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# Temperature- and Light-Regulated Gas Transport in a Liquid Crystal Polymer Network

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## Abstract

Azobenzene-containing liquid crystal polymer networks (LCNs) are developed for temperature- and light-regulated gas permeation. The order in a chiral- nematic LCN (LCN\*) is found to be essential to couple the unique structure of the membrane and its gas permeation responses to external stimuli such as temperature and varying irradiation conditions. An LCN membrane polymerized in the isotropic phase exhibits enhanced N<sub>2</sub> permeation with increasing temperature, like most traditional polymers, but barely responds to exposure with 455 and 365 nm light. In sharp contrast, a reversible decrease of N<sub>2</sub> transport is observed for the LCN\* membrane of exactly the same chemical composition, but molecularly ordered, when submitted to an elevated temperature. More importantly, alternating in situ illumination with 455 and 365 nm light modulates reversibly N<sub>2</sub> permeation performance of the LCN\* membrane, through the trans–cis isomerization of azo moieties. The authors postulate that, besides the anisotropic deformation of LCN\*, the decreased order in LCN\* membrane caused by external stimuli (i.e., increasing temperature or UV light illumination) is responsible for an inhibition of gas permeation. These results show potential applications of liquid crystal polymers in the gas transport and separation, and also contribute to the development of “smart” membranes.

Keywords: azobenzene, gas permeation, isomerization, liquid crystal polymer network, stimuli-responsive membranes

## 1. Introduction

Polymer membranes are widely used for separation and purification processes. The advantages of using polymers are manifold. They easily comply with large scale manufacturing under relatively

mild conditions. And, most importantly, they allow chemical functionalization making them versatile for numerous applications.[1] An ideal membrane should serve as a molecular scale filter that produces pure permeate A on the permeation side from the mixture of A and B, with maximized mass transport and selectivity.[2] However, conventional polymer membranes are unable to approach such high efficiency, for instance, a general trade-off has always existed between mass transport and selectivity.[3] Accordingly, the focus of the active research in the field has been directed to the development of chemically different polymers with novel structures that can overcome existing challenges or access applications that are not yet practiced commercially.[4–6] Liquid crystal polymer networks (LCNs) form relatively new classes of intelligent materials due to the combination of self-assembled molecular morphology and stimuli-responsive properties.[7–9] Our approach here is to develop LCN membranes whose gas transport behavior can be regulated by changes in their environment, i.e., temperature and light. Especially light is an attractive stimulus, since it proved to be a versatile and controllable energy source for driving a wide range of nanoscale molecular systems.[10–12] The advantages of employing LCNs as gas permeation membranes are as follows:[13] 1) topologically defect-free polymeric membranes can be easily formed, since the in situ polymerization freezes the desired molecular order that is previously established in the low viscous monomeric state; 2) designable order of mesogens can give uniform and tailored membrane structures and corresponding gas transport properties; and 3) good chemical resistance of these polymers enable the process stability even in a harsh environment. However, there have been limited reports on the use of these polymers for gas permeation applications. Major efforts have focused on the research of polymer dispersed liquid crystal (PDLC) systems and liquid crystals-polymer composite membranes. [14–17] These systems successfully demonstrated that obvious deviations in their permeation performance corresponds to the liquid crystal phase transitions. Nevertheless, one of the unfavorable properties of these composite membranes could be inhomogeneities on microscopic level, as the liquid crystal molecules are physically dispersed or blended within the polymer matrix. On longer terms the low molar mass liquid crystals tend to evaporate, especially when the membrane is subjected to heat or vacuum processes. Therefore, here we seek to create gas permeation membranes using pure polymeric networks with photo responses and temperature responses inherently encoded in the membrane structures.

