Electronic Supplementary Material (ESI) for Polymer Chemistry

No Matter the Order of Monomer Addition For the Synthesis of Well-Defined Block Copolymers by Sequential Group Transfer Polymerization Using *N*-Heterocyclic Carbenes as Catalysts

Jean Raynaud,[a,b] Na Liu,[a,b] Maréva Fèvre,[a,b] Yves Gnanou [a,b] and Daniel Taton*[a,b]

[a] *Centre National de la Recherche Scientifique, Laboratoire de Chimie des Polymères Organiques, 16 avenue Pey-Berland, F-33607 Pessac cedex, France; E-mail: taton@enscbp.fr*

[b] *Université de Bordeaux, Laboratoire de Chimie des Polymères Organiques, IPB-ENSCBP, F-33607 Pessac cedex, France*

SUPPLEMENTARY INFORMATION

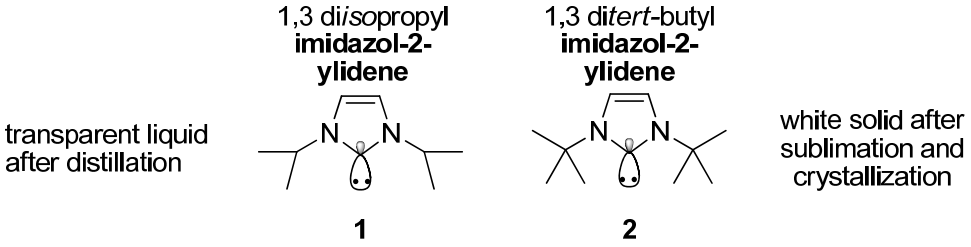
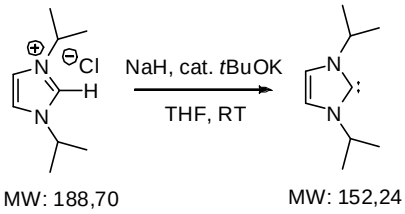


Figure 1. Two NHCs synthesized from the "imidazol-2-ylidene" family

1,3-diisopropyl imidazol-2-ylidene (1). A 150-mL round-bottom flask equipped with a stir bar was charged with 2.0 g (10.6 mmol) of 1,3-di*iso*propyl imidazolium chloride, solid potassium *tert*-butoxide (90 mg, 0.8 mmol) and sodium hydride (600 mg, corresponding to 15 mmol of pure NaH) as a 60%wt dispersion in silicon oil. The flask was kept under vacuum. Then, 20 mL of freshly distilled THF were added dropwise to the suspension at room temperature. A dark gray solution was obtained immediately. The mixture was stirred for 5 h, then filtrated under vacuum (fritted glass filter, porosity G5) and volatiles were removed under vacuum. The obtained pale viscous liquid was subsequently distilled under vacuum to provide NHC **1** as a clear liquid (1.3 g, 81% yield): ^{1}H NMR (THF-d_8) δ 1.45 (s, C$\underline{H}_3$, 12 H), 4.45 (m, C$\underline{H}$(CH$_3$)$_2$, 2 H), 6.95 (s, NC$\underline{H}$C, 2 H); ^{13}C NMR δ 24.8 (s, $\underline{C}$H$_3$), 52.9 (s, $\underline{C}$H-(CH$_3$)$_2$), 116.5 (s, N$\underline{C}$HC), 212.9 (s, N$\underline{C}$N).



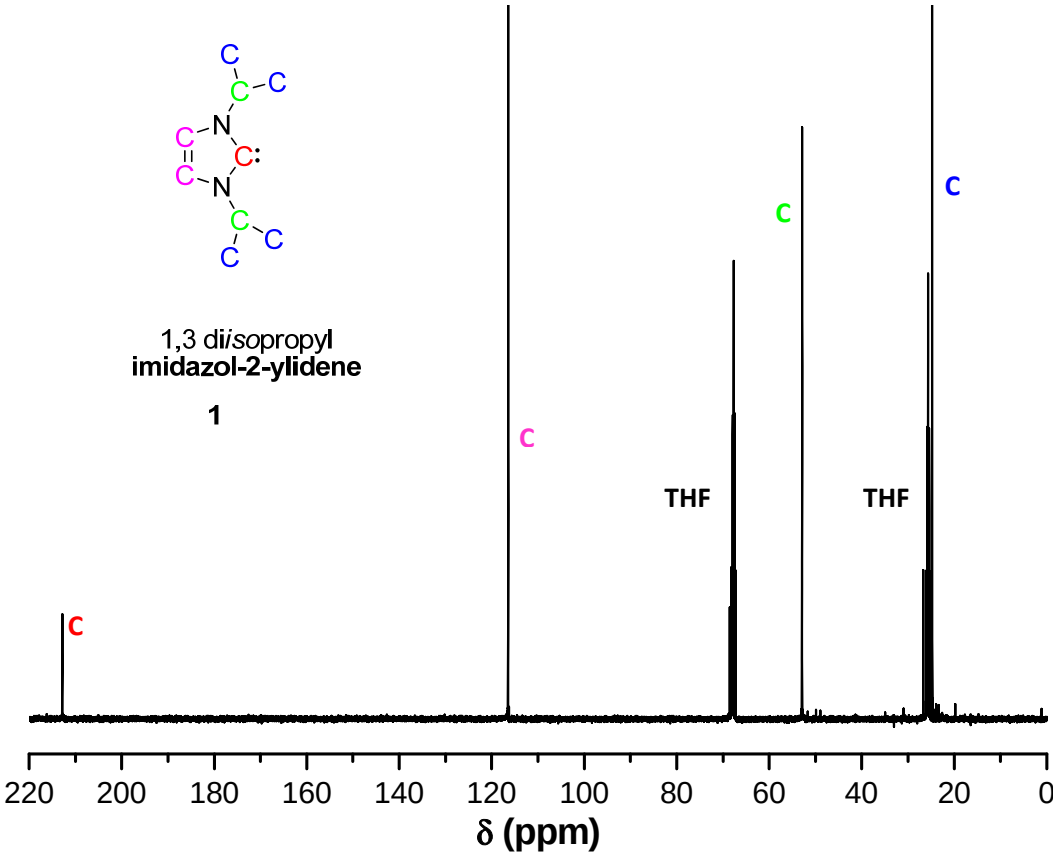


Figure 2. NMR ^{13}C (THF-d_8) of 1,3 di*iso*propyl imidazol-2-ylidene (NHC **1**)

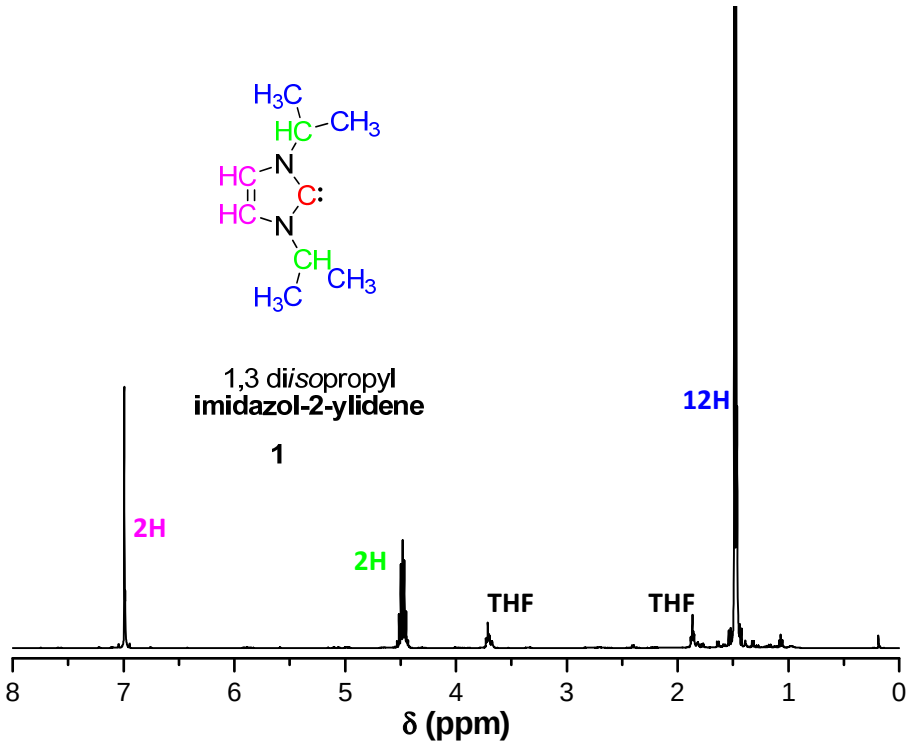
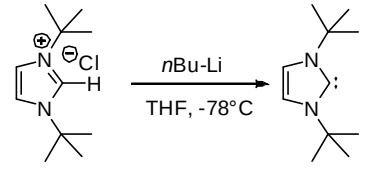


