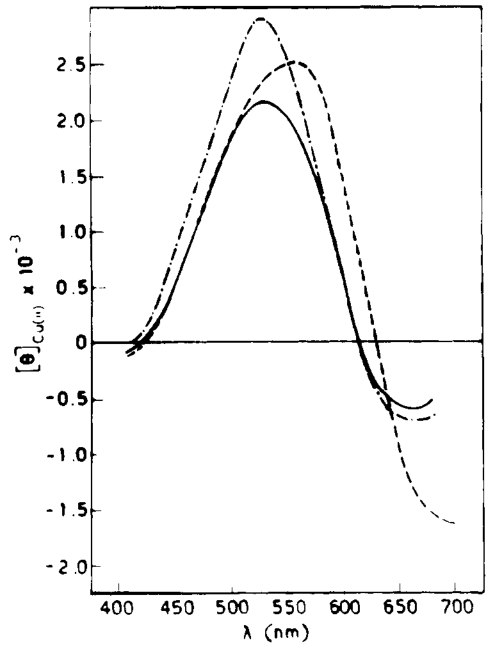

Figure 8. CD spectra of the low-pH cupric complexes of (L-His)$_n$ and poly(L-diaminobutyric acid) in the visible region: (—) (L-His)$_n$–Cu(II) (from ref 2); (···) (L-His)$_n$–Cu(II) (our measurements); (- - -) (L-diaminobutyric acid)$_n$–Cu(II) (from ref 9).

range and at the very low Cu/peptide ratio used by Wasylishen and Cohen, instead of complex I a complex in which imidazole nitrogens only are coordinated to Cu(II) is formed immediately after addition of the metal ions. Significantly, between pH 3.5 and 4.0, the transformation of this complex into complex I is very slow, so that the above NMR measurements very probably refer to the former. At pH ~5 the rate of formation of complex I is much faster, so that the decreased relaxation effect of Cu(II) on (L-His)$_n$ above pH 3.5 can be explained by the presence of increasing amounts of complex I in the mixture with consequent slower exchange of cupric ions which are bound to deprotonated peptide nitrogens.

Acknowledgment. The authors are indebted to Mrs. Clara Benvegnu' for her skillful technical assistance.

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Mechanophotochemistry

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ABSTRACT: A model is presented for materials that deform due to exposure to light. This model is based on the conclusions drawn from mechanochemistry that chemically induced ionizations cause changes in the dimensions of porous polyelectrolytic gels. The mechanophotochemical properties of poly[*p*-(*N*,*N*-dimethylamino)-*N*-γ-D-glutamanilide], that displays up to 35% dilation in each dimension when exposed to light, are presented as proof of the correctness of the model.

Dilation and contraction of synthetic fibers due to changes in the state of ionization of polyelectrolytic gels have been observed as early as 1950.[1] The authors noticed that expansion of polyacrylic acid gels could be induced by suspension in alkali solutions, while restoration of the original size took place when the solution was titrated with acid. Very spectacular were the experiments on threads of poly(vinyl phosphate).[2] On addition of strong alkali the threads elongated to about three times their original length, while subsequent addition of acid caused rapid reversion to the original length. A proposal was put forward to utilize this phenomenon for conversion for chemical into mechanical energy.[3] Continued research in the field of "mechanochemistry" produced deeper understanding of the phenomenon[4,5,6] and many more materials were reported to be suitable for conversion of chemical energy into mechanical motion.[4] Two distinguishable contractile and elastic mechanisms govern the phenomenon. One of these is restricted to amorphous polymers and the other to crystalline polymers. In the former the initial and the deformed states are both amorphous, while in the latter the polymer undergoes a crystal to amorphous transition (or vice versa). Excellent reviews describing these mechanisms in great detail have appeared in the literature.[5,7]

When a polymer having a random network structure is elongated, the chain's end-to-end vector both increases in length and aligns itself in the direction of the elongation. Simultaneously, the number of configurations that the chains could have assumed prior to the application of the stress is diminished, leading to a decrease in entropy. It is to a large measure this change in entropy that is responsible for the retractive force. It should be pointed out that in a non-cross-linked network the individual chains have an option of rearrangement in a way that avoids the decrease in entropy and thus does not exhibit an elastic response. Too much cross-linking, on the other hand, stiffens the material and renders it inflexible.

