

Self-Assembled Structures of Azobenzene Amphiphiles: A New Photorecording Medium

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SYNOPSIS

The self-assembly of azobenzene amphiphiles by themselves and in the presence of a non-ionic polymer has been studied. The conditions that yield homeotropic and uniaxial films, i.e., the optical properties of a single crystal, by spin-coating were identified. It is shown that these films constitute a very sensitive write and erase recording medium. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Organic, photorecording materials are of considerable technological interest for many purposes, such as detectors or optical storage media. Materials containing azoaromatic moieties belong to the more promising systems. In several articles, the suitability of polymers containing azobenzene derivatives for reversible photorecording has been reported.¹⁻¹¹ Natansohn et al.¹⁰ gave an extensive survey of the literature in their recent article. Most of these studies were performed with the azobenzene moiety being a part of a side-chain liquid crystalline (lc) polymer. A combination of field and surface effects is generally used to achieve a uniform homogeneous orientation of the azobenzene chromophores throughout the sample with the director of the lc phase parallel to the film plane.

The photorecording mechanism in these systems is based on the fact that the photosensitive azo groups are present as an equilibrium of the *cis* and the *trans* isomers with the equilibrium strongly shifted to the thermally more stable *trans* isomer. Upon irradiation with light, the isomerization equilibrium is shifted as the *trans* isomer undergoes a fast photoinduced *trans-cis* isomerization into the *cis* form. This causes a change in the geometry of the azo group-bearing molecule from a straight rod-

like shape to a bent form. In the investigated lc side-chain polymers, the change of shape induces an instant local loss in the order of the mesophase. This reorientation is maintained even after the formed *cis* isomers have reverted back to *trans* isomers. Erasure is achieved by heating the film above the clearing temperature.¹⁻⁸ Irradiation with a polarized laser beam causes the optical axis of the lc polymer to turn perpendicular to the polarization plane.³

Natansohn et al. showed that a long-term macroscopic dichroism can also be induced in amorphous polymers containing azoaromatic groups, when the material was irradiated with polarized light.⁹⁻¹¹ A *trans-cis-trans* reorientation process continued as long as a component of the electric dipole moment of the azo group lay in the direction of the polarization of the beam. Molecules that had reached a reorientation perpendicular to the polarization direction were inert to further photoexcitation, leading to an excess of molecules with this orientation with time. Erasure was obtained by irradiating the sample with circularly polarized light. Writing times were typically 1 s, and erasure times, 0.1 s, at a laser intensity of 40 mW/mm².¹¹ This is similar to the reported writing time of less than 0.2 s for the formation of holograms in lc side-group copolymers at a laser intensity of 100 mW/mm².⁴

The photoresponse of Langmuir-Blodgett (L-B) films has also received interest.¹²⁻¹⁹ In general, the L-B deposition process results in tightly packed azobenzene groups oriented nearly parallel to the surface normal that will restrict the *trans-cis* isomerization. The needed larger cross section has been

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obtained by complexing the azobenzene amphiphile to a polymer present in the subphase,¹² decoupling the azobenzene unit from a larger polar head group by a suitable spacer,^{13,17} using lc homo- or copolymers,^{16,19} and expanding the L-B layers by a pretreatment with UV light.¹⁴

Self-assembling systems, such as self-assembling amphiphilic multilayers,²⁰⁻³⁰ offer a different solution to obtain highly oriented chromophores. Here, the ordering is inherently attributed to the systems and is achieved spontaneously rather than by the action of external fields or by successive depositions of layer after layer. Thus, during the past years, the preparation of aqueous solutions of artificial, amphiphile-based bilayer membranes has been reported in numerous papers. Phospholipid-mimicking compounds, such as quarternary alkylammonium salts, are discussed^{20,21,27,30} as well as amphiphiles incorporating a variety of rodlike moieties, as biphenyl or azobenzene groups.^{21,23,25} Further, it has been demonstrated that casting these materials on solid substrates and allowing them slowly to dry creates anisotropic multilayer aggregates.^{23,25,26} The potential value of these systems for optical applications is evident. However, a satisfactory optical quality will demand absence of scattering domain borders.

The goal of large monodomains is not easily reached. The aqueous solutions generally show a lyotropic polymorphism, which is passed through upon evaporation of the water. This causes problems due to phase transformations in the mesophase system. Particularly, first-order phase transitions, such as crystallization in the dry state, seem to lead to scattering polydomain structures of low optical quality. Further, a mesomorphic phase structure of multilayer aggregates is basically liquid and mechanically unstable. Immobilization of the systems is therefore a condition for their use as novel functional materials. The use of polymerizable amphiphiles, which are cross-linked after aggregation,^{25,28} has not prevented subsequent crystallization of the side chains.

CONCEPT

In this article, we present an approach, which specifically targets the above-discussed problems and produces well-ordered macromolecules of the azo group-containing materials. Starting from well-known self-assembling multilayer systems with rigid rodlike azo moieties, the combination of two well-known methods was chosen to prevent crystallization and to immobilize the systems. The first method

was to use mixtures of homologous amphiphiles rather than one pure amphiphilic species in analogy with the practice in small molecule liquid crystals. The formation of mesomorphic glasses should become very probable, particularly, if the drying occurs fast and supercooling is effective.

The second method was to add water-soluble polymers to the amphiphile solutions. The addition of poly(vinyl alcohol) (PVA)^{22,25} and the complexation of ionic amphiphiles with ionic polymers²⁴ have been reported previously. Several effects can generally be expected from the addition of water-soluble polymers. The polymer additive will enhance the viscosity both in the solution and in the dry state. Particularly, in the dry state, a significant reduction of all diffusion processes can be anticipated, which will decrease the tendency of the amphiphiles to phase separate and crystallize. The increase in the solution viscosity will make spin-coating feasible and allow the use of this simple, efficient technique^{31,32} for the production of even, thin layers on glass or other substrates.

