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 μl or 100 μL 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 × 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 × 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 the shape factor, 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 ±10 μg (Denver Instruments).
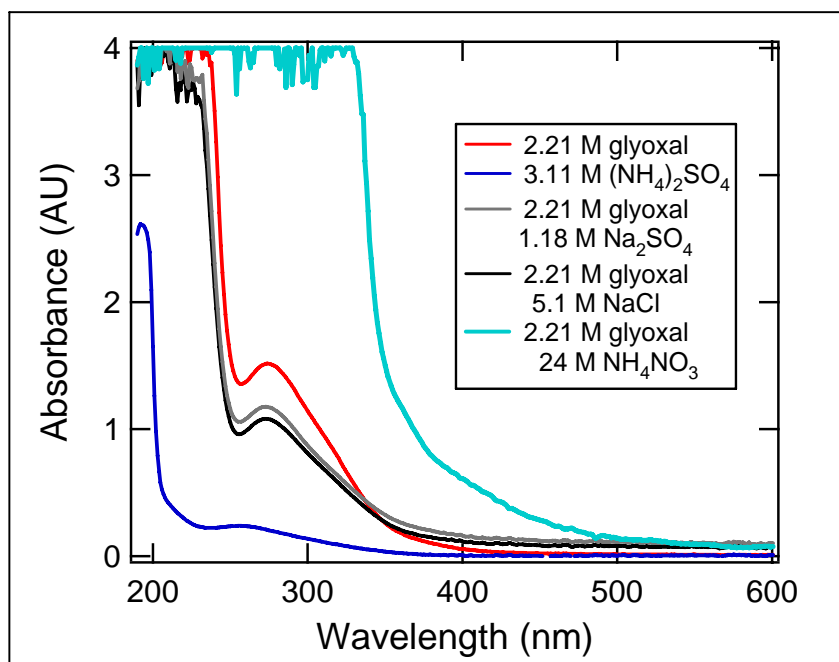
2. Results of control experiments

Figure S1. UV/Vis spectra of control solutions. Measurements made 24 h after mixing**.**
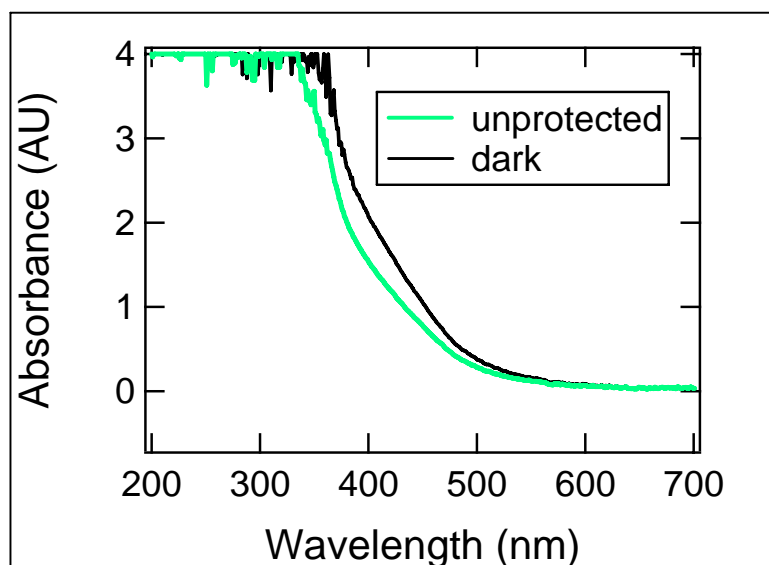
Figure S2. Results of control experiment for ambient light. An aqueous solution containing 2.21 M glyoxal and 3.11 M ammonium sulfate was allowed to react for 24 h in a Pyrex vessel covered with aluminum foil. The resulting UV/Vis spectrum is shown along with the corresponding curve from Figure 2a, in which the sample was not protected from ambient light.
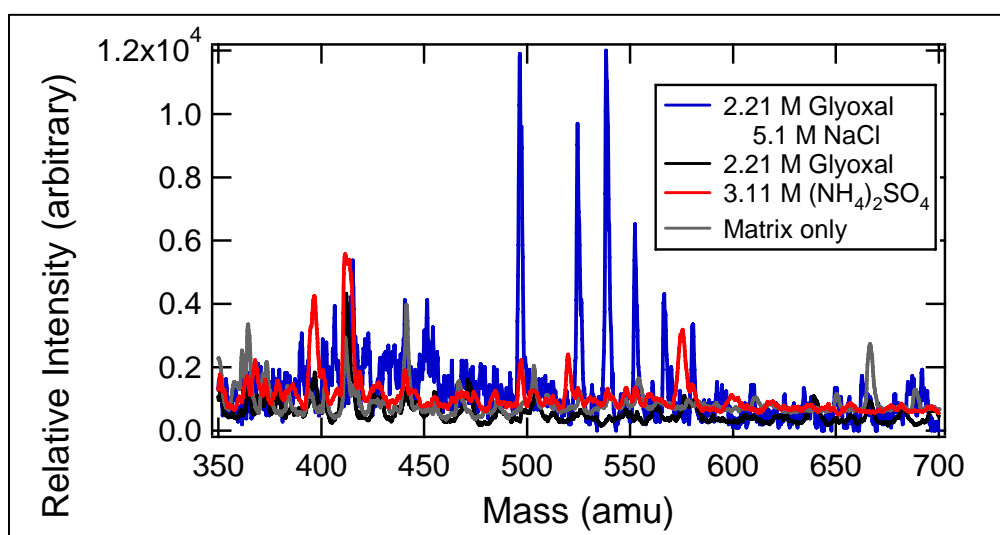

