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Reversible Switching of the Shear Modulus of Photoresponsive Liquid Crystalline Polymers

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Liquid crystalline polymers (LCP) have attracted recent interest due to their ability to combine the properties of small molecule liquid crystals and those of a polymer[1]. Liquid crystalline moieties can be designed to exhibit a conformational change on the molecular level in response to thermal[2, 3], pH[3], electrical[4] or optical[5, 6] stimulation. Liquid crystalline polymeric materials benefit from the rheological integrity that the polymer component provides to the system. Siloxane based LCPs present specific advantages associated with the very low glass transition temperature (T_g) of the siloxane backbone[7,8], allowing for the materials to retain their properties over a wide temperature range, particularly at room temperature.

The utilization of photoisomerization of LC moieties to produce actuator materials was first proposed by deGennes[5]. This class of materials can be stimulated by exposure to particular wavelengths of electromagnetic radiation (e.g. visible light), resulting in molecular rearrangements that manifest the desired effects. The molecular conformational change can lead to a change in the rheological or dimensional properties of the materials, resulting in photoresponsive shape memory polymers[9] or films that exhibit a bending actuation when one surface is exposed to light [8, 10]. There are several examples of molecules that have

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garnered great interest for their abilities to photoisomerize and thus generate useful properties in polymers[11, 12]. One such class of molecules is azobenzene-containing moieties, which have been found to undergo a *trans* to *cis* photoisomerization upon exposure to UV (366 nm) light. The moiety relaxes to the equilibrium *trans* conformation when the UV irradiation is removed; this relaxation can also be accelerated with heat or exposure to longer wavelength light (> 540 nm). The photoisomerization of azo moieties incorporated into a polymer matrix have been shown to disrupt the stability of nematic[13] and smectic[14] LC mesophases. Thus, a reversible and isothermal smectic to isotropic transition can be achieved by disrupting the smectic LC mesophase through the isomerization of the azo moieties[11, 15].

Here we will demonstrate the effects of UV stimulation upon the morphology and rheological properties of azo-containing siloxane-based LCPs. To date, a very limited number of studies have addressed the light-tunable rheological properties of photoresponsive polymeric systems. Among them, the recent work by Ketner et al.[16] revealed the remarkable potential of aqueous micellar solutions whose viscosity can drop by more than four orders of magnitude upon UV exposure. The limiting factor in their study is the irreversible character of the transformation. In the present work, we demonstrate reversible rheological property changes. Such properties are of particular interest for light activated damping mechanisms, actuable armor, and related applications in fields such as robotics and sensors. Here we investigate azo-containing moieties attached to a siloxane polymer backbone that can undergo a reversible conformational change upon exposure to UV light. This molecular rearrangement disrupts the LC phase, which affects the global conformation of the chain, allowing for dynamic switching of the rheological properties of the system.

The polymer backbone used for this study is a poly-(vinylmethylsiloxane) (PVMS) with a number average molecular weight (M_n) of 14,800 g/mol and a polydispersity index (PDI) of 1.23[17]. The homopolymer can be modified with a broad range of attachment percentages using previously reported approaches that rely on Pt catalyzed hydrosilyation. Azo-containing LC moieties were attached to the polymer backbone with an attachment percent of 67%, yielding a polymer with a total molecular weight of 80,700 g/mol. This functionalized siloxane polymer will be referred to as $LCP_{azo}81$, see Figure 1a. The smectic to isotropic transition temperature (T_{iso}) of $LCP_{azo}81$ was measured via differential scanning calorimetry (DSC) to be T_{iso} = 124°C.

Small-angle X-ray scattering (SAXS) was used to characterize the morphological response of the liquid crystalline polymers to UV stimulation. To achieve sufficient LC response over reasonable timeframes, the LCP film was first heated to 100°C, close to the clearing point temperature, in the absence of UV light using a commercially available SabreTube furnace[18], which was custom mounted for in-situ X-ray experiments. A *trans* to *cis* conformational change was induced by exposing the LCP film to UV light while holding the temperature constant, resulting in a disruption of the smectic LC mesophase and a corresponding decrease in the scattering intensity. Figure 1b shows a schematic diagram of the LCP in the *trans* conformation, resulting in a smectic LC mesophase; Figure 1c shows a schematic diagram of the LCP in the *cis* conformation, resulting in an isotropic LC mesophase.

With increasing UV exposure time, a decrease in the scattering intensity from the smectic layers is observed; Figure 2 shows 1-D scattering profiles as a function of UV exposure time. The low *q* scattering arises from the larger smectic layers, which are disrupted more readily leading to a shift in the peak with continued exposure; the larger smectic layers are less tightly packed and thus the photoisomerization has a lower enthalpic barrier that has to be overcome. A similar phenomenon was previously observed in similar systems, where larger smectic layers had a lower smectic to isotopic transition temperature[17].