## 2. Results and Discussion

### 2.1. Design of the Temperature and Photo-responsive Membrane

Our approach involves the use of a liquid crystal mixture (Figure S1, Supporting Information) that can selectively form amorphous or helically structured polymer membranes, as the order of liquid

crystals either in isotropic phase or chiral nematic (or cholesteric) phase can be preserved by in situ photopolymerization. The cholesteric phase exhibits heli-coidal molecular order of planar aligning rodlike mesogenic molecules and is characterized by a helical pitch ( $p$ ), the distance corresponding to a  $360^\circ$  rotation of the meso- gens along the helix director.[18] The cross section view of a cholesteric LCN\* membrane has been revealed in Figure S2 in the Supporting Information, and the pitch is represented by the multiple parallel lines in the scanning electron microscopy (SEM) image. If the pitch is of the same order of magnitude as the wavelength of visible light, corrected for the refractive index determined wavelength change in the medium, the cholesteric phase selectively reflects light and shows a color in the visible range, according to the equation,  $\lambda=np$ , where  $n$  is the mean refractive index of the liquid crystal.[19] The inset in Figure S2a in the Supporting Information shows the texture of the LCN\* membrane as observed by polarized optical microscopy (POM) in reflection mode. The typical “oily streaks” structure of the cholesteric phase point to a planar orientation with the helix axes orthogonal to the surface of the film. Accordingly, the central reflection band of the LCN\* membrane characterized by UV-vis is 640–720 nm, corresponding to a pitch  $p$  of around 420 nm. Noticeably, liquid crystal networks display a strong coupling between the scalar order parameter of the molecules

and mechanical strain. Compared to the uniaxially aligned nematic and smectic phase, mechanical deformations of the polymer with cholesteric molecular order can be minimized in the membrane planar direction, as expansional changes related to the vectoral order parameter of the successive layers cancel each other out.[20] Therefore, here we have designed and prepared our permeation membranes based on the LCN\* polymer and for reference we made an isotropic polymer membrane of exactly the same chemical composition but polymerized in the isotropic state of the monomer mixture. While the helicoidal molecular structure of the membrane can be easily obtained by adding an adjusted amount of chiral dopant to the LC mixture, one of the most straightforward approaches to induce light responsiveness in the network is to introduce photo-responsive molecular switches, such as azobenzene moieties, into its covalent structure. Azobenzene derivatives are thoroughly investigated photo-switches that undergo an oscillating trans–cis isomerization with ultraviolet (UV) and visible light/ heat. The isomerization can provide large geometrical changes and also a remarkable alteration in polarity, because the dipole moments of the trans- and cis-isomers of non-substituted azobenzene are around 0 and 3.1D, respectively, and from trans- to cis- state, the molecular length changes from 9 to 5.5 Å. [21,22] As shown in Figure S1 in the Supporting Information, the switch is incorporated into the polymer main chain through copolymerizable methacrylate groups. It has been shown that in an LCN, already a low concentration of azobenzene

moieties (e.g., 2–6 wt%) the conformational change of azobenzene molecules is amplified to macroscopic level,[23] and thus the concentration was set to 4 wt% to provide large photoinduced effects.

