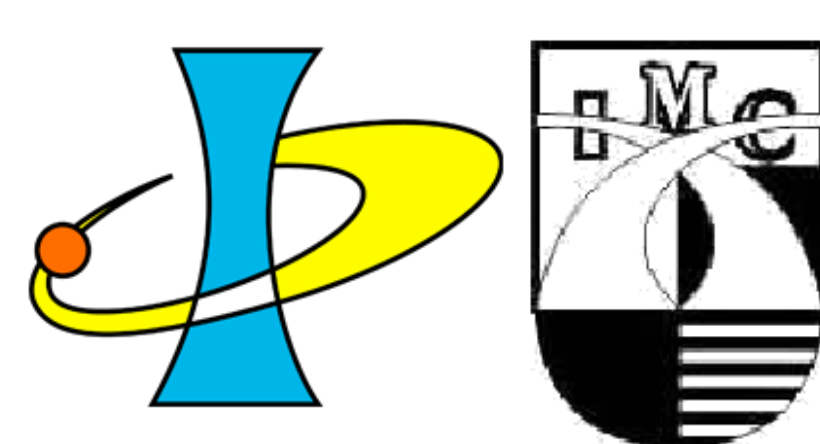


# Physico-Chemical Properties of Fluorinated Oligo(azomethine)s with Azo Groups in the Main Chain



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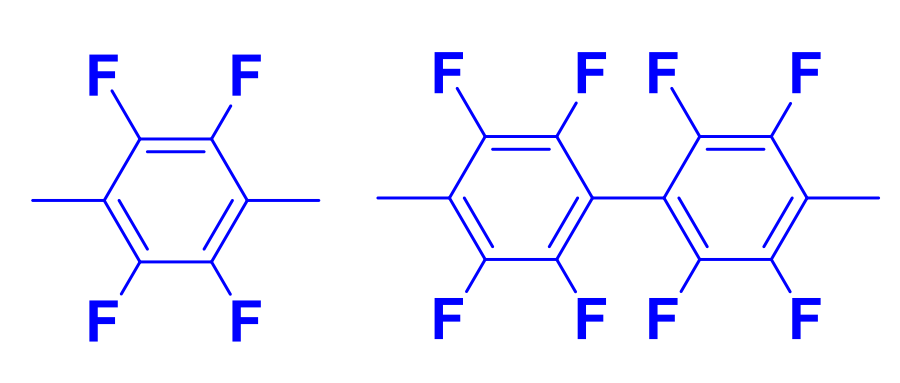
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**Abstract:** We report the synthesis and optical behavior of photoactive fluorinated azo-based oligo(azomethine)s (Azo-Oam). The desired oligomers were prepared by polycondensation of octafluorobiphenylene-containing diamine with excess of tetrafluorobenzene- or octafluorobiphenylene-based bis-hydroxybenzaldehydes. The repeating unit of the oligomers was targeted as n=7 by controlling the molar ratio of initial monomers. Importantly, the oligomers can be solution cast into flexible solid films with tensile strength in the range 13-20 MPa. The studied Azo-Oam showed a remarkable response to both optical and chemical stimuli. Thus, the *trans-cis* photoisomerization of azobenzene units occurs in Azo-Oam solid films as well as absorption maxima of the obtained oligomers can be regulated by changing the pH of a medium and a solvent concentration. It was studied that the irradiation of the synthesized oligomers leads to the emergence of birefringence in their films. The highly stable diffraction gratings based on Azo-Oam's films were fabricated which can be stored for the long time.

