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Photosensitive thiol–ene composition for DLP 3D printing of thermally stable polymer materials

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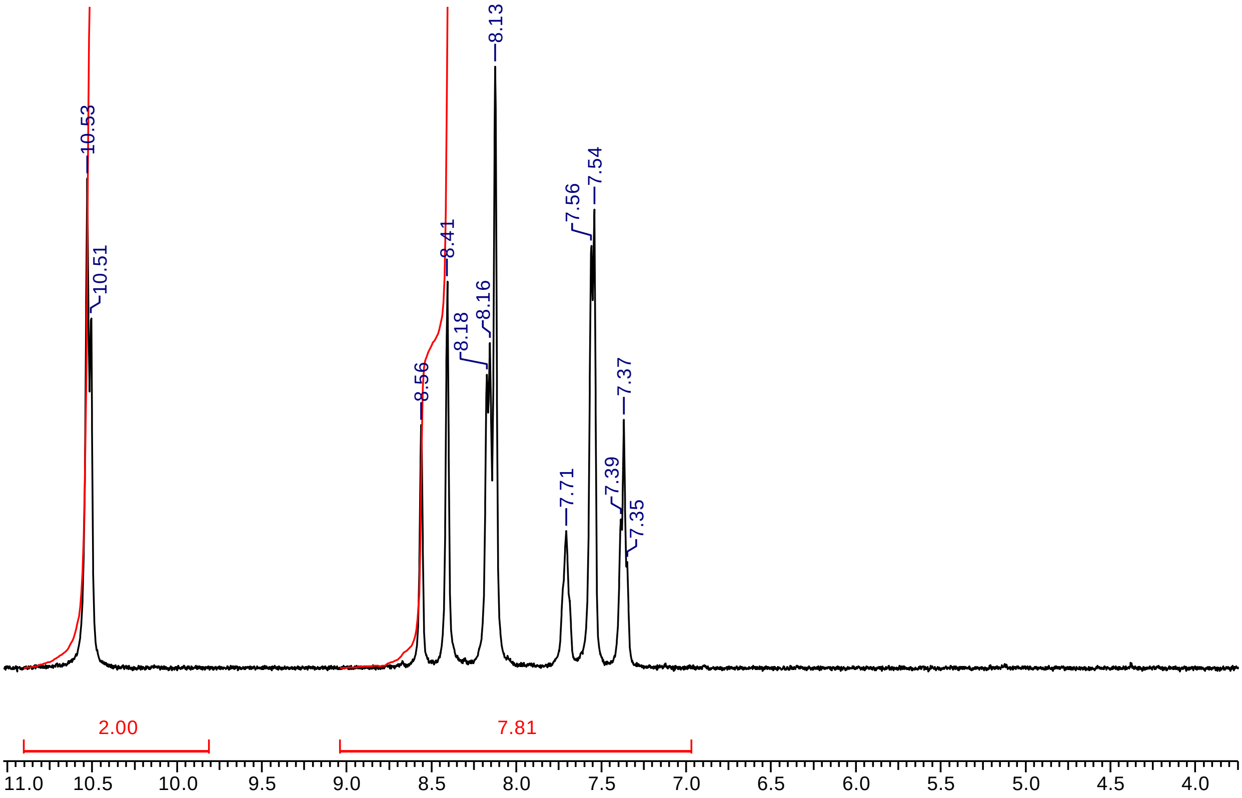

Figure S1 ^{1}H NMR spectrum of poly[*N*,*N*′-(1,3-phenylene)isophthalamide].

