Optical Properties of Multistimuli Responsive Fluorinated Oligo(azomethine)s with Azo Groups in the Main Chain

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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.

The advantages of combining azo- and azomethine group in the polymer chain

—N=N—

- ✓ Good distribution of electron density
- ✓ Nonlinear optical properties
- ✓ Photo induced *trans-cis*-transitions

—C(H)=N—

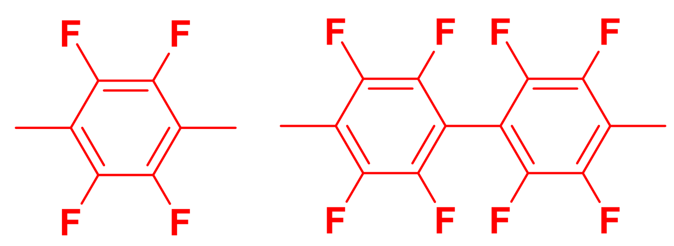
- ✓ Liquid-crystal properties
- ✓ Piezo and pyroelectric properties
- ✓ Fiber formation
- ✓ Low dielectric anisotropy

—N=N— + —C(H)=N—

- ✓ High optical sensitivity
- ✓ Bathochromic shift
- ✓ Good complexing ability
- ✓ Tautomeric transitions

The aim of this work is to study the optical properties of azo-containing olygoazomethines (Azo-Oam) with fluorinated fragments

The advantages of fluorine-containing polymers



- ✓ High thermal and thermooxidative stability
- ✓ Improved chemical resistance
- ✓ Low surface energy
- ✓ Low moisture uptake
- ✓ Low refractive index
- ✓ High optical transparency
- ✓ Good mechanical properties
- ✓ High electronegativity
- ✓ Low dielectric constant

