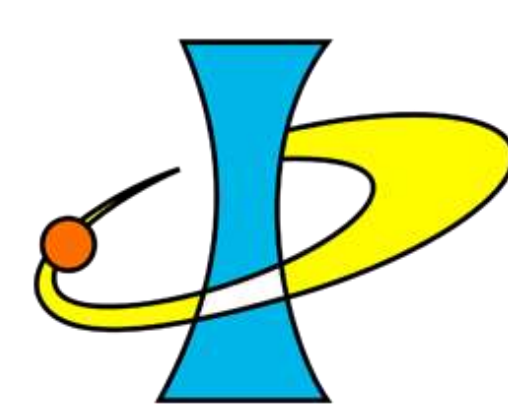




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Novel photoswitchable azobenzene-based fluorinated aromatic polyether

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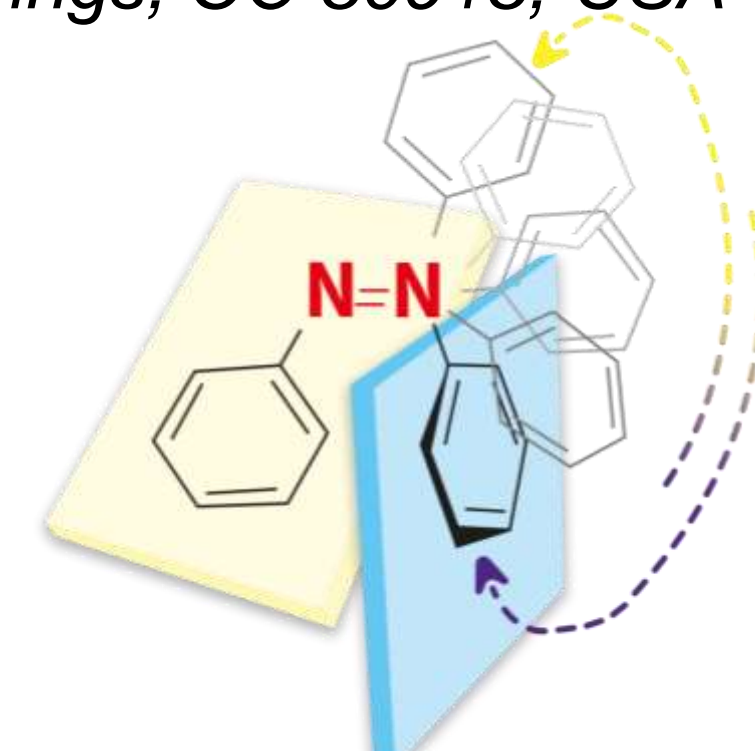
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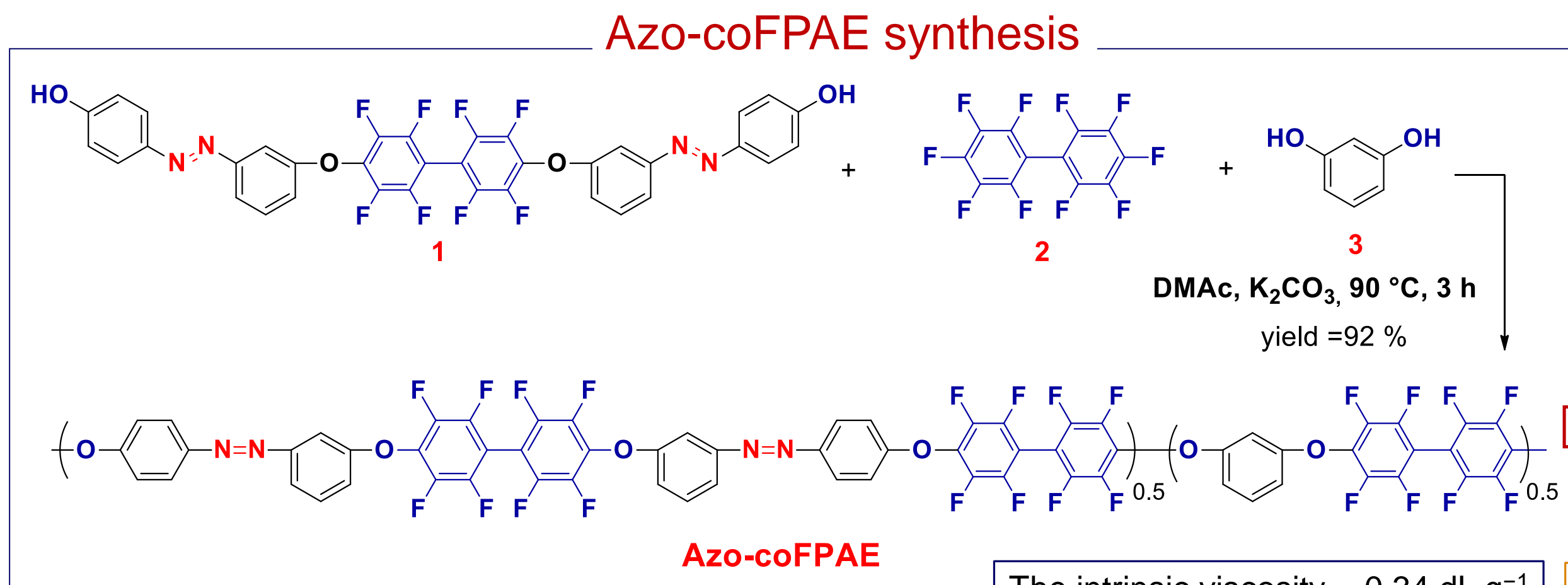
INTRODUCTION

