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Supporting Information

Bilayer solvent and vapor-triggered actuators made of cross-linked polymer architectures via Diels-Alder pathways

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Materials For the production of the films *α,ω*-dihydroxyl poly(ε-caprolactone) (PCL-diol; CAPA2402, $\overline{\mathrm{M}}_n = 4000$ g mol^{-1} and PDI = 1.48) and *α,α',ω,ω'*-tetrahydroxyl poly(ε-caprolactone) (PCL-tetraol; CAPA4801, $\overline{\mathrm{M}}_n = 8000$ g mol^{-1} and PDI = 1.48) were used. The PCL oligomers chain end-functionalization was realized using 1-(3-hydroxylpropyl)-1H-pyrrole-2,5-dione [MAL(OH), prepared from 3-aminopropan-1-ol (Acros), exo-3,6-epoxy-1,2,3,6-tetrahydrophtalic anhydride (Sigma Aldrich) and ethanol 96% vol (VWR)] and furfuryl isocyanate (Sigma Aldrich). Multi-walled carbon nanotubes NC7000 (MWCNTs, Nanocyl, length of 1.5 μm and diameter of 9.5 nm) were used as nanofillers for the production of the nanocomposite films. Dichloromethane, chloroform ($CHCl_3$) and ethanol (EtOH) were supplied by Merck.

Synthesis of chain end-functionalized PCL The synthesis of chain end-functionalized PCL and the production of the thermo-reversible PCL-based networks were done respecting the procedure in our previous study.[1] In brief, PCL-tetraol oligomers were end-functionalized with furfuryl moeities [PCL(FUR)$_4$] in bulk overnight in presence of an excess of furfuryl isocyanate (1.5 eq.) at 110 °C in 250 ml pre-conditioned flask under inert atmosphere. Afterwards, the oligomers were dissolved in CH_2Cl_2 and poured in an excess of cold methanol in order to remove out the excess of the non-reacted furfuryl isocyanate. For the synthesis of maleimide functionalized

PCL [PCL(MAL)$_2$], PCL-diol, 1-(3-hydroxylpropyl)-1H-pyrrole-2,5-dione and methylene diphenyl diisocyanate were introduced into a 15 cm^3 twin-screw DSM micro-compounder at 55 °C with twin-screws rotation speed of 30 rpm under nitrogen flow. The reaction was completed in 40 min with constant temperature of 140 °C and rotation speed of 70 rpm. The residual protected maleimide chain end groups were deprotected and furan was removed by placing the polymer matrix in an oven under vacuum at 110 °C overnight.

Production of thermo-reversible PCL-based networks The thermo-reversible network was produced using reactive extrusion technique. PCL(FUR)$_4$ was introduced in a 15 cm^3 twin-screw DSM micro-compounder in presence of PCL(MAL)$_2$ (stoichiometric ratio between furfuryl and maleimide functions) at 55 °C with rotation speed of the twin-screws of 30 rpm under nitrogen flow. The reaction was completed in 30 min at 80 °C and rotation speed of 70 rpm. Afterwards, the obtained network was placed in oven at 65 °C in order to complete the Diels-Alder coupling reactions. The MWCNTs containing polymer network, were obtained adding the corresponding nanofiller (5 wt% with respect to the total polymer amount) to PCL(FUR)$_4$ solution in CHCl$_3$. After the evaporation of the solvent under stirring the material was placed under vacuum at room temperature and the mixture was introduced in a 15 cm^3 twin-screw DSM micro-compounder in the presence of PCL(MAL)$_2$ while subject to conditions described previously.

Equations

$D_s (\%) = (W_t - W_d)/W_d \times 100$ equation (S1),

where D_s is the degree of swelling, W_t is the weight of the swelled film at a given time t of swelling and W_d is the weight of the dry film (before swelling).

$D_d (\%) = (W_{eq} - W_d)/(W_{eq} - W_t) \times 100$ equation (S2),

where D_d is the degree of deswelling, W_{eq} is the weight of the swelled film at equilibrium, W_d is the weight of the film before swelling and W_t is the weight of the film at a given time t of deswelling. Both the D_s and the D_d, were calculated after the second cycle of swelling/deswelling of the samples.

