SUPPORTING INFORMATIONS

High Tg, Non-Poled Photorefractive Polymers

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**Synthesis and characterization** of Poly[(S)-(−)-3-methacryloyloxy-N-[3-(9-ethylcarbazolyl)]pyrrolidine-co-(S)-3-methacryloyloxy-1-(4’-nitro-4-azobenzene)pyrrolidine] 50/50 \{poly[(S)-(−)-MECP-co-(S)-MAP-N] 50/50\} (compound 2)

**Chemicals**

Methacryloyl chloride (Aldrich) was distilled (bp 95°C) under dry nitrogen in the presence of traces of 2,6-di-tert-butyl-p-cresol as polymerization inhibitor before use.

Toluene, chloroform, dichloromethane and tetrahydrofuran (THF) were purified and dried according to the reported procedures\(^1\) and stored over molecular sieves (4 Å) under nitrogen.

Triethylamine (Aldrich) was refluxed over dry CaCl\(_2\) for 8 h, then distilled (b.p. 89°C) under nitrogen atmosphere. 2,2’-Azobisisobutyronitrile (AIBN) (Aldrich) was crystallized from abs. ethanol before use.

All other reagents and solvents (Aldrich) were used as received without further purification.

**Monomers**
(S)-3-Methacryloyloxy-1-(4‘-nitro-4-azobenzene)pyrrolidine [(S)-MAP-N] was prepared as previously reported\(^2\) and crystallized from absolute ethanol; yield 47%.

(S)-(−)-3-Methacryloyloxy-N-[3-(9-ethylcarbazolyl)]pyrrolidine [(S)-(−)-MECP] was synthesized as previously reported\(^3\) and crystallized from absolute ethanol; yield 56%. [α]\(^{25}\) = −8.0° (c=1.005 in CHCl\(_3\)).

Structures of these monomers are shown in Scheme S1.

![Scheme S1](image_url)

**Scheme S1.** Molecular structures of monomers and synthesis of polymeric compound 2
Synthesis and characterization of compound 2

The copolymerization reaction was carried out in glass vials using AIBN (2 wt% with respect to the monomers) as thermal initiator and dry THF as solvent (1 g of monomers in 15 mL of THF). Feed at 50% molar content of (S)-MAP-N and (S)-(−)-MECP was prepared and introduced into vials under a nitrogen atmosphere, submitted to several freeze-thaw cycles, and allowed to polymerize at 60 °C for 72 h (Scheme S1). The polymerization process was stopped by pouring the reaction mixture into a large excess of methanol and the precipitate collected by filtration. The solid polymeric product was repeatedly redissolved in THF and reprecipitated again with methanol. The last traces of unreacted monomers and oligomeric impurities were eliminated from the products by Soxhlet extraction with methanol. The material was finally dried to constant weight at 60 °C for 4 days under high vacuum.

The polymer was obtained in 65% yield. $\bar{M}_n = 6700$; $\bar{M}_w / \bar{M}_n = 1.5$; $T_g = 203 ^\circ C$; $T_d = 328 ^\circ C$.

The conversion was determined gravimetrically and the product was characterized by FT-IR, $^1H$- and $^{13}C$ NMR.

The final molar composition of the copolymer was determined from the $^1H$ NMR spectrum by comparing the integrated peak areas in both the aromatic and aliphatic regions of (S)-MAP-N and (S)-(−)-MECP resonances. To confirm the obtained result, a quantitative analysis based on UV-vis spectrum was also carried out. The averaged molar content of (S)-MAP-N in the copolymer (50% mol) reflects the feed composition, indicating similar reactivities of the two methacrylate monomers.
^1^H-NMR (CDCl\textsubscript{3}): 8.35-7.80 (m, 7H, arom. 5-H carbazole, azoarom. ortho to nitro groups, azoarom. 3-H and 2’-H), 7.50-6.80 (m, 8H, arom. carbazole and azoarom. ortho to amino group), 5.20 (m, 2H, pyrrolidine 3-CH), 4.30 (m, 2H, N-CH\textsubscript{2}-CH\textsubscript{3} carbazole), 3.80-3.50 (m, 8H, pyrrolidine 2- and 5-CH\textsubscript{2}), 2.10-0.90 (m, 17H, pyrrolidine 4-CH\textsubscript{2}, N-CH\textsubscript{2}-CH\textsubscript{3} of carbazole and backbone CH\textsubscript{3} and CH\textsubscript{2}) ppm.