Figure 3. NMR ^{1}H (THF-d_8) of 1,3 di*iso*propyl imidazol-2-ylidene (NHC **1**)

1,3-ditert-butyl imidazol-2-ylidene (2). A 150-mL round-bottom flask equipped with a stir bar was charged with 2.0 g (9.2 mmol) of 1,3-di*tert*-butyl imidazolium chloride, and 20 mL of freshly distilled THF. The dispersion was stirred for 0.5h. Then, 7 mL of a 2M solution of *n*Bu-Li in cyclohexane (14 mmol) was added dropwise at -78°C. A turbid solution was obtained immediately. The mixture was allowed to warm up and stirred for 2 h, then filtrated under vacuum (fritted glass filter, porosity G5) and volatiles were removed under vacuum. The obtained pale solid was subsequently sublimed under vacuum to provide NHC **2** as a white crystalline solid (1.3 g, 78% yield): ^{1}H NMR (THF-d_8) δ 1.6 (s, C*H*$_3$, 18 H), 7.15 (s, NC*H*C, 2 H); ^{13}C NMR δ 31.8 (s, -*C*H$_3$), 56.3 (s, *C*(CH$_3$)$_3$), 115.7 (s, N*C*HC), 213.4 (s, N*C*N).



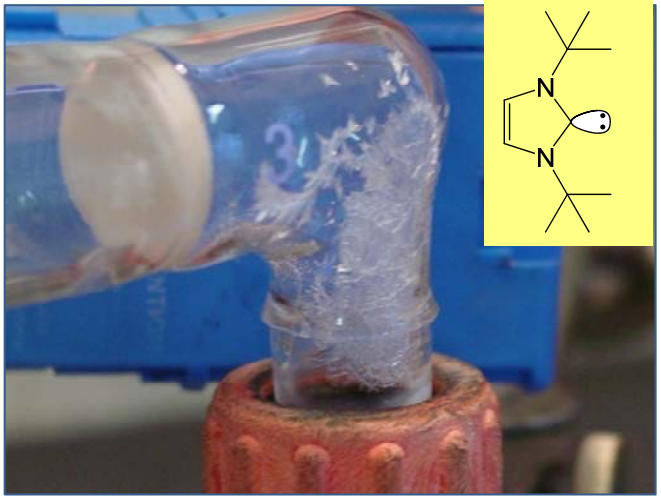


Figure 4. Crystallization of the NHC 2 after the fritted filter

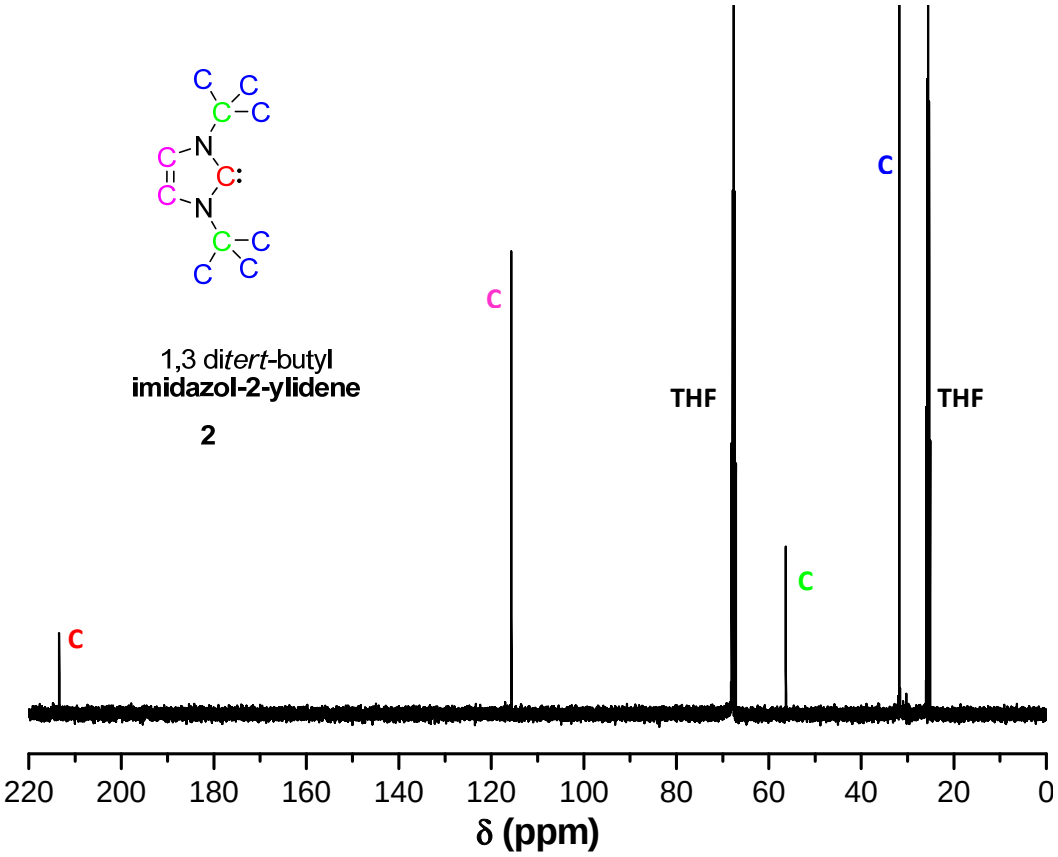


Figure 5. NMR ^{13}C (THF-d_8) of 1,3 di*tert*-butyl imidazol-2-ylidene (NHC **2**)

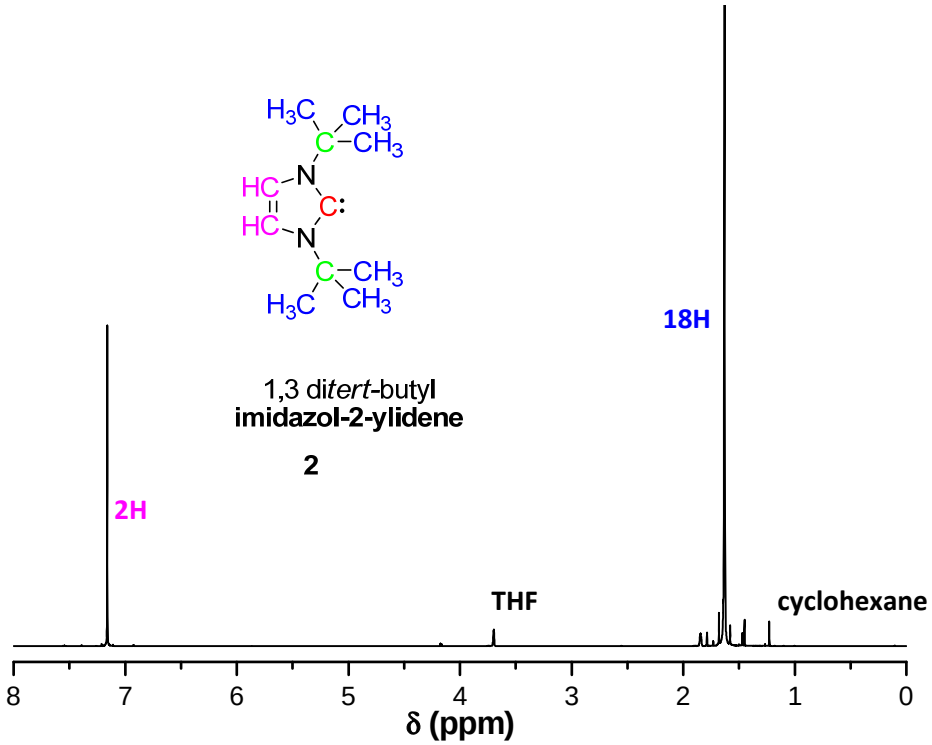


Figure 6. NMR ^{1}H (THF-d_8) of 1,3 di*tert*-butyl imidazol-2-ylidene (NHC **2**)