The curvature upon swelling and the degree of deformation and recovery in those experiments were calculated using the length of the bilayer before and after swelling (L) as well as the angle upon bending (α) and the radius (r) of the imaginary circle drown around the bended film as shown (Figure 4D in the manuscript). Therefore, for the curvature measurement, equation

(S3) was used as described in the literature[2] and equations (S4) and (S5) in the case for the deformation and recovery degree:

$C = 1/r$ equation (S3),

where C is the curvature on swelling and r is the radius of the circle described around the bended bilayer;

$R_d\ (\%) = (L_{eq}/L_d) \times 100$ equation (S4),

where R_d is the degree of deformation, L_{eq} is the length of the curve of the swelled film at equilibrium and L_d is the length of the dry film (before swelling).

$R_r\ (\%) = ((L_{eq}/L_t)/(L_{eq}/L_d)) \times 100$ equation (S5),

where R_r is the degree of recovery, L_{eq} is the length of the curve of the swelled film at equilibrium, L_t is the length of the curve of the swelled at a given time t and L_d is the length of the dry film (before swelling).

$L = d \times \pi \times (\alpha/360)$ equation (S6),

where L is the length of the curve, d is the diameter of the circle described around the bended bilayer and α as the angle upon bending as presented in Figure 4 in the manuscript.

Mechanical tests The tensile characteristics were evaluated using a Zwick/Roell Z 2.5 apparatus (Germany load cell 2 mV/V, type Xforce P) with nominal force of 2.5 kN using test Xpert II software and strain rate of 1 mm/min. Before the test, the specimens were kept for 24h at 21 °C and cut in dumbbell-shape respecting D368-5 Standard. It was established out that the maximal deformation at break was 600% with Young modulus of 130 MPa and ultimate strain of 32 MPa (Figure S1).

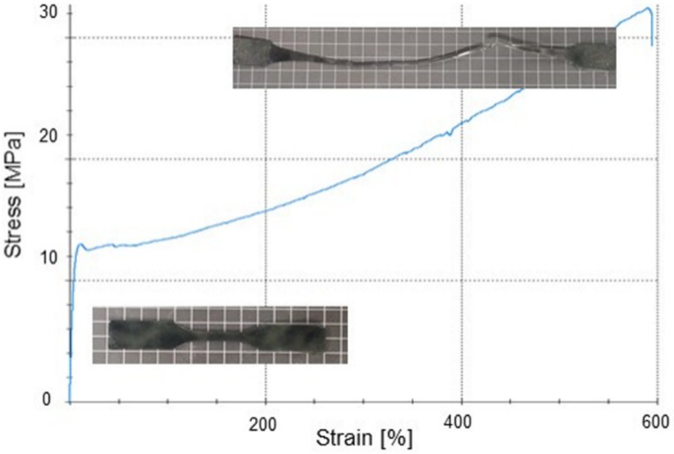

Figure S1. Digital images of PCL/PCL-MWCNT bilayer film before and after mechanical test and corresponding stress-strain curve.

Bilayer compression production Influence of the monolayer composition (furan and maleimide moieties content) on the bilayer production capacity (Figure S2). Due the highter crosslinking degree in the case of the layers containing PCL(MAL)$_2$-PCL(FUR)$_4$ [compared to PCL(MAL)$_2$-PCL(FUR)$_2$] the best sample for bilayer actuator production was the one where one of the layer is PCL(MAL)$_2$-PCL(FUR)$_4$ and the other PCL(MAL)$_2$-PCL(FUR)$_4$/MWCNT (Figure S2d).

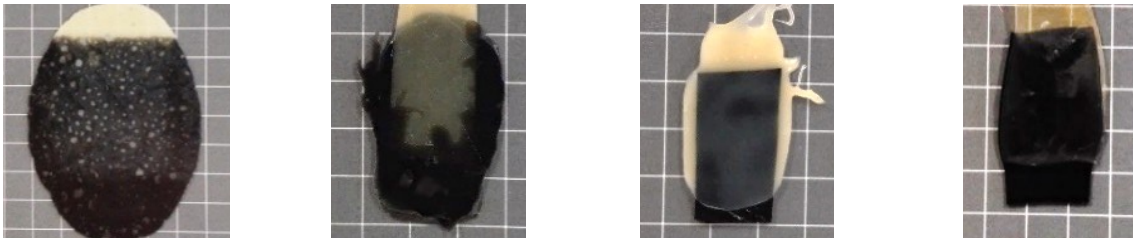
(a) (b) (c) (d)

