

Supporting Information

**Title: Atmospheric pulsed plasma copolymerization of acrylic monomers:
kinetics, chemistry and applications.**

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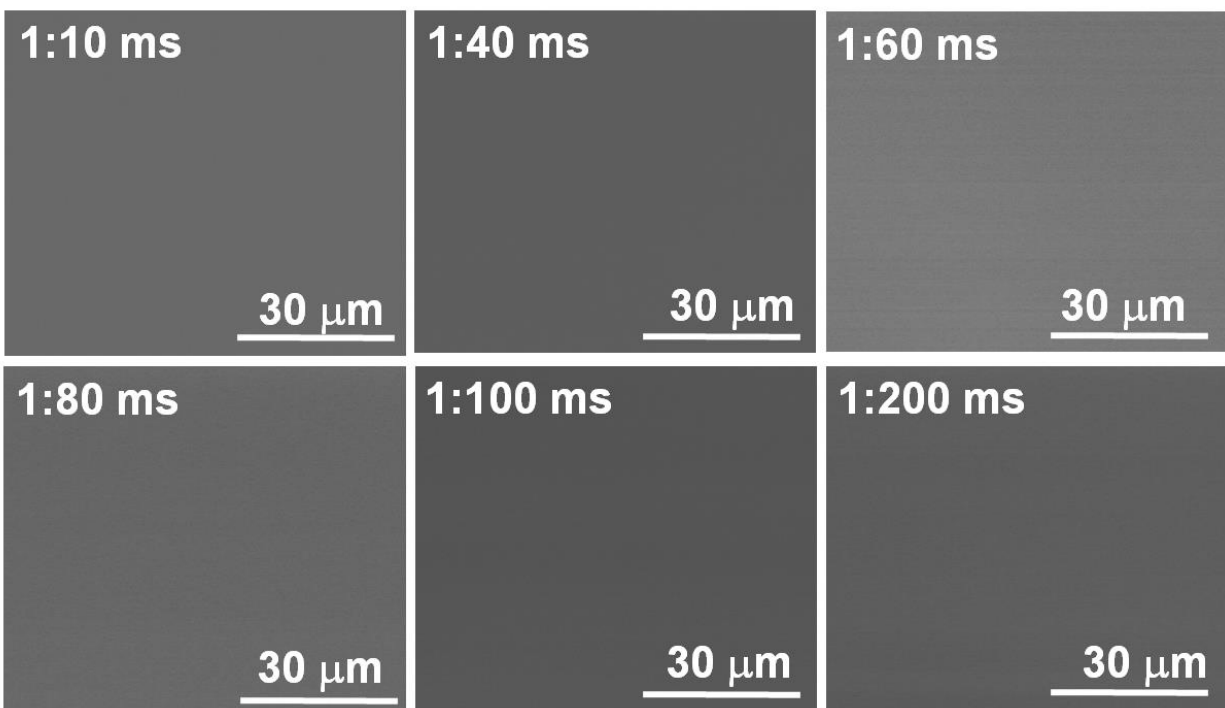
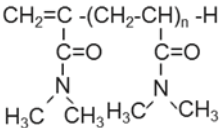
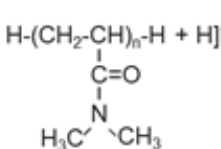
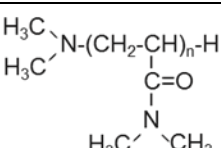
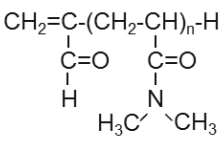


Figure S1. SEM pictures of DMA-homopolymers deposited at a fixed 1 ms t_{on} and t_{off} values ranging from 10 ms to 120 ms.

Table S1. Ion assignments of oligomers (m/z) detected by ESI-HRMS analysis of DMA homopolymer deposited at 1 ms t_{on} and 60 ms t_{off} .

