Supplementary Material

Triblock copolymers as versatile constituents of double stimuli-responsive ionic-liquid-based aqueous biphasic systems

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Methods

Correlation equation

Equation S1 was used to fit the experimental binodal data:

$$[PE] = A.\exp\left(B[Ch][C_2O_2]\right) \quad \text{(S1)}$$

In this equation, [PE] and [Ch][C_2O_2] indicate the weight percentage of PE and IL, respectively, while *A* and *B* are the fitting parameters.

Extent of the ABS stimulus-responsive region

Equations S2 and S3 were used to calculate the distance between binodal curves at extreme conditions of temperature and pH, respectively, thus providing the temperature- and pH-responsive regions extents.

$$\Delta 25℃ - 45℃ = \sqrt{(x_{25℃} - x_{45℃})^2 + (y_{25℃} - y_{45℃})^2} \quad \text{(S2)}$$

$$\Delta pH5 - pH7 = \sqrt{\left(x_{pH5} - x_{pH7}\right)^2 + \left(y_{pH5} - y_{pH7}\right)^2} \quad \text{(S3)}$$

where *y* and *x* denote the weight percent of PE and IL, respectively, in the considered mixture compositions.

Results

Determination and characterization of ABS

Table S1 Experimental binodal data in weight percent (wt%) for the system composed of PE 6200 (1) + [Ch][C_2O_2] (2) + H_2O at pH 5.

pH 5					
25°C		**35°C**		**45°C**	
wt% 1	wt% 2	**wt%** 1	wt% 2	**wt%** 1	wt% 2
44.82	11.61	48.84	8.49	46.53	5.62
37.61	13.15	45.11	8.80	41.42	6.03
33.58	14.09	43.95	9.01	36.73	6.61
29.24	15.47	36.53	9.39	21.34	7.26
24.37	15.96	32.67	9.72		
22.16	16.32				
19.54	16.65				
15.88	16.73				

Table S2 Experimental binodal data in weight percent (wt%) for the system composed of PE 6200 (1) + [Ch][C_2O_2] (2) + H_2O at pH 6.

pH 6					
25°C		**35°C**		**45°C**	
wt% 1	wt% 2	wt% 1	wt% 2	wt% 1	wt% 2
45.06	10.80	43.59	8.18	43.41	4.98
41.42	11.91	41.62	9.12	41.66	5.74
36.99	12.65	37.73	9.90	32.36	6.32
32.31	13.41	34.83	10.18	30.82	6.34
29.54	15.08	31.58	10.77	26.89	6.73
25.69	15.79	27.05	11.39		
23.48	16.13	23.95	11.40		
21.58	16.54	22.45	11.75		
20.13	16.88	20.48	12.05		
18.41	17.16	18.69	12.17		
17.41	17.69	15.95	12.33		
15.29	17.93				
14.58	18.18				

Table S3 Experimental binodal data in weight percent (wt%) for the system composed of PE 6200 (1) + [Ch][C_2O_2] (2) + H_2O at pH 7.

pH 7					
25°C		**35°C**		**45°C**	
wt% 1	wt% 2	wt% 1	wt% 2	wt% 1	wt% 2
45.16	10.89	33.13	9.82	34.39	4.30
41.68	11.51	28.23	10.36	32.63	4.86
39.24	12.56	18.39	10.55	28.48	5.82
37.82	12.90	15.72	10.57	27.91	6.15
35.91	13.28	13.96	10.80	27.64	6.29
34.21	13.75				
32.56	14.05				
31.12	14.44				
28.47	14.95				
24.92	15.62				
22.98	16.03				
20.72	16.26				
19.60	16.72				
17.94	16.86				
16.52	17.07				

Table S4 Experimental binodal data in weight percent (wt%) for the system composed of PE 6400 (1) + [Ch][C_2O_2] (2) + H_2O at pH 5.

pH 5					
25°C		**35°C**		**45°C**	
wt% 1	wt% 2	wt% 1	wt% 2	wt% 1	wt% 2
34.40	23.82	30.83	22.70	22.00	17.64
29.37	25.80	28.86	22.87	20.89	18.09
27.16	27.23	27.34	23.57	20.27	18.20
26.04	28.09	26.08	23.85	19.36	18.24
24.75	28.58	24.43	24.15	18.67	18.37
23.92	29.23	23.62	24.43	18.10	18.47
23.28	29.29	22.09	24.64	17.30	18.45
22.24	29.79	21.39	25.14	16.78	18.56
19.30	31.42	20.73	25.32	15.44	18.87
16.99	32.20	19.06	25.75	13.98	18.92
16.53	32.43	18.37	25.90	13.42	18.94
16.03	32.72	17.36	26.19	12.70	19.17
15.55	33.11	16.77	26.47	12.13	19.25
15.30	33.24	16.38	26.67	11.70	19.43
15.00	33.31	15.88	26.86	11.27	19.51
14.69	33.52	15.38	26.99	10.97	19.56
14.38	33.67	14.91	27.25	10.59	19.60
13.77	33.95	13.87	27.44		
13.43	34.25	13.42	27.57		
13.18	34.32	12.63	27.86		
12.94	34.48	12.37	28.04		
12.61	34.58	11.98	28.18		
12.31	34.62	11.67	28.28		
12.00	34.95	10.92	28.42		
11.70	35.12	10.65	28.52		
11.35	35.26	10.39	28.59		
11.00	35.19	10.15	28.76		
10.65	35.63	9.78	28.98		
10.47	35.81	9.48	29.02		
10.02	36.01	9.26	29.10		
9.79	36.10	8.89	29.22		
		8.51	29.35		
		8.32	29.47		
		8.07	29.53		
		7.89	29.58		

