Imprinted polymers for chiral resolution of (+/-)-ephedrine, 3: the use of alternative functional monomers.

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Supplementary Information

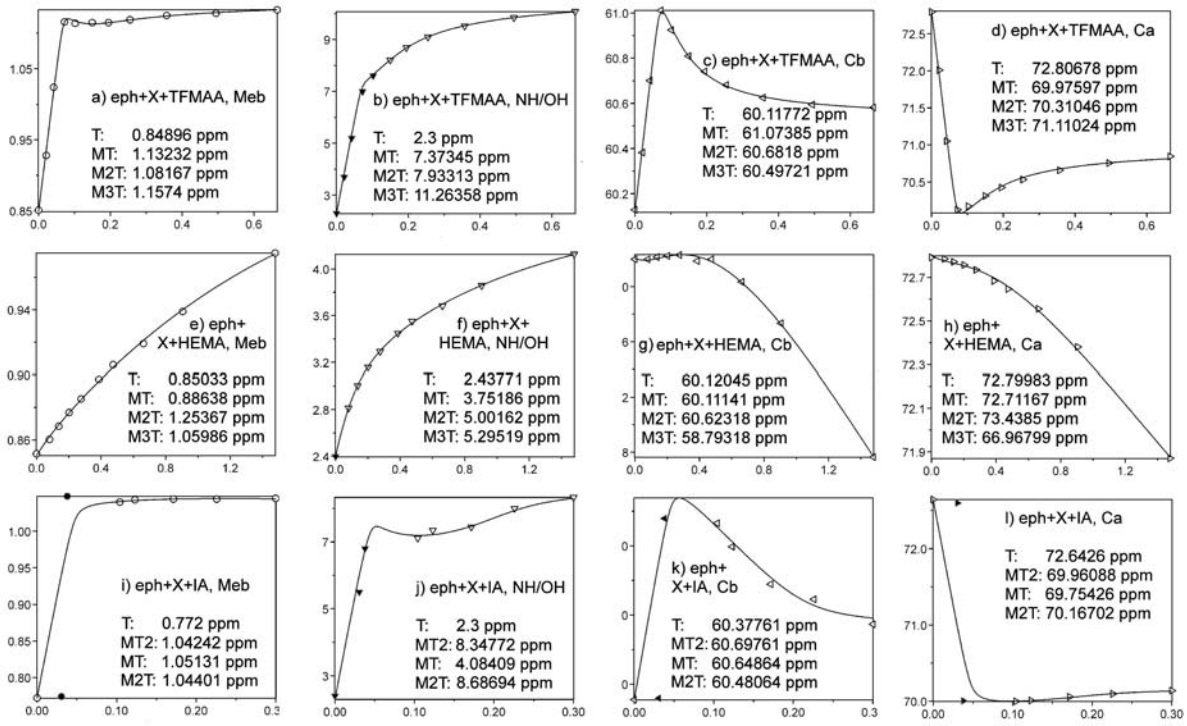

Figure S1 Titration of 0.1 M (-)-ephedrine with different monomers in the presence of 2.0 M EDMA: a)-d) TFMAA in chloroform-*d* (11 data points per nucleus, $\mathbf{T}_{total}$ adjusted to 0.07 M); e)-h) HEMA in chloroform-*d* (10 data points per nucleus); i)-l) IA in acetonitrile-d_3 (8 data points per nucleus, 2 concentrations ignored for fit due to precipitation). Changes in chemical shift for Me^b protons, NH/OH protons, C^b carbons, and C^a carbons. For each graph, the horizontal axis shows the concentration of monomer in M, and the vertical axis shows chemical shift, δ, in ppm. The fitted values for δ are shown for each curve. Filled symbols represent points which were ignored for the global fitting..

