

Supporting Information

Nucleophilic degradation of Diazinon in thermoreversible polymer-polymer aqueous biphasic systems

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Table S1. Experimental data for the binodal weight fraction percentage of the ABS formed by PPG 400 (1) + PEG (2) + water (3) at (298 ± 1) K and atmospheric pressure.

PEG 600			PEG 1000		
$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$
71.74	7.39	20.87	68.07	6.81	25.12
65.93	9.27	24.80	63.83	7.82	28.35
61.76	9.92	28.32	61.23	8.84	29.93
59.30	10.76	29.95	57.86	9.55	32.59
57.14	11.58	31.28	55.78	10.39	33.83
54.13	13.23	32.64	50.76	11.53	37.71
52.00	13.77	34.23	49.11	12.23	38.65
50.39	14.35	35.25	45.08	13.22	41.71
48.83	14.86	36.31	43.73	13.77	42.50
47.37	15.43	37.20	41.37	14.61	44.02
45.23	16.60	38.17	40.05	15.15	44.80
41.50	17.79	40.70	39.03	15.58	45.39
39.78	18.87	41.36	37.51	16.54	45.95
38.67	19.29	42.04	36.53	16.90	46.57
37.35	19.93	42.72	34.09	17.93	47.98
36.36	20.26	43.39	30.92	19.35	49.73
34.97	20.99	44.03	29.05	20.71	50.24
33.88	21.66	44.47	26.93	22.21	50.86
32.43	22.59	44.98	24.93	23.65	51.43
31.40	23.14	45.46	68.07	6.81	25.12
30.03	23.82	46.15			
29.09	24.36	46.55			
26.88	26.18	46.93			
25.19	27.59	47.22			
22.99	29.79	47.22			
20.91	32.11	46.99			

Table S2. Experimental data for the binodal weight fraction percentage of the ABS formed by PPG 400 (1) + PEG (2) + water (3) at (298 ± 1) K and atmospheric pressure.

PEG 2000			PEG 4000			PEG 6000		
$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$
67.02	2.27	30.71	78.67	1.15	20.18	71.11	0.99	27.90
64.04	3.17	32.78	63.77	1.76	34.47	58.86	1.91	39.23
61.75	4.05	34.20	60.24	2.26	37.49	54.80	2.72	42.48
59.35	4.87	35.78	58.29	2.95	38.76	52.42	3.51	44.08
57.15	5.60	37.25	56.69	3.51	39.80	49.36	5.05	45.59
55.21	6.33	38.46	55.47	4.10	40.44	47.53	5.71	46.76
51.82	7.67	40.51	53.04	4.56	42.39	45.94	6.29	47.77
49.59	8.11	42.30	50.98	5.63	43.39	44.41	6.91	48.68
47.49	9.17	43.34	49.74	6.06	44.20	42.39	8.07	49.54
46.17	9.62	44.21	48.54	6.48	44.98	41.06	8.55	50.39
44.34	10.56	45.10	46.79	7.31	45.90	39.88	9.03	51.09
43.35	10.99	45.66	45.79	7.69	46.53	38.02	10.10	51.88
41.96	11.30	46.74	44.64	8.09	47.27	36.56	10.85	52.59
40.95	11.68	47.36	43.64	8.45	47.91	35.17	11.33	53.50
39.45	12.51	48.03	42.33	9.17	48.50	34.16	12.04	53.79
37.88	13.34	48.78	41.51	9.46	49.04	32.54	13.14	54.32
36.38	13.89	49.73	40.72	9.80	49.48	31.25	13.96	54.78
34.71	14.92	50.38	39.61	10.48	49.91	29.89	14.73	55.37
33.66	15.5322	50.81	38.80	10.75	50.45	28.41	15.83	55.76
30.92	17.22	51.86	37.76	11.35	50.89	27.37	16.65	55.98
28.86	18.34	52.80	36.17	12.14	51.70	25.77	18.05	56.18
26.489	20.63	52.88	34.88	13.00	52.13	23.62	20.21	56.18
25.01	21.55	53.44	33.98	13.54	52.48	18.75	25.34	55.90
21.35	25.22	53.43	32.45	14.48	53.07			
16.42	30.98	52.60	31.34	15.01	53.65			
			29.94	15.82	54.25			
			28.07	17.00	54.93			
			24.82	19.92	55.27			
			22.48	22.51	55.01			

