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Electronic supplementary information

Thermoresponsive Icy Road Sign by Light Scattering and Enhanced Fluorescence

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Video.MP4

Video of prototype warning ice sign illustrating temperature response, fast contrast switching, flexibility and temperature dependant fluorescence response.

Experimental

Multi-well plate and camera apparatus to measure the phase transition of polystyrene in a solvent

The phase separation experiments took place in a square aluminium plate with 36 wells (volume 0.25 mL), each with a circle of black card fixed to the bottom to aid with contrast during the measurement. The top five rows were covered with an anti-reflective coated glass slide, held in place by double-sided tape, to prevent solvent evaporation and stop ice formation directly on the plate. A well filled with pure solvent was designated for measuring the temperature directly during the experiment. To record the temperature, a k-type temperature probe was submerged in the solvent filled well and held in place vertically by a 3D-printed stand. During the phase transition experiment, the aluminium plate was cooled and heated by a thermoelectric cooler.

The phase transition of the polymer solutions was determined using photographs taken as the plate was cooled. Photographs were saved in RAW format (.NEF) to allow for total control of the analysis process. A Nikon D5100 camera fitted with a 18-55 mm VR lens was used. The lens' aperture width was set to 3.5mm (F-stop F11) to increase the depth of feel, producing a sharper image. A narrower aperture also reduces chromatic aberration, a colour distortion that occurs when wavelengths of light passing through the lens have different refractive indices and do not converge at the same focal point. The ISO of the camera was fixed to 100 to reduce noise artifacts. The shutter was not fixed and used to determine the exposure of the image. To measure the exposure, matrix metering was used, this mode considers the entire picture frame and calculates an average value. The white balance was determined automatically by the camera and fixed during the experiment. During polymer phase separation, the transmission of light through the liquid decreases as more light is scattered and opacity increases. Photographs of the change in contrast from a black well to a white well were analysed and the cloud point was calculated (see following section).

Ambient light during the measurement will heavily impact on the contrast value. To ensure consistent lighting, a lightbox was fabricated. The thermoelectric cooler and aluminium plate were placed inside an open-topped box (30 cm x 30 cm x 30 cm) made of white PVC foam board. On the left and right sides of the box, a cut-out (24 cm x 24 cm) was covered with non-woven fabric interfacing that acted as an optical diffuser. Two desk lamps were positioned outside the box behind the fabric interfacing. The light box was lit with LED globe blubs (17 W, 6400 K, 200° 1520 lm, 16.4 cm x 12.0 cm). The DLSR camera was positioned directly above the aluminium plate using a tripod. To prevent the interference of ambient light, four retort stands (height 77cm) were placed around the open-topped box in a 50 cm square and black cloth was draped over the retort stands.

To measure the phase transition of samples, the polymer was first dissolved in the solvent. The chosen ratio of polymer and solvent was combined and mixed in a rotary mixing oven at 60 °C overnight. Once dissolved, 0.2 mL of each polymer solution was added to a single well on the aluminium plate. The temperature of the plate was then lowered from 20 to -20 °C at a rate of 0.2 °C min^{-1} and a photograph of the plate was taken every 5 minutes using the camera's timer function. Below 10 °C, condensation was removed with an ethanol-soaked swab between each image.

Measurement of the phase transition using image analysis

On completion of the experiment the photographs were analysed using ImageJ software. Images were recorded in RAW format to negate any compression or lighting effect introduced by the camera converting to JPEG. The RAW files were process use the DCRaw Reader imagej plugin (v.1.5.), white balance was not adjusted, colour space was set to raw and images were read as 8-bit. Adaptive homogeneity-directed was the chosen interpolation method to minimize colour artifacts. The images were converted to 32-bit to maximise colour depth and then converted to greyscale. The mean grey value for a 50 pixel diameter circle in each liquid filled plate well was analysed in each image (figure S2). From this a plot of G/G_0 vs temperature was produced for each polymer/solvent combination, where G is the mean grey value and G_0 is the lowest value recorded in each data set.

Results

Table S1 Experimental quantities of styrene and comonomers used for bulk polymerisations

	PSMMA_0.5	**PSMMA_1.0**	**PSMAA_2.0**	**PSMMA_2.3**	**PSMMA_5.0**	**PSMMA_10**
Styrene/ g	7.961	7.918	7.85	7.816	7.606	7.2
Methyl methacrylate / g	0.04	0.04	0.04	0.04	0.04	0.04
	PSEMA_0.5	**PSEMA_1.0**	**PSEMA_2.0**	**PSEMA_2.3**	**PSEMA_5.0**	
Styrene / g	7.96	7.92	7.84	7.818	7.606	
Ethyl methacrylate / g	0.041	0.08	0.16	0.185	0.401	
	PSEA_0.5	**PSEA_1.0**	**PSEA_2.0**	**PSEA_2.3**	**PSEA_5.0**	
Styrene / g	7.961	7.927	7.844	7.832	7.604	
Ethyl acrylate / g	0.042	0.081	0.16	0.185	0.401	
	PS2EHA_0.5	**PS2EHA_1.0**	**PS2EHA_2.0**	**PS2EHA_2.3**		
Styrene / g	7.96	7.927	7.842	7.99		
2-Ethyhexyl acrylate / g	0.041	0.08	0.161	0.188		
	PSLA_0.5	**PSLA_1.0**	**PSLA_2.0**	**PSLA_2.3**		
Styrene / g	7.965	7.922	7.841	7.913		
Lauryl acrylate/ g	0.04	0.081	0.16	0.187		
	PSNIPAM_0.5	**PSNIPAM_1.0**	**PSNIPAM_2.0**	**PSNIPAM_2.3**		
Styrene / g	7.965	8.078	7.928	7.828		
N-Isopropylacrylamide / g	0.04	0.082	0.164	0.185		

