

The kinetics of cationic polymerization at the air/water interface

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Hydronium ions, H_3O^+ , at the topmost layers of the air-acidic water interface can transfer H^+ to species whose proton affinity (PA) is larger than that of gaseous water ($\text{PA} = 165 \text{ kcal mol}^{-1}$) due to the less hydrated coordination.^{1,2} This interface-specific acid-catalyst induces cationic polymerizations of unsaturated hydrocarbons even in the presence of water, which is an effective quencher.^{3,4} Cationic polymerizations are generally described by following reactions.

Initial proton transfer reaction: $\text{R (gas)} + \text{H}_3\text{O}^+ (\text{int}) \rightarrow \text{RH}^+ (\text{int}) + \text{H}_2\text{O (int)}$

Chain-propagation reaction: $\text{R}_n\text{H}^+ (\text{int}) + \text{R (gas)} \rightarrow \text{R}_{n+1}\text{H}^+ (\text{int})$

Chain-transfer reaction: $\text{R}_n\text{H}^+ (\text{int}) + \text{R (gas)} \rightarrow \text{R}_n (\text{int}) + \text{RH}^+ (\text{int})$

Termination reactions: $\text{RH}^+ + (\text{H}_2\text{O})_m (\text{liq}) \rightarrow \text{RH-OH} + \text{H}^+(\text{H}_2\text{O})_{m-1} (\text{liq})$, and

$\text{R}_n\text{H}^+ + \text{Cl}^- (\text{int}) \rightarrow \text{R}_n\text{H-Cl (int)}$

Here, we investigated the competing reactions at the truly early stages of polymerization at the air-water interface. Carbocations were directly detected by surface-selective mass spectrometry ~10 micro seconds after exposure of various reactive gases to acidic water microjets ($1 < \text{pH} < 5$).

The extent of oligomerization was found to follow the order: 2-methyl-1,3-butadiene (isoprene, ISO) >> 1,3-butadiene > 1,4-pentadiene >> 1-pentene. Since ISO has an electron-donating methyl group adjacent to a C=C bond, it acts as a more effective nucleophile than 1,3-butadiene. Furthermore, we found that carbocations contain conjugated C=C bonds (ISO, 1,3-butadiene, 1,4-pentadiene), can be stabilized by the resonance, leading to successful oligomerization.

H-containing products were observed during the experiments on pure D_2O microjets, showing the chain-transfer reaction competed with the chain-propagation reaction. Multiple D- or H-substitutions were not observed, suggesting the termination reaction and re-ionization of oligomers did not occur under the present conditions. Furthermore, we found that the presence of an excess amount of NaCl does not disturb the oligomerization. These results suggest that termination processes involving the reaction of carbocations with interfacial water would not be important in the observed oligomerization process. The chemistry occurring at the topmost layers of water within a nanometer of the surface, where the water density sharply decreases, would be essentially different from the bulk chemistry.

References

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