

SUPPORTING INFORMATION

Self-aggregation, H-bonding, and Photoresponse in Film and Solution States of Azobenzene Containing Polyurea

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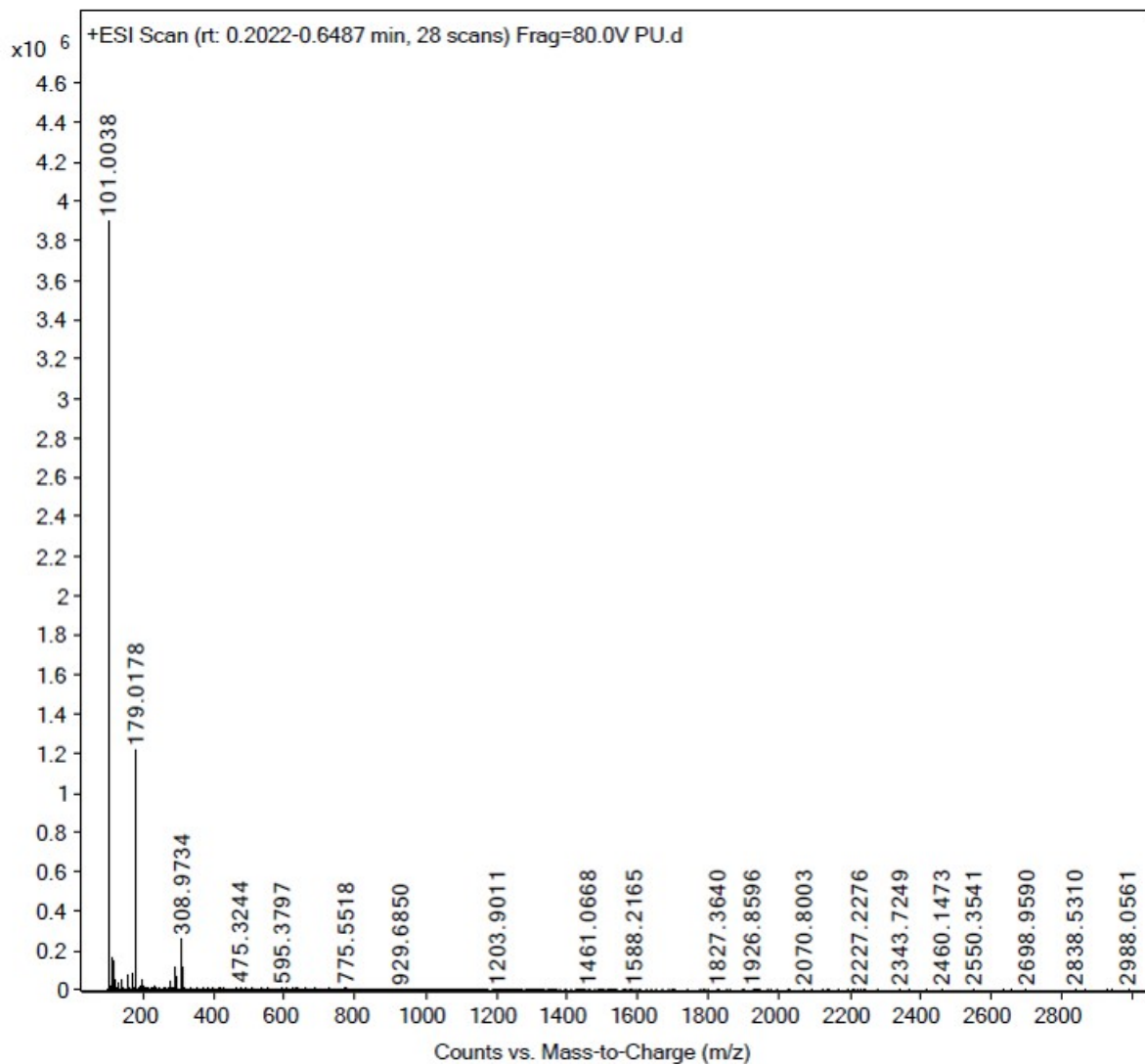


Figure S1: Electrospray ionization (ESI) spectrum of azo-PU. The average molecular weight was calculated using the first nine peaks of this spectrum using the free version of ESIprot Online software)