Table 1 Characteristics of block copolymers obtained via sequential group transfer polymerization in THF using NHCs as catalyst s and MTS as initiator

Exp.	Monomer	[M] (mmol)	[NHC1] (µmol)	[MTS] (mmol)	M_n th.[a] (g/mol)	M_n exp.[b] (g/mol)	NMR[c] M_n^{exp}(g/mol)	Time (h)	D[d] (M_w/M_n)
1[f]	*t*BA	27	6	0.25	14200	14100*(THF)	14800	4	1.22
	DMA	19			21800	23700*(THF)	21300	48	1.2
2	*t*BA	10	6	0.25	5300	5800*(THF)	5500	4	1.19
	MMA	12			10300	11500*(THF)	11900	48	1.27
3	nBA	10	5 NHC**2**	0.25	5300	5200*(THF)	5400	3	1.35
	MMA	12			10300	9800*(THF)	10500	48	1.4
4[f]	*t*BA	20	2.5	0.1	26000	28500*(THF)	30000	5	1.24
	DMAEMA	9			40000	36000*(THF)	36700	96	1.23
5[f]	MMA	25	12.5	0.25	10000	9300*(THF)	9300**	3	1.1
	DMA	29			19300	23000(THF)	16900	96	1.09
6	DMA	19	12.5	0.25	7600	79400(DMF)	6600	24	1.31
	DMAEMA	27			24400	126000(DMF)	17600	216	1.4
7	DMA	39	12.5	0.25	15400	20600(DMF)	12400	24	1.15
	MMA	38			30600	87500(DMF)	23900	120	1.3
8	DMAEMA	12	12.5	0.25	7500	8800(DMF)	6300	18	1.16
	DMA	42			24000	31000(DMF)	13000	216	1.29
9	MMA	35	12.5	0.25	13800	11200*(THF)	11200**	3	1.07
	DMAEMA	18			25000	26000(DMF)	22000	72	1.1
10	MMA	37	25	0.5	7500	6400*(THF)	6400**	3	1.12
	DMAEA	20			13200	8300(DMF)	11000	96	1.3
11	DMAEMA	9	12.5	0.25	5800	2000(DMF)	3400	24	1.24
	DMAEA	10			11500	6200(DMF)	4800	72	1.21
12[f]	MMA	100	12.5	0.25	40000	43000(THF)	43000**	24	1.08
	MAN	100			67000	71000(THF)	-	72	1.18
13	MMA	7.5	11.6	0.23	3300	3000	3200	24	1.16
	*t*BA	5.5			4500	4100	4600	72	1.12
	DMA	4.8			5500	5200	5300	168	1.09

[a] M_n^{theo} are obtained by calculation, 2nd value being systematically the sum of both blocks. [b] M_n^{exp} are determined by SEC in DMF (PS calibration), or in THF (*) (PMMA calibration) for PMMA blocks. [c] ^{1}H NMR has been used to determine block molar masses when chain ends (MTS remains) were identifiable. ** M_n^{exp} of PMMA's obtained by SEC in THF (PMMA calilbration) are re-used for the ^{1}H NMR calculation of both block molar masses. [d] SEC analyses in THF or in DMF, according the nature of the polymer have been used. [f] The first block (PMMA or P*t*BA) has voluntarily been chosen long enough to allow the block copolymerization in THF, without need of DMF addition during the overall synthesis.

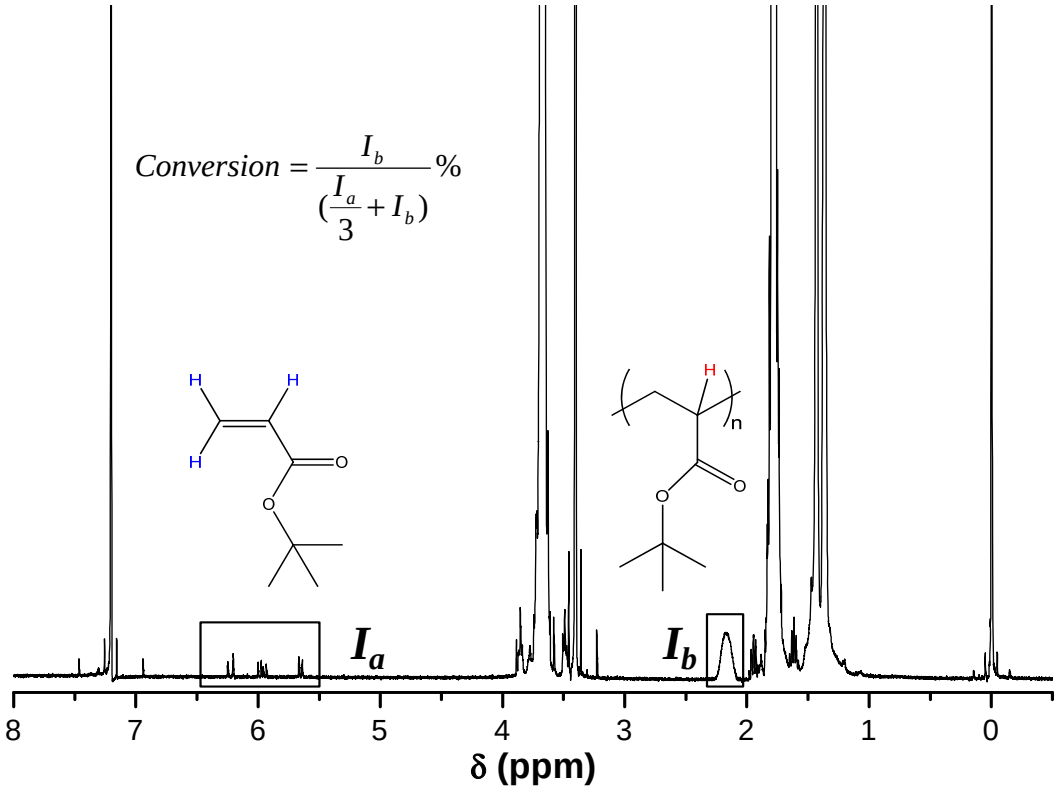


Figure 7. NMR ^{1}H ($CDCl_3$) to determine the monomer conversion during GTP of *t*BA catalyzed by NHC **1** or **2** in THF

