Photoinduced Tension of Polymers

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Synopsis

Photoirradiation of polymer films at constant length induced a fast tension reduction (time scale: seconds) followed by slow tension buildup (time scale: minutes). Immediately after irradiation, fast tension buildup was followed by slow tension decay. Cycles were repeatable without significant hysteresis loss. The amplitude of both phenomena are intensity-dependent in the ultraviolet–visible spectral regions; both phenomena are thermal rather than photochemical effects. Light-absorbing chromophores in the polymer structure, or in additives such as dyes, lead to absorption of light and internal conversion into heat. The classical, rapid thermal expansion (or contraction) on heating (or cooling) leads to the fast relaxation (or buildup) of tension. The elastic, entropic response of the sample with its longer relaxation time leads to slow buildup (or decay) of tension. Fast and slow responses are observed sequentially with film of extensively crosslinked Riston photopolymer resist or with Kapton polyimide film, whereas, in experiments with latex rubber, the rubbery behavior dominates.

INTRODUCTION

Mechanical and conformational changes have been induced in polymers by: changing their degree of ionization,[1] ion exchange,[2] redox reactions in dialluric acid–alloxan gels,[3] ionic strength changes in collagen fibers,[4] and chemical complexation.[5] Photoinduced mechanical effects such as shrinkage/dilation have been attributed to *cis–trans* isomerism of azo groups, whether dissolved in the polymer matrix, incorporated as pendant groups, or as part of the polymer backbone.[6] Similar effects have been attributed to the spiropyran–merocyanine isomerization.[7] Evidence has accumulated that indicates that other mechanisms may contribute to photochemically induced changes in addition to the clearly demonstrated photochemical isomerizations. Agolini and Gay[8] concluded that the reversible photo/thermal contractile behavior of azo aromatic polymers was controlled by a process other than the cis/trans isomerization of the in-chain azo group. Smets, Bracken, and Irie[9] showed that the spiropyran–merocyanine isomerization is not the cause of the sample contraction. Although conversion of energy stored in the chromophores, which could lead to local heat effects, was suggested as a possibility, the authors preferred cis/trans isomerization of the ring-opened merocyanine form as the explanation of the reversible contractile process. Matejka and co-workers[10] studied the effect of radiation on the mechanical behavior of crosslinked styrene/maleic anhydride polymer containing pendant azo groups. Their work showed a considerable influence of thermal effects, previously obscured or ignored by other workers, in addition to the effect of photoisomerization of the photochrome.

Sarbolouki and Fedors[11] showed that thin polymer films acted as intensity-dependent photo mechanical transducers.

The present work shows that photoirradiation of polymer films at constant length induces previously unrecognized tension changes caused by classical thermal expansion/contraction effects and by competing elastic entropic effects. These photoinduced tensions (PIT) appear to be generally applicable to a broad range of polymers.

EXPERIMENTAL

Apparatus

Figure 1 shows a schematic of the apparatus used. A 100-W mercury lamp, Model B-100A Black Ray (Ultraviolet Products, Inc.) or a 1000-W high-pressure mercury lamp (General Electric Model AH-6) with a quartz–water infrared absorbing filter was used to irradiate self-supporting films held by lever action Instron grips (50 g load capacity) connected to a Gould UC-2 Pressure Transducer, a UL-4 Gould Load Cell, a Gould Transducer–Amplifier 13-4615-50 and Power Amplifier 11-4113-01, and a two-channel recorder. Initially, experiments conducted in open air yielded noisy signals; therefore, films were irradiated in an insulated cylindrical chamber with a black interior.

Film Samples

Sample strips (3 in. $\times$ 0.25 in.) of unexposed Riston 3010 photopolymer resist film (1 mil), Riston 3015 (1.5 mil), and Riston 3020 (2 mil) were exposed through the Mylar polyester film cover sheet to 220 mJ cm^2 light energy, at 365 nm wavelength, after which the Mylar and polyolefin cover films were peeled away to leave the crosslinked resist film for the PIT experiments. The composition of these photocrosslinkable resists has been described by Cohen.[12]
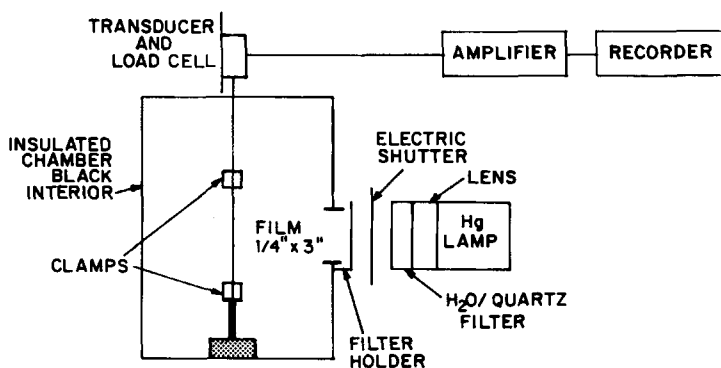