Table S2 Experimental quantities of styrene and xylene for bulk and solution polymerisations

	PS0%XY	PS20%XY	PS40%XY	PS60%XY	PS80%XY
Styrene / g	9.9060	8.0060	4.7966	10.0053	5.0326
Xylene / g	0	2.0511	3.1980	15.0051	20.009

Table S3 Styrene copolymer experimental composition and molecular weight characterisation

	Experimental wt% of X component in PS-*co*-X	Experimental mol% of X component in PS-*co*-X	M_n x 10^5/ g.mol^{-1}	M_w x 10^5/ g.mol^{-1}	Đ
PS	0	0	1.42	3.09	2.18
PS-*co*-PMMA	2.34	2.43	1.61	3.35	2.09
	3.24	3.36	1.75	3.22	1.84
	4.83	5.02	1.72	3.27	1.90
	5.05	5.24	1.56	3.18	2.04
	9.99	10.35	1.70	3.00	1.76
	16.71	17.27	1.33	2.73	2.05
PS-*co*-PEMA	1.70	1.56	1.81	3.44	1.90
	2.51	2.30	1.94	3.46	1.78
	3.62	3.32	1.79	3.29	1.84
	4.43	4.05	1.75	3.45	1.97
	7.45	6.84	1.85	3.36	1.82
PS-*co*-EA	2.22	2.31	1.79	3.61	2.01
	3.11	3.23	2.07	3.82	1.84
	3.61	3.75	2.14	3.92	1.83
	3.83	3.97	1.96	3.54	1.81
	6.24	6.47	2.00	3.65	1.82
	10.74	11.13	2.00	3.83	1.92
PS-*co*-2EHA	1.38	0.78	1.77	3.10	1.75
	2.44	1.39	1.79	3.08	1.72
	3.00	1.72	1.32	3.18	2.41

	3.93	2.26	2.02	7.60	3.76
PS-*co*-LA	1.54	0.67	1.95	3.71	1.90
	2.04	0.89	1.77	3.40	1.92
	3.08	1.36	2.40	3.93	1.64
	5.88	2.64	1.97	3.83	1.94
PS-*co*-NIPAM	2.53	2.33	1.51	3.66	2.42
	2.73	2.52	1.15	3.52	3.06
	3.24	2.99	1.63	3.79	2.33
	3.30	3.05	1.55	4.38	2.82

Table S4 Polystyrene molecular weight characterisation for phase separation experiments in 1,2-cyclohexane dicarboxylic acid diisononyl ester

	M_w x 10^5/ g.mol^{-1}	M_n x 10^5/ g.mol^{-1}	M_p x 10^5/ g.mol^{-1}	Đ
PS0%XY	3.99	1.95	3.55	2.05
PS20%XY	3.48	1.71	3.02	2.04
PS40%XY	2.90	1.29	2.57	2.24
PS60%XY	2.10	0.96	1.87	2.18
PS80%XY	1.15	0.44	1.02	2.64

Table S5 Summary of copolymer weight fraction and temperature critical phase conditions for PS copolymer in dioctyl phthalate

	Experimental mol% of X component in PS-*co*-X	UCST (Copolymer weight fraction)	UCST (temperature) / °C
PS	0	0.106	7.91
PS-*co*-PMMA	2.43	0.121	-1.91
	3.36	0.116	-3.14
	5.02	0.102	-1.77
	5.24	0.098	-2.92
	10.35	0.100	-6.64
	17.27	0.092	-11.10
PS-*co*-PEMA	1.56	0.096	0.06

	2.30	0.116	-3.72
	3.32	0.131	-5.15
	4.05	0.097	-4.26
	6.84	0.070	-11.34
PS-*co*-PEA	2.31	0.103	0.70
	3.23	0.106	0.29
	3.75	0.095	0.37
	3.97	0.113	-2.09
	6.47	0.102	-6.28
	11.13	0.070	-11.42
PS-*co*-2EHA	0.78	0.110	1.22
	1.39	0.101	-1.29
	1.72	0.101	-5.87
	2.26	0.022	-6.08
PS-*co*-PLA	0.67	0.113	-0.39
	0.89	0.114	-3.38
	1.36	0.063	-7.80
	2.64	0.073	-8.95
PS-*co*-PNIPAM	2.33	0.056	1.39
	2.52	0.103	-1.37
	2.99	0.120	-5.11
	3.05	0.092	-4.95