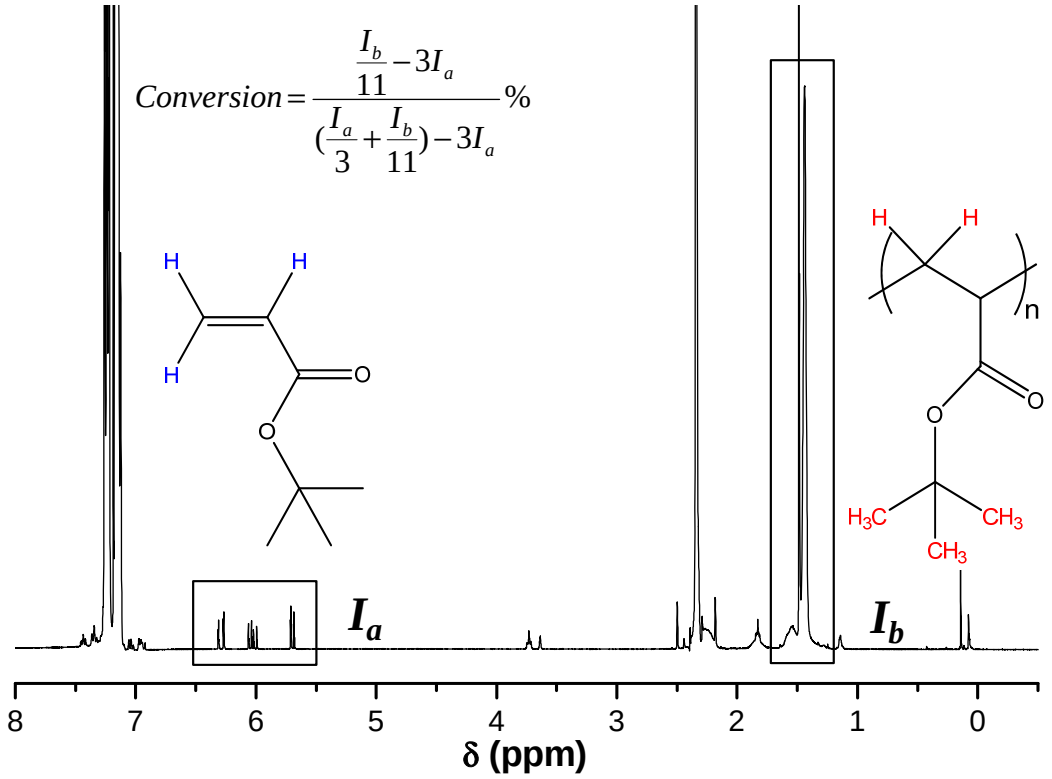


Figure 8. NMR ^{1}H ($CDCl_3$) to determine the monomer conversion during GTP of *t*BA catalyzed by NHC **1** or **2** in toluene

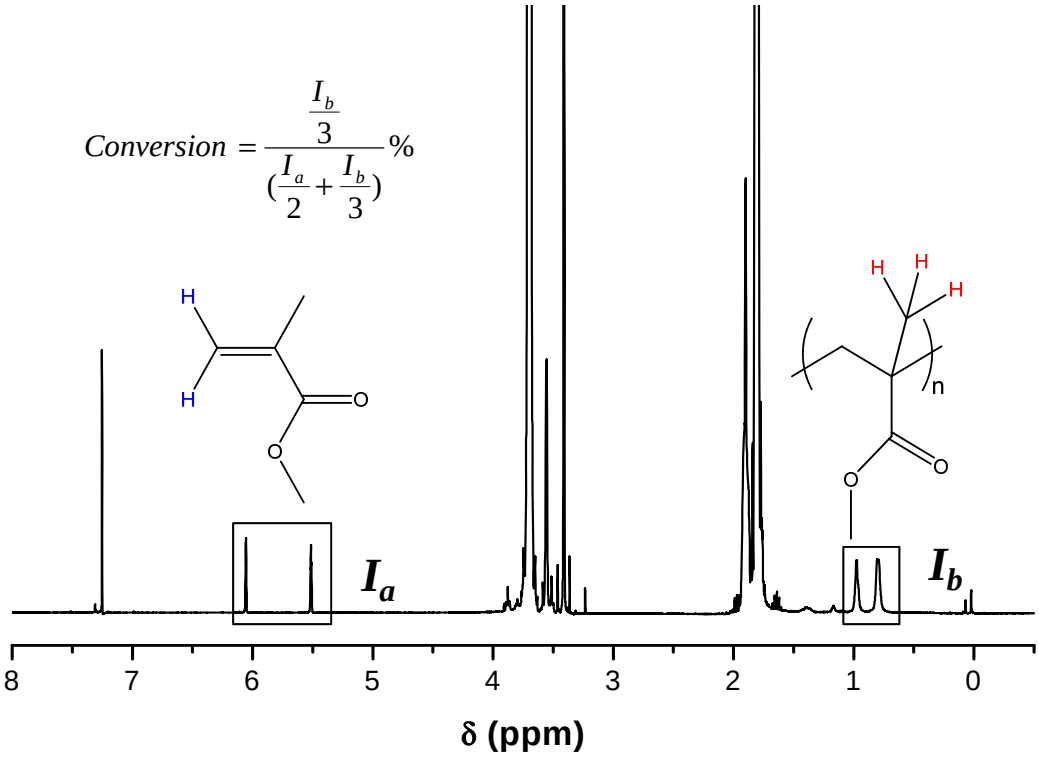


Figure 9. NMR ^{1}H ($CDCl_3$) to determine the monomer conversion during GTP of MMA catalyzed by NHC **1** or **2** in THF

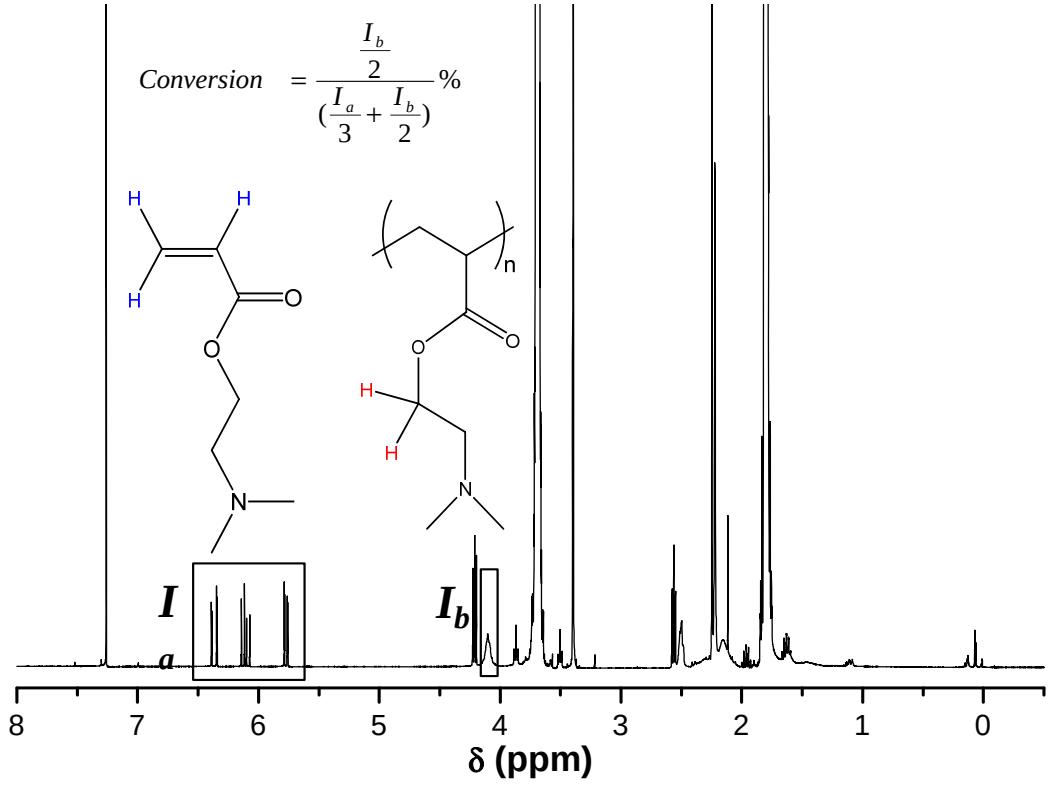


Figure 10. NMR ^{1}H ($CDCl_3$) to determine the monomer conversion during GTP of DMAEA catalyzed by NHC **1** or **2** in THF

