Supplementary Information for

Nanostructural Changes in Crystallizable Controlling Units Determine the Temperature-Memory of Polymers†

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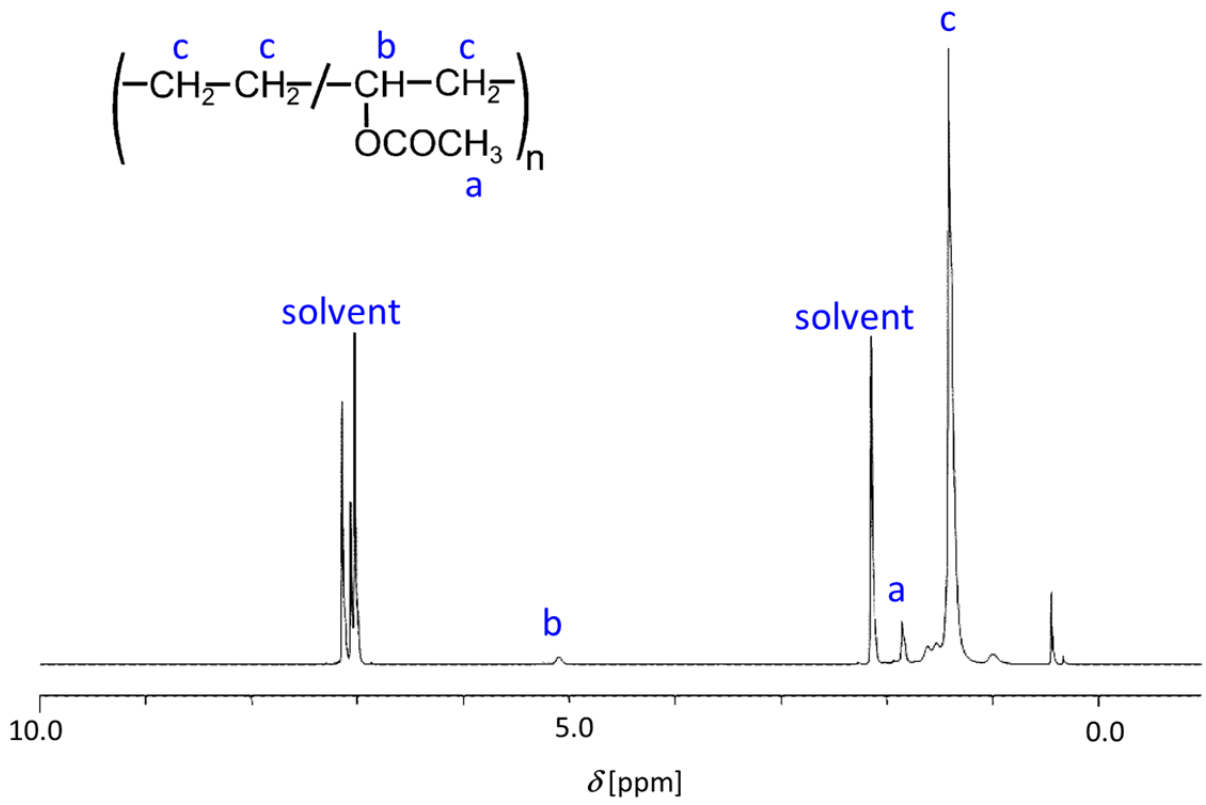
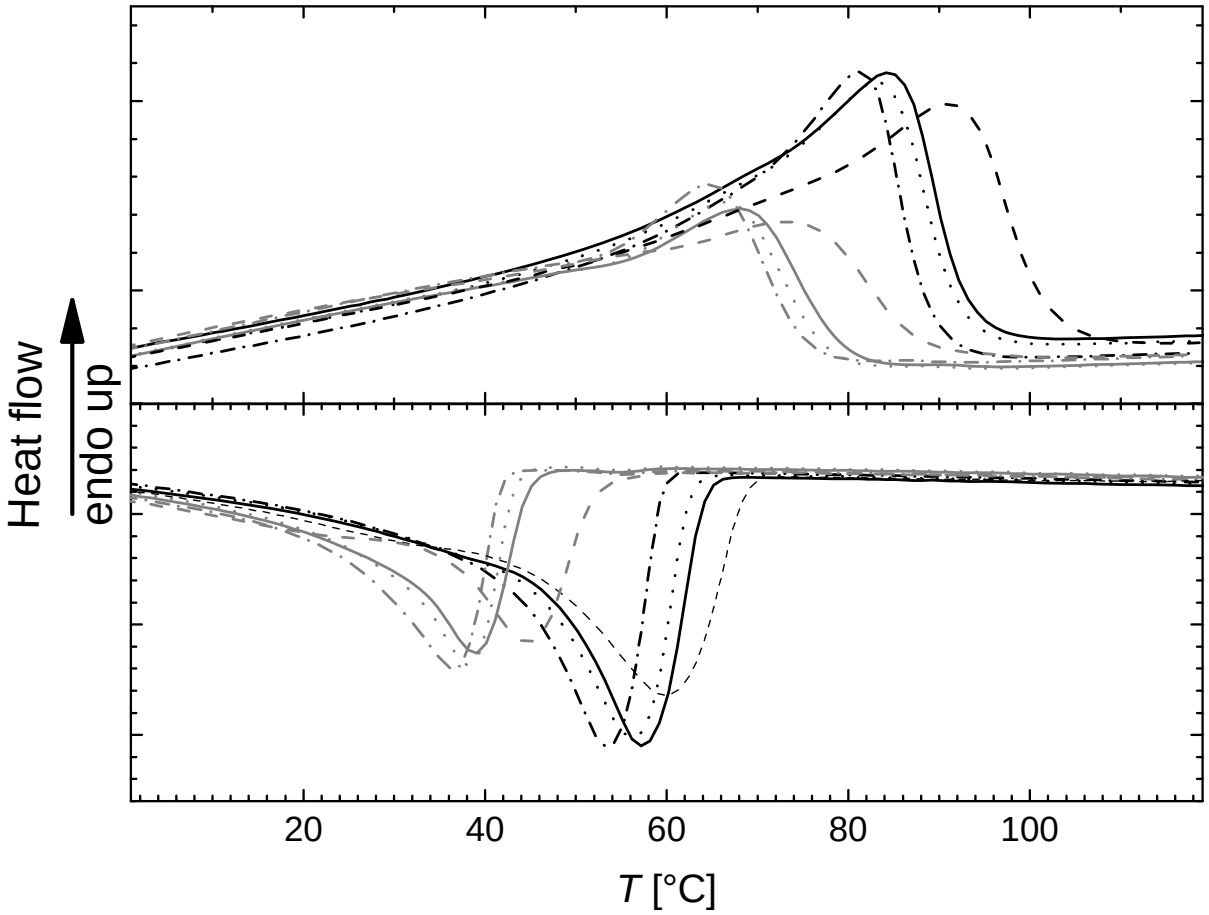
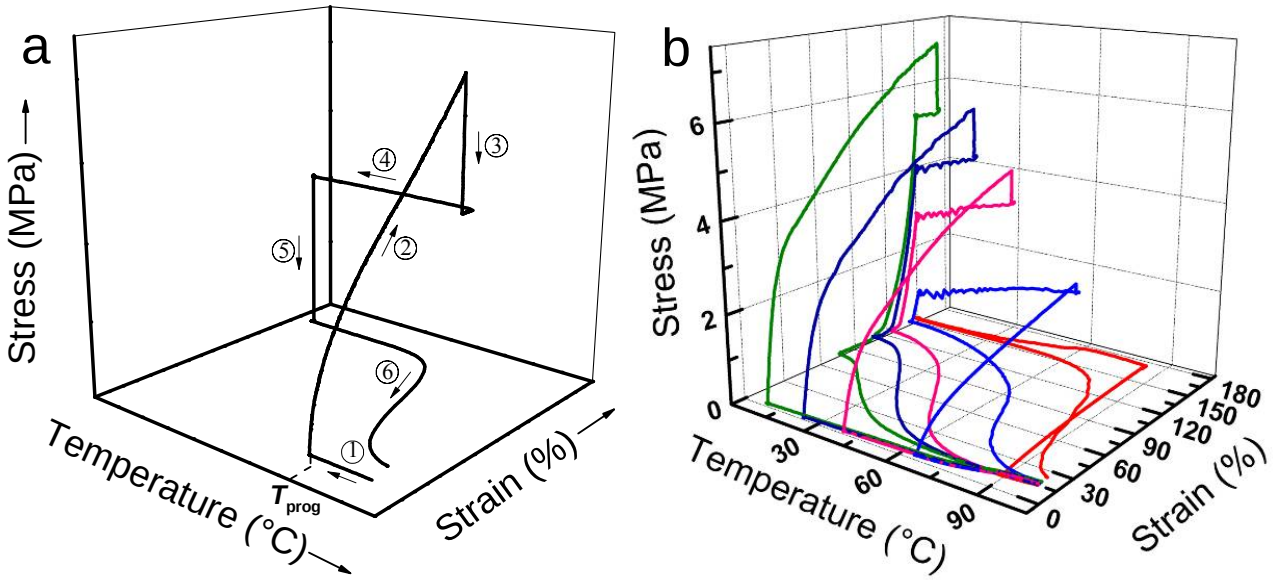