## 2.2. Temperature-Induced Permeation

We have designed and fabricated a permeation set-up for the membrane gas transport test at controllable conditions, as depicted in Figure 1. Dynamic mechanical temperature analysis (DMTA) was performed on isotropic and cholesteric LCN membranes to determine their glass transition temperature ( $T_g$ ), which was 75 and 65 °C, respectively, while the storage modulus below and above  $T_g$  was not much affected by the molecular order (Figure S3, Supporting Information). After equilibration of the membranes at the operational pressure difference between the feed and permeate side (e.g.,  $\Delta p \approx 0.8$  bar), we recorded the N<sub>2</sub> transport through the membrane over time by a gas chromatography instrument (GC). The N<sub>2</sub> peak area from GC result was used to quantitatively analyze the real time N<sub>2</sub> permeation through the membrane. The pressure difference between feed and permeate side was optimized and constant at 0.8 bar, in order to prevent visible deformation of the thin LCN membranes ( $\approx 20 \mu\text{m}$  thickness). For the isotropic LCN membrane, the gas transport increased by 6% as the temperature increased right above the  $T_g$ , as shown in Figure 2a. It is completely comparable to conventional polymer membranes, i.e., increasing temperature normally decreases the gas solubility in polymers but increases the gas diffusivity in the polymer, resulting in an overall increased gas permeation.[2] The permeation ( $P$ ) of gas molecules through the dense polymer membrane is usually described by the well-known “solution–diffusion” process, i.e.,  $P \approx SD$  where solubility ( $S$ ) and diffusivity ( $D$ ) are governed by thermodynamic and kinetic/transport factors, respectively.[5,24] But in sharp contrast to the isotropic membrane, N<sub>2</sub> transport through the cholesteric LCN membrane decreased (by 8%) by increasing the temperature right above the  $T_g$  (Figure 2b). This should be attributed to the different structures of these membranes (amorphous vs helicoidally ordered), since the chemical composition of the membranes has been designed to be identical. Upon heating, both films expand, thus increasing the diffusional path length. The chiral-nematic films are known to expand anisotropic with most of the volume increase manifesting itself as a linear coefficient along the helix axes, unlike the isotropic film which expands equally in all dimensions. An estimate based on the data in reference 13 revealed a thickness increase of around 0.7% for the isotropic film and around 2.5% for the LCN\* film. This difference alone is not enough to explain the remarkable opposite thermal response of both films. We therefore speculate that the difference in molecular packing, especially at room temperature is co-responsible for leading to a higher N<sub>2</sub> permeability of the LCN\* at low temperatures. The difference in packing and

corresponding less relaxational freedom of the polymer chains as limited by the mesogenic organization leads to an enhanced free volume, which also is manifested in the lower glass transition temperature of the LCN\* film. Upon passing the glass transition, the mesogenic order decreases and the mobility of the polymer chains increases compared to the isotropic case and both materials converge to the same permeability. As a net result, the decreased order of the LCN\* at elevated temperature leads to a decreased permeability.

### 2.3. Photoinduced Permeation

After we demonstrated regulation of nitrogen permeation by temperature, we will focus in the following section on controlling nitrogen transport through both the isotropic and chiral-nematic liquid crystal network under varying illumination conditions. Alternating irradiation with 455 and 365 nm light, the in situ measured permeation-time profile of the LCN\* membrane exhibits a “zigzag” pattern as shown in Figure 3a. The figure shows 3 cycles but can be repeated multiple times. Keeping the azobenzene in its predominantly trans state by exposing with 455 nm light enhances the permeability while populating the photostationary state of the cis state by illuminating with 365 nm light reduces the transparency of the membrane for N<sub>2</sub>. In comparison, similar light irradiations on the isotropic LCN membrane does not cause any obvious changes in its N<sub>2</sub> permeation performance (Figure 3b), even when we significantly increase the light intensity. These measurements revealed a strong correlation between photoinduced gas permeation performance and the molecular structure of the membrane. In addition, as shown in Figure 3c, first shining blue light and switching to UV irradiation on the cholesteric LCN membrane, the permeation value dropped quickly (by 9%). Then extinguishing the UV light, the permeation slowly reverted to the initial state, within several hours (corresponding to the time scale for the cis–trans isomerization of azobenzene moieties in dark).[25] Under the different illumination conditions, the temperature of the membrane is subjected to changes, thus the real time temperature on the membrane was recorded by an infra-red camera. Exposure to 455 nm light and then only 365 nm light with the same irradiation intensity, the temperature of the LCN\* membrane shows a marginal change (44–48 °C). For reference we performed a membrane permeation test in dark while heating the membrane to the same values using an internal heater (i.e., the temperature control device as shown in Figure 1). As result, the permeation of the LCN\* membrane showed only a negligible difference. After exposure, the 365 nm light was switched off, the temperature of the LCN\* membrane dropped quickly to temperatures close to room temperature (in several minutes) as shown in Figure 3c. Mimicking this temperature drop in a “dark” experiment shows that the permeation of the membrane increased rapidly to its initial equilibrium value (Figure 3d). This is in contrast with what is seen in Figure 3c, where the same

temperature drop does not lead to a rapid increase of the permeation. Here the nitrogen diffusion is still dominated by the cis state of the azobenzene and the corresponding lower degree of order of the LCN\*.