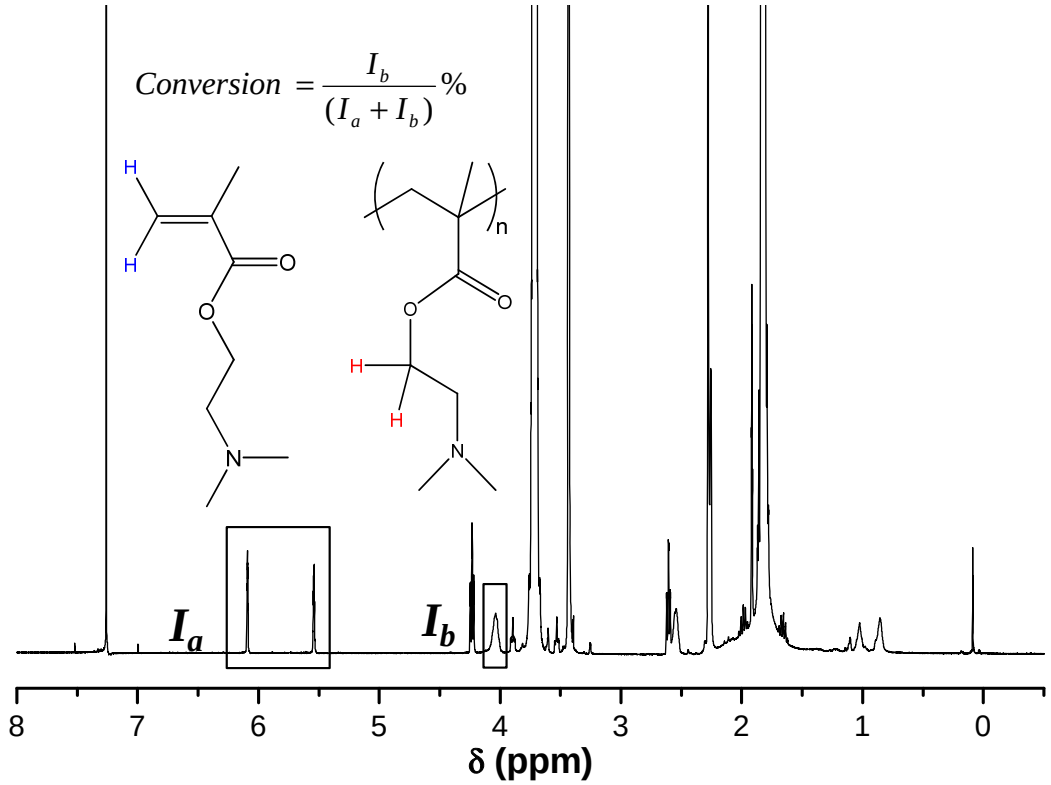


Figure 11. NMR ^{1}H ($CDCl_3$) to determine the monomer conversion during GTP of DMAEMA catalyzed by NHC **1** or **2** in THF

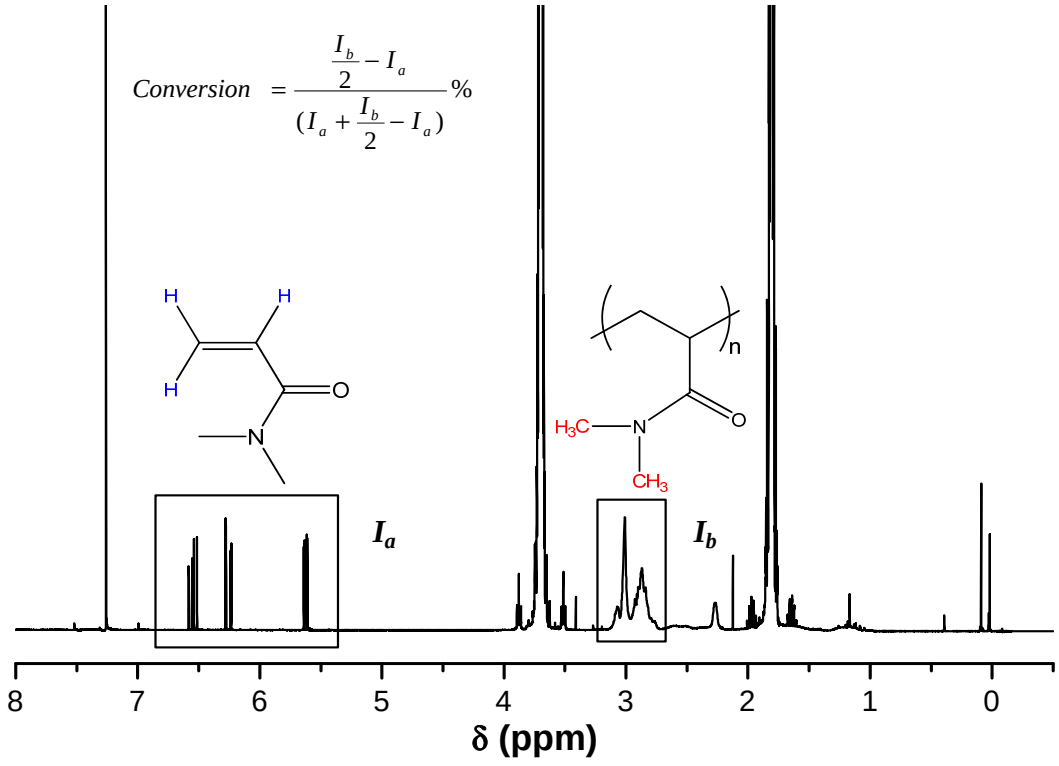


Figure 12. NMR ^{1}H ($CDCl_3$) to determine the monomer conversion during GTP of DMA catalyzed by NHC **1** or **2** in THF

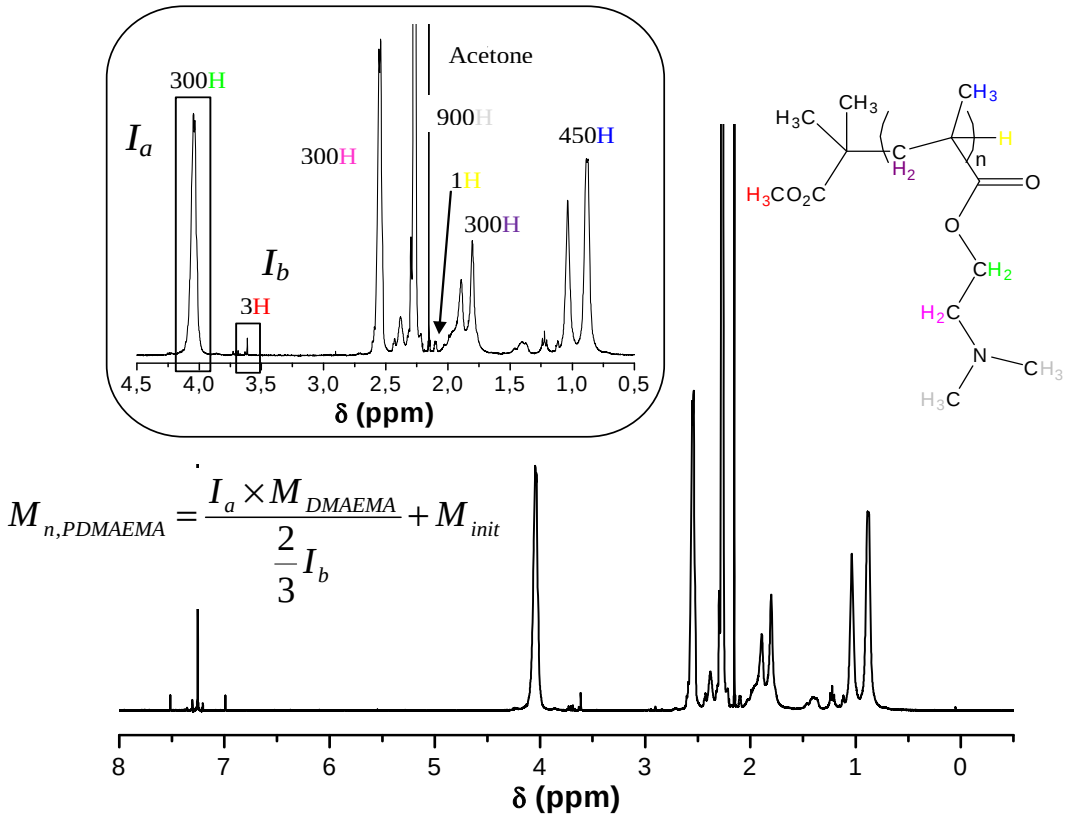


Figure 13. NMR ^{1}H ($CDCl_3$) of PDMAEMA, determination of its molar mass (equation)