Fig. 1. Schematic diagram of the apparatus for measuring photoinduced tension in films at constant length.
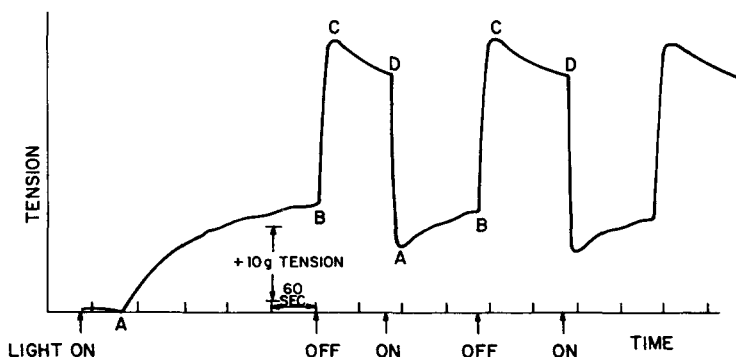
Fig. 2. PIT response curve for exposed Riston 3020. Lamp intensity 5.6 mW/cm²; pretension 5.0 g; chamber temperature 23°C; calibration 10 cm = 25.0 g.

Photoinduced Tension (PIT) Response Curves

Figure 2 shows PIT response curves for exposed Riston 3020 using the lower-intensity mercury lamp. The film was initially loaded with about 5 g. When the light was turned on, a small drop in tension resulted which began a rapid increase after about a 60-s lag. At point B the shutter was closed; the tension increased rapidly to point C, and then it decayed from C to D. At D the light was turned on, and a sudden drop in tension resulted to point A after which it increased to point B. After the initial cycle, cycle ABCDA was repeated up to 30 times without any apparent shift in the tension changes for the various segments of the curve.

The temperature of the system was measured in two separate ways. First, a thermocouple was placed next to the film surface, but not in direct contact with the film. This thermocouple recorded a maximum difference of 1–2°C between conditions in which the light was off and on. Second, a small thermocouple (0.12 mm diameter wire) was embedded between two layers of unexposed Riston 3020. The film was exposed to 200 mJ/cm² of UV light, and the exposed film with embedded thermocouple was mounted for PIT measurements. The rise time (or fall time) of the internal temperature was 5 s upon opening (or closing) the shutter. The corresponding temperature shifts observed internally reached up to ±8°C with the 100-W light source. The latter range reflects the internal heating and cooling which occurred with photoirradiation of the crosslinked polymer.

Curve analysis of a typical PIT cycle for Riston 3020 is shown on Figure 3. Two competing processes occur: the rapid drop in tension line DA vs. slow buildup curve AB when the light was turned on; rapid increase in tension line BC vs. slower decay curve CD when the light was turned off. Faster processes occur on the seconds time scale. The two slower processes had similar time constants (min) and similar tension changes.

Mechanism Studies

Light Intensity Effects. It is necessary to define the role which light intensity and wavelength distribution played to understand the mechanism of the photoinduced tension. Experiments with neutral density filters are
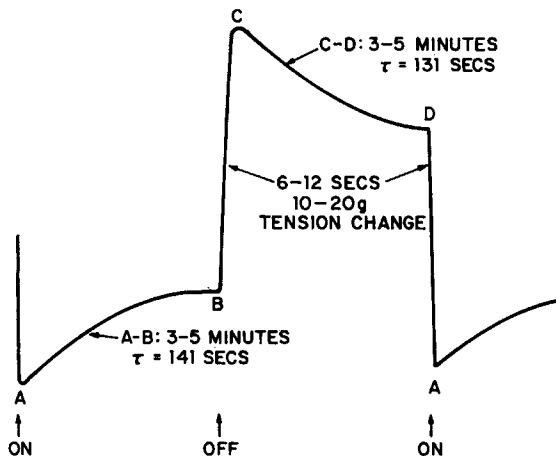
Fig. 3.   Analysis of PIT response curve.

shown on Figure 4 in which the tension displacement for each part of the PIT cycle is plotted against relative light intensity. An excellent linear correlation was obtained at all intensities for the BC and DA portions of the PIT cycle and above a small threshold intensity for the AB and CD portions.