Table S5 Experimental binodal data in weight percent (wt%) for the system composed of PE 6400 (1) + [Ch][C_2O_2] (2) + H_2O at pH 6.

pH 6					
25°C		**35°C**		**45°C**	
wt% 1	wt% 2	wt% 1	wt% 2	wt% 1	wt% 2
35.30	18.85	19.09	18.60	30.05	10.37
23.47	21.13	17.89	18.67	23.70	12.72
17.16	23.30	16.67	18.85	17.52	13.49
16.39	23.63	15.31	18.98	14.55	13.63
15.58	23.90	13.62	19.29	10.42	13.65
13.82	24.41	12.66	19.52	9.65	13.91
13.31	24.51	12.19	19.58	8.60	13.92
12.31	24.93	11.41	19.63	7.17	13.99
11.07	25.15	10.87	19.77	6.72	14.06
10.82	25.41	10.31	19.88		
10.29	25.55	9.78	20.05		
9.95	25.59	8.38	20.27		
9.72	25.70	8.02	20.28		
9.43	25.76	7.18	20.35		
8.92	25.93	6.84	20.43		
8.68	25.96	6.63	20.72		
8.51	25.99				
8.29	26.07				

Table S6 Experimental binodal data in weight percent (wt%) for the system composed of PE 6400 (1) + [Ch][C_2O_2] (2) + H_2O at pH 7.

pH 7					
25°C		**35°C**		**45°C**	
wt% 1	wt% 2	wt% 1	wt% 2	wt% 1	wt% 2
31.85	14.72	29.60	12.27	29.81	8.37
26.81	17.07	25.60	13.38	25.12	9.86
21.86	18.92	23.28	14.73	23.49	10.23
19.28	20.03	21.08	15.58	18.01	11.42
16.40	20.62	17.66	15.92	12.59	11.72
14.58	21.98	14.67	17.21	11.60	11.80
12.23	22.35	12.46	17.38	9.99	11.87
11.00	22.75	11.51	17.54	6.68	12.07
10.55	22.83	10.71	17.58	6.41	12.10
10.10	23.19	10.31	17.77		
9.87	23.17	9.73	17.91		
9.48	23.23	9.26	18.09		
9.28	23.25	8.97	18.14		
9.07	23.29	7.90	18.30		
8.69	23.46				
8.23	23.57				

Table S7 Correlation parameters used to describe the experimental binodal data of the system composed of PE 6200 + [Ch][C_2O_2] + H_2O at pH 5.

T	$A \pm \sigma$	$B \pm \sigma$	R^2
25°C	$2.92\times10^{2} \pm 1.82\times10^{2}$	$-1.58\times10^{-1} \pm 4.44\times10^{-2}$	0.9244
35°C	$8.05\times10^{2} \pm 8.01\times10^{2}$	$-3.28\times10^{-1} \pm 1.11\times10^{-1}$	0.9691
45°C	$4.53\times10^{2} \pm 3.22\times10^{2}$	$-3.99\times10^{-1} \pm 4.44\times10^{-1}$	0.9019

Table S8 Correlation parameters used to describe the experimental binodal data of the system composed of PE 6200 + [Ch][C_2O_2] + H_2O at pH 6.

T	$A \pm \sigma$	$B \pm \sigma$	R^2
25°C	$2.10\times10^{2} \pm 4.73\times10^{1}$	$-1.39\times10^{-1} \pm 1.61\times10^{-2}$	0.9702
35°C	$2.55\times10^{2} \pm 1.34\times10^{2}$	$-2.04\times10^{-1} \pm 5.18\times10^{-2}$	0.8969
45°C	$1.67\times10^{2} \pm 1.51\times10^{2}$	$-2.61\times10^{-1} \pm 1.87\times10^{-1}$	0.8654

Table S9 Correlation parameters used to describe the experimental binodal data of the system composed of PE 6200 + [Ch][C_2O_2] + H_2O at pH 7.

T	$A \pm \sigma$	$B \pm \sigma$	R^2
25°C	$2.25\times10^{2} \pm 6.19\times10^{1}$	$-1.42\times10^{-1} \pm 2.04\times10^{-2}$	0.9489
35°C	$1.09\times10^{5} \pm 5.39\times10^{5}$	$-8.21\times10^{-1} \pm 6.79\times10^{-1}$	0.8253
45°C	$5.67\times10^{1} \pm 6.31\times10^{0}$	$-1.15\times10^{-1} \pm 2.06\times10^{-2}$	0.9904

Table S10 Correlation parameters used to describe the experimental binodal data of the system composed of PE 6400 + [Ch][C_2O_2] + H_2O at pH 5.

