Electronic Supplementary Information

The Influences of Monomer Structure and Solvent on the Radical Copolymerization of Tertiary Amine and PEGylated Methacrylates

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Index

1. Alcoholysis of DMAEMA at 70 °C in ethanol. 3
2. Copolymerization data 4
   2.1. Poly(DEAEMA-*co*-PEGMA$_{23}$) 5
   2.2. Poly(DEAEMA-*co*-EEMA$_1$) 5
   2.3. Poly(DEAEMA-*co*-MMA) 7
   2.4. Poly(DMAEMA-*co*-PEGMA$_9$) 9
   2.5. Poly(DMAEMA-*co*-PEGMA$_{23}$) 11
   2.6. Poly(BMA-*co*-PEGMA$_9$) 13
3. Reactivity ratios for the copolymerizations of TAMAs and methacrylate monomers in different solvents 15

1. Alcoholysis of DMAEMA at 70 °C in ethanol.

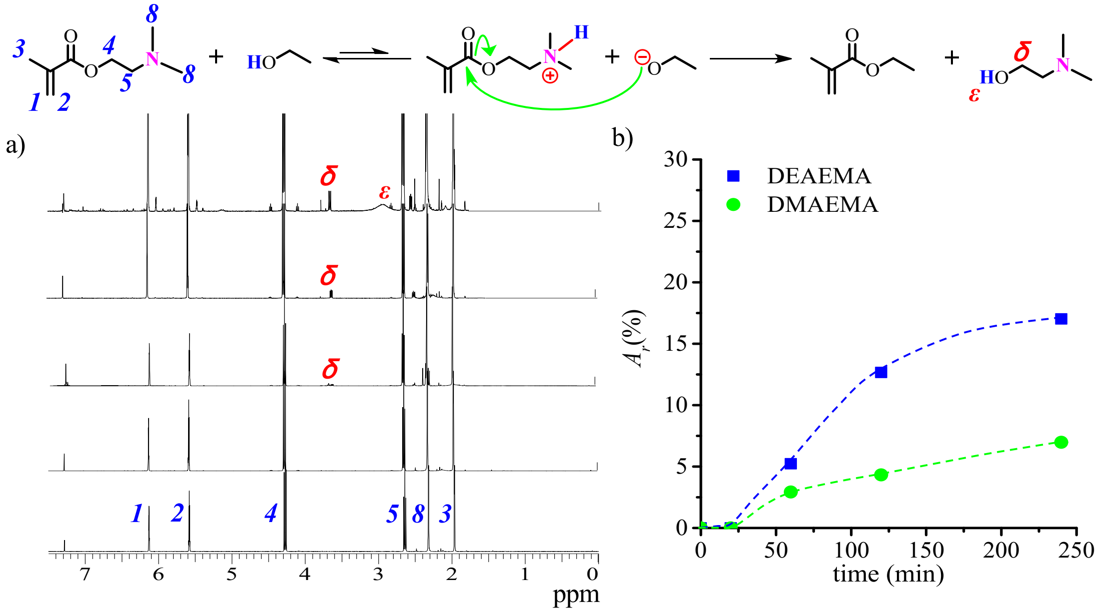

Figure S1. Alcoholysis of DMAEMA at 70 °C in ethanol. a) ^{1}H-NMR spectra of DEAEMA at 4 h, and b) relative degree of alcoholysis (A_r) of DEAEMA and DMAEMA.