Small and large amplitude oscillatory shear tests (denoted SAOS and LOAS respectively) were performed at 100°C ($T < T_{iso}$) to characterize the rheological properties of the liquid crystalline polymer (LCP) in response to stimulation with UV light. To do so, we used a parallel plate photocuring accessory (20 mm diameter) mounted on an Advanced Rheometric Expansion System (ARES) strain controlled rheometer (TA Instruments, New Castle DE, USA) together with the ARES Peltier control system. A Dymax Blue Wave 200 light source was used for UV exposure experiments (λ = 365 nm; output power: 10mW/cm^2). Exposing the LCP to UV light during oscillatory shear experiments significantly affects the viscoelastic behavior of the system. Strain amplitude sweep tests, with amplitudes ranging from $1\% \leq \gamma_o \leq 1000\%$, were performed at a frequency of ω = 1 rad/s on the LCP without and with exposure to UV light as illustrated in Figure 3. In the case of the exposure to UV light represented by the open symbols, the signals obtained for strain amplitudes less than 5% are close to resolution of the force rebalanced transducer on the rheometer. The unexposed material (UV off and shielded from ambient light) shows a linear viscoelastic response for strain amplitudes up to ~4%, above which the dynamic moduli begin to decrease slowly with increasing strain amplitude. In Figure 3, we can see that exposure to UV light lowers the modulus by close to an order of magnitude and extends the linear viscoelastic regime of the LC melt to a strain amplitude of about 20%. Both the storage (G') and loss (G'') moduli are lower with exposure to UV light; however, the extent of this reduction depends on the imposed strain amplitude. Within the linear viscoelastic regime the relative decrease in the storage modulus $(G'_{off})/(G'_{on})$ and loss modulus $(G''_{off})/(G''_{on})$ is comparable. For strain amplitudes $1\% \leq \gamma_o \leq 4\%$: $(G'_{off})/(G'_{on}) = 8.4 \pm 0.9$, and $(G''_{off})/(G''_{on}) = 7.0 \pm 1.1$. As the strain amplitude is increased into the nonlinear viscoelastic regime the elastic modulus of the LCP network begins to decrease dramatically and is more than an order of magnitude lower than without exposure to UV light at strain amplitudes greater than 100% and in the nonlinear viscoelastic regime, $(G'_{off})/(G'_{on}) \gg (G''_{off})/(G''_{on})$. Frequency sweep experiments were performed with a strain amplitude of 2% at 100°C with and without exposure to UV light and are shown in Figure S4 of the Supporting Information.

The transient response of this photo-rheological polymer melt to UV irradiation was investigated using in-situ UV dynamic oscillatory shear experiments. The effects of repeated exposure to UV irradiation on the storage and loss moduli at 100°C are shown for both small (γ_o = 2%) and large (γ_o = 100%) strain amplitudes in Figures 4a and 4b, respectively. The experiment began without UV exposure, and once the steady state was reached the LCP was exposed to UV light, resulting in a decrease in G' and G''. Once a new steady state was established (after a period of approximately 500 s) the UV light was turned off so that the system could relax back to its initial state. The decay in both the integrated scattering intensity and the storage modulus (G') can be described by an exponential as a first order approximation (details provided in supporting information).

The viscoelastic properties of the LCP melt are dependent upon the morphology of the system; when the azo moieties are in their equilibrium *trans* conformation, the smectic LC mesophase provides inter-chain interactions that reinforce the LCP, leading to higher values of the storage and loss moduli. In general, it is known that smectic LC phases have a high viscosity; the closely-packed and ordered smectic layers present additional resistance to deformation that is manifest as a higher shear modulus. Upon exposure to UV irradiation a local *trans* to *cis* isomerization is induced, resulting in a disruption of the smectic LC mesophase and a subsequent decrease in the storage and loss moduli. This effect is most prominent at larger strain amplitudes; the large imposed deformation helps to disrupt the long range order of the mesogens. The reversibility of the system is demonstrated by the rapid relaxation of the rheological properties upon removal of the UV light. Multiple cycles of this switching response can be achieved at strain amplitudes of 2% or 100%.

Close examination of Figure 4a and 4b shows that the photorheological evolution in the properties of the LCP melt is more complex in the nonlinear viscoelastic regime than a simple exponential decay[29]. Upon UV irradiation, at short times the elastic modulus G' decreases approximately linearly with time and the loss modulus G'' initially climbs. As the UV irradiation continues, the order of the LC mesophase is increasingly disrupted by the shearing and both the loss and storage modulus decrease dramatically. The nonlinear nature of the viscoelastic response at large strains can be more clearly demonstrated by Lissajous plots of the stress $\sigma(t)$ and strain $\gamma(t)$ at a given frequency ω[20]. When represented in this form, a perfectly elastic material response would appear as a straight line with a slope equal to the elastic modulus. For strain amplitudes of 2% the response is clearly linearly viscoelastic, both with and without UV exposure, as shown by the elliptical trajectories in Figure 5a. Exposure to UV light leads to a decrease in the slope of the curves which indicates an elastic softening because of the disruption of the LC smectic mesophase. This is in agreement with the results shown in Figures 3 and 4 and the relative decrease in the storage modulus is $(G'_{off})/(G'_{on}) \approx 9.4$. In the linear viscoelastic regime both the viscous and elastic contributions to the complex modulus $G^*(\omega)$ are affected to equal extents following exposure to UV light. The decrease in the linear viscoelastic moduli over a range of frequencies can be described by a single vertical shift factor that depends on the intensity and duration of the UV irradiation. An example of this shifting is shown in the supporting material (Figure S4).