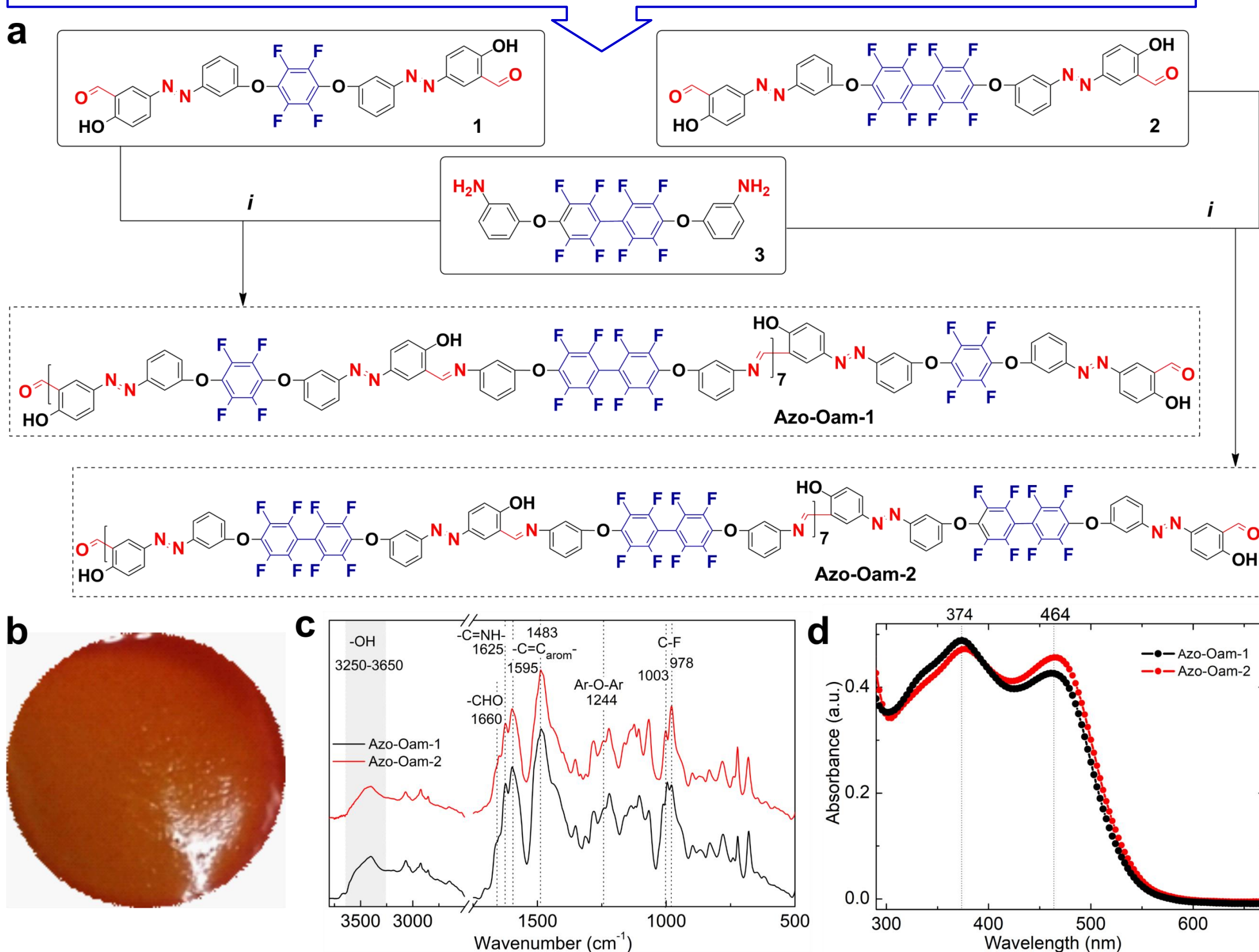
**Advantages of combining azo and azomethine groups in the molecule conjugation system**      **The advantages of fluorine-containing polymers**

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|---|--|---|
| <p><b>—N=N—</b></p> <ul style="list-style-type: none"> <li>✓ Good distribution of electron density</li> <li>✓ Nonlinear optical properties</li> <li>✓ Photo induced <i>trans-cis</i>-transitions</li> </ul> | <p><b>—C=N—<br/>H</b></p> <ul style="list-style-type: none"> <li>✓ Liquid-crystal properties</li> <li>✓ Piezo and pyroelectric properties</li> <li>✓ Fiber formation</li> <li>✓ Low dielectric anisotropy</li> </ul> | <p><b>—N=N— + —C=N—<br/>H</b></p> <ul style="list-style-type: none"> <li>✓ High optical sensitivity</li> <li>✓ Bathochromic shift</li> <li>✓ Good complexing ability</li> <li>✓ Tautomeric transitions</li> </ul> |
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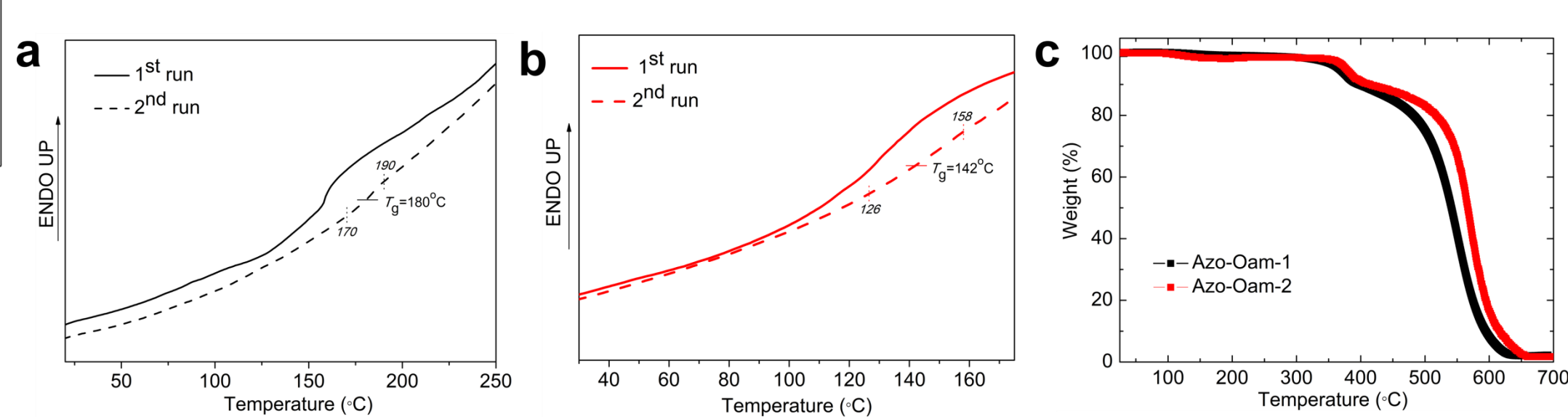