Closely related to the elasticity mechanism is the swelling of an amorphous network in an open thermodynamic system. In the absence of an externally applied force, the deformation results from the free energy of interaction between the chain units of the network and monomeric species of the medium in which it is immersed. Changes in the chemical and thermodynamic nature of the medium will alter the quantity of swelling of the network. This change in swelling manifests itself in a uniform dilation or contraction in all three dimensions. Thus, in amorphous polyelectrolytes the driving force for the isotropic deformation is osmotic in origin.

The relationship between the macroscopic size of the polymer and the relative configuration of the individual polymeric molecular chains, as described in connection with the elastic response, can explain the contraction mechanism due to a phase transition. In contrast with an amorphous polymer, in the crystalline network the individual chain axes are rather well oriented and the end-to-end vectors are far larger. In many cases, stretching of polymers produces crystallites with chain axes parallel to the direction of the elongation. This crystallization reduces the retractive forces which are associated with the residual amorphous regions since the mean degree of extension $r/r_{\max}$ is reduced. Conversely when a crystalline polymer melts, the dimension in the direction of alignment has to shrink considerably. Alteration of the chemical environment in a way that would produce ionizations of the functional groups or diminish the intrachain hydrogen bonding that may be a factor in the lattice formation may produce a phase transition accompanied by contraction. The opposite change should lead to lengthening. Therefore, crystalline polymers that have functional groups that can be altered in response to a change in the chemical environment can be used as working substances for the direct conversion of chemical energy into mechanical energy. Such a mechanical–chemical system should be far more sensitive and be a superior mechanochemical converter than one based on the former mechanism mentioned.[5] In some respects such materials can be regarded as artificial muscles, yet one should bear in mind that in natural muscle the deformations are constant in volume and due to a totally different mechanism.

This article deals with induction of mechanical deformations in materials by "photochemistry" rather than "chemistry". The observation of such effects has been previously reported in the literature. A spiropyran polymer developed by Vanderwijer and Smets[9] as a photochromic material was found to display a 3% light-induced deformation. Lovrein[10] reported a photoviscosity effect of various polymer–dyes combinations. A decrease in viscosity was effectuated by light in solutions containing chrysophenine, a bis(azobenzene) dye that is known to undergo a cis–trans photoisomerization, and poly(methyacrylic acid). Van Der Veen and Prins[11] amplified Lovrein's work and reported that poly(methyacrylic acid) gels buffered with (*p*-phenylazophenyl)trimethylammonium iodide, a cis–trans photoisomerizable dye, show a 10% elongation when irradiated for 10 min with a focused intense source of light. Unfortunately, these results, interesting and important as they are, are not easy to understand and interpret. It would seem that "mechanophotochemistry" could also be constructed by a more systematic approach based on the well-developed foundations of "mechanochemistry". These physical properties are conferred by: (a) high polymeric amorphous or crystalline structure, (b) the distinguishing feature of porous cross-linked gel matrices, and (c) a suitable combination of ionizable groups. While principles "a" and "b" seem to be absolutely unalterable, "c" seems to be amenable to control and to variation. The changes in macroscopic dimensions that are imposed on the material by the ionized groups associated with the polymeric backbone certainly are not dependent on the method which caused the ionization. Thus, it is immaterial whether the ionization occurred due to chemical changes in pH, chemical or electrochemical oxidations and/or reductions, or photoionization. However, the demands imposed on the photoionization reaction are rather stringent. It must produce a charged species whose lifetime is long enough to permit the polymer to deform. Mechanochemistry is notorious for its sluggishness, with rearrangement times of the order of seconds. Therefore, the choice for a suitable photoionization reaction is limited. One may consider a dynamic model whereby the incident light produces a statistical concentration of short-lived ions or zwitterions that is sufficient to cause deformations. It seems that this last approach would require rather intense light sources for production of meaningful ion concentrations, and the deformation would persist practically only when the light is on. Thus a desideratum would be that the induced charged ion should be stable.

