review by Irie[8] for more detail. The focus of the section that follows is on studies demonstrating changes in separation properties such as permeability.

Some of the earliest contributions applying the concept of photoresponsive polymer membrane behavior to protein separations have been reported by Ishihara and coworkers. Applications involving azoaromatic polymers have emerged with the development of photocontrolled adsorption[55] and cell adhesion[56] chromatography. Both techniques use a photoresponsive adsorbent which is capable of altering the adsorption or adhesion characteristics of substances with

ultraviolet irradiation. For example, the amount of lysozyme adsorbed onto a 2-hydroxyethylmethacrylate/p-phenyl-azoacrylanilide copolymer was found to decrease upon irradiation with ultraviolet light. Elution of the lysozyme was possible by photoirradiation of a column packed with this adsorbent. Similarly, in the dark, erythrocytes were sorbed onto an adsorbent composed of poly(2-hydroxyethylmethacrylate) containing phenylazobenzene side groups grafted onto the surface of controlled pore glass. Separation from the absorbent was possible with ultraviolet irradiation.

The swelling degree of a polymeric hydrogel membrane has been an important factor in the regulation of permeation rates for drugs. Consequently, the effects of photoirradiation on the swelling behavior of amphiphilic poly(2-hydroxyethylmethacrylate) containing phenylazobenzene side groups[57] were investigated. The swelling degree of a polymer membrane, containing 2.4 mole% azo groups, in water at 25°C was decreased from 14% (measured in the dark) to an equilibrium value of 7.3% after one hour of irradiation with ultraviolet light. This behavior was attributed to the solvation of the hydroxyl group of the polymer with water. A large dipole moment was induced across the azo bond of phenylazobenzene upon photoisomerization. The hydroxyl group of the polymer was thought to interact with the dipole of the cis form of phenylazobenzene, stripping solvated water molecules from the hydroxyl group. The photo-transition of the membrane was examined using spectroscopic methods. The absorption maximum (trans) at 325 nm decreased; whereas, a peak at 420 nm (cis) increased upon exposure to ultraviolet light. An increase in the swelling degree to the original level was observed after irradiation with visible light for 6 hours.

An increase in the mole fraction of phenylazobenzene from 0.018 to 0.387 resulted in a rapid decrease in the swelling degree from 22% to 12% in the dark and from 16% to 8% under ultraviolet irradiation. The deswelling degree decreased gradually from approximately 7.4% to 3.3% with an increase of the azobenzene moiety under ultraviolet irradiation. No change in the swelling behavior was noted with swollen membranes of undyed poly(2-hydroxyethylmethacrylate).

These property changes have suggested that membrane properties can be controlled by the incorporation of photoisomerizable molecules into polymeric membranes. A most intriguing application to these observations was in the photoinduced permeation of proteins[58]. A membrane of poly(2-hydroxyethylmethacrylate) containing 2 mole% p-phenylazobenzoyl side groups was swollen in a phosphate buffer (pH 7.4) at 30°C, and positioned in a separation cell (described in the article). A 50-80% reduction in protein permeability was observed when the membrane was irradiated with ultraviolet light (350 ± 50 nm). Larger reductions were observed for higher molecular weight substances. For example, the reduction in chymotrypsin (MW = 23000) permeability was larger than for lysozyme (MW = 14500), which was larger than insulin (MW = 6000). The permeation of albumin (MW = 60000) was not observed. This was attributed to the relatively large size of the albumin molecule. The permeation of solute through a polymer membrane is greatly dependent on the molecular size of the solute. The decrease in the permeability of the proteins induced by ultraviolet irradiation was due to the decrease in the degree of swelling of the polymer membrane.

Sato et al.[59-62] have investigated the permeability of a membrane made of poly(L-glutamic acid) containing 15.5 mole% pararosaniline (a triphenylmethane leucohydroxide derivative) pendant groups. The permeability of styrene glycol increased ca. 50% upon uv irradiation. The permeability decreased when returned to the dark. Irradiation of the material caused the photodissociation of the leucohydroxide, giving a carbon cation and a hydroxyl group. The hydroxyl groups changed the local pH, causing the increased ionization of the L-glutamic acid groups. This was observed to change the polymer configuration from random coil to a helix. The change in polymer chain configuration was proposed as the cause for the observed increase in swelling upon irradiation. Related studies have been performed using poly(L-glutamic acid) containing azobenzene-4-sulfonic acid residues[63].