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| <ul style="list-style-type: none"> <li>✓ High thermal and thermooxidative stability</li> <li>✓ Improved chemical resistance</li> <li>✓ Low surface energy</li> <li>✓ Low moisture uptake</li> </ul> | <ul style="list-style-type: none"> <li>✓ Low refractive index</li> <li>✓ High optical transparency</li> <li>✓ Good mechanical properties</li> <li>✓ High electronegativity</li> <li>✓ Low dielectric constant</li> </ul> |
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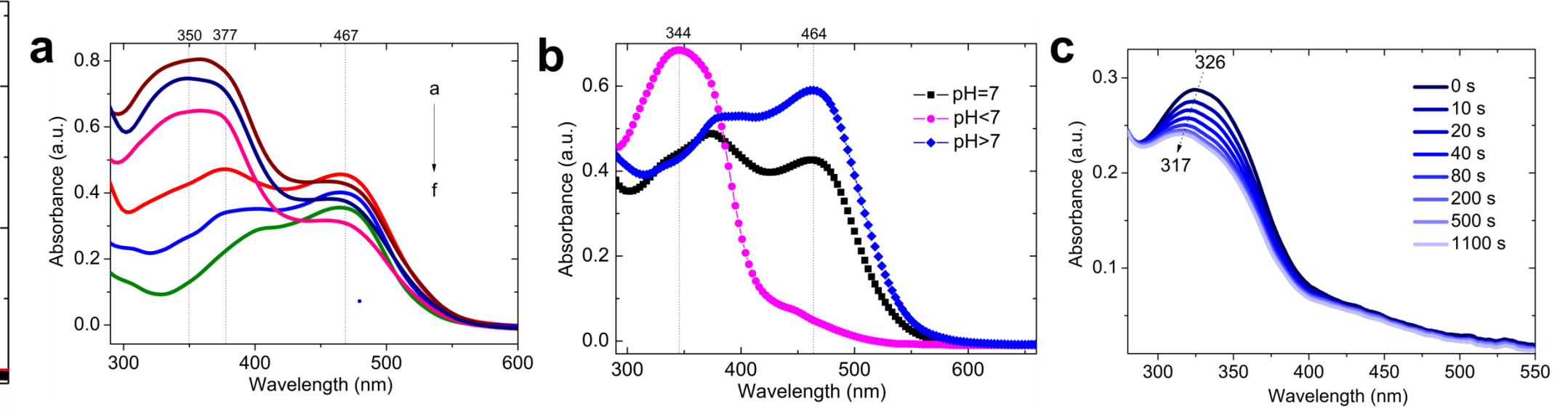
The aim of this work is to study the optical properties of azo-containing oligoazomethines (Azo-Oam) with fluorinated fragments