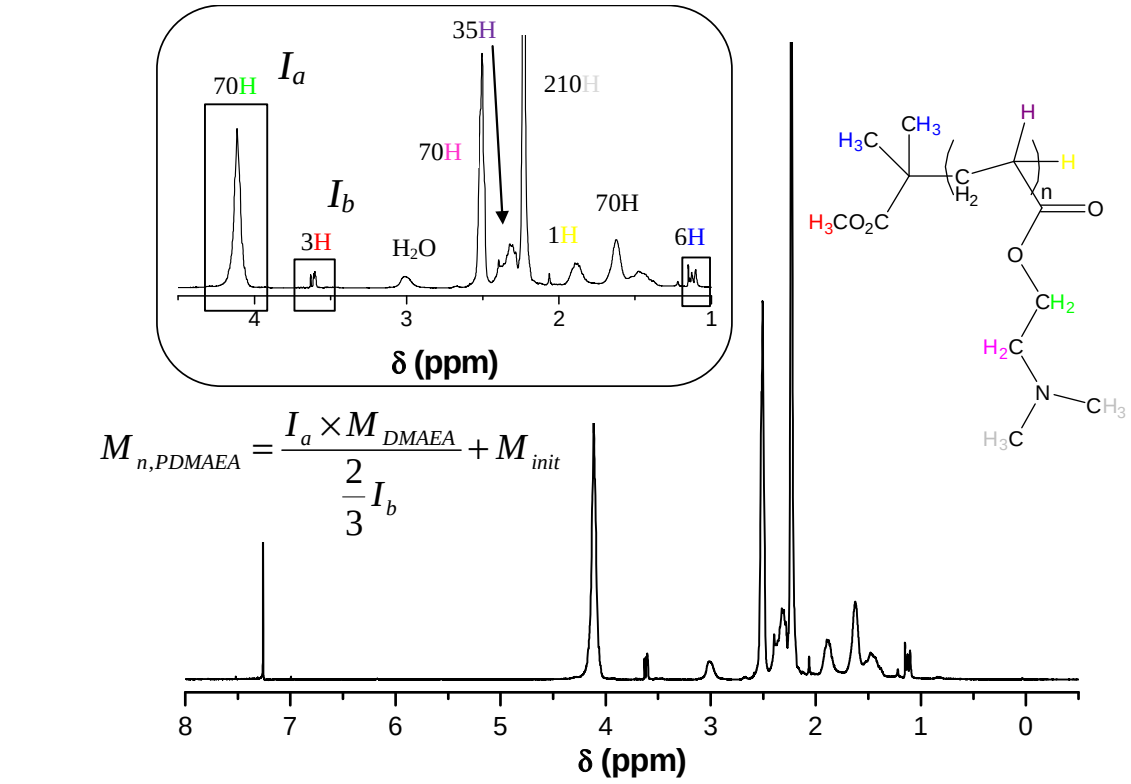
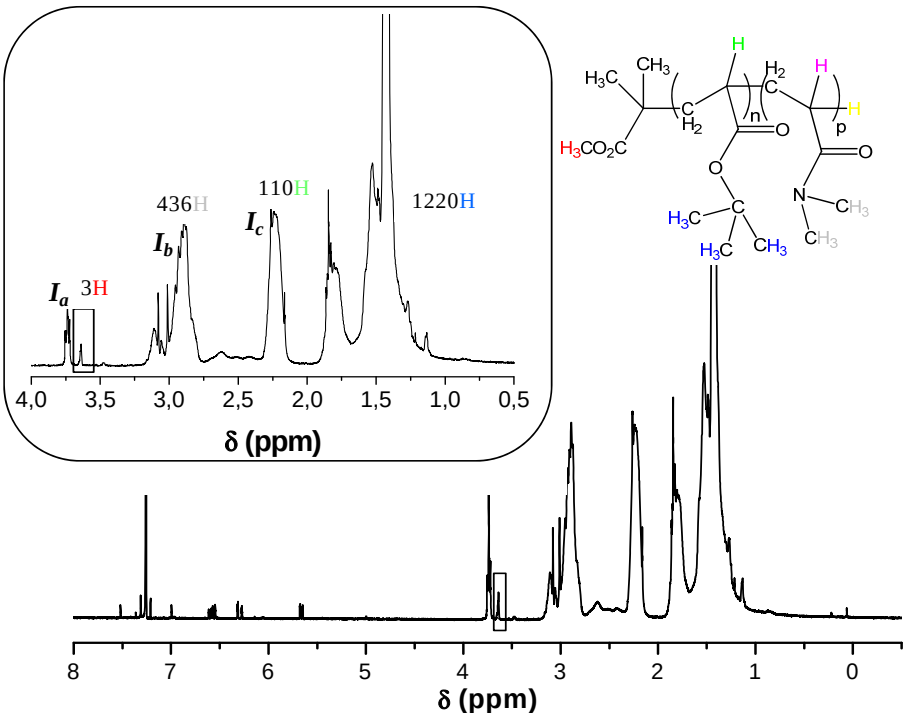
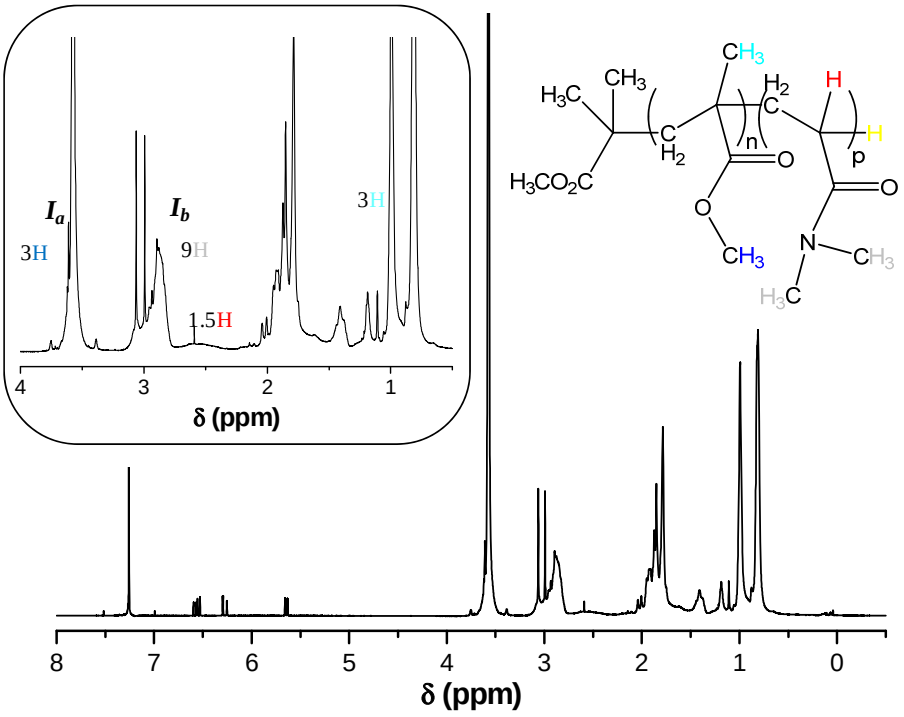