Ion assignments	$D_{100}E_0$, m/z
$\begin{array}{c} \text{CH}_2=\text{C}-(\text{CH}_2-\text{CH})_n-\text{H} + \text{HJ}^+ \\ \qquad \qquad \\ \text{C}=\text{O} \qquad \text{C}=\text{O} \\ \qquad \qquad \\ \text{N} \qquad \qquad \text{N} \\ / \ \backslash \qquad / \ \backslash \\ \text{H}_3\text{C} \ \text{CH}_3 \ \text{H}_3\text{C} \ \text{CH}_3 \end{array}$	199.1441 (n=1), 298.2125 (n=2), 397.2809 (n=3) 496.3493 (n=4) 595.4178 (n=5) 694.4862 (n=6)
$\begin{array}{c} \text{H}-(\text{CH}_2-\text{CH})_n-\text{H} + \text{HJ}^+ \\ \\ \text{C}=\text{O} \\ \\ \text{N} \\ / \ \backslash \\ \text{H}_3\text{C} \ \text{CH}_3 \end{array}$	201.1597 (n=2), 300.2282 (n=3), 399.2966 (n=4), 498.3650 (n=5), 597.4334 (n=6), 696.5018 (n=7),
$\begin{array}{c} \text{H}_3\text{C} \\ \\ \text{H}_3\text{C}-\text{N}-(\text{CH}_2-\text{CH})_n-\text{H} + \text{HJ}^+ \\ \\ \text{C}=\text{O} \\ \\ \text{N} \\ / \ \backslash \\ \text{H}_3\text{C} \ \text{CH}_3 \end{array}$	145.1335 (n=1), 244.2019 (n=2), 343.2704 (n=3), 442.3388 (n=4), 541.4072 (n=5), 640.4756 (n=6), 739.5440 (n=7),
$\begin{array}{c} \text{CH}_2=\text{C}-(\text{CH}_2-\text{CH})_n-\text{H} + \text{HJ}^+ \\ \qquad \qquad \\ \text{C}=\text{O} \qquad \text{C}=\text{O} \\ \qquad \qquad \\ \text{H} \qquad \qquad \text{N} \\ \qquad \qquad / \ \backslash \\ \qquad \qquad \text{H}_3\text{C} \ \text{CH}_3 \end{array}$	156.1019 (n=1) 255.1703 (n=2), 354.2387 (n=3), 453.3071 (n=4), 552.3756 (n=5), 651.4440 (n=6), 750.5124 (n=7),

Table S2. Ion assignments of oligomers (m/z) detected by AP-MALDI-HRMS analyses of different DMA/EGDMA plasma copolymers deposited at 1 ms t_{on} and 60 ms t_{off} .