T	$A \pm \sigma$	$B \pm \sigma$	R^2
25°C	$3.70\times10^{2} \pm 6.56\times10^{1}$	$-9.66\times10^{-1} \pm 5.86\times10^{-3}$	0.9711
35°C	$1.91\times10^{3} \pm 3.65\times10^{2}$	$-1.81\times10^{-1} \pm 7.51\times10^{-3}$	0.9866
45°C	$2.56\times10^{4} \pm 2.18\times10^{4}$	$-3.95\times10^{-1} \pm 4.59\times10^{-2}$	0.9590

Table S11 Correlation parameters used to describe the experimental binodal data of the system composed of PE 6400 + [Ch][C_2O_2] + H_2O at pH 6.

T	$A \pm \sigma$	$B \pm \sigma$	R^2
25°C	$1.14\times10^{3} \pm 2.81\times10^{2}$	$-1.84\times10^{-1} \pm 1.09\times10^{-2}$	0.9825
35°C	$1.87\times10^{5} \pm 2.62\times10^{-10}$	$-4.95\times10^{-1} \pm 9.86\times10^{-4}$	0.9880
45°C	$6.46\times10^{2} \pm 2.23\times10^{2}$	$-2.91\times10^{-1} \pm 1.35\times10^{-1}$	0.7435

Table S12 Correlation parameters used to describe the experimental binodal data of the system composed of PE 6400 + [Ch][C_2O_2] + H_2O at pH 7.

T	$A \pm \sigma$	$B \pm \sigma$	R^2
25°C	$2.64\times10^{2} \pm 8.87\times10^{1}$	$-1.38\times10^{-1} \pm 1.75\times10^{-2}$	0.9439
35°C	$3.15\times10^{2} \pm 1.59\times10^{2}$	$-1.87\times10^{-1} \pm 3.35\times10^{-2}$	0.9185
45°C	$3.77\times10^{2} \pm 2.88\times10^{2}$	$-2.92\times10^{-1} \pm 1.23\times10^{-1}$	0.8115