Table S3. Experimental data for the binodal weight fraction percentage of the ABS formed by PPG 400 (1) + PEG (2) + water (3) at (298 ± 1) K and atmospheric pressure.

PEG 8000			PEG 10000			PEG 20000		
$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$
72.41	0.83	26.76	55.10	2.38	42.52	50.98	1.74	47.28
58.91	2.51	38.58	51.98	3.06	44.96	49.03	2.36	48.61
54.29	3.01	42.69	50.05	3.83	46.12	47.36	3.01	49.63
52.12	3.60	44.28	48.09	4.78	47.12	44.86	4.20	50.94
49.35	4.89	45.76	46.43	5.51	48.06	43.06	4.72	52.22
47.24	6.23	46.52	44.74	6.12	49.14	41.60	5.30	53.10
45.78	6.55	47.67	43.21	6.84	49.94	39.94	6.27	53.79
44.89	6.89	48.22	41.89	7.34	50.78	38.08	7.08	54.84
43.96	7.27	48.77	40.64	7.99	51.37	33.13	9.85	57.02
43.11	7.58	49.31	39.36	8.60	52.04	31.51	10.81	57.68
42.29	7.92	49.79	38.25	9.07	52.68	26.99	14.21	58.80
40.76	8.48	50.76	37.15	9.43	53.44	23.01	16.90	60.09
39.58	8.68	51.74	35.29	10.47	54.24			
38.80	9.09	52.11	32.62	11.61	55.77			
38.11	9.35	52.53	27.21	15.29	57.50			
37.48	9.62	52.91	24.89	17.27	57.84			
36.83	9.90	53.28	20.83	20.12	59.06			
35.97	10.40	53.63						
35.41	10.63	53.96						
34.58	11.19	54.23						
33.64	11.63	54.73						
32.84	12.12	55.05						
32.19	12.51	55.30						
31.03	13.13	55.84						
30.29	13.71	56.00						
28.51	14.91	56.58						
27.07	15.64	57.29						
25.31	17.15	57.54						
23.24	19.16	57.60						
21.10	21.65	57.25						

The binodal curves were determined by the weight quantification of all components added ($u(m) = 10^{-4}$ g), in which the weight mass fractions corresponding to the cloud and limpid points were used to describe each binodal curve. The experimental solubility curves were correlated using equation 1:

$$[PPG] = A \exp[(B[PEG]^{0.5}) - (CPEG^3)] \quad (1)$$

where PPG and PEG represent the PPG 400 and each PEG weight fraction percentages, respectively, and A, B, and C are constants obtained by regression. Equation 1 is a mathematical description based on a mass balance approach widely used to correlate the experimental binodal/solubility curves of ABS, originally proposed by Merchuk et al.¹ According to Freire et al.,² and although other equations have been proposed to correlate solubility curves of ternary systems, equation 1 is amongst the ones that better fit to the experimental data of ABS, and as such has been applied in the current work.

Table S4. Adjusted parameters and respective standard deviations (σ) obtained by the fitting of the experimental data of ABS composed by PPG 400 (1) + PEG (2) + water (3) at (298 ± 1) K and atmospheric pressure, by equation 1.

