Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Amphiphilic-Zwitterionic Block Polymers

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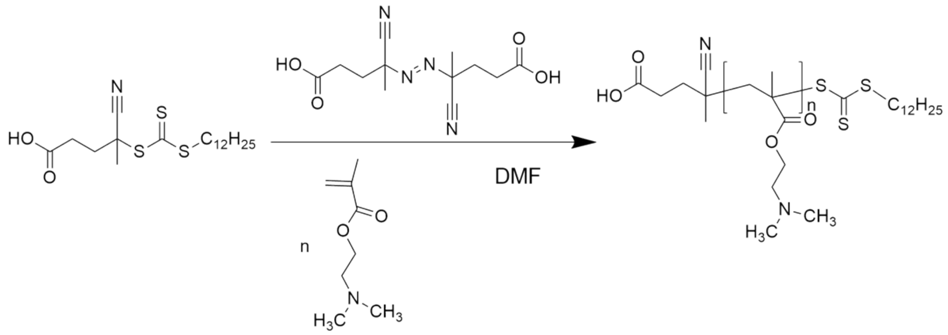
1) Kinetic Study for Synthesis of Poly(dimethyl aminoethyl methacrylate)

A kinetic study of the synthesis of macro chain transfer agents containing dimethyl aminoethyl methacrylate (Scheme S.1) has been performed to study the reaction time required to achieve the Poly(dimethyl aminoethyl methacrylate) (D) block with targeted molecular weight and low dispersity. A commercially available chain transfer agent (CTA) was chosen containing a trithiocarbonate group which is less susceptible than the dithioester group to nucleophilic attack from the tertiary amine group present in the monomer. The CTA contains a methylene group that provides a distinct traceable signal in ^{1}H-NMR, not overlapping with any of the polymer characteristic signals, for end-group analysis and DP measurements.

scheme S.1: Homopolymerisation of PDMAEMA (D)



Synthesis of poly DMAEMA was performed under a nitrogen atmosphere at 60°C. Selected quantities of CTA and initiator are dissolved in DMF (10ml) in a 50 ml round bottom flask. The solution was purged under nitrogen for 20 min. Into the purged solution, purified DMAEMA (10ml) was added. [CTA]:[Initiator] ratio was 10:1. [Monomer] to [CTA] and [initiator] ratio was maintained so that the molecular weight of the targeted polymer was 350,000 g/mol. The resulting stock solution was kept under nitrogen flow for a further 10 min more to ensure complete removal of dissolved oxygen. The flask was then transferred to a stir plate pre-heated to 60°C. An aliquot of 0.5 ml of the reaction mixture was removed with a nitrogen flushed syringe every 2 hours. ^{1}H-NMR and DMF-GPC measurements were performed on the crude aliquot to observe changes in monomer concentration to determine % conversion, molecular weight, and dispersity (Table S.1).

Table S.1: Kinetic study data for homopolymer block

Time	**conversion [%]**	**Đ**	**M_n [KDa]**
2 h	11	1.9	28
4 h	19	1.6	41
6 h	26	1.5	56
8 h	28	1.5	61
10 h	34	1.4	71
11 h	32	1.5	65
14 h	48	1.5	90
16 h	44	1.3	98
18 h	44	1.4	90
20 h	37	1.4	85
22 h	46	1.4	91