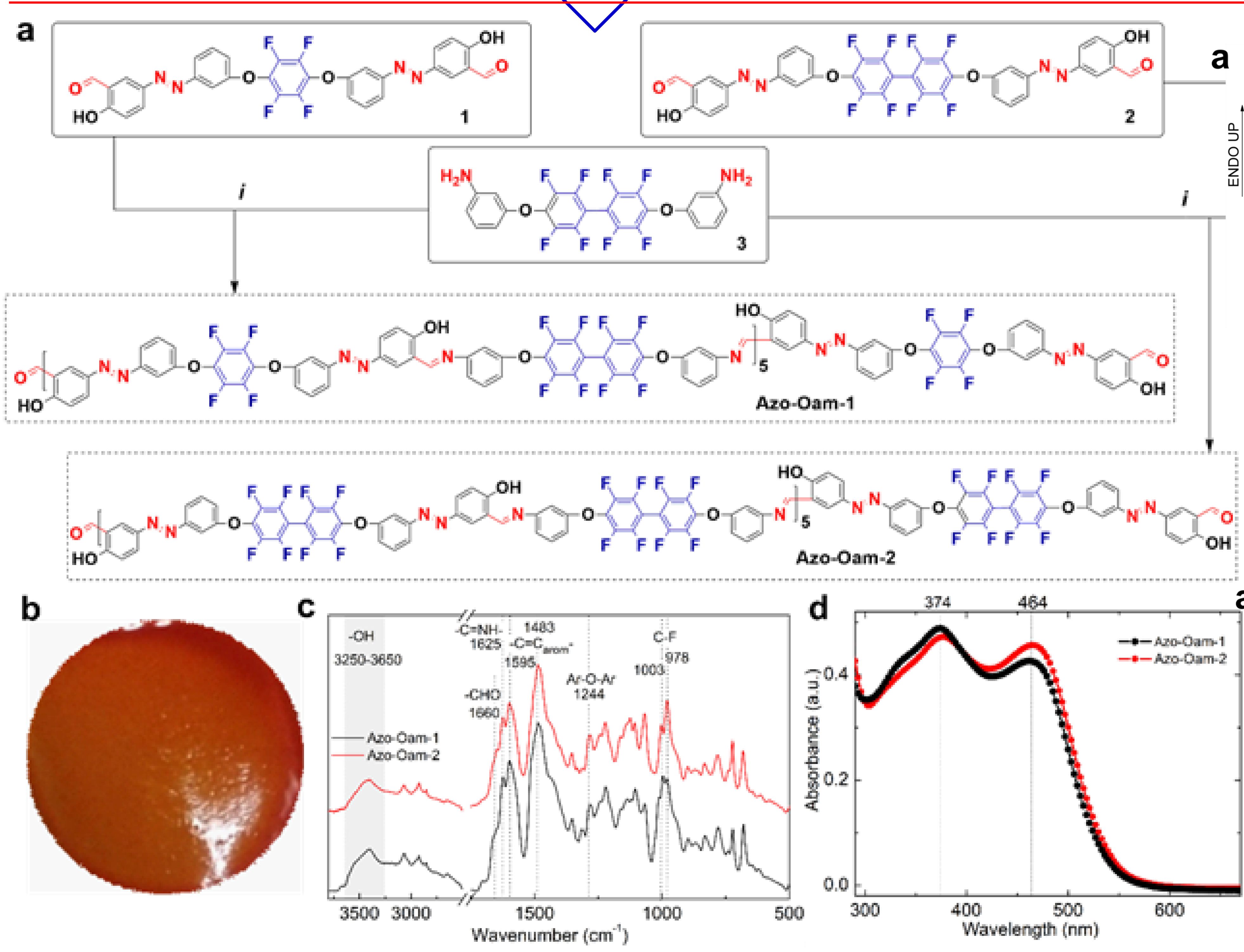


Figure 1. a) Synthesis of Azo-Oam-1 and Azo-Oam-2 oligomers: (i) DMAc, 110 ° C, 24 h. Yield about 86% for both oligomers after reprecipitation. b) Digital image of self-standing Azo-Oam-2 oligomer (thickness 100 μm). c) FTIR spectra of synthesized Azo-Oam oligomers; d) UV-vis absorbance spectra of oligomers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

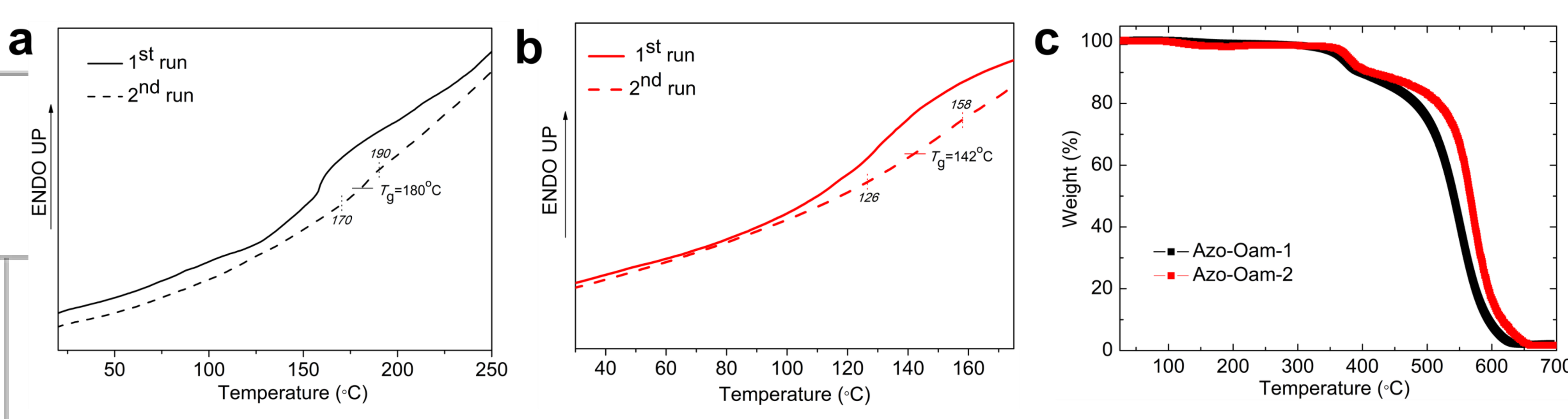


Figure 2. DSC traces (heat flow vs. temperature) of oligomers Azo-Oam-1 (a) and Azo-Oam-2 (b) recorded for film samples; depicted are the first heating and second heating runs. (DSC curves are offset for clarity). Air atmosphere, heating rate of 20°C/min. c) TGA curves of Azo-Oam-1 and Azo-Oam-2 in an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

