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Polybenzimidazole-based thiol-ene photosensitive composition for DLP 3D printing

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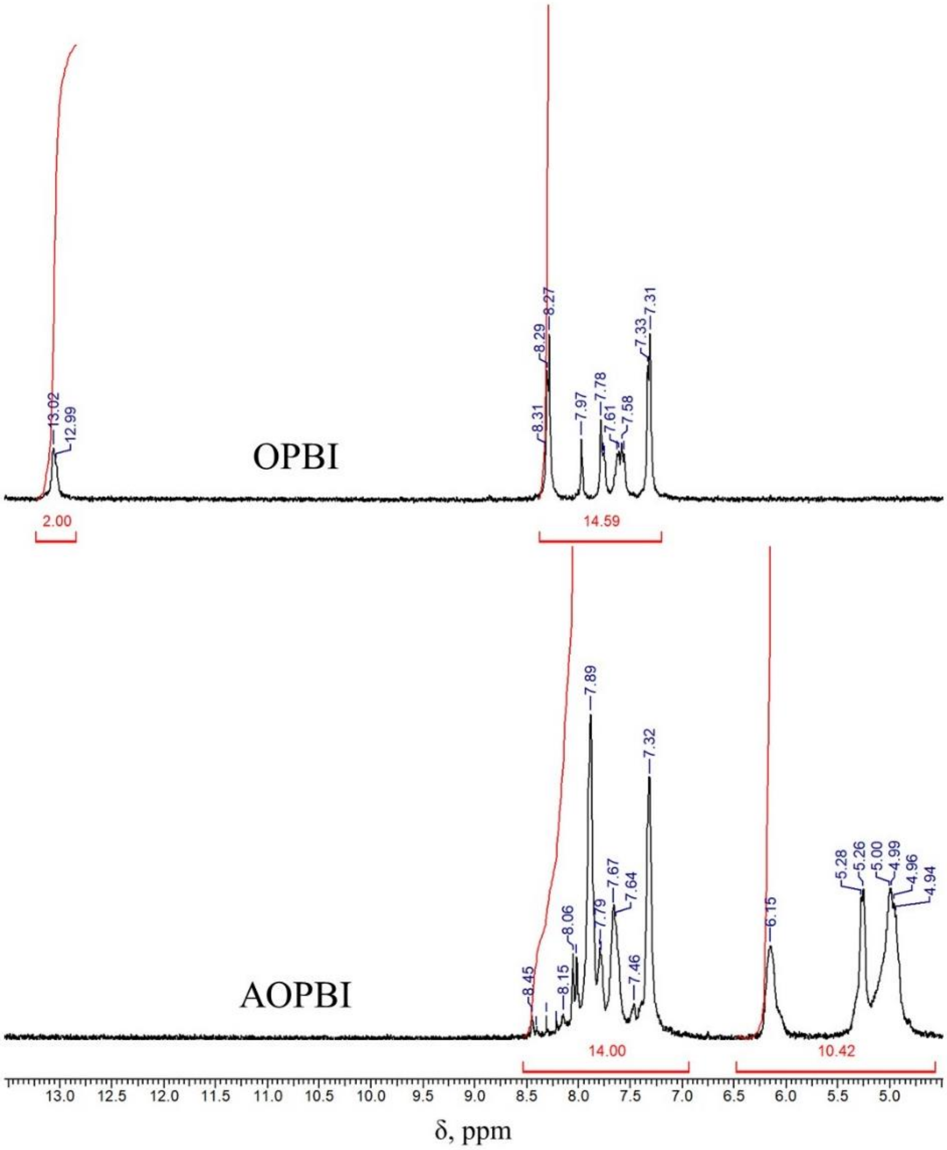

Figure S1 ^{1}H NMR spectra of poly(2,2'-(*p*-oxydiphenylene)-5,5'-dibenzimidazole) (OPBI) and *N*-allyl-functionalized poly[2,2'-(*p*-oxydiphenylene)-5,5'-dibenzimidazole] (AOPBI).