For the larger strain amplitudes of 100%, we observe pronounced distortions from ellipticity in the shape of the Lissajous curves in Figure 5b (both with and without UV exposure) indicating nonlinear behavior. The large amplitude deformations induce a macroscopic orientation of the LC smectic mesophase leading to the nonlinear viscoelastic behavior. This more complex material response can be described in multiple ways; for example, in terms of higher order Fourier coefficients[21] or using the Chebyshev representation introduced by Ewoldt et al.[20] to describe non linear elastic and viscous responses. Using the latter approach we can quantify both the first order changes in the modulus of the material and the evolution in the nonlinear strain-stiffening response using a series of elastic material coefficients e_1, e_3, …. The ratio of the third-order to first-order elastic Chebyshev coefficient increases with UV exposure: from $(e_3^{off}/e_1^{off}) = 5.5 \times 10^{-2}$ to $(e_3^{on}/e_1^{on}) = 8.9 \times 10^{-2}$, which indicates an increase in the *relative* degree of elastic nonlinearity of the material upon UV irradiation. However, the *absolute* strength of the elastic network of the material is decreased because of the disruption of the smectic mesophase. Quantitative analysis of the Lissajous curves shows that both the linear and nonlinear coefficient decrease after exposure to UV light with $(G'_{off})/(G'_{on}) = (e_1^{off}/e_1^{on}) = 14.9$ and $(e_3^{off}/e_3^{on}) = 9.2$. Similar analysis of the viscous contributions to the oscillating stress in Figure 5b show an increase in the relative degree of viscous nonlinearity on UV irradiation. Under the combined actions of UV light and large strain the material is thus broken down from a predominately-elastic LC material with a high modulus to a weakly nonlinear viscoelastic gel-like response.

This study has demonstrated the ability to reversibly alter the morphology of side chain liquid crystalline polymers containing azo moieties through stimulation with UV light. The UV light induces a *trans* to *cis* isomerization, which disrupts the smectic LC mesophase, as shown by the in-situ SAXS experiments. This morphological rearrangement can be used to manipulate the rheological properties of the material over several orders of magnitude. In both the linear viscoelastic regime (strain amplitude of $\gamma_o \leq 4\%$) and in the nonlinear viscoelastic regime (strain amplitude of 100%), we have shown that UV irradiation can be used to reversibly modify and control the storage (G′) and loss (G″) moduli of the material. Future work includes investigating the effects of LC architecture and attachment percentage upon the responsive properties of this class of materials as well as the temperature dependence of the photorheological response.

Experimental Section

The synthesis of the poly(vinylmethylsiloxane) homopolymer has been previously reported[17, 22]. A detailed description of the synthesis of the LC moieties can be found in the supporting information. Solvent-cast films were prepared from a 2 wt% solution of LCP in toluene, resulting in films approximately 100μm thick. A Dymax Blue Wave 200 light source with a Thorlabs, Inc. FGUV W53199 ultraviolet (UV) filter, with peak at transmission at 360 nm, was used for UV exposure experiments. Information regarding the transmission spectrum of the FGUV filter is provided in the supporting information. The power output measured at the point where the sample is mounted for the UV rheometry experiments was 10mW/cm2. A TA Instruments Q1000 was used for differential scanning calorimetry (DSC), the heating and cooling rate was 10°C min-1 in all cases. Small-angle X-ray scattering (SAXS) experiments were performed at the G1 beamline at the Cornell High Energy Synchrotron Source (CHESS). The wavelength of the X-rays was 1.239Å, and silver behenate was used to calibrate the sample to detector distance with a first order scattering vector of q of 1.076nm-1 (with $q = 4\pi \sin\theta/\lambda$ where 2θ is the scattering angle and λ is the wavelength). A slow-scan CCD-based X-ray detector, home built by Drs. M.W. Tate and S.M. Gruner of the Cornell University Physics Department, was used for data collection. All scattering data were processed and analyzed using Polar software (Stonybrook Technology and Applied Research Inc., NY, USA). The SAOS and LAOS measurements were performed at the Hatsopoulos Microfluids Laboratory in the Massachusetts Institute for Technology (MIT). We used a parallel plate photocuring accessory mounted on an Advanced Rheometric Expansion System (ARES) strain controlled rheometer (TA Instruments, New Castle DE, USA). The photocuring accessory consists of an upper tool with a reflecting mirror directing the UV source towards the quartz lower plate (20 mm diameter) which is in contact with the sample. The lower plate is made of copper with a thin coating (6.35 μm) of a chromium based material (Micro-E, Electrolizing Inc.) and was used with the ARES Peltier control system.

