

Degradation processes in the cellulose/N-methylmorpholine-N-oxide system studied by HPLC and ESR. Radical formation/recombination kinetics under UV photolysis at 77 K

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Abstract

Degradation processes of N-methylmorpholine-N-oxide monohydrate (NMMO), cellulose and cellulose/NMMO solutions were studied by high performance liquid chromatography (HPLC) and electron spin resonance (ESR) spectroscopy. Kinetics of radical accumulation processes under UV ($\lambda = 248$ nm) excimer laser flash photolysis was investigated by ESR at 77 K. Beside radical products of cellulose generated and stabilized at low temperature, radicals in NMMO and cellulose/NMMO solutions were studied for the first time in those systems and attributed to nitroxide type radicals $\sim\text{CH}_2\text{-NO}\cdot\sim\text{-CH}_2\sim$ and/or $\sim\text{CH}_2\text{NO}\cdot\text{-CH}_3\sim$ at the first and methyl $\cdot\text{CH}_3$ and formyl -CHO radicals at the second step of the photo-induced reaction. Kinetic study of radicals revealed that formation and recombination rates of radical reaction depend on cellulose concentration in cellulose/NMMO solutions and additional ingredients, e.g., Fe(II) and propyl gallate. HPLC measurements showed that the concentrations of ring degradation products, e.g., aminoethanol and acetaldehyde, are determined by the composition of the cellulose/NMMO solution. Results based on HPLC are mainly maintained by ESR that supports the assumption concerning a radical initiated ring-opening of NMMO. © Springer Science+Business Media B.V. 2007.

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Keywords

Cellulose, ESR, Flash photolysis, High performance liquid chromatography (HPLC), N-methylmorpholine-N-oxide, Radicals