Figure S2. Digital images of bilayer films produced from monolayers with different furan and maleimide moieties content: PCL(MAL)$_2$-PCL(FUR)$_2$ and PCL(MAL)$_2$-PCL(FUR)$_2$/MWCNT (a), PCL(MAL)$_2$-PCL(FUR)$_4$ and PCL(MAL)$_2$-PCL(FUR)$_2$/MWCNT (b), PCL(MAL)$_2$-PCL(FUR)$_2$ and PCL(MAL)$_2$-PCL(FUR)$_4$/MWCNT (c) and PCL(MAL)$_2$-PCL(FUR)$_4$ and PCL(MAL)$_2$-PCL(FUR)$_4$/MWCNT (d).

Differential scanning calorimetry The thermal properties of the films were studied using differential scanning calorimetry (DSC, DSC Q2000 apparatus from TA Instruments, USA) under nitrogen flow in the range from -80 °C to 65 °C with heat rate of 10 °C min^{-1}. The degree of PCL crystallinity was calculated using equation (S7) and presented in Table S1.

χ_c^{PCL}, % = $[(\Delta H_m^{PCL} - \Delta H_{cc}^{PCL})/(\Delta H_m^{PCL,0} \times W^{PCL})] \times 100$ equation (S7),

where ΔH_m^{PCL} is the melting enthalpy, ΔH_{cc}^{PCL} is the enthalpy at the temperature of cold crystallization, ΔH_m^0 is the melting enthalpy when PCL is in a 100% crystalline state [$\Delta H_m^{PCL,0}$ = 139.5 J g^{-1}]^3 and W^{PCL} is the weight fraction of PCL in the sample.

Table S1. Values of T_m, ΔH_m^{PCL} and χ_c^{PCL} for PCL and PCL-MWCNT films.

Sample	T_m [°C]	ΔH_m^{PCL} [J g^{-1}]	χ_c^{PCL} [%]
PCL	52.4	59.4	42.6
PCL-MWCNT	51.9	60.0	45.2

The degree of swelling of mono- and bilayer films used for thermo-mechanical studies with DMTA are presented in Table S2.

Table S2. Degree of swelling of mono- and bilayer films after immersion for 1 and 3 min in $CHCl_3$ and after immersion in 3 min and 30 min in $CHCl_3$ and EtOH, respectively.

Sample	D_s [%]		
	1 min in $CHCl_3$	3 min in $CHCl_3$	3 min in $CHCl_3$ and 30 min in EtOH
PCL	49	180	21
PCL-MWCNT	32	160	26
PCL/PCL-MWCNT	92	205	27

Solvent induced shape-memory Fast solvent-triggetred shape recovery was observed after suitable programming (spiral like) of PCL film upon subsequent immersion in $CHCl_3$ (Figure S3).

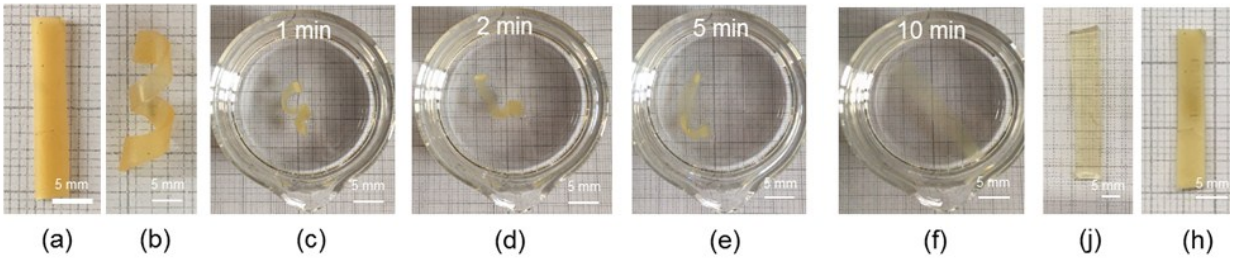

Figure S3. Digital images of different shape recovery step of PCL film in $CHCl_3$: permanent shape (a), spiral temporary shape (b), shape changes upon immersion (c-f), swelling state of the film after 10 min in $CHCl_3$ (j) and recovery after immersion for 90 min in EtOH (h).

References

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