

## SUPPORTING INFORMATION

The basic centers in PA **13** ( $\text{ZH}_2^{\pm-}$ ) (0.31-0.53 mmol repeating unit) in water (200  $\text{cm}^3$ ) were titrated by stepwise addition of 0.05–0.15 mL of  $\approx 0.1$  M NaOH or HCl (Table S1). Log  $K_i$ s were calculated using the Henderson–Hasselbalch equation (eqn (2) in Scheme 3).

**Table S1** Protonation of polymer **13** ( $\text{ZH}_2^{\pm}$ ) at 23 °C.

run	$\text{ZH}_2^{\pm}$ (mmol)	$C_T^a$ (mol $\text{dm}^{-3}$ )	$\alpha$ -range	pH-range	Points <sup>b</sup>	Log $K_i^{o,c}$	$n_i^c$	$R^2,^d$
1	0.3080 ( $\text{ZH}_2^{\pm}$ )	+0.1222	0.13-0.58	3.05-2.57	22	2.65	0.47	0.9927
2	0.4400 ( $\text{ZH}_2^{\pm}$ )	+0.1222	0.064-0.65	3.15-2.51	25	2.63	0.45	0.9895
3	0.5280 ( $\text{ZH}_2^{\pm}$ )	+0.1222	0.087-0.65	3.13-2.47	26	2.59	0.52	0.9939
Average						2.62 (3)	0.48 (4)	
Log $K_3^e = 2.62 - 0.52 \log [(1-\alpha)/\alpha]$ For the reaction: $\text{ZH}_2^{\pm} + \text{H}^+ \xrightleftharpoons{K_3} \text{ZH}_3^+$								
1	0.3080 ( $\text{ZH}_2^{\pm}$ )	-0.09594	0.82-0.13	4.08-7.22	13	5.63	2.16	0.9907
2	0.4400 ( $\text{ZH}_2^{\pm}$ )	-0.09594	0.82-0.13	4.01-7.45	18	5.55	2.21	0.9978
3	0.5280 ( $\text{ZH}_2^{\pm}$ )	-0.09594	0.87-0.13	3.87-7.45	22	5.58	2.20	0.9971
Average						5.59 (4)	2.19 (3)	
Log $K_2^e = 5.59 + 1.19 \log [(1-\alpha)/\alpha]$ For the reaction: $\text{ZH}^{\pm-} + \text{H}^+ \xrightleftharpoons{K_2} \text{ZH}_2^{\pm}$								
1	0.3080 ( $\text{ZH}_2^{\pm}$ )	-0.09594	0.89-0.27	9.10-10.65	11	10.09	1.13	0.9883
2	0.4400 ( $\text{ZH}_2^{\pm}$ )	-0.09594	0.87-0.36	9.07-10.33	12	10.08	1.14	0.9924
3	0.5280 ( $\text{ZH}_2^{\pm}$ )	-0.09594	0.90-0.27	9.05-10.63	08	10.19	1.18	0.9945
Average						10.12 (6)	1.15 (3)	
Log $K_1^e = 10.12 + 0.15 \log [(1-\alpha)/\alpha]$ For the reaction: $\text{Z}^= + \text{H}^+ \xrightleftharpoons{K_1} \text{ZH}^{\pm-}$								

<sup>a</sup> Titrations with NaOH and HCl are described by (-)ve and (+)ve values, respectively; <sup>b</sup> Data points used; <sup>c</sup> Parentheses include the standard deviations in the last digit; <sup>d</sup>  $R$  = Correlation coefficient; <sup>e</sup>  $\log K_i = \log K_i^o + (n_i - 1) \log [(1 - \alpha)/\alpha]$ ;