PEG	$A \pm \sigma$	$B \pm \sigma$	$10^5 (C \pm \sigma)$
600	164.59 ± 10.60	-0.31087 ± 0.0205	1.2917 ± 0.3046
1000	186.65 ± 18.32	-0.37780 ± 0.0333	1.5678 ± 0.7469
2000	101.37 ± 4.12	-0.25705 ± 0.0159	1.9863 ± 0.4823
4000	97.30 ± 4.29	-0.27732 ± 0.0169	1.2500 ± 0.0726
6000	88.79 ± 3.71	-0.26639 ± 0.0186	1.5268 ± 0.8773
8000	94.46 ± 3.01	-0.29438 ± 0.0126	1.0922 ± 0.4046
10000	79.32 ± 3.21	-0.23231 ± 0.0176	3.9440 ± 0.9196
20000	67.97 ± 2.31	-0.21017 ± 0.0175	4.7372 ± 1.2990

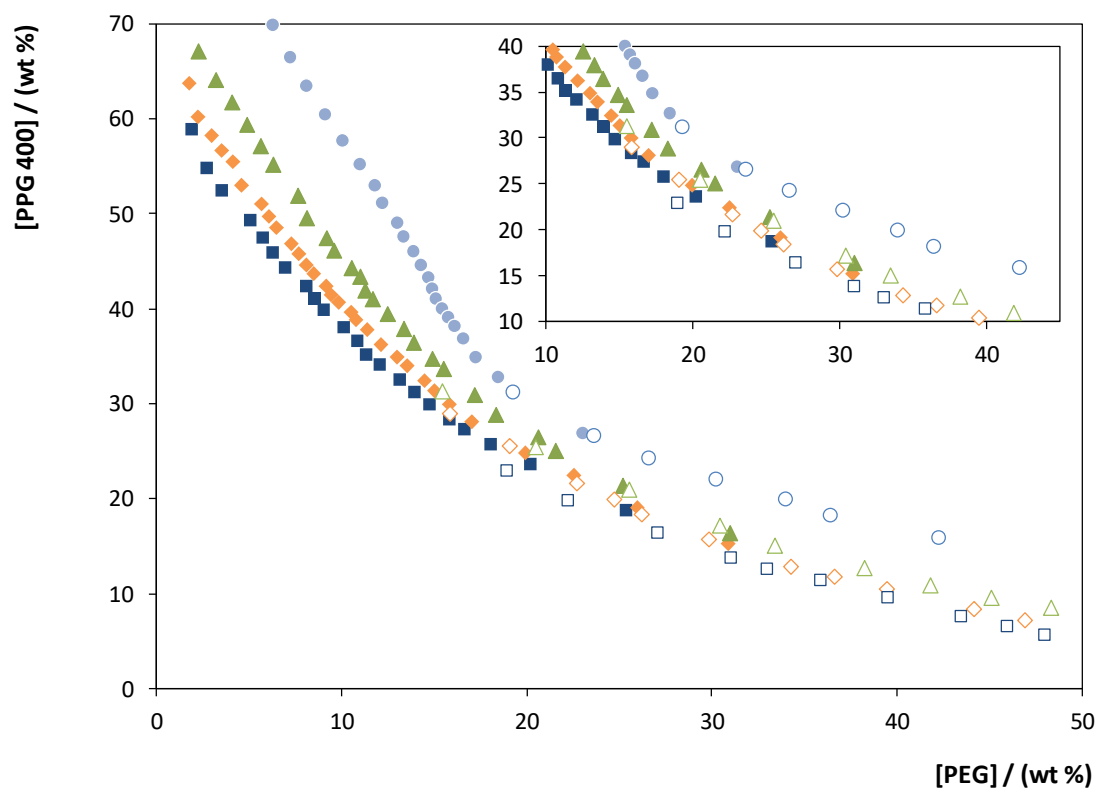


Figure S1. Phase diagrams for the systems composed of PPG 400 + PEG + H₂O at 298 K determined in this work: PEG 600 (●); PEG 2000 (▲); PEG 4000 (◆); PEG 6000 (■); and reported in the literature³: PEG 600 (○); PEG 2000 (△); PEG 4000 (◇); PEG 6000 (□);

Table S5. Standard deviation between the experimental solubility data obtained in this work to those reported in the literature³ corresponding to the weight fraction percentage of PPG in each ABS he ABS formed by PPG 400 + PEG + water at 298 K reported in literature. The experimental data of this work was determined by the fitting by equation (1) to the same weight fraction percentages of PEG reported in the literature.