2. Copolymerization data

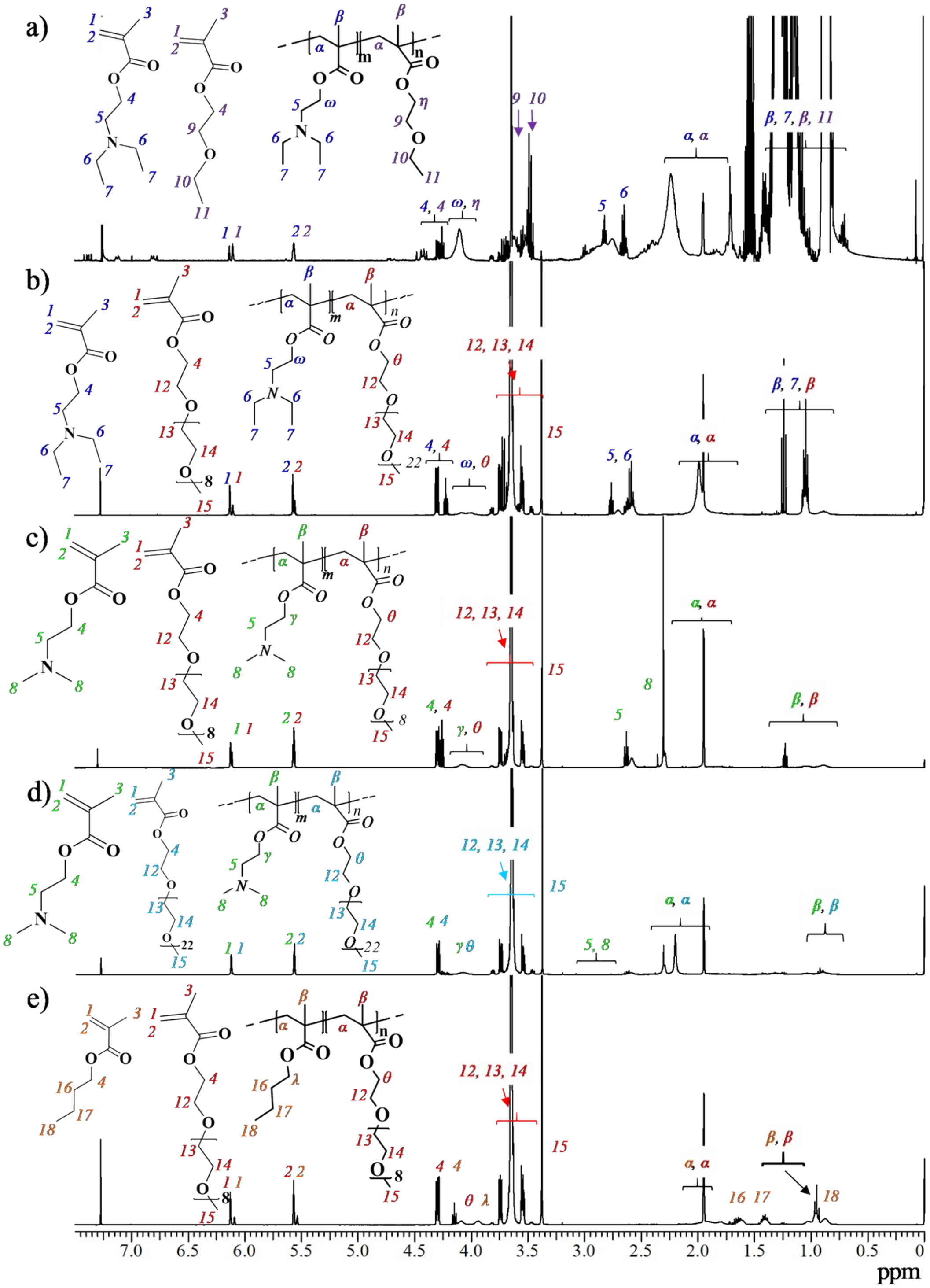

Figure S2. ^{1}H-NMR spectra of: a) Poly(DEAEMA-*co*-EEMA$_1$), b) Poly(DEAEMA-*co*-PEGMA$_{23}$), c) Poly(DMAEMA-*co*-PEGMA$_9$), d) Poly(DMAEMA-*co*-PEGMA$_{23}$), e) Poly(BMA-*co*-PEGMA$_9$). Copolymerization unpurified at 20 min in ethanol with initial monomer composition 50:50 mol% at 70 °C using ACVA as initiator.

2.1. Poly(DEAEMA-*co*-PEGMA$_{23}$)

Table S1. Conversion and copolymer composition of poly(DEAEMA-*co*-PEGMA$_{23}$ in ethanol, at 70 °C, with [ACVA]$_0$ = 0.0016 mol L^{-1} and ratio [ACVA]$_0$:[monomers]$_0$ = [1:100].

Mol frac DEAEMA (f_{DEAEMA})[a]	Mol frac PEGMA$_{23}$ ($f_{PEGMA_{23}}$)	Conversion (%)	Copolymer composition (F_{DEAEMA})	Standard deviation (σ) *n=3*
0.9	0.1	12	0.83	± 0.020
0.7	0.3	18	0.66	± 0.036
0.5	0.5	14	0.48	± 0.042
0.2	0.8	18	0.22	± 0.021
0.1	0.9	13	0.11	± 0.029

2.2. Poly(DEAEMA-*co*-EEMA$_1$)

Figure 2a shows the ^{1}H-NMR spectrum for the copolymer product isolated from polymerization of a 50:50 mol% ratio of DEAEMA:EEMA$_1$ at a reaction time of 20 min. ^{1}H-NMR (500 MHz, CDCl$_3$): δ (ppm) 4.09 (–C**H$_2$**OOC–), 3.61-3.52 (–C**H$_2$OCH$_2$**–), 2.81-2.68 (–C**H$_2$**N(C**H$_2$**)$_2$–), 1.83-1.71 (–C**H$_2$**– backbone chains) and 1.21-0.57 (–N(CH$_2$)$_2$–C**H$_3$**, –OCH$_2$C**H$_3$**, –C**H$_3$** backbone chains). As mentioned above, the conversion of the copolymerization of DEAEMA and EEMA$_1$ was calculated using Equation (2) with the parameter definitions $\alpha = \int\left(H_\omega + H_\eta\right)$ and $\beta = \int H_4$ of the non-purified samples for DEAEMA and EEMA$_1$, respectively **(Figure S2a)**.