Ion assignments	D ₁₀₀ E ₀ m/z	D ₈₅ E ₁₅ m/z	D ₇₅ E ₂₅ m/z
$\text{CH}_2=\text{C}-(\text{CH}_2-\text{CH})_n-\text{H} + \text{HJ}^+$ 	199.1441 (n=1), 298.2125 (n=2), 397.2809 (n=3) 496.3493 (n=4) 595.4178 (n=5) 694.4862 (n=6) 793.5546 (n=7) 892.6230 (n=8)	199.1441 (n=1), 298.2125 (n=2), 397.2809 (n=3) 496.3493 (n=4) 595.4178 (n=5) 694.4862 (n=6)	199.1441 (n=1), 298.2125 (n=2), 397.2809 (n=3) 496.3493 (n=4) 595.4178 (n=5)
$\text{H}-(\text{CH}_2-\text{CH})_n-\text{H} + \text{HJ}^+$ 	201.1597 (n=2), 300.2282 (n=3), 399.2966 (n=4), 498.3650 (n=5), 597.4334 (n=6), 696.5018 (n=7), 795.5702 (n=8) 894.6386 (n=9) 993.7071 (n=10) 1092.7755 (n=11)	201.1597 (n=2), 300.2282 (n=3), 399.2966 (n=4), 498.3650 (n=5), 597.4334 (n=6), 696.5018 (n=7),	201.1597 (n=2), 300.2282 (n=3), 399.2966 (n=4), 498.3650 (n=5), 597.4334 (n=6),
$\text{H}_3\text{C}-\text{N}(\text{CH}_3)-(\text{CH}_2-\text{CH})_n-\text{H} + \text{HJ}^+$ 	145.1335 (n=1), 244.2019 (n=2), 343.2704 (n=3), 442.3388 (n=4), 541.4072 (n=5), 640.4756 (n=6), 739.5440 (n=7), 838.6124 (n=8), 937.6808 (n=9)	145.1335 (n=1), 244.2019 (n=2), 343.2704 (n=3), 442.3388 (n=4), 541.4072 (n=5), 640.4756 (n=6),	145.1335 (n=1), 244.2019 (n=2), 343.2704 (n=3), 442.3388 (n=4), 541.4072 (n=5), 640.4756 (n=6),
$\text{CH}_2=\text{C}-(\text{CH}_2-\text{CH})_n-\text{H} + \text{HJ}^+$ 	156.1019 (n=1) 255.1703 (n=2), 354.2387 (n=3), 453.3071 (n=4), 552.3756 (n=5), 651.4440 (n=6), 750.5124 (n=7), 849.5808 (n=8), 948.6492 (n=9)	156.1019 (n=1) 255.1703 (n=2), 354.2387 (n=3), 453.3071 (n=4), 552.3756 (n=5), 651.4440 (n=6),	156.1019 (n=1) 255.1703 (n=2), 354.2387 (n=3), 453.3071 (n=4), 552.3756 (n=5), 651.4440 (n=6),

$\text{H}-(\text{CH}_2-\text{CH})_n- (\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{C}=\text{O}}{\text{C}}})_m-\text{H} + \text{H}]^+$ $\begin{array}{c} \text{H}_3\text{C}-\text{N}-\text{CH}_3 \\ \\ \text{C}=\text{O} \\ \\ \text{O} \\ \\ (\text{CH}_2)_2 \\ \\ \text{O} \\ \\ \text{C}=\text{O} \\ \\ \text{C}-\text{CH}_3 \\ \\ \text{CH}_2 \end{array}$		300.1805 (n=1, m=1) 399.2490 (n=2, m=1) 498.2698 (n=1, m=2) 498.3174 (n=3, m=1) 597.3382 (n=2, m=2) 597.3858 (n=4, m=1) 696.4066 (n=3, m=2) 696.4542 (n=5, m=1) 795.4274 (n=2, m=3)	300.1805 (n=1, m=1) 399.2490 (n=2, m=1) 498.2698 (n=1, m=2) 498.3174 (n=3, m=1) 597.3382 (n=2, m=2) 597.3858 (n=4, m=1) 696.3590 (n=1, m=3) 795.4274 (n=2, m=3)
$\text{CH}_2=\text{C}-(\text{CH}_2-\text{CH})_n- (\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{C}=\text{O}}{\text{C}}})_m-\text{H} + \text{H}]^+$ $\begin{array}{c} \text{H}_3\text{C}-\text{N}-\text{CH}_3 \quad \text{H}_3\text{C}-\text{N}-\text{CH}_3 \\ \quad \quad \\ \text{C}=\text{O} \quad \text{C}=\text{O} \\ \quad \quad \\ \text{O} \quad \quad \text{O} \\ \quad \quad \\ (\text{CH}_2)_2 \\ \\ \text{O} \\ \\ \text{C}=\text{O} \\ \\ \text{C}-\text{CH}_3 \\ \\ \text{CH}_2 \end{array}$		397.2333 (n=1, m=1) 496.3017 (n=2, m=1) 595.3225 (n=1, m=2) 595.3701 (n=3, m=1) 694.3909 (n=2, m=2) 793.4117 (n=1, m=3)	397.2333 (n=1, m=1) 496.3017 (n=2, m=1) 595.3225 (n=1, m=2) 595.3701 (n=3, m=1) 694.3909 (n=2, m=2) 793.4117 (n=1, m=3) 991.5009 (n=1, m=4)
$\text{H}_3\text{C}-\text{N}-(\text{CH}_2-\text{CH})_n- (\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{C}=\text{O}}{\text{C}}})_m-\text{H} + \text{H}]^+$ $\begin{array}{c} \text{H}_3\text{C}-\text{N}-\text{CH}_3 \\ \\ \text{C}=\text{O} \\ \\ \text{O} \\ \\ (\text{CH}_2)_2 \\ \\ \text{O} \\ \\ \text{C}=\text{O} \\ \\ \text{C}-\text{CH}_3 \\ \\ \text{CH}_2 \end{array}$		343.2227 (n=1, m=1) 442.2912 (n=2, m=1) 541.3120 (n=1, m=2) 541.3596 (n=3, m=1) 640.3804 (n=2, m=2) 640.4280 (n=4, m=1)	343.2227 (n=1, m=1) 442.2912 (n=2, m=1) 541.3120 (n=1, m=2) 541.3596 (n=3, m=1) 640.3804 (n=2, m=2) 640.4280 (n=4, m=1)