PEG 600 /wt%				PEG 2000 /wt%			
PEG ³	PPG ³	PPG (this work)	σ	PEG ³	PPG ³	PPG (this work)	σ
19.29	31.12	38.30	5.08	15.47	31.26	34.27	2.13
23.64	26.62	30.61	2.83	20.50	25.41	26.68	0.90
26.61	24.21	25.96	1.24	25.51	20.98	19.90	0.76
30.22	22.01	20.86	0.81	30.41	17.16	14.05	2.20
34.01	19.91	16.16	2.65	33.43	15.06	10.92	2.93
36.40	18.19	13.53	3.29	38.23	12.71	6.82	4.17
42.25	15.85	8.24	5.38	41.82	10.93	4.50	4.55
				45.13	9.61	2.90	4.74
				48.36	8.46	1.79	4.71
				50.36	7.30	1.29	4.25
Average σ		Maximum σ		Average σ		Maximum σ	
3.04		5.38		3.13		4.74	
PEG 4000				PEG 6000			
PEG ³	PPG ³	PPG (this work)	σ	PEG ³	PPG ³	PPG (this work)	σ
15.86	28.92	30.68	1.24	18.96	22.88	25.08	1.56
19.11	25.50	26.63	0.83	22.22	19.73	21.39	1.18
22.68	21.63	22.45	0.58	27.06	16.35	16.41	0.04
24.70	19.87	20.31	0.31	31.04	13.80	12.75	0.74
26.19	18.40	18.80	0.29	33.02	12.63	11.09	1.09
29.81	15.66	15.37	0.20	35.86	11.39	8.91	1.75
34.30	12.81	11.57	0.87	39.50	9.53	6.50	2.15
36.61	11.84	9.84	1.41	43.46	7.58	4.38	2.26
39.46	10.43	7.90	1.78	45.99	6.59	3.30	2.32
44.17	8.40	5.24	2.23	47.98	5.60	2.60	2.12
46.90	7.24	4.01	2.28				
50.23	5.53	2.80	1.93				
Average σ		Maximum σ		Average σ		Maximum σ	
0.96		2.28		1.52		2.32	

Table S6. Experimental data for the binodal weight fraction percentage of the ABS formed by PPG 400 (1) + PEG 600 (2) + water (3) at different temperatures and atmospheric pressure.

288 K			298 K			308 K			313 K		
100w ₁	100w ₂	100w ₃	100w ₁	100w ₂	100w ₃	100w ₁	100w ₂	100w ₃	100w ₁	100w ₂	100w ₃
75.61	6.36	18.03	76.48	6.49	17.03	74.34	3.85	21.81	54.96	5.05	39.99
71.00	7.67	21.33	71.74	7.39	20.87	66.41	4.49	29.10	47.75	6.01	46.24
68.83	8.71	22.47	65.93	9.27	24.80	62.98	5.34	31.68	42.69	6.74	50.57
64.34	10.93	24.73	61.76	9.92	28.32	59.99	6.20	33.81	33.30	9.09	57.61
61.46	11.79	26.75	59.30	10.76	29.95	57.14	6.97	35.89	27.53	12.05	60.43
57.58	13.63	28.78	57.14	11.58	31.28	51.94	8.29	39.77	23.35	15.55	61.09
54.71	15.00	30.28	54.13	13.23	32.64	49.78	9.03	41.18	22.05	19.35	58.60
51.74	16.20	32.07	52.00	13.77	34.23	42.22	10.88	46.89	19.90	22.33	57.77
49.85	16.81	33.34	50.39	14.35	35.25	40.27	11.97	47.76	17.72	24.66	57.62
47.53	17.86	34.61	48.83	14.86	36.31	37.80	12.61	49.59	15.65	28.40	55.95
42.89	19.70	37.41	47.37	15.43	37.20	31.78	15.39	52.82			
39.41	20.74	39.85	45.23	16.60	38.17	27.65	16.90	55.44			
38.10	21.41	40.49	41.50	17.79	40.70	23.54	19.83	56.62			
35.02	23.19	41.79	39.78	18.87	40.70	21.57	22.46	55.97			
29.93	27.21	42.87	38.67	19.29	41.36	18.82	24.98	56.20			
			37.35	19.93	42.04	17.76	28.28	53.97			
			36.36	20.26	42.72	15.82	31.978	52.20			
			34.97	20.99	43.39						
			33.88	21.66	44.03						
			32.43	22.59	44.47						