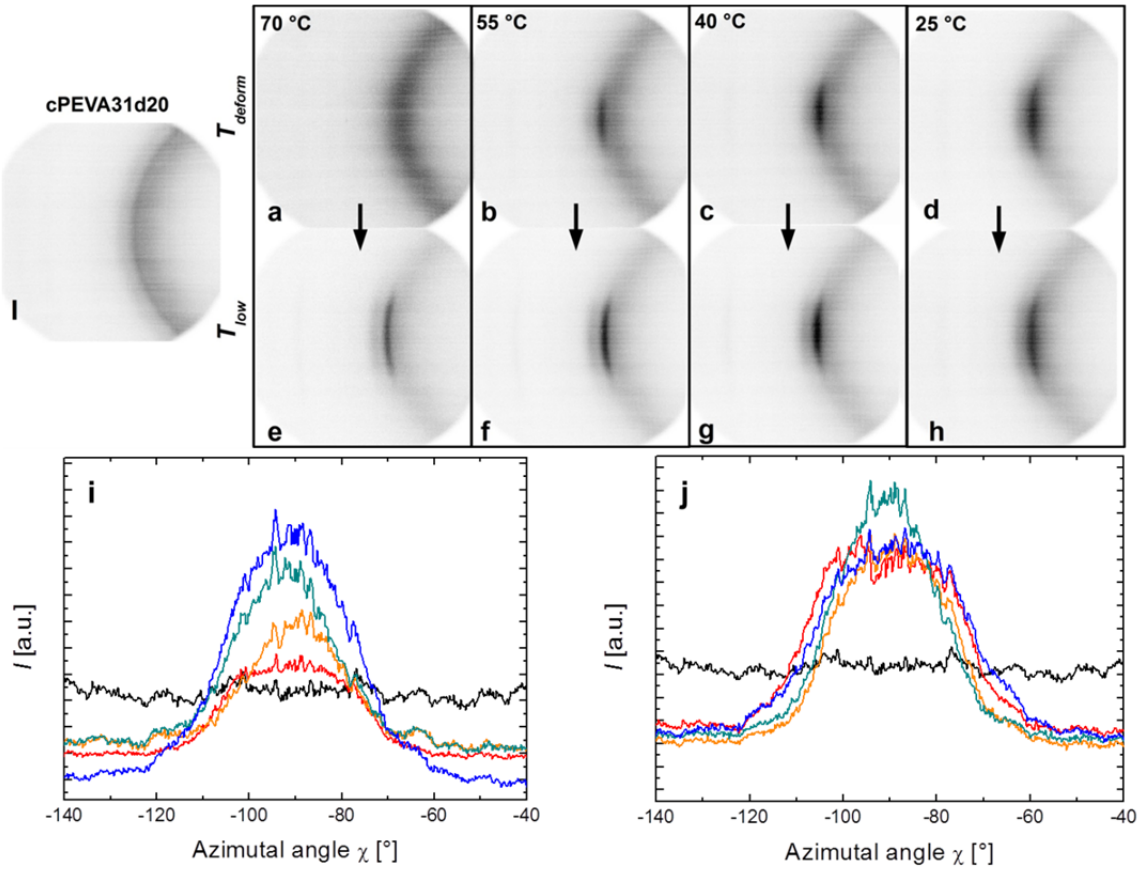
SI Figure 1. 500 MHz ^{1}H-NMR spectrum of cPEVA31D10 with assigned chemical shifts utilized for calculation of the average segment length of PE sequence. a: –$COOCH_3$- (methylene protons near the carboxyl group, δ = 1.8 ppm); b: -CH- (methylene protons near the carboxyl group, δ = 5.0 ppm); c: -CH_2- (linear methylene protons, δ = 1.3-1.6 ppm). The solvent (toluene-d_8) appears at δ = 2.2 and 7.1 ppm.



SI Figure 2: DSC thermograms of copolymer starting materials, PEVA20 (dashed black line), PEVA31 (dashed grey line) and crosslinked cPEVAs with different composition. cPEVA20D05 (solid black line), cPEVA20D10 (dotted black line), cPEVA20D20 (dash-dotted black line) and cPEVA31D05 (solid grey line), cPEVA31D10 (dotted grey line), and cPEVA31D20 (dash-dotted grey line) at heating and cooling rates of 20 $K \cdot min^{-1}$.