Wave Length Distribution Effects. Corning glass filters were selected to:

1. Transmit ultraviolet light between 330 and 400 nm (CS-7-51).
2. Transmit visible light between 390 and 490 nm (CS-5-59 plus CS-3-75).
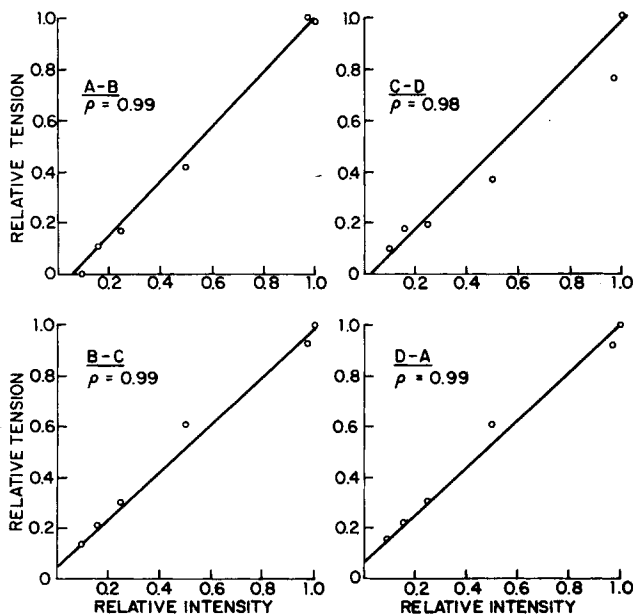3. Transmit visible light greater than 390 nm (CS-3-75).

Fig. 4.   Dependence of PIT response on incident intensity. The ordinate is $(T - T_{initial})/(T_{max} - T_{initial})$.

4. Transmit visible light greater than 520 nm (CS-3-69).

When these filters were used with the 100-W mercury lamp, a linear correlation between displacement and relative intensity was obtained for the fast processes (BC; DA). However, the light flux was inadequate for useful intensity dependence measurements of the slower AD and CD processes. PIT response curves were measured using the 1000-W mercury lamp where the incident intensity was attenuated with neutral density filters (NDF) as well as colored glass filters. Absolute intensity measurements of lamp output proved to be unreliable because of excessive intensity fluctuations with the 1000-W lamp. However, a "built-in" standard was available in these tests since tension changes in the fast processes had already been shown to be proportional to intensity at all the wavelengths mentioned above. Table I shows that correlation coefficients ranged from 0.88 to 0.94 for the slow process vs. the fast process. Therefore, all processes of the photoinduced tension cycle are linearly dependent upon intensity in the ultraviolet–visible spectral regions.

Thermal Effects. Heating and cooling of film with the lamp on–off cycles must certainly play an important role in the PIT phenomenon. Previous workers have recognized this effect[9–11] and have demonstrated expansion–contraction cycling at high temperature using an oven.[8] A Riston 3020 film sample was immersed in a water bath and exposed to high intensity light. Figure 5 shows that the PIT cycle was virtually eliminated. Tension changes were, therefore, induced because of temperature differentials created between the film and its environment.

OTHER POLYMERS

Kapton Polyimide Film

At low intensity, Kapton film showed a modified PIT response curve. Tension increased rapidly with the light on and decayed rapidly with the light off, but the offsetting slow process did not appear. Instead, tension continued to drop, albeit slowly and with greatly reduced magnitude, while the light was on and to increase with the light off. Further work is required to understand these small, slow tension changes.

With the high intensity lamp, Kapton film showed the same PIT behavior as the Riston photopolymer (Fig. 6), indicating that some threshold power was needed to induce tension buildup with light or decay in the dark. A chemically crosslinked polymer is not a requirement since Kapton is a linear

TABLE I
Correlation of Slow PIT Rates vs. Fast Rate[a]

Slow rate	Fast rate	Slope	Correlation coeff
(C–D)	(D–A)	0.75	0.93
(C–D)	(C–B)	0.77	0.94
(B–A)	(C–B)	0.81	0.88
(B–A)	(D–A)	0.93	0.88

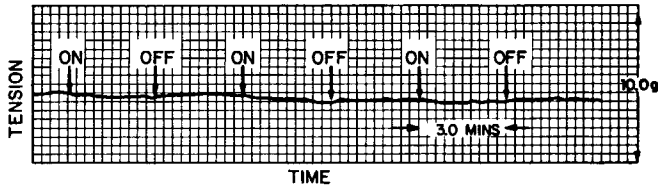[a] Riston 3020, 1000-W AH-6 Hg Lamp.