Table S6 Summary of copolymer weight fraction and temperature critical phase conditions for PS in 1,2-Cyclohexane dicarboxylic acid diisononyl ester

	M_w x 10^5/ g.mol^{-1}	UCST (Copolymer weight fraction)	UCST (temperature) / °C
PS0%XY	3.99	0.128	18.45
PS20%XY	3.48	0.129	17.42
PS40%XY	2.90	0.123	16.77
PS60%XY	2.10	0.109	13.64
PS80%XY	1.15	0.118	-3.24

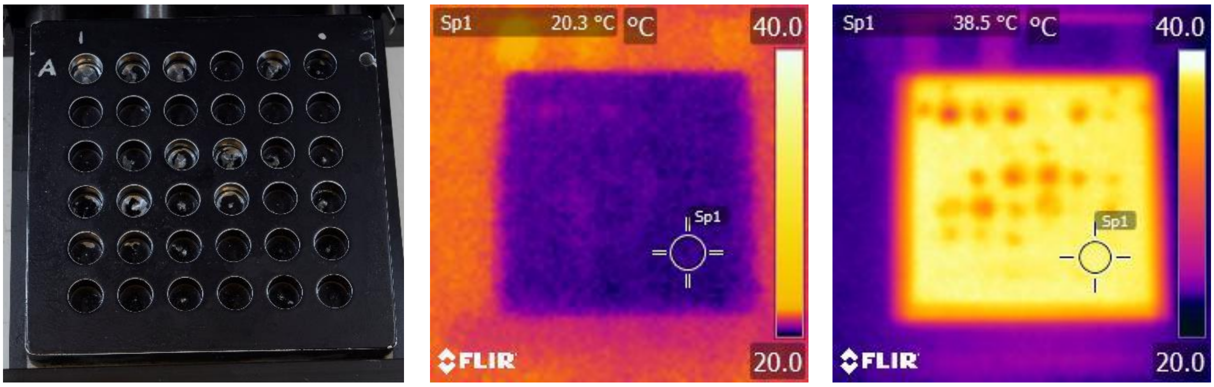

Figure S1 Thermal imaging camera showing equal temperature across the plate reader. (Left) A matt black painted plate was required because infra-red radiation from camera's lens is reflected by polished surfaces and recorded instead of surface radiation. (Middle) Thermal image of plate on thermoelectric module set to 20 °C. (Right) Thermal image of plate on thermoelectric module set to 40 °C. Cooler spots are a distortion from polished surface where black paint was not applied.

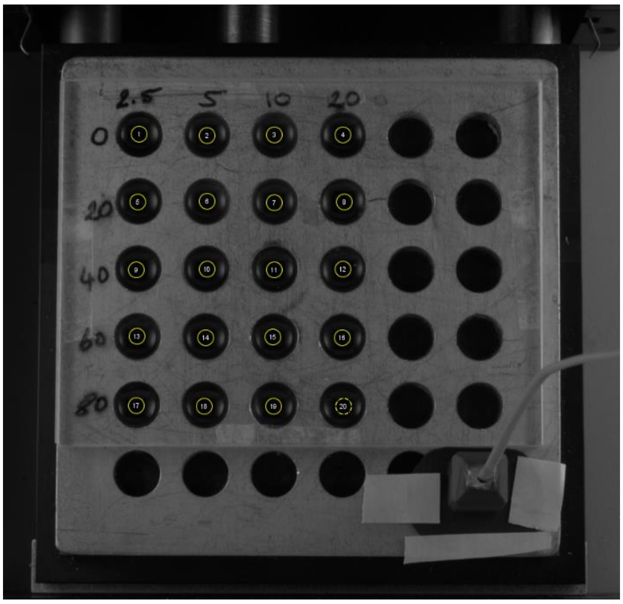

Figure S2 Screenshot of image analysis for determining mean grey value for each PS/DINCH mixture at a given temperature, analysis carried out using ImageJ software.