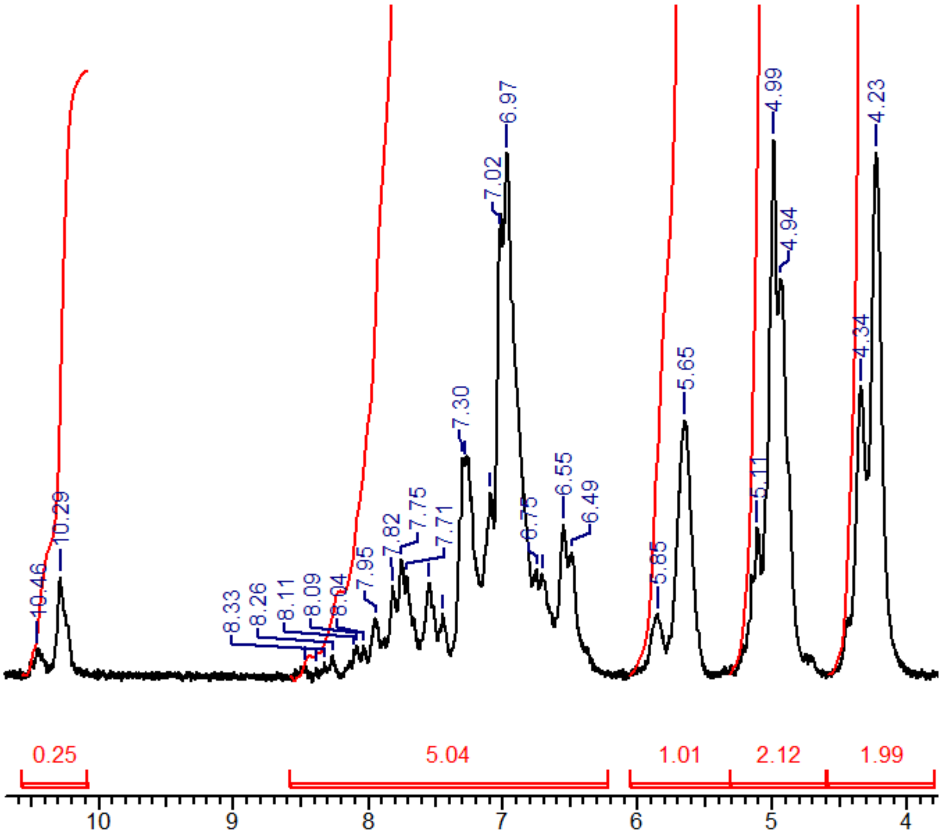

Figure S2 ^{1}H NMR spectrum of *N*-allyl-functionalized poly[*N*,*N′*-(1,3-phenylene)-isophthalamide].

Experimental Part

*Synthesis of poly[*N,N′*-(1,3-phenylene)isophthalamide] (MPA) and N-allyl-functionalized poly-[*N,N′*-(1,3-phenylene)isophthalamide] (AMPA)*

MPA was obtained by polycondensation of equimolar amounts of *m*-phenylenediamine and isophthaloyl chloride in a solution of *N,N*-dimethylacetamide according to the previously described procedure.[s1] η_{inh} = 1.20 dl g^{-1} (*N,N*-dimethylformamide, 20°C). ^1H NMR spectrum (δ, ppm): 10.5 (N–H). Calculated for $C_{14}H_{10}N_2O_2$ (%): C, 70.59; H, 4.20; N, 11.76. Found (%): C, 69.91; H, 4.61; N, 11.69.

For the synthesis of AMPA, initially 0.16 g (4 mmol) of NaH (60% in mineral oil) was stirred in 40 ml of DMSO at 75°C for 1 hour. The resulting homogeneous solution was cooled to 40°C and 0.476 g (2 mmol) MPA was added. Stirring was continued for 48 hours at this temperature. During this time, the color of the solution changed from yellow to dark red, which is due to the formation of a polyanion. Then, 0.346 ml (4 mmol) of allyl bromide was added to the reaction solution, and the synthesis was carried out for 24 hours at 40°C. The resulting homogeneous light orange solution was poured into excess THF. The precipitated light yellow polymer was filtered, washed several times with THF, and dried in vacuum at 45°C. η_{inh} = 0.75 dl g^{-1} (*N,N*-dimethylformamide, 20°C). ^1H NMR spectrum (δ, ppm): 4.3 ($–N–CH_2–$), 5.0 ($–CH=CH_2$) and 5.7 ($–CH=CH_2$).

Preparation of photosensitive composition and photocured films

To prepare a photosensitive composition, AMPA was dissolved in NMP with vigorous stirring at room temperature. PETMP was added to the resulting solution and stirring was continued for 1 hour. After complete homogenization, photoinitiator Irgacure 819 and hydroquinone were added. The mixture was stirred for an additional 12 hours. The resulting photosensitive composition contained 20.0 wt% AMPA, 16.2 wt% PETMP, 2.0 wt% Irgacure 819, 0.1 wt% hydroquinone and 61.7% NMP.

To obtain photocured films, the composition with a thickness of 150 µm was irradiated with a LED (power – 10 W, wavelength – 405 nm) for 30 seconds. After that, the sample was dried in air at 20°C for 72 hours, and then in vacuum at 40°C for 24 hours, 60°C for 12 hours, 100°C for 4 h and 200°C for 1 hour.

Characterization methods

^{1}H NMR spectra of polymers were recorded on a Varian Inova 400 spectrometer (Varian). DMSO-d_6 was used as a solvent; and TMS was used as an internal standard. The thermal stability of the materials obtained by the TGA method was evaluated on a STA 449 F3 synchronous thermal analyzer (Netzsch) at a heating rate of 10°C min^{-1}. The study of the mechanical characteristics of the materials was carried out using an Instron 3367 testing machine at a temperature of 20°C and a humidity of about 50% at a stretching rate of 2 mm min^{-1}, the dimensions of the samples were 50×5×0.1 mm^3, the number of parallel measurements was 5.

DLP 3D Printing Process

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 – 30 seconds, exposure time of subsequent layers – 15 seconds. After printing, the sample was additionally irradiated for 1 minute with a LED (power – 10 W, wavelength – 405 nm), and then dried in air at 20°C for 72 hours and in vacuum at 40°C for 24 hours, 60°C for 12 hours, 100°C for 4 hours and 200°C for 1 hour.

References

S1 D. S. Dudova, K. N. Bardakova, B. C. Kholkhoev, B. D. Ochirov, E. N. Gorenskaia, I. A. Farion, V. F. Burdukovskii, P. S. Timashev, N. V. Minaev and O. S. Kupriyanova, *J. Appl. Polym. Sci.*, 2018, **135**, 46463.