Inoue and coworkers[64,65] created photoresponsive membranes from a polyvinyl/polypeptide graft copolymer containing azoaromatic

groups. Specifically, the polymer had a poly(butyl methacrylate) backbone with grafted branches of a copolypeptide of β-p-phenylazobenzyl L-aspartate and β-benzyl L-aspartate. The permeation rate of mandelic acid through this membrane increased by a factor of 6 with UV irradiation and was decreased again by subsequent irradiation with visible light. Smaller increases in permeability were observed for other substrates such as acetone, benzamide, N-((benzyloxy)carbonyl)-D,L-alanine, and biphenyl. The observed changes in permeability were related to conformational changes in polymer. The polymer was inverted from a left-handed helix in the dark adapted state to a right-handed helix in the UV-irradiated state. This inversion was induced by the cis-trans isomerization of the azoaromatic moiety.

A different approach was taken by Koch et al.[66] using the liquid-crystalline polymer poly[4-propoxyphenyl 4-(6-acryloyloxyhexyloxy)cinnamate] and the side-chain crystallizable copolymers poly[4-(6-acryloyloxyhexyloxy)cinnamic acid-co-hexadecyl acrylate] (PAAA). UV-irradiation eliminated the liquid-crystalline order in these polymers due to the photoresponse of the cinnamic acid groups. The activation energy for permeation of 1-butanol through polyamide composite membranes containing a thin film of these polymers was increased by UV-irradiation for temperatures below 48.8°C but decreased for temperatures greater than 48.8°C.

Perhaps the largest photoinduced change in polymer membrane properties was observed for the photocontrolled permeation of water through a porous poly(vinyl alcohol) membrane coated with a polyacrylamide gel containing a triphenylmethane leucocyanide[33]. This is essentially an asymmetric membrane with the permeability controlled by the polyacrylamide gel. As discussed above, the leucocyanide groups are ionized upon irradiation, leading to ion-ion repulsion and expansion of the polymer matrix. The photostimulated dilation and contraction of a polyacrylamide gel containing 1.9% mole% of pendant triphenylmethane leucocyanide was pronounced. Upon irradiation, the gel dilated, or swelled, to 18 times (1800%) its original weight at 25°C and an initial pH of 6.5. In the dark, the gel slowly contracted to

the initial weight. This caused up to a 60-fold increase in the permeability of water through the membrane. In the dark the permeability again decreases. The addition of NaCl to the water quenched the photoeffect by suppressing the photostimulated swelling of the gel.

As the above studies indicate, there is a great potential for further development in gel membrane systems. A primary advantage of these systems is their large photoresponse which results from the potential amplification of changes in the photochrome. In general, polymer solubility is strongly dependent on the polarity of the polymer[67]. If the sample is near the critical solubility, small changes in polarity can have a significant affect on solubility. In a similar manner, the degree of swelling of a gel is expected (as observed) to be affected by the changes in polarity induced by changes in the photochrome. This helps explain the 18-fold change in swelling which was observed for the polyacrylamide gel containing only 1.9 mole% pendant triphenylmethane leucocyanide groups. This pronounced photomodulation of properties should stimulate continued interest in these exciting materials.

Photocontrol of Gas Separations

Photoresponsive polymeric membranes have also been studied as controllable gas separation membranes. The development of a gas separation membrane in which permeability and selectivity are controlled in real time has significant implications. In particular, a controllable membrane could be "fine-tuned" to optimize its permselectivity for difficult separations. In addition, membrane properties could be adjusted to match changing operating conditions. This would be particularly advantageous for a membrane used in a batch process. In addition, the ability to reproducibly and controllably modify membrane properties provides a new tool for developing structure-function relationships for membrane materials.

We have studied the ability of ultraviolet radiation to reversibly modify the permeability and diffusivity of gases through nonporous membranes composed of ethyl cellulose (EC) modified with 18-46% p-

phenylazobenzoyl chloride (PAB/EC)[35,36]. Measurements with argon, carbon dioxide, carbon monoxide, helium, hydrogen, nitrogen, and oxygen were performed at temperatures from 30-85°C using the "time-lag" method[68,69]. A diffusion cell was specially constructed with a quartz window to allow the entire membrane to be irradiated during measurements. A detailed description of this apparatus is given elsewhere[36].