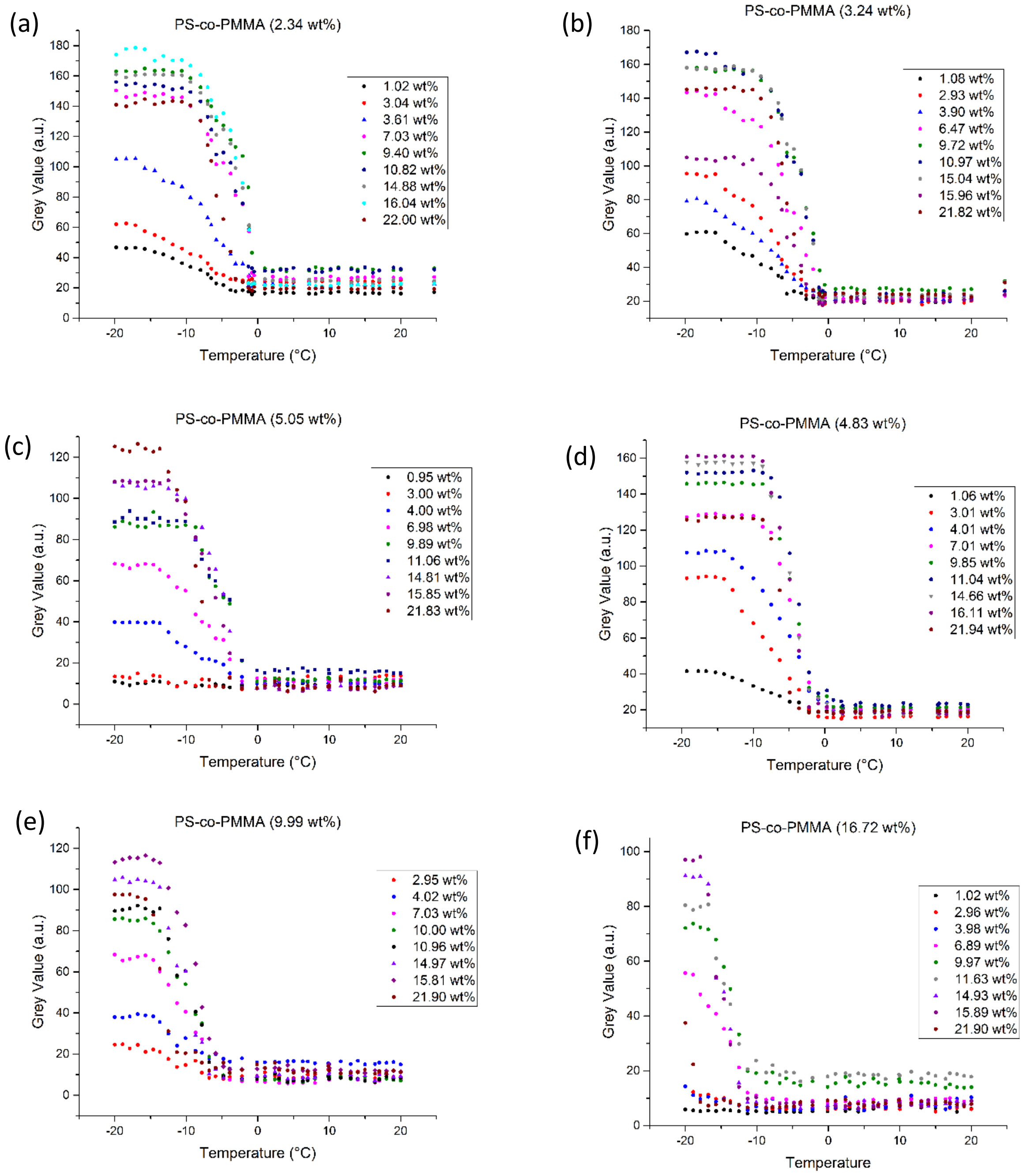

Figure S3 Phase change curves for poly(styrene-*co*-methyl methacrylate) (P(S-*co*-PMMA) polymers in dioctyl phthalate, the grey values recorded from photographic analysis are plotted against the sample temperature. Each graph contains the phase change curves of a range of polymer/solvent compositions in weight percentage polymer (see insets). Percentage moles and weight of methyl methacrylate units in the P(S-*co*-PMMA) copolymer for each series is as follows; (a) 2.43 mol%, 2.34 wt% (b) 3.36 mol%, 3.24 wt% (c) 5.02 mol%, 4.83 wt% (d) 5.24 mol%, 5.05 wt% (e) 10.35 mol%, 9.99 wt% (f) 17.27 mol%, 16.71 wt%.