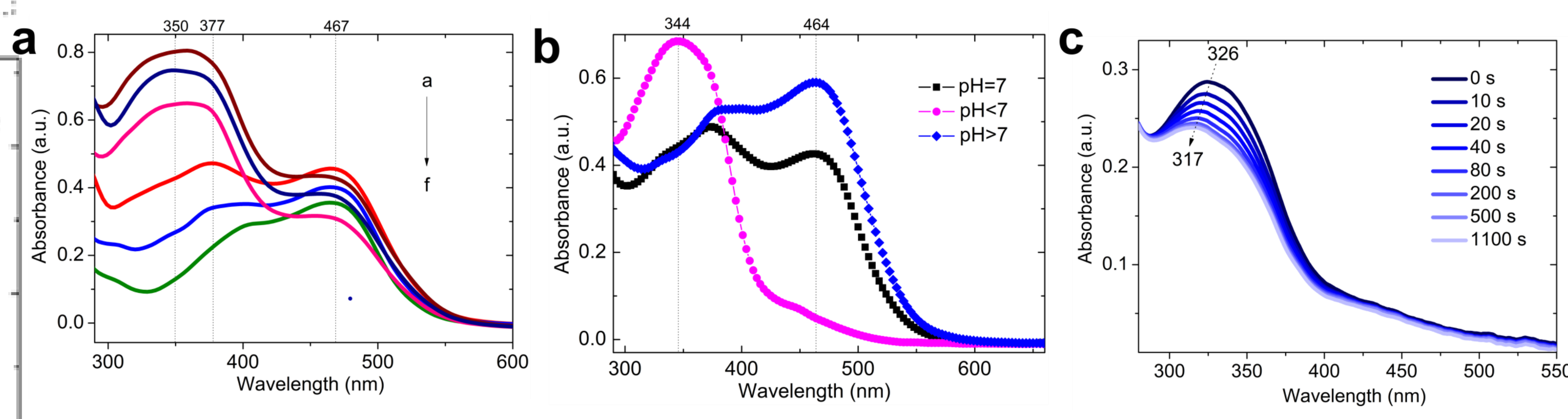
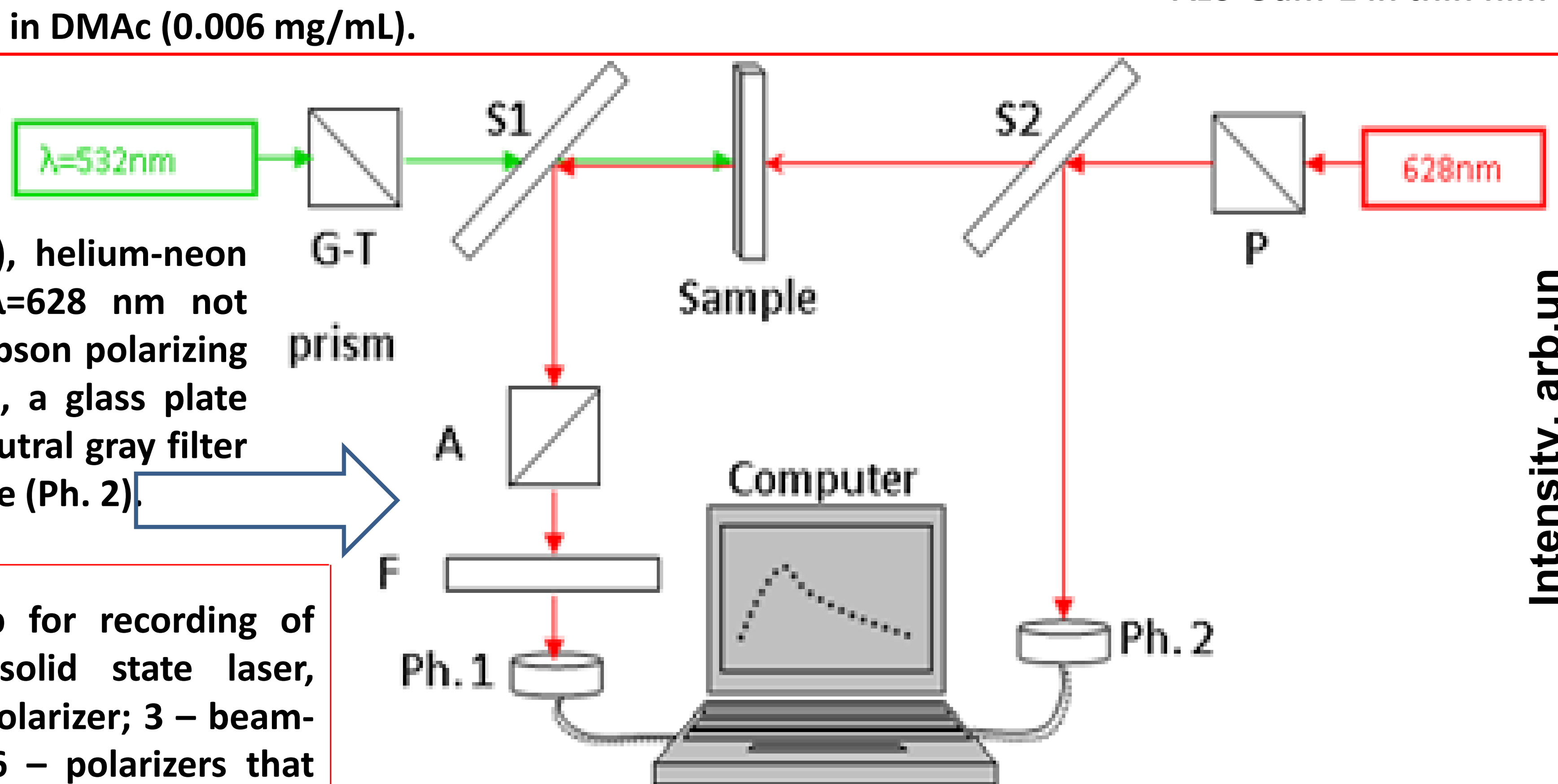