As shown in **Figure S3a**, a slight increase in the polymerization rate was observed when the EEMA$_1$ fraction in the initial comonomer mixture was increased from 30 to 50 to 70 mol%. In **Figure S3b** the values $(k_p/\langle k_t\rangle^{1/2})_{cop}$ for the three compositions, as summarized in **Table 1** (are in the References Section, main manuscript)and determined from the slopes of the lines in **Figure S3b**. From the limited data, a linear increase with regard to the initial DEAEMA monomer composition was obtained, $(k_p/\langle k_t\rangle^{1/2})_{cop} = 0.826 + 0.781 f_{DEAEMA}$.

The composition of the monomer in the copolymer was estimated by Equation (3) using the following parameters: $\psi = \int H_{5,6} \big/ 6$ and $\Omega = \int H_{9,10} \big/ 4$ for DEAEMA and EEMA$_1$, respectively, and the values are presented in **Table S2**. This system shows that experimental data (symbols) behavior very close to the azeotropic line for (*i.e.*, $F_{DEAEMA} = f_{DEAEMA}$) **(Figure S3c)**. F_{DEAEMA} is slightly lowered below the diagonal for $f_{DEAEMA} > 0.5$, and slightly elevated above the diagonal for $f_{DEAEMA} < 0.5$. This azeotropic behavior is consistent with the estimated reactivity ratios of $r_{DEAEMA} = 0.61 \pm 0.06$ and $r_{EEMA1} = 0.92 \pm 0.09$ calculated by the *NLLS* method, with the azeotropic composition estimated as $f^{A}_{DEAEMA} = 0.17$ using Equation (4). With both reactivity ratios lower than unity, the copolymer has a very slight tendency towards an alternating behavior. Furthermore, since $r_{DEAEMA} < r_{EEMA1}$, EEMA$_1$ monomer is slightly more reactive than DEAEMA over much of the composition range such that the copolymer will be enriched in EEMA$_1$.

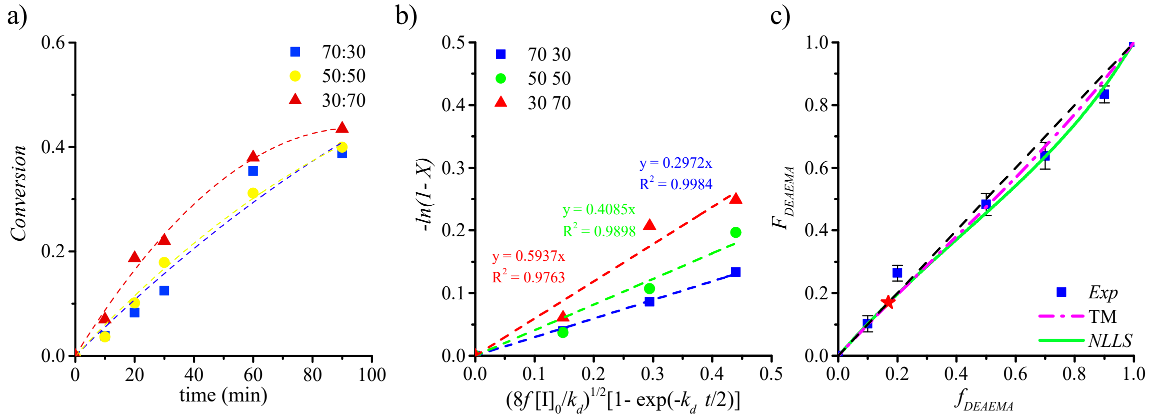

Figure S3. Kinetic characteristics of the copolymerization of poly(DEAEMA-*co*-EEMA$_1$) in ethanol at 70 °C. a) Evolution of the conversion profiles using three initial monomer ratios DEAEMA:EEMA$_1$ (mol%:mol%) (labels). b) Linear fitting of conversion expression for 3 different initial monomer composition, dotted lines are the linear regressions. c) Copolymer composition as a function of the DEAEMA initial composition. Experimental data (symbols) and the theoretical predictions (lines). Azotropic composition (red star).

Table S2. Conversion and copolymer composition of poly(DEAEMA-*co*-EEMA$_1$) in ethanol, at 70 °C, with $[\mathrm{ACVA}]_0 = 0.0016\ \mathrm{mol\ L}^{-1}$ and ratio $[\mathrm{ACVA}]_0$:$[\mathrm{monomers}]_0$ = [1:100].

