

Supporting Information

Structural Heterogeneity in Polymeric Nitric Oxide Donor Nanoblended Coatings for Controlled Release Behaviors

Hyejoong Jeong^a, Kyungtae Park^a, Jae-Chan Yoo^b and Jinkee Hong^{a,*}

^a Department of Chemical and Biomolecular Engineering, Yonsei University, Seoul 03722, Republic of Korea

^b Biotechnology Research Center, JCBIO Co., LTD & Avison Biomedical Research Center (ABMAC), Yonsei University, Seoul 03722, Republic of Korea



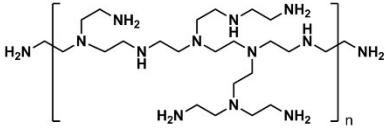
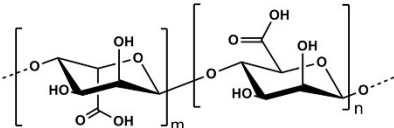
	BPEI  (Branched polyethylene imine)	ALG  (Alginic acid)
Chemical Structures		
MW	25,000	75,000 ^a
pKa	8.5 ^b	3.4 ^c
pH	9	8 or 4

Table S1. Chemical properties of polyelectrolytes in the table. a. Estimated molecular weight of alginate written in the experiment section, b. pKa value of BPEI[1] c. pKa value of ALG[2,3]