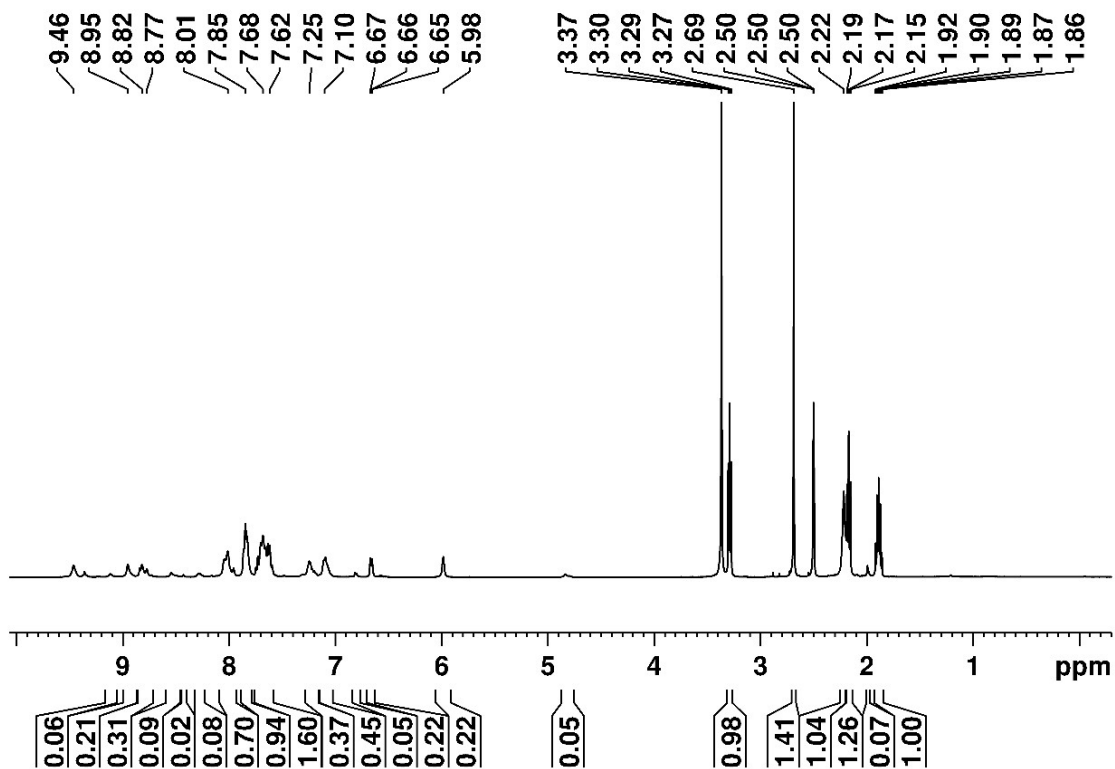


Figure S2: ^1H NMR spectrum of azo-PU powder in $\text{DMSO-}d_6$. The spectrum shows chemical shifts between 6 and 9.5 ppm which correspond to the protons in urea group, while the multiple peaks between δ 1.86 - 2.69 ppm correspond to the resonance peaks of the methyl protons [1, 2].