Acknowledgments

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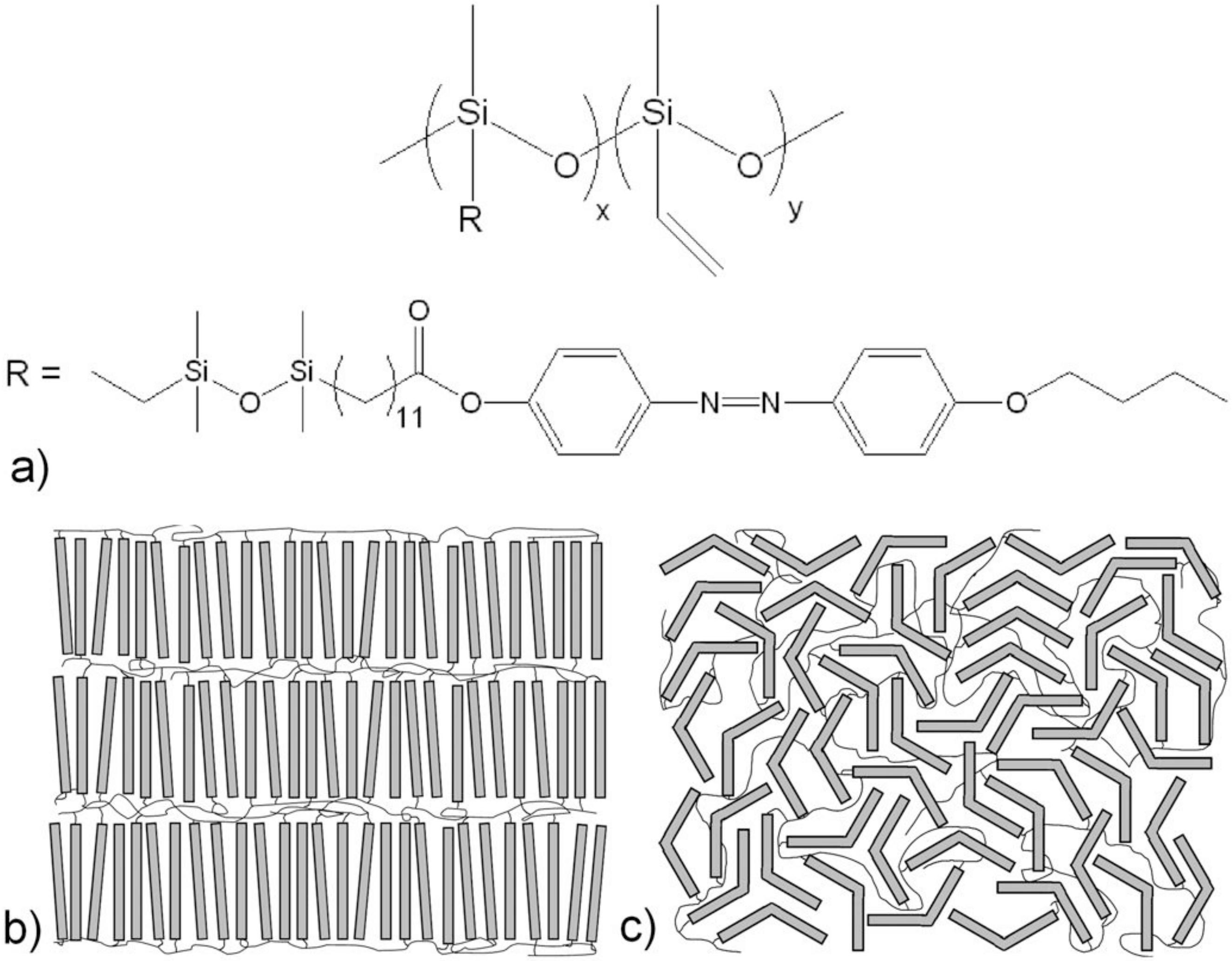


Figure 1.

a) Chemical structure of the side chain liquid crystalline polymer, where x and y are random and R is the azobenzene-containing moiety. Schematic of LCP in b) the *trans* conformation and c) the *cis* conformation, resulting in smectic and isotropic LC mesophases, respectively.