Figure S3. MALDI-MS spectra of control solutions. Measurements were made several days after mixing.

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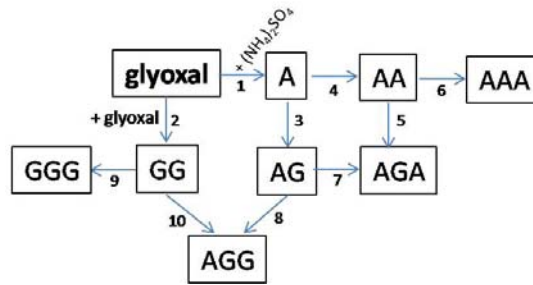
Scheme S1. Glyoxal reaction pathway. 'A' denotes a reaction product of glyoxal and ammonium sulfate, and 'G' denotes glyoxal.

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

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

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

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

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

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

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

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

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

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

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, rate constant data are not available for each step in this system, all the rate constants were assumed to be equal. With each rate constant set to a value of 5×10^{-4} l·mol^{-1}·min^{-1} the model roughly reproduced the time evolution of products observed in Figure 1(b). The results are shown in Figure S4.
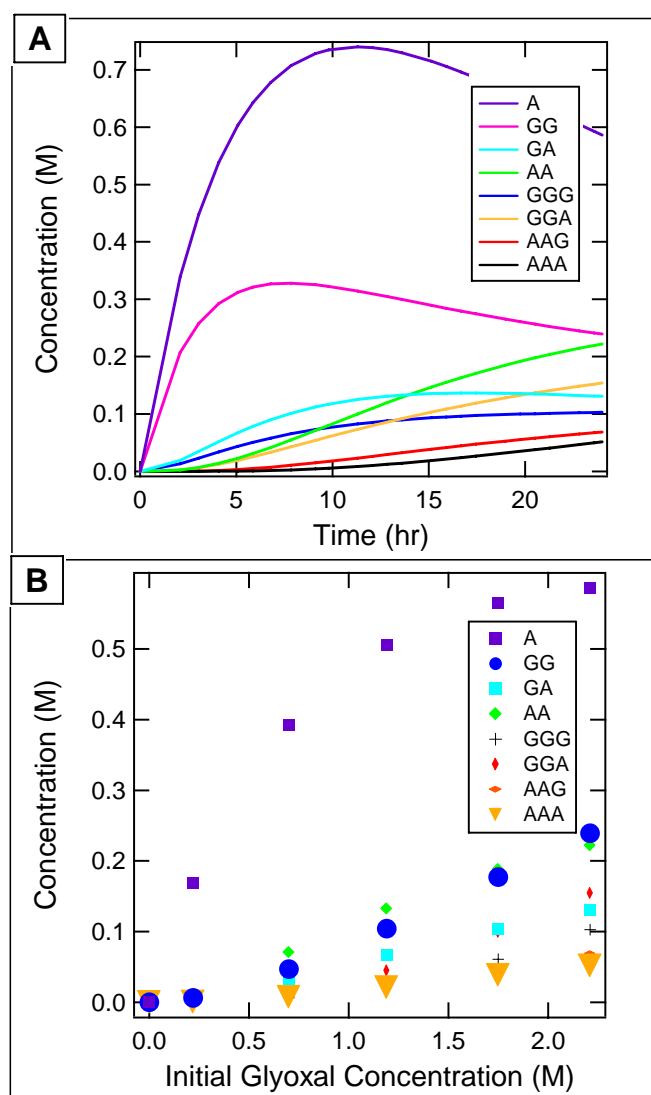
Figure S4. Output of simplified kinetics model. Concentrations of first, second, and third-generation product species is shown as a function of (a) time, for an initial glyoxal concentration of 2.21M and (b) initial glyoxal concentration at 24 h.

References

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