SI Figure 3: a) Quantification of temperature-memory effect with schematic illustration of the TMCP and recovery module under stress-free conditions. The TMCP for programming of the cPEVAs consisted of the following steps: After preconditioning, the sample was heated to T_{high} and cooled to T_{deform} (step 1) leading to a partial crystallization of the domains depending on the applied T_{deform}. In the step 2 the sample was deformed to ε_m at T_{deform}, and was held isothermally for 10 min under constant strain to allow structural reorganization of the fixing segments (step 3). In step 4, the sample was cooled to T_{low} = 0 °C under constant strain conditions and held isothermally for 10 min. Then in step 5, the stress was released to σ = 0 MPa at T_{low}, and the fixed temporary shape ε_u was obtained. For the shape recovery the specimen was reheated to T_{high} under stress-free conditions leading to step 6.
b) Temperature-memory effect. Stress-temperature-strain curves obtained from cyclic, thermomechanical tensile tests for cPEVA20D10 with stress-free recovery at various deformation temperatures: T_{deform} = 10 °C (green), 25 °C (blue), 40 °C (pink), 65 °C (light blue) and 90 °C (red). Fixed parameters: T_{low} = 0 °C, T_{high} = 100 °C, and ε_m = 150%.



SI Figure 4: Equatorial section of the wide-angle scattering patterns of cPEVA31D20 following the temperature-memory effect (**a-h**) during TMCP. Left: T_{low} = 10 °C and ε = 0%; **a-d**: T_{deform} (as indicated) and ε_m = 150%; **e-h**: T_{low} = 10 °C and ε_u (temporary shape); **i** and **j**: Azimuthal profiles of the (110) diffraction from: in **i:** non-deformed (black), **a** (red), **b** (orange), **c** (dark cyan) and **d** (blue); in **j**) non-deformed (black), **e** (red), **f** (orange), **g** (dark cyan) and **h** (blue).

SI Table 1: Temperature-memory properties of the cPEVA20 series.

Sample ID	Stress-free recovery				
	T_{deform} [a] [°C]	$\sigma(\varepsilon_m)$ [b] [MPa]	R_f [c] [%]	R_r [d] [%]	T_{sw} [e] [°C]
cPEVA20D05	90	0.26	104	100	89
	65	1.81	97	98	69
	40	3.75	83	97	43
	25	4.62	74	99	28
	10	5.80	53	100	16
cPEVA20D10	90	0.42	101	100	87
	65	1.95	103	100	68
	40	4.31	84	100	43
	25	5.60	74	99	31
	10	7.02	51	100	16
cPEVA20D20	90	0.85	100	100	79
	65	1.94	97	99	68
	40	4.49	83	99	44
	25	5.36	75	99	36
	10	7.32	52	100	23

a)T_{deform} and fixed parameters: T_{low} = 0 °C, T_{high} = 100 °C, heating rate = 2 K·min^{-1}, cooling rate = 5 K·min^{-1} and ε_m = 150%; **b**) $\sigma(\varepsilon_m)$: stress at ε_m; **c**) R_f: shape fixity rate; **d**) R_r: shape recovery rate; **e**) T_{sw}: switching temperature.

SI Table 2: Temperature-memory properties of the cPEVA31 series.

Sample ID	Stress-free recovery				
	T_{deform} [a] [°C]	$\sigma(\varepsilon_m)$ [b] [MPa]	R_f [c] [%]	R_r [d] [%]	T_{sw} [e] [°C]
cPEVA31D05	70	0.38	116	96	71
	55	0.66	106	97	60
	40	1.67	92	96	41
	25	2.48	82	99	26
	10	3.51	62	87	12
cPEVA31D10	70	0.61	110	99	68
	55	0.82	105	98	60
	40	2.17	90	98	41
	25	3.17	79	100	26
	10	4.48	57	100	14
cPEVA31D20	70	0.91	106	100	66
	55	0.93	102	98	61
	40	2.35	89	98	42
	25	3.41	78	99	28
	10	4.78	58	96	12

a) T_{deform} and fixed parameters: T_{low} = 0 °C, T_{high} = 80 °C, heating rate = 2 K·min^{-1}, cooling rate = 5 K·min^{-1} and ε_m = 150%; **b**) $\sigma(\varepsilon_m)$: stress at ε_m; **c**) R_f: shape fixity rate; **d**) R_r: shape recovery rate; **e**) T_{sw}: switching temperature.