## 2.4. Temperature and Photo-response Mechanism

At this moment it is of interest to consider the temperature of the exposed membranes in relation to their glass transition temperature. So far, all illumination experiments are apparently carried out below the glass transitions as given in Figure S3 in the Supporting Information. However, it is known for azobenzene modified LCNs that photo-softening might occur when the embedded photo-switch is isomerized reducing the  $T_g$  under illumination.[26] And indeed, as seen in Figure 4, when the membranes are subjected to the illumination condition, we used in our permeability experiments, a shift in modulus and glass transition is measured. When exposing the isotropic membrane to blue or UV light, the glass transition temperature shifts from 75 to 65 °C, as derived from the maximum in  $\tan\delta$ . For the LCN\* membrane the decrease of the glass transition temperature is even larger, from 65 to 45 and 40 °C, when exposed to UV and blue light, respectively. Consequently, the permeation of the LCN\* is measured around the glass transition for both the 365 and the 455 nm exposure. Nevertheless, populating the azobenzene cis state promotes a decrease of the order parameter and reduces the N<sub>2</sub> permeation. This is in correspondence with the effect of the reduced order parameter by increasing the temperature in the foregoing experiment. For the isotropic membrane the temperature rise gives an increase of the permeability (Figure 2a), but this is not observed for the light exposed membrane (Figure 3b). This can be partly explained by the fact that the temperature remains below the glass transition temperature. But even when we increase the light intensities (Figure 3b), thereby raising the temperature to just above the glass transition, this does not reveal a change in permeability within the accuracy of the experiment. We may conclude that the increased diffusional mobility by temperature is counter-balanced by the oscillatory trans–cis conversion of the azobenzene and its influence on the molecular dynamics of the whole network.

## 3. Conclusion

We have designed and synthesized liquid crystal polymers for the temperature- and photoinduced reversible regulation of their gas permeation. These stimuli-responsive membranes showed a strong correlation between the membrane structures and their permeation performance. When temperature was applied as a real time stimulus, the liquid-crystalline ordered membranes revealed a completely opposite response in comparison with their isotropic analogue: when heated

above their glass transition temperature reversible promotion of N<sub>2</sub> permeation was observed for the isotropic membranes while the cholesteric LCN\* membrane shows an inhibition of the permeation under similar temperature conditions. The change from the glassy to the rubbery state and an accompanying decrease in the molecular order reduced the N<sub>2</sub> mobility in this film. We hypothesize that the main cause originates from a higher glassy diffusion rate in the ordered network by an initially higher free volume and molecular voids as the network forms in the more rigid ordered state of the monomers. When heated to the rubbery state the voids fill as the order parameter reduces and the LCN\* cannot benefit from a higher diffusional mobility as normally observed in isotropic polymers. Under alternative blue and UV light irradiation, negligible changes in the permeation performance were observed for the isotropic LCN membrane, but trans–cis isomerization of azo moieties in the ordered cholesteric LCN\* allowed photoinduced reversible regulation on the permeation. Also, here the reduction of the order parameter under UV illumination condition and the trans to cis dynamics of the azobenzene tend to close the molecular voids and reduce the diffusional mobility of nitrogen. As soon as the mesogenic molecular rods in the network are brought back into their higher order position the polymer network opens itself for enhanced gas transport. Due to the combination of meso- morphic and macromolecular behavior, we anticipate that gas permeation and transport properties of these intelligent LCN polymers can be further enhanced by controlling parameters related to the order, orientation, connectivity and distribution of the different domains of liquid crystals.