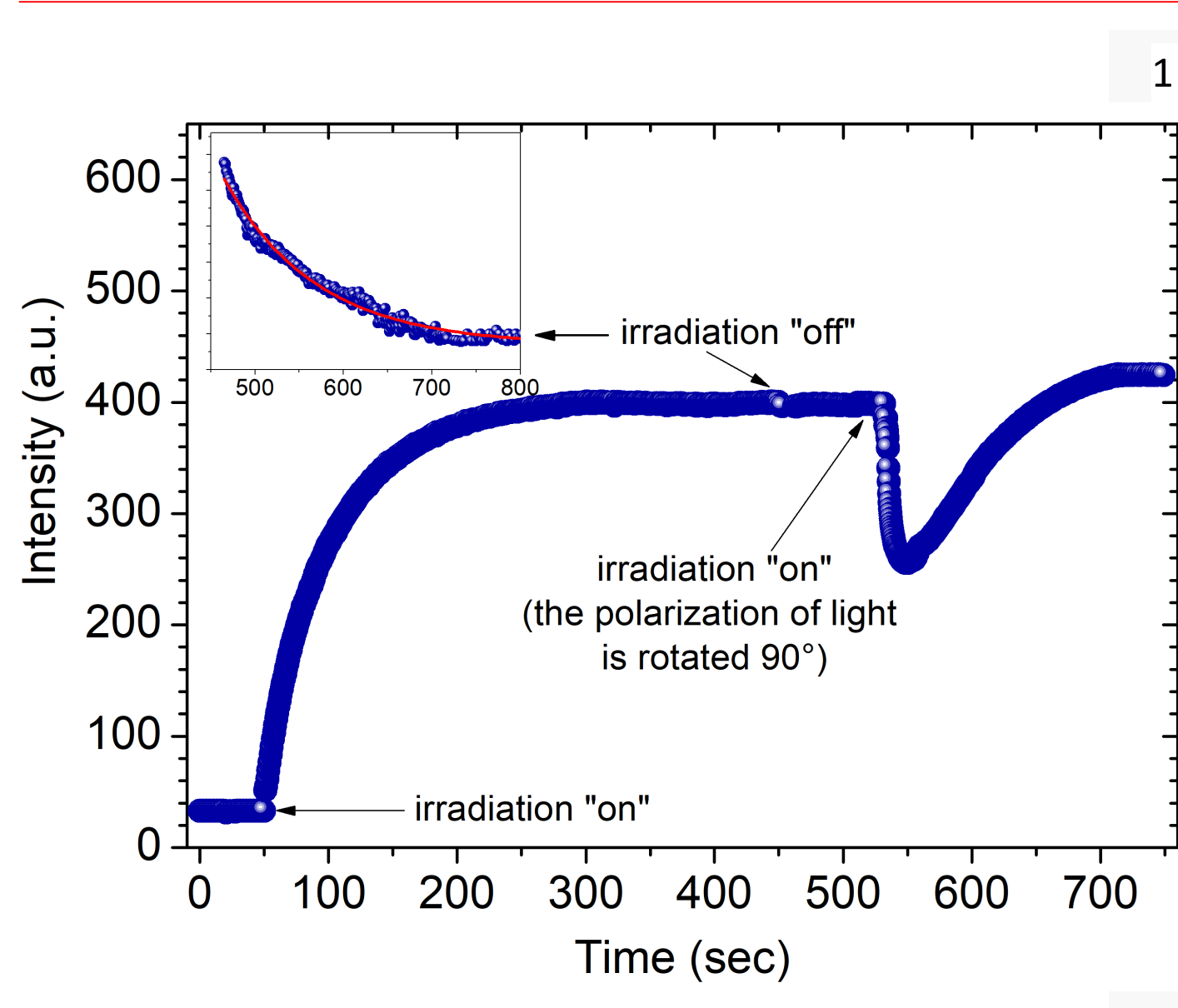
**Figure 1.** a) Synthesis of Azo-Oam-1 and Azo-Oam-2 oligomers: (i) DMAc, 110 °C, 24 h. Yield about 86% for both oligomers after reprecipitation. b) Digital image of self-standing Azo-Oam-2 oligomer (thickness ~100 μm). c) FTIR spectra of synthesized Azo-Oam oligomers; d) UV-vis absorbance spectra of oligomers Azo-Oam-1 and Azo-Oam-2 in DMAc (0.006 mg/mL).