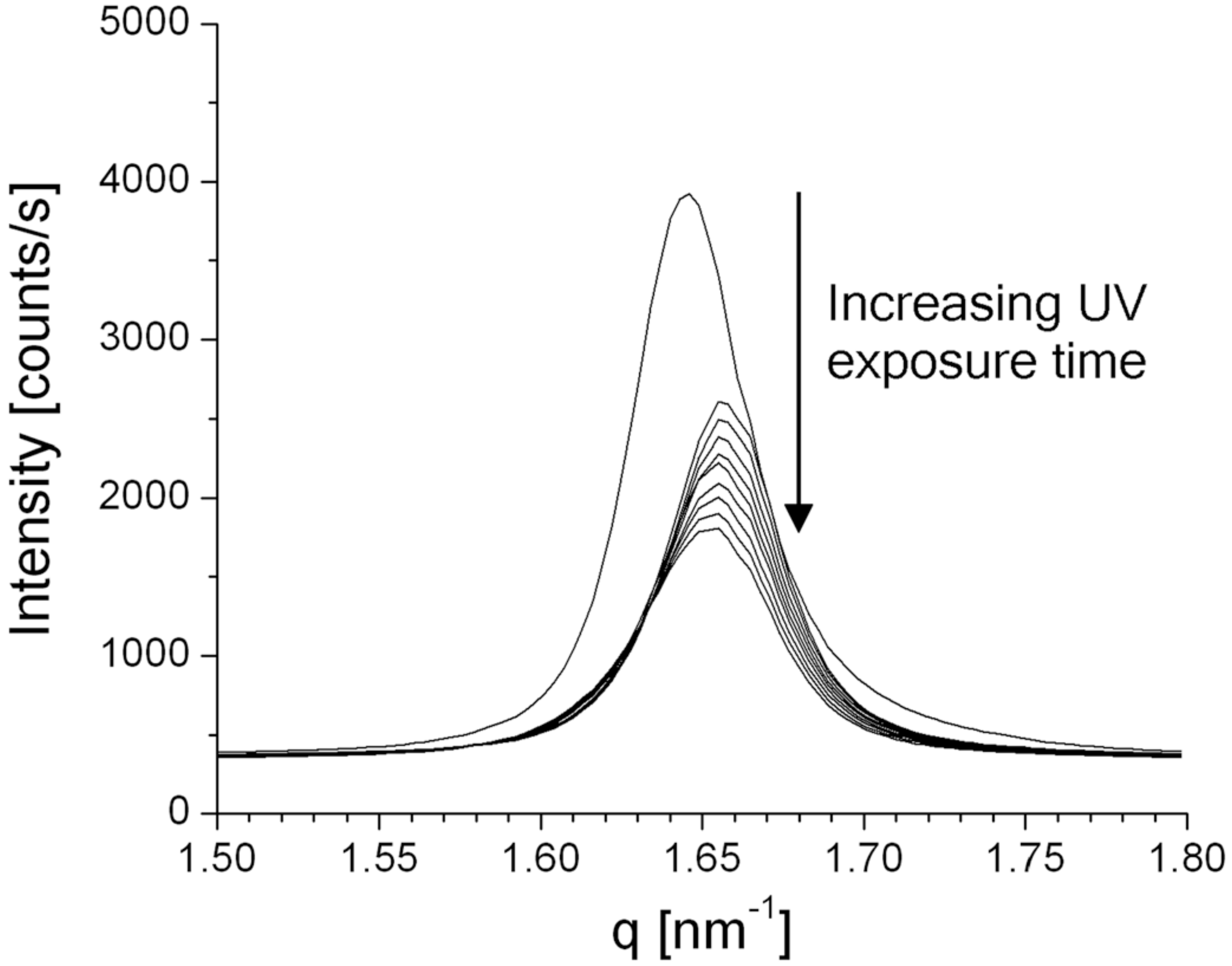


Figure 2.

Morphological response to UV light measured by small-angle X-ray scattering (SAXS). 1-D scattering curves as a function