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Supporting Information

Azobenzene-Containing Liquid Crystalline Block Copolymer Supramolecular Complexes as a Platform for Photopatternable Colorless Materials

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Experimental section

Materials

THF and ethyl ether were purchased from Aldrich, they were dried over KOH and distilled over an additional portion of KOH. Synthesis of LC triblock copolymers were performed by reversible addition-fragmentation transfer polymerization (Scheme 1) as described previously.[1] AzoOH was synthesized by an azocoupling reaction according to[2].

Preparation of supramolecular complex films

To prepare triblock copolymer supramolecular complexes, a triblock copolymer and AzoOH were dissolved separately in freshly distilled THF. The obtained solutions were mixed in a desired proportion to achieve the required degree of complexation. The mixture was kept in dark for 12 hours to ensure forming hydrogen bonds between pyridine and phenol groups. Then this solution was used for the preparation of complex films, In case of optical measurements, films were prepared with the spin-coating method but for TEM and FTIR measurements, the drop-casting method was used.

Instrumental measurements

Polarizing optical microscopic (POM) observations were conducted on an Axio Vert. A1 (Carl Zeiss) microscope equipped with a CCD camera and a hot stage.

The phase transition temperatures of the polymers were studied by differential scanning calorimetry (DSC) with a PerkinElmer DSC-7 thermal analyzer with a scanning rate of 10 K/min. Samples were prepared as 10–20 mg pellets. Samples were first heated above isotropic melt to remove thermal history.

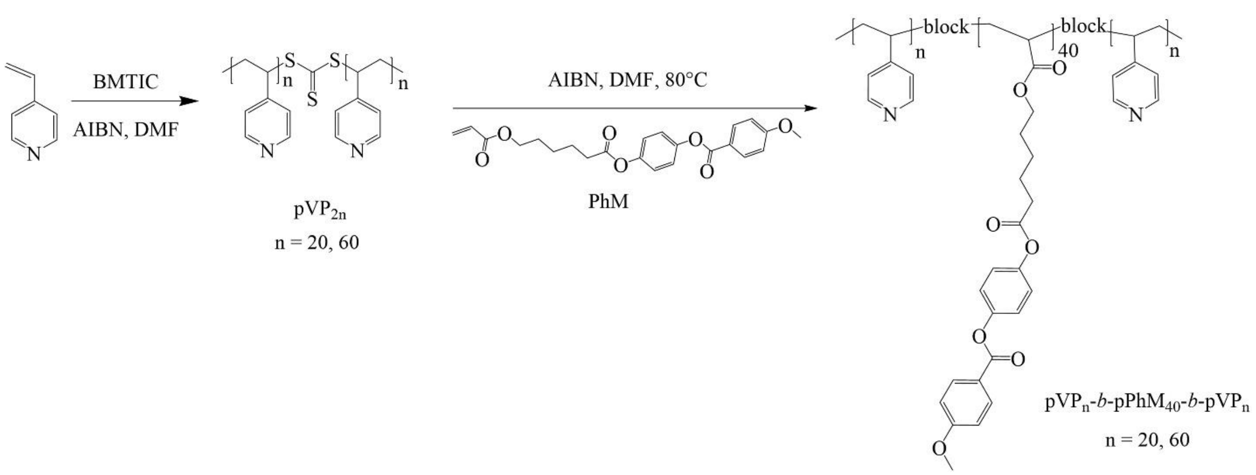
To prepare samples of the composites for TEM measurements following procedure was used. Firstly, using dispersion of composite in chloroform films were prepared by drop-casting on PTFE substrate. Then, samples were embedded in an epoxy resin and cured overnight. The sample was subsequently microtomed to a thickness of about 50 nm using a Reichert-Gung ultramicrotome with a diamond knife (Diatome) at room temperature. The microtomed sections were floated on water and subsequently placed on copper grids. To obtain contrast during TEM, the samples were stained with iodine for 1 h. TEM images were taken with a LEO 912 AB Omega transmission electron microscope (Carl Zeiss) operating at an accelerating voltage of 100 kV.

Polarized absorbance UV spectra of the composites were recorded by UNICAM UV-500 spectrophotometer equipped with a rotating polarizer. Photoorientation processes were induced with a KLM-473/h-150 laser operating at 473 nm. An incident light intensity was equal to 70 mW/cm^2 as measured with a LaserMate-Q (Coherent) intensity meter. Dichroism, *D*, of the complex films was calculated from the spectra through the following equation:

$$D = \frac{A_{\perp} - A_{\parallel}}{A_{\perp} + A_{\parallel}}$$

where $A_{\parallel}$ and $A_{\perp}$ stand for optical absorbance at 377 nm or 260 nm upon irradiation with a linearly polarized light along the directions parallel and perpendicular to the exciting light polarization direction (457 nm), respectively.