Binodal curves representations: temperature and pH effect

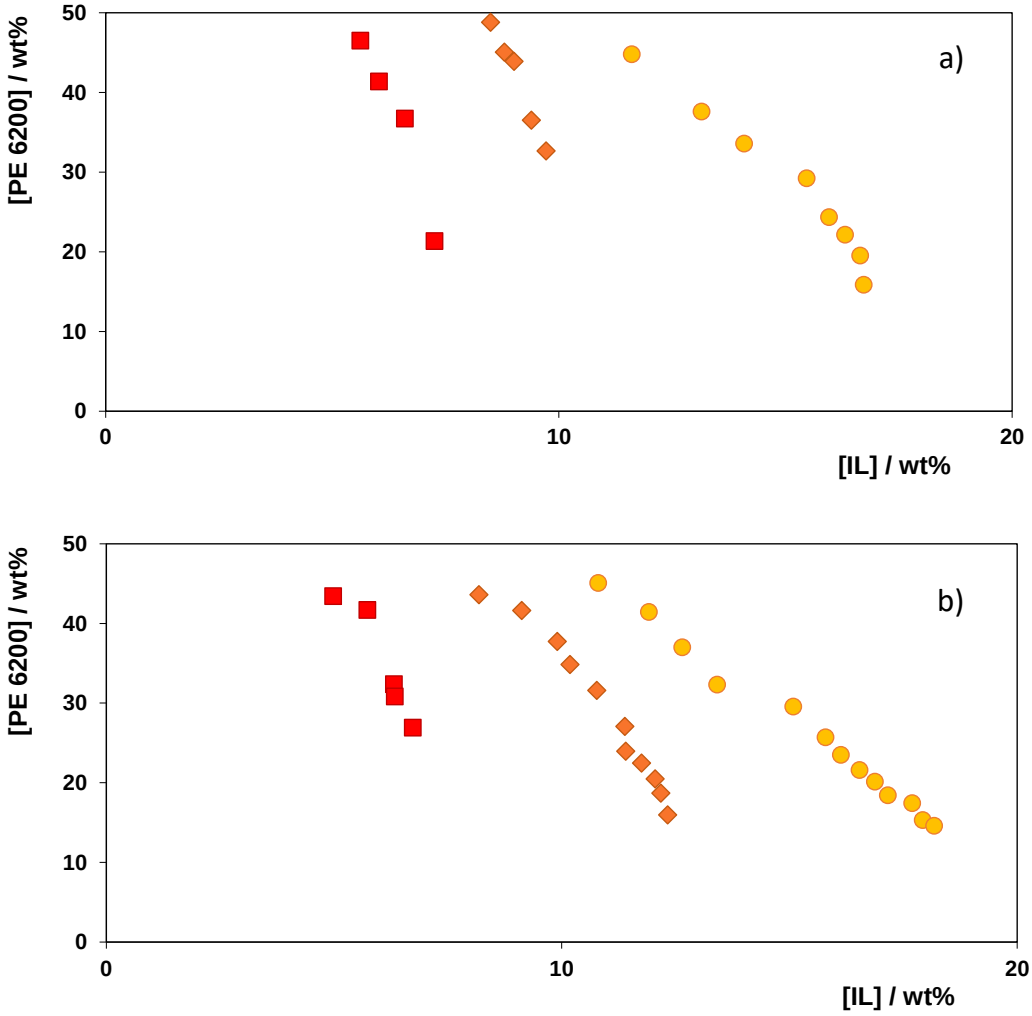


Figure S1 Binodal curves of the systems composed of PE 6200 + [Ch][C_2O_2] + H_2O at a) pH 5 and b) pH 6 at 25°C (●), 35°C (◆) and 45°C (■).

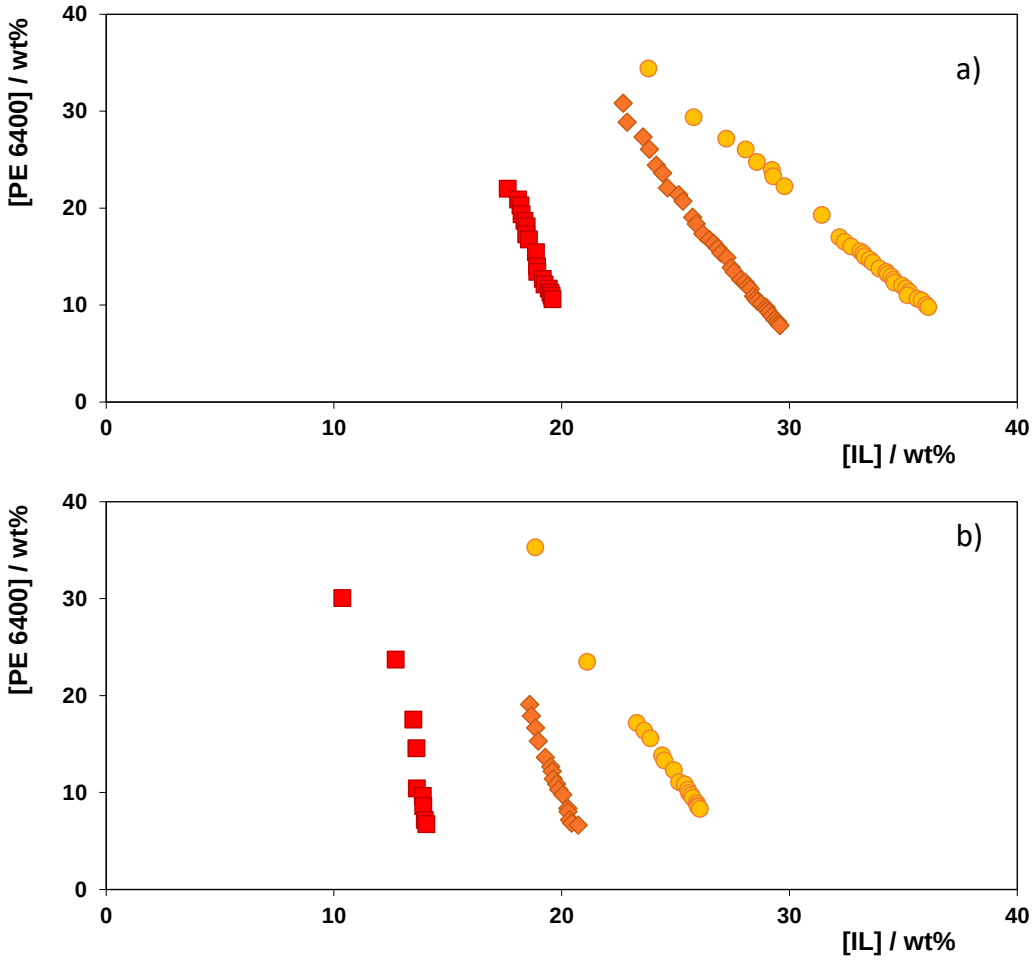


Figure S2 Binodal curves of the systems composed of PE 6400 + [Ch][C_2O_2] + H_2O at a) pH 5 and b) pH 6 at 25°C (●), 35°C (◆) and 45°C (■).

