Supporting Information

RAFT polymerisation of *N*-vinylformamide and corresponding double hydrophilic block copolymers

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Table of contents

Table S1. RAFT polymerization of NVF in DMSO with CTA1 at different initial concentrations at 35°C. $[NVF]_0 = 4.5$ mol L^{-1}, $[V\text{-}70]_0 = 5.4$ mmol L^{-1}. 3

Table S2. RAFT polymerization of NVF at 35°C in DMSO aiming for different $M_{n,th}$. $[V\text{-}70]_0/[CTA1]_0 = 0.33$. $[NVF]_0 = 4.5$ mol L^{-1} (30% wt NVF in DMSO). 4

Table S3. RAFT polymerization of NVF at 35°C in DMSO aiming for $M_{n,th.} = 100$ kg mol^{-1}. $[NVF]_0 = 4.5$ mol L^{-1}, $[CTA1]_0 = 3.2$ mmol L^{-1}, $[V\text{-}70]_0 = 2.7$ mmol L^{-1}.....4

Table S4. Block polymerization of NVF at 35°C in DMSO using PDMA-CTA2, PVCL-CTA2 and PNIPAAm-CTA2 as macro-RAFT agents. $[NVF]_0 = 4.5$ mol L^{-1}. $[V\text{-}70]_0/[macro\text{-}CTA]_0 = 0.33$. 5

Table S5. ^{1}H DOSY-NMR analysis data of the block copolymers and their first block. 5

Fig. S1. ^{1}H NMR spectrum of a crude mixture of NVF polymerization with CTA1 (Table S1 entry 13). Measured on a 300MHz apparatus. 6

Fig. S2. Evolution of SEC-RI traces of PNVF with NVF conversion for RAFT polymerization with CTA1 at 35°C (V-70 initiation) aiming for different $M_{n,th}$: (a) 100 kg mol^{-1}, (b) 50 kg mol^{-1}, (c) 20 kg mol^{-1}, (d) 10 kg mol^{-1} and (e) 5 kg mol^{-1}. 7

Fig. S3. Evolution of (a) $M_{n,SEC}$, $Đ$ and (b) SEC-RI traces with monomer conversion for the RAFT polymerization of NVF in DMSO(data taken from Table S3). 8

Fig. S4. SEC-RI traces of (a) PDMA-*b*-PNVF, (b) PVCL-*b*-PNVF, (c) PNIPAAm-*b*-PNVF and corresponding first blocks. 9

Fig. S5. Dynamic light scattering measurements at (a) 25°C and (b) 35°C of PNIPAAm-*b*-PNVF block copolymer at a concentration of 0.5 mg mL^{-1} in ultrapure water. 10

Fig. S6. ^{1}H NMR spectra of (a) PVCL-*b*-PNVF, (b) PVCL-CTA2, (c) PNIPAAm-*b*-PNVF and (d) PNIPAAm-CTA2 analyzed via DOSY-NMR (Table S4). Measured on a 500MHz apparatus. 11

Table S1. RAFT polymerization of NVF in DMSO with CTA1 at different initial concentrations at 35°C. $[NVF]_0 = 4.5$ mol L^{-1}, $[V\text{-}70]_0 = 5.4$ mmol L^{-1}.

Entry	Targeted M_n (g mol^{-1})	Time (h)	Conversion [a] (%)	$M_{n,th}$ [b] (g mol^{-1})	$M_{n,SEC}$ [c] (g mol^{-1})	$Đ$
1	-	2	22	-	192000	1.62
2		4	30	-	183000	1.44
3		8	80	-	221000	1.36
4		16	95	-	225000	1.40
5		24	95	-	200000	1.82
6	50000	2	36	18000	22100	1.03
7		8	80	39800	40100	1.03
8		24	93	46200	47800	1.13
9	20000	1.5	13	2500	4700	1.21
10		2	15	3100	6300	1.18
11		4	43	8700	10400	1.17
12		7	58	11700	13200	1.15
13		16	75	15100	14800	1.33
14		24	80	16100	18200	1.23
15	6000	4	27	1700	5100	1.14
16		7	42	2600	4000	1.19
17		16	60	3700	5100	1.19
18		24	66	4000	5100	1.26

[a]calculated by ^{1}H NMR, [b]$M_{n,th}=[NVF]_0/[CTA1]_0 * M_{NVF} * Conv. + M_{CTA1}$, [c]$M_{n,SEC}$ measured with RI-MALS detection. M_{NVF} =71 g mol^{-1}; M_{CTA1} =161 g mol^{-1}.