## Acknowledgements

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## Conflict of Interest

The authors declare no conflict of interest.

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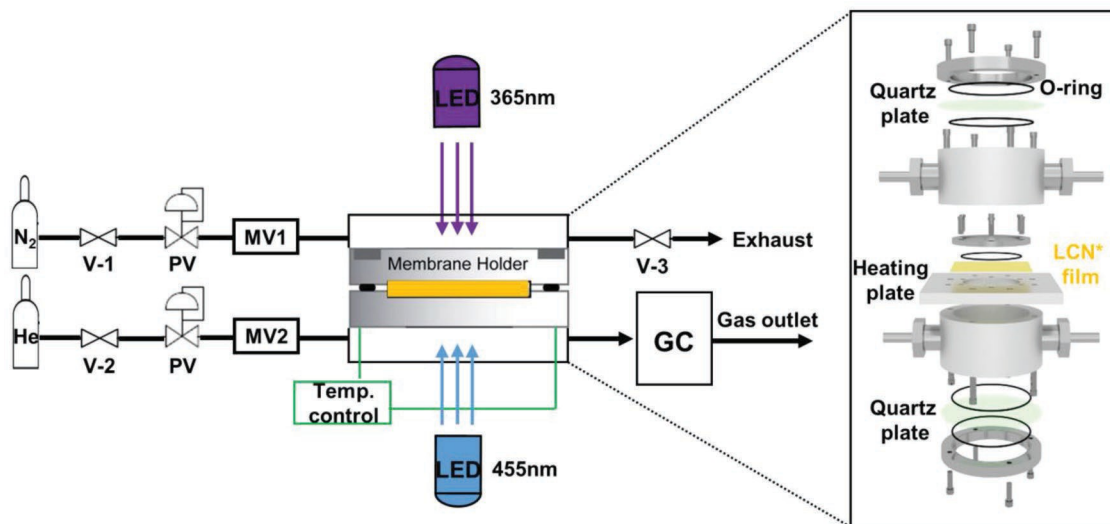


Figure 1.

Design of N<sub>2</sub> gas permeation set-up and the gas permeation cell with in situ irradiation and temperature control over the measurements. (V: valve; PV: pressure reducing valve; MV: manual valve; GC: gas chromatograph).

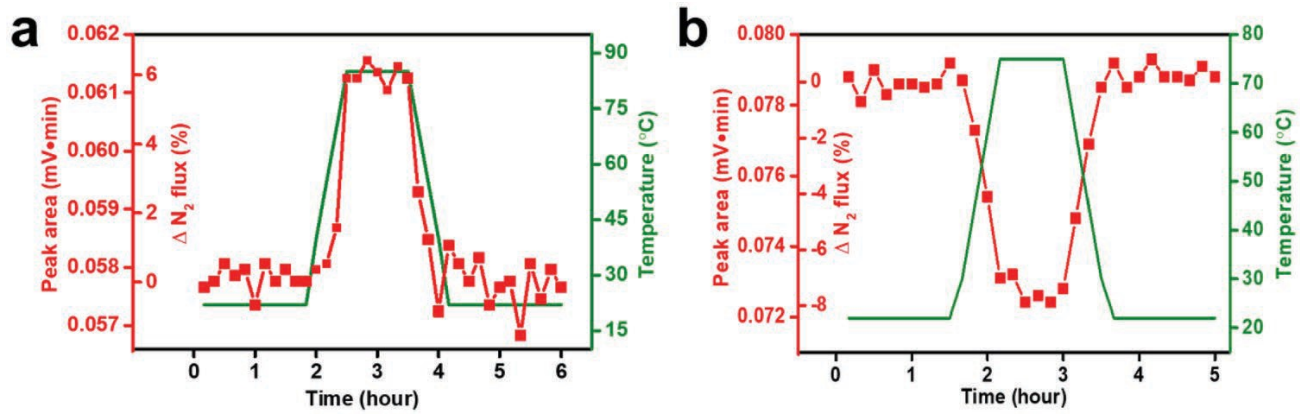


Figure 2.