^1^3^C-NMR (THF-d\textsubscript{8}): 176.9 (C=O ester), 157.3 (arom. C-NO\textsubscript{2} of (S)-MAP-N), 151.4, 148.7 and 144.7 (arom. C=N=N-C and C-N-CH\textsubscript{2} of (S)-MAP-N), 142.9 (arom. C\textsubscript{10} carbazole), 141.1 (arom. C\textsubscript{13} carbazole), 133.9 (arom. C\textsubscript{3} carbazole), 126.8 (arom. 3’-C of (S)-MAP-N), 125.7 (arom. C\textsubscript{7} carbazole), 125.0 and 123.3 (arom. 2’-C and 3-C of (S)-MAP-N), 124.5 and 123.7 (arom. C\textsubscript{11} and C\textsubscript{12} carbazole), 120.9 (arom. C\textsubscript{5} carbazole), 118.5 (arom. C\textsubscript{6} carbazole), 113.2 (arom. C\textsubscript{2} carbazole), 112.5 (arom. 2-C of (S)-MAP-N), 109.6 (arom. C\textsubscript{1} carbazole), 108.9 (arom. C\textsubscript{8} carbazole), 103.0 (arom. C\textsubscript{4} carbazole), 75.5 (pyrrolidine 3-CH), 55.2 (CH\textsubscript{2}-C main chain), 54.0 (pyrrolidine 5-CH\textsubscript{2}), 47.4 (pyrrolidine 2-CH\textsubscript{2}), 45.9 (CH\textsubscript{2}-C main chain), 37.7 (N-CH\textsubscript{2}-CH\textsubscript{3} carbazole), 31.6 (pyrrolidine 4-CH\textsubscript{2}), 19.8 and 17.9 (CH\textsubscript{3} methacrylic main chain), 14.0 (N-CH\textsubscript{2}-CH\textsubscript{3} carbazole) ppm.

FT-IR (KBr): 3105, 3092 and 3047 (\nu_{\text{CH}} arom.), 2974, 2969 and 2928 (\nu_{\text{CH}} aliph.), 1725 (\nu_{\text{C=O ester}), 1602 and 1516 (\nu_{\text{C=C}} arom.), 1334 (\delta_{\text{CH}}), 788 and 721 (\delta_{\text{CH}} 1,2,4-trisubst. arom. ring), 744 (\delta_{\text{CH}} 1,2-disubst. arom. ring) cm\textsuperscript{-1}.

Physicochemical Measurements

^1^H- and ^1^3^C-NMR spectra were obtained at room temperature, in 5-10% CDCl\textsubscript{3} solutions, using a Varian NMR Gemini 300 spectrometer. Chemical shifts are given in ppm relative to tetramethylsilane (TMS). ^1^H-NMR spectra were run at 300 MHz by using the following experimental conditions: 24,000 data points, 4.5 kHz spectral width, 2.6 s acquisition time, 128
transients. $^{13}$C-NMR spectra were recorded at 75.5 MHz, under full proton decoupling, by using the following experimental conditions: 24,000 data points, 20 kHz spectral width, 0.6 s acquisition time, 64,000 transients.

FT-IR spectra were recorded with a Perkin-Elmer 1750 spectrophotometer, equipped with an Epson Endeavour II data station, on sample prepared as KBr pellets.

Number average molecular weight of the polymers ($\bar{M}_n$) and their polydispersity indexes ($\bar{M}_w/\bar{M}_n$) were determined in THF solution by SEC using a HPLC Lab Flow 2000 apparatus, equipped with an injector Rheodyne 7725i, a Phenomenex Phenogel 5-micron MXL column and a UV-VIS detector Linear Instrument model UVIS-200, working at 254 nm. The calibration curve for the MXL column was obtained by using monodisperse polystyrene standards in the range 800-35000.

Optical activity measurements were carried out at 25 °C on CHCl$_3$ solutions, using a Perkin Elmer 341 digital polarimeter, equipped with a Toshiba sodium bulb, with a cell path length of 1 dm. Specific and molar rotation values at the sodium D line are expressed as deg·dm$^{-1}$·g$^{-1}$·cm$^{-3}$ and deg·dm$^{-1}$·mol$^{-1}$·dL, respectively.

UV-vis absorption spectra were recorded at 25 °C on a Perkin Elmer Lambda 19 spectrophotometer on CHCl$_3$ solutions by using a cell path length of 0.1 cm. Azoaromatic and carbazole chromophores concentrations of about 5·10$^{-4}$ mol L$^{-1}$ were used.