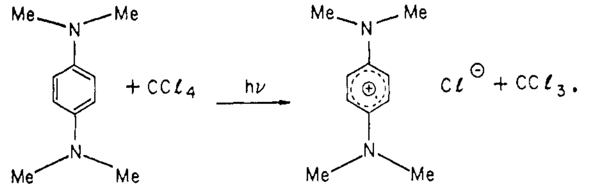

Figure 1. The photoionization of *N*,*N'*-tetramethyl-*p*-phenylenediamine in carbon tetrachloride.

With the above-mentioned considerations in mind, a photoionization reaction that conforms with the specified needs and is of wide scope was chosen.[12-14] *N*,*N*-Tetramethyl-*p*-phenylenediamine is photoionizable to a stable ion radical in the presence of an acceptor such as carbon tetrachloride,[12] as shown in Figure 1. As indicated in the references cited, other groups besides phenylenediamine follow the course of the same photoreaction: groups like tetrathiafulvalene, tetraselenafulvalene,[14] ferrocene,[13] and many leuco dyes. For reasons of simplicity and availability phenylenediamine was chosen as the photoionizable group. *N*,*N*-Dimethyl-*p*-phenylenediamine can be easily connected to a polymer via the unsubstituted amine group to form amides. The resulting amides are different from *p*-phenylenediamine and an initial investigation was undertaken to obtain information on the photochemistry of such amides in the presence of carbon tetrachloride. This study is detailed in a following section and it showed that photoionization occurs for such amides too. It should be stressed that while under certain conditions the photoreaction is irreversible photochemically or thermally, the ion radical is reducible both chemically and electrochemically.

For the satisfaction of requirements "a" and "b" discussed above, a poly(γ-x glutamate), where x represents the photoionizable group mentioned above, was chosen. This polymer backbone has been employed successfully

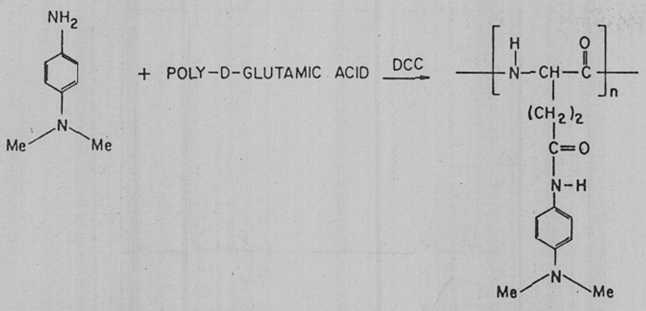

Figure 2. The reaction sequence that was used for the synthesis of the mechanophotochemical system.

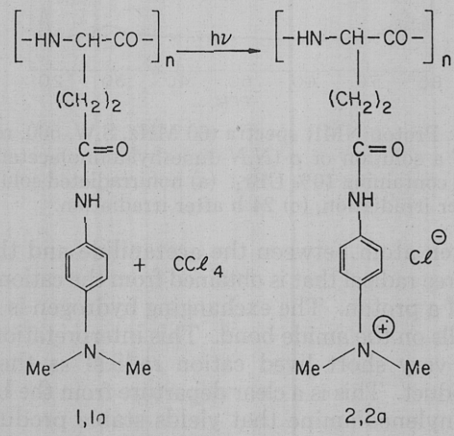

Figure 3. The photochemical reaction that leads to mechanophotochemistry.

in mechanochemistry[8] and has the added advantage of being orientable in magnetic[15] and electric fields. The latter property may yield some bonuses in the future.

Accordingly, poly-4-(*N*,*N*-dimethylamino)-*N*-γ-D-glutamanilide (**1**) was synthesized by the reaction sequence shown in Figure 2. This polymer **1** was subsequently cross-linked to a gel **1a** by 2,6-bis(bromomethyl)-naphthalene. It was expected that irradiation of **1a** in the presence of carbon tetrabromide or carbon tetrachloride would produce photooxidation of the anilide that branches off the backbone as shown in Figure 3. In turn, the photoionization was expected to trigger mechanical deformations, in line with the rules of mechanochemistry.