	Species	Nucleus: chemical shift / ppm																		
		CHx	CHy	Meb	Nme	Hb	Ha	NH/ OH	MeC	Cu	Cv	COOH	Cmeb	CNMe	Cb	Ca	C3	C4	C2	C1
no X	M	6.5794	6.8509	-	-	-	-	nu	120.96	130.72	134.987	164.946 [a]	-	-	-	-	-	-	-	-
	M2	6.60283	6.88861	-	-	-	-	nu	121.006	130.923	135.421	167.505 [a]	-	-	-	-	-	-	-	-
	T*	-	-	0.82997	2.47784	2.79516	4.75101	2.36109	-	-	-	-	14.3402	34.0744	60.4099	73.0355	126.126	127.053	128.087	141.537
	MT	nu	nu	1.12194	2.75539	3.23257	5.40627	8.59651	nu	nu	nu	167.965	8.40208	30.9328	61.8849	70.4267	125.716	127.521	128.388	139.839
	M2T	nu	nu	1.05791	2.77951	3.33776	5.33259	7.14893	nu	nu	nu	165.988	8.91437	31.3619	61.3742	71.1676	125.654	127.593	128.357	139.483
	M3T	nu	nu	1.11817	2.84557	3.52002	5.38628	12.9533	nu	nu	nu	164.266	8.04144	31.17	61.3346	71.7768	125.552	128.066	128.697	138.646
with EDMA	M	nu	nu	-	-	-	-	-	nu	nu	nu	159.768	-	-	-	-	-	-	-	-
	M2	nu	nu	-	-	-	-	-	nu	nu	nu	163.9	-	-	-	-	-	-	-	-
	T*	-	-	0.84896	2.46379	2.7819	4.75365	2.3 [b]	-	-	-	-	13.653	33.4893	60.1177	72.8068	nu	nu	nu	141.693
	MT	nu	nu	1.13232	2.81608	3.34503	5.44718	7.37345	nu	nu	nu	167.236	7.97375	30.363	61.0739	69.976	nu	nu	nu	139.788
	M2T	nu	nu	1.08167	2.80949	3.38344	5.35377	7.93313	nu	nu	nu	165.132	8.67992	30.7684	60.6818	70.3105	nu	nu	nu	139.925
	M3T	nu	nu	1.1574	2.93918	3.62665	5.39956	11.2636	nu	nu	nu	162.988	7.94293	30.7156	60.4972	71.1102	nu	nu	nu	138.865

Table S1 Fitted chemical shifts for titrations with TFMAA in d-chloroform. - = nucleus not present in species, nu = data not used. Shifts for T* calculated from titration of ephedrine with TFMAA ignoring dimerisation of ephedrine. [a] Shifts calculated from self titration of TFMAA then used as constant parameters for fitting titration of ephedrine with TFMAA. [b] Shifts manually estimated and used as constant parameters for fitting titration of ephedrine with TFMAA.

