XVII ICMS 22-25.09.2024 Wojanów, Poland

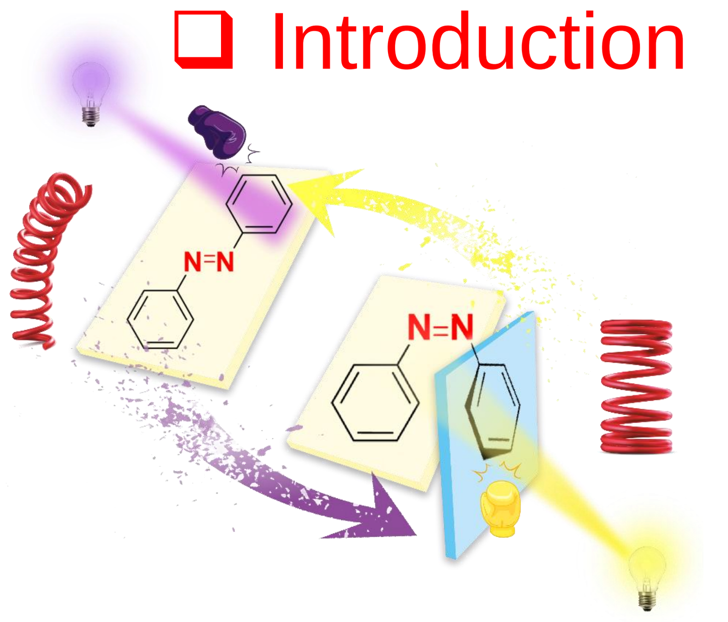
NATO OTAN This activity is supported by: The NATO Science for Peace and Security Programme

Synthesis and optical properties of new azobenzene-containing side-chain fluorinated poy(arylene ether)

I.M. Tkachenko [1], Yu.I. Kurioz [2], R.M. Kravchuk [2,3], D.V. Litoshenko [2,4], V. G. Nazarenko [2,3], V. V. Shevchenko [1]

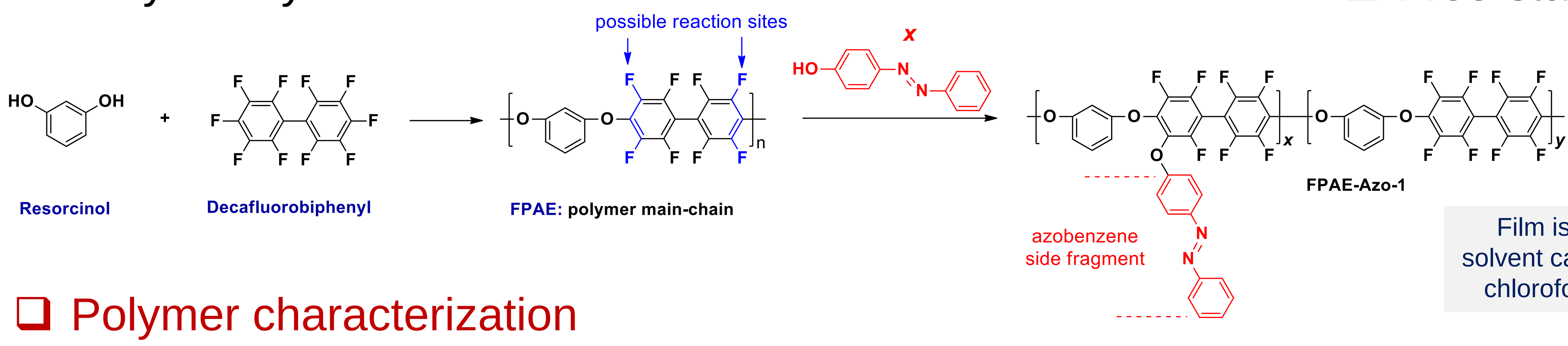
[1] Institute of Macromolecular Chemistry, Kyiv, Ukraine (ttkachenkoim@gmail.com), [2] Institute of Physics, Kyiv, Ukraine
[3] Institute of Physical Chemistry, PAS, Warsaw, Poland [4] Taras Shevchenko National University of Kyiv, Kyiv, Ukraine

❑ Introduction



Considerable attention is devoted to the preparation and performance of fluorinated poly(aryl ether)s (FPAEs) due to their high temperature resistance, stability, and low optical propagation loss. The structure of FPAEs with perfluoroaromatic fragments, especially biphenylene ones, provides opportunities for functionalization not only on non-fluorinated aromatic units but also on fluorinated aromatic fragments using nucleophilic agents. Therefore, FPAEs could hold promise for covalently attaching azo groups to their side chains, thus preventing chromophore aggregation and preserving their optical and electro-optical properties. The most attractive feature of azobenzene-containing side chain polymers is the large and reversible photoinduced birefringence, making them suitable for numerous applications in photonics and holographic storage.