Results and Discussion

Polymeric films 1.15 mil thick were prepared from **1a** and irradiated as outlined in the Experimental Section. Figure 4 is a photograph of such a film in three different stages of deformation. In (a) the film is shown prior to the exposure and in (b) and (c) the same film was photographed following two different exposure times. The magnification of the camera and the frame were kept constant for all three cases and therefore one observes the actual deformations that the material experiences due to the irradiation. Though not shown in the photograph, the thickness of the film expands proportionately. The observed dilations are plotted in Figure 5 as a function of exposure time. These films displayed a maximum light-induced deformation of 35 ± 2% in each dimension. This represents a volume change of 146%. There was no prealignment of the polymer on the molecular scale and therefore anisotropy of the deformation was neither expected nor observed. Care was exercised to prevent any externally imposed stress or strain on the sample during the irradiation. This was the reason for the choice of experimental conditions that permitted the films to be freely suspended in an envelope of liquid diluent. However, due to the fixed geometry and shape of the film, some regions have more freedom to deform than others (for instance the outside boundaries) and therefore stresses develop during the irradiation. Due to these stresses, the irradiated sample tends to curl. The additional benefit that was drawn from the liquid envelope was the constant temperature that was maintained during the exposure. Throughout the irradiation the temperature was maintained at 27 °C to make certain that the observed effect was due to actinic radiation as opposed to a thermal effect. A thermal effect was also discounted on the basis of a control experiment where the film and the diluent were heated in the dark to 60 °C for 5 min. Under these conditions no deformations were observed. It was also noticed that the rate of the deformation is dependent on the intensity of the light source. These experiments lead to the conclusions that the observed effect is due to photochemistry and that the experiments were conducted with light sources whose intensities were low enough to command the rate, rather than have the mechanical response of the polymer dictate the rate.

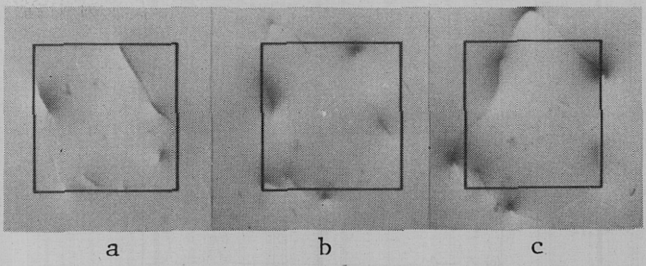

Figure 4. Mechanophotochemistry in action. Photographs of a piece of film of photodeformable material following various exposure times to UV light. The frame side is 2 mm. In (a) there has been no exposure and the film is smaller than the frame. In (b) and (c) the frame was kept constant and the films were irradiated. Notice that the exposed material is larger than the frame.

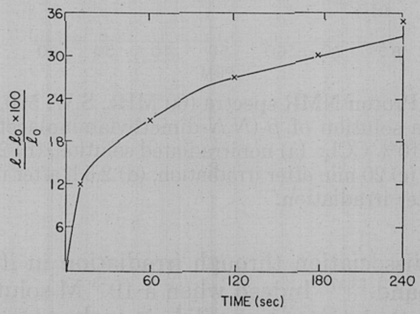

Figure 5. Plot of observed deformations vs. exposure time. l_0 represents initial length and l represent final length.

In order to determine whether a photoionization reaction as shown in Figure 1 is taking place along the polymeric backbone, some of the results were compared with those obtained for *p*-(*N*,*N*-dimethylamino)acetanilide.[16] This molecule is almost identical with the photoactive group that branches off the polymeric backbone. Therefore it was expected that a clear understanding of the photochemistry of the acetanilide would shed light on the photochemistry of polymer **1** and gel **1a**. With this notion in mind the photochemistry of *p*-(*N*,*N*-dimethylamino)-acetanilide was compared to that of *p*-phenylenediamine first.