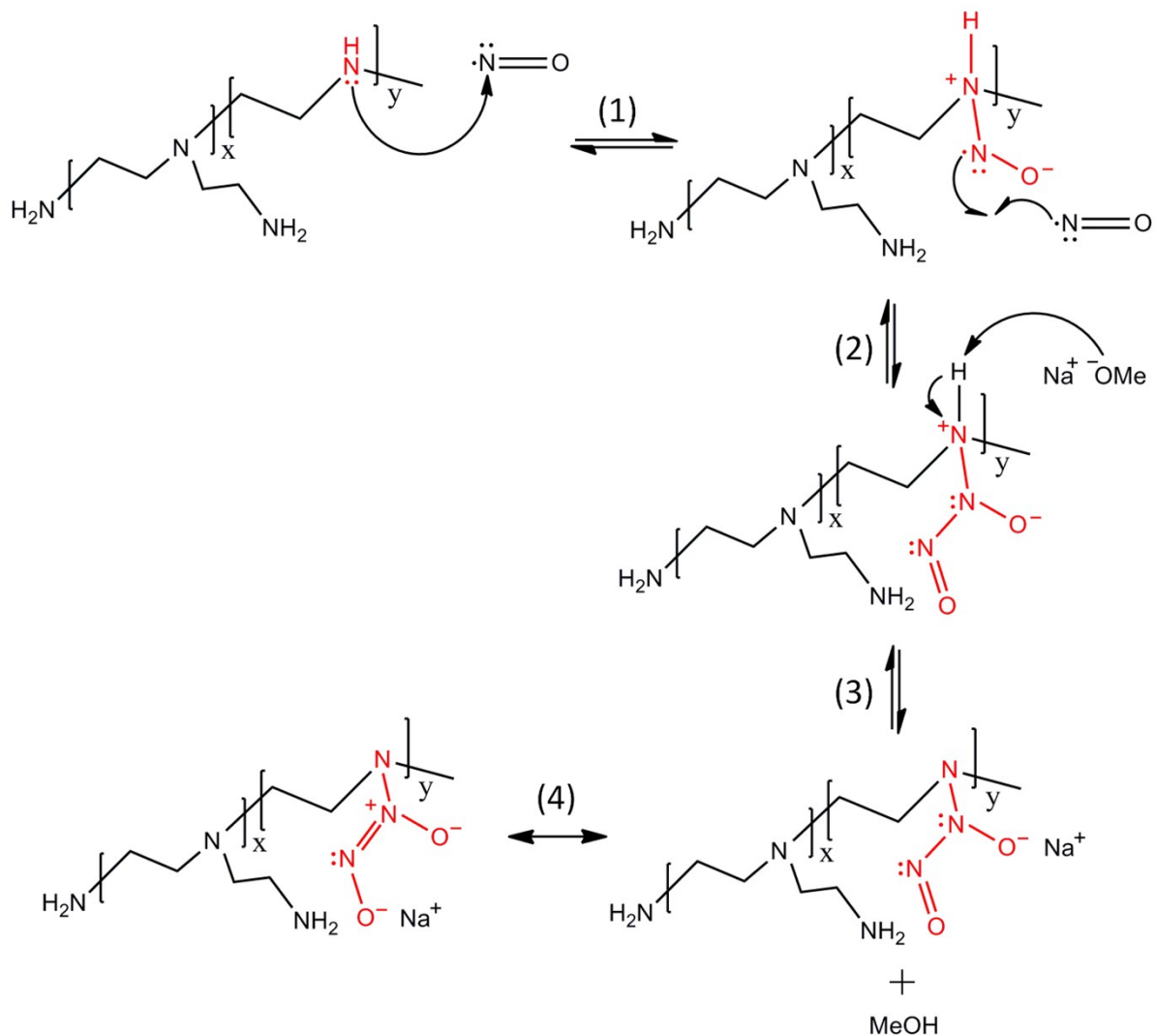


Figure S1. Mechanism of *N*-diazeniumdiolate formation on (BPEI/ALG) nanoblended coatings.

(modified from Drago and Schoenfisch et al.[4-7])

Sodium methoxide (NaOMe) which is a strong base catalyst, leading the deprotonation of the amino nitrogen and following dominant *N*-diazeniumdiolate formation due to the shift of equilibrium at third step (3).

N-diazeniumdiolate species includes a *N*-diazeniumdiolate anion and an ammonium counteraction, where the ammonium counteraction is from either an adjacent amine on the same structure or a second molecule containing an amine site.

Number of bilayers (n)	Film1: (BPEI9/ALG8) _n			Film2: (BPEI9/ALG4) _n		
	Mass (ug·cm ⁻²)	Thickness (cm)	Density (ug·cm ⁻³)	Mass (ug·cm ⁻²)	Thickness (cm)	Density (ug·cm ⁻³)
2.5	0.60	-	-	1.11	1.17.E-06	9.57.E+05
4.5	0.90	1.33E-06	6.76E+05	6.37	6.15.E-06	1.04.E+06
6.5	2.29	4.22E-06	5.42E+05	14.93	1.45.E-05	1.03.E+06
8.5	4.46	1.19E-05	3.76E+05	38.53	6.96.E-05	5.54.E+05
10.5	8.15	2.70E-05	3.02E+05	66.87	1.13.E-04	5.94.E+05

Table S2. Density of Film 1 and Film2 according to each number of bilayer, calculated by mass and thickness results.

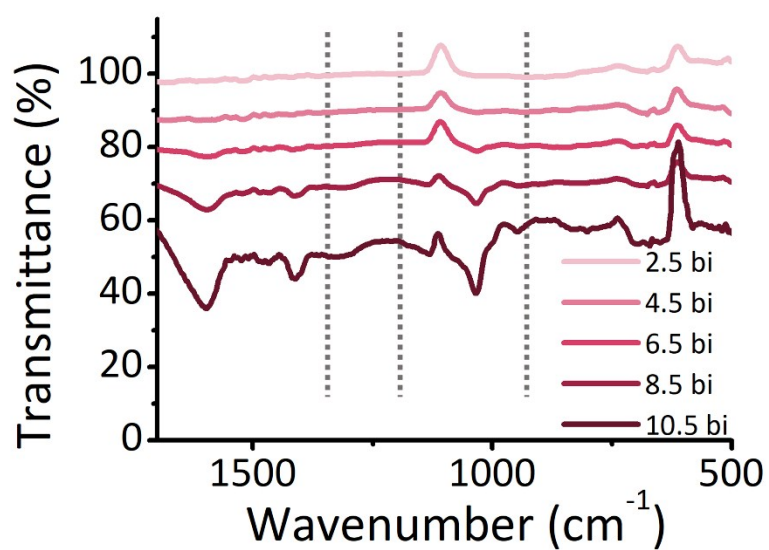


Figure S2. FT-IR spectra of Film 1; (BPEI9/ALG8)_n nanoblended coatings (n=2.5, 4.5, 6.5, 8.5, 10.5) before *N*-diazeniumdiolate generation. The specific parts to be compared with the spectra after generation of *N*-diazeniumdiolate are indicated by gray-dotted lines.

