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Structural information and quantification of oligomeric components in secondary organic aerosols

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In recent years it has been recognized that high molecular weight compounds, or oligomers, are major constituents of secondary organic aerosols (SOA). The formation mechanisms, the chemical structure and the quantity of these oligomers are only poorly understood. We investigated the formation of oligomers in secondary organic aerosols generated from 1,3,5-trimethylbenzene, alpha-pinene and isoprene as gaseous precursors in smog chamber experiments. The formation rate of oligomers in SOA is comparable with chain reaction kinetic regimes well-known from polymer chemistry. The molecular size and structure of the oligomers were analyzed with laser mass spectrometry and electrospray ionization mass spectrometry. Mass pattern typical for oligomers are measured with both techniques, as well as temporal changes of the oligomer molecular size distribution with increasing ageing. Tandem mass spectrometry measurements along with accurate mass determination were performed to get insights into the structure of the oligomers. Due to a lack of appropriate quantification standards for these oligomers, mass spectrometric methods cannot be used for quantification of the oligomer mass fraction in SOA particles. A quantification of the water soluble oligomer mass fraction in SOA was performed after size exclusion chromatographic separation of the oligomers from lower molecular weight compounds followed by a coupling of the electrospray mass spectrometer with an evaporative light scattering detector (ELSD). While the mass spectrometer gives qualitative information of the oligomer content of the different fractions, the ELSD simultaneously quantifies the oligomer fraction. ELSD is a novel quantification method for atmospheric samples, which is almost independent on the chemical properties of the analyzed compounds

and thus ideally suited to quantify compounds with unknown chemical properties and structure such as the oligomers analyzed here.