Table S2. RAFT polymerization of NVF at 35°C in DMSO aiming for different $M_{n,th}$. $[V\text{-}70]_0/[CTA1]_0 = 0.33$. $[NVF]_0 = 4.5$ mol L^{-1} (30% wt NVF in DMSO).

Entry	Targeted M_n (g mol^{-1})	Time (h)	Conversion [a] (%)	$M_{n,th}$ [b] (g mol^{-1})	$M_{n,SEC}$ [c] (g mol^{-1})	$Đ$
1	100000	4	20	20300	17300	1.34
2		8	33	33300	29100	1.32
3		16	42	42400	43600	1.28
4		24	58	58500	53200	1.38
5	50000	2	14	7100	10700	1.18
6		4	24	12000	14600	1.19
7		8	43	21400	23300	1.12
8		16	57	28400	29600	1.19
9		24	66	32800	34300	1.19
10	10000	2	27	2800	5300	1.12
11		4	46	4700	5400	1.11
12		8	70	7100	8400	1.07
13		16	84	8400	9300	1.13
14		24	89	8900	8400	1.23
15	5000	2	35	1900	2600	1.12
16		4	57	2900	4300	1.01
17		8	79	4000	5900	1.10
18		16	90	4500	6200	1.05
19		24	92	4600	5300	1.03

[a]calculated by ^{1}H NMR, [b] $M_{n,th}=[NVF]_0/[CTA1]_0*M_{NVF}*Conv.+M_{CTA1}$, [c] $M_{n,SEC}$ measured with a RI-MALS detection. M_{NVF}=71 g mol^{-1}; M_{CTA1}=161 g mol^{-1}.

Table S3. RAFT polymerization of NVF at 35°C in DMSO aiming for $M_{n,th.}$= 100 kg mol^{-1}. $[NVF]_0 = 4.5$ mol L^{-1}, $[CTA1]_0 = 3.2$ mmol L^{-1}, $[V\text{-}70]_0 = 2.7$ mmol L^{-1}.

Entry	Targeted M_n (g mol^{-1})	Time (h)	Conversion [a] (%)	$M_{n,th}$ [b] (g mol^{-1})	$M_{n,SEC}$ [c] (g mol^{-1})	$Đ$
1	100000	2	18	18100	20700	1.31
2		4	32	32100	39200	1.19
3		8	51	51100	53900	1.18
4		16	79	79000	74300	1.22
5		24	87	87000	79500	1.22

[a]calculated by ^{1}H NMR, [b] $M_{n,th}=[NVF]_0/[CTA1]_0*M_{NVF}*Conv.+M_{CTA1}$, [c] $M_{n,SEC}$ measured with a RI-MALS detection. M_{NVF}=71 g mol^{-1}; M_{CTA1}=161 g mol^{-1}.

Table S4. Block polymerization of NVF at 35°C in DMSO using PDMA-CTA2, PVCL-CTA2 and PNIPAAm-CTA2 as macro-RAFT agents. $[NVF]_0 = 4.5$ mol L^{-1}. $[V\text{-}70]_0/[\text{macro-CTA}]_0 = 0.33$.

Entry	Polymer	Target. M_n (g mol^{-1})	Time (h)	Conv.[a] (%)	$M_{n,th}$ [b] (g mol^{-1})	$M_{n,SEC}$ [c] (g mol^{-1})	$Đ_{SEC}$	$M_{n,A4F}$ [c] (g mol^{-1})	$Đ_{AF4}$
1	PDMA-CTA2	5000	16	99	5000	6200	1.30	9900	1.23
2	PDMA-*b*-PNVF	32700	16	83	28100	-	-	28900	1.21
3	PVCL-CTA2	5000	16	99	5000	6400	1.11	6000	1.04
4	PVCL-*b*-PNVF	36000	16	82	30600	-	-	37200	1.27
5	PNIPAAm-CTA2	5000	16	99	5000	6300	1.31	9800	1.28
6	PNIPAAm-*b*-PNVF	40300	16	81	33800	-	-	46800	1.18

[a]calculated by ^{1}H NMR. [b]$M_{n,th}=[\text{Monomer}]_0/[\text{macro-CTA}]_0 * M_{Monomer} * \text{Conv.} + M_{n,macro\text{-}CTA}$; [c] measured with a RI-MALS detection.

Table S5. ^{1}H DOSY-NMR analysis data of the block copolymers and their first block.