No changes in any of the separation parameters were observed upon ultraviolet irradiation of a pure EC membrane[35]. For the majority of gases (argon, carbon dioxide, carbon monoxide, helium, hydrogen, and oxygen), irradiation of the PAB/EC membrane caused no significant changes in the separation properties. However, for nitrogen, the diffusivity during ultraviolet irradiation decreased by as much as 18% relative to the non-irradiated membrane. The percent change in diffusivity increased with an increase in the PAB loading. The extent of this photoresponse was also dependent on temperature. For example, upon ultraviolet irradiation, no measurable changes from the non-irradiated values were noted for 18% PAB/EC. However, the diffusion coefficient for nitrogen gas in 27% and 46% PAB/EC membranes decreased 6.4% and 8.5%, respectively, at 30°C; 6.7% and 11%, respectively, at 35°C; and 12% and 18%, respectively, at 40°C. At 50°C and above, the irradiated measurements were equivalent to the non-irradiated measurements. These decreases in diffusivity were completely reversible, returning to pre-irradiated values upon exposing the membrane to darkness for 12 to 16 hours[35].

The photoisomerization of the azo bond in the 46% PAB/EC membrane was indicated by a decrease in the area of the trans peak (370 nm) and an increase in the area of the cis peak (440 nm) upon irradiation with ultraviolet light (365 nm) for 1 hour. This resulted in isomerization of 19% of the PAB groups to the cis state at 30°C, reaching a maximum of 30% cis at 40°C, and then decreasing to 11% at 50°C. The decrease in the cis population at 50°C coincided with the decrease in the photoresponse, and has been attributed to the onset of the cis-to-trans back-reaction[35]. The relationship between the fraction of PAB

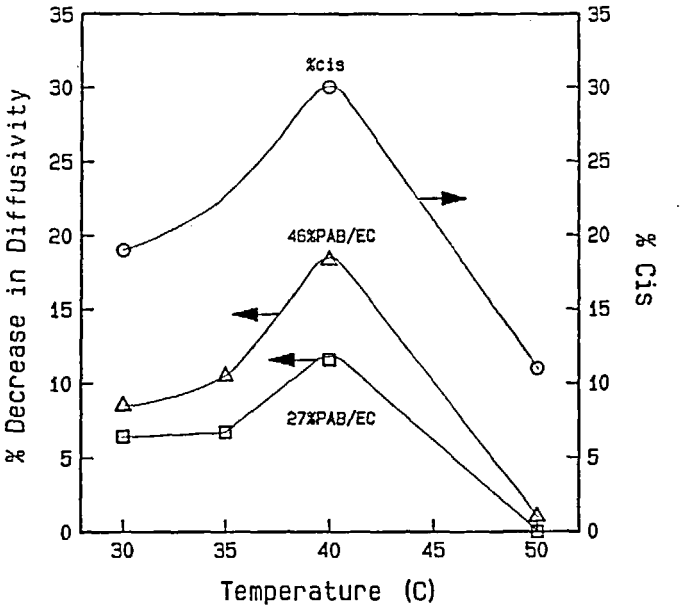


FIGURE 1

Change in diffusivity of N_2 in PAB/EC and fraction of PAB groups in the cis state in PAB/EC as a function of temperature (adapted from reference 35).

groups in the cis state and the observed photoresponse as a function of temperature is shown in Figure 1. This behavior suggested that the observed decrease in diffusivity was directly related to the concentration of the cis-azobenzene moieties in the membrane. Hence, the incorporation of photoresponsive moieties into a polymeric membrane provided a reversible method to modify the diffusivity of nitrogen in a gas separation membrane.

While the gas separation membranes did demonstrate the feasibility of the photoresponsive control of membrane properties, the magnitude of the response was too small to be of practical use. In addition, while changes were observed in both the solubility and diffusivity, no

change was observed in permeability. Consequently, no photoresponsive change in the selectivity of these membranes is expected. Examination of this system suggests several ways to design better photoresponsive polymer systems for gas separations. The polymer matrix, the choice of photochrome, and the location of the photochrome, and the location of the photochrome (sidechain vs. crosslink) are variables which need to be considered. For example, in the present study, a glassy polymer was used as the polymer matrix. In such a rigid matrix, small changes in polymer properties are not surprising. Greater changes in polymer configuration would be expected for polymers above their glass transition temperature. For room temperature evaluation, poly(ethyl acrylate) is a good candidate (T_g = -24°C). Functional groups are available for incorporating photochromic moieties as sidechains, or the ethyl acrylate can be copolymerized with a monomer containing the photochrome.

For gas separation membranes, a photochrome, such as a spirobenzopyran, with a more pronounced change in polarity and/or configuration is recommended. Large changes in polymer configuration have also been exhibited by incorporating spirobenzopyrans as crosslinks in the polymer network. Smets et al.[70] have reported that poly(ethyl acrylate) containing bis-spiropyran reversibly contracted by as much as 2.3% in length under isothermal conditions upon ultraviolet irradiation. Samples were under a constant load and had glass-transition temperatures between -18°C to -15°C. The materials were irradiated for approximately 10 minutes, and full recovery was achieved within 30 minutes in darkness. Under comparable conditions, films of poly(ethyl acrylate) networks crosslinked with a dimethylacryloylaminoazobenzene produced a contraction of 0.15% to 0.25% in the length of the film[71]. This illustrates the larger potential effect of spirobenzopyrans on polymer behavior in comparison to azoaromatic compounds.