Mol frac DEAEMA (f_{DEAEMA})	Mol frac EEMA$_1$ (f_{EEMA1})	Conversion (%)	Copolymer composition (F_{DEAEMA})	Standard deviation (σ) *n=3*
0.9	0.1	15	0.83	± 0.027
0.7	0.3	8	0.64	± 0.043
0.5	0.5	10	0.48	± 0.035
0.3	0.7	19	0.26	± 0.026
0.1	0.9	18	0.10	± 0.025

2.3. Poly(DEAEMA-*co*-MMA)

The synthesis of poly(DEAEMA-*co*-MMA) was carried out under the conditions already mentioned, to serve as a model system. **Figure S4** shows the ^{1}H-NMR spectrum for the copolymerization, at a reaction time of 20 min. ^{1}H-NMR (500 MHz, CDCl$_3$): δ (ppm) 4.19 (–C**H$_2$**OOC–), 3.68 (–**OCH$_3$**), 2.95-2.50 (–**CH$_2$**N(C**H$_2$**)$_2$–), 1.83-1.59 (–C**H$_2$**– backbone chains and 1.28-0.85 (–N(CH$_2$)$_2$–C**H$_3$**, –C**H$_3$** backbone chains). The copolymer composition of the copolymerization of DEAEMA with MMA was estimated by Equation (3), using the parameters $\psi = \int H_{5,6}/6$ and $\Omega = \int H_{\tau}/3$, and the values are presented in **Table S3.**

The values of the estimated reactivity ratios were calculated by TM and *NLLS* method are shown in **Table 2**. The reactivity ratios estimated by *NLLS* are r_{DEAEMA} =0.90 ± 0.18 y r_{MMA} = 0.53 ± 0.11. The r_{DEAEMA} and r_{MMA} values strongly suggest that the copolymer contains more DEAEMA than in the initial condition (**Figure S5**). Like $r_{DEAEMA} \times r_{MMA} < 1$, meaning that the copolymerization is inclined to form random copolymers. **Figure S5** details the behavior of the system via a plot of the copolymer composition *versus* initial composition. It is evident from the plot that this system shows azeotropic behavior at high initial fraction of DEAEMA. The azeotropic composition was estimated by Equation (4), resulting in f_{DEAEMA}^{A} =0.83 (**Figure S5**).

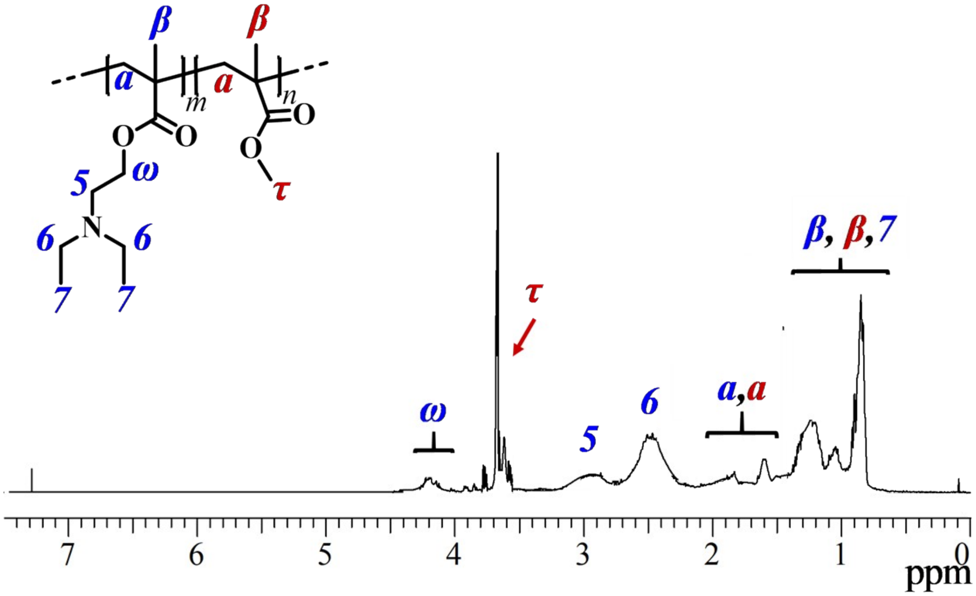

Figure S4. ^{1}H-NMR spectra of poly(DEAEMA-*co*-MMA**)**. Copolymerization at 20 min in ethanol with initial monomer composition 50:50 mol% at 70 °C using ACVA as initiator.