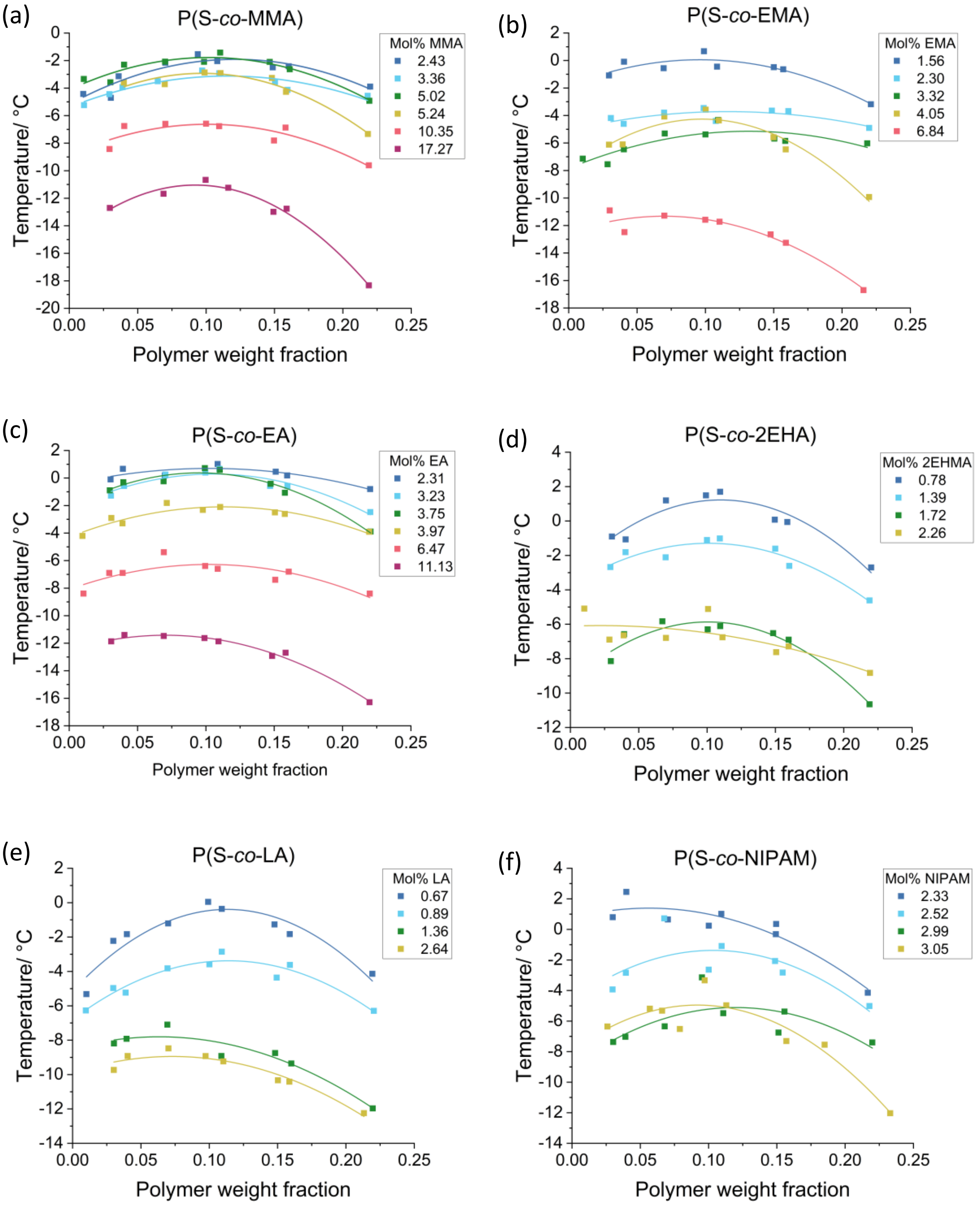

Figure S4 Phase diagrams for polystyrene copolymers in dioctyl phthalate (DOP) as a function of polymer composition. The mole percentages of comonomer in the PS copolymers of each series are shown in the inset legends (a) Poly(styrene-*co*-methyl methacrylate), (b) poly(styrene-*co*-ethyl methacrylate), (c) poly(styrene-*co*-ethyl acrylate), (d) poly(styrene-*co*-2-ethylhexyl acrylate), (e) poly(styrene-*co*-lauryl acrylate), (f) poly(styrene-*co*-N-isopropylacrylamide). Data points have been fit with second order polynomials.