of exposure to UV light, the scattering intensity decreases with increasing exposure time

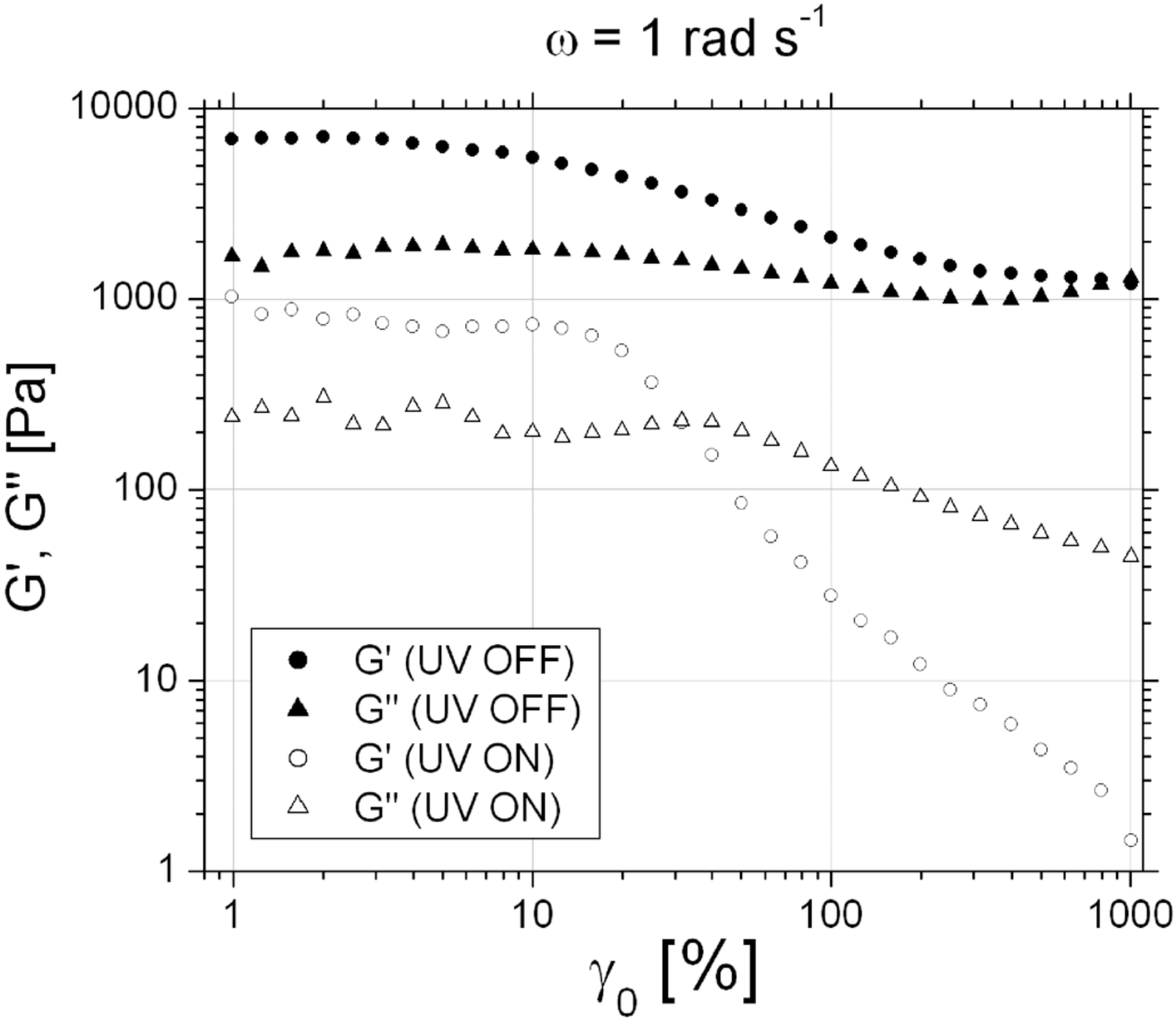
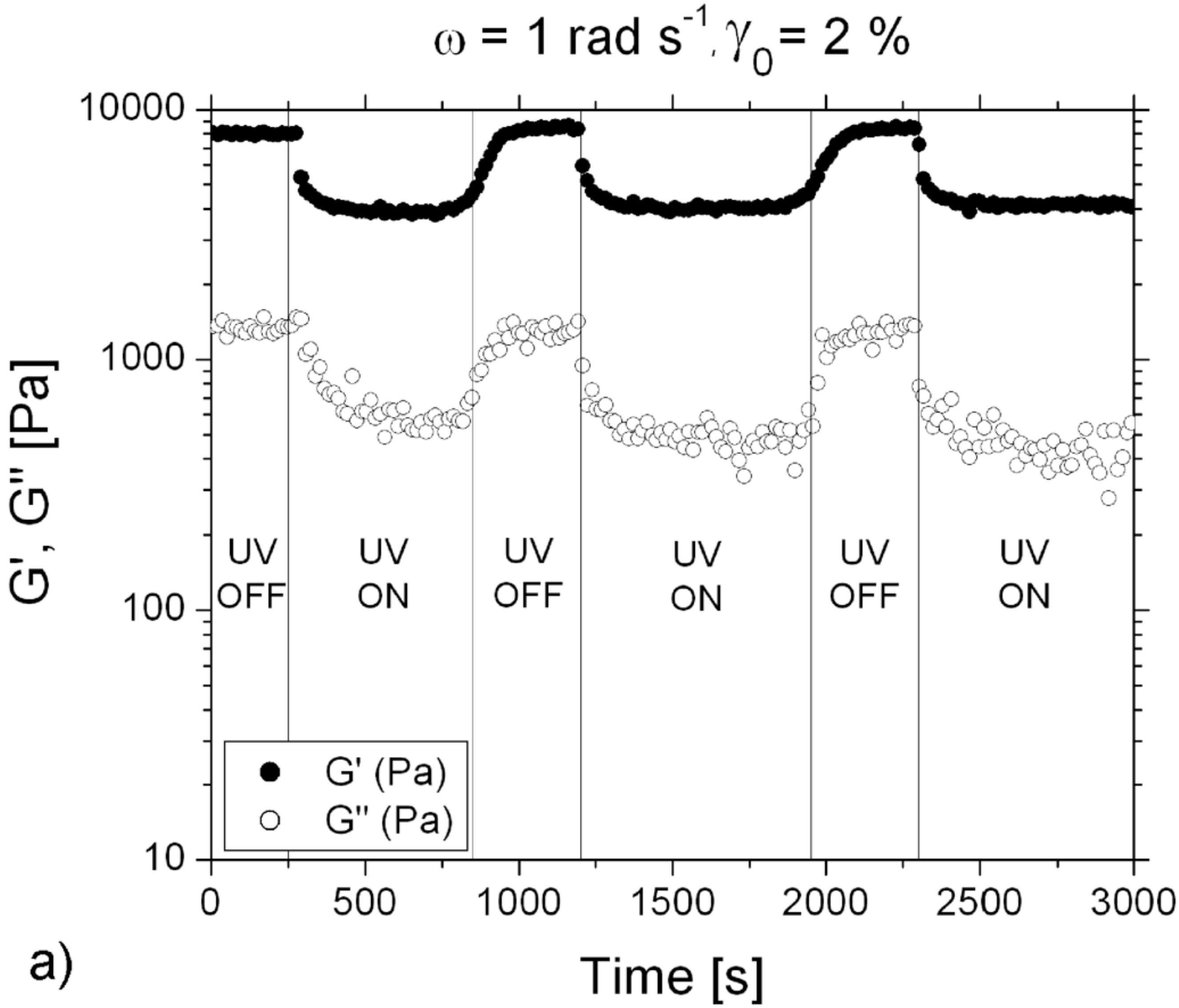