MATERIALS

In our research, we concentrated on two homologous amphiphiles (Fig. 1). Both have a rigid, rodlike azobenzene group as the core and with a hydrophobic dodecyl chain on one side and, on the other side, a hydrophilic di(hydroxyethyl) ammonium-terminated alkyl chain of 10 (**A-1**) or 6 (**A-2**) carbon atoms length. The synthesis followed procedures reported in the literature.^{13,21}

Both amphiphiles gave clear homogeneous dispersions in water after ultrasonication in the concentration range of 0–50 wt %. Their solubility in most organic solvents is limited, including polar solvents such as alcohols (less than 5 wt % in ethanol, methanol, and isopropanol). However, they are readily soluble in water/alcohol mixtures.

The restricted solubility of the amphiphiles made us choose three structurally different water-soluble polymers as polymers, viz., PVA (T_g 99°C, MW 86,000), poly(vinyl pyrrolidone) (PVP) (T_g 175°C, MW 10,000–1,000,000), and hydroxypropylcellulose (HPC) (T_g 130°C, MW 10,000–1,000,000).

SAMPLE PREPARATION

The amphiphiles were dispersed in water, alcohol, or mixtures thereof by ultrasonication at a concentration from 5 to 50 wt %. The desired amount of

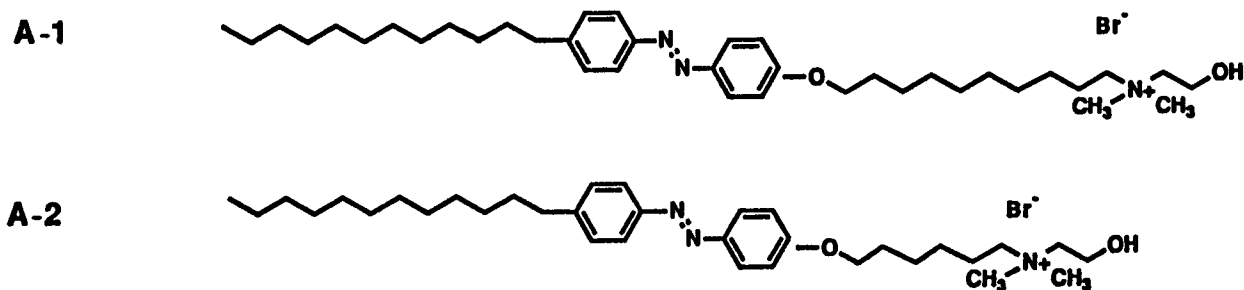


Figure 1 Structure of azobenzene amphiphiles 10-[4-[[4-(dodecyl)phenyl]azo]phenoxy]-*N*-(2-hydroxyethyl)-*N,N*-dimethyl-1-decanaminium bromide (**A-1**) and 6-[4-[[4-(dodecyl)phenyl]azo]phenoxy]-*N*-(2-hydroxyethyl)-*N,N*-dimethyl-1-hexanaminium bromide (**A-2**).

the water-soluble polymer was added to the sonicated dispersion of the amphiphile(s) and the solution was tumbled overnight to assure homogeneity. The solutions were filtered under pressure immediately before use. In the case of amphiphile-polymer solutions, the solid content was adjusted to give a viscosity suitable for spin-coating and generally kept below 20 wt %.

Glass (or quartz) slides, 2.5 × 2.5 in., were cleaned either by an ultrasonic wash in a dilute detergent solution or by 50°C 50% nitric acid solution followed by extensive rinsing with Millipore deionized water. The slides were stored under water until used. Glass slides cleaned by either method gave identical results. Glass slides hydrophobized by a vapor-phase exposure to hexamethyldisilazane were used in a few cases.

The glass slides were full-flooded with solution and then spin-coated at 500–5000 rpm for 2 min to evaporate the water. The spin-coated samples were finally dried overnight at room temperature in the open atmosphere.

CHARACTERIZATION METHODS

Optical Microscopy

Optical microscopy was performed on a Leitz Orthoplan polarizing microscope equipped with a Mettler hot stage. Orthoscopy was used to observe the quality of the spin-coated films and to detect dust particles and textures of the samples. Conoscopy was used to determine the optical character, i.e., the number and orientation of the optical axes.

Film Thickness

Film thickness was determined with a Dektak IIA. The film was carefully scratched with a tilted scalpel

blade and the height difference across the scratch determined at three different locations.

Differential Scanning Calorimetry (DSC)

DSC experiments were performed on a Perkin-Elmer differential scanning calorimeter DSC 7. In general, spin-coated films were used in the analysis. The films from several identical samples were scraped off with a razor blade to yield the needed amount of material (~ 10 mg) and transferred to the interior of the pans. The scan protocol included a cooling below 0°C, followed by a first heating cycle, a cooling cycle, and a renewed heating cycle at 20°C/min.

UV-VIS Spectroscopy

UV-VIS spectroscopy was performed to determine the local environment of the azobenzene chromophores and their order. A Perkin-Elmer Lambda 9 UV-VIS spectrophotometer was used. Film samples were spun onto quartz glass to allow transmission in the low UV range.

X-ray Diffraction

Grazing-angle high-resolution X-ray diffraction experiments were performed to determine the presence of possible multilayer structures and their relative order and layer thickness. Most experiments were performed with a high-resolution two-circle Huber diffractometer using monochromatized CuK α radiation. Step scans were performed from 1° to 30° with 0.05° to 0.1° step size for 120 s (total 10–13 h).

A few studies were performed using synchrotron radiation at the XIIB beam line at the National Synchrotron Light Source with a collection of the

X-ray diffraction patterns in 10 min. This allowed time-resolved elevated temperature diffraction studies to be performed.