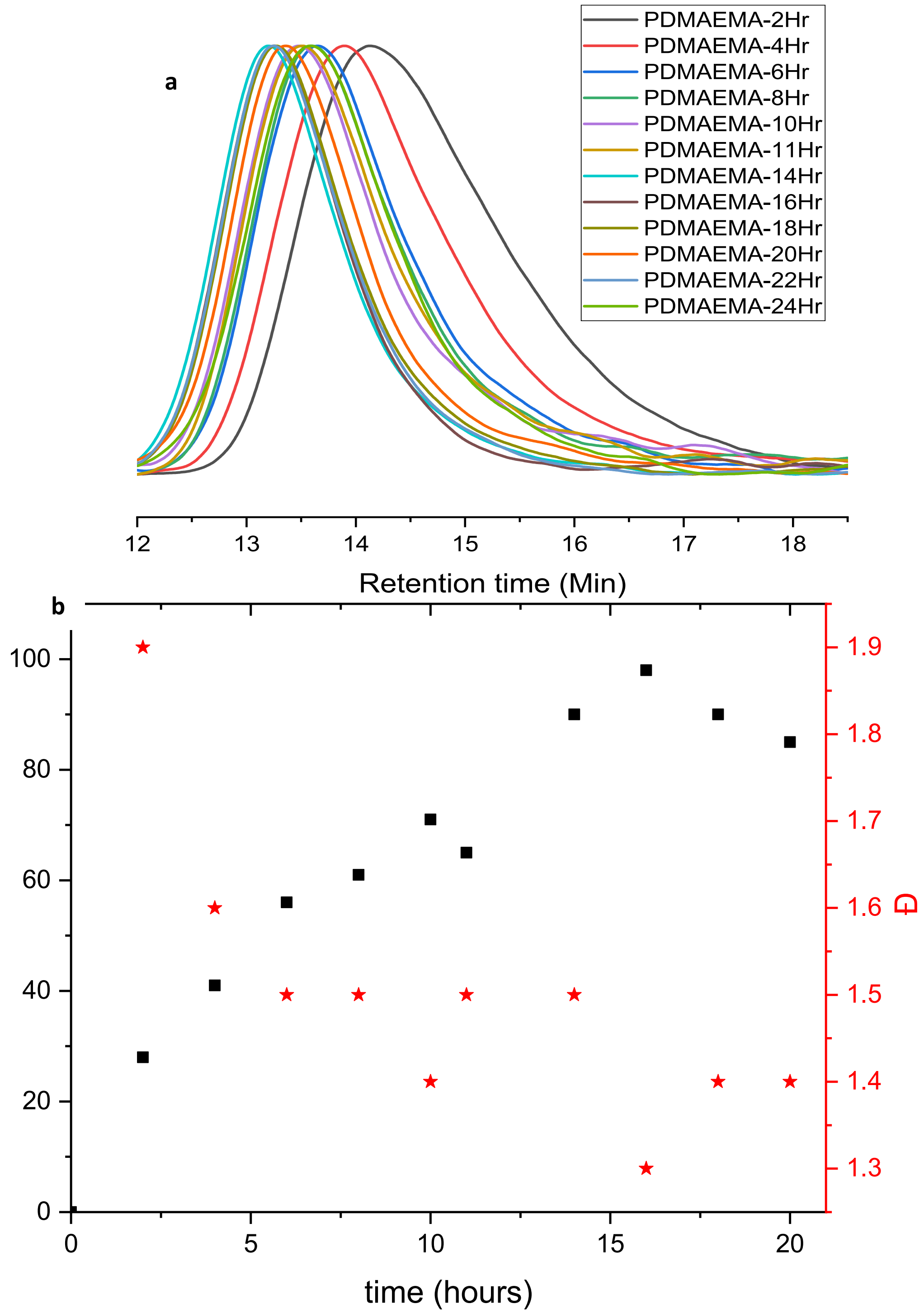
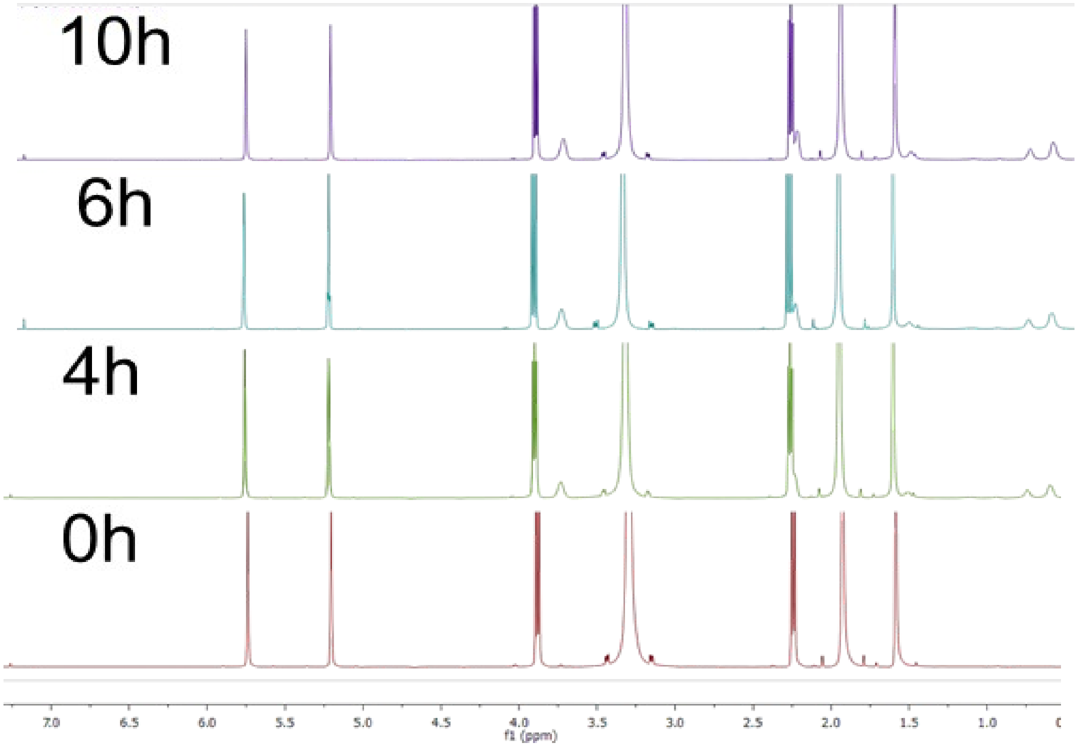


Figure S.1: a) GPC trace of the crude aliquot at 2hr interval b) M_n and Đ plot as indicated by GPC values