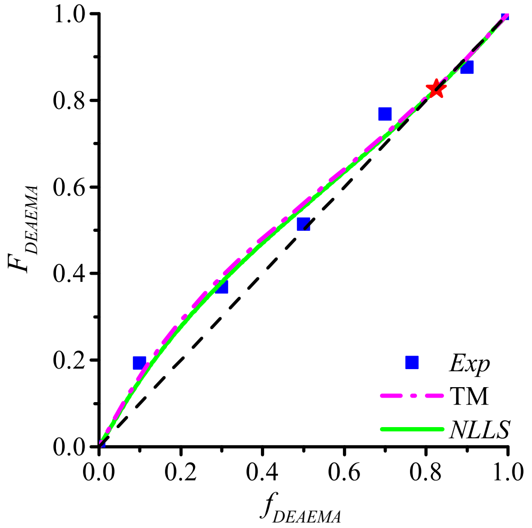

Figure S5. Kinetic characteristics of the copolymerization of poly(DEAEMA-*co*-MMA) in ethanol at 70 °C. Copolymer composition as a function of the DEAEMA initial composition. Experimental data (symbols) and the theoretical predictions (lines).

Table S3. Conversion and copolymer composition of poly(DEAEMA-*co*-MMA) in ethanol, at 70 °C, with $[ACVA]_0 = 0.0016$ mol L^{-1} and ratio $[ACVA]_0$:$[monomers]_0$ = [1:100].

Mol frac DMAEMA (f_{DEAEMA})	Mol frac MMA (f_{MMA})	Conversion (%)	Copolymer composition (F_{DEAEMA})
0.9	0.1	15	0.87
0.7	0.3	14	0.77
0.5	0.5	17	0.51
0.3	0.7	13	0.37
0.1	0.9	18	0.19

2.4. Poly(DMAEMA-*co*-PEGMA$_9$)

Figure 2c shows the ^{1}H-NMR spectrum of poly(DMAEMA-*co*-PEGMA$_9$) (initial monomer composition of 50:50 mol%) obtained at 20 min of reaction: ^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 4.09 (–C**H$_2$**OOC–), 3.64 (–(C**H$_2$**C**H$_2$**O)$_8$–), 3.38 (–OC**H$_3$**), 2.72-2.39 (–C**H$_2$**N(C**H$_3$**)$_2$), 1.89-1.82 (–C**H$_2$**– backbone chains), 1.26-0.88 (–C**H$_3$** backbone chains). Conversion was estimated by using Equation (2) with the parameter definitions

$\alpha = \int (H_\gamma + H_\theta)$ and $\beta = \int H_4$ of the non-purified samples for DMAEMA and PEGMA$_9$, respectively (**Figure S2c**). **Figure S6a** shows an increase in the polymerization rate when the initial monomer composition of PEGMA$_9$ increases from 70:30, 50:50, to 30:70 mol%. The values of $(k_p / \langle k_t \rangle^{1/2})_{cop}$ were obtained by fitting, **Figure S6b**, they are shown in **Table 1**.

The experimental data were obtained by Equation (3), using the parameters $\psi = \int H_{5,8} / 8$ and $\Omega = \int H_{15} / 3$, and the values are presented in **Table S4.** This system shows in **Figure S6c** a behavior almost overlapping with the azeotropic line (dashed line); hence, at any initial monomer composition the copolymer formed has the same composition as the monomers in the initial conditions. No compositional drift is presented under this condition.

The experimental results presented in **Table S4** were treated by the estimation methods already mentioned in previous sections (TM and *NLLS*) for the system of poly(DMAEMA-*co*-PEGMA$_9$). The copolymerization parameters calculated using the *NLLS* method were r_{DMAEMA}=0.83 ± 0.01 and r_{PEGMA9}=1.08 ± 0.02, which are shown in **Table 2**. It was observed that the value computed by all the methods for the reactivity ratio are very similar, being the *NLLS* the most exact method with the R^2 =0.99, **Figure S6c**.

The calculated reactivity ratios predict a random copolymerization, but very close to ideal behavior, frequently seen when monomers with similar chemical structure are used, *i.e.* r_{BMA} = 0.96 with r_{MMA}= 1.04 in bulk.[39] However, in this case, both monomers present clearly a dissimilarity, while DEAEMA has a short side-chain with tertiary amine functionality, PEGMA$_9$ is a macromonomer with a long side-chain and ether functionalities distributed along the chain, **Scheme 1**. Therefore, important kinetic phenomena must be involved in this polymerization system, which will be discussed in posterior sections.