	Species	Nucleus: chemical shift / ppm																						
		Mea	CH2f	CH2e	CHcx	CHcy	Meb	Nme	Hb	Ha	NH+OH	Ca	Cf	Ce	Cc	Cb	COOR	Cmeb	CNMe	Cb	Ca	C3	C4	C2	C1
no X	M	1.9678	3.88189	4.30431	5.61013	6.1526	-	-	-	-	2.01564	18.3609	61.4809 [a]	66.467	126.097	136.066	167.8 [a]	-	-	-	-	-	-	-	-
	M2	1.8948	3.69793	4.11277	5.55121	6.1472	-	-	-	-	8.64202	16.6496	57.1377 [a]	64.471	124.755	134.917	166.854 [a]	-	-	-	-	-	-	-	-
	T*	-	-	-	-	-	0.83353	2.48182	2.79806	4.75449	2.20509	-	-			-	-	14.3252	34.0579	60.4193	72.9867	126.115	127.045	128.098	141.51
	MT	nu	nu	nu	nu	nu	0.87326	2.48386	2.81656	4.80336	2.95	nu	60.9278	nu	nu	nu	167.597	13.6849	33.6859	60.4763	73.0566	126.021	127.079	128.084	141.381
	M2T	nu	nu	nu	nu	nu	1.26481	2.43945	2.91177	5.12184	6.90422	nu	55.7521	nu	nu	nu	168.557	7.91335	30.4315	60.8635	74.543	125.787	127.461	128.192	141.323
	M3T	nu	nu	nu	nu	nu	1.02549	2.88398	3.53541	5.40421	4.41445	nu	59.2371	nu	nu	nu	165.258	7.58479	29.4516	59.6034	68.0074	124.289	126.527	127.397	138.913
with EDMA	M	nu	nu	nu	nu	nu	-	-	-	-	-	nu	nu	nu	nu	nu	167.135	-	-	-	-	-	-	-	-
	M2	nu	nu	nu	nu	nu	-	-	-	-	-	nu	nu	nu	nu	nu	163.713	-	-	-	-	-	-	-	-
	T*	-	-	-	-	-	0.85033	2.46552	2.78201	4.75187	2.43771	-	-	-	-	-	-	13.6843	33.4995	60.1205	72.7998	125.72	126.469	127.563	141.679
	MT	nu	nu	nu	nu	nu	0.88638	2.4804	2.81512	4.80581	3.75186	nu	nu	nu	nu	nu	166.559	13.1765	33.1746	60.1114	72.7117	125.659	126.463	127.551	141.593
	M2T	nu	nu	nu	nu	nu	1.25367	2.49568	2.94806	5.21858	5.00162	nu	nu	nu	nu	nu	164	7.58867	29.7108	60.6232	73.4385	125.15	126.955	127.583	141.147
	M3T	nu	nu	nu	nu	nu	1.05986	3.01775	3.76368	5.56066	5.29519	nu	nu	nu	nu	nu	173.733	6.19607	28.6268	58.7932	66.968	124.243	125.816	126.87	138.695

Table S2 Fitted chemical shifts for titrations with HEMA in d-chloroform. - = nucleus not present in species, nu = data not used. Shifts for T* calculated from titration of ephedrine with HEMA ignoring dimerisation of ephedrine. [a] Shifts calculated from self titration of MAA then used as constant parameters for fitting titration of ephedrine with HEMA.

	Species	Nucleus: chemical shift / ppm																			
		Hd	Hc1	Hc2	Meb	Nme	Hb	Ha	NH/OH	Cd	Cc	Cb	Ca	Ce	Cmeb	CNMe	Cb	Ca	C3	C4	C2	C1
no X	M	3.27496	5.75247	6.23553	-	-	-	-	9.3	36.4037	127.985	134.008	166.413 [a]	170.923 [a]	-	-	-	-	-	-	-	-
	M2	3.39121	5.89813	6.39142	-	-	-	-	9.3	36.1546	130.322	132.776	169.418 [a]	174.708 [a]	-	-	-	-	-	-	-	-
	T*	-	-	-	0.76303	2.38502	2.72107	4.69402	2.28423	-	-	-	-	-	13.0724	32.9044	60.1347	72.5695	125.857	126.385	127.564	142.509
	MT2	nu	nu	nu	1.00589	2.7331	3.40864	5.22698	5.27495	nu	nu	nu	174.346	178.462	8.28135	30.4598	60.2839	69.7745	128.469	127.235	127.969	140.159
	MT	nu	nu	nu	1.00462	2.70945	3.38618	5.28251	5.6 [b]	nu	nu	nu	176.548	170.584	8.19222	30.1604	60.5656	69.4498	120.14	127.073	127.992	139.86
	M2T	nu	nu	nu	0.99742	2.72638	3.41304	5.17313	7.92027	nu	nu	nu	169.793	173.589	8.45306	30.5934	60.2289	69.9544	127.17	127.326	128.027	139.673
with EDMA	M	nu	nu	nu	-	-	-	-	-	nu	nu	nu	167 [b]	172.063	-	-	-	-	-	-	-	-
	M2	nu	nu	nu	-	-	-	-	-	nu	nu	nu	170 [b]	174.113	-	-	-	-	-	-	-	-
	T*	-	-	-	0.772	2.406	2.732	4.718	2.3 [b]	-	-	-	-	-	13.3036	33.2036	60.3776	72.6426	125.99	126.513	127.708	142.632
	MT2	nu	nu	nu	1.04242	2.78192	3.42781	5.31697	8.34772	nu	nu	nu	177.499	176.252	8.43061	30.6549	60.6976	69.9609	124.771	127.295	128.137	140.333
	MT	nu	nu	nu	1.05131	2.79379	3.44093	5.33329	4.08409	nu	nu	nu	173.454	172.61	8.57733	30.6173	60.6486	69.7543	126.785	127.16	128.1	140.564
	M2T	nu	nu	nu	1.04401	2.79578	3.46798	5.26065	8.68694	nu	nu	nu	170.26	173.486	8.57485	30.8287	60.4806	70.167	125.826	127.412	128.16	139.917