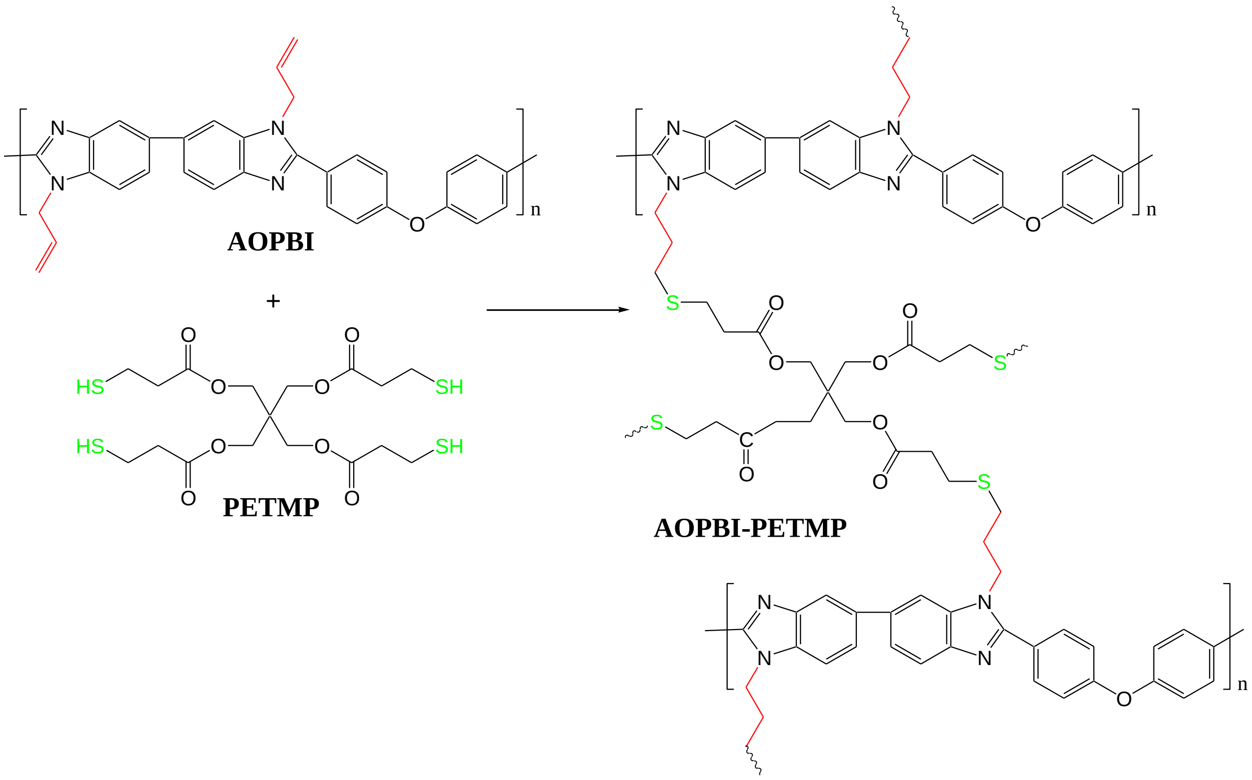

Figure S2 Schematic illustration of the synthesis of AOPBI-PETMP by UV-initiated thiol-ene polymerization of AOPBI and PETMP.

Experimental Part

Materials

Methanesulfonic acid (MSA, ≥99.5%, Sigma-Aldrich), P_2O_5 (chemically pure grade, KhimReaktivSnab, Russia), 4,4'-oxybis(benzoic acid) (OBA, 99%, Sigma-Aldrich), 3,3'-diaminobenzidine (DAB, ≥98%, Sigma-Aldrich), sodium hydride (NaH, 60% dispersion in mineral oil, Sigma-Aldrich), allyl bromide (97%, Sigma-Aldrich), pentaerythritol tetrakis(3-mercaptopropionate) (PETMP, >95%, Sigma-Aldrich), photoinitiator Irgacure 819, hydroquinone (≥99%, Sigma-Aldrich) and all solvents were used without additional purification. For preparation of Eaton's reagent (ER), a mixture of P_2O_5 (3 g) and MSA (20 ml) was stirred at 60°C up to complete homogenization.

Characterization methods

The ^{1}H NMR spectra were recorded on a Varian Inova 400 spectrometer (400 MHz) in DMSO-d_6 with TMS as the internal reference. The ^{1}H NMR peak integral ratio was used to evaluate the degree of *N*-allylation. The IR spectra were recorded with ALPHA spectrometer (Bruker) in the wavenumber range 4000-400 cm^{-1}. Average molecular weight and polydispersity index were determined by gel permeation chromatography on Malvern GPC max TDA 305 using polystyrene as calibration standards (eluent – DMF containing 0.01 M LiCl). Thermal gravimetric analysis (TGA) was performed with STA 449 C14/G Jupiter device (Netzsch) at a heating rate of 10 K min^{-1}. The mechanical characteristics of the materials were determined with an Instron 3367 testing machine at room temperature and approximately 50% humidity at an extension velocity of 2 mm min^{-1}; the specimen size was $40\times5\times0.1$ mm^3. The gel-fraction content of UV cured material was measured through *N*-methyl-2-pyrrolidone (NMP) extraction. The pre-weighted sample was immersed into NMP at 20°C for 24 hours. Afterward, the insoluble polymer was dried in a vacuum oven at 100°C to the constant weight.