		m=1) 739.4012 (n=1, m=3) 739.4488 (n=3, m=2)	m=1) 739.4488 (n=3, m=2)
$ \begin{array}{c} \text{CH}_2=\text{C}-(\text{CH}_2-\text{CH})_n - (\text{CH}_2-\text{C})_m - \text{H} + \text{HJ}^+ \\ \begin{array}{ccc} & & \\ \text{C}=\text{O} & \text{C}=\text{O} & \text{C}=\text{O} \\ & & \\ \text{H} & \text{N} & \text{O} \\ & / \backslash & \\ & \text{H}_3\text{C} \quad \text{CH}_3 & (\text{CH}_2)_2 \\ & & \\ & & \text{O} \\ & & \\ & & \text{C}=\text{O} \\ & & \\ & & \text{C}-\text{CH}_3 \\ & & \\ & & \text{CH}_2 \end{array} \end{array} $		354.1911 (n=1, m=1) 453.2595 (n=2, m=1) 552.2803 (n=1, m=2) 552.3279 (n=3, m=1) 651.3487 (n=2, m=2) 651.3964 (n=4, m=1) 750.3695 (n=1, m=3) 750.4648 (n=5, m=1) 849.4379 (n=2, m=3)	354.1911 (n=1, m=1) 453.2595 (n=2, m=1) 552.2803 (n=1, m=2) 552.3279 (n=3, m=1) 651.3487 (n=2, m=2) 651.3964 (n=4, m=1) 750.4171 (n=3, m=2) 750.3695 (n=1, m=3)