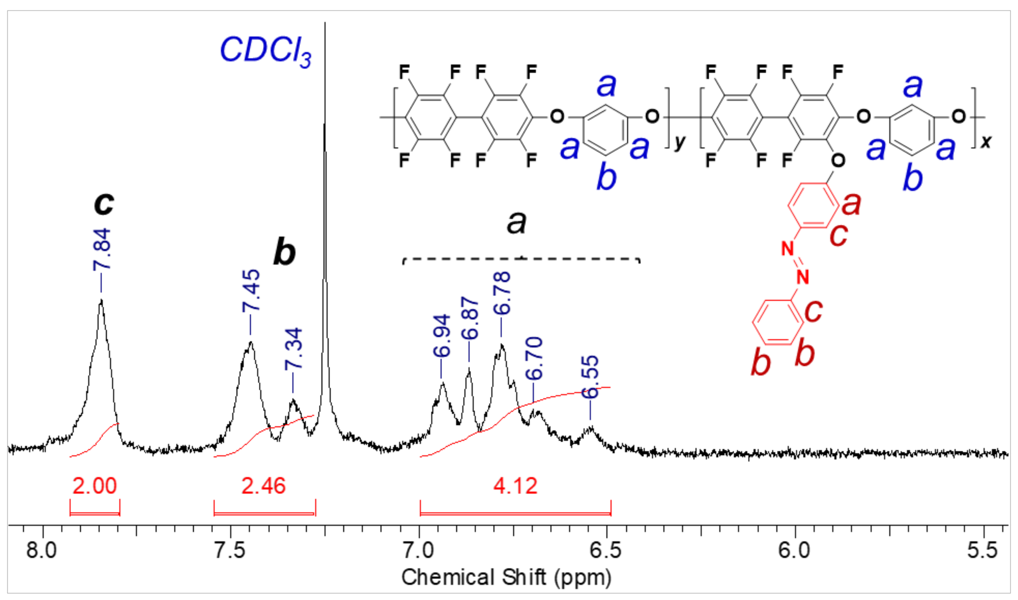
❑ Polymer synthesis



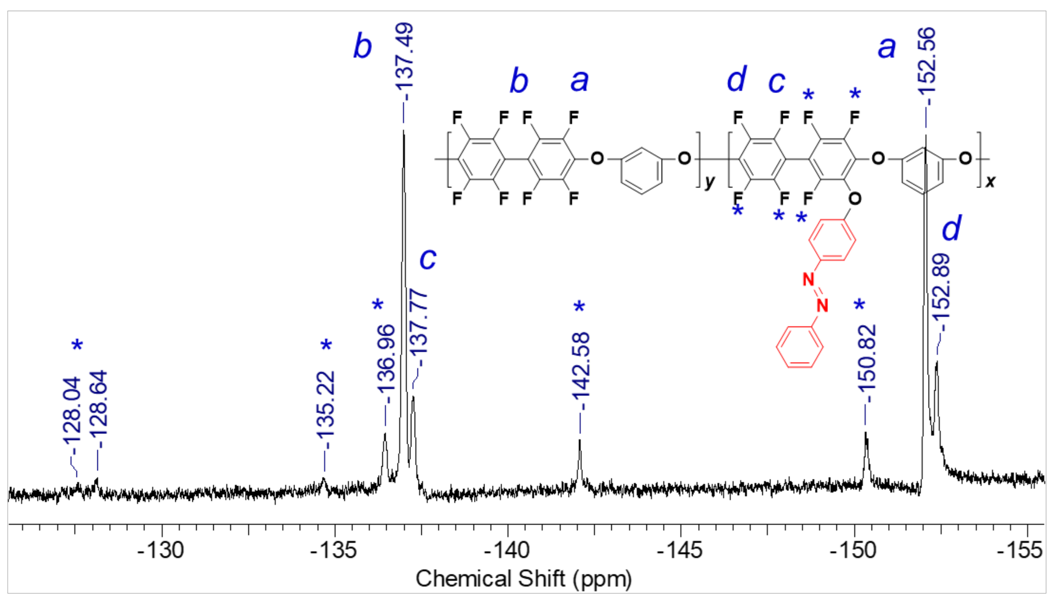
❑ Free-standing film of FPAE-Azo-1

❑ Polymer characterization

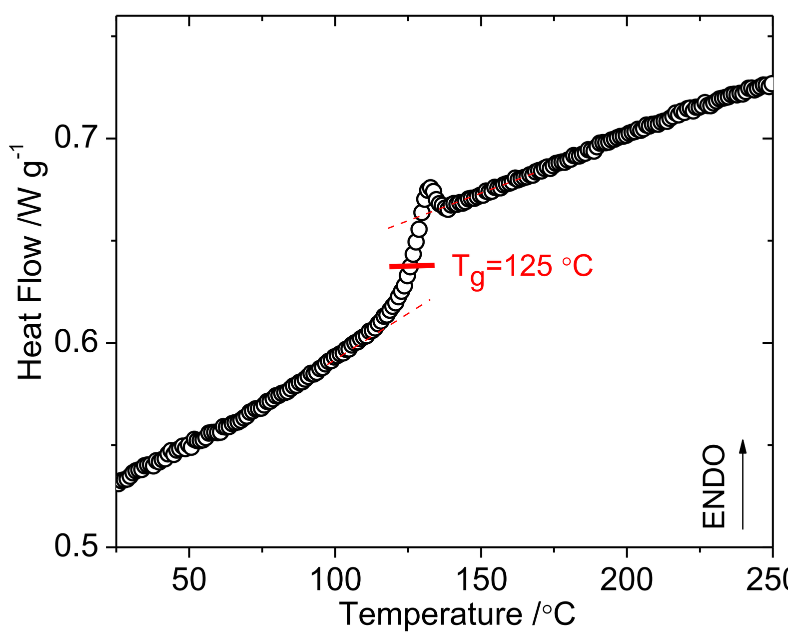