Table S7. Experimental data for the binodal weight fraction percentage of the ABS formed by PPG 400 (1) + PEG 20000 (2) + water (3) at different temperatures and atmospheric pressure.

288 K			298 K			308 K			313 K		
$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$	$100w_1$	$100w_2$	$100w_3$
75.61	6.36	18.03	50.98	1.74	47.28	48.89	1.83	49.28	46.98	1.47	51.54
71.00	7.67	21.33	49.03	2.36	48.61	47.33	2.32	50.35	39.57	3.02	57.41
68.83	8.71	22.47	47.36	3.01	49.63	45.75	2.81	51.44	35.58	3.83	60.59
64.34	10.93	24.73	44.86	4.201	50.94	44.51	3.20	52.29	33.64	4.91	61.45
61.46	11.79	26.75	43.06	4.72	52.22	42.63	3.55	53.83	31.80	5.77	62.42
57.58	13.63	28.78	41.60	5.30	53.10	40.42	4.57	55.01	29.39	6.89	63.72
54.71	15.00	30.28	39.94	6.27	53.79	35.95	5.66	58.39	21.20	10.66	68.14
51.74	16.20	32.07	38.08	7.08	54.84	34.53	6.55	58.92	19.18	12.95	67.87
49.85	16.81	33.34	33.13	9.85	57.02	32.65	6.88	60.47	14.69	17.23	68.08
47.53	17.86	34.61	31.51	10.81	57.68	30.54	8.17	61.29	11.79	20.77	67.43
42.89	19.70	37.41	26.99	14.21	58.80	28.84	8.73	62.43	9.73	25.02	65.25
39.41	20.74	39.85	23.01	16.90	60.09	26.68	9.73	63.59			
38.10	21.41	40.49				25.16	10.51	64.32			
						21.18	14.95	63.87			
						19.31	17.22	63.47			
						17.27	20.55	62.18			
						14.43	24.07	61.50			

Table S8. Adjusted parameters and respective standard deviations (σ) obtained by the fitting of the experimental data of ABS composed by PPG 400 (1) + PEG 600 (2) + water (3) at different temperatures and atmospheric pressure, by equation 1.

Temperature (K)	$A \pm \sigma$	$B \pm \sigma$	$10^5 (C \pm \sigma)$
288	125.81 ± 13.93	-0.19839 ± 0.0369	2.4000 ± 0.6933
298	164.59 ± 10.60	-0.31087 ± 0.0205	1.2917 ± 0.3046
308	167.65 ± 15.66	-0.41731 ± 0.0362	0.3221 ± 0.0786
313	179.18 ± 50.71	-0.54274 ± 0.1082	2.4419 ± 1.9113

Table S9. Adjusted parameters and respective standard deviations (σ) obtained by the fitting of the experimental data of ABS composed by PPG 400 (1) + PEG 20000 (2) + water (3) at different temperatures and atmospheric pressure, by equation 1.