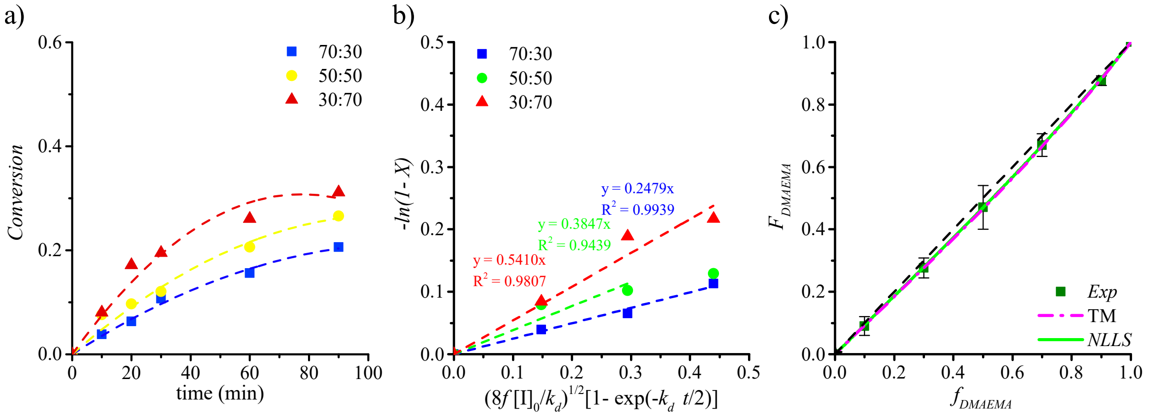

Figure S6. Kinetic characteristics of the copolymerization of poly(DMAEMA-*co*-PEGMA$_9$) in ethanol at 70 °C. a) Evolution of the conversion profiles using three initial monomer ratios DMAEMA:PEGMA$_9$ (mol%:mol%) shown in the labels, dashed lines denote tendencies. b) Linear fitting of conversion expression for 3 different initial monomer composition, dotted lines are the linear regressions. c) Copolymer composition as a function of the DMAEMA initial composition. Experimental data (symbols) and the theoretical predictions (lines).

Table S4. Conversion and copolymer composition of poly(DMAEMA-*co*-PEGMA$_9$) in ethanol, at 70 °C, with $[\text{ACVA}]_0 = 0.0016$ mol L^{-1} and ratio $[\text{ACVA}]_0:[\text{monomers}]_0 = [1:100]$.

Mol frac DMAEMA (f_{DMAEMA})	Mol frac PEGMA$_9$ (f_{PEGMA_9})	Conversion (%)	Copolymer composition (F_{DMAEMA})	Standard deviation (σ) *n=3*
0.9	0.1	15	0.87	± 0.015
0.7	0.3	6	0.67	± 0.036
0.5	0.5	10	0.47	± 0.070
0.3	0.7	17	0.27	± 0.032
0.1	0.9	15	0.09	± 0.030

2.5. Poly(DMAEMA-*co*-PEGMA$_{23}$)

^{1}H-NMR spectrum for a copolymerization experiment of a 50:50 mol% ratio of DMAEMA:PEGMA$_{23}$, at a reaction time of 20 min, is shown in **Figure 2d**. ^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 4.39-4.03 ($–\mathbf{CH_2}OOC–$), 3.57 ($–(\mathbf{CH_2CH_2}O)_{22}–$), 3.31 ($–O\mathbf{CH_3}$), 2.98

($–CH_2N(CH_3)_2$), 2.14 ($–CH_2–$ backbone chains), 1.19-0.81($–CH_3$ backbone chains). The conversion of DMAEMA and $PEGMA_{23}$ in the copolymerizartion was calculated using Equation (2) with the same parameter definitions α and β of the non-purified samples for DMAEMA and $PEGMA_9$, as mentioned before, **Figure S2d**. Varying the initial monomer composition of DMAEMA:$PEGMA_{23}$ 30:70, 50:50 and 70:30 (mol%:mol%) the conversion profiles show an increase when higher $PEGMA_{23}$ initial composition was used in the recipe (30:70 mol%:mol%), **Figure S7a**. A summary of the values of $(k_p/\langle k_t\rangle^{1/2})_{cop}$ calculated by linear fitting, **Figure S7b**, are shown in the **Table 1**.

To determine the chemical composition of the copolymer (mol%), a similar procedure to that used in the previous system was performed. Equation (3) was estimated, by using the same parameters ψ and Ω as for poly(DMAEMA-*co*-$PEGMA_9$) system, and the values are presented in **Table S5**. **Figure S7c** shows the variation in the copolymer composition as a function of the comonomer initial composition of DMAEMA, in which the experimental data (symbols) are found with a behavior very close to the azeotropic line in compositions with lower than 70 mol% of DMAEMA in initial conditions.

Table S5 show the molar compositions of the copolymer and the reactivity ratio estimated by the TM and *NLLS* methods are summarized in **Table 2**, with the *NLLS* method resulting in the best prediction for the experimental data (**Figure S7c**). The estimated copolymerization parameters using the *NLLS* method were $r_{DMAEMA} = 0.52 \pm 0.09$ and $r_{PEGMA23} = 0.76 \pm 0.14$. The initial fraction at which the azeotropic composition of the system is exactly obtained is $f_{DMAEMA}^{A} = 0.33$ (**Figure 7c**). Since $r_{DMAEMA} < 1$ and $r_{PEGMA23} < 1$, it is assumed that the copolymer shows a random addition of comonomers, with tendency to alternation.