The absorption spectra of *p*-(*N*,*N*-dimethylamino)-acetanilide in carbon tetrachloride and in carbon tetrabromide were investigated. These spectra revealed that in the halogenated solvent the absorption is shifted somewhat toward the visible. The shift may be due to a weakly bound π-donor–haloalkane complex that can

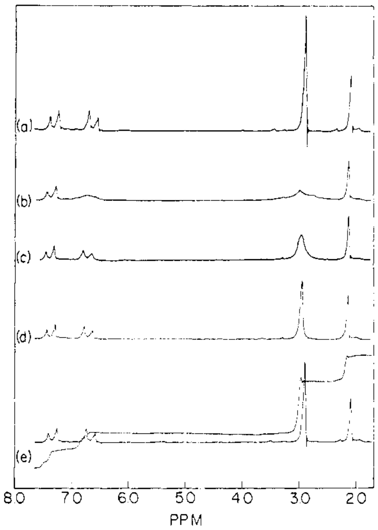

Figure 6. Proton NMR spectra (60 MHz, S.W. 500, reference Me_4Si) of a solution of *p*-(*N*,*N*-dimethylamino)acetanilide in $DCCl_3$ and 10% CCl_4: (a) nonirradiated solution, (b) 2 min after irradiation, (c) 20 min after irradiation, (d) 2.5 h after irradiation, (e) 24 h after irradiation.

undergo dissociation through irradiation in its charge-transfer band.[13,17] Indeed when a 10^{-3} M solution of *p*-(*N*,*N*-dimethylamino)acetanilide in carbon tetrachloride was irradiated with a 0.5 m W/cm^2 UV light source at 3650 Å a blue precipitate formed, just as *N*,*N*′-tetramethyl-*p*-phenylenediamine yields Wurster's Blue Salts under identical conditions.[12] A charge-transfer complex and dissociative reduction of the organic halide by the amine were proposed to be involved in the mechanism for the photoionization of the latter.[12] However, as the well-documented case of photoreduction of aromatic ketones by amines suggests,[19] the dissociating complex may well be an exciplex. In addition, it was shown that the oxidized anilide displays an EPR signal[18] characteristic of a free radical. However, an irradiated solution of chloroform containing 10% carbon tetrachloride and 10% *p*-(*N*,*N*-dimethylamino)acetanilide showed a very weak EPR signal that seemed to be unstable. The NMR spectra of irradiated solutions of the above-mentioned anilide and deuterated chloroform containing 10% carbon tetrachloride were most revealing and are shown in Figure 6. As can be clearly seen the irradiation produces a free radical that is localized on the amine nitrogen rather than delocalized as in the case of *p*-phenylenediamine (Figure 1). NMR spectra with broadened signals such as Figure 6b are not without precedent. Degenerate electron exchange between *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD) and Wurster's Blue (WB), the product derived from TMPD by one-electron oxidation, causes a similar line broadening.[20,21] The rate of electron exchange for TMPD–WB in acidic solutions was calculated to be 2.5×10^4 L mol^{-1} s^{-1} [20] while in organic solvents $(2 \pm 1) \times 10^8$ L mol^{-1} s^{-1}. The rate of electron exchange between *p*-(*N*,*N*-dimethylamino)acetanilide and the photoproducts cannot be calculated from the NMR spectra because the relative concentrations are not known. The series of spectra indicate that the photoproduct is transient since the amount of exchange diminishes slowly with time. The slow decomposition of the free radical into unidentified products leads to the original spectrum as can be seen in Figure 6e. The half-lifetime of the photoproduct has been estimated to be in the order of minutes. According to a different interpretation of the spectra in Figure 6[22] that seems plausible, the broadening is due to an exchange of a hydrogen atom between the acetanilide and the zwitterionic free radical that is obtained from the cation radical by loss of a proton. The exchanging hydrogen is the one that dwells on the amide bond. This interpretation would imply a very short lived cation radical as the initial photoproduct. This is a clear departure from the behavior of *p*-phenylenediamine that yields stable products. In polar solvents such as dimethylformamide or dimethyl sulfoxide the photochemical reaction of the anilide is identical with the photochemical reaction in chloroform, as shown in Figure 7, but the electron exchange seems to persist longer. One may venture to argue that the unidentified product from the decomposition of the irradiated anilide is an ammonium salt due to the requirements of electroneutrality and the presence of the chloride or bromide ions that were produced in the course of the irradiation.