RESULTS AND DISCUSSION

Properties of Pure Amphiphiles

Spin-coated films of the pure azobenzene amphiphiles rapidly developed a crystalline texture with drying at ambient conditions. The crystallization could be suppressed by storage of the samples under high humidity. Optical microscopy and DSC both of powders and spin-coated films of **A-1** and **A-2** showed an extended thermotropic polymorphism. Table I lists the observed transition temperatures and their enthalpies within parentheses. DSC scans for powders and films showed that the spin-coated samples exhibited the same transitions as those of the powders but with much broader peaks during the first cycle (Fig. 2). The phase structure of cr2 is either crystalline or highly ordered smectic, as judged from the textures observed in the polarizing microscope and the comparatively high DSC phase transition enthalpy. The small supercooling suggests an lc phase. High fluidity and the tendency to orient homeotropically and the low phase transition enthalpy suggest that lc2 is a nematic phase.

Small-angle X-ray scattering of spin-coated films of **A-1** and **A-2** gave diffraction patterns exhibiting strong crystalline lines. Indexing of the lines showed a repeat distance for the **A-1** film with an average layer thickness of 5.3 nm, and for the **A-2** film, of 4.7 nm. Molecular models showed the extended chain length of the **A-1** and **A-2** molecules to be 4.7 and 4.1 nm, respectively. This would suggest that the amphiphiles form either highly tilted or interdigitated bilayers.

The UV-VIS spectra of dilute water and methanol solutions showed absorption maxima at about 335 and 350 nm, respectively, for both amphiphiles. Kunitake et al.²³ reported a λ_{\max} of 300 nm for H-aggregates (crystalline bilayers with the chromophores perpendicular to the layer plane), 330–340 nm for lc bilayers and 355 nm for monomeric and 360–390 nm for J-like aggregates (tilted chromophores) of azobenzene amphiphiles. The amphiphiles thus formed bilayers in the water solutions although light scattering suggested aggregate sizes less than 10 nm, i.e., liposomes were not present. (Kunitake et al.'s studies suggested small globular or disklike aggregates that are most probably small bilayer fragments for azobenzene amphiphiles of a similar structure as that of ours.³⁰) Spin-coated films of **A-1** and **A-2** showed broad peaks that could be resolved into two peaks at a λ_{\max} of about 307 and 380 nm (**A-1**) and 320 and 380 nm (**A-2**). Ringsdorf et al.¹⁹ also observed for their L-B deposited lc side-chain polymers a very broad π - π^* transition of the azobenzene resulting from different surroundings and aggregational states of the chromophores in the L-B film. A hypsochromic shift relative to the chromophore in dilute solution will only occur if the chromophores are tilted less than 35.3° from the normal.³³

Studies of mixtures of **A-1** and **A-2** showed that the crystallization was strongly delayed in samples with a weight ratio of **A-1** to **A-2** of 9/1 to 7/3. The UV-VIS of fresh films of **A-1/A-2** in a ratio of 4/1 showed a single transition peak at 343 nm, typical of an lc phase. DSC of scraped-off spin-coated films showed during the first heating cycle several very weak transitions with enthalpies less than 2 J/g. Small-angle X-ray diffraction showed very few broad peaks, which again suggested the formation of an lc phase.

Table I Bulk-Phase Transitions of Pure Amphiphiles as Determined by DCS and Thermal Microscopy

Sample	Methods	Phase Transition Behavior ^a							
A-1 , powder	Microscopy	cr1	70°C	cr2 (?)	150°	lc1	165°C	lc2	> 220°C
A-1 , powder	DSC		75°C (77.3)		157°C (20.7)		164°C (2.6)		
A-1 , film	DSC		50°C (0.6), 72°C (67.8)		154°C (18.5)		164°C (2.5)		
A-2 , powder	Microscopy	cr1	65°C	cr2 (?)	141°C	lc1	215°C	lc2	> 230°C
A-2 , powder	DSC		-16.4°C (3.0), -10°C (~ 1)		135°C (28.5)				
A-2 , film	DSC		-6°C (~ 2.0)		137°C (27.2)				

^a Transition temperatures (°C) and enthalpies of transitions [J/g] in parentheses. cr1: crystalline; cr2 (?): crystalline or highly order smectic; lc1 and lc2: liquid crystalline.