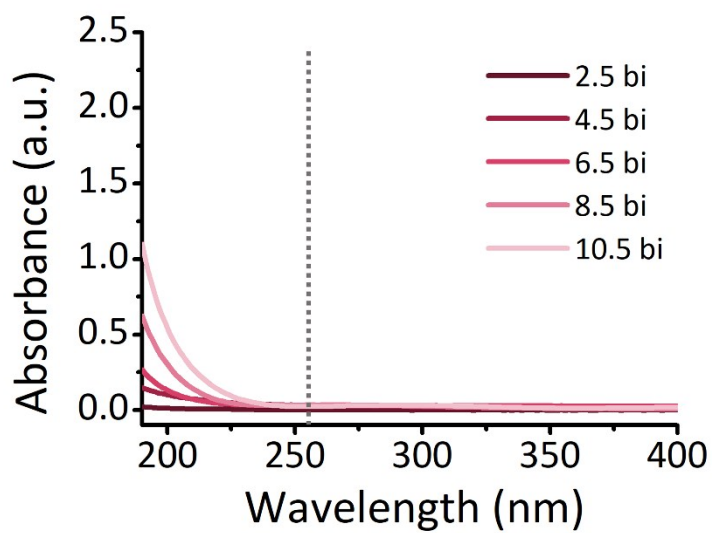


Figure S3. UV-vis absorbance of Film1; (BPEI9/ALG8)_n nanoblended coatings (n=2.5, 4.5, 6.5, 8.5, 10.5) before *N*-diazeniumdiolate generation. 252 nm of wavelength is indicated by gray dotted line.

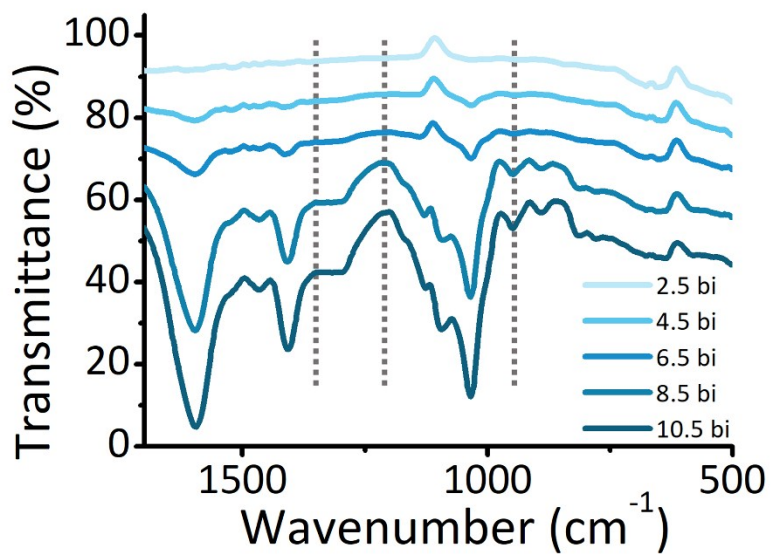


Figure S4. FT-IR spectra of Film2; (BPEI9/ALG4)_n nanoblended coatings (n=2.5, 4.5, 6.5, 8.5, 10.5) before *N*-diazeniumdiolate generation. The specific parts to be compared with the spectra after generation of *N*-diazeniumdiolate are indicated by gray-dotted lines.