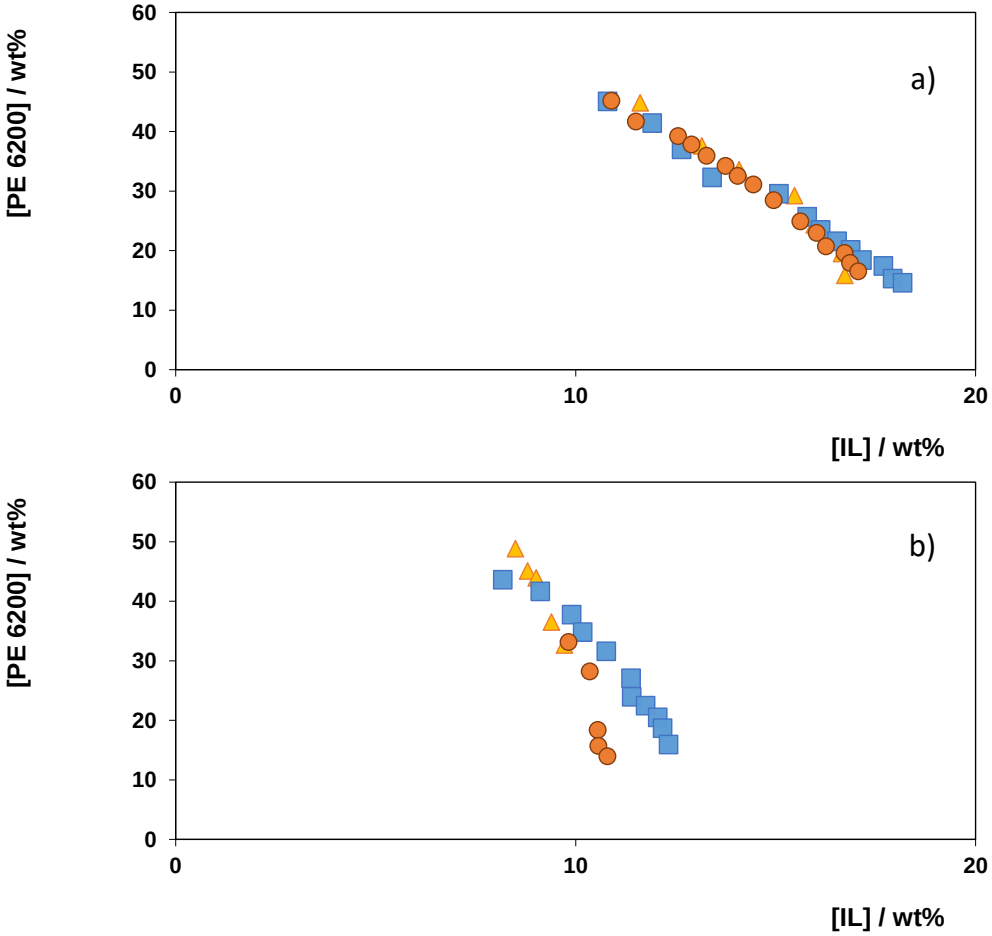


Figure S3 Binodal curves of the systems composed of PE 6200 + [Ch][C_2O_2] + H_2O at pH 5 (▲), pH 6 (■) and pH 7 (●) at a) 25°C and b) 35°C.

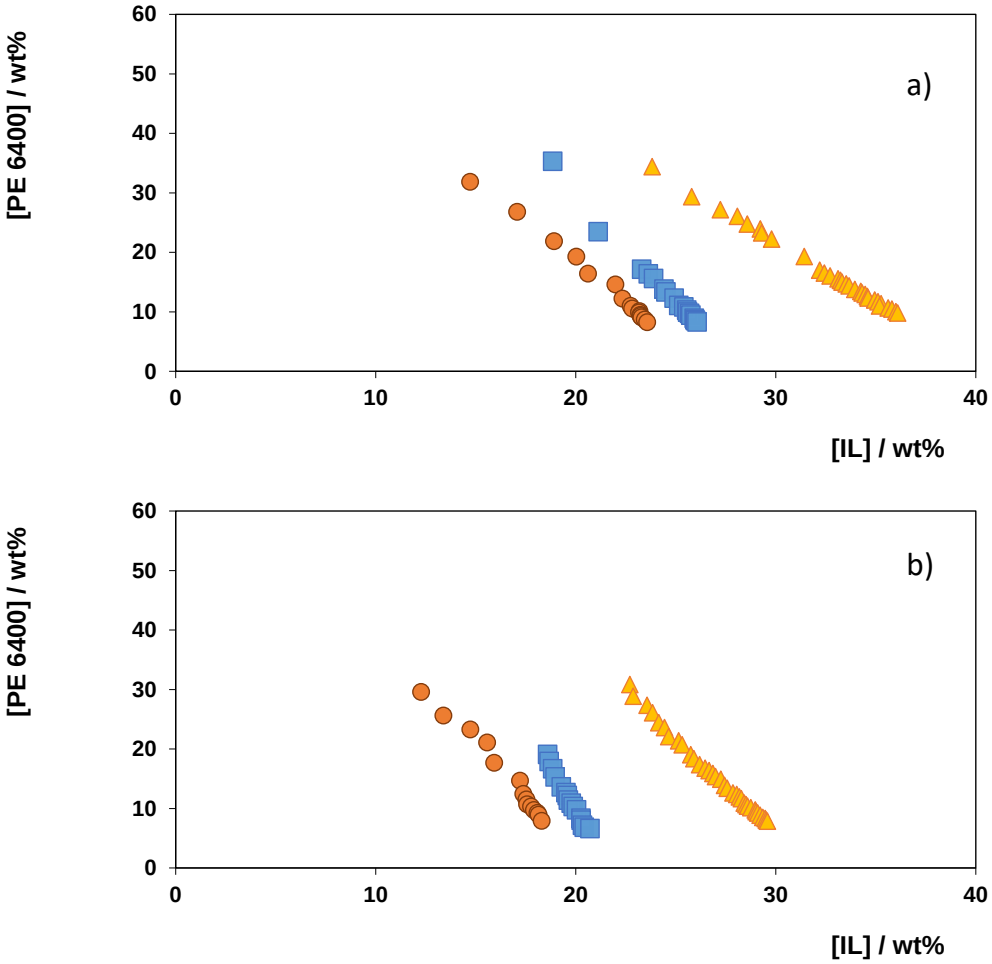
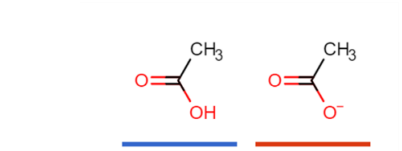