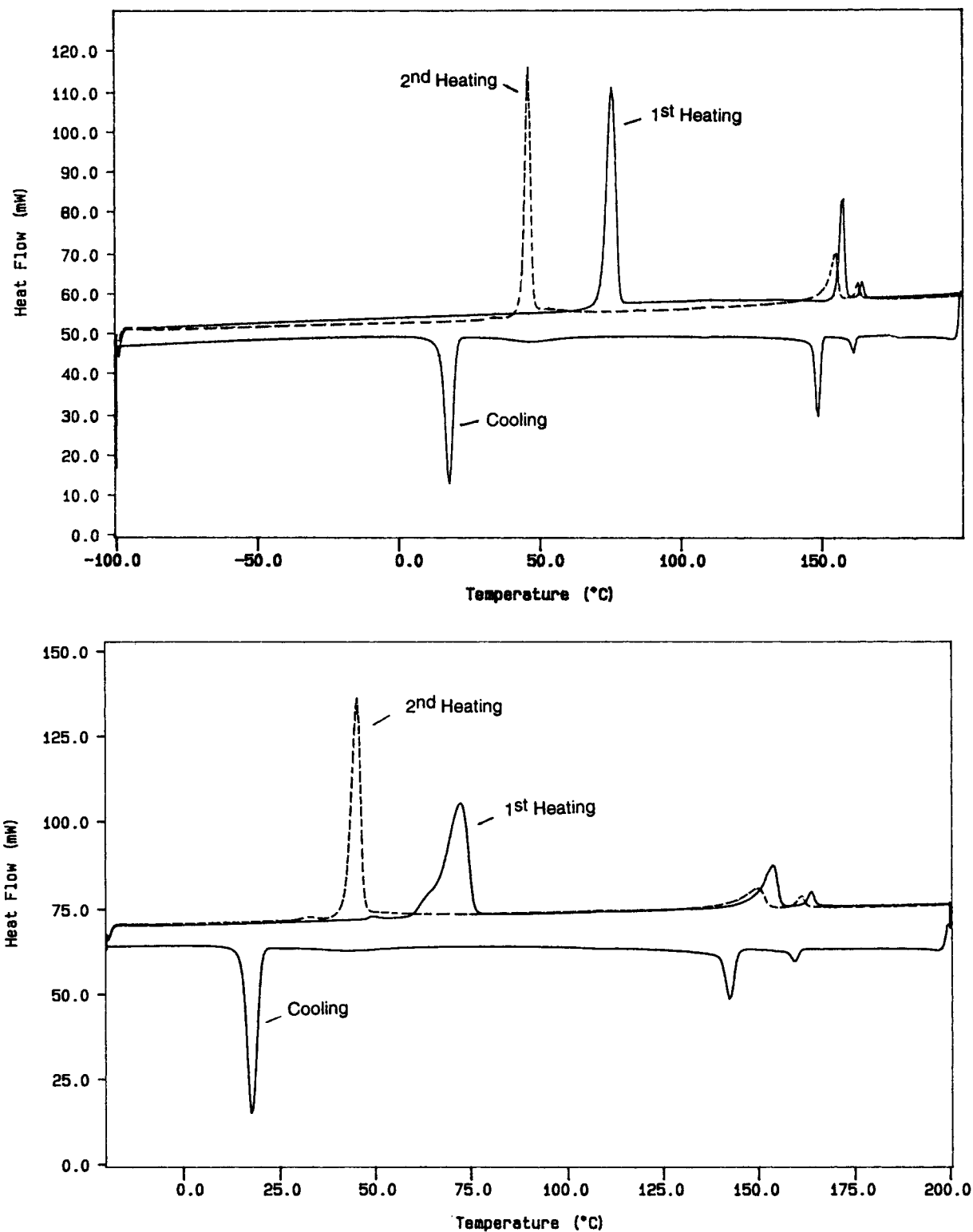


Figure 2 DSC scans showing thermal transitions during a first heating cycle, a cooling cycle, and a second heating cycle for a (A) powder and (B) spin-coated film of azobenzene amphiphile A-1.

This confirmed that the idea to mix two different amphiphiles to suppress crystallization was, at least to a certain extent, valid. It also confirmed our assumption that the two homologs **A-1** and **A-2** due to their similar chemical structure are compatible in the mesophase.

Mixtures of Azobenzene Amphiphile and Polymers

In a first series of experiments, solutions of the azobenzene amphiphile, **A-1**, and the water-soluble polymer, HPC (MW 1,000,000), were prepared with the weight ratio **A-1** to HPC varied from 100 : 0 to 50 : 50 and spin-coated to yield film thicknesses of 1 μm or less. All films containing more than 80 wt % of **A-1** gave cloudy films. Microscopic observation under polarized light showed these films to be crystalline.

Compositions containing 75 wt %, or less, gave films with excellent optical clarity. Microscopy showed the samples to be homogeneous, homeotropic, and uniaxial with the optical axis perpendicular to the film surface. UV-VIS of the thinner films showed an absorption maximum at 330 nm, which agrees with a perpendicular orientation of the chromophores.

All films did, however, develop birefringence after some days storage under ambient conditions. It thus appeared to be necessary to suppress the crystallization of the azobenzene amphiphiles by using a mixture of **A-1/A-2**. Samples were accordingly prepared with a varied ratio of **A-1/A-2** but with a constant ratio of HPC, MW 1,000,000, to the cumulated content of amphiphiles at 1 : 3. Homeotropic, uniaxial samples were obtained with **A-1/A-2** ratios between 9/1 and 7/3. Samples with a higher ratio than 9/1 or a lower ratio than 7/3 became opaque and scattering within several days due to crystallization of some or all of the amphiphile molecules. The best results were obtained with ratio of **A-1/A-2** of 4/1.

The UV-VIS spectrum of a 0.7 μm -thick film containing amphiphile ($A = \mathbf{A-1/A-2} = 4/1$) and HPC in the ratio 3/1 showed an absorption maximum at 330 nm. DSC of a film with the same A/P composition showed only very broad transitions during the first heating cycle.

In another series, the amphiphile ratio **A-1** : **A-2** was kept constant at 4/1 and the polymer content was varied. It was found that samples with an amphiphile/polymer ratio higher than 4/1 tended either to crystallize or to form an lc texture. Stable,

homeotropic, uniaxial samples were obtained with polymer contents of 25 wt % up to approximately 60 wt %. This shows that these polymer contents immobilized the "multilayer structure" significantly without interfering with its formation. Samples with an even higher polymer content were not birefringent.

Type of Polymer

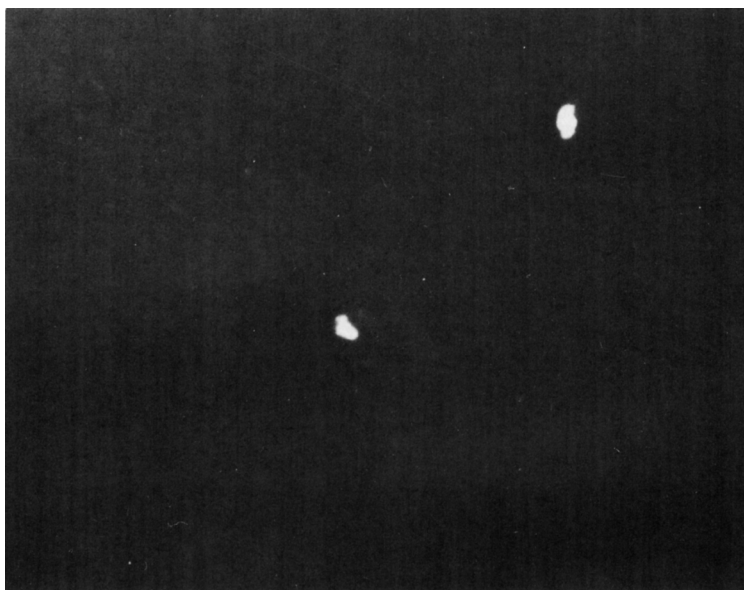
We decided next to study in more detail the influence of type and molecular weight of the polymer. Three different polymers were tested: PVP, HPC, and PVA. PVA did not yield optically clear films. The results for PVP and HPC were very similar. Films with the same A/P ratio of 3/1 and with polymers of MW 1,000,000 gave, thus, the same absorption maximum and very similar DSC spectra and X-ray diffractions.