Figure 3.

Strain amplitude sweep without (solid symbols) and with (open symbols) exposure to UV light. The storage modulus (G′) is represented by the circles and the loss modulus (G″) is represented by the triangles. The data were obtained at 100°C at an angular frequency of ω = 1 rad/s.


ω = 1 rad s-1, γ0 = 2 %
10000
1000
100
10
G', G'' [Pa]
UV OFF
UV ON
UV OFF
UV ON
UV OFF
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● G' (Pa)
○ G'' (Pa)
0
500
1000
1500
2000
2500
3000
Time [s]
a)

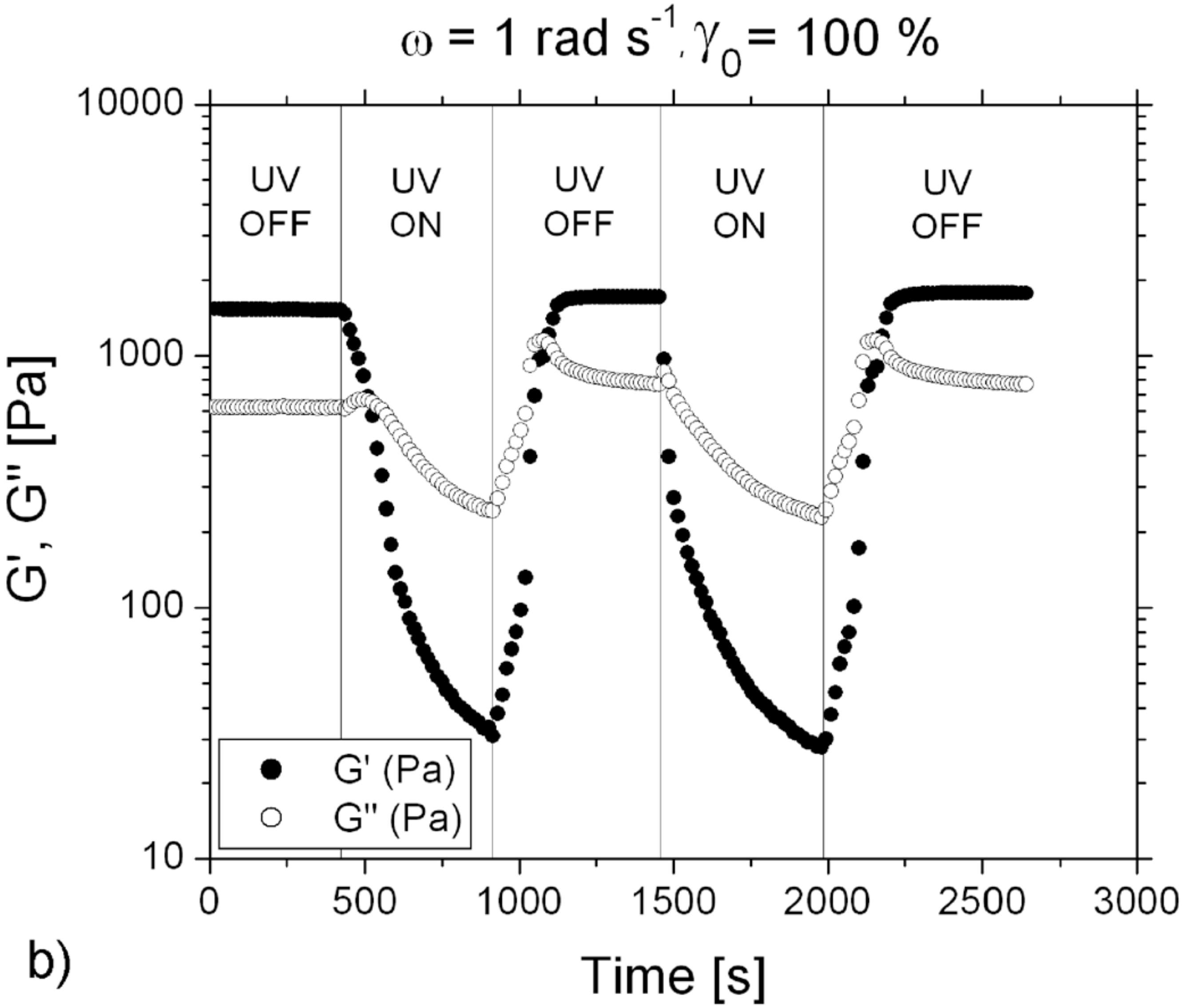
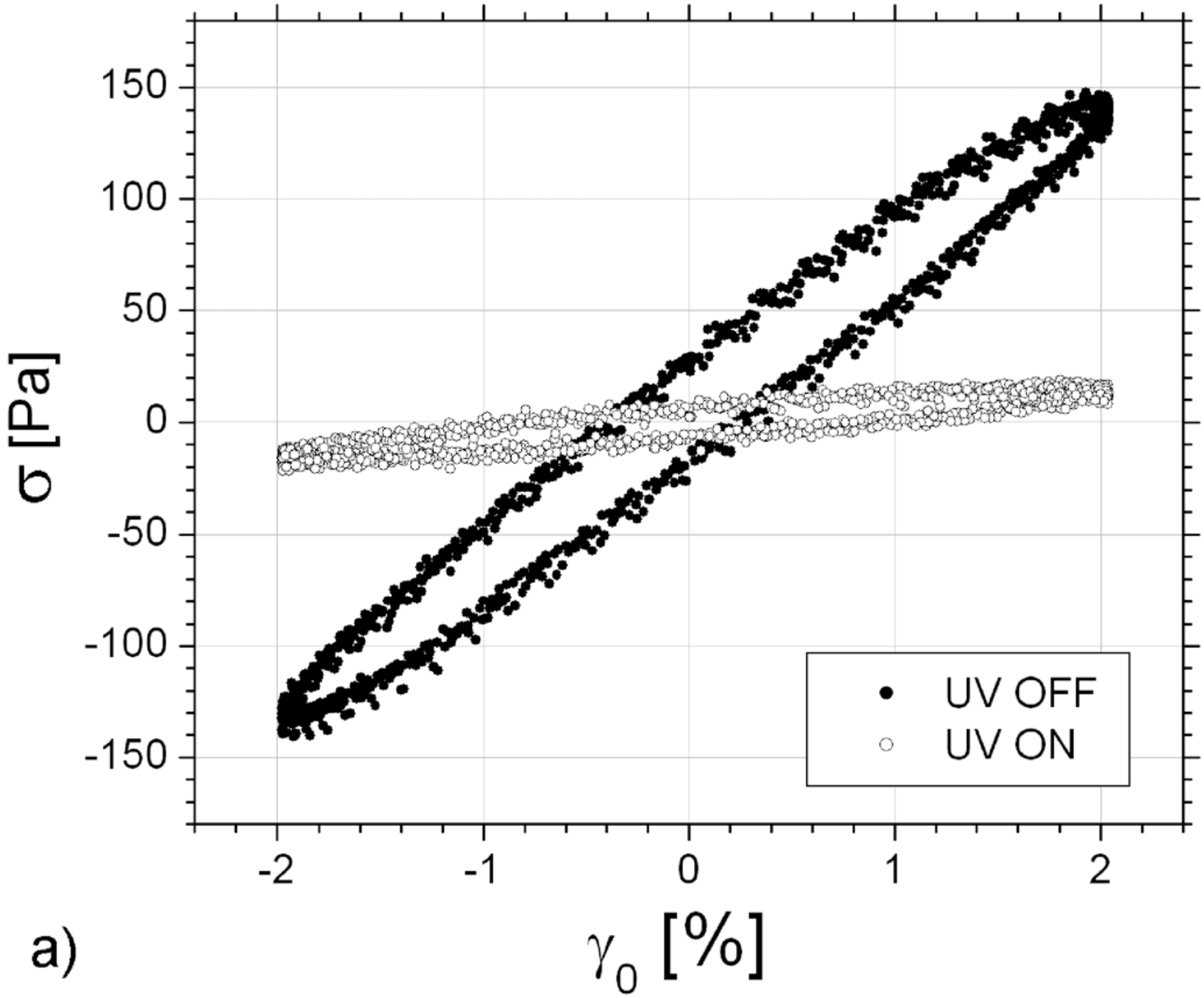