Figure 3. a) UV-vis spectra of Azo-Oam-2 at various concentrations (*a-f*) in DMAc. The concentration (*a-f*) of Azo-Oam-2 in DMAc solutions was about 15.0 (*a*), 13.8 (*b*), 11.0 (*c*), 6.0 (*d*), 4.5 (*e*) and 3.5 (*f*) μg mL⁻¹. b) UV-vis spectra of Azo-Oam-1 in DMAc at acidic (pH<7), neutral (pH=7) 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. Experimental setup for observe the dynamics of birefringence in the Azo-Pam films: irradiating laser with a wavelength of 532 nm (green color), helium-neon laser (He-Ne) with the wavelength λ=628 nm not absorbed by the polymer, a Glan-Thompson polarizing prism (G-T prism), a quartz wafer (S1), a glass plate (S2), a polarizer (P), a analyzer (A), a neutral gray filter (F), a photodiode (Ph. 1), test photodiode (Ph. 2).



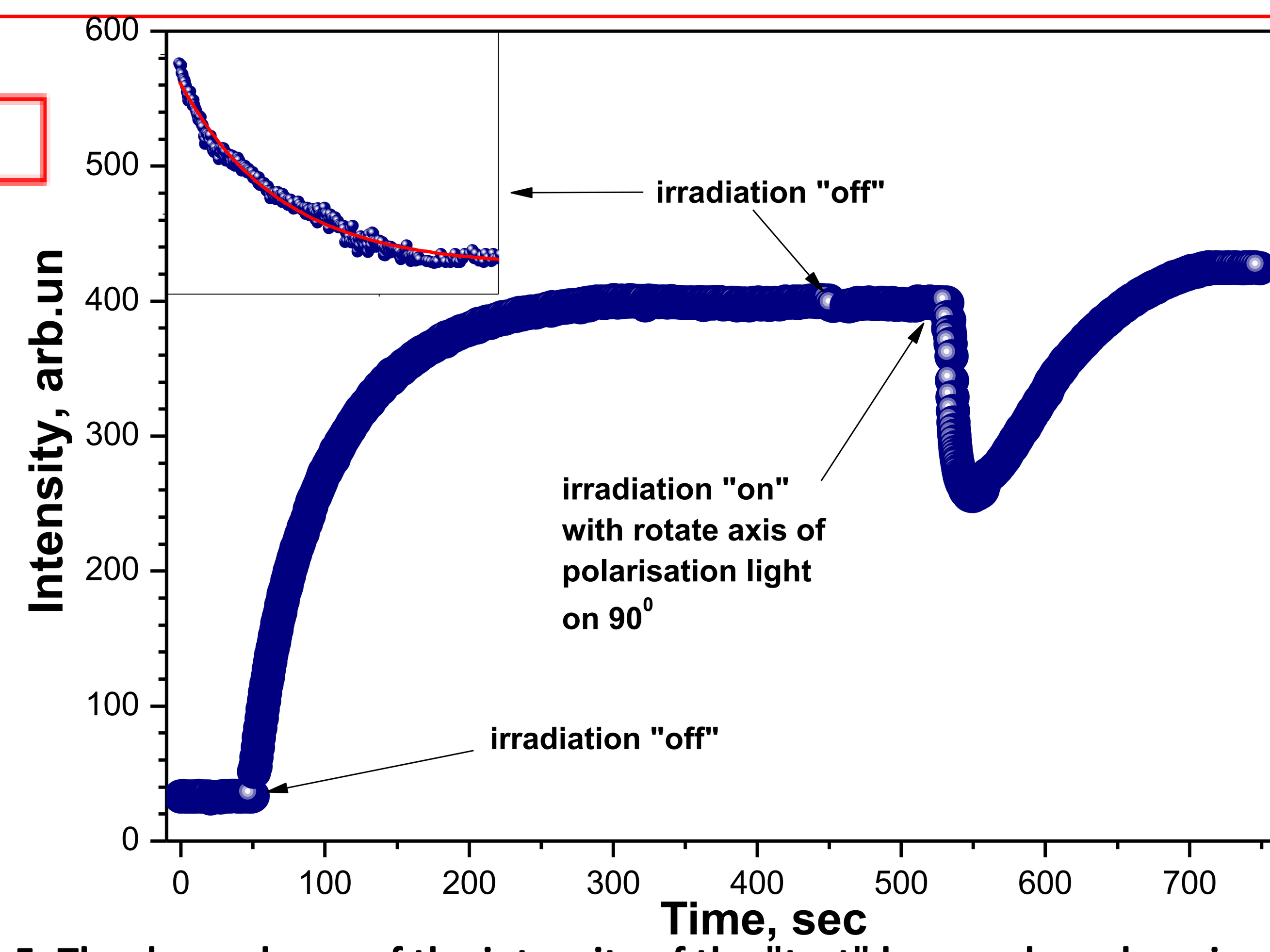
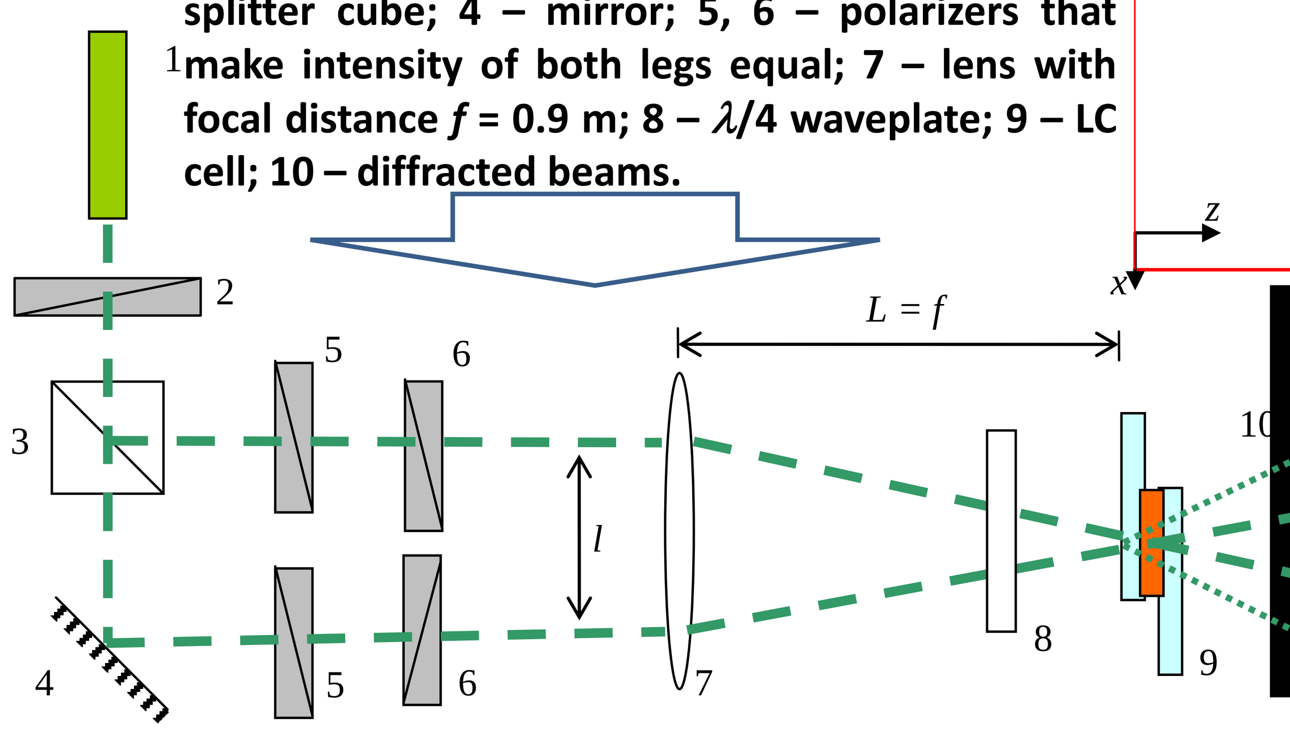