Fig. 5. PIT response curve for Riston 3020 immersed in water. 1000-W mercury lamp plus filter CS-7-51.

polyimide with a low level of crystallinity and a high glass transition temperature.[13] Sarbolouki and Fedors[11] reported PIT curves for Kapton, which may have been on the verge of showing tension buildup (the slow process) with the light on. However, the cycling times they used were too short to confirm response curves which we report. Higher lamp intensity should have given the PIT response curves that we report.

Latex Rubber

White and red latex rubber film strips showed a small increase in tension with light (Fig. 7). The tension then decayed, probably as a result of creep. The rate of decay dropped with the light off, and a small increase in tension resulted in a second cycle with the light on. The low glass transition temperature of latex is probably responsible for the different shape of these PIT curves.

DISCUSSION

The slow time scale of these two tension-forming and tension-relaxation steps imply that molecular motion changes in the polymer are occurring. These molecular motions result from the conversion of light into heat energy which is then transferred to the polymer matrix. The Riston photopolymer contains a blue/green dye selected to improve image contrast over copper when it is used as a resist. Similarly, Kapton polyimide film is yellow from chromophores, apparently formed during manufacture. White and red latex rubber film also contain moieties, which absorb light energy and convert it to heat. It is not necessary to invoke a cis–trans isomerism mechanism
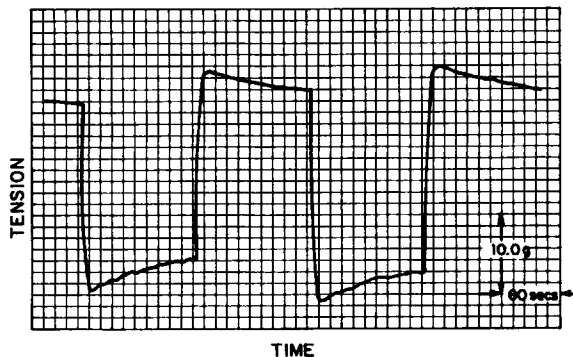

Fig. 6. PIT response curve for Kapton polyimide film. Illuminated with 1000-W mercury lamp plus CS-7-51 Corning Filter plus 0.75 neutral density filter.
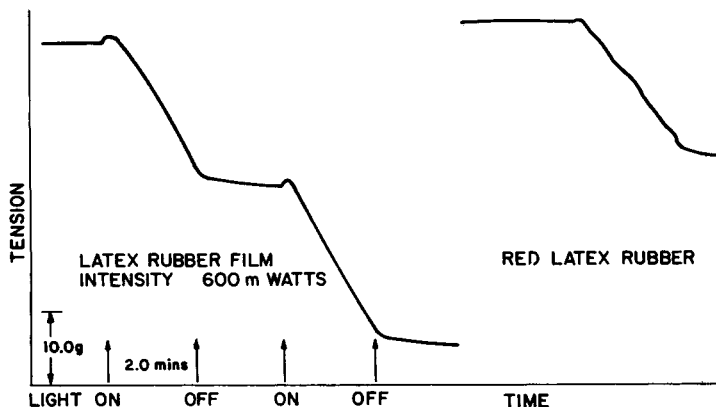
Fig. 7.   PIT response curve for latex rubber. White latex: no filters. Red latex: 0.5 plus 0.75 neutral density filters, plus filter CS-3-69.

with these groups, or ring opening mechanisms with merocyanine/spiro-pyran groups to obtain these kinds of tension changes.

The origin of the fast steps in the observed PIT response curve is the thermal expansion and contraction of the sample. This conclusion was also reached by Sarbolouki and Fedors.[11] It is supported by the observation reported above that immersion in water suppresses the fast steps. The time scale is, of course, determined by the rate at which the thermal steady state is established (seconds in our experiments). The actual dimensional changes occur on the time scale of atomic vibrations (10^{-11}–10^{-13} s). Additional support comes from the order of magnitude estimates of the observed temperature changes of the film in air, the time scale of the fast steps, and the magnitude of the tension evolved. Our picture of the fast steps can be succinctly illustrated with this latter calculation.