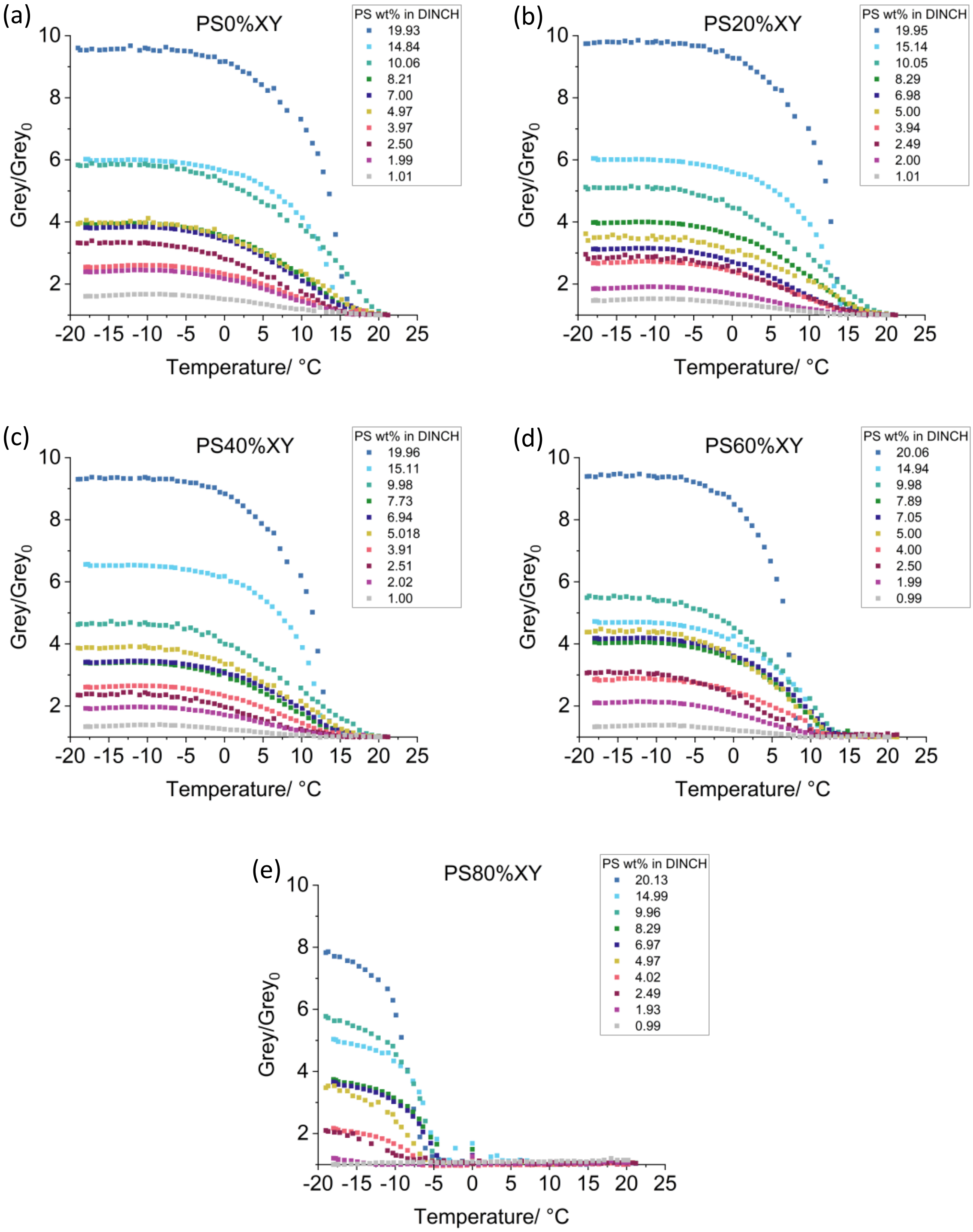

Figure S5 Phase change curves for polystyrene in 2-cyclohexane dicarboxylic acid diisononyl ester (DINCH), the grey values were recorded from photographic analysis and plotted against the sample temperature. Each plot displays a range of polymer/solvent compositions in weight percentage polymer (see insets). The polystyrene molecular weight was varied for each series, the weight average molecular weights are as follows (a) 400,000 g.mol^{-1}, (b) 348,000 g.mol^{-1}, (c) 290,000 g.mol^{-1}, (d) 210,000 g.mol^{-1}, (e) 115,000 g.mol^{-1}.

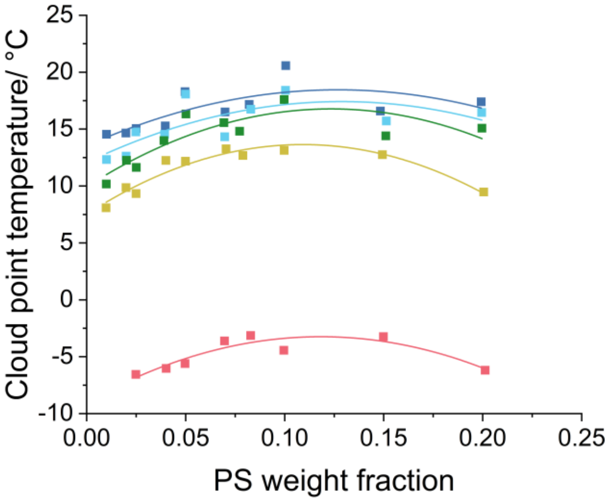

Figure S6 Phase diagram for polystyrene in 2-cyclohexane dicarboxylic acid diisononyl ester (DINCH) as a function of molecular weight. The polystyrene weight average molecular weights are as follows; 400,000 g.mol^{-1} (dark blue), 348,000 g.mol^{-1} (turquoise), 290,000 g.mol^{-1} (green), 210,000 g.mol^{-1} (yellow), 115,000 g.mol^{-1} (pink). Data points have been fit with second order polynomials.

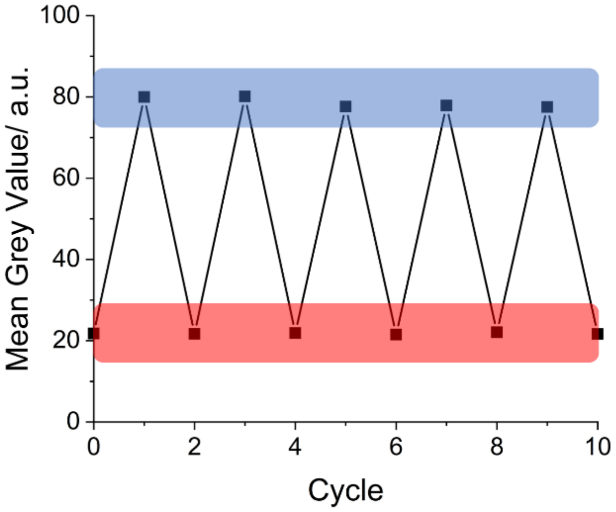

Figure S7 Reversable contrast change of patch quantified by mean grey value cycled between 10 °C and 0 °C with 60 second intervals, middle acetate sheet thickness of 100 µm. The grey value of the patch was measure using the photographic plate reader method.