Furthermore, since $r_1 < r_2$ and it is evident that the copolymer is enriched with PEGMA$_{23}$ for $f_{DMAEMA} > 0.4$.

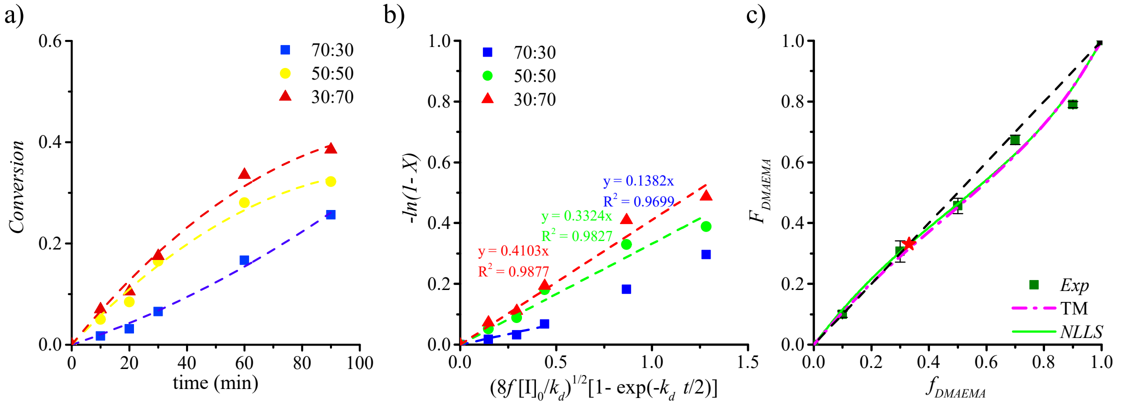

Figure S7. Kinetic characteristics of the copolymerization of poly(DMAEMA-*co*-PEGMA$_{23}$) in ethanol at 70 °C. a) Evolution of the conversion profiles using three initial monomer ratios DMAEMA:PEGMA$_{23}$ (mol%:mol%) shown in the labels, dashed lines denote tendencies. b) Linear fitting of conversion expression for 3 different initial monomer composition, dotted lines are the linear regressions. c) Copolymer composition as a function of the DMAEMA initial composition. Experimental data (symbols) and the theoretical predictions (lines). Azotropic point (red star).

Table S5. Conversion and copolymer composition of poly(DMAEMA-*co*-PEGMA$_{23}$) in ethanol, at 70 °C, with $[\text{ACVA}]_0 = 0.0016$ mol L^{-1} and ratio $[\text{ACVA}]_0:[\text{monomers}]_0 = [1:100]$.

Mol frac DMAEMA (f_{DMAEMA})	Mol frac PEGMA$_{23}$ ($f_{PEGMA_{23}}$)	Conversion (%)	Copolymer composition (F_{DMAEMA})	Standard deviation (σ) *n=3*
0.9	0.1	17	0.79	± 0.010
0.7	0.3	3	0.67	± 0.015
0.5	0.5	8	0.45	± 0.025
0.3	0.7	11	0.30	± 0.035
0.1	0.9	18	0.10	± 0.010

2.6. Poly(BMA-*co*-PEGMA$_9$)

Figure 2e shows the ^{1}H-NMR spectrum for a copolymerization experiment at 20 min of reaction using a 50 mol% of BMA monomer in the initial condition. ^{1}H-NMR (500 MHz, CDCl$_3$): δ (ppm) 4.09-3.94 (–C**H$_2$**OOC–), 3.63 (–(C**H$_2$**C**H$_2$**O)$_8$–), 3.38 (–OC**H$_3$**), 1.90-1.80

(–C**H₂**– backbone chains), 1.61-1.41(–C**H₂**C**H₂**CH₃), 1.02-0.86 (–C**H₃** backbone chains) and 0.57 (–CH₂C**H₃**). **Figure S8a** shown profiles of conversion for the copolymerization of BMA with PEGMA₉ were estimated using the parameters $\alpha = \int(H_\theta + H_\lambda)$ and $\beta = \int H_4$ in Equation (2), samples were taken at 20 min of reaction time (**Figure S2e)**. In **Figure S8b** is shown that as the BMA content is increasing the values $(k_p/\langle k_t\rangle^{1/2})_{cop}$ are also increased, contrary to all the previous systems, they are shown in **Table 1**.

The composition of the copolymer was obtained by Equation (3) with parameters: $\psi = \int H_\lambda \big/ 2$ and $\Omega = \int H_{15} \big/ 3$ for BMA and PEGMA₉, respectively, and the values are presented in **Table S6.** The variation in the copolymer composition as a function of the BMA comonomer initial composition is shown in **Figure S8c**. It can be seen that the experimental data (symbols) for the copolymer started with 10 mol% of BMA in the initial deviates from the azeotropic line showing that the copolymer is enriched in BMA units when BMA is added at molar initial fractions lower than 50 mol%.