Photocontrol in Synthetic Bilayer Membranes

Bilayer membranes which surround cells and subcellular organelles are highly selective permeable structures. These membranes

function in defining and partitioning the cellular volume, regulate the molecular and ionic composition of the intracellular medium, and control mass and information transport into and out of the cell. In addition, they are involved in cellular division, energy conversion processes, chemical synthesis, and an assortment of biochemical response mechanisms. The function of these membranes is controlled by specific chemical and physical stimuli. For example, electrical signals are generated by photoreceptors, such as rods and cones, which convert light into atomic motion and then into a nerve impulse. Acetylcholine acts as a neurotransmitter in communicating nerve impulses between nerve cells. Common features associated with these and similar processes involve detection of the stimulus by a highly specific protein receptor, an induced conformational change in the receptor, followed by restoration of the receptor (reversibility).

The remarkable activity of these natural biomembrane signaling processes has lead to the design and preparation of synthetic bilayer membranes which are capable of responding to signals. Controllable changes in bilayer membrane functions have been induced by pH, temperature and glucose concentration[72-78]. The pH-dependent adsorption of hydrophobic poly(carboxylic acids), such as poly(2-ethylacrylic acid), on Dipalmitoylphosphatidylcholine (DPPC) vesicle membranes permitted the rapid and quantitative release of vesicle contents[72]. The structural properties of the phospholipid vesicle membrane were modified by complexation with the poly(carboxylic acids). This complexation was strongly dependent on the pH of the medium, and was controlled by variation in polymer chemical structure and tacticity.

Similarly, membrane permeability has been regulated using a photoresponsive DPPC liposome membrane containing an azobenzene chomophore[79,80]. Such a system produced vesicles which increased water and bromothymol blue (BTB) permeabilities upon exposure to ultraviolet light. For example, the release rates of BTB from the cis-azoliposomes were approximately 2 and 5 faster than those from the trans-azoliposomes at 50°C and 20°C, respectively. A perturbation in

the membrane structure, which was attributed to the trans-cis conformation change of the azobenzene chromophore, resulted in a shrinkage of the DPPC liposomes. Channel formation due to liposomal shrinkage was responsible for the increase in permeation across the membranes. Initial shrinkage rates of the liposomes containing the azobenzene chromophores were doubled upon trans-cis photoisomerization at 25°C ([azobenzene]/[DPPC] = 0.1). Sato et al.[81] reported that for L-α-dimyristoyl phosphatidylcholine liposomes containing an azoaromatic chromophore the permeability of potassium cations was increased 5000-fold by UV irradiation. Subsequent irradiation with visible light decreased the permeability to its original value.

The release of an aqueous space marker, carboxyfluorescein (CF), has been photocontrolled from light-sensitive liposomes prepared by reactions of retinoylimidazolide with phosphatidylcholines (PC)[82]. These liposomes released 100% of the entrapped space marker within 30 to 120 seconds upon irradiation with ultraviolet light at 25°C. Liposomes which were not irradiated, showed leakages on the order of 10% to 50% after 30 minutes at temperatures between 20°C to 40°C. The release of the space marker from retinoic acid/PC liposomes was at least 50 times slower than from light-sensitive liposomes. For example, only 60% leakage of CF was obtained after 37 minutes of irradiation at 37°C. This suggested that a difference in photoregulation existed between incorporating the chromophore in the membrane versus building the membrane from the chromophore. As an aside, the rate of CF leakage from the light-sensitive liposomes was reduced in the absence of oxygen. No further details were reported.

Upon further investigations, 100% release of CF from similar retinoid photosomes required up to 300 seconds of irradiation at 25°C in buffered solutions[83]. In the absence of light, the release of CF ranged from 0.1 to 2% per minute. Other aqueous space markers showed similar results. The quantitative release of sucrose, however, required 700-800 seconds of irradiation. The light-induced leakage rates decreased with a decrease in the concentration of the chromophore in the membrane.