10h
6h
4h
0h
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

a

The percent conversion (Table S.1) of the poly DMAEMA was studied through ^{1}H-NMR by calculating the relative ratio of the methylene proton alpha to the carbonyl group of the pendant group of the unreacted monomer and polymer. This study shows a linear increase in polymer formation up to 10 h with a slowing in the rate of increase of molecular weight over time (Figure S.2). A similar trend is followed by molecular weight and as analyzed by GPC using DMF as eluent with PMMA standards (Figure S.1). The overall dispersity values were low, but it gradually reduced for the first 10 h and after that it became constant. This study demonstrates that the polymerization remained controlled for the initial 10 h time, after that the rate of polymerization drops. This observation is attributed to two factors: 1) reduction is the concentration of the unreacted monomer,

b

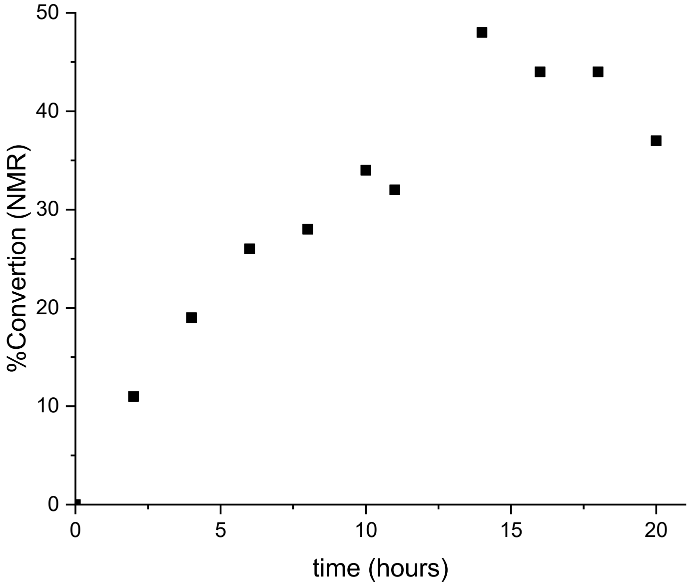


Figure S.2: a) ^{1}H-NMR spectra of the crude aliquot at different time interval b) Percent conversion plot as calculated from the unreacted monomer to polymer peak ratio

2) possible nucleophilic attack of the tertiary amine on the trithiocarbonyl end-group on the CTA, terminating the chain-end. Based on this observation, the selected duration of polymerization reactions was fixed at 10 h.

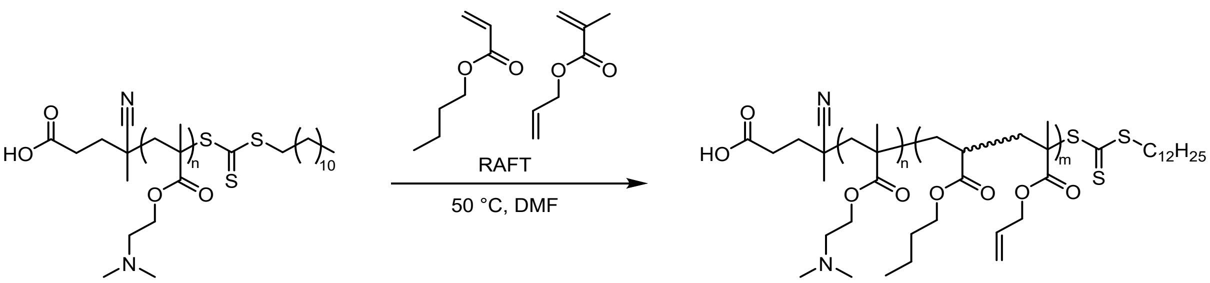
Table S.2:Reactant composition of different batches of homopolymerization synthesis

Sample name	Monomer			Chain Transfer Agent			Initiator			Solvent
	Vol. (ml)	MMol	Equiv.	Mass (g)	MMol	Equiv.	Mass (g)	MMol	Equiv.	Vol (ml)
D_{290}	80	474.78	1319	0.1454	0.36	1	0.0101	0.04	0.1	80
D_{260}	70	415.43	1065	0.1598	0.39	1	0.0111	0.04	0.1	70
D_{223}	70	415.43	704	0.2397	0.59	1	0.0166	0.06	0.1	70
D_{110}	35	207.72	461.6	0.1798	0.45	1	0.0125	0.04	0.1	35
D_{64}	50	296.74	233.65	0.5136	1.27	1	0.0357	0.12	0.1	50
D_{25}	50	296.74	116.82	1.0272	2.54	1	0.0713	0.24	0.1	50

2) Kinetic Study for Synthesis of Poly[(dimethyl aminoethyl methacrylate)-*b*-Poly(n-butyl acrylate-*ran*-allyl methacrylate)]

A kinetic study of the chain extension of poly DMAEMA with hydrophobic Poly(n-butyl acrylate-ran-allyl methacrylate) block (HyphB) has been performed to determine the reaction times required to achieve a diblock copolymers with targeted molecular weight and low dispersity (Scheme S.2). Purified PDMAEMA from previously described steps were used as macro CTAs.