Figure 14. NMR ^{1}H ($CDCl_3$) of PDMAEA, determination of its molar mass (equation)



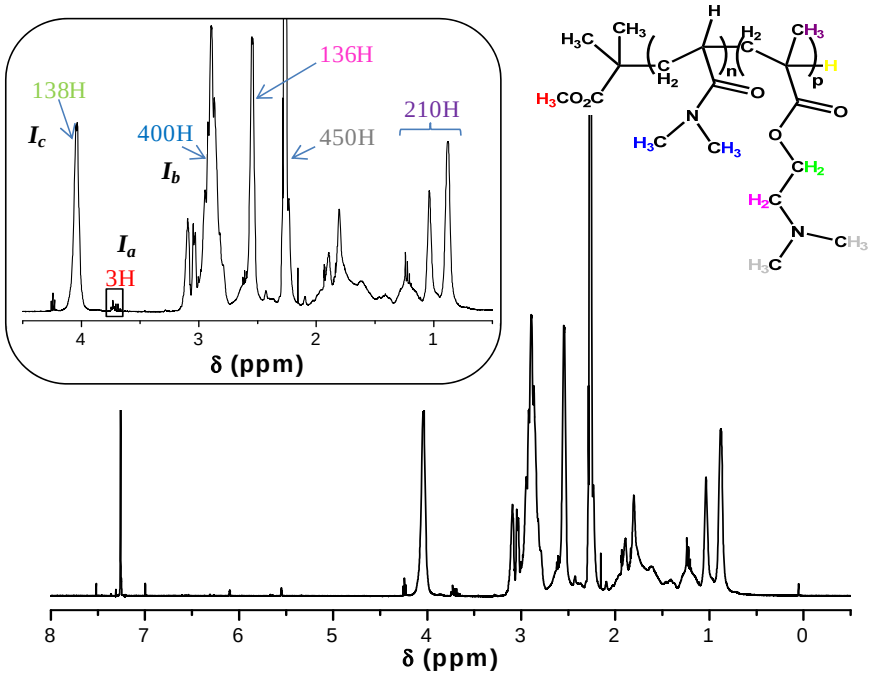
$$M_{n,block(PtBA)} = \frac{3I_c \times M_{tBA}}{I_a} \qquad M_{n,block(PDMA)} = \frac{I_b \times M_{DMA}}{2I_a}$$

Figure 15. NMR ^{1}H ($CDCl_3$) of P*t*BA-*b*-PDMA, determination of the molar mass of each block (equations)



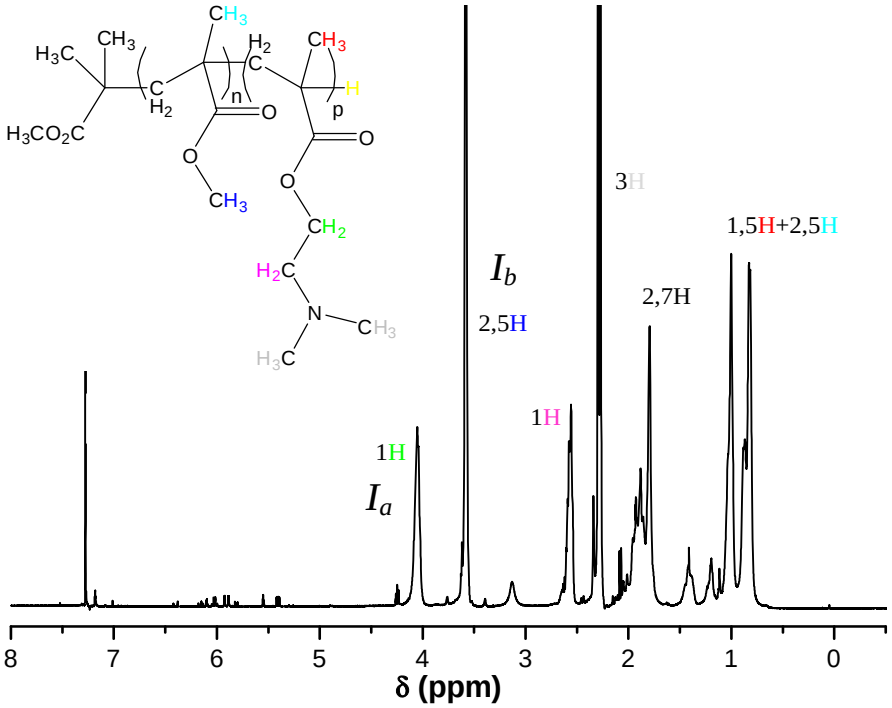
$$M_{n,block(PDMA)} = \frac{I_b \times M_{DMA}}{2 \times I_a} \times \frac{M_{n,block(PMMA)obtained\_by\_SEC}}{M_{MMA}}$$

Figure 16. NMR ^{1}H ($CDCl_3$) of PMMA-*b*-PDMA, determination of the molar mass of the PDMA block (equation)



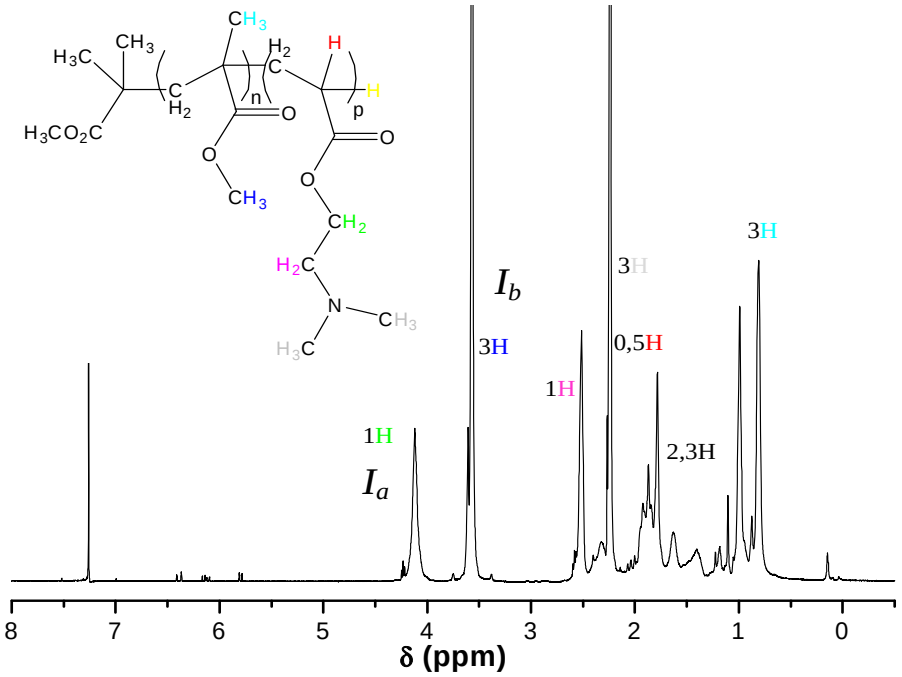
$$M_{n,block(PDMAEMA)} = \frac{I_c \times M_{DMAEMA}}{\frac{2}{3} I_a} \quad M_{n,block(PDMA)} = \frac{I_b \times M_{DMA}}{2 I_a}$$

Figure 17. NMR ^{1}H ($CDCl_3$) of PMADAME-*b*-PDMA, determination of the molar mass of each block (equations)