Azobenzene-based poly(arylene ether)s (PAEs) are versatile for developing stable materials with manipulable macroscopic properties using light. These polymeric systems undergo reversible photochemical reactions of azo groups to switch between trans and cis isomers, impacting the materials world. Incorporating perfluorinated aromatic units improves chemical and thermal stability, as well as optical and electro-optical properties. However, the importance of azo-containing fluorinated PAEs (FPAEs) is often overlooked in the literature, despite their unique properties crucial for modern high-tech applications.

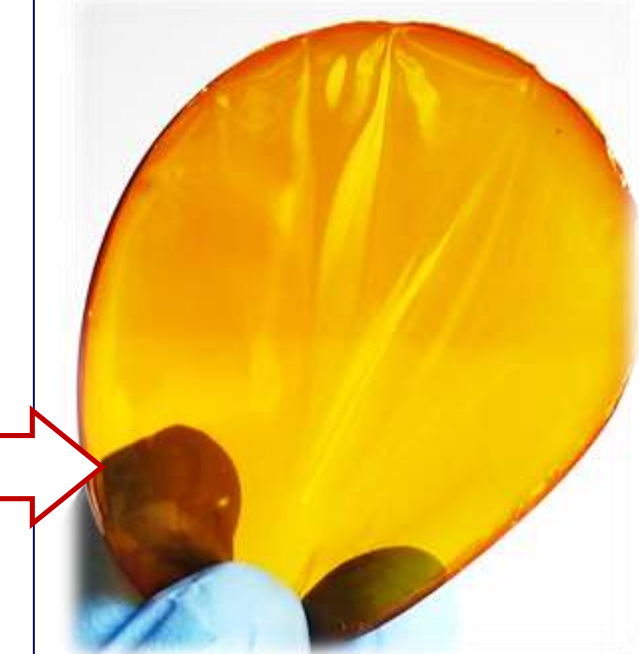


Aim

The study aims to explore the design of a new copolymeric azo-based FPAE (**Azo-coFPAE**), with azobenzene and octafluorobiphenylene fragments in the main chain. The Azo-coFPAE undergoes comprehensive studies on its chemical structure, mechanical and thermal properties, photoinductive birefringence and photoisomerization behaviors.