scheme S.2: Synthesis of HyPhB



Chain extension of Macro CTA of 6,200 g/mol molecular weight was performed under nitrogen atmosphere at 60°C. The 10:1 molar ratio of macro CTA and initiator are dissolved in DMF (10 ml) in a 50 ml round bottom flask. The solution was purged under nitrogen for 20 min. In the purged solution, purified *n*-butyl acrylate (nBA)(10 ml) and allyl methacrylate (AMA) (0.26ml) were added in an amount to target a 19:1 n-BA:AMA molar ratio in the random copolymer block amount. [nBA plus AMA] to [CTA] and [initiator] ratio was maintained so that the molecular weight of the targeted polymer was 25,500 g/mol. 80% of the total reaction volume consisted of the reaction solvent The stock solution was kept under nitrogen flow for a further 10 min to ensure complete removal of dissolved oxygen. The flask was then transferred to a stir plate pre-heated to 60 °C. An aliquot of 0.5 ml of the reaction mixture was removed with a nitrogen flushed syringe every 2 hours. ^{1}H-NMR and GPC analysis with DMF eluent were performed on the crude aliquots to observe change in percent conversion of monomer, molecular weight, and dispersity (Table S.3).

Table S.3: Kinetic study of synthesis of PDMAEMA-b-P(BA-ran-AMA)

	DMF-GPC				^{1}H-NMR					
time	**PDMAEMA**	**Di-Block Copolymer**			**PnBA**		**PAMA**		**Di-Block Copolymer**	
	D.P.	**M_n [g/mol]**	**M_w [g/mol]**	**Đ**	**D.P.**	**conversion [%]**	**D.P.**	**conversion [%]**	**conversion (monomer signal) [%]**	**M_n [g/mol]**
0 h	40	800	1,000	1.3	0	0	0	0	0	0
2 h	40	4,100	5,400	1.3	42	29	2	75	27	11,800
4 h	40	8,600	12,900	1.5	76	53	5	93	49	16,500
6 h	40	13,400	24,700	1.8	105	66	8	93	64	20,600
8 h	40	15,600	39,300	2.5	103	76	8	93	73	20,400
10 h	40	18,000	52,300	2.9	128	80	8	93	80	23,600
12 h	40	22,000	81,600	3.7	151	85	8	93	83	26,500
22 h	40	23,300	192,700	8.3	142	93	8	93	92	25,400