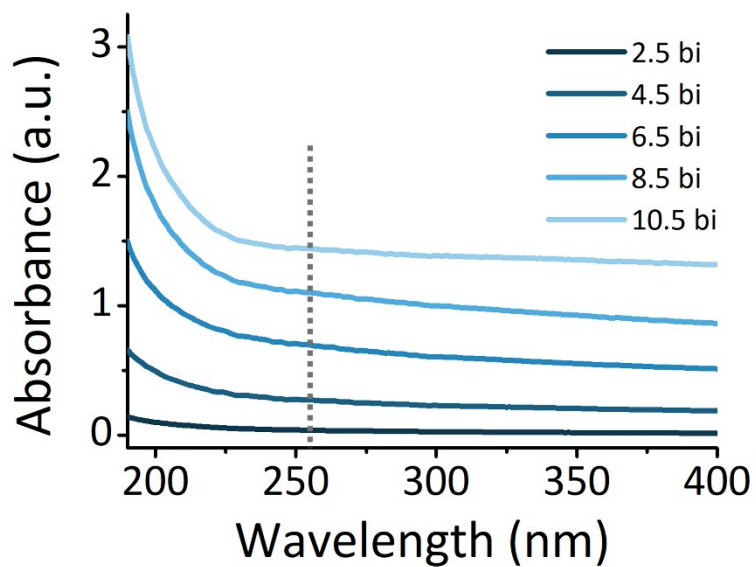


Figure S5. UV-vis absorbance of Film2; (BPEI9/ALG4)_n nanoblended coatings (n=2.5, 4.5, 6.5, 8.5, 10.5) before *N*-diazoniumdiolate generation. 252 nm of wavelength indicated by gray dotted line.

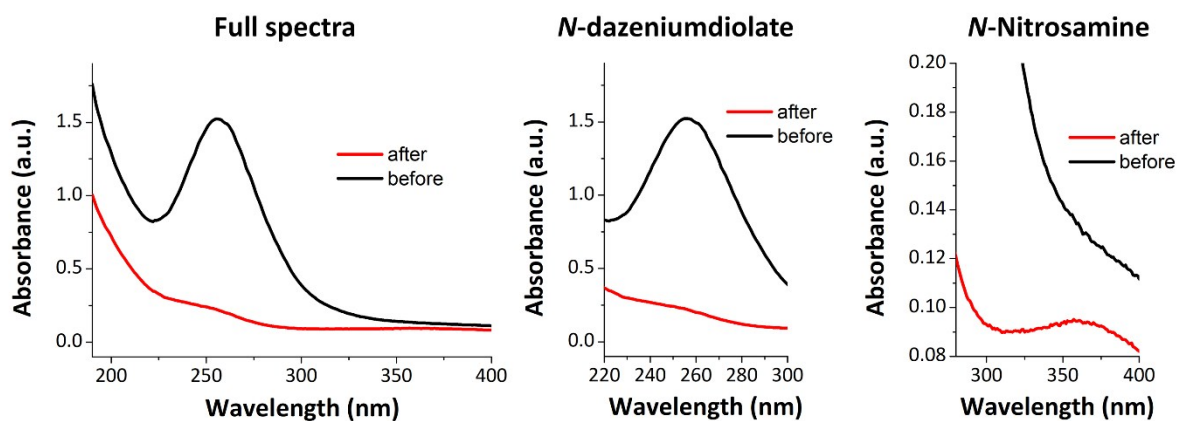


Figure S6. UV-vis absorbance of Film 1; (BPEI9/ALG8)_{10.5} nanoblended coating after NO release. From the full spectra, the regions of *N*-diazoniumdiolate and *N*-nitrosamine were each magnified as individual graphs. Black spectrum indicates the film before NO release and red spectrum indicates after NO release at 37°C in PBS for 43 hours.

Compared with the absorbance at 252 nm of both spectra, it can be seen that 13.7% of *N*-diazoniumdiolate was remained after NO release. The peak of *N*-nitrosamine was detected at around 350 nm.

References

- [1] J. M. Silva, S. G. Caridade, R. R. Costa, N. I. M. Alves, T. Groth, C. Picart, R. L. Reis, J. O. F. Mano 2015 *Langmuir* **31** 11318
- [2] S. Choosakoonkriang, B. A. Lobo, G. S. Koe, J. G. Koe, R. Middaugh 2003 *J. Pharm. Sci.* **92** 1710
- [3] K. Y. Lee, D. J. Mooney, 2012 *Prog. Polym. Sci.* **37** 106
- [4] R. S. Drago, R. O. Ragsdale, D. P. Eyman 1961 *J. Am. Chem. Soc.* **83** 4337
- [5] R. S. Drago 1962 *Adv. Chem.* **36** 143
- [6] R. O. Ragsdale, B. R. Karstetter, R. S. Drago 1965 *Inorg. Chem.* **4** 420
- [7] H. Zhang, G. M. Annich, J. Miskulin, K. Stankiewicz, K. Osterholzer, S. I. Merz, R. H. Bartlett, M. E. Meyerhoff 2003 *J. Am. Chem. Soc.* **125** 5015