^{1}H NMR



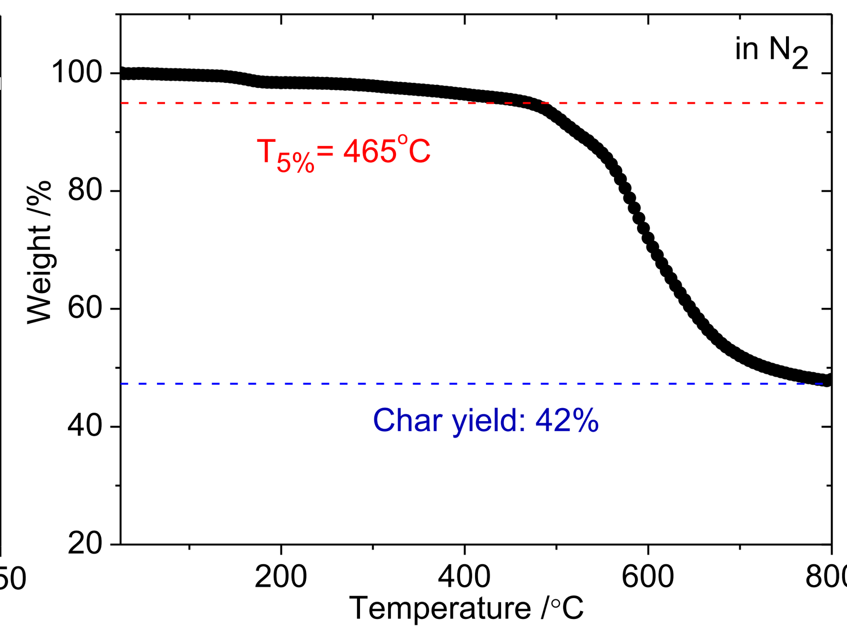
^{19}F NMR



DSC



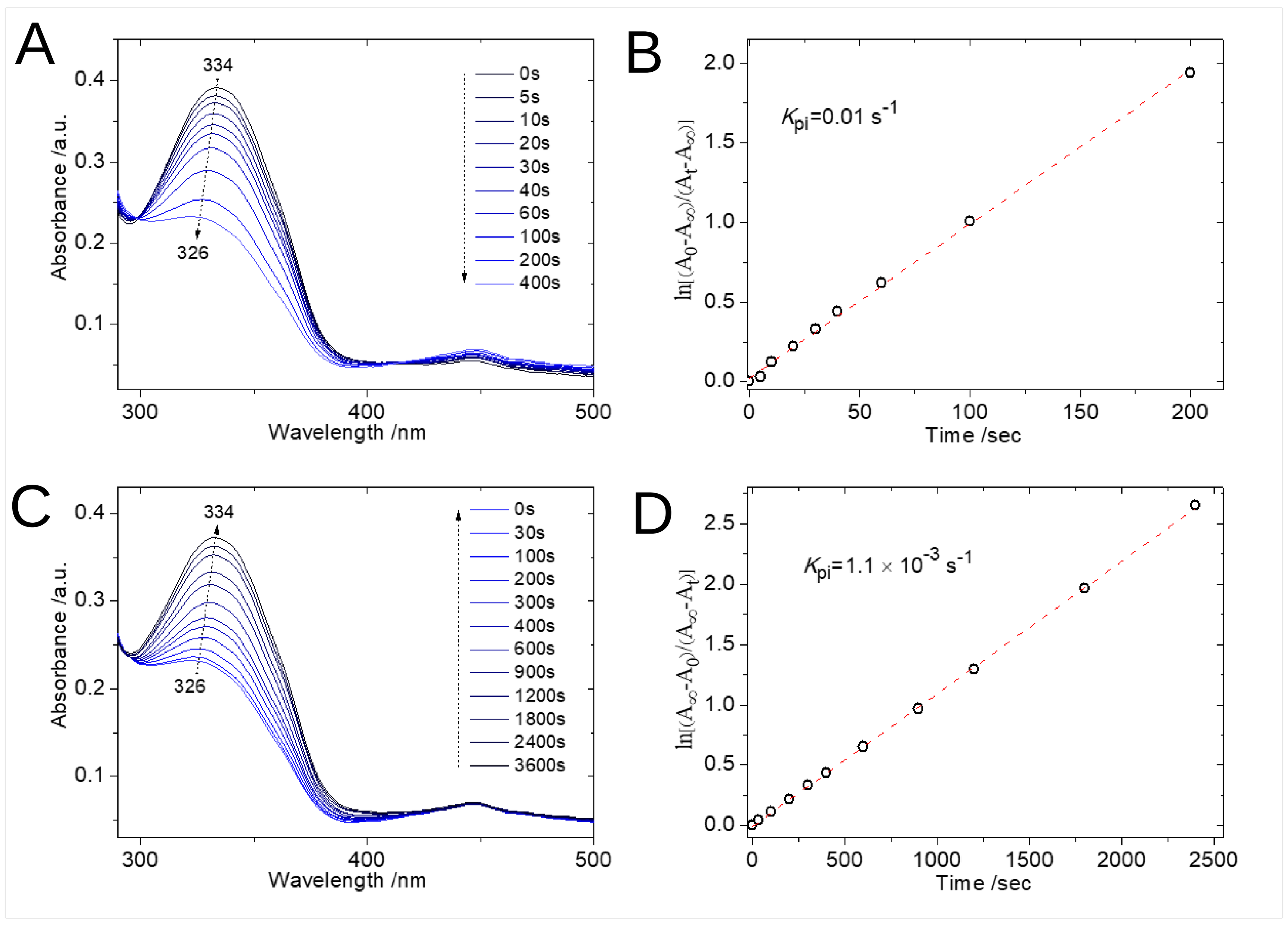
TGA



The success of the synthesis of the FPAE-Azo-1 is confirmed with ^{1}H NMR and ^{19}F NMR, as well as FTIR spectroscopy techniques.

DSC shows the amorphous nature of the polymer (T_g=125°C) while TGA demonstrates good thermal stability ($T_{5\%\ weight\ loss}$ =465°C)