Entry	Polymer	$M_{n,SEC}$[a] ($M_{n,A4F}$[a]) (g mol^{-1})	Diffusion coefficient of first block[b] (µm² s^{-1})	Diffusion coefficient of second block[b] (µm² s^{-1})
1	PDMA-CTA2	6200 (9900)	33.2 ± 0.4 (c)	-
2	PDMA-*b*-PNVF	(28900)	4.0 ± 0.6 (c)	3.8 ± 0.4 (f+g)
3	PVCL-CTA2	6400 (6000)	58 ± 3 (c)	-
4	PVCL-*b*-PNVF	(37200)	2.5 ± 0.3 (a+e+f)	2.5 ± 0.3 (h+i)
5	PNIPAAm-CTA2	6300 (9800)	32.6 ± 0.5 (e)	-
6	PNIPAAm-*b*-PNVF	(46800)	3.4 ± 0.6 (e)	2.9 ± 0.4 (h+i+c)

[a] measured with a RI-MALS detection; [b] determined by DOSY-NMR technique applied on the attributed ^{1}H NMR signals of Fig. 6 for PDMA-CTA2 and PDMA-*b*-PNVF and of Fig. S4 for the two other copolymers.

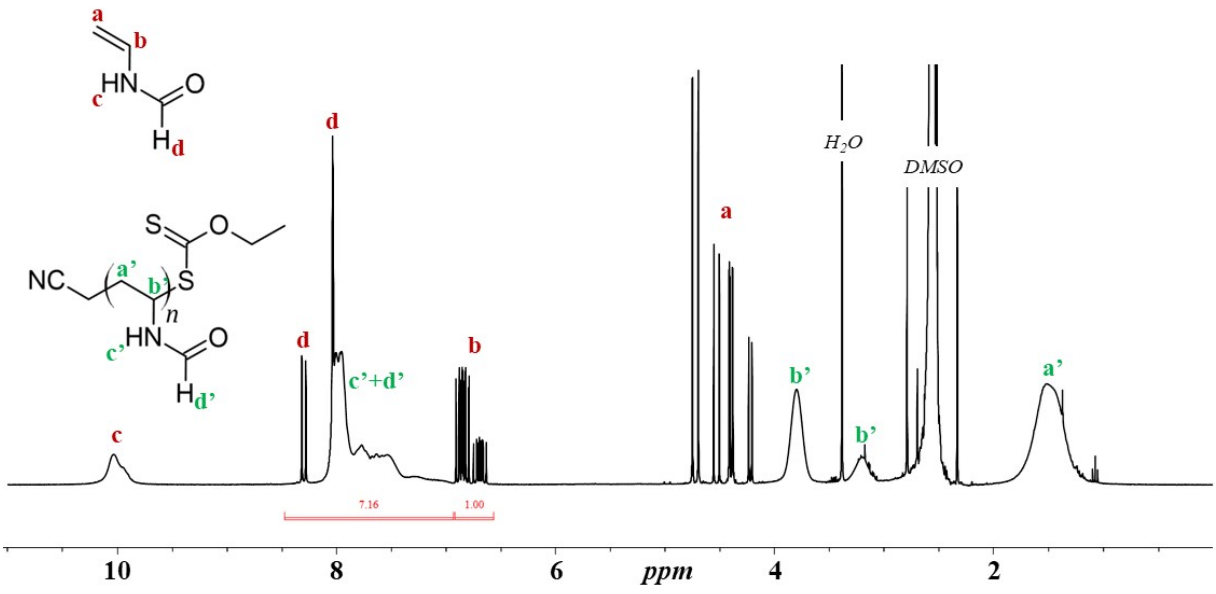
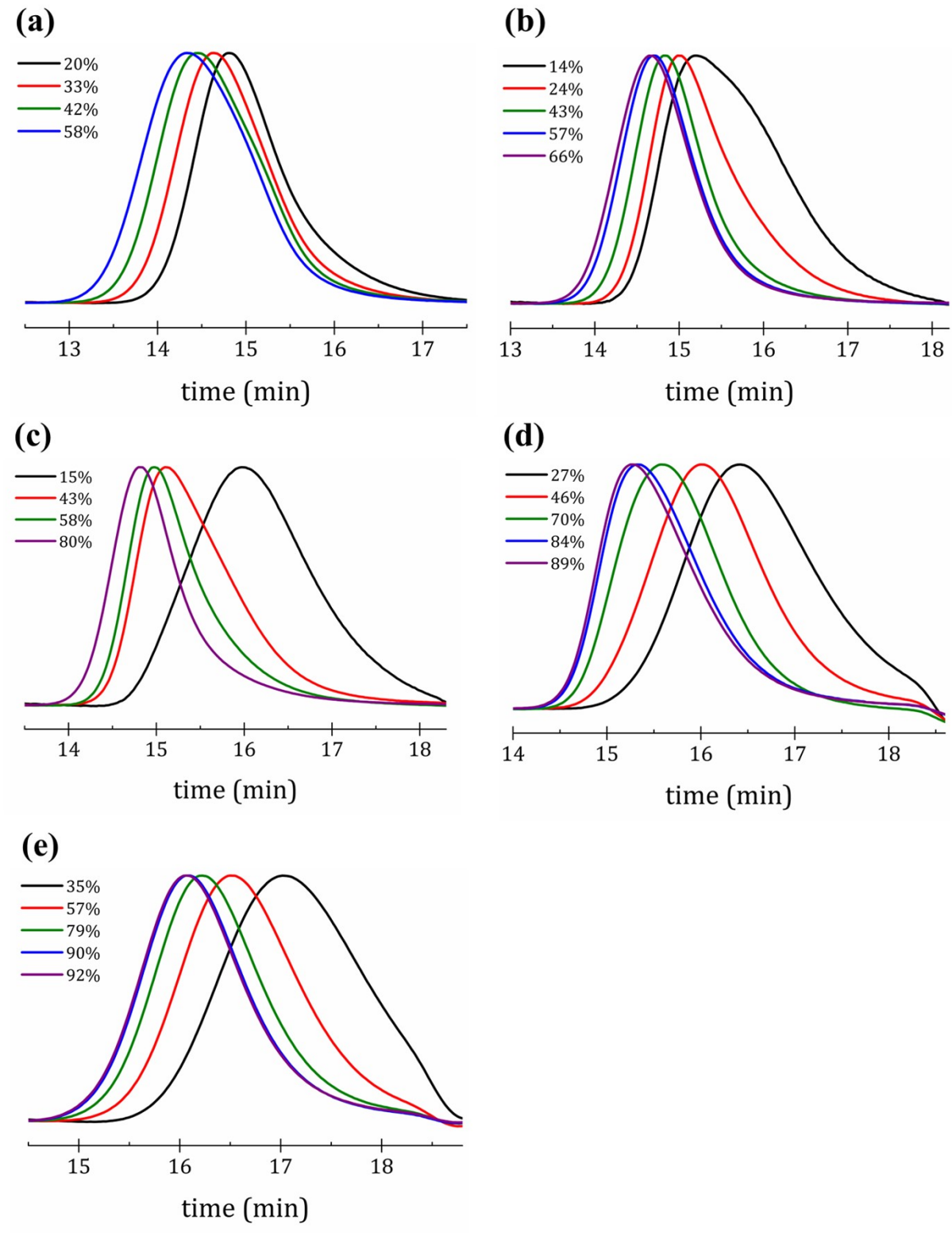