The infrared spectra were measured with a Thermo Nicolet IR200 FTIR spectrometer by 150 scans at a resolution of 2 cm^{-1}. The samples were drop-cast on KBr plates and dried overnight at room temperature.



Scheme 1. Synthetic route of pVP_n-b-$pPhM_{40}$-b-pVP_n triblock copolymers.

Table S 1. Properties of polymer samples under study.

Samples	**Microphase separation***	**Glass transition temperature, °C**	**Phase behavior****	$\boldsymbol{D}_{\mathbf{max}}$
TBC60-Azo0.50	L	31/86	N 120 (0.3) I	0.32
TBC20-Azo0.50	U	30	N 121 (0.3) I	0.40
pVP60-Azo0.50	-	87	amorphous	0.28
pVP20-Azo0.50	-	81	amorphous	0.27
p($VP_{20}Azo_{20}PhM_{40}$)	-	43	amorphous	0.12
$pPhM_{40}$	-	31	N 131 (0.8) I	-

*L is a lamellar structure, U is an unclear type of a microphase separated structure, but it contains discrete azobenzene-containing microphases.

**N is a nematic phase, SmA is a smectic phase A, and I is a isotropic melt. Isotropization enthalpy (in J g^{-1}) is given in brackets.

Figures

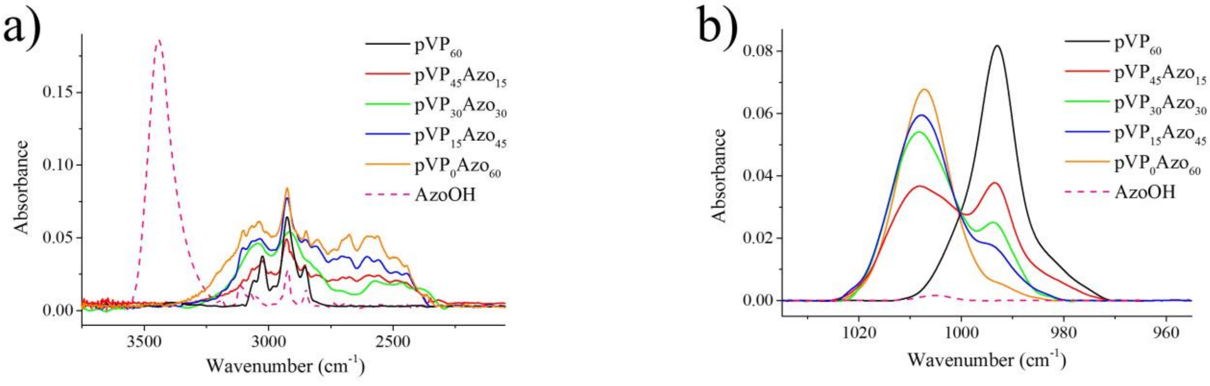


Fig. S 1. FTIR spectra of series of the complexes pVP60-Azo0.50 (x = 0.25, 0.50, 0.75, 1.0), AzoOH and pVP_{60} at wavenumber regions 1040-950 cm^{-1} (a) and 3600-2200 cm^{-1}(b).