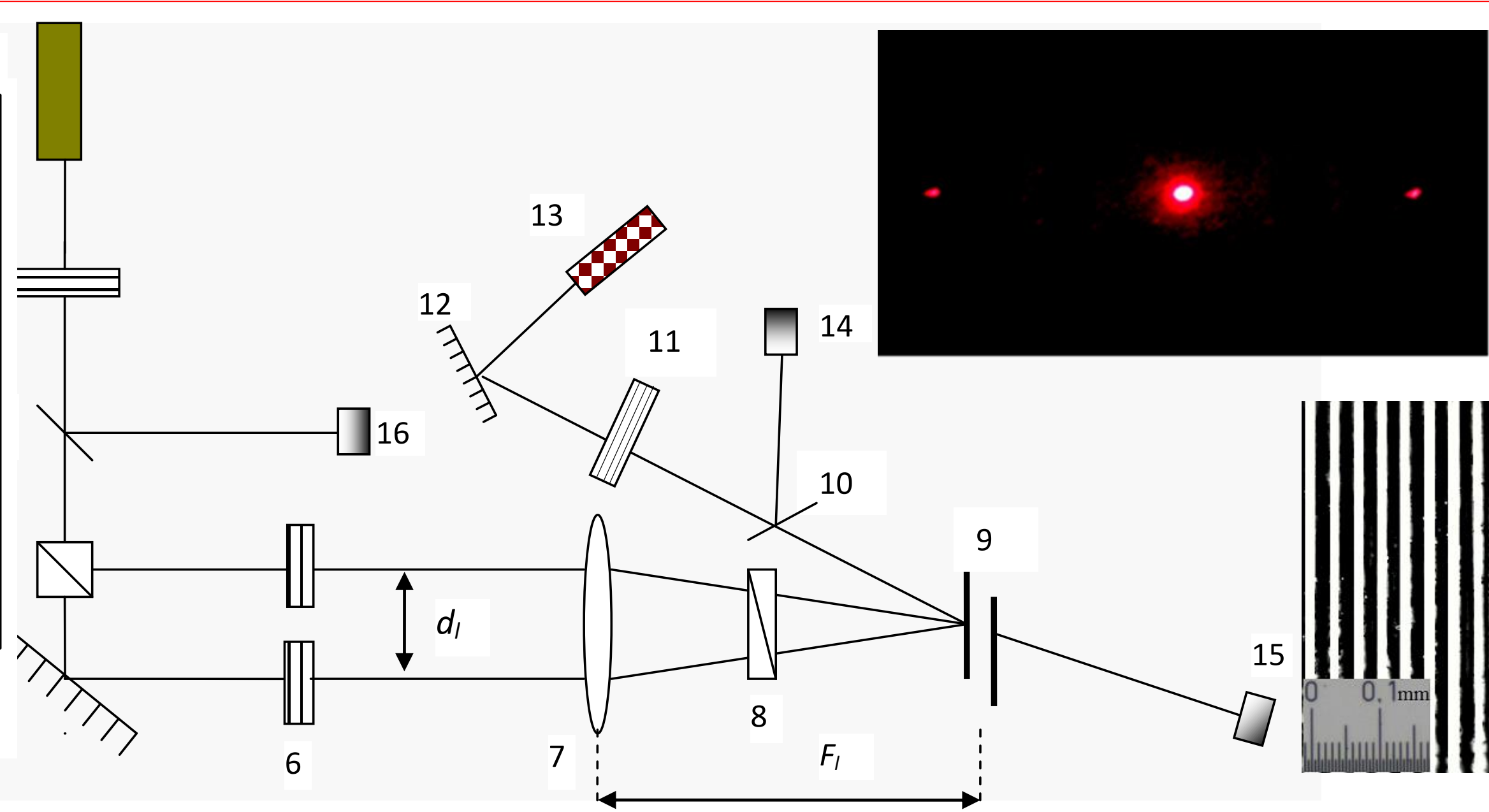
**Figure 2.** DSC traces (heat flow vs. temperature) of oligomers Azo-Oam-1 (a) and Azo-Oam-2 (b) recorded for film samples; depicted are the first heating and second heating runs. (DSC curves are offset for clarity). Air atmosphere, heating rate of 20°C/min. c) TGA curves of Azo-Oam-1 and Azo-Oam-2 in an air atmosphere (heating rate: 20 °C/min with a temperature from 25 to 700°C).