Figure 5. The dependence of the intensity of the "test" beam when changing the birefringence on the time of irradiation of polymers Azo-Oam-I

Figure 6. Experimental set-up for recording of gratings. 1 – diode-pump solid state laser, $I \leq 100$ mW, $\lambda = 532$ nm; 2 – polarizer; 3 – beam-splitter cube; 4 – mirror; 5, 6 – polarizers that make intensity of both legs equal; 7 – lens with focal distance $f = 0.9$ m; 8 – $\lambda/4$ waveplate; 9 – LC cell; 10 – diffracted beams.



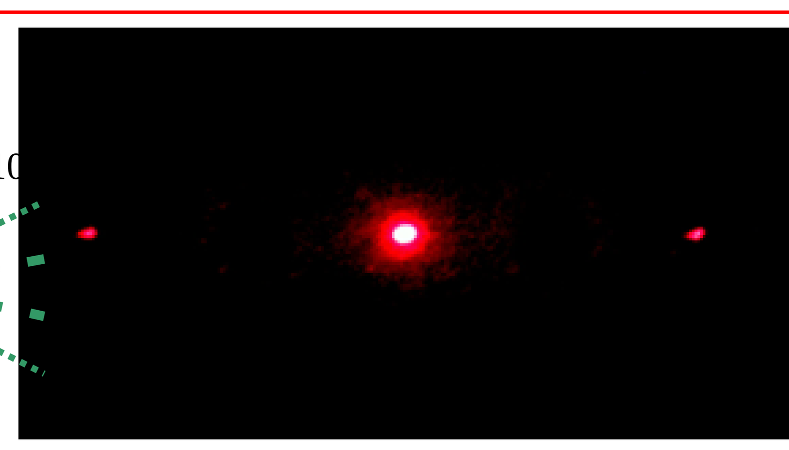


Figure 7. Diffraction patterns for Azo-Oam-I film from test beam

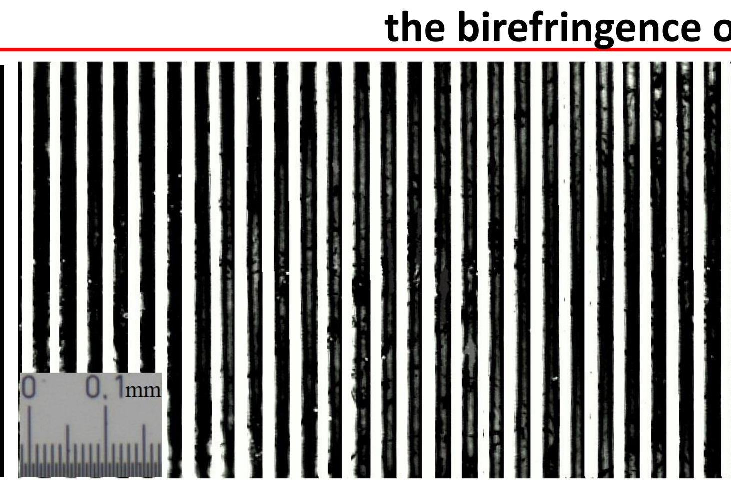


Figure 8. The photo of a diffraction grating Azo-Oam-I film in polarization microscope,

Conclusions: We have developed synthetic route for a novel meta-linked aromatic oligomer with the aldehyde end groups and possessing both azo and azomethine groups as well as mono- and biphenylene perfluorinated aromatic units. It was found that after the irradiation by the polarized light the resulting oligomer acquired time stable anisotropic properties. Moreover, holographic gratings (efficiency of diffraction about 2 %.) were observed in the oligomer film irradiated with two polarized beams.