The molecular weight of the polymer has a strong influence on the stability of the self-assembled multilayer aggregate. Particularly, it was found that the tendency of spin-coated samples to form an lc texture increased with decreasing MW. Stable samples were obtained with molecular weight higher than 60,000 for HPC and 40,000 for PVP. The different molecular weights also influenced the dynamics of the spin-coating process. This was illustrated by the effect that dust grains or other impurities had on the quality of the samples. If a polymer with high MW was used, dust grains appeared as birefringent spots on the black homeotropic background in the polarizing microscope [Fig. 3(A)]. An increasing birefringent trace was observed with decreasing MW of the polymer [Fig. 3(B)], which implies a distorted boundary layer extending far into the self-assembled material. Most interestingly, this trace was deformed in the way that it yielded a frozen picture of the hydrodynamic shielding effect of the grain during spin-coating.

Film Thickness

A more systematic study of the influence of film thickness was also performed. It was found that the film thickness has a high influence on the prevention of texture formation in samples, the composition of which was chosen to suppress crystallization. In samples thinner than 0.3 μm , a texture was never observed, no matter what the composition. With layers thicker than 3.0 μm , a long-term stable texture-free self-assembly was not achieved. Layers with thicknesses less than 1.5 μm were homeotropic

A



B

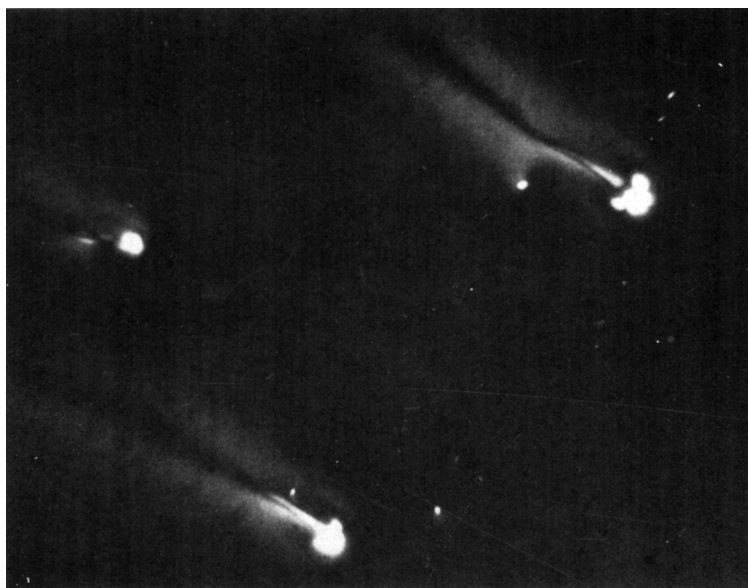


Figure 3 Microphotographs of spin-coated films composed of 75 wt % of a 4 : 1 mixture of azobenzene amphiphiles **A-1** and **A-2** and 25 wt % of PVP of MW (A) 360,000 and (B) 10,000 viewed under cross-polarized light. Bright spots are dust particles that cause a birefringent trace in case B.

and uniaxial and long-term stable, if the above-discussed composition regimen and medium-to-high MW polymers were used and if the samples were kept at temperatures below approximately 45°C. This influence of the layer thickness could result either from an orientation effect from adsorbed monolayers of the amphiphile molecules at the glass–film and film–air interfaces or from a slower evaporation of water in thicker films yielding time for relaxations to occur.

Structure of Self-assembled Films

UV-VIS spectroscopy and the optical properties of the homeotropic uniaxial films and their pure amphiphile analogs suggest that the chromophores are oriented next to each other perpendicular to the surface most probably in an interdigitated bilayer.

Our general observation is that the described self-assembling materials have a very strong tendency to orient themselves homeotropically on the glass surface even in the presence of certain polymers. Two effects can contribute to that behavior. First, there is a very strong anchoring effect of the hydrophilic groups of the cationic amphiphiles, **A-1** and **A-2**, on hydrophilic glass surfaces. This was confirmed by experiments, where alcoholic amphiphile solutions were dropped onto a glass surface and the solvent was slowly evaporated. Homeotropic alignment resulted. Dendritic patterns resulted if a hydrophobic substrate was used under the same conditions. Spin-coating of the amphiphile–polymer solutions gave, however, continuous homeotropic uniaxial films also on hydrophobized glass surfaces.

The UV-VIS data and the light-scattering experiments as well as Kunitake et al.'s observation for similar systems suggest that the amphiphile molecules are present in the spin-coating solutions in the form of submicron (less than 10 nm) bilayer aggregates. During the spin-coating process, the initially dilute, amphiphile/polymer solution becomes more concentrated, as the solvent rapidly evapo-

rates. It can be assumed that this leads to the intermediate formation of a lamellar lyotropic mesophase at some higher concentration. If domains of a lamellar phase form during the spin-coating, the mechanical force acting on lamellar mesophase domains would cause an alignment parallel to the mechanical field. Especially in the case of polar anchoring, this would lead effectively to the observed alignment of the layers parallel to the glass surface.

Since most samples were optically clear during the spin-coating process and immediately thereafter, it can be assumed that this orientation is originally obtained in all spin-coated samples. Optically opaque, scattering samples are the result of secondary processes, i.e., crystallization of the amphiphiles and the formation of lc textures. They may happen in time periods of a few seconds up to several months after spin-coating. The occurrence of these deteriorations depends strongly on the composition of the spin-coated materials and many formulations resulted in long-term stable, well-ordered samples. The formation of lc textures might be an indication of changes in the phase structure caused by fluctuations in residual water content or the occurrence of kinetically hindered reorientation processes.

