Electronic Supplementary Information for

Maximizing the Symbiosis of Static and Dynamic Bonds in Self-Healing Boronic Ester Networks

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Table S1. All prepared compositions listed by ratio of the functional groups, thiol for DODT

DODT	PTMP	VPBE	APD	TEGDVE
75	25	99	1	-
75	25	97	3	-
75	25	95	5	-
75	25	20	-	80
75	25	15	-	85
75	25	10	-	90
75	25	3	-	97
75	25	2	-	98
75	25	1	-	99
75	25	20	1	79
75	25	-	-	100

and PTMP and vinyl for VPBE, APD, and TEGDVE.

DODT: 3,6-dioxa-1,8-octanedithiol; **PTMP:** pentaerythritol tetrakis(3-mercaptopropionate); **VPBE:** 4-((allyloxy)methyl)-2-(4-vinylphenyl)-1,3,2-dioxaborolane; **APD:** 3-allyloxy-1,2-propanediol; **TEGDVE:** tri(ethylene glycol) divinyl ether

Table S2. DSC results of low glass transition temperature polymers showing T_g values belowroom temperature.

Free Diol (%)	Permanent x-linker (%)	Tg (°C)
5	-	-25.2
3	-	-20.0
1	-	-20.1
-	80	-55.3
-	85	-52.6
-	90	-51.0
5	80	-52.0



Figure S1. Percent mass change of the network that contained 95:5 VPBE:APD while immersed in water.

Table S3. Characteristic relaxation times for different sample compositions.

Free Diol (%)	Permanent x-linker (%)	Humidity (%)	τ (s)
5	-	0	25
3	-	0	100
1	-	0	110
0	0	0	93
-	80	0	116
-	85	0	123
-	90	0	127
-	97	0	109
-	98	0	114
-	99	0	104
5	80	0	146
5	-	23	7.3
3	-	23	41
1	-	23	92
0	0	23	107
-	80	23	62
-	85	23	78
-	90	23	83
-	97	23	85
-	98	23	105
-	99	23	82
5	80	23	69
5	-	85	1.8
3	-	85	1.3
1	-	85	0.7
0	0	85	1.9
-	80	85	2.7
-	85	85	3.2
-	90	85	3.4
-	97	85	6.1
-	98	85	6.9
-	99	85	7.4
5	80	85	5.0

The characteristic relaxation time (τ) was determined via a modified Maxwell model as the time required for the stress (σ) to reach 37% (1/e) of its original value (σ_0) after accounting for the stress that the sample cannot physically relax (σ_{plateau}) due to any permanent (*i.e.*, non-dynamic) network structure, *i.e.*, $\tau = (1/e)(\sigma_0 - \sigma_{\text{plateau}})$. The plateau stress was approximated as the final stress at 300 s. Longer relaxation times have a larger error due to this approximation, but trends remain evident.



Figure S2. Water absorption of samples containing both free diol and permanent crosslinker, 20:79:1 VPBE:TEGDVE:APD.