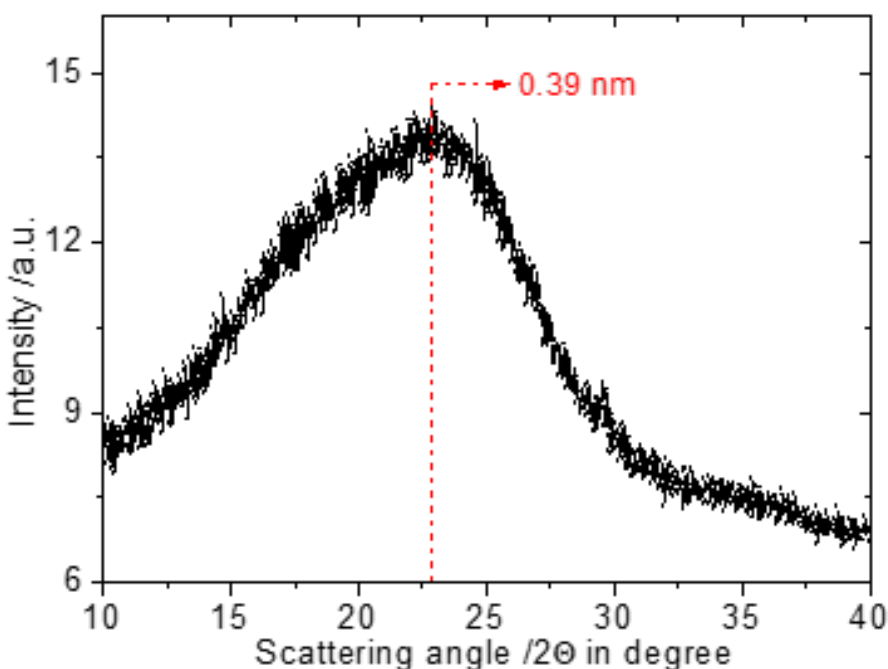


Solvent cast Azo-coFPAE film

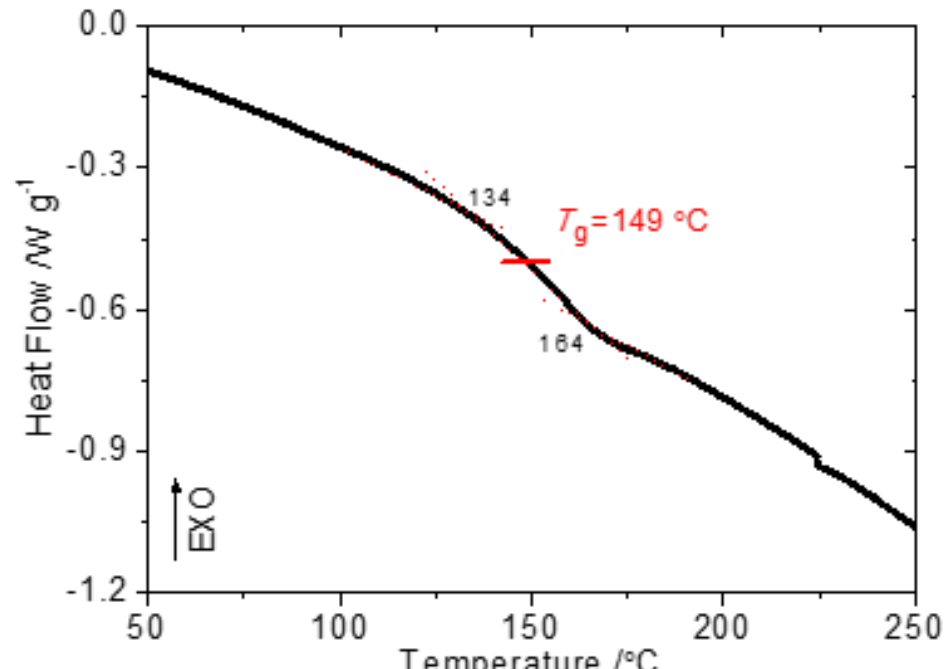


Stress at break: **62 MPa**;
Elongation at break: **5%**;
Young modulus: **1.45 GPa**