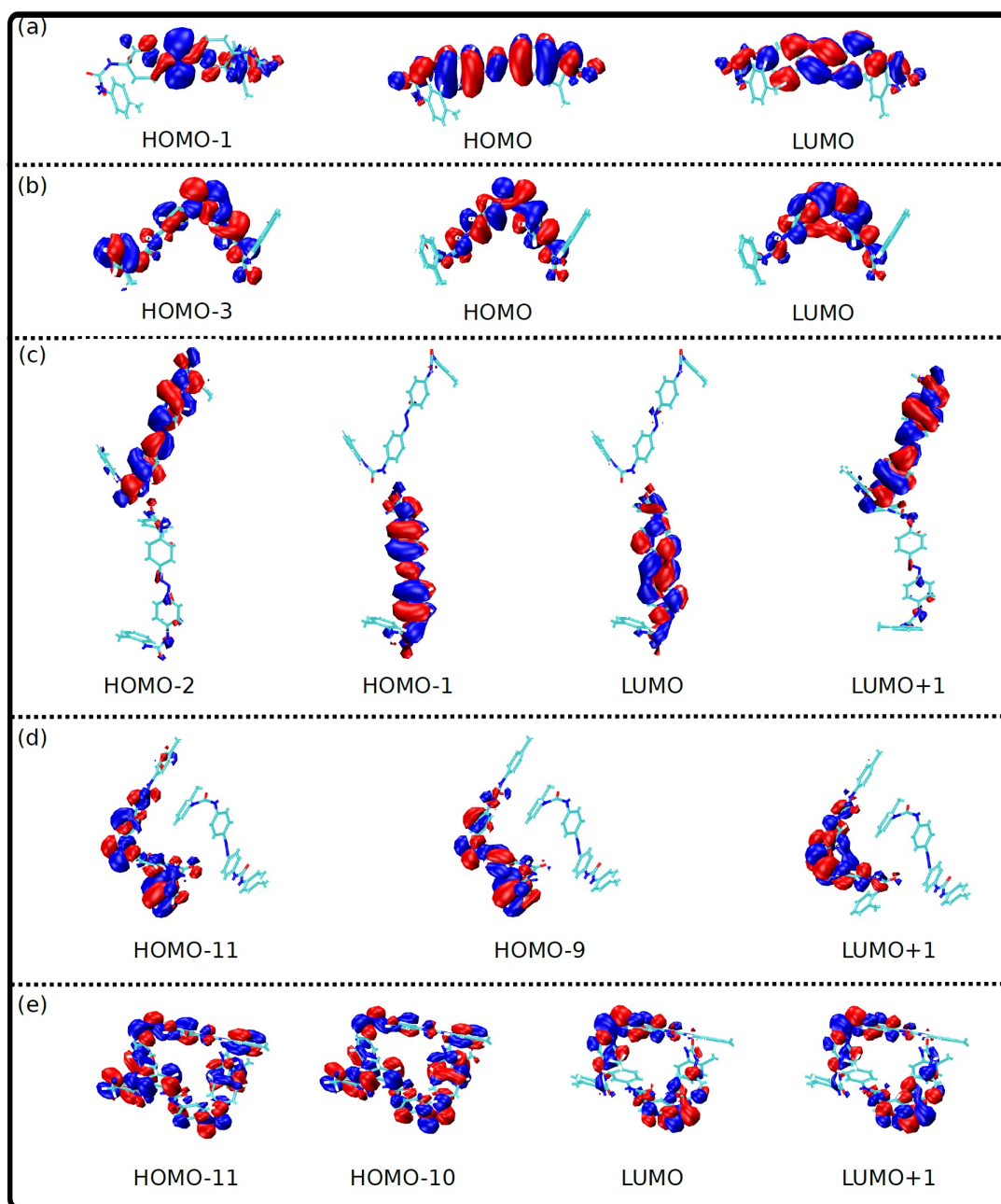


Figure S3: Molecular orbital (orbital type) iso-surface for: (a) trans-monomer in gas phase, (b) cis-monomer in gas phase, (c) trans-dimer in DMF, (d) H-aggregated cis-dimer *without* hydrogen bonding and (e) H-aggregated cis-dimer *with* hydrogen bonding (iso-value 0.02, colours show opposite spin).