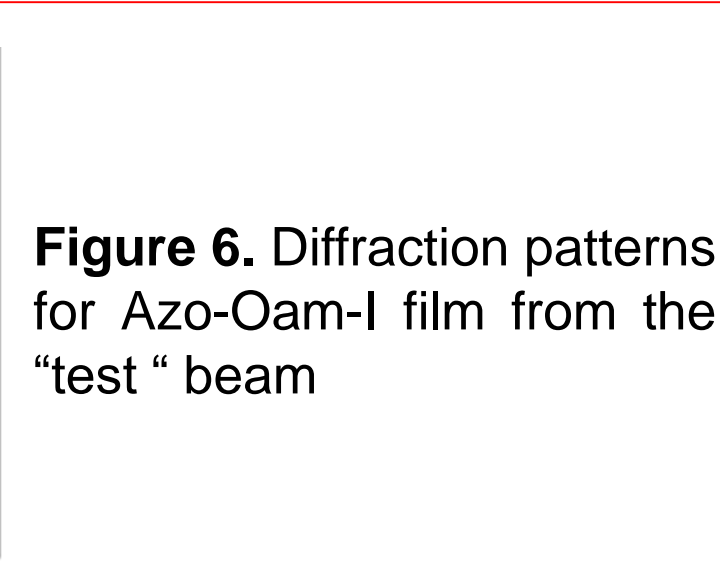
**Figure 3.** a) UV-vis spectra of Azo-Oam-2 at various concentrations (a-f) in DMAc. The concentration (a-f) of Azo-Oam-2 in DMAc solutions was about 15.0 (a), 13.8 (b), 11.0 (c), 6.0 (d), 4.5 (e) and 3.5 (f) μg mL<sup>-1</sup>. b) UV-vis spectra of Azo-Oam-1 in DMAc at acidic (pH<7), neutral (pH=7) and alkaline medium (pH>7). c) *Trans-cis* photoisomerization of Azo-Oam-1 in thin film (λ=370 nm, P 3.4 mW)



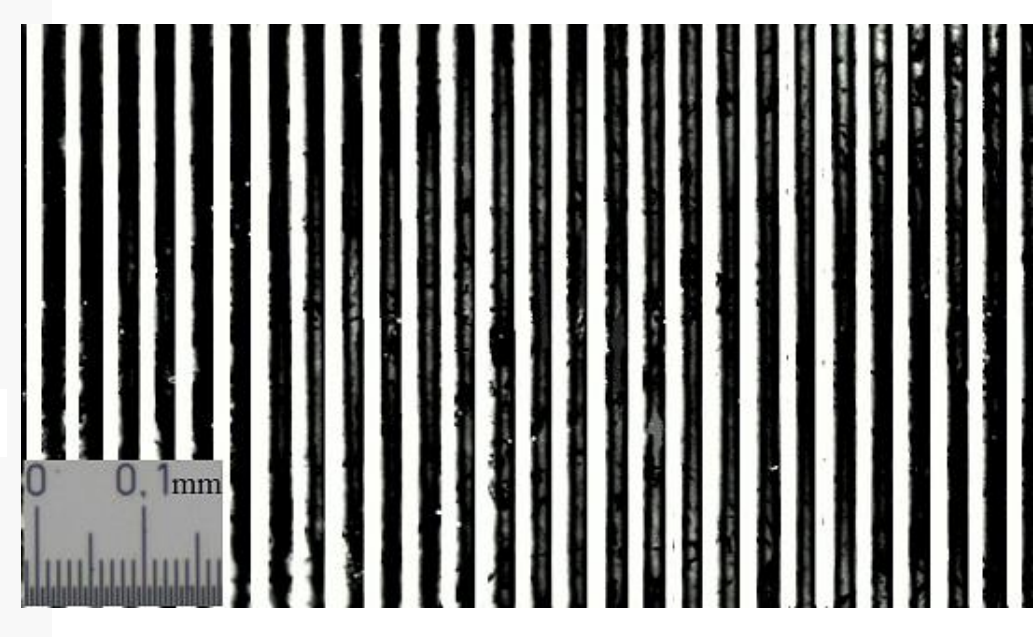
**Figure 4.** The dependence of the intensity of the "test" beam when changing the birefringence on the time of irradiation and position of polarize light of polymer Azo-Oam-1



**Figure 5.** Experimental set-up: 1 – DPS Laser (λ = 532 nm); 2– λ/2-waveplates; 3, 10 – beam-splitter plates; 4 – beam-splitter cube; 5, 12 – mirrors; 6, 8, 11 – polarizer; 7 – lens; 9 – sample; 13 – He-Ne laser (λ = 632.8 nm); 14, 15, 16 – photodiodes.



**Figure 6.** Diffraction patterns for Azo-Oam-1 film from the "test" beam



**Figure 7.** The photo of a diffraction grating in polarization microscope, the film of Azo-Oam-1 (scale 0,1 mm)