Temperature (K)	$A \pm \sigma$	$B \pm \sigma$	$10^5 (C \pm \sigma)$
288	71.05 ± 2.22	-0.17694 ± 0.0146	2.3483 ± 0.5609
298	67.97 ± 2.31	-0.21017 ± 0.0175	4.7372 ± 1.299
308	79.88 ± 4.39	-0.33809 ± 0.0263	0.3547 ± 0.3869
313	73.01 ± 4.80	-0.35600 ± 0.0324	1.9387 ± 1.3476

Table S10. Extraction efficiencies ($EE\%$) of Diazinon in each 35 wt% PPG 400 + 15 wt% PEG + 50 wt% H₂O ABS at (313 ± 1) K.

PEG / (g.mol ⁻¹)	$EE\%_{\text{Diazinon}} \pm \sigma$
600	54.49 ± 0.67
1000	73.82 ± 1.51
2000	86.56 ± 0.81
4000	89.70 ± 0.20
6000	90.74 ± 0.03
8000	91.01 ± 0.01
10000	92.78 ± 0.59
20000	93.71 ± 0.19

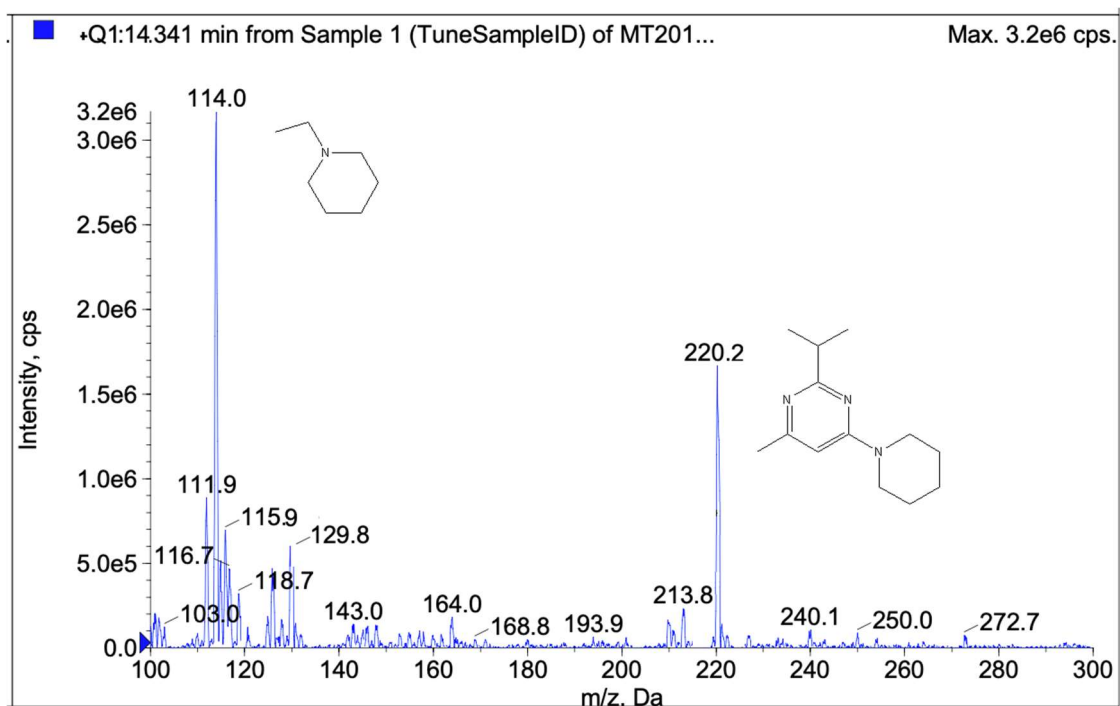


Figure S2. ESI-MS/MS(+) of the products **3** and **5** of $m/z=113.12$ and 219.17 , from the nucleophilic degradation of diazinon in the ABS system.