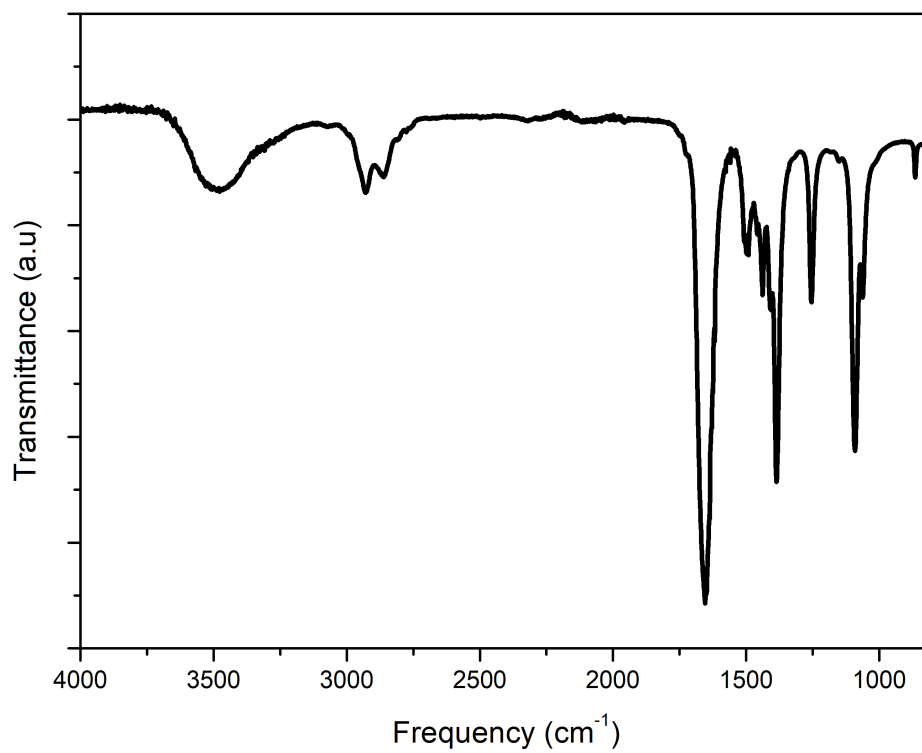


Figure S4: IR spectrum of cis isomer of azo-PU solution. The spectrum of cis azo-PU solution was recorded after exposing azo-PU solution to 365 nm light for 20 min.

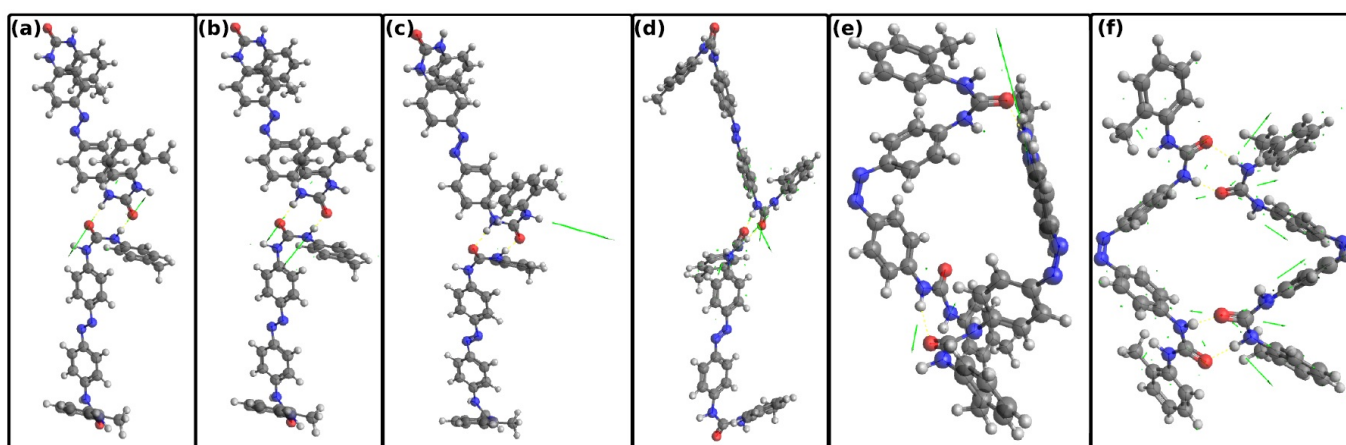


Figure S5: Force vectors for vibrational modes along N-H bond stretching, force vectors shown as green arrows: (a) trans dimer in DMF phase (at 3284 cm^{-1}) representing $\text{C}=\text{O}\leftrightarrow\text{N-H}$ anti-symmetric stretching, (b) trans dimer in DMF phase (at 3309 cm^{-1}) representing $\text{C}=\text{O}\leftrightarrow\text{N-H}$ symmetric stretching, (c) trans dimer in DMF phase 3575 cm^{-1} representing N-H symmetric stretching and (d) H-aggregated cis-dimer in DMF solvent (at 3487 cm^{-1}).