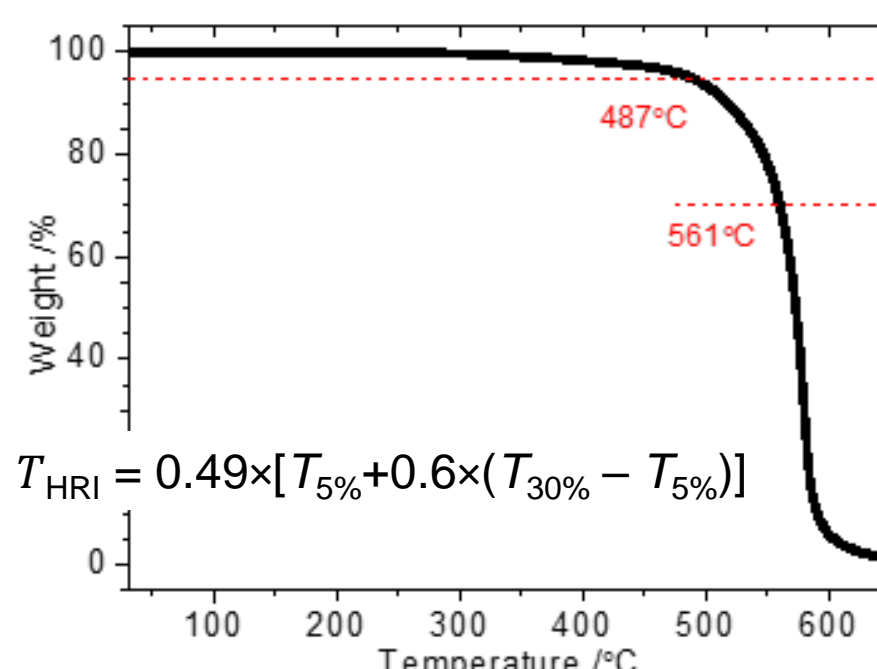
Wide-angle X-ray diffraction pattern



Differential scanning calorimetry

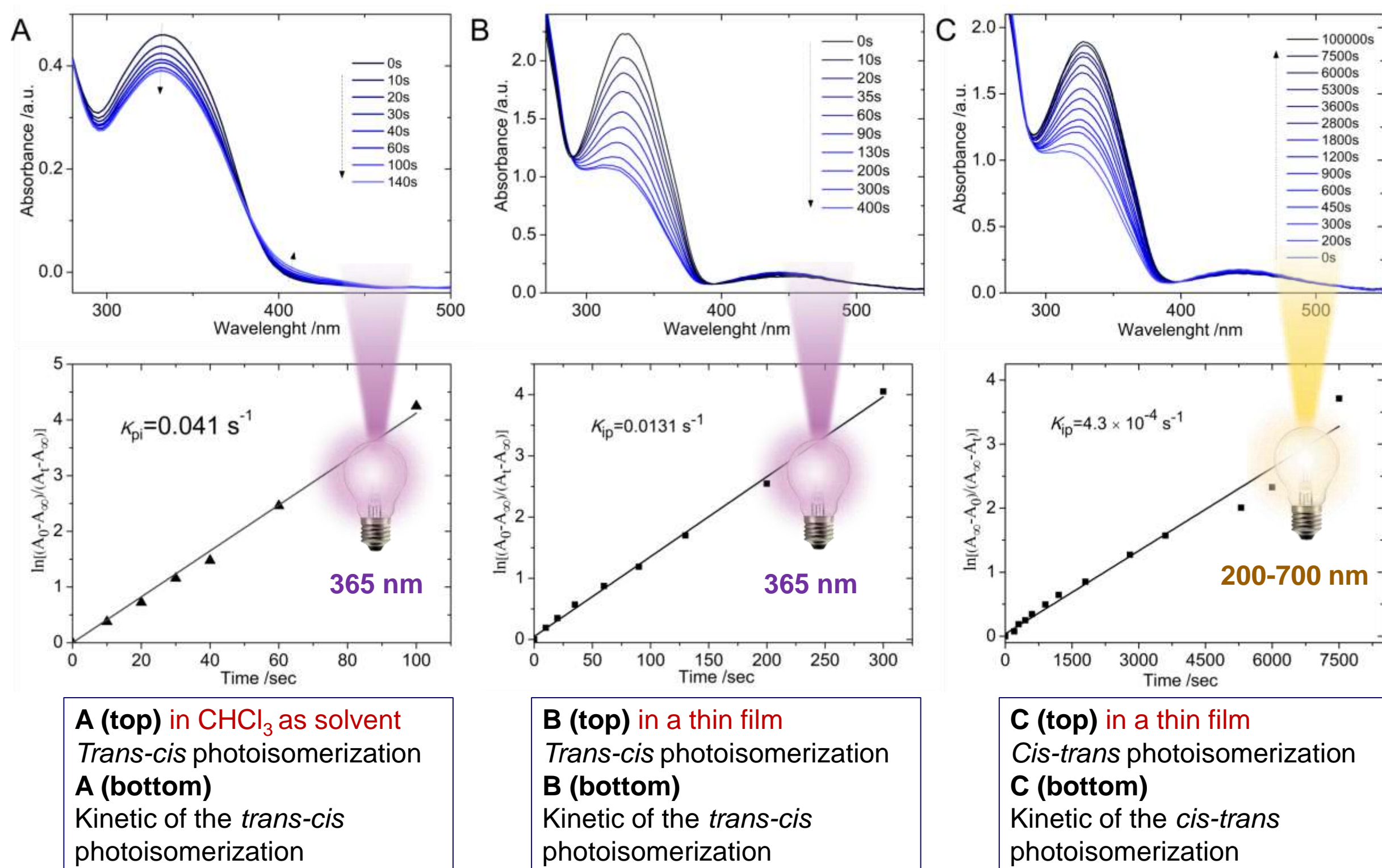


Thermogravimetric analysis



- WAXD study revealed that the Azo-coFPAE was amorphous. An amorphous halo at $2\theta = 22.8^\circ$ ($d = 0.39$ nm)
- Polymer showed a glass transition temperature (T_g) at 149 °C ($\Delta C_p = 0.7015$ J g⁻¹ K⁻¹) (DSC analysis)
- The TGA results show that the temperature at 5% weight loss ($T_{5\%}$) was 487°C. The heat-resisting index (HRI) = 260.4 °C. ($T_{30\%} = 561^\circ\text{C}$)