Another possible film-forming process would be that the amphiphile molecules exist in the water solutions as disklike submicron bilayer aggregates and that these “disks” remain more or less intact through the spin-coating process. The aggregates become evenly distributed in a continuous polymer matrix of a comparatively even thickness due to the shear orientation of the polymer chains during the spin-coating. These bilayer aggregates would not scatter light significantly due to their submicron size.

Recording of Birefringent Spots

The evaluation of the recording properties of the composite films was focused on films that were homeotropically ordered and optically uniaxial. The films were irradiated with a vertically polarized ar-

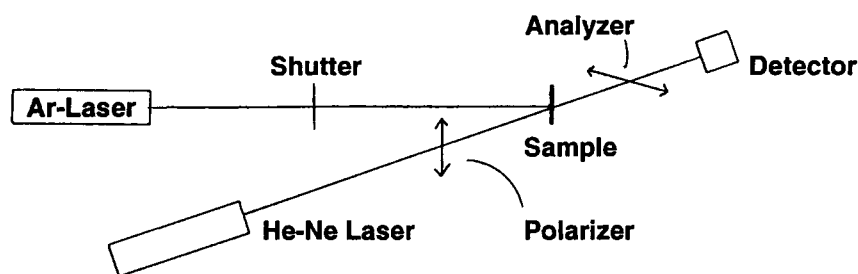


Figure 4 Experimental setup for recording birefringent dots.

Time variation

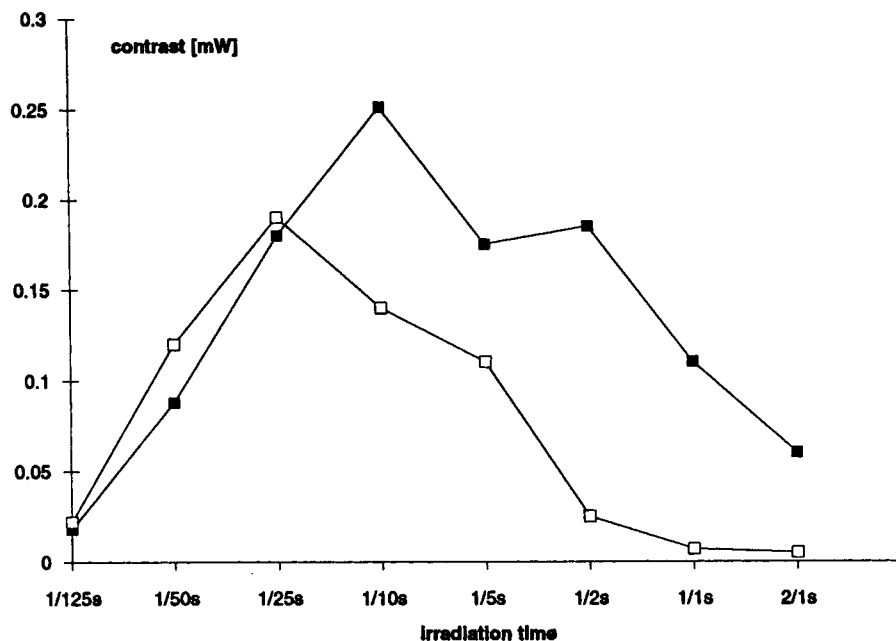


Figure 5 Induced birefringence vs. irradiation time for films composed of 75 wt % a 4 : 1 mixture of azobenzene amphiphiles A-1 and A-2 and 25 wt % of PVP: (—■—) MW 10,000; (—□—) MW 1,000,000.

gon laser at $\lambda = 351.1$ nm at powers of 0.1–0.5 W corresponding to laser intensities of 20–100 mW/mm² at the sample. The beam was impinging the film perpendicularly to the film plane, i.e., along the

optical axis of the homeotropically oriented films. The irradiation time could be varied by using different shutter speeds or by repeated exposures at a given shutter speed. The birefringence of the formed

Repeated Irradiations on One Spot

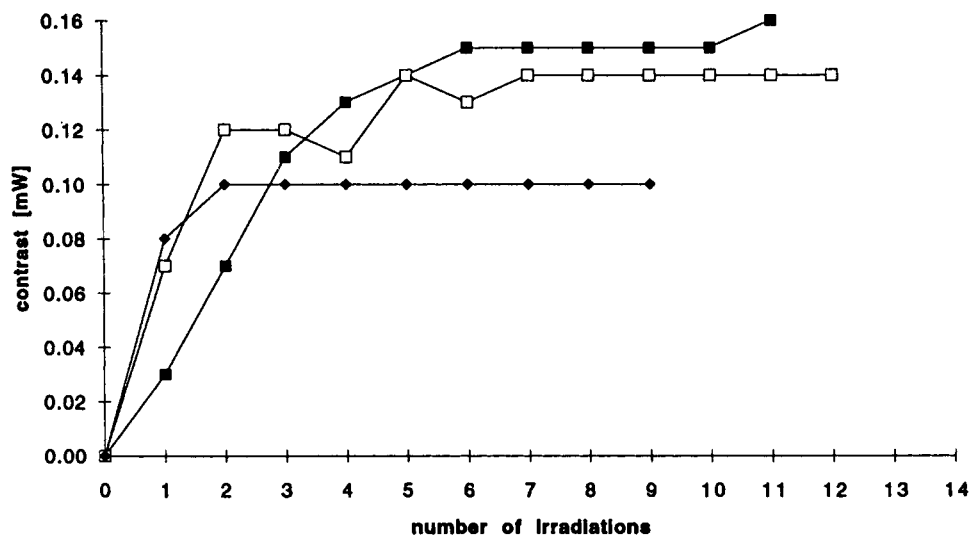
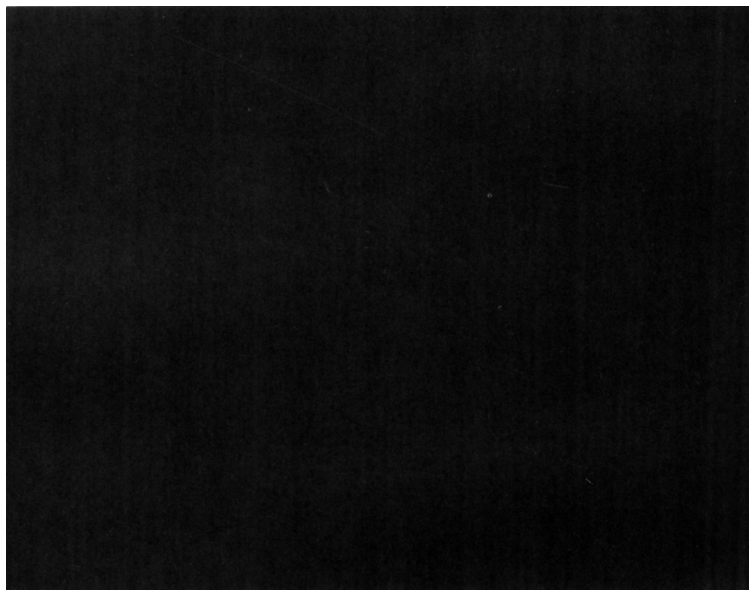