Figure S4 Binodal curves of the systems composed of PE 6400 + [Ch][C_2O_2] + H_2O at pH 5 (▲), pH 6 (■) and pH 7 (●) at a) 25°C and b) 35°C.

Speciation curve of acetic acid

The speciation curve was retrieved from Marvin version 22.18, ChemAxon (https://www.chemaxon.com).



pH	5	25.9 %	74.1%
	6	3.38 %	96.62 %
	7	0.35 %	99.65 %

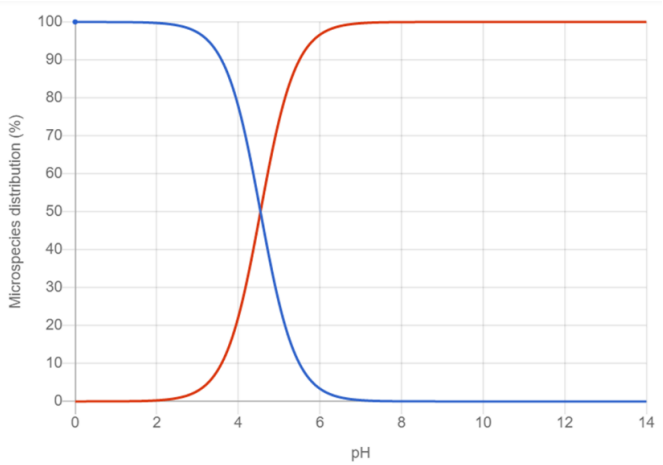


Figure S5 Speciation curves of acetic acid as a function of pH and microspecies distribution.