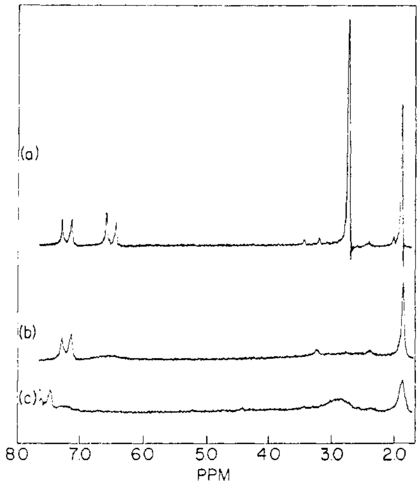

Figure 7. Proton NMR spectra (60 MHz, S.W. 500, reference Me_4Si) of a solution of *p*-(*N*,*N*-dimethylamino)acetanilide in $Me_2SO\text{-}d_6$ containing 10% CBr_4: (a) nonirradiated solution, (b) 2 min after irradiation, (c) 24 h after irradiation.

It remained to be proven that the photoproducts carry charge too. For this purpose the conductivity of a solution containing *p*-(*N*,*N*-dimethyl)acetanilide and carbon tetrabromide in DMF was measured in the dark and at intervals while it was irradiated with a 0.5 mW/cm^2 UV light source at 3650 Å. The results are plotted in Figure 8a and suggest that the radical produced causes the conductivity to increase. Conductivity of solutions is always ionic and therefore the inevitable conclusion is that the photochemical reaction produces charged species. These results show that a required photoionization occurs.

p-(*N*,*N*-Dimethylamino)acetanilide serves as a model for the photochemical behavior of polymers 1 and **1a**. Evidence was mounted in support of this notion and the reaction shown in Figure 3. Solutions containing 75% chloroform and 25% carbon tetrachloride as solvent and polymer 1 as solute were irradiated with the same light source that was mentioned above. Precipitate formed (2) that showed 61% incorporation of chloride, possibly a counterion, compared with the calculated value (one chloride per anilide site corresponds to 100%). The visible spectrum of polymer 2 in DMF was close to that of *p*-(*N*,*N*-dimethylamino)acetamidinium chloride, though weaker. Solid precipitate 2 displayed an EPR signal 35 G wide at 3300 G. No hyperfine splitting was observed probably because of the solid state of the material, in contrast with the reported solution study of the cation radical.[23] Conductivity measurements of solutions of polymer 1 in DMF containing carbon tetrabromide showed the same behavior as did solutions containing the model

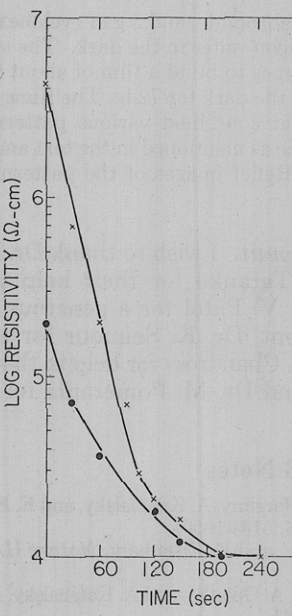

Figure 8. Resistivity vs. time for a continuously irradiated solution of: (a, top) ×, *p*-(*N*,*N*-dimethylamino)acetanilide and CBr_4 2.4 × 10^{-2} M in DMF, and (b, bottom) O, poly[*p*-(*N*,*N*-dimethylamino)-*N*-γ-D-glutamanilide] and CBr_4 2.4 × 10^{-2} M in DMF. The conductivity of the solutions is increased due to photochemical generation of ions.