With the light on, a steady state is rapidly attained in which a significant fraction (ca. 0.5) of the incident intensity is absorbed and converted to heat. This heat is dissipated by transfer to the surrounding atmosphere, and the net flux supports a temperature difference between the film and its surroundings. Because it is held at constant length, the film cannot expand in response to this temperature difference so that compressive stresses arise. Since the temperature difference is small (ca. 8°C), the resulting stresses are correspondingly small, and we may plausibly suppose that the film will respond linearly, so that

$$\sigma = \epsilon E \qquad (1)$$

Here, σ is the stress, E is the modulus of elasticity, and ϵ is the strain. The strain is purely thermal so that

$$\epsilon = \alpha_L(\Delta T) \qquad (2)$$

where α_L is the linear thermal expansion coefficient of the film and the temperature difference is taken to be $\Delta T = T_{air} - T_{film}$ to endow σ with the proper sign. The tension τ which is actually measured is related to the

stress through the cross-sectional area of the film, A, and the acceleration due to gravity, g. Combining all these relations, one finds

$$\tau = A\alpha_L E(\Delta T)g^{-1} \tag{3}$$

For an order of magnitude calculation, we may approximate the mechanical properties of the Riston 3020 film (α_L, E) by those for poly(methyl methacrylate).[14] Thus, $\tau \approx -70$ g which has the correct sign and about the right magnitude (see Fig. 2).

This explanation of the fast processes in terms of simple thermal expansion and contraction is consistent with all the other information at hand. Such a process is clearly reversible when the light is extinguished and should give rise to no detectable hysteresis so long as the strains are small. Moreover, τ is linearly dependent upon ΔT, which can readily be shown to depend linearly on light intensity in the steady state.

In a similarly consistent but less detailed fashion, the slow steps of the PIT response curve can be ascribed to an elastic, entropic response of the noncrystalline portions of the film. This response is completely equivalent to the well-known property of natural and synthetic rubbers, which, once stressed beyond the point of their thermoelastic inversions,[15] tend to contract when heated and expand when cooled. In the cases we have examined, this response can only be observed under well-chosen conditions.

In the case of the latex rubber films, complications arise. Foremost is the phenomenon of creep that is so evident in Figure 7. The low extent of crosslinking and comparatively low glass transition temperature of the latex rubbers are consistent with the enhanced creep of these samples. The low glass transition temperature is also evident in the altered response curve at very short times, where ordinary thermal expansion or contraction is no longer visible. We may speculate that, under grossly different experimental conditions, the latex rubber films would give rise to PIT response curves similar to those obtainable with Kapton and Riston films under our conditions. However, we have no evidence to support this speculation and can only comment that the latex rubbers appear to behave like well-known, poorly crosslinked elastomers do when heated under load.

In Riston photopolymer resists and Kapton polyimide films, sufficient intensity must be provided to create stresses which exceed the point of thermoelastic inversion. This is why Kapton at low illumination intensity and Riston at very low intensity do not show slow steps reacting in opposition to the preceding fast steps of the PIT response curve.

This process may be plausibly indentified with the slow steps of the observed response curves by appealing to the likely (but uncertain) properties of the amorphous regions in semicrystalline polymers. Ambient temperatures are well below the nominal glass transition temperatures (in contrast to the latex rubbers), so that any changes should be slow. However, variations in states of internal stress, concentrations of plasticizers (particularly in the case of the complex Riston 3020 system), effective crosslink (probably crystallite) density, and other factors preclude quantification of any feature beyond the sign of the evolved tension in the slow steps. Still, it can be definitely stated that an explanation in these terms is consistent

with the observed linear dependence of the retractive force on light intensity (via the temperature) and the lack of hysteresis after initial pretensioning. An accompanying phase transition analogous to stress-induced crystallization of natural rubber is also possible. Such a process would likely lead to some hysteresis, so we do not consider it a likely feature of the systems studied here. Such a phase transition would enhance the magnitude of the slow response.

Elastic character around room temperature is usually not associated with high T_g, high modulus polyimides, and even less so with crosslinked structures, such as photopolymerized compositions. Since PIT behavior occurred with these compositions, it appears to be a general phenomenon determined by the small but significant rubberlike, elastic component in all polymers.

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