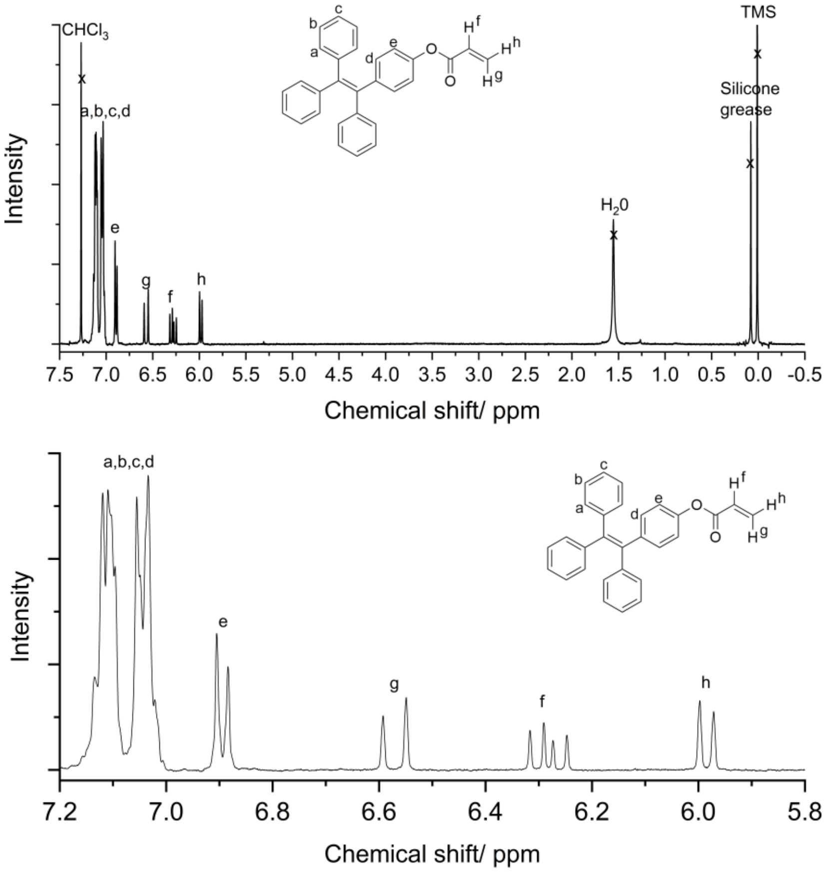

Figure S8 ^{1}H NMR spectra for 4-(1,2,2-triphenylvinyl)phenyl acrylate) (TPE-acrylate). (a) Full sample spectra between -0.5 and 7.5 ppm (b) magnified spectra between 5.8 and 7.2 ppm.

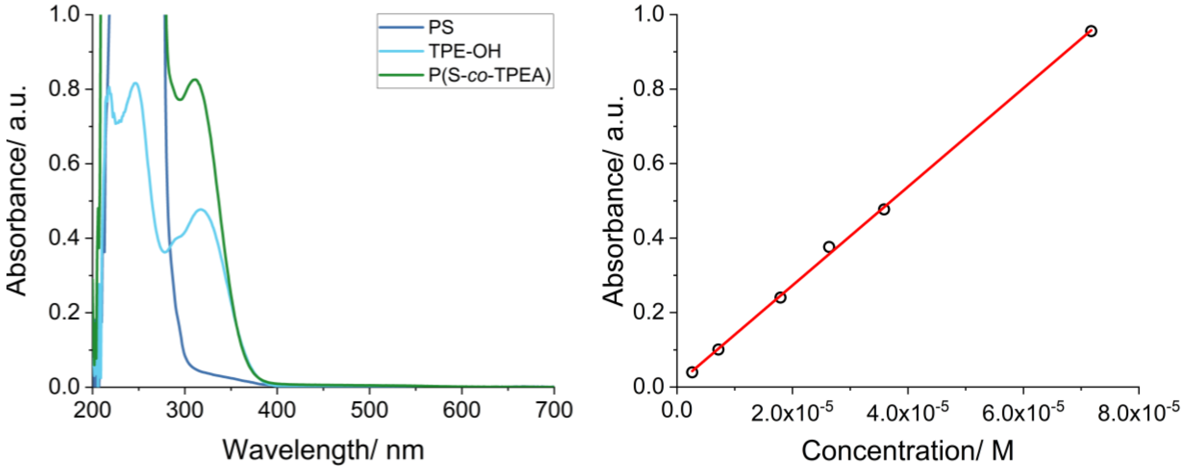

Figure S9 UV-Vis spectra of polystyrene (dark blue, 24.24 mg/mL), 1-(4-hydroxyphenyl)-1,2,2-triphenylethylene (TPE-OH, light blue, 0.0125 mg/mL) and P(S-*co*-TPEA) (green, 24.26 mg/mL) in stabiliser-free THF measured at 25 °C. (b) Calibration curve of 1-(4-hydroxyphenyl)-1,2,2-triphenylethylene in stabiliser-free THF at 25 °C. Linear fit is shown in red, with R-squared value of 0.99918 and molar extinction coefficient of 13240 M^{-1} cm^{-1}.