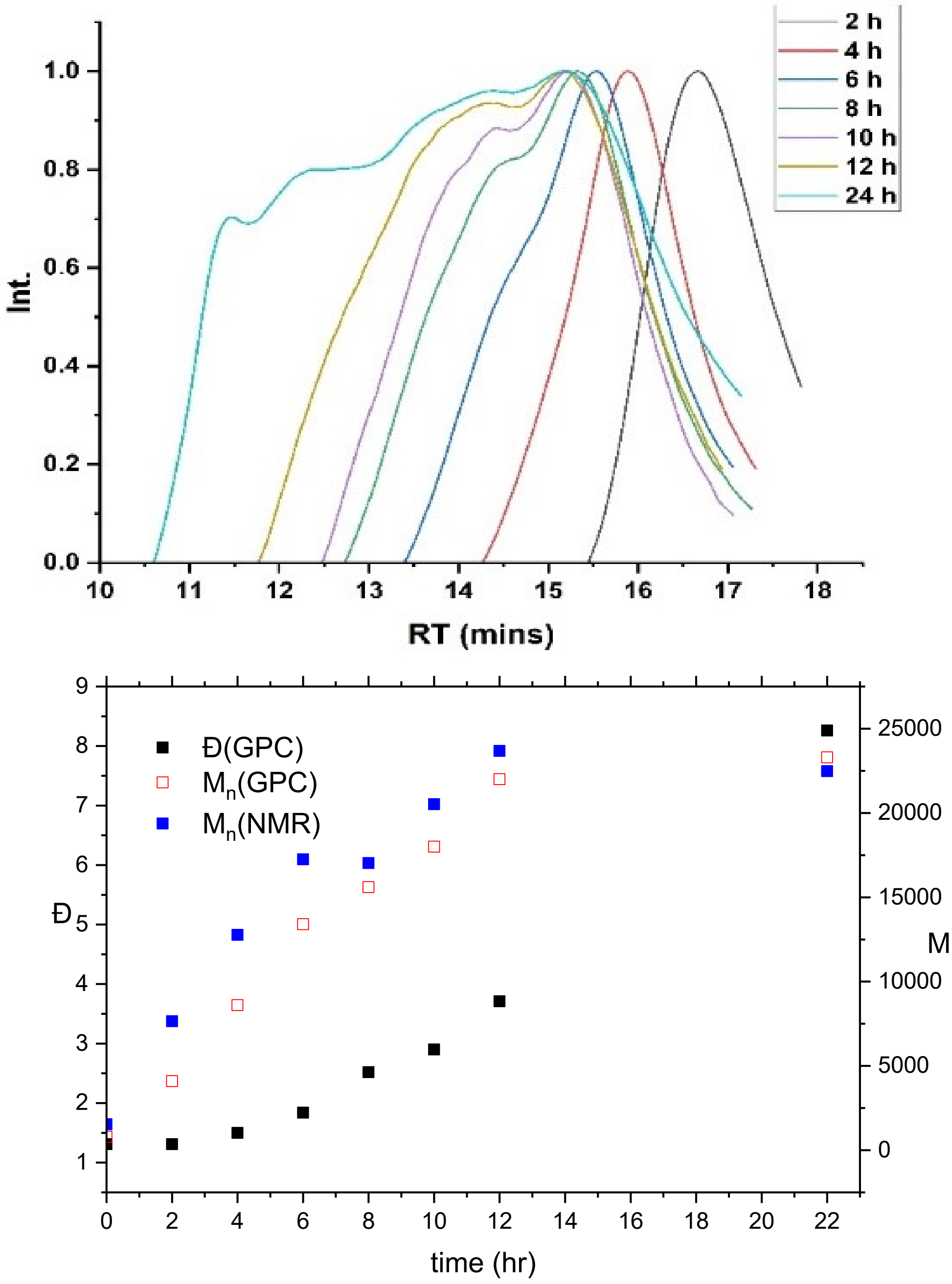
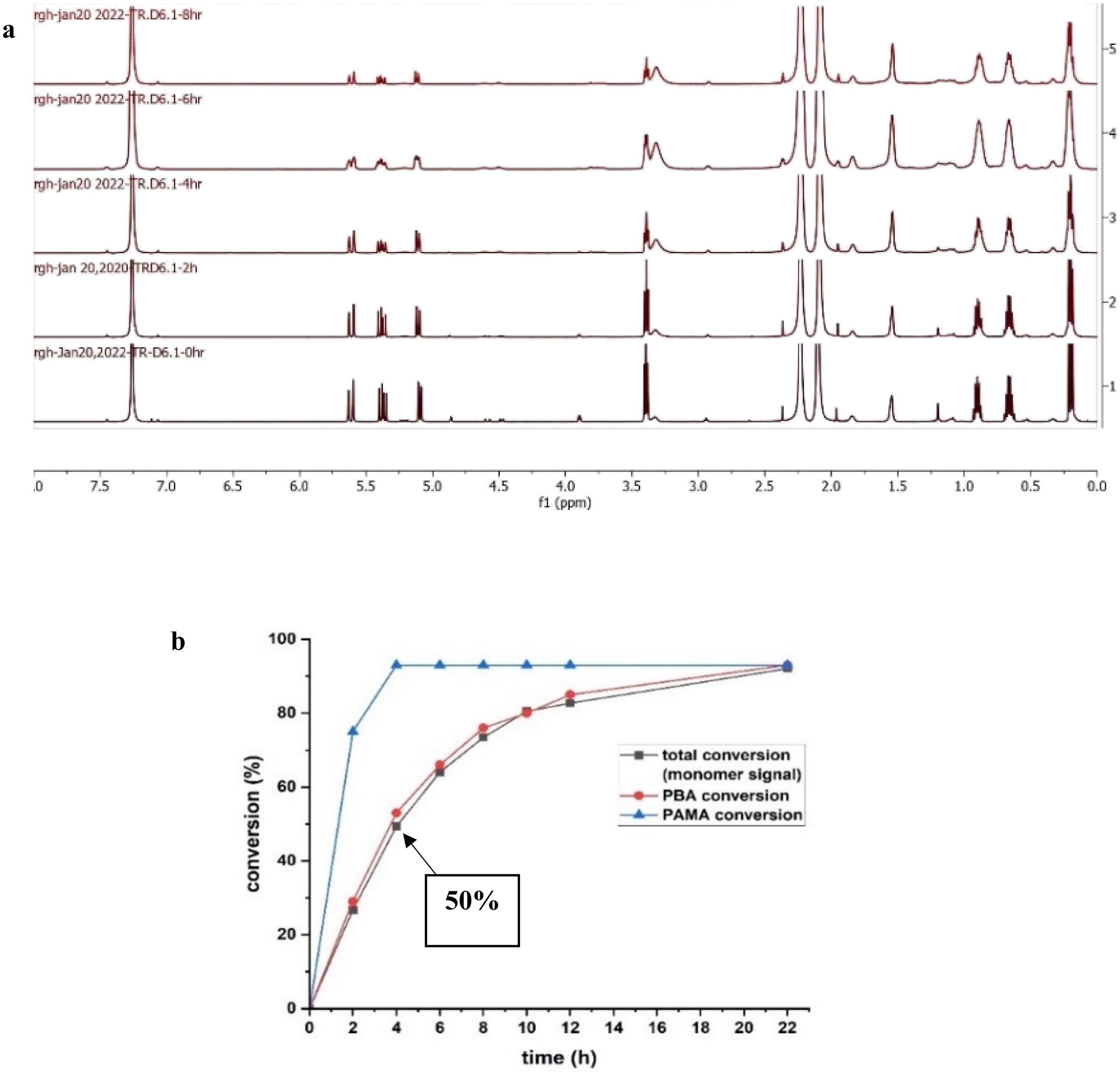