Fig. S1. ^{1}H NMR spectrum of a crude mixture of NVF polymerization with CTA1 (Table S1 entry 13). Measured on a 300MHz apparatus.

$$Conversion\ (\%) = \frac{\left(d + c^{'} + d^{'}\right) - b}{\left(d + c^{'} + d^{'}\right) + b} \times 100$$



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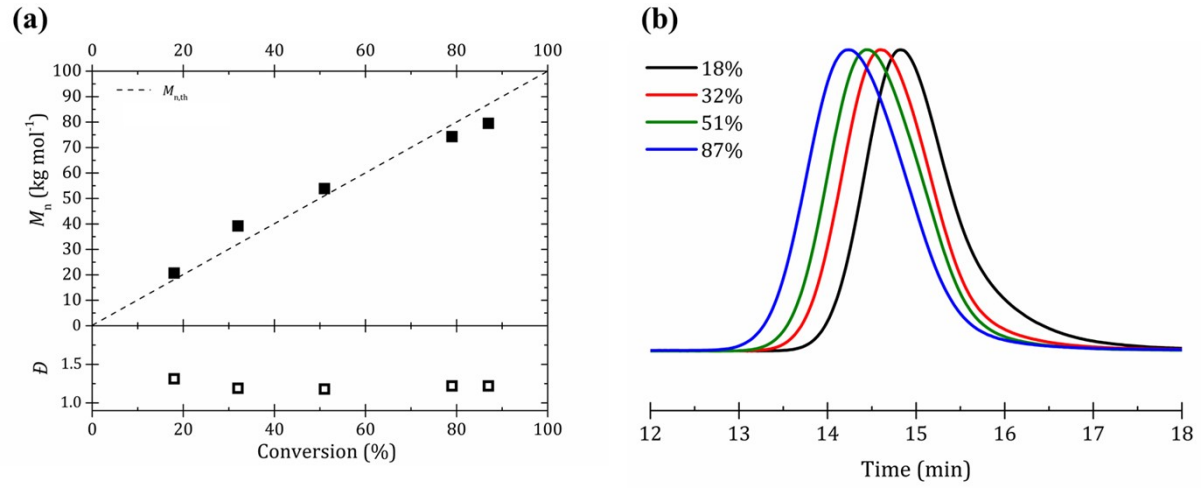