Figure 6 Induced birefringence vs. number of 1/125 s pulses at different laser powers: (—■—) 20 mW/mm²; (—□—) 40 mW/mm²; (—◆—) 100 mW/mm².

A



B

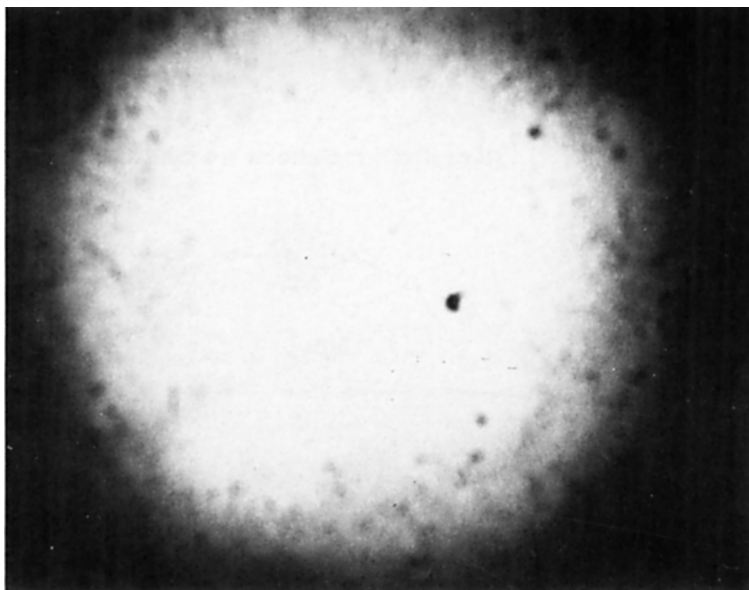
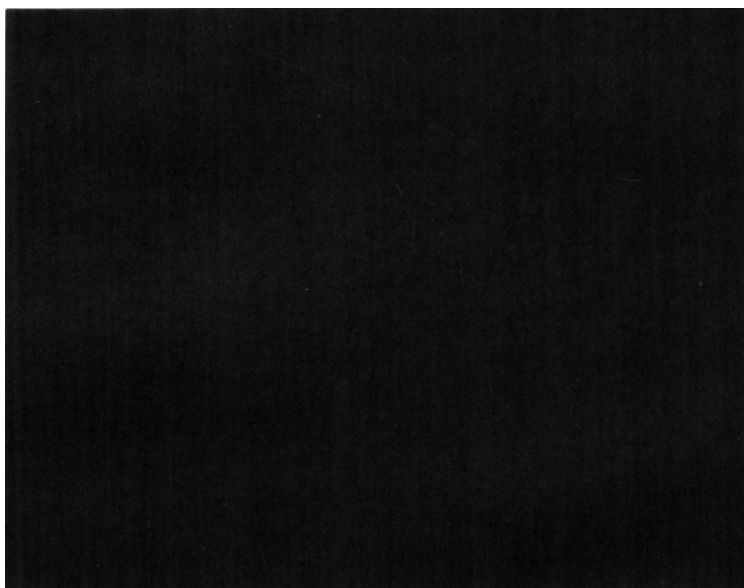


Figure 7 Microphotographs of a spin-coated film composed of 75 wt % of a 4 : 1 mixture of azobenzene amphiphiles **A-1** and **A-2** and 25 wt % of PVP of MW 1,000,000 viewed under cross-polarized light (A) before irradiation, (B) after irradiation, (C) after erasure with a 90° rotated beam, and (D) after repeated irradiation with original beam orientation at 351.1 nm for 1/25 s at 20 mW/mm².

C



D

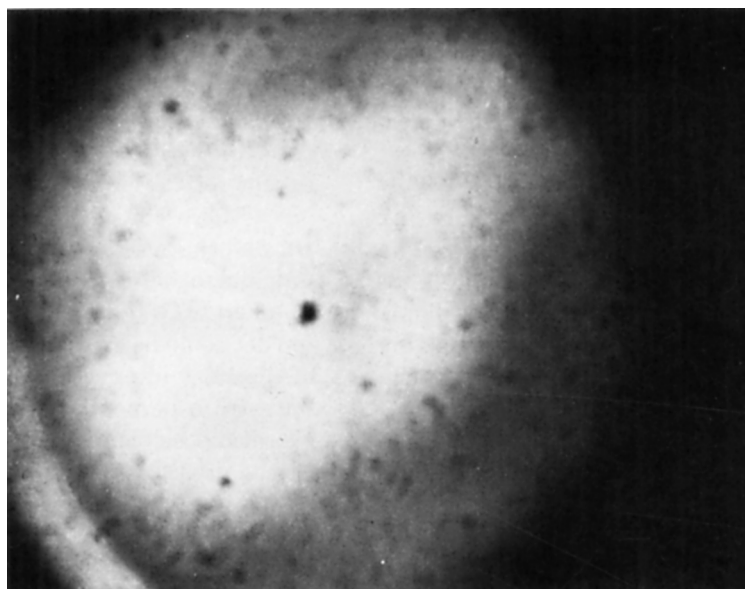


Figure 7 (Continued from the previous page)

dot was monitored using the 632.8 nm beam of a He-Ne laser beam and a detector (Fig. 4). The polarizer and analyzer in the He-Ne laser beam path were crossed to give full extinction before irradiation of the sample with the argon laser beam.