Table S3 Fitted chemical shifts for titrations with IA in d3-acetonitrile. - = nucleus not present in species, nu = data not used. Shifts for T* calculated from titration of ephedrine with IA ignoring dimerisation of ephedrine. [a] Shifts calculated from self titration of IA then used as constant parameters for fitting titration of ephedrine with IA. [b] Shifts manually estimated and used as constant parameters for fitting titration of ephedrine with IA.

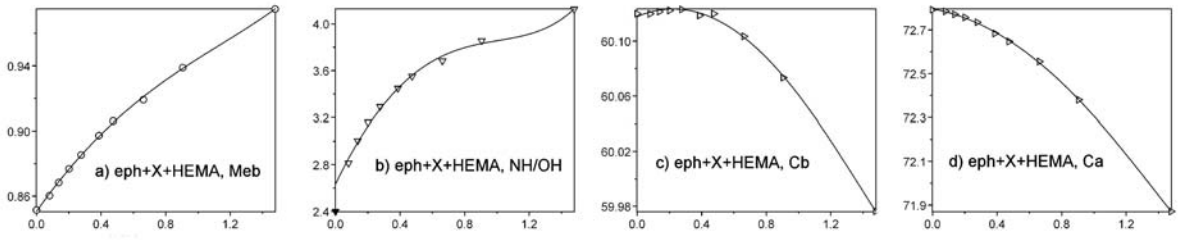

Figure S2 Titration of 0.1 M (-)-ephedrine with HEMA in the presence of 2.0 M EDMA in chloroform-*d* (10 data points per nucleus); i)-l) IA in Changes in chemical shift for Me^b protons, NH/OH protons, C^b carbons, and C^a carbons. For each graph, the horizontal axis shows the concentration of monomer in M, and the vertical axis shows chemical shift, δ, in ppm. Filled symbols represent points which were ignored for the global fitting.

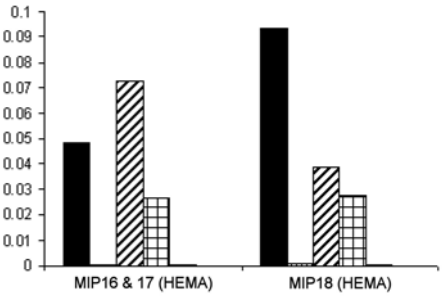

Figure S3. Speciation in the prepolymerisation mixtures with HEMA, recalculated using the association constants in Table 2 and an additional association to give MX with bMX = 3 M-1.. Vertical axis represents concentration in M of free **M** (filled), $\mathbf{M_2}$ (vertical bars), free **T** (diagonal bars), **MT** (chequered), $\mathbf{M_2T}$ (horizontal bars) and $\mathbf{M_3T}$ (unshaded). For these calculations, a spreadsheet was constructed in Excel, and [**M**]free and [**T**]free were varied iteratively until the equations [**M**]total-[**M**]free-2[$\mathbf{M_2}$]-[**MT**]-2[$\mathbf{M_2T}$]-3[$\mathbf{M_3T}$]-[**MX**]=0, [**X**]total-[**MX**]-[**X**]=0 and [**T**]total-[**T**]free-[**MT**]-[$\mathbf{M_2T}$]-[$\mathbf{M_3T}$]=0 were all satisfied to 6 decimal places.