Heparan Sulfate Degradation via Reductive Homolysis of its *N*-Chloro Derivatives

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SUPPLEMENTARY DATA

N-Chloro derivative	Hyperfine splitting (mT)[1]			Assigned structure of trapped radical
	a(N, NO)	*a*(H)	*a*(other)	
[2-^{13}C]-GlcNH_2 chloramine	1.55	2.50	0.66 (^{13}C)	C-2 carbon-centered radical (adduct isomer)
	1.56	2.34	0.67 (^{13}C)	C-2 carbon-centered radical (adduct isomer)
	1.53	2.28	0.80 (^{13}C)	C-2 carbon-centered radical (adduct isomer)
[2-^{13}C]-GlcNH_2 dichloramine	1.48	1.83	0.34 (N)	*N*-chloroaminyl radical ($^{\bullet}$NCl-R)
GlcNSO_3 *N*-chlorosulfonamide	1.61	2.32	-	C-2 carbon-centered radical (adduct isomer)
	1.61	2.14	-	C-2 carbon-centered radical (adduct isomer)
Polymer-derived chloramines	1.57[2]	2.34[2]	-	carbon-centered radical
	1.57	1.86	-	$CO_2^{\bullet-}$
Polymer-derived dichloramines	-	-	-	no substrate-derived adducts detected
Polymer-derived *N*-chlorosulfonamides	1.50[2]	2.70[2]	-	carbon-centered radical
	2.10[2]	1.70[2]	-	unidentified
	7.0[2] (total width)			unidentified
	1.57	1.86	-	$CO_2^{\bullet-}$

[1] Hyperfine coupling constants $\pm$ 0.01 mT

[2] Approximate value due to broad nature of spectral lines

Table 1. Substrate-derived DMPO adducts detected by EPR spectroscopy upon decomposition of monosaccharide and polymer *N*-chloro derivatives in the presence of DMPO.

N-Chloro derivative	Hyperfine splitting (mT)[1]			Assigned structure of trapped radical
	a(N, NO)	*a*(H)	*a*(other)	
$GlcNH_2$ chloramine, polymer-derived $GlcNH_2$ chloramines, $GlcNH_2$ dichloramine, polymer-derived $GlcNH_2$dichloramines	-	-	-	no substrate-derived adducts detected
$GlcNSO_3$ *N*-chlorosulfonamide	1.52	0.05	0.18 (N)	C-2 carbon-centered radical (adduct isomer)
	1.53	-	0.18 (N)	C-2 carbon-centered radical (adduct isomer)
	1.50	0.08	0.22 (N)	C-2 carbon-centered radical (adduct isomer)
	1.47	-	-	$SO_3^{\bullet-}$
Polymer-derived $GlcNSO_3$ *N*-chlorosulfonamides	1.50[2]			carbon-centered radical
	>1.50[2,3]	-	-	carbon-centered radical
	1.47	-	-	$SO_3^{\bullet-}$

[1] Hyperfine coupling constants $\pm$ 0.01 mT.

[2] Approximate value due to broad nature of spectral lines

[3] Tentative assignment, see text

Table 2. Substrate-derived MNP adducts detected by EPR spectroscopy upon decomposition of monosaccharide and polymer *N*-chloro derivatives in the presence of MNP.

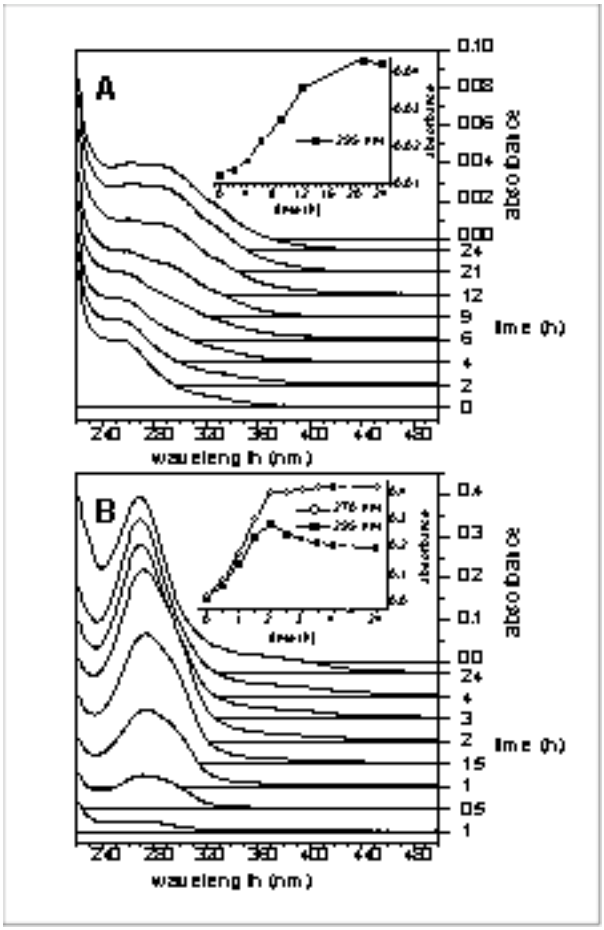

Figure 6. Formation of chromophores upon decomposition of polymer *N*-chloro derivatives. UV-vis absorbance spectra of samples were obtained after 10-fold dilution in phosphate buffer. (A) dnsp-HP chloramines (406 μM) + Cu^{2+} (10 μM), 37°C, aerobic conditions; *inset* – absorbance values at 295 nm. (B) p-HP NCl (2.01 mM) + Cu^{2+} (10 μM), 37°C, aerobic conditions; *inset* – absorbance values at 270 and 295 nm.