Irradiation with 20 mW/mm² continually for increasing times gave increased birefringence of the recorded dot to a certain point after which longer times led to a decreasing brightness (Fig. 5). Microscopy of the recorded dots showed them to be

birefringent and polarized parallel to the incident laser beam and to exhibit an extreme biaxiality. After long irradiation times, samples made with PVP became again isotropic, whereas samples made with HPC showed a crystallized texture. At higher laser powers, the recorded dot in PVP samples showed a black hole in the center where, due to the laser beam profile, the energy is highest. Conoscopy of the "black hole" showed that this area had returned to its uniaxial state. The HPC samples showed a crystallized central area.

Irradiation of samples containing polymers of different molecular weight showed that the contrast of the dot increased with decreasing molecular weight (Fig. 5). This could be explained with a higher local mobility in samples with lower molecular weights. PVP and HPC showed basically the same behavior.

When an increasing amount of light energy was applied to the sample in many short pulses intermittent with a long resting time, the contrast increased up to a saturation level (Fig. 6). A higher final contrast was obtained with a lower laser power. This suggests that the loss in contrast observed in the continuous irradiation case was caused by a heating of the irradiated area, resulting in a reorientation.

Both sets of experiments showed the systems to have a high sensitivity with well-defined dots obtained with a low laser energy (0.1 mWs/mm^2). This was surprising since there has to be a very low overlap between the vertically oriented laser beam and the perpendicularly oriented dipole moments of the chromophores. Calculations show that the used laser energy will only heat up the sample $1\text{--}2^\circ\text{C}$. This temperature increase is not expected to cause any change in the uniaxial orientation of the azobenzene amphiphiles.

Finally, the irradiation angle between the sample plane and the beam was varied from 90° to 22° by rotating the sample. The dot size changed from circular to oval and the contrast decreased with decreasing angle. The orientation of the birefringence did not change. This was surprising since the interaction of the polarized laser beam with the ordered azo-dye molecules was expected to show some dichroism.

The wavelength dependence was also studied by comparing the energy needed to record a birefringent dot of the same intensity as obtained optimally at 351.1 nm . The film sensitivity at $\lambda = 333.6 \text{ nm}$ was approximately the same as at 351.1 nm . At 363.8 nm , 10 times higher energy was required to give a dot of equivalent intensity. Much higher energies were required to record laser marks with visible laser

lines. Five seconds' exposure at a power of 100 mW/mm^2 was thus needed at 472.7 nm . Very high energies were required for any recording to occur at 514.5 nm . The resulting spots, although still polarized with the beam, were much larger than the nominal beam size. The sensitivity of the films increased with thickness at the visible wavelengths.

Write/Erase Methods

The results of the different irradiation times indicated that it should be possible to erase the laser marks with the very same writing beam by a saturation in the case of PVP-containing composite films. This saturation method was demonstrated using the 351.1 nm line by writing a dot with a low energy (0.1 mWs/mm^2), erasing the dot with higher energy ($\sim 20 \text{ mWs/mm}^2$), and then writing again on the erased area. The contrast of the second dot was markedly lower than the first dot, implying that some degradation of the material had taken place. The most probable mechanism for this erasing is a local heating of the recorded area, leading to enough mobility to cause the azobenzene amphiphiles to adopt the orientation of the surrounding undisturbed self-assembled molecules. Erasing with other laser beams of the same size but of different wavelengths might therefore also be possible but was not investigated.

Another method to perform write/erase cycles is similar to the method of Natansohn et al.⁹⁻¹¹ In this case, the writing and erasing beam were identical except for the polarization plane being rotated by 90° . Microscopical analysis of the erased area showed that a transformation back to the original uniaxial, quasi-isotropic state had taken place [Fig. 7(A) and (C)]. Experiments showed that the written dot could be extinguished by a second irradiation of the same intensity and time as the writing beam but with a perpendicular polarization direction. It was also possible to rewrite a good quality dot in the erased area [Fig. 7(D)]. This process worked basically the same in films with polymers of different molecular weight and both in PVP- and HPC-containing films as long as the used laser energies were not high enough to cause erasing in the PVP and crystallization in the HPC samples. It is worth noting that the erasure leads to the reformation of a uniaxial orientation in our system, whereas Natansohn et al.'s samples returned to the original random orientation. The sensitivity of the self-assembled systems are also much higher. Our needed energy for both recording and erasing is 0.1 mWs/

mm², and Nathansohn et al.'s¹¹, 40 and 4 mWs/mm², respectively.

CONCLUSIONS

Self-assembly of azobenzene amphiphiles in the presence of certain water-soluble polymers has been shown to yield a unique write/erase recording material within certain compositions and film thicknesses. The films resulting from spin-coating are homeotropic and uniaxial and thus appear to exhibit the optical properties of a single crystal. They show very high sensitivity and fast recording of birefringent dots. Erasure can be achieved equally fast by rotating the beam 90° and restoring the original homeotropic uniaxial orientation of the chromophores. It is remarkable that this process allows a fast switching between a quasi-isotropic and birefringent state, especially since the average orientation of the electric dipole moment of the chromophores is perpendicular to the polarization plane of the writing beam. It has not been possible to determine the microscopic arrangement of the components in these self-assembled composite films. No simple answers have been found to what happens in the sample during writing and erasing.

This paper is dedicated in memory of Dr. Alan Buckley whose strong support and encouragement were essential for the pursuit of this research. Drs. P. J. Harget and C. Saw are acknowledged for their X-ray diffraction studies and Dr. H. N. Sung for performing the light-scattering experiments. Dr. R. Norwood is thanked for his valuable comments to this paper.

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Received August 11, 1993

Accepted January 9, 1994