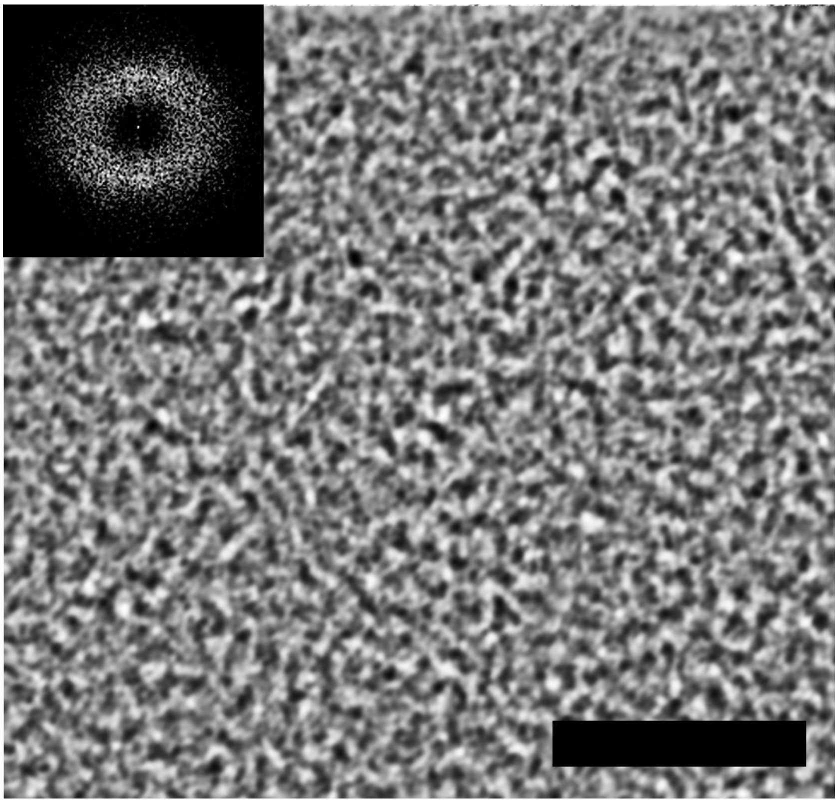


Fig. S 2. TEM images cross sections of the TBC20-Azo0.5 film. The sample was annealed at 140 °C for 3 h and stained with iodine for 1 h. The inset is a corresponding FFT image. Scale bar: 100 nm.

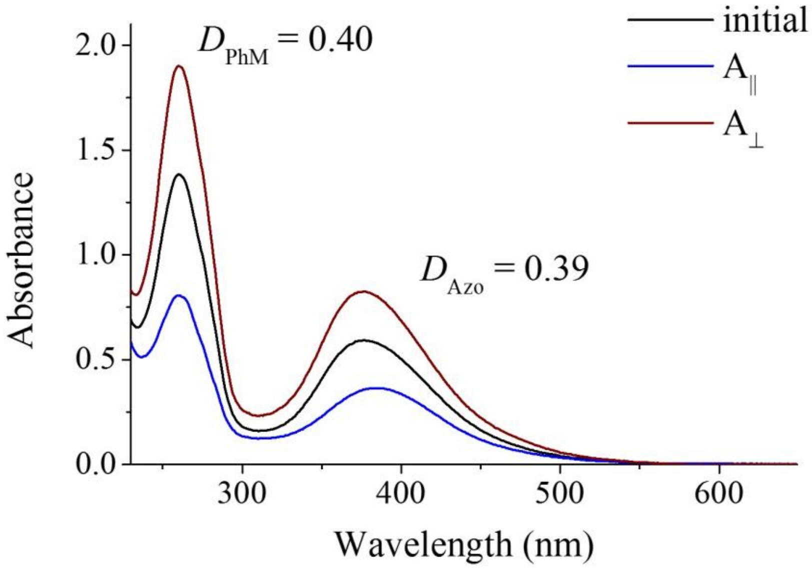


Fig. S 3. Polarized absorbance spectra of the TBC20-Azo0.5 film irradiated with linearly polarized light (457 nm, 70 mW/cm^2).

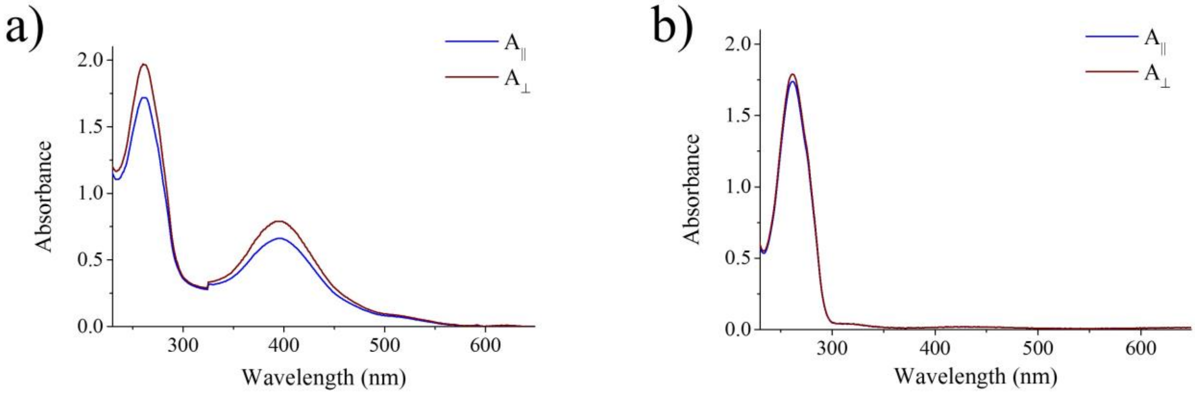


Fig. S 4. Polarized absorbance spectra of the $p(VP_{20}Azo_{20}PhM_{40})$ *film irradiated with linearly polarized light (457 nm, 70 mW/cm*^{2}*) before (a) and after (b) rinsing in ethyl ether.*

References

1 M. A. Bugakov, N. I. Boiko, E. V. Chernikova, S. S. Abramchuk and V. P. Shibaev, *Polym. Sci. Ser. C*, 2018, **60**, 3–13.

2 A. Priimagi, J. Vapaavuori, F. J. Rodriguez, C. F. J. Faul, M. T. Heino, O. Ikkala, M. Kauranen and M. Kaivola, *Chem. Mater.*, 2008, **20**, 6358–6363.