compound *p*-(*N*,*N*-dimethylamino)acetanlide (see Figure 8b). Thus the conclusion that in the polymer poly[*p*-(*N*,*N*-dimethylamino)-*N*-γ-D-glutamanilide] (1) the same photoionization reaction occurs as in the case of *p*-(*N*,*N*-dimethylamino)acetanilide. Additional indications pointing to this conclusion were obtained by exploration of the wetability (contact angle) change of the surface of a film of polymer 1, due to irradiation in the presence of carbon tetrachloride. A glass substrate was covered with a film of polymer 1. The contact angle of a drop of water on that film was 54°. The film was covered with carbon tetrachloride. Since the polymer is not soluble in the solvent, only the surface layer was in contact with the liquid. The film was irradiated with the same light source as mentioned above for several minutes and the solvent was removed. The new contact angle measured 40°, a decrease of 14°. This suggests that the surface polarity increased due to the irradiation, again in support of the photoionization reaction. All the experiments that were mentioned in this paragraph corroborate the photochemical reaction shown in Figure 3. In line with previous studies of the photooxidation reaction[12] it was found that oxygen does not inhibit the photoionization or in any way effect the rate. Oxygenated and degassed samples showed the same photoactivity.

The spectral changes, incorporation of chloride, and the electron spin resonance signal that resulted when polymer 1 was irradiated were obtained also with cross-linked gel **1a**, indicating that the reaction that takes place in solution with polymer 1 and in gel **1a** are one and the same. Based on the evidence presented above about the similarity of behavior between polymer 1 and our model molecule *p*-(*N*,*N*-dimethylamino)acetanilide, it is concluded that gel polymer **1a** reacts as expected and as shown in Figure 3.

It is the photoionization reaction that is responsible for the observed deformations of polymer **1a**. In the introduction and elsewhere[5] it was pointed out that in crystalline polymers induced ionizations should lead to phase transition and contraction of the material. However, the observed deformations described in this paper were opposite, namely dilations. Furthermore, examination of the films between cross-polarizers under the microscope did not reveal any crystallinity or alignment. Therefore, it is concluded that the responsible mechanism operating in these experiments is the one that is restricted to amorphous polymers. In effect the exposed material becomes bibulous. Excess liquid that envelopes the film prior to the irradiation is absorbed into the film upon irradiation, due to the changes in the chemical and thermodynamic interaction that are introduced. The incorporation of additional liquid diluent in the gel matrix causes additional swelling. This explanation is supported by the observation that in the absence of diluents no dilations were observed. The large deformations observed are similar in magnitude to chemically induced deformations. Furthermore, the size of deformation that was reported to occur with polyglutamic acid[8] is identical with the maximum mechanophotochemical dilation observed for poly[*p*-(*N*,*N*-dimethylamino)-*N*-γ-D-glutamanilide] (**1a**). It is not yet clear to what extent this is a coincidence or significant.

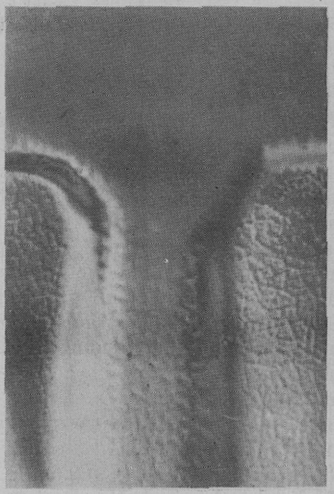

Figure 9. Relief image produced on a film due to exposure through a mask. The exposed regions are raised relative to the rest of the surface.

The relationship between the amount of cross-linking and photodeformability was cursorily investigated. It was observed that films that contained 5% cross-linking were too stiff to be distorted by photochemistry while the films that contained 1.5% cross-linking did show deformability. Hence, the tradeoff between mechanical rigidity and deformability that was observed in mechanochemistry holds, not surprisingly, for mechanophotochemistry too. No attempts have as yet been made to reverse dilated polymer **2a** to its original size **1a**. In principle[23] this should be accomplished by a simple reduction, either chemical or electrochemical. In the future, we intend to focus our efforts on this aspect of the phenomenon since its demonstration may carry some technological importance.

For one application relief images on fixed planar surfaces were required. Initial attempts to prepare such images failed due to peeling and cracking of cast films. To prevent these difficulties, the films were chemically bound to silicon supports by 3-chloropropyltriethoxysilane, and carbon tetrabromide was imbedded in them. Solventless films were irradiated through masks that contained variouos designs and were subsequently immersed in DMF to obtain swelling. Relief images that reproduced the exposed pattern were obtained (see Figure 9); however, stresses are visible.