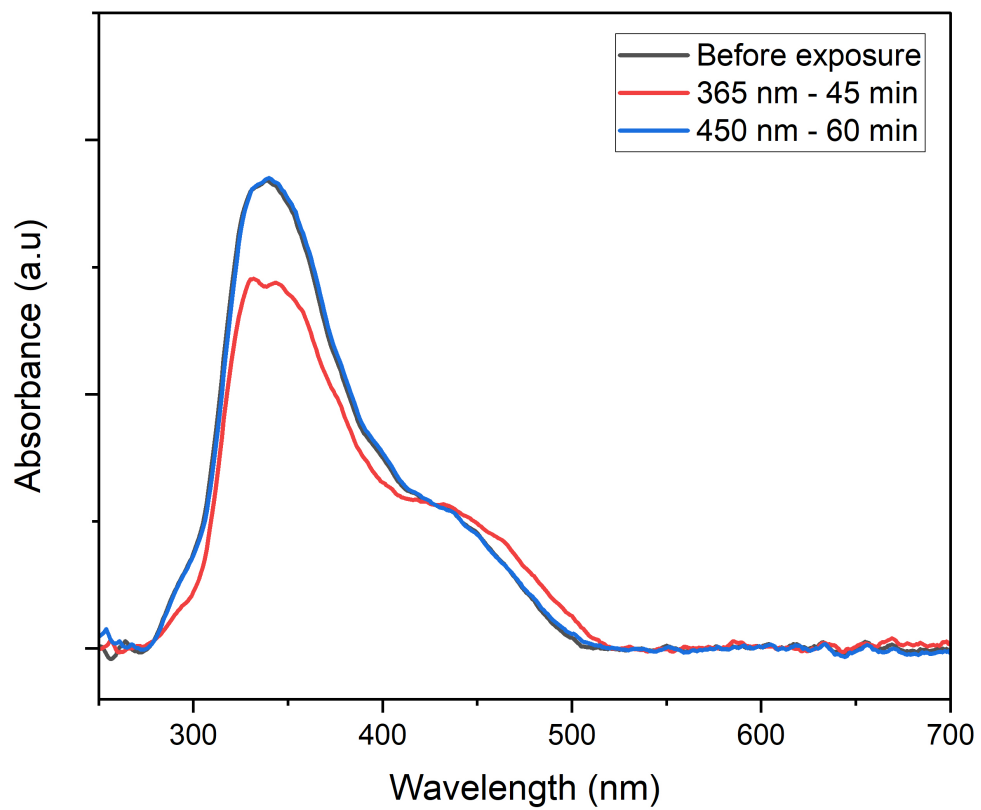


Figure S6: UV-visible absorbance spectra of azo-PU thin film when subjected to 365 nm light for 45 min followed by 450 nm light for 60 min