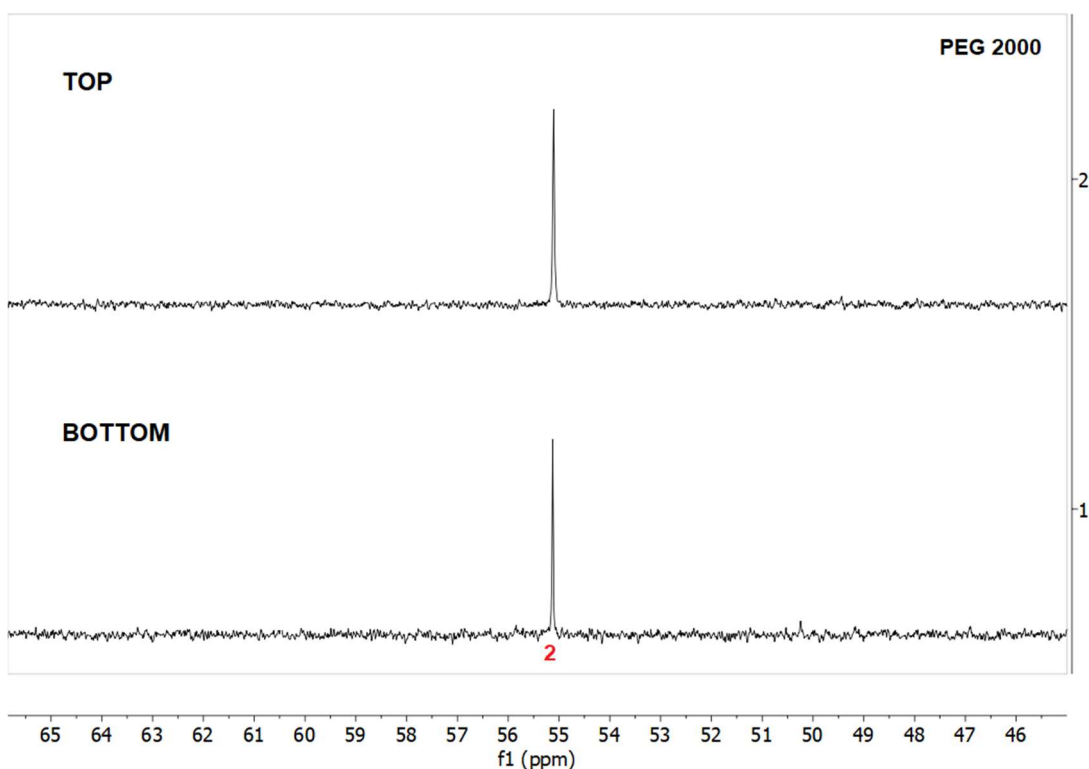


Figure S3. ^{31}P -NMR spectra of both phases of the ABS composed of 35 wt% PPG 400 + 15 wt% PEG 2000 + 50 wt% H₂O used as a reaction medium of nucleophilic degradation of Diazinon with piperidine.

Kinetics details

The rate law for all the reactions studied is given by eqn (2), where P and S represent one of the products and diazinon. The rate constants (k_{obsd}) were obtained in the presence of total piperidine excess (at least 10 folder) and are shown in Table S11.

$$\frac{d[P]}{dt} = k_{obsd} [S] \quad (2)$$

From rate constants values (k_{obsd}), the half-lives ($t_{1/2}$) of degradation of diazinon were obtained in the different ABS by using eqn (3):

$$t_{1/2} = \frac{\ln 2}{k_{obs}} \quad (3)$$

Table S11. Pseudo-first-order rate constants (k_{obs}) and second-order rate constant (K_2) for the degradation of diazinon in the ABS.

	$10^4 k_{OBS} / \text{min}^{-1}$	$10^3 K_2 / \text{M}^{-1}\text{min}^{-1}$
PPG 600	7.52 ± 0.13	1.87 ± 0.03
PPG 2000	5.40 ± 0.41	1.37 ± 0.04
PPG 20000	3.72 ± 0.02	0.94 ± 0.05

Second order rate constant (K_2) were calculated by eq 4, were k_0 is the rate constant for solvolysis and [pip] is the concentration of piperidine.

$$k_{obs} = k_0 + K_2[\text{pip}] \quad (4)$$

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