Binodal curves representations: Polymer effect

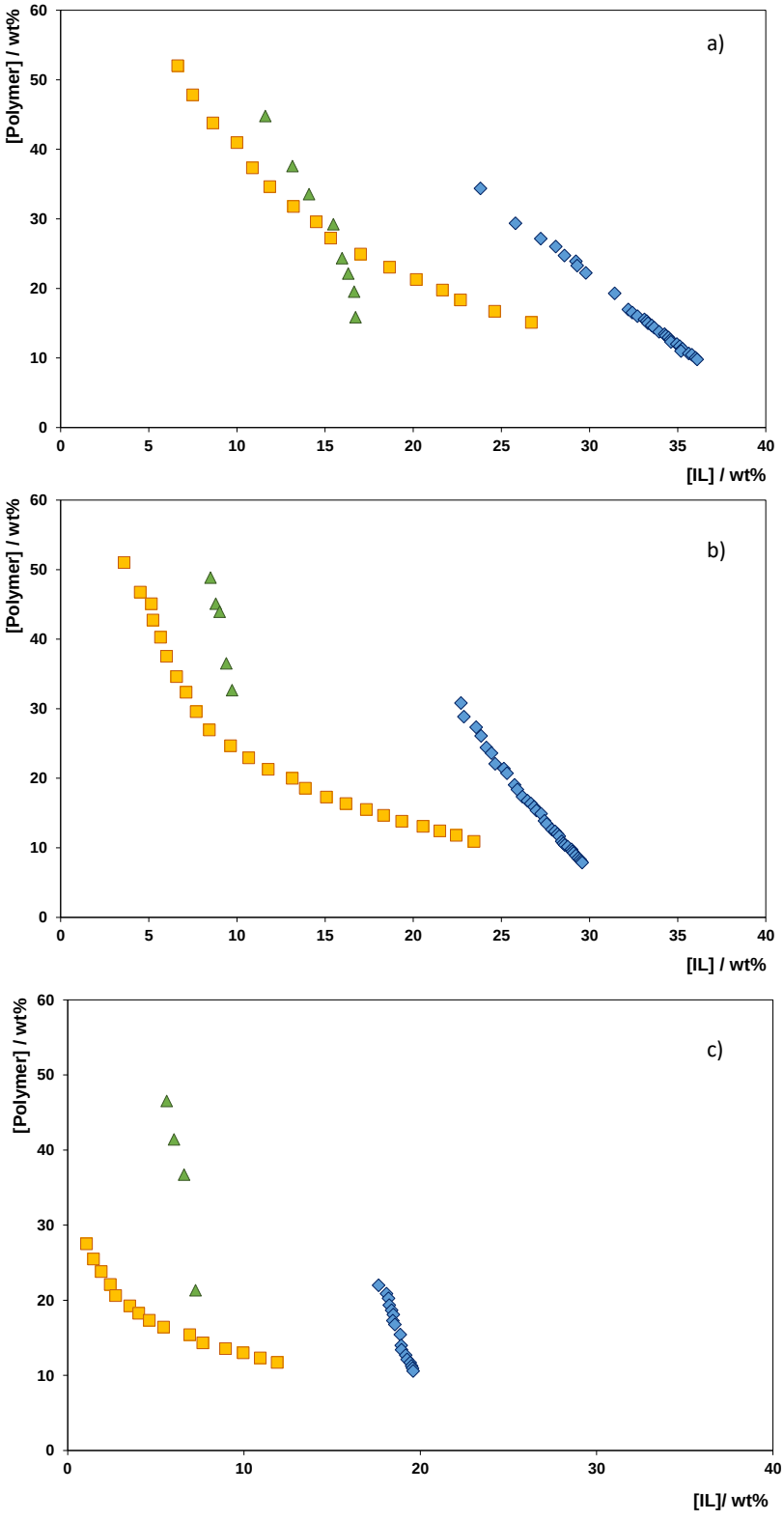


Figure S6 Binodal curves of the systems composed of polymer + [Ch][C_2O_2]+ H_2O at pH 5 at a) 25°C, b) 35 °C and c) 45°C: PE 6200 (▲); PE 6400 (◆); PPG 400 (■). Binodal data for the [Ch][C_2O_2] + PPG 400 + H_2O system is obtained from Rufino et al. ACS Sustain. Chem. Eng. (2023) 10.1021/acssuschemeng.3c00059.

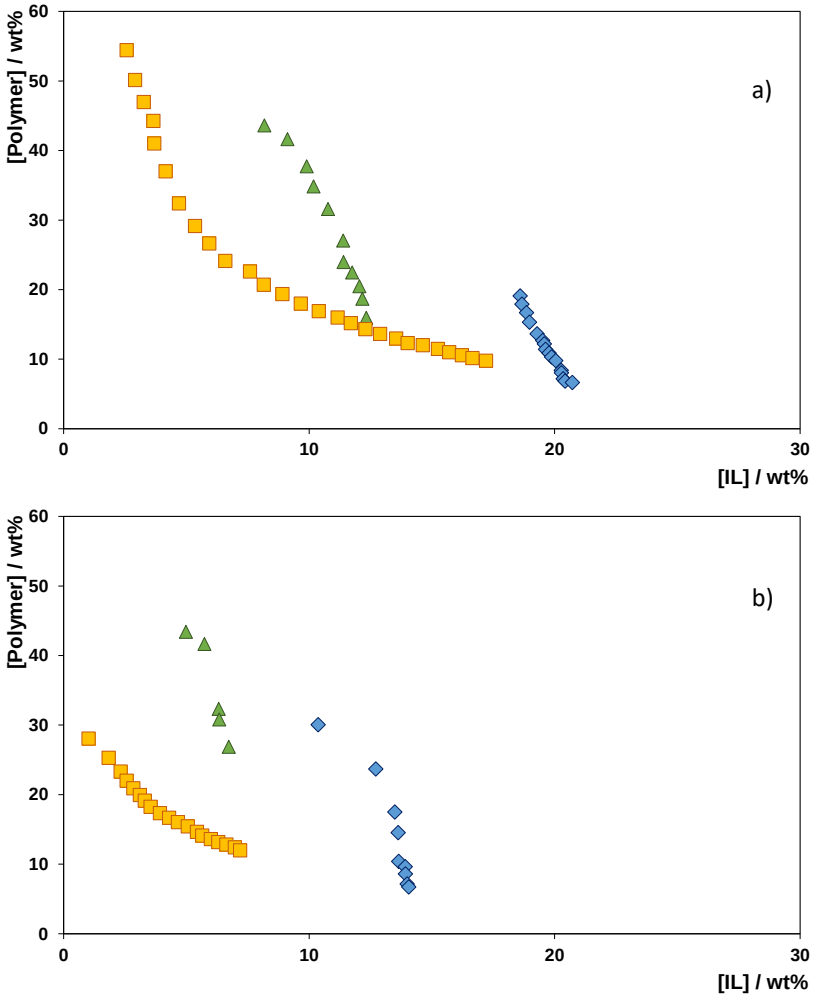


Figure S7 Binodal curves of the systems composed of polymer + [Ch][C_2O_2]+ H_2O at pH 6 at a) 35°C and b) 45°C: PE 6200 (▲); PE 6400 (◆); PPG 400 (■). Binodal data for the [Ch][C_2O_2] + PPG 400 + H_2O system is obtained from Rufino et al. ACS Sustain. Chem. Eng. (2023) 10.1021/acssuschemeng.3c00059.