N<sub>2</sub> permeation measured real-time at different temperatures: the polymer film polymerized in the isotropic phase a) and in the cholesteric phase b).

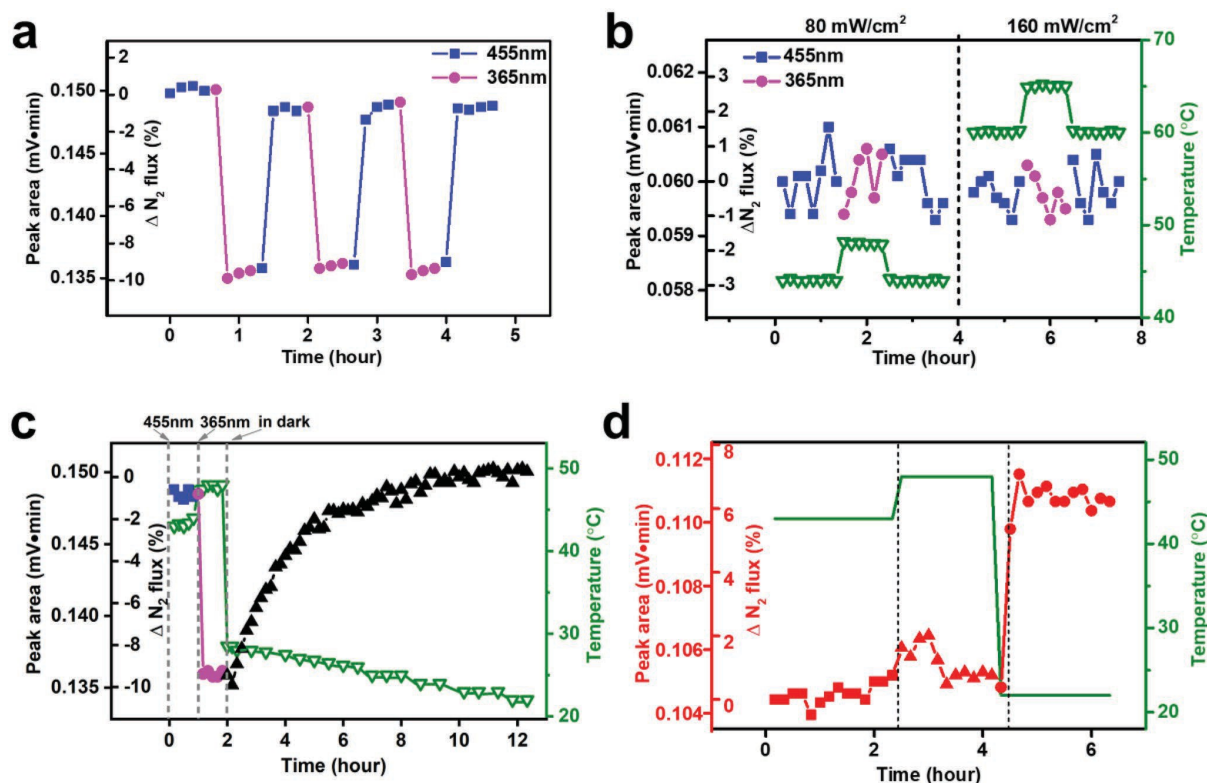


Figure 3.

N<sub>2</sub> permeation during in situ illumination of a) the LCN\* membrane and b) the LCN membrane polymerized in isotropic state: alternating irradiation with blue light (455 nm, 80 mW cm<sup>-2</sup>) and UV light (365 nm, 80 mW cm<sup>-2</sup>), for the isotropic membrane the light intensity was further increased to 160 mW cm<sup>-2</sup>; c) first a brief exposure with blue light, then switched to UV light and then light off while simultaneously the temperature is recorded on the LCN\* membrane; d) N<sub>2</sub> permeation through an LCN\* membrane at different temperatures in dark to mimic the heating effect of illumination.