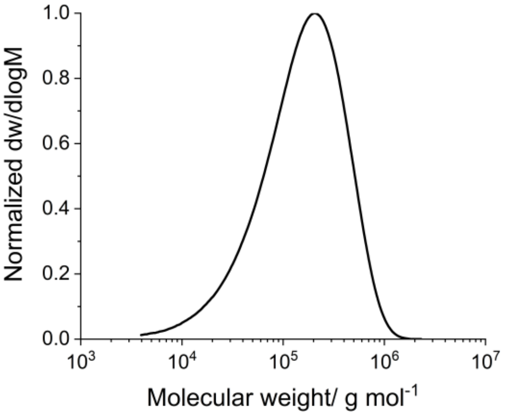

Figure S10 Molecular weight distribution of poly(styrene-*co*-4-(1,2,2-triphenylvinyl)phenyl acrylate) in THF. M_n = 84,000 g.mol^{-1}, M_w = 219,000 g.mol^{-1}, Đ = 2.6

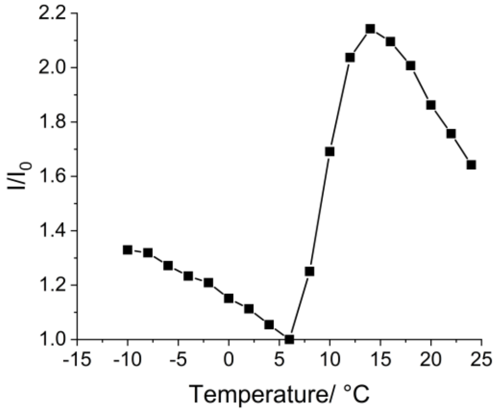

Figure S11 Normalised fluorescence intensity of P(S-*co*-TPEA)/DINCH 10 % w/w, as a function of temperature, cooled at rate of 0.2 °C min^{-1}. Excitation wavelength 350.00 nm, using a cuvette of pathlength 1cm and detector angle 90° to incident beam.

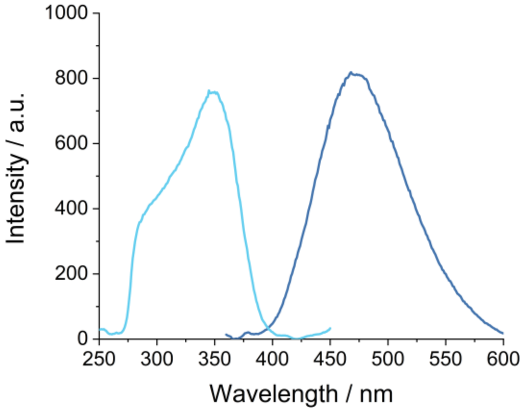

Figure S12 Absorption (light blue) and emission (dark blue) spectra of P(S-*co*-TPEA)/DINCH 10 % w/w at 2 °C. Absorption spectra was measured at an emission wavelength of 470.00 nm, emission spectra was measured at an excitation wavelength of 350.00 nm.

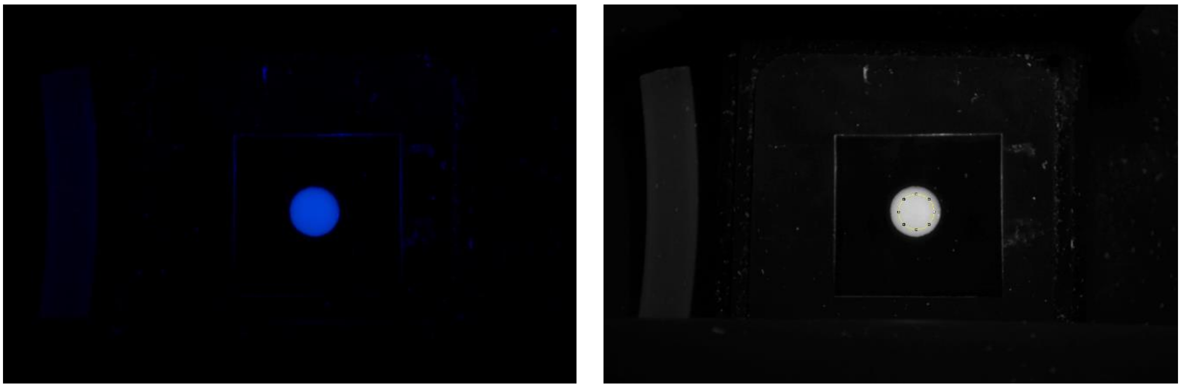

Figure S13 Images of P(S-*co*-TPEA)/DINCH prototype ice warning sign under UV-light. Unprocessed image (left) and image converted to grey-scale and area of grey value measurement shown in yellow (right).