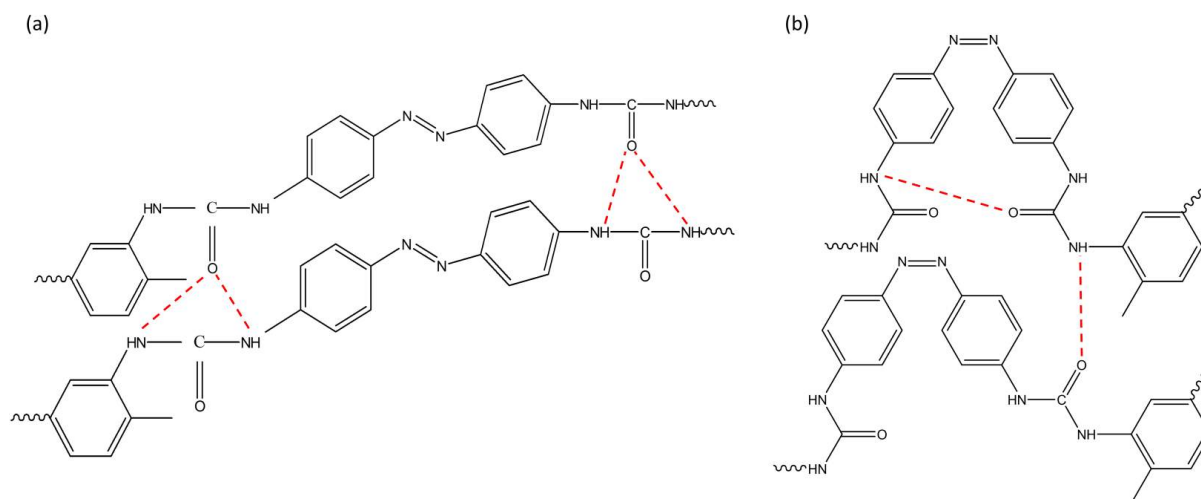


Figure S7: Hydrogen bonding possibilities, denoted by the red dashed lines, that can exist in dimers of (a) trans azo-PU and (b) cis azo-PU. The coplanarity of azo groups and aromatic rings in trans azo-PU provides greater chances of hydrogen atoms being proximal and bonded to the electronegative oxygen atoms, but the out-of-plane configuration in cis azo-PU makes it more difficult. We note that these are 2-D schematics; the azo group and urea groups in cis azo-PU are actually in different planes in 3-D.

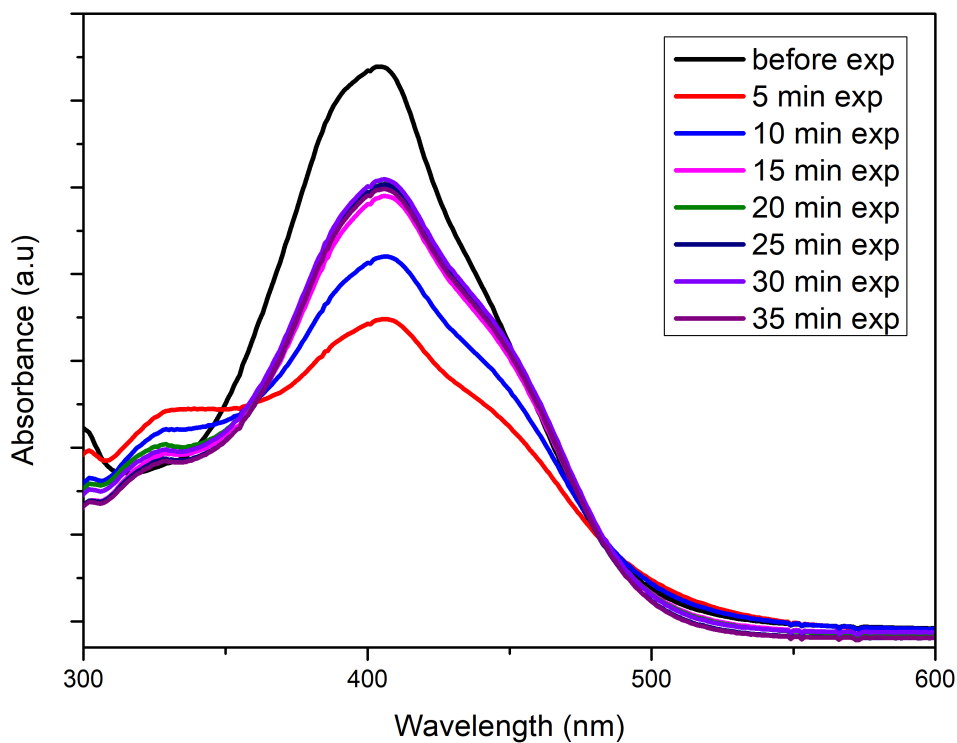


Figure S8: Time dependent UV-visible absorption spectra of azo-PU solution in DMF. The solution was exposed to UV light of 365 nm and the photostationary state was observed to occur at around 20 min. The cis/trans ratio may be estimated based on the changes in intensities of the absorption peaks over different times of 365 nm UV irradiation [3, 4, 5]. It is assumed that all the trans isomers were converted to the cis form after sufficiently long exposure, and this is used as a reference state. This may be a reasonable assumption, as cis isomers have greater stability in solution compared to azo-PU in solid state. Since the two bands overlap before exposure of azo-PU solution, the cis/trans ratio cannot be calculated precisely prior to exposure. The cis : trans ratios were estimated as 57.9 : 42.1, 75.8 : 24.2, and 99.2 : 0.8 after 5, 10, and 15 min of UV exposure. Finally, at 20 min of UV exposure (the photostationary state), 100% cis isomers is attained, which is the reference state for the calculation.

References

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