Apart from being of scientific interest, mechanophotochemistry may attract the attention of technologists interested in such applications as printing, photocopying, actinometry, and others.

Experimental Section

Poly[*p*-(*N*,*N*-dimethylamino)-*N*-γ-D-glutamanilide](1). Poly(D-glutamic acid) (Miles-Yeda Ltd. mol wt 12 400), 0.5 g, was dissolved in 50 mL of dry DMF and 2 g of freshly distilled *N*,*N*-dimethyl-*p*-phenylenediamine was added. The solution was cooled to 0 °C and 1 g of DCC was added with stirring. Stirring was continued at 0 °C for 1 h and at room temperature for an additional 24 h. One milliter of dry methanol was added and stirring was continued for an additional h. The precipitate was filtered off and the filtrate was evaporated to dryness at 35 °C (0.01 mm) (bath temperature). The residue was dissolved in THF and filtered in a drybox under nitrogen. Diethyl ether was added to the solution and the precipitate was filtered and collected under nitrogen. The collected solid was further purified by precipitation from THF with diethyl ether. Anal. Calcd for $(C_{13}H_{17}N_3O_2)_n$: C 62.90; H, 6.85; N, 16.93. Found: C, 62.69; H, 7.64; N, 14.54.

Poly[*p*-(*N*,*N*-dimethylamino)-*N*-γ-D-glutamanilidinium chloride] (2). Poly[*p*-*N*,*N*-dimethylamino)-*N*-γ-D-glutamanilide] (1), 100 mg, was dissolved in 3 mL of chloroform and 1 mL of carbon tetrachloride was added. The solution was filtered and irradiated for 10 min with a 3650 Å UV light source (0.5 mW/cm^2). The precipitate was collected by filtration Anal. Calcd for $(C_{13}H_{17}ClN_3O_2)_n$: Cl calulated on basis of 1, 10.97. Found: 6.74.

The solid displayed an electron spin resonance signal at 3300 G of 35-G width (no hyperfine splitting was observed).

Preparation of Films (1a). Poly[*p*-(*N*,*N*-dimethylamino)-*N*-γ-D-glutamanilide] (1), 120 mg, was dissolved in 400 mg of THF. 2,6-Bis(bromomethyl)naphthalene, 2.35 mg (to provide for 1.5 M % cross-linking), in 100 mg of THF was added and a film was cast on a glass slide. To prevent fast evaporation the film was kept in a chamber saturated with THF vapors. It took about 1 day to evaporate the solvent and for the cross-linking reaction to take place. The dry film thickness was 1.15 mil.

Irradiation and Measurements. Films of **1a** with approximate area of 4 mm^2 were swollen in *N*,*N*-dimethylformamide. The excess liquid was replaced in the dark with a 5% solution of carbon tetrabromide in *N*,*N*-dimethylformamide and photographed under the microscope, following a 5 min waiting period. The films were irradiated at a distance of 1 in. with a source of "black light" rated at 1680 μW/cm^2 at 3650 Å, 18 in. away. During the irradiation the films were freely suspended in the liquid to prevent stress and strain and kept in a constant temperature bath at 27 °C. At the end of the irradiation period (as specified) the films were photographed again and the dilations measured from the photographs.

Sililation of Silicon Wafers and Chemically Surface Bound Films. 3-Chloropropyltriethoxysilane (10 g) was dissolved in 50 mL of xylene and refluxed under nitrogen. A wafer of silicon 2.5 in. in diameter was placed in the vapor area. Reflux was continued for 5 h.[24] The wafer was rinsed with dry xylene. A solution containing 0.6 g of polymer **1**, 7.83 mg of 2,6-bis(bromomethyl)naphthalene (predissolved in 0.3 g of cyclohexanone), 0.6 g of carbon tetrabromide, and 3 g of cyclohexanone was spin coated onto the silicon wafer in the dark. The spin coating was repeated several times to build a film of about 5 μm. The film was left to react in the dark for 72 h. The films were irradiated through masks that contained various patterns with a 1680 μW/cm^2 light source as mentioned in the text and immersed into DMF for 5 min. Relief images of the patterns exposed were obtained.

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