Figure S.3: a) GPC trace of the crude aliquot at 2 h interval b) M_n and Đ plot as indicated by GPC values.

a



percent conversion of the *n*-butyl acrylate and allyl methacrylate were studied

b

throug -NMR by calculating relative ratios of the methylene proton alpha to the carbon oup of the pendant group of the unreacted monomers and polymer (Figure 2.8 a). Butyl acrylate exhibits a linear increase in percent conversion for an initial 4 h with

Figure S.4: a) ^{1}H-NMR spectra of the crude aliquot at different time intervals b) percent conversion plot as calculated from the unreacted monomer to polymer ratio.

gradual reduction in rate of increase in percent conversion. For allyl acrylate, the rate of increase in percent conversion is high and reaches almost 95% in the initial 4 h, after which it becomes constant due to a very low monomer concentration (Figure S.4, b). The analysis by GPC with DMF as eluent utilizing PMMA standards shows a gradual increase in molecular weight up to 4 h with gradual decrease in the rate of increase over time whereas the opposite trend is followed by dispersity as studied (Figure S.3, b). The overall dispersity was initially low then it increases exponentially after 4 hrs. The GPC chromatogram also shows an appearance of a shoulder at higher molecular weight (Figure S.3, a). This observation can be attributed to the fact that initially the vinyl unit of the allyl methacrylate were reacting with the chain-end of the macro CTA, but with the reduction of the monomer concentration, radical generation begins to happen from the allyl group resulting in branching and crosslinking of the pendent sidechains. Based on this observation, the duration of the polymerization reaction was fixed at 4 h.

Table S.4: Reactant composition for different batches of parent block copolymer synthesis

Sample name	n-Butyl Acrylate			Allyl Methacrylate			Macro Chain Transfer Agent			Initiator			DMF
	Vol. (ml)	MMol	Equiv.	Vol. (ml)	MMol	Equiv.	Mass (g)	MMol	Equiv.	Mass (g)	MMol	Equiv.	Vol (ml)
D_{290}-b-$HyPhB_{185}$	57.02	395.96	990	1.62	12.07	30	20.0000	0.40	1	0.0112	0.04	0.1	236
D_{260}-b-$HyPhB_{150}$	60.14	417.62	1129	1.82	13.58	37	15.0000	0.37	1	0.0105	0.04	0.1	248
D_{223}-b-$HyPhB_{312}$	54.99	381.83	1364	1.82	13.58	48	10.0000	0.28	1	0.0080	0.03	0.1	294
D_{110}-b-$HyPhB_{480}$	68.43	475.16	1584	1.24	9.29	31	8.000	0.30	1	0.0090	0.03	0.1	279
D_{064}-b-$HyPhB_{360}$	64.15	445.46	1437	1.34	9.96	32	5.0000	0.31	1	0.0088	0.03	0.1	262
D_{025}-b-$HyPhB_{265}$	69.28	481.10	1604	1.80	13.44	45	3.0000	0.30	1	0.0084	0.03	0.1	227

3) COSY-NMR Analysis of A-Z Block Polymers

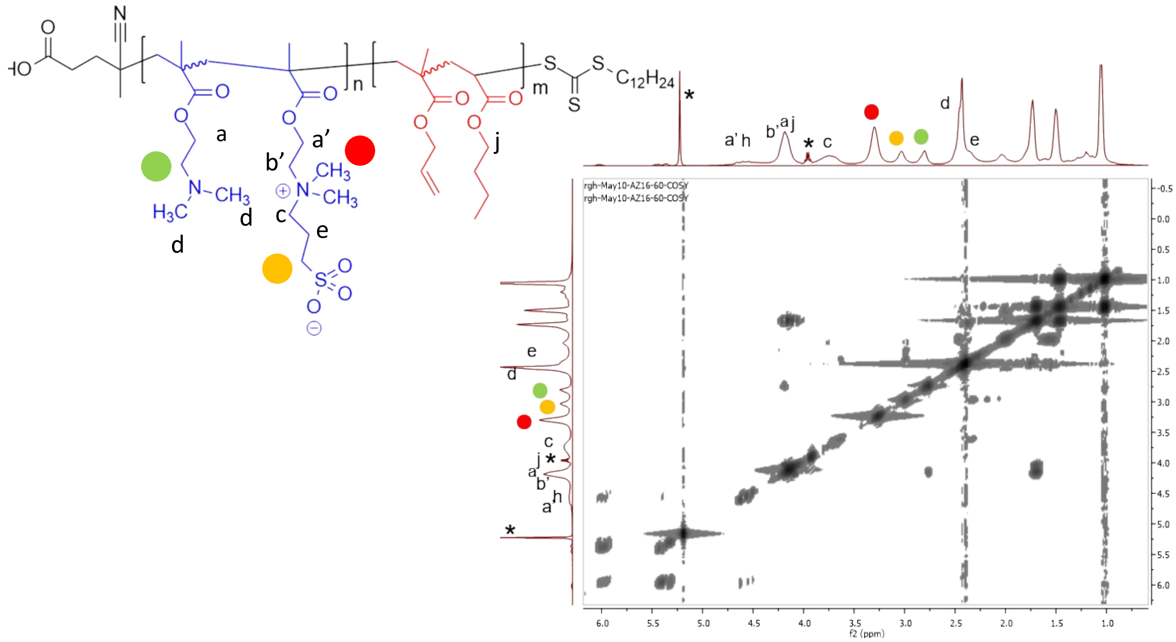


Figure S.5: Representative COSY-NMR of A-Z block copolymer (D-^{54}S)$_{223}$-b-(HyPhB)$_{312}$