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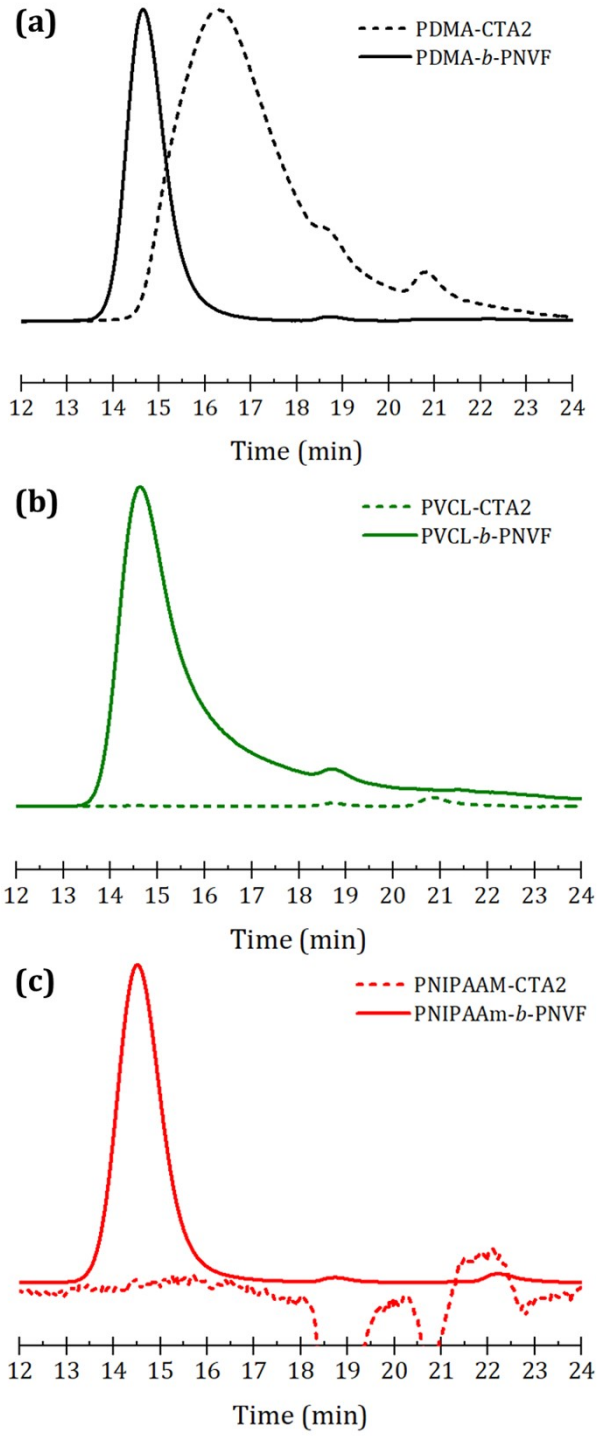

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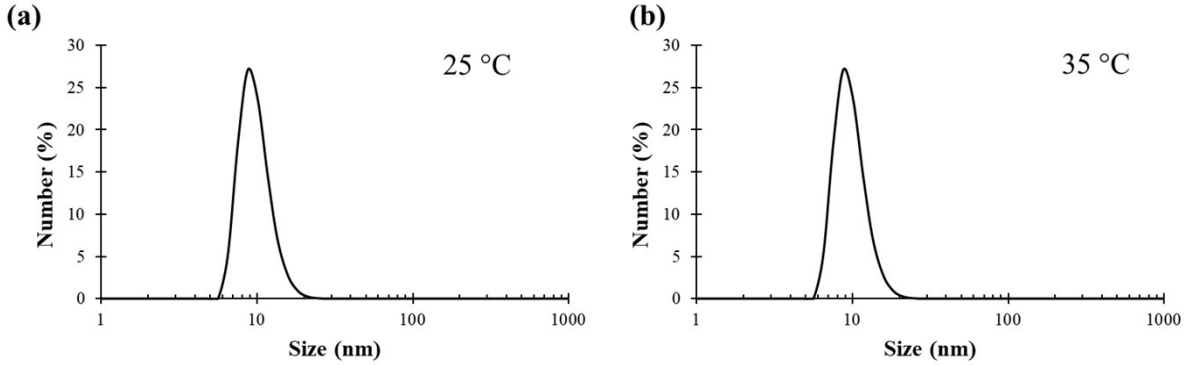

