

Light-absorbing secondary organic material formed by glyoxal in aqueous aerosol mimics

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Supplementary Material

1. Experimental Details of Surface Tension Measurements

Pendant drop tensiometry (PDT) was used to measure surface tension. The PDT apparatus used in this study is similar to that described by Anastasiadis et al (1987). Drops were generated at the tip of a glass capillary tube using a 25 μ l or 100 μ L syringe, which was mounted inside an enclosed cell with quartz windows. Droplet volume was selected to be the largest stable volume (and thus most elongated drop) possible before detachment would occur. For each drop, images were acquired at 1 min intervals to ensure that drop shape had reached steady state before analysis. Images are acquired using a TV zoom lens (Fujinon) coupled to a Pulnix model TM-7CN video camera. The optics are focused using a 0.5 mm \times 0.5 mm ruled grid, which also provides a basis for image calibration. The signal from the video camera is captured and digitized using a video board, run by in-house software. In the highest-resolution mode, the image is comprised of a 640 \times 480 pixel RGB array. Software routines written in-house and executed in MATLAB 7.0 (the MathWorks, Inc.) were used for edge detection using the method of Canny (1986) and image postanalysis. The method of several selected planes was used for determining H based on the diameter of the drop at five intervals along the drop axis (Juza, 1997).

To infer surface tension values from PDT data, it is desirable to know the density of the test solution to high precision. Solution density was measured using an analytical balance readable to within $\pm 10 \mu\text{g}$ (Denver Instruments).

2. Results of control experiments

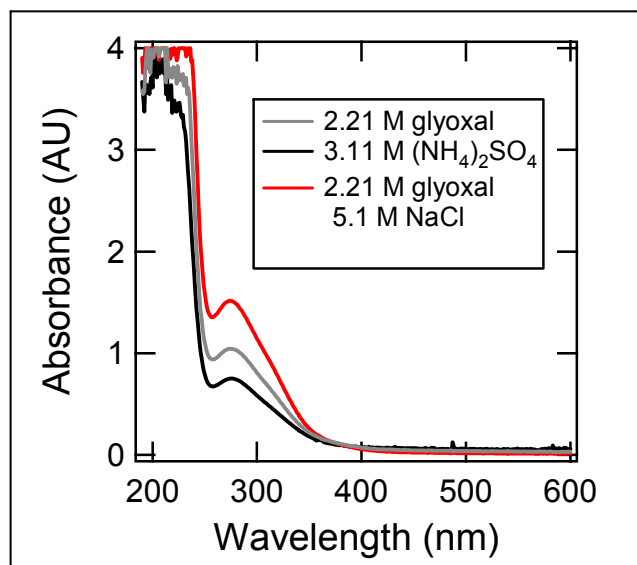


Figure S1. UV/Vis spectra of control solutions.

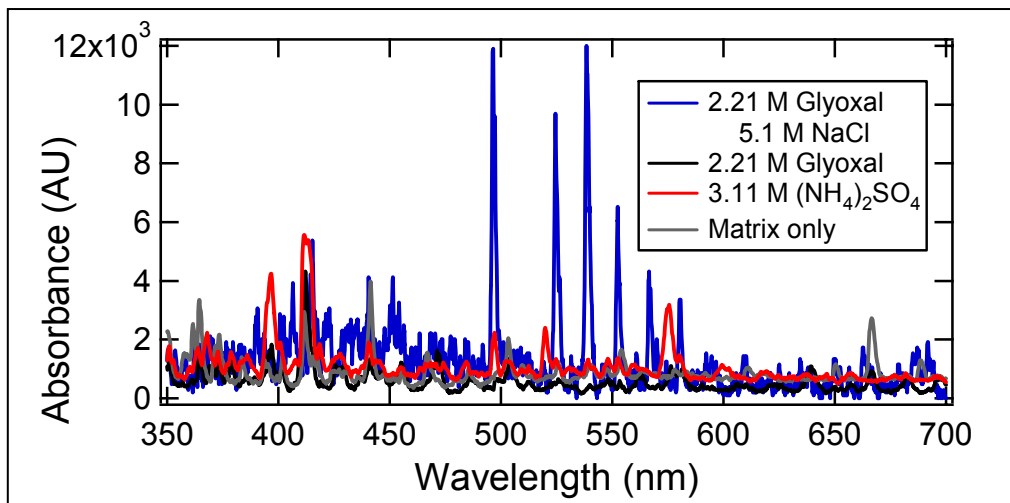
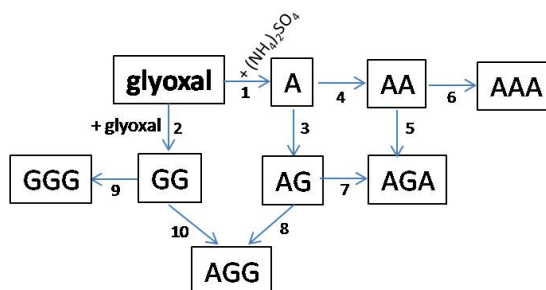


Figure S2. MALDI-MS spectra of control solutions.

3. Kinetics analysis of polymerization reactions

In order to develop a qualitative sense of the kinetics of the polymerization reactions active in the glyoxal-ammonium sulfate system, we constructed a simplified reaction network (shown in Scheme S1) that includes glyoxal being processed by ammonium sulfate to produce a molecule “A”, and successive addition reactions between A and G to form molecules consisting of up to 3 monomer units.