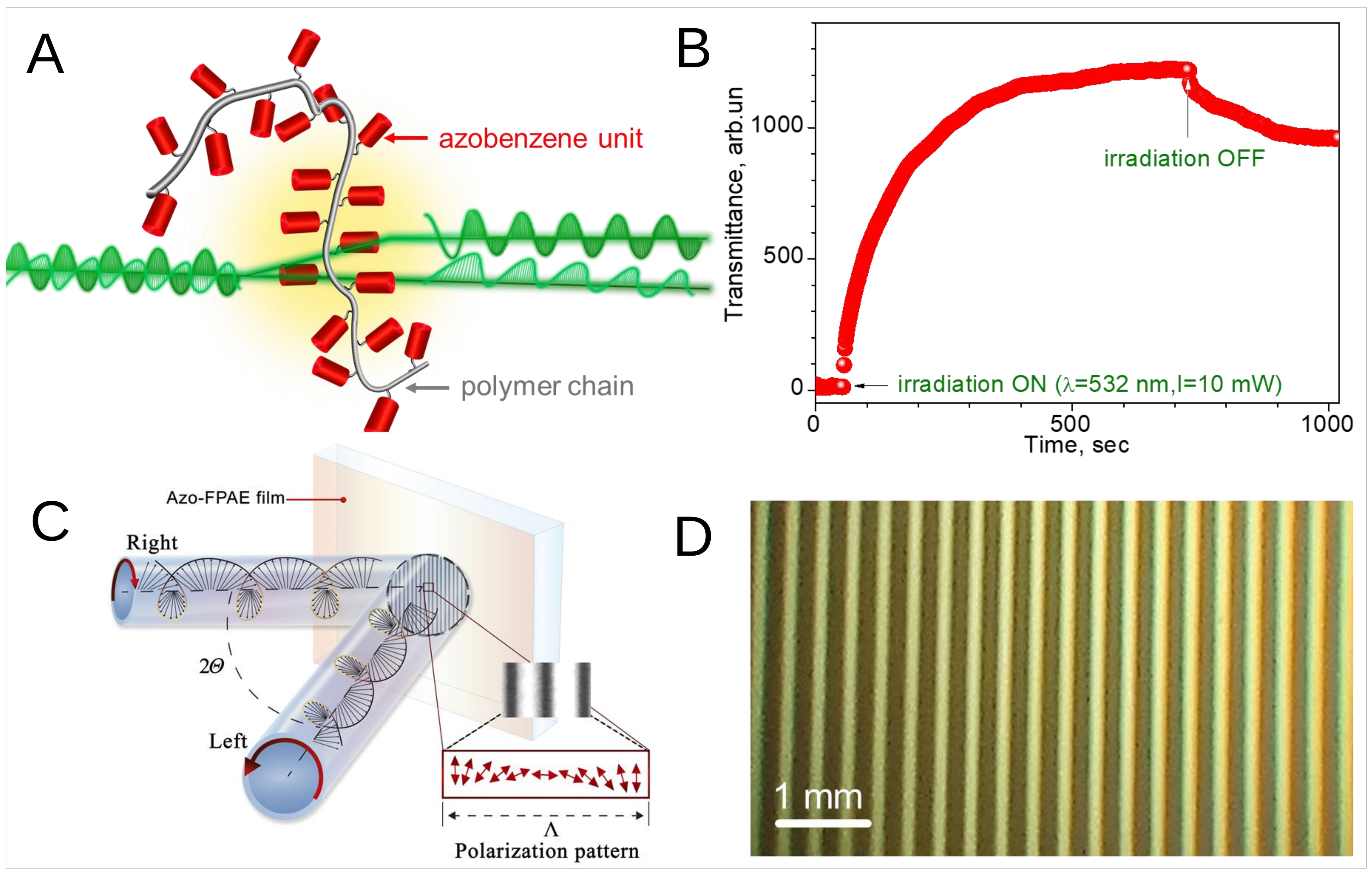
❑ Photoisomerization Behavior in Thin Film



A. *Trans-cis* isomerization in film (λ = 365 nm, 3-4 mW);
B. Kinetic of the *trans-cis* photoisomerization
C. *Cis-trans* photoisomerization (deuterium lamp, λ = 275 ± 25 nm, 8-12 mW)
D. Kinetic of the *cis-trans* photoisomerization.

Photoinduced conversion between trans and cis configurations in polymer proceeds almost completely in both directions

❑ Birefringence Measurements. Diffraction grating



A. 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.
B. Birefringence kinetics in film (λ = 532 nm, P ~10 mW) buildup and relaxation curves.
C. Scheme of a polarization holographic exposure using right- and left-handed circularly polarized beams
D. Photo of diffraction grating with a resolution of 30 lines per mm in a polarization microscope.

Conclusions

● The developed FPAE-Azo-1 is amorphous in nature and has good tersomtability and film forming properties. ● Polymer shows reversible *trans-cis* photoisomerization behavior in both solution and solid film ● Under the irradiation of a green laser, the FPAE-Azo-1 film exhibits photoorientation ability, leading to the acquisition of anisotropic properties. ● The film shows the formation of efficient diffraction gratings. ● These findings highlight the potential for designing stimuli-responsive and optically active materials as intelligent on-off photoswitches.

Acknowledgments This work was supported by NASU projects 0123U100832 and 0124U001912, NATO SPS project G6030. VGN and RMK thank the long-term program of support of the Ukrainian research teams at the Polish Academy of Sciences carried out in collaboration with the U.S. National Academy of Sciences with the financial support of external partners via the agreement No. PAN.BFB.S.BWZ.356.022.2023. YuIK thanks the American Physical Society (IRTAP-Ukraine)