The glass transition temperatures of the polymers ($T_g$) were determined by differential scanning calorimetry (DSC) on a TA Instruments DSC 2920 Modulated apparatus, adopting a temperature program consisting of three heating and two cooling ramps starting from room temperature (heating/cooling rate 10° C/min under a nitrogen atmosphere). Each sample (5-9 mgr) was heated up to only 250 °C in order to avoid thermal decomposition.
The initial thermal decomposition temperature ($T_d$) was determined on the polymeric samples with a Perkin-Elmer TGA-7 thermogravimetric analyzer by heating the samples in air at a rate of 20° C/min.
Figure S1. TGA thermograms of compound 1 (a) and 4 (b).
Figure S2. Time dependence of light transmission through a 20 µm thick oxidized sample of compound 1. The light is linearly polarized, with intensity $I = 0.8 \text{ W cm}^{-2}$ and $\lambda = 633 \text{ nm}$, and its propagation direction is along the sample normal.
Optically Induced Diffraction Gratings

Amorphous thin films were prepared by spin-coating solutions of the polymers in THF onto clean fused silica substrates. The films were then dried by heating above 60 °C under vacuum for 12 h. The film thicknesses, measured by a Tencor P-10 profilometer, were in the range 300-400 nm. The writing beam was formed by expanding and collimating a 5 mW circularly polarized argon laser beam (Spectra Physics model 165) at 488 nm to a diameter of 3 mm giving a power density of 100 mW cm\(^2\). These power levels were not high enough to produce permanent surface damage as would be caused in the case of ablation. This beam was incident onto the sample holder which consisted of a sample stage set at right angles to a front surface mirror. The portion of the beam which strikes the mirror is reflected back into the sample to interact with the direct beam and form an interference pattern on and throughout the sample. The light in the interference pattern is absorbed by the polymer film and the formation of a grating has been observed. The grating spacing is easily controlled by selecting the incidence Lloyd’s angle (α).

![Figure S3. 2D AFM image 10x10 µm (A) and relative 3D AFM image (B) of a 400 nm thick film of 1 after inscription at room temperature of surface relief grating (SRG) using a Lloyd’s mirror arrangement (with Lloyd’s angle α of 14°) to superimpose left and right circularly polarized interfering beams at 488 nm (100 mW cm\(^2\)) on the sample surface.](image-url)
The surface of the polymer films was observed with a Nanoscope II atomic force microscope (AFM) in Tapping™ mode. The surface gratings produced are permanent as long as the temperature of the sample is kept below its Tg.
Measurement of the Phase Shift between Interference Pattern and Refractive Index Grating

Measurements were carried out as described in the experimental section. Typical experimental results are illustrated below in Figures S4 and S5.

**Figure S4.** Time dependence of the light intensity of the two writing beams as a function of time during the translation of the grating, starting at $t = 0.3\,\text{s}$

**Figure S5.** Sum and difference of the two writing beams shown in Fig. S4. From the difference it is possible to extract the phase between the PR grating and the interference pattern while the sum gives evidence of a less intense grating in phase with the interference fringes.
Birefringence of Mechanically Oriented Samples

Samples of compounds 2 and 3 were prepared as described in the experimental section. They were cooled to a temperature low enough to become quite viscous but high enough to allow stretching by pulling the two glass substrates in opposite directions. Samples were then allowed to cool to room temperature. The resulting polymers appeared highly birefringent when observed at the optical microscope between crossed polarizers. Their birefringence was first analyzed at the optical microscope using a tilting compensator in line with the optical beam. As both compounds absorb in the visible, we were not able to obtain a clear birefringence measurement with this method, but we were nonetheless able to establish that birefringence was of the order the resolution of our compensator, which is $5 \times 10^{-3}$ for the thickness of our samples.

Given the low values of birefringence, we could then use for its measurement the set up described in the experimental section, with the stretching direction normal to the p-plane. Measurements were affected by a large error, as the alignment by mechanical stretching is not very reproducible. Results changed for different samples of the same compound and for different areas within the same sample. The measured birefringence ranges were:

$\Delta n = 1-4 \times 10^{-3}$ for compound 2

$\Delta n = 4-7 \times 10^{-3}$ for compound 3

Even if this is only a rough measurement, it is evident how the two compounds, assuming they were given a similar orientational order by the stretching, do not show a very different birefringence.
References