4) FTIR Analysis of A-Z Block Polymers

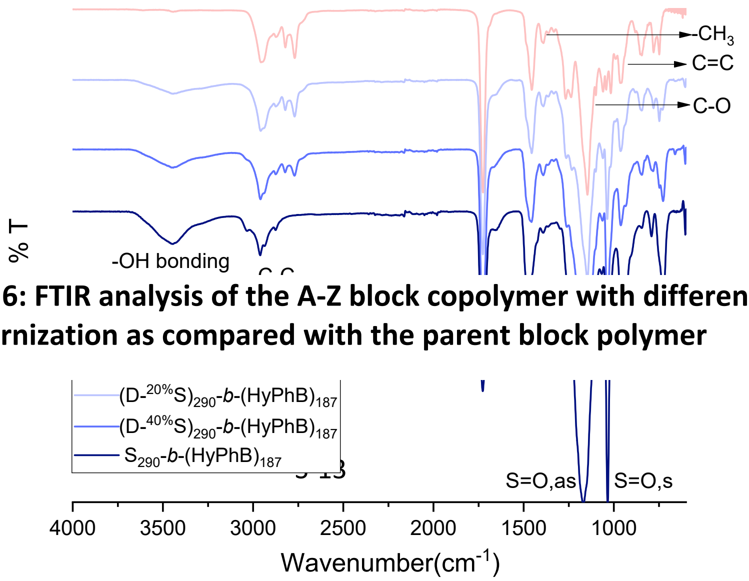


Figure S.6: FTIR analysis of the A-Z block copolymer with different percentages of quaternization as compared with the parent block polymer