Scheme S1. Glyoxal reaction pathway. ‘A’ denotes a reaction product of glyoxal and ammonium sulfate, and ‘G’ denotes glyoxal.

Considering the addition reactions depicted in scheme S1 we get the following rate law expressions:

$$\frac{d[G]}{dt} = -k_1[(NH_4)_2SO_4][G] - k_2[G]^2 - k_3[A][G] - k_5[AA][G] - k_8[AG][G] - k_9[G][GG]$$

$$\frac{d[A]}{dt} = k_1[(NH_4)_2SO_4][G] - k_3[A][G] - k_4[A]^2 - k_6[A][AA] - k_7[A][AG] - k_{10}[A][GG]$$

$$\frac{d[GG]}{dt} = k_2[G]^2 - k_9[G][GG] - k_{10}[A][GG]$$

$$\frac{d[AG]}{dt} = k_3[A][G] - k_8[AG][G] - k_7[A][AG]$$

$$\frac{d[AA]}{dt} = k_4[A]^2 - k_5[AA][G] - k_6[A][AA]$$

$$\frac{d[AGA]}{dt} = k_5[AA][G] + k_7[A][AG]$$

$$\frac{d[AAA]}{dt} = k_6[A][AA]$$

$$\frac{d[GGG]}{dt} = k_9[G][GG]$$

$$\frac{d[AGG]}{dt} = k_8[AG][G] + k_{10}[A][GG]$$

These 9 simultaneous differential equations were solved numerically using POLYMATH 6.1, setting the initial glyoxal and ammonium sulfate concentrations to 2.21 M and 3.11 M respectively. Since to our knowledge no rate constant data is available for this system, all the rate constants were assumed to be equal. With each rate constant set to a value of $5 \times 10^{-4} \text{ l} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$ the model roughly reproduced the time evolution of products observed in Figure 1(b). The results are shown in Figure S3.

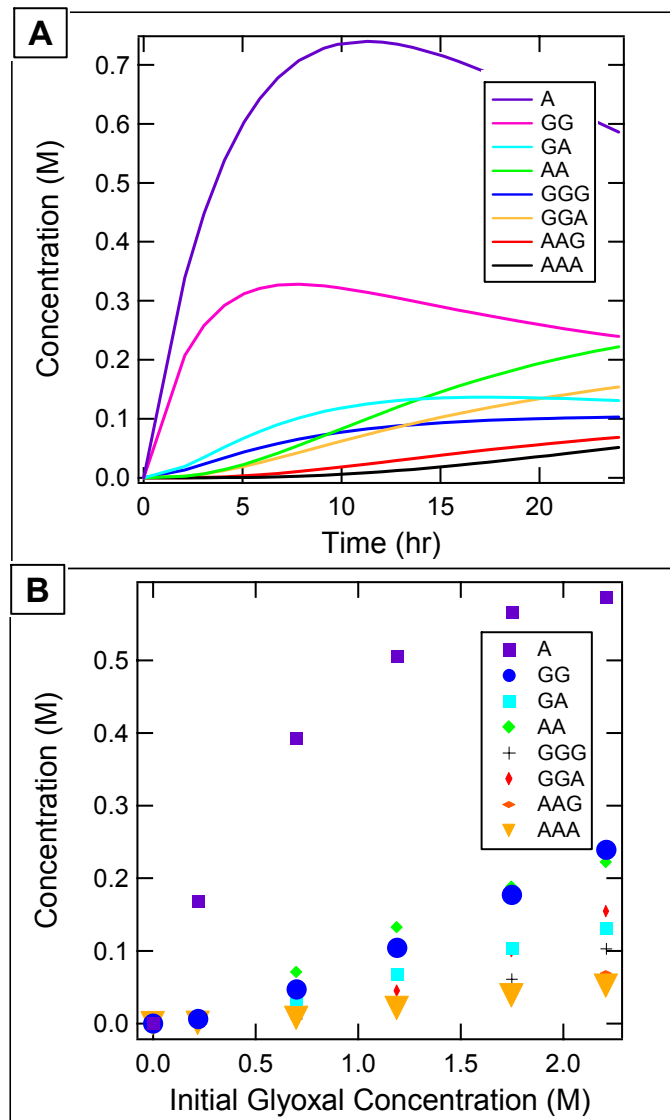


Figure S3. Output of simplified kinetics model. Concentrations of first, second, and third-generation product species is shown as a function of (a) time and (b) initial glyoxal concentration.

References

- Anastasiadis, S. H., Chen, J. K., Koberstein, J. T., Siegel, A. F., Sohn, J. E., and Emerson, J. A.: The Determination of Interfacial-Tension by Video Image-Processing of Pendant Fluid Drops, *J. Colloid Interface Sci.*, 119(1), 55-66, 1987.
- Canny, J.: A Computational Approach to Edge Detection, *IEEE Trans. Patt. Anal. Mach. Intell.*, 8, 679-714, 1986.
- Juza, J.: The pendant drop method of surface tension measurement: Equation interpolating the shape factor tables for several selected planes, *Czech. J. Phys.*, 47(3), 351-357, 1997.