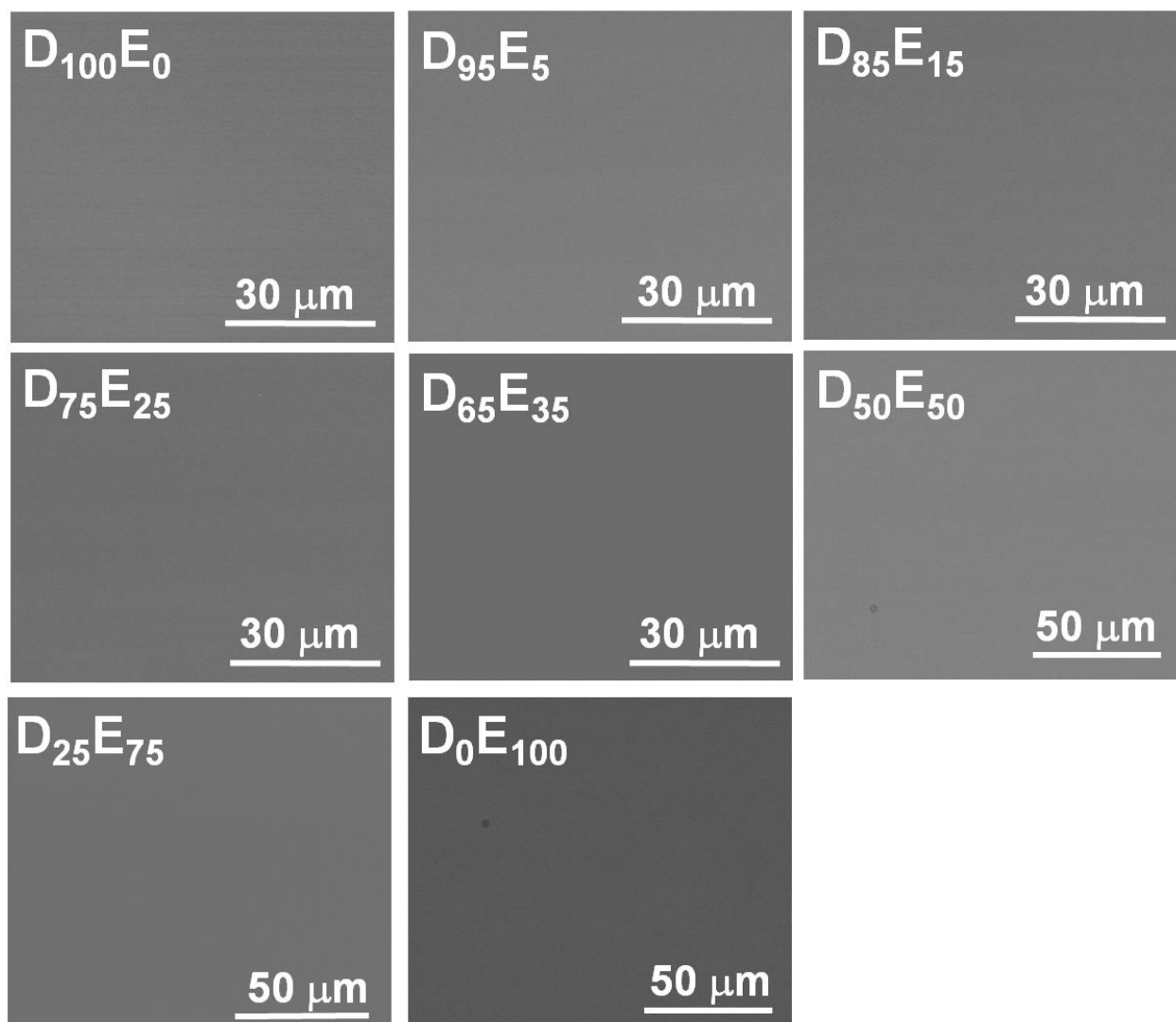


Figure S2. SEM pictures of plasma polymer films deposited from different DMA/EGDMA precursor mixtures, at a fixed 1 ms t_{on} and a fixed 60 ms t_{off} .

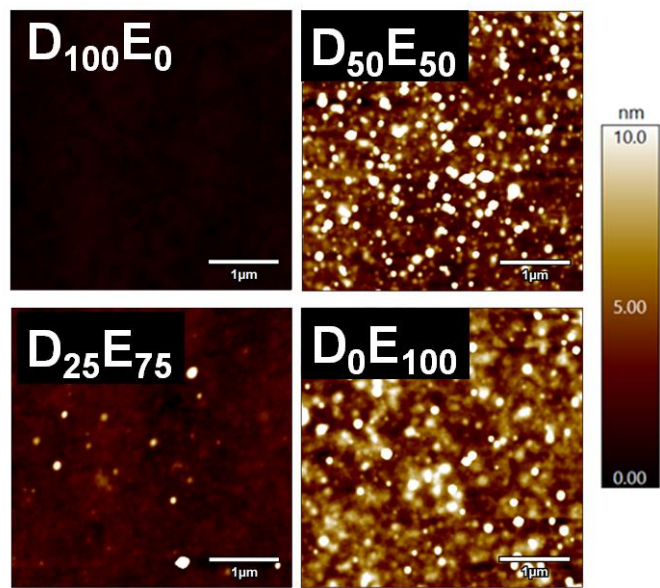


Figure S3. AFM pictures of plasma polymer films from pure DMA, pure EGDMA and different DMA/EGDMA mixtures.