Figure 4.

a) Rheological dynamic properties measured over several exposure cycles at a strain amplitude of 2%; b) rheological dynamic properties measured over an exposure cycle at a strain amplitude of 100%. The storage modulus (G′) is represented by the solid circles and the loss modulus (G″) is represented by the open circles. The data were obtained at 100°C at an angular frequency of ω = 1 rad/s.


150
100
50
0
-50
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σ [Pa]
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0
1
2
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a)

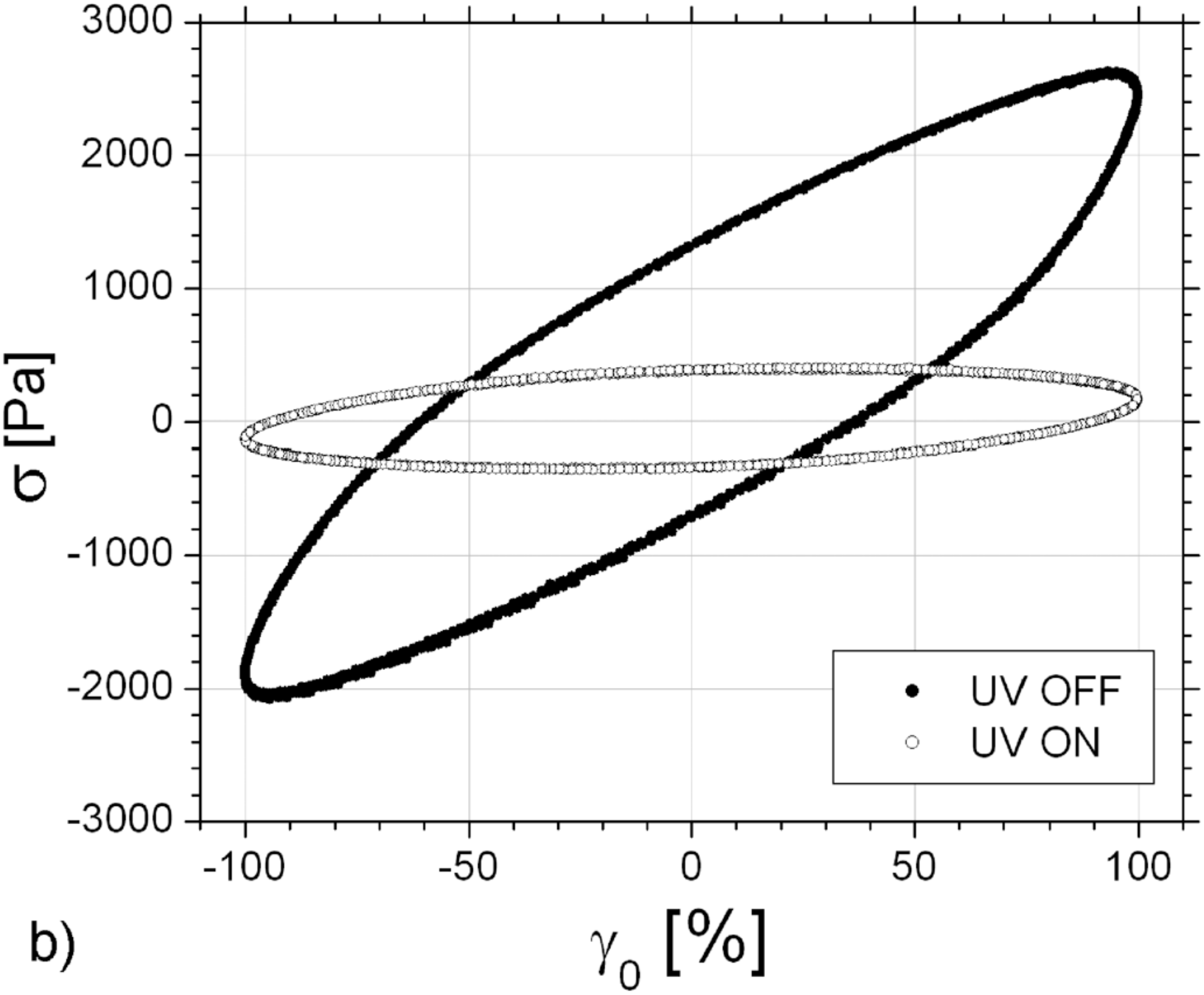

Figure 5.

Lissajous figure of the shear stress σ as a function of the oscillatory strain for a maximum strain amplitude of a) 2% and b) 100%. The steady state data were obtained at 100°C with (open symbols) and without (solid symbols) exposure to UV light at an angular frequency of ω = 1 rad/s and after a UV exposure time of 750s corresponding to a) 33τ and b) 8τ, where τ is determined according to equation (2).