Comparable results were obtained from the photo-induced leakage of calcein from DPPC containing a synthetic photochromic phospholipid, Bis-Azo PC[84]. Large unilamellar vesicles (LUV) containing trapped calcein were prepared from a mixture of DPPC with 6% (w/w) Bis-Azo PC. Instantaneous release of the vesicle contents occurred as a result of the photoisomerization of the lipid dispersions containing Bis-Azo PC in the trans photostationary state by irradiating samples with a high pressure mercury arc lamp. The cis photostationary state was achieved within minutes after exposure. Reisomerization from the cis to the trans state was accomplished by exposure to unfiltered visible light from a tungsten lamp. Visualization of the extent of calcein leakage from vesicles was possible using an ultraviolet hand lamp (360 nm). Approximately 35% leakage of the calcein was observed after a 3 minute exposure. Fusion of the unilamellar vesicles was observed upon irradiation. Photoisomerization resulted in the fusion of photochromic liposomes with those of the pure DPPC lipid, resulting in the formation of larger, more highly cooperative structures. Applications for localized drug delivery as an adjunct to phototherapy has been suggested from this behavior.

Tirrell and coworkers have investigated the binding of photochromic polyelectrolytes to phosphatidylcholine membranes as a method of photoinducing changes in vesicle permeabilities[85-89]. Binding was accomplished by suspending the vesicles in the polyelectrolyte solution or by linking the polyelectrolyte to the vesicle surface by chemical reaction. Unilamellar vesicles of egg yolk phosphatidylcholine (EYPC) were treated with a dark-adapted (trans) or an irradiated (cis) photochromic polyelectrolyte composed of 2-ethylacrylic acid and N-[4-(phenylazo)phenyl]methacrylamide[85]. Samples were prepared in an aqueous buffered solution at a pH of 7.55. The permeability of calcein through the vesicle of the irradiated sample was identical to the polyelectrolyte-free EYPC vesicle. The percent calcein released from the vesicle was approximately 4% after 100 seconds. A 3-fold increase in the percent of calcein released was observed from the dark-adapted sample, reaching approximately 11% after 100 seconds. These results were consistent with the calorimetric phase transition behavior

of treated DPPC membranes. The irradiated sample produced a transition similar to the pure DPPC membranes, indicating minimal membrane reorganization. The dark-adapted sample, however, was disordered.

A similar investigation was performed using a polyelectrolyte composed of 2-ethylacrylic acid and a spirobenzopyran (PESP)[87]. Samples were examined under thermostated conditions at 5 ± 1°C in an aqueous buffered solution at a pH of 7.22. When dark-adapted PESP (in the merocyanine conformation) was added to a EYPC vesicle, 28% of the entrapped calcein was released. The merocyanine was converted to the spirobenzopyran by irradiation with visible light ($\lambda \geq 410$ nm), increasing the release of calcein to 48% after 2 minutes. A pH-dependency on phase behavior was observed from calorimetry on DPPC suspended in aqueous buffered solutions of PESP. At high pH (8.50 and 9.17), the shape of the transition was not dependent on the photostationary state of PESP. However, at pH ≤ 7.74, addition of the irradiated PESP lead to a broader transition than for the addition of the dark-adapted PESP. This behavior showed that the structural properties of the phospholipid vesicle membrane had been modified by complexation with the poly(carboxylic acid), as previously reported[72]. Complexation was absent at high pH. As pH was decreased, the complexation was more apparent, resulting in the reorganization of the bilayer vesicle structure.

Water-soluble, photosensitive dicarboxydiphenyliodonium salts have been used as an alternative to the azoaromatic or spirobenzopyran chromophores[89]. Vesicular PC suspensions prepared in dilute aqueous solutions of poly(2-ethylacrylic acid) and 3,3'-dicarboxydiphenyliodonium disulfate resulted in the quantitative release of calcein after 2 minutes of ultraviolet irradiation (254 nm). The pH of the sample changed from 7.7 (initial) to 6.69 (final) as the result of irradiation. The release of calcein from the polymer-free control remained constant at 20% prior to, and upon irradiation. The release of the vesicle contents was attributed to the photoinduced acidification of the PC suspensions.

SUMMARY

Initial results with photoresponsive membranes have been mixed. The most encouraging results have been observed in systems where the relatively small photoresponse of the photochromic moiety was multiplied into a large change in system properties (i.e. swollen hydrogel membranes and bilayer membranes). Additional investigation, however, is needed to better elucidate the effects of polymer/photochrome structure and synergy on the control of polymer properties. If these systems are to be utilized in commercial separation applications, the mode of irradiation will need to be seriously considered. Will uv light adversely affect or degrade the material being separated? The polymer matrix may also be degraded (or altered) by exposure to uv light. What is the lifetime of the polymer matrix upon exposure to uv irradiation? These questions, and many more, remain to be answered.

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