Table S6 presents the experimental results of the molar compositions in the copolymer, obtained by Equation (3). The estimations are summarized in **Table 2**, being $r_{BMA} = 0.55 \pm 0.13$ and $r_{PEGMA9} = 0.38 \pm 0.09$ for the best fit to the experimental data, **Figure S8a**. The estimated values for the reactivity ratio for both methods are very similar. The azeotropic point was estimated at $f_{BMA}^{A} = 0.58$.

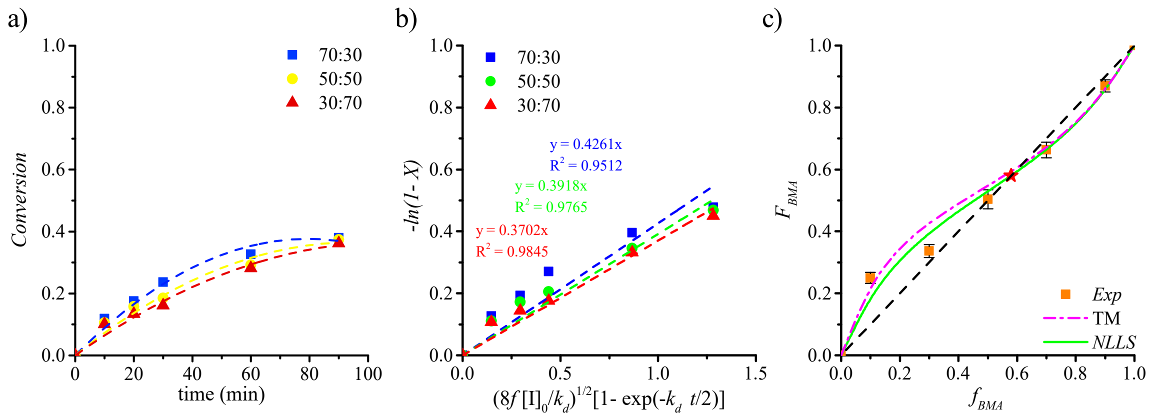

Figure S8. Kinetic characteristics of the copolymerization of poly(BMA-*co*-PEGMA$_9$) in ethanol at 70 °C. a) Conversion profiles at three initial monomer compositions BMA:PEGMA$_9$ (mol%:mol%) shown in the labels, dashed lines denote tendencies. b) Linear fitting of conversion expression for 3 different initial monomer composition, dotted lines are the linear regressions. c) Copolymer composition as a function of the BMA initial composition. Experimental data (symbols) and the theoretical predictions (lines). Azotropic point (red star).

Table S6. Conversion and copolymer composition of poly(BMA-*co*-PEGMA$_9$) in ethanol, at 70 °C, with [ACVA]$_0$ = 0.0016 mol L^{-1} and ratio [ACVA]$_0$:[monomers]$_0$ = [1:100].

Mol frac BMA (f_{BMA})	Mol frac PEGMA$_9$ (f_{PEGMA_9})	Conversion (%)	Copolymer composition (F_{BMA})	Standard deviation (σ) *n=3*
0.9	0.1	19	0.87	± 0.020
0.7	0.3	18	0.66	± 0.025
0.5	0.5	16	0.50	± 0.031
0.3	0.7	13	0.34	± 0.021
0.1	0.9	19	0.25	± 0.017

3. Reactivity ratios for the copolymerizations of TAMAs and methacrylate monomers in different solvents

Table S7. Reactivity ratios for the copolymerizations of TAMAs (M$_1$) and methacrylate monomers (M$_2$), solvent, relative polarity (ζ), and temperature. (the references 22, 23 and 24 are in the References Section, main manuscript).

M$_1$	M$_2$	Solvent	ζ	r_1	r_2	T (°C)	Ref.
DEAEMA	PEGMA$_9$	*p*-dioxane	0.16	0.91 ± 0.12	0.75 ± 0.09	70	T.W.
DEAEMA	PEGMA$_9$	THF	0.21	0.96 ± 0.13	0.81 ± 0.11	66	T.W.

DEAEMA	MMA	DMF	0.39	0.94	0.99	75	[24]
DEAEMA	MMA	EtOH	0.65	1.40 ± 0.23	0.73 ± 0.13	70	T.W.
DEAEMA	PEGMA$_9$	EtOH	0.65	0.79 ± 0.07	0.71 ± 0.07	70	T.W.
DMAEMA	MMA	$CHCl_3$	0.26	1.13	1.07	60	[22]
DMAEMA	MMA	DMF	0.39	0.92	0.85	70	[23]