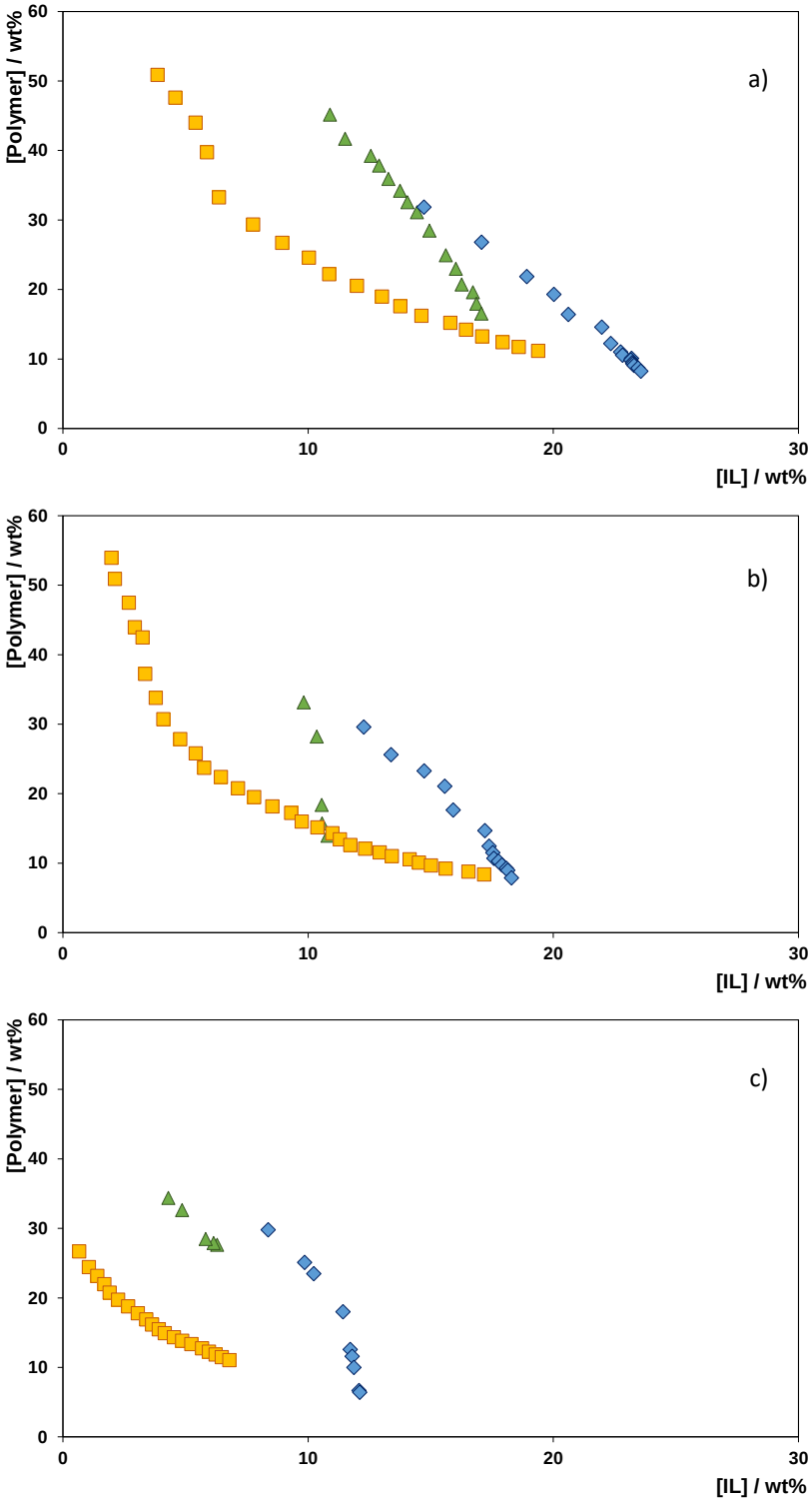


Figure S8 Binodal curves of the systems composed of polymer + $[Ch][C_2O_2]$+ H_2O at pH 7 at a) 25°C, b) 35 °C and c) 45°C: PE 6200 (▲); PE 6400 (◆); PPG 400 (■). Binodal data for the $[Ch][C_2O_2]$ + PPG 400 + H_2O system is obtained from Rufino et al. ACS Sustain. Chem. Eng. (2023) 10.1021/acssuschemeng.3c00059.

Partition of dyes

Table S13 Extraction efficiencies of Sudan III ($EE_{\text{Sudan III}}$, %) and E133 (EE_{E133}, %) obtained with the double stimuli-responsive ABS composed of [Ch][C_20_2] + PE 6400 and [Ch][C_2O_2] + PPG 400 for comparison purposes. Data for the [Ch][C_2O_2] + PPG 400 + H_2O system is obtained from Rufino et al. ACS Sustain. Chem. Eng. (2023) 10.1021/acssuschemeng.3c00059.

System	[Ch][C_2O_2] + PE 6400		[Ch][C_2O_2] + PPG 400	
Stimulus	EE_{E133}%	$EE_{\text{Sudan III}}$%	EE_{E133}%	$EE_{\text{Sudan III}}$%
Temperature	28.02 ± 1.20	100	98.02 ± 1.36	100
pH	91.45 ± 2.18	73.14 ± 4.19	94.08 ± 1.68	96.32 ± 9.57