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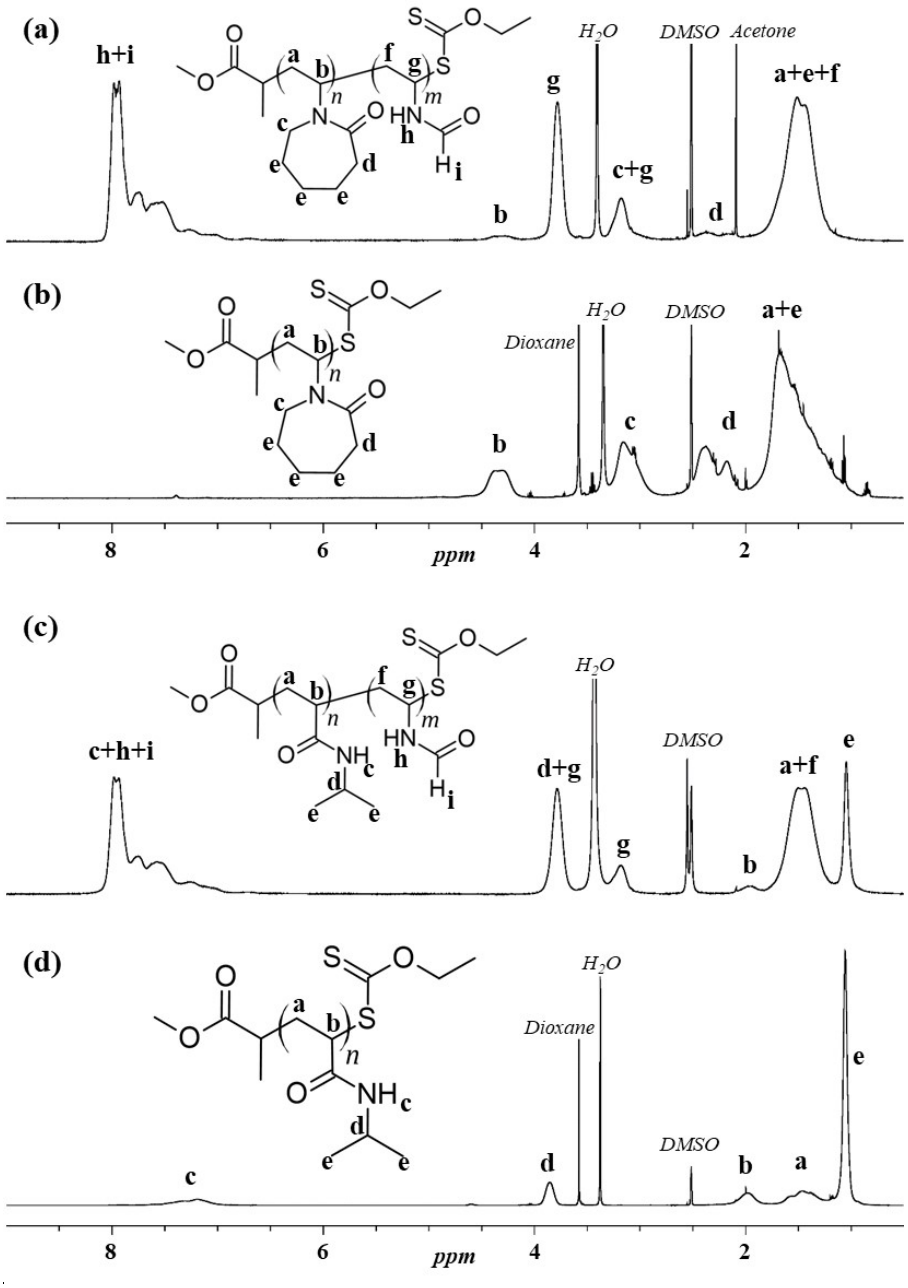

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