Synthesis of OPBI and AOPBI

OPBI was prepared by polycondensation of DAB and OBA in ER at 140 °C (Figure S2), as described [M. Ueda, M. Sato and A. Mochizuki, *Macromolecules*, 1985, **18**, 2723].
η_{inh} = 2.40 dl g^{-1} (DMF, 20 °C). M_w = 120 000, M_w/M_n = 1.52.

For the synthesis of AOPBI, OPBI (2 g, 5 mmol) was mixed with NMP (100 ml) under vigorous stirring at 50 °C until complete dissolution. Then NaH (60% dispersion in mineral oil, 0.6 g, 15 mmol) was added, and the temperature was gradually raised up to 80 °C. Then stirring was continued at this temperature for more 4 h. Upon deprotonation, the initial light brown OPBI solution changed to a very deep red with a noticeably higher viscosity. After that the mixture was cooled to 40 °C, and allyl bromide (1.296 ml, 15 mmol) dissolved in NMP (20 ml) was added. The reaction mixture was stirred at 40 °C for 72 h. The resulting yellow-orange solution was poured into the stirred water (2 dm^{-3}), and the yellow beige precipitate was filtered. The obtained polymer was washed with water (5×300 ml) and finally with acetone (3×200 ml). The substance was dried in a vacuum oven at 40 °C for 5 days. η_{inh} = 1.79 dl g^{-1} (DMF, 20°C).

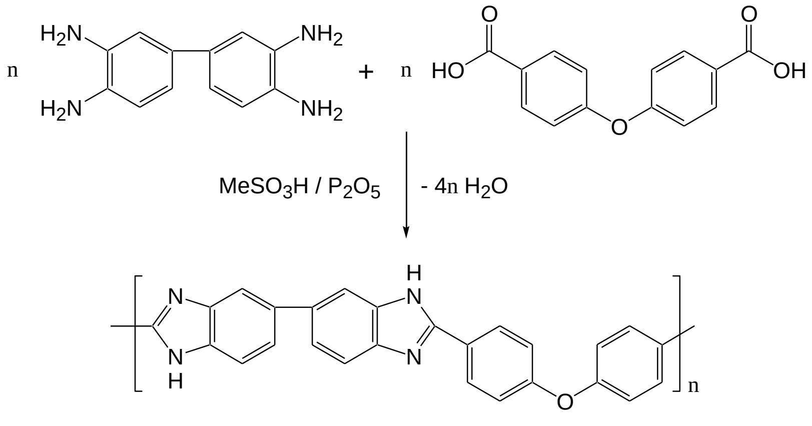

Figure S3 Schematic illustration of the synthesis of OPBI.

Preparation of photosensitive composition and photocured films

For the preparation of photosensitive composition, AOPBI (1.92 g, 4 mmol) was dissolved in NMP or *N*,*N*-dimethylacetamide (20 ml) under magnetic stirring at room temperature for 1 h. Then PETMP (0.976 g, 2 mmol) was added. After complete homogenization, Irgacure 819 (0.1738 g) and hydroquinone (0.0028 g) were added, and stirring was continued for more 12 h. The resulting homogeneous mixture was ready to use without further purification.

Film materials based on OPBI and AOPBI were obtained by solution casting method. Typically, OPBI or AOPBI (0.5 g) was dissolved in *N*,*N*-dimethylacetamide (10 ml) under magnetic stirring at room temperature for 2 h. The resulting homogenous solution was uniformly distributed over a glass support and dried at room temperature for 72 h. Then the films were peeled off from the support and additionally dried in a vacuum oven at 100 °C for 12 h and at 200 °C for 2 h in order to remove traces of the solvent. Photocured film was prepared as follows: photosensitive thiol-ene composition (8 ml) was uniformly distributed over a glass support and irradiated with an UV LED (395-400 nm, 10 W) for 10 min. The sample was then air dried at 30 °C for 48 h and then heated in a vacuum oven to 60 °C for 24 h, 100 °C for 4 h and at 200 °C for 2 h.

DLP 3D printing and post-processing

The formation of three-dimensional structures was carried out on a commercial DLP 3D printer Anycubic Photon Mono. A 30 ml vessel made of anodized aluminum with a bottom made of FEP film was used as a bath for the composition. Printing of three-dimensional structures was carried out with the following parameters: printing step 50 μm, exposure time of the first five layers – 60 seconds, exposure time of subsequent layers – 30 seconds. After printing, the sample was additionally irradiated for 10 minutes with a LED (395-400 nm, 10 W), and then dried in air at 30 °C for 48 h and in vacuum at 60°C for 24 h, at 100 °C for 4 h and at 200 °C for 2 h.