Photoisomerization of Azo-coFPAE copolymer in solution and thin film

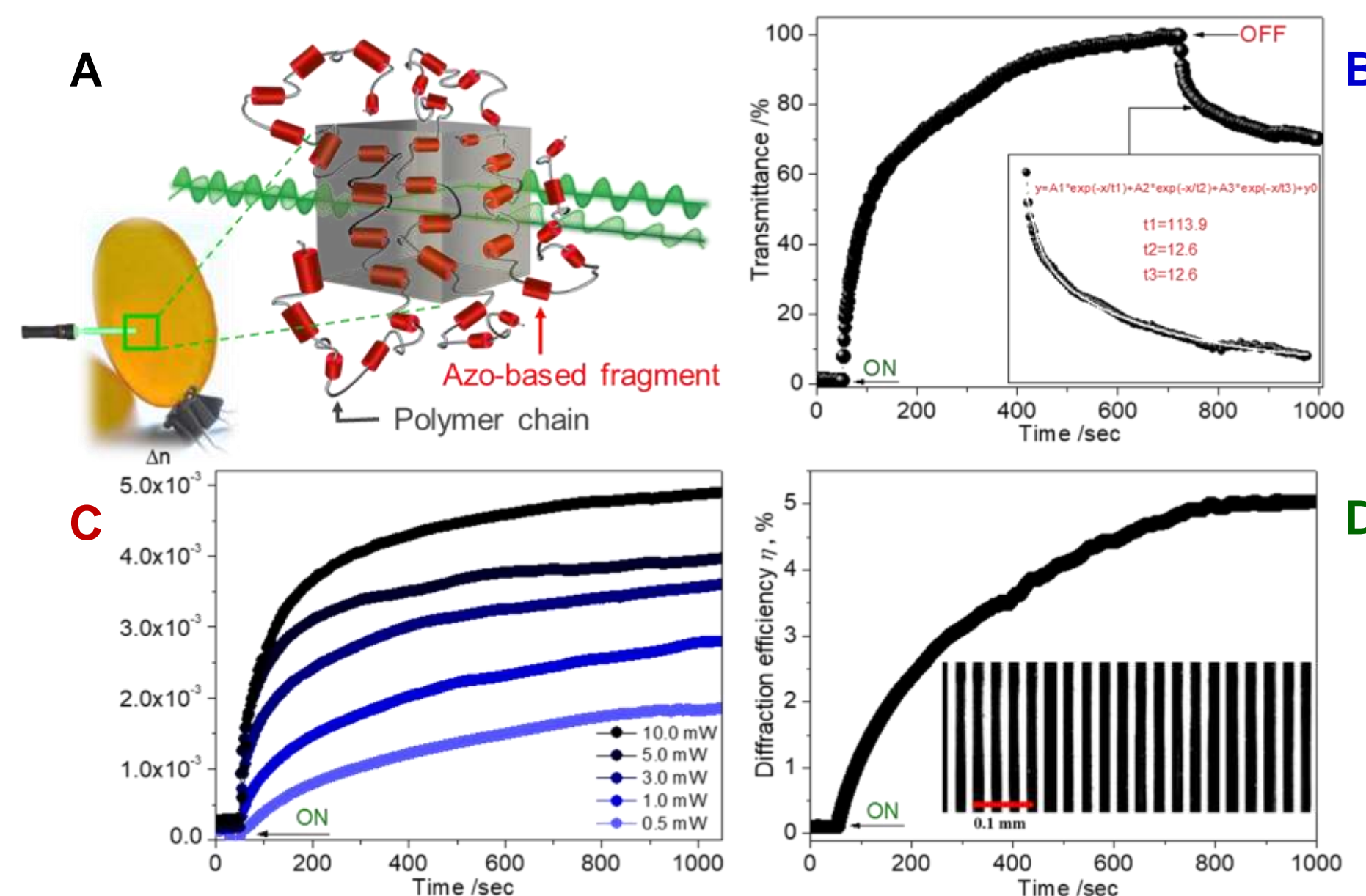


- In comparing *trans-to-cis* photoisomerization in solution and film state, a significant fraction of azobenzene units remained trans in chloroform after reaching the photostationary state (around 140 s).
- Photoisomerization of Azo-coFPAE in a film was slower (rate constant k_{pi} of 0.0131 s⁻¹).
- Conversion between *trans* and *cis* configurations in the copolymer film occurred almost completely in both directions (see Figures B and C).

Conclusions

• Azo-coFPAE, a copolymer with reversible *trans-cis* photoisomerization behavior in both solution and solid film, was synthesized. • Under the irradiation of a green laser, the Azo-coFPAE film exhibited photoorientation ability, leading to the acquisition of anisotropic properties and achieving birefringence levels of up to 5.0×10^{-3} . • The Azo-coFPAE film showed the formation of efficient diffraction gratings. • These findings highlight the potential for designing stimuli-responsive and optically active materials as intelligent on-off photoswitches.

Birefringence measurements and diffraction grating writing



- During *trans-cis-trans* isomerization, azobenzene units in the polymer change orientation perpendicular to the incident light's polarization, creating birefringence in the illuminated film.
- Birefringence kinetics in Azo-coFPAE film: buildup and relaxation curves. **Inset:** Decay of birefringence fitted with a tri-exponential function (white solid line). ($\lambda = 532$ nm, $P \sim 10$ mW)
- Photoinduced birefringence curves as a function of the writing laser power ($\lambda = 532$ nm) for Azo-coFPAE film (thickness of 18 μm).
- Dependency of diffraction efficiency for Azo-coFPAE film on irradiation time. **Inset:** photo of an Azo-coFPAE diffraction grating with a resolution of 30 lines per mm in a polarization microscope.

Acknowledgements

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