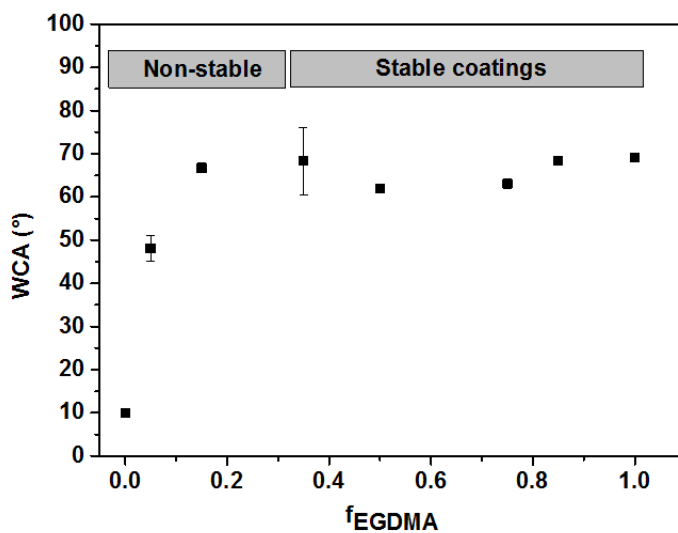


Figure S4. Water Contact Angle (WCA) values as a function of the amount of EGDMA in the feed (f_{EGDMA}).

The WCA evolution as a function of the f_{EGDMA} is reported in **Figure S4**. Increasing EGDMA content in the feed up to 20 mol% led to an increase in the film hydrophobicity, from 10° for pure DMA-films, up to 70° , a value close to the pure EGDMA-film one. In addition, coatings issued from f_{EGDMA} superior or equal to 35 mol% presented similar wetting properties, with a WCA of about 70° . Such results suggested the existence of a thin EGDMA-based layer on the topmost surface of the coating.

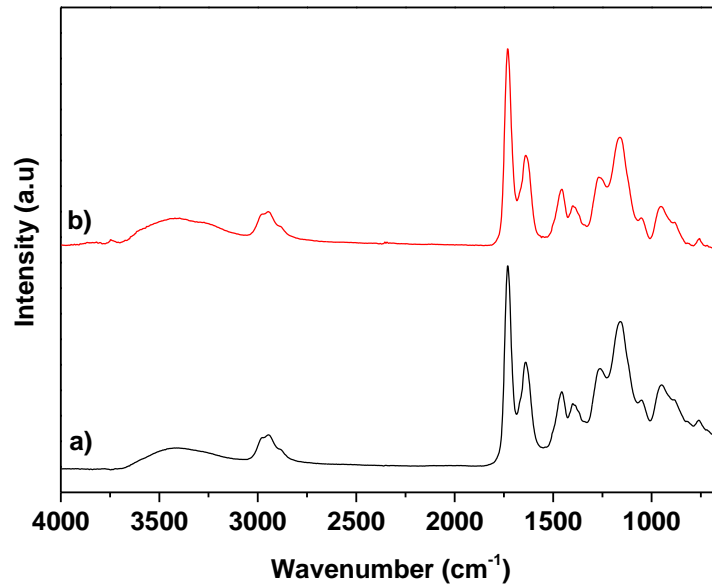


Figure S5. IR spectra of D₆₅E₃₅ films as deposited (a) and after 2h20 water immersion tests (b).