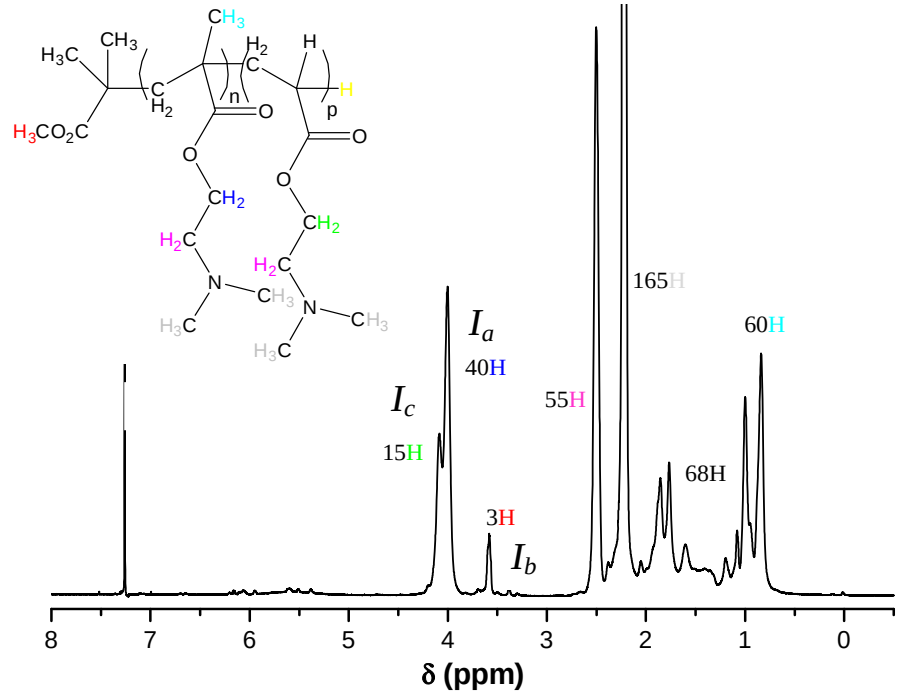
$$M_{n,block(PDMAEMA)} = \frac{I_a \times M_{DMAEMA} \times 3}{2 \times I_b} \times \frac{M_{n,block(PMMA)obtained\_by\_SEC}}{M_{MMA}}$$

Figure 18. NMR ^{1}H ($CDCl_3$) of PMMA-*b*-PMADAME, determination of the molar mass of the PMADAME block (equation)



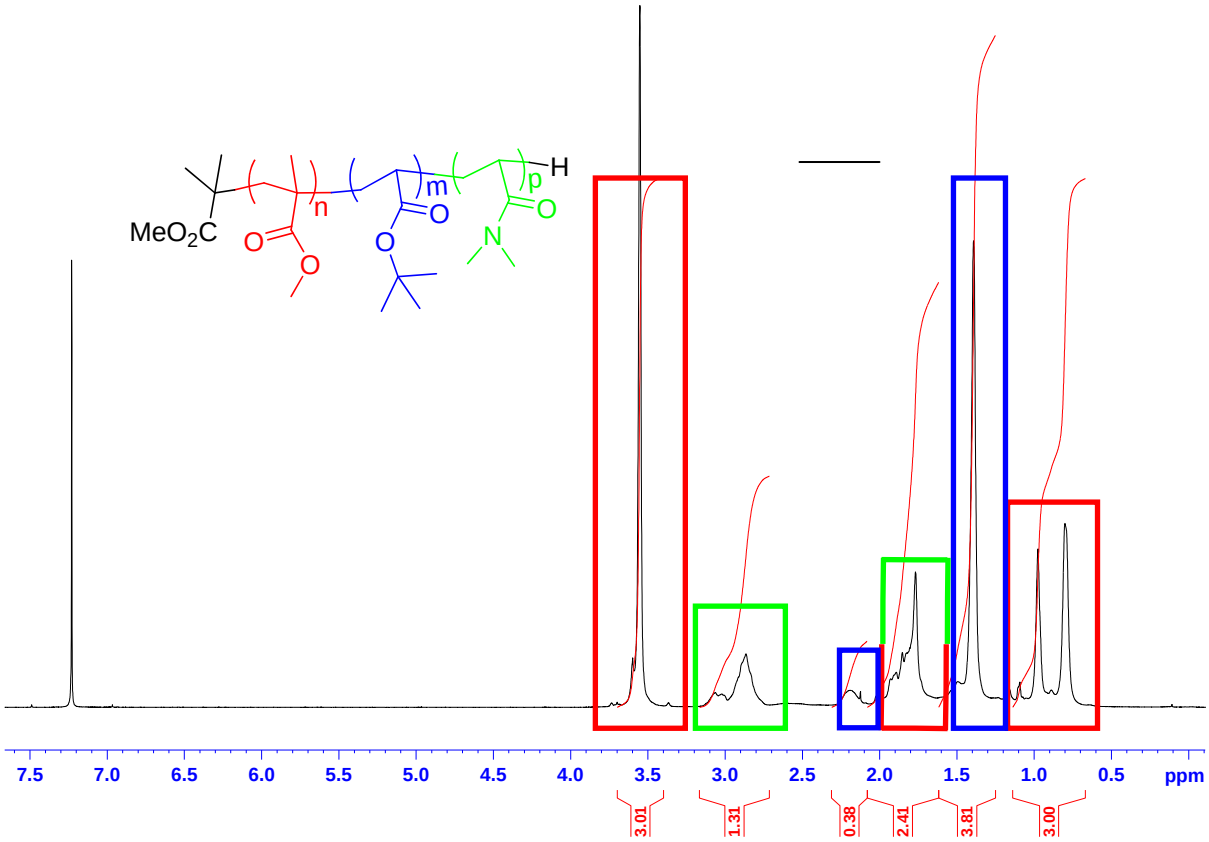
$$M_{n,block(PDMAEA)} = \frac{I_a \times M_{DMAEA} \times 3}{2 \times I_b} \times \frac{M_{n,block(PMMA)obtained\_by\_SEC}}{M_{MMA}}$$

Figure 19. NMR ^{1}H ($CDCl_3$) of PMMA-*b*-PDMAEA, determination of the molar mass of the PDMAEA block (equation)



$$M_{n,block(PDMAEMA)} = \frac{I_a \times M_{DMAEMA}}{\frac{2}{3} I_b} + M_{init} \quad M_{n,block(PDMAEA)} = \frac{I_c \times M_{DMAEA}}{\frac{2}{3} I_b}$$

Figure 20. NMR ^{1}H ($CDCl_3$) of PDMAEMA-*b*-PDMAEA, determination of the molar mass of each block (equations)



$$M_{n,block(PDMA)} = \frac{I_{green} \times M_{DMA} \times 3}{6 \times I_{red}} \times \frac{M_{n,block(PMMA)obtained\_by\_SEC}}{M_{MMA}}$$

$$M_{n,block(PtBA)} = \frac{I_{blue} \times M_{tBA} \times 3}{9 \times I_{red}} \times \frac{M_{n,block(PMMA)obtained\_by\_SEC}}{M_{MMA}}$$

Figure 21. NMR ^{1}H ($CDCl_3$) of PMMA-*b*-P*t*BA-*b*-PDMA, determination of the molar mass of each block (equations)

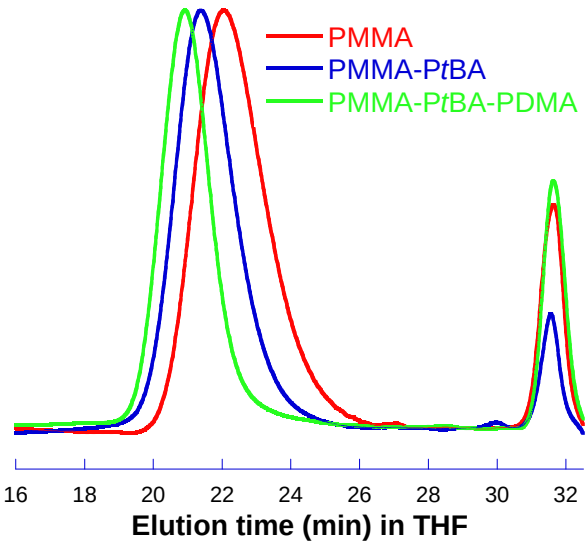


Figure 22. SEC trace (RI detector) of the corresponding triblock PMMA-*b*-P*t*BA-*b*-PDMA