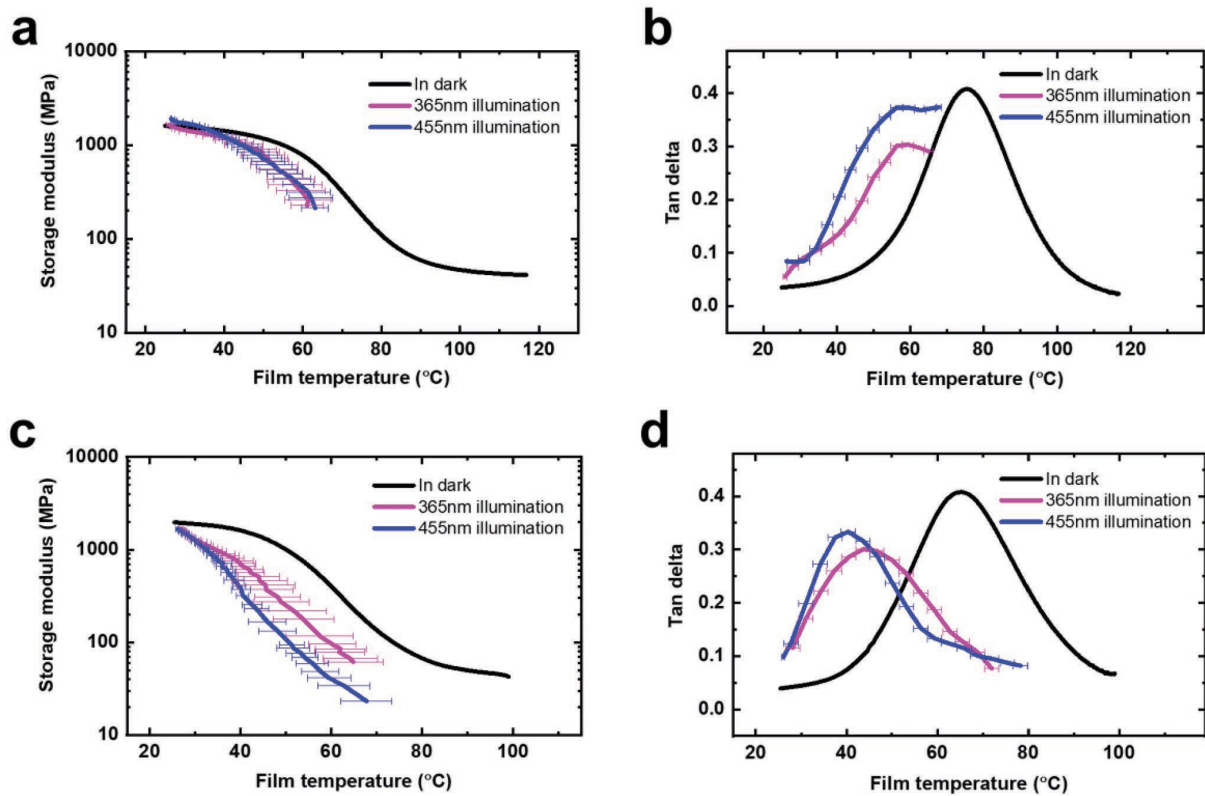


Figure 4.

Mechanical properties of membranes with isotropic molecular order in dark and under illumination: a) comparison of the storage modulus and b) tan delta. Mechanical properties of LCN\* film in dark and under illumination: c) comparison of the storage modulus and d) tan delta. For the mechanical property tests with separate light (455 or 365 nm) illumination on the films, the light intensity was gradually and slowly increased for a desired temperature increase ( $\approx 0.4 \text{ } ^\circ\text{C min}^{-1}$ ) of the films. The error bars show the total spread of the data.