5) TGA Analysis of A-Z Block Polymers

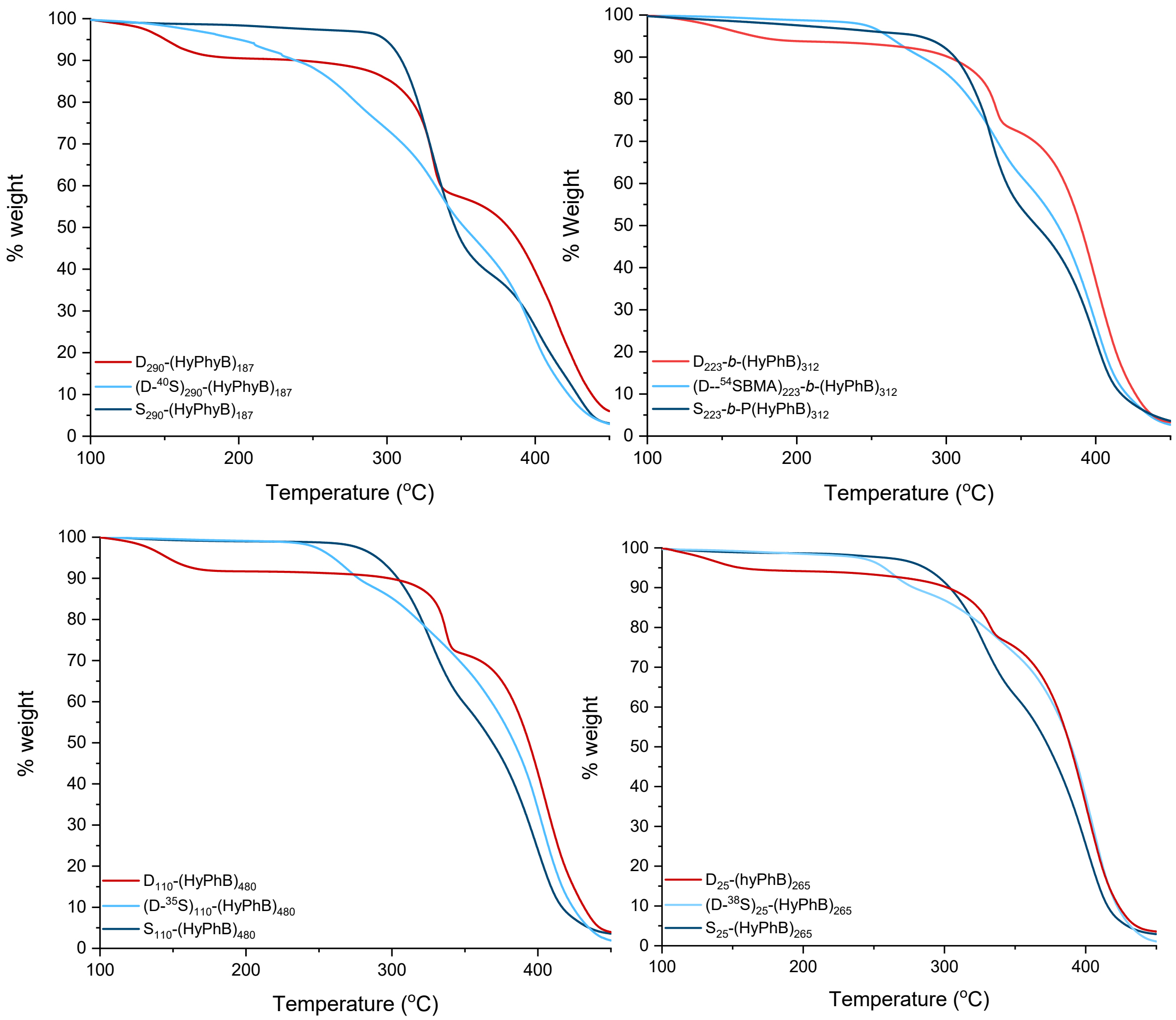


Figure S.7: TGA analysis of the A-Z block copolymer as compared with that of the parent block copolymer

6) DSC Analysis of A-Z Block Polymers

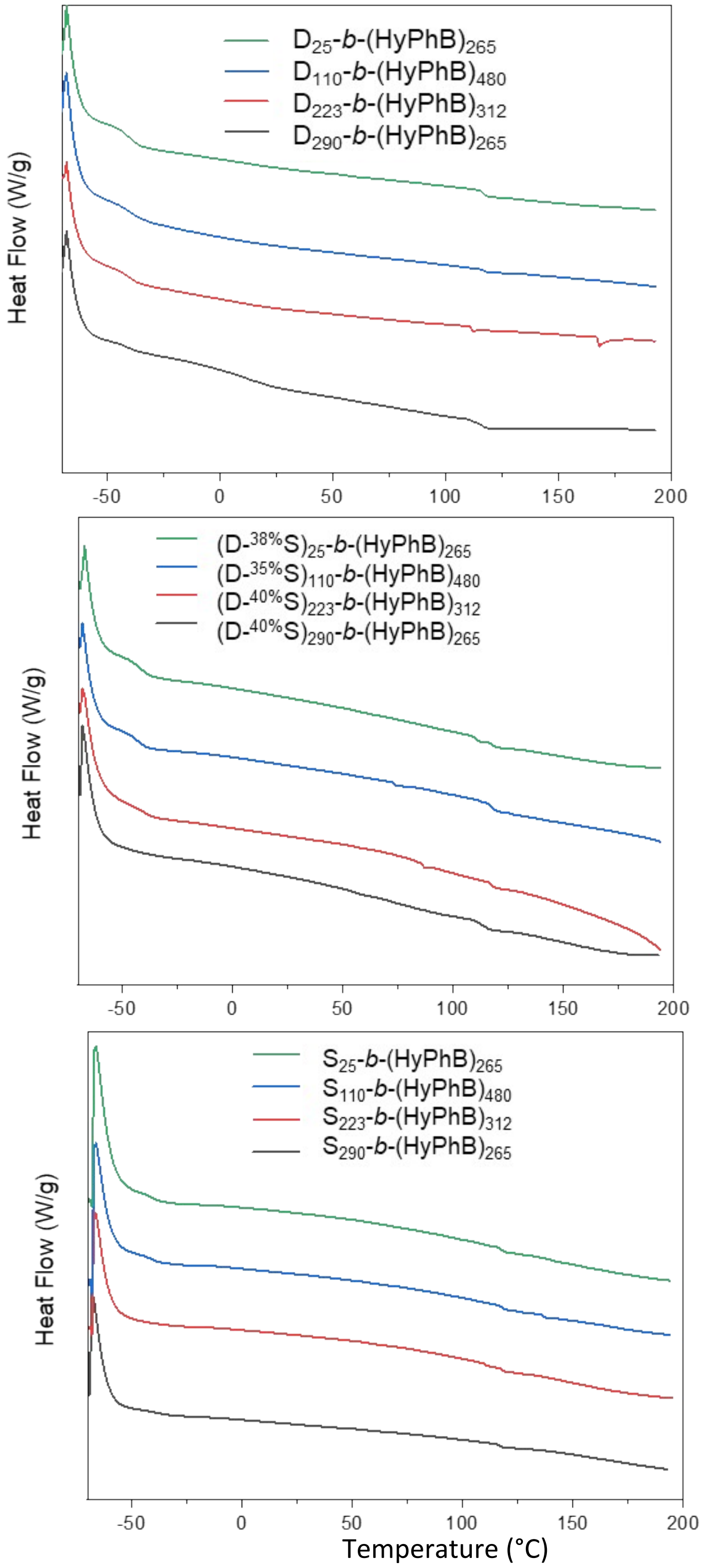


Figure S.8: DSC analysis of the A-Z block copolymer as compared with that of the parent block copolymer