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APPENDIX A

DETERMINATION OF CHN IN COPOLYMER BY ELEMENTAL ANALYSIS

Compositions of starch-g-polyacrylamide after saponification with a 5% potassium hydroxide solution for various periods of time are shown in Table A-1.

Table A-1 Compositions of Starch-g-polyacrylamide after Saponification

Period of Saponifiaction Time	Sample NO.	Composition of the Elements (%)		
(minute)		Carbon	Hydrogen	Nitrogen
0	1	46.499	6.978	10.982
(unsaponified sample)	2	46.611	6.761	10.998
	3	46.144	6.992	10.928
	Average	46.418	6.910	10.968
30	1	43.463	6.417	10.573
	2	43.717	6.696	10.549
	3	43.396	6.273	10.550
_	4	43.770	6.427	10.481
	Average	43.587	6.453	10.538
60	1	42.268	6.570	9.630
	2	42.558	6.786	9.740
	Average	42.413	6.679	9.685

Table A-1 Composition of Starch-g-polyacrylamide after Saponification (continued)

Period of Saponifiaction Time	Sample NO.	Composition of the Elements (%)		
(minute)		Carbon	Hydrogen	Nitrogen
90	1	41.372	6.438	9.173
	2	41.650	6.286	9.383
	3	41.629	5.965	9.355
`	Average	41.550	6.230	9.304

These data were analyzed by CHNS/O analyzer (Perkin Elmer PE 2400 Series II).

APPENDIX B

INTERACTION OF RADIATION WITH WATER

The Formation of Primary Free-Radical Products in Water Radiolysis

The overall process of producing chemical changes by the use of ionizing radiation starts with the bombardment of water or aqueous solution by the radiation and terminates with the reestablishment of chemical equilibrium. This process is usually divided into three stages.

1) The physical stage consists of energy transfer to the system. Its duration is of the order of 10⁻¹⁵ sec or less. The incident radiation produces, indirectly, ionization of water,

$$H_2O \longrightarrow e^- + H_2O^+$$
 (B.1)

as well as directly excitation,

$$H_2O \longrightarrow H_2O^{\bullet}$$
 (B.2)

2) The physicochemical stage consists of processes which lead to the establishment of thermal equilibrium in the system. Its duration is usually taken to be of the order of 10⁻¹¹ sec or less. Electron ejected in the ionization process become thermalized and hydrated:

$$e \rightarrow e_{therm} \rightarrow e_{aq}$$
 (B.3)

The H₂O⁺ ions undergo a proton transfer reaction with neighboring water molecules,

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH$$
 (B.4)

and the H_3O^+ becomes hydrated; hence, the point of formation an the initial spatial distribution of $H_3O^+_{aq}$ and OH are essentially the same and different from those for e^-_{aq} . If the volume in which they arose is considered to be spherical, then the radius for the initial distribution of the hydroxyl radicals and $H_3O^+_{aq}$ is about three times smaller than that of the hydrated electrons.

The dissociation of excited water molecules gives the hydrogen atom and hydroxyl radical as main products,

$$H_2O^{\bullet} \rightarrow H + OH$$
 (B.5)

It also gives a low yield of hydrated electrons and, eventually, molecular hydrogen. It seems, however, that the contribution of excited water molecules to the formation of primary free-radical products in water radiolysis is of minor importance in comparison with that of the ionization processes.

3) The chemical stage consists of diffusion away from the point of origin and chemical reaction of primary species (e⁻_{aq}, OH, H₃O⁺_{aq}, and H), and leads to the establishment of chemical equilibrium. It begins in the spur about 10⁻¹¹ sec after the passage of the radiation and about 10⁻¹⁰ sec in the bulk of the solution. Table B-1 summarizes important chemical reactions of the primary species.

The expression for radiation-induced water decomposition,

$$H_2O \longrightarrow H_3O_{aq}^+, OH, e_{aq}^-, H, H_2O_2, H_2$$
 (B.6)

represents the state in irradiated water about 10⁻⁹ sec after the passage of high energy radiation, when the reactions in the spurs, blobs, and short tracks are practically terminated. These products are found in irradiated water irrespective of the type and energy of radiation.

When dilute aqueous solutions are irradiated practically all the energy absorbed is deposited in water molecules and the observed chemical changes are brought about *indirectly* via the molecular and, particularly, the radical products. *Direct* action due to energy deposited directly in the solute is generally unimportant in dilute solutions. At higher solute concentrations direct action may be significant, and there is some evidence that excited water molecules may transfer energy directly to the solute [1].

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Table B-1 Reactions of Free Radicals in Irradiated Water

	R	eaction	Rate Constant,	pH
			M ⁻¹ sec ⁻¹	-2
$e_{aq} + e_{aq}$	2H2O	$H_2 + 2OH^-$	5.5 x 10°	13.3
			5 x 10 ⁹	10-13
			6 x 10 ⁹	11
$e_{aq} + H$	H2O	$H_2 + OH^-$	2.5 x 10 ¹⁰	10.5
			3 x 10 ¹⁰	10.9
e aq + OH	\rightarrow	OH.	3 x 10 ¹⁰	11
$e_{aq} + O$	→	2OH ⁻	2.2 x 10 ¹⁰	13
$e_{aq} + H_3O^+$	\rightarrow	$H + H_2O$	2.06 x 10 ¹⁰	2.1-4.3
			2.36×10^{10}	4-5
			2.2 x 10 ¹⁰	-
			2.26 x 10 ¹⁰	4.1-4.7
$e_{aq} + H_2O_2$	\rightarrow	OH + OH	1.23 x 10 ¹⁰	7
			1.36 x 10 ¹⁰	11
			1.1 x 10 ¹⁰	-
			1.3 x 10 ¹⁰	11
e _{aq} + HO ₂ -	\rightarrow	O - + OH.	3.5 x 10°	13
e _{aq} + H ₂ O	->	H + OH.	16	8.3-9.0
Н + Н	→	H_2	1.5 x 10 ¹⁰	0.2-0.8 N H ₂ SO ₄
			1.0 x 10 ¹⁰	2.1
			7.75 x 10 ⁹	3
			1.3 x 10 ¹⁰	0.4-3
			1.25 x 10 ¹⁰	2-3
Н + ОН	\rightarrow	H ₂ O	3.2×10^{10}	0.4-3

Table 2.2 Reactions of Free Radicals in Irradiated Water (continued)

	R	eaction	Rate Constant	рН
			M ⁻¹ sec ⁻¹	
H + OH	→	e aq	1.8 x 10 ⁷	11.5
			2.2×10^7	11-13
$H + H_2O_2$	\rightarrow	$H_2O + OH$	5 x 10 ⁷	acid
			1.6 x 10 ⁸	0.4-3
			9 x 10 ⁷	2
			4 x 10 ⁷	-
OH + OH	\rightarrow	H_2O_2	6 x 10 ⁹	0.4-3
			4 x 10 ⁹	7
			5 x 10 ⁹	-
O. + O.	\rightarrow	O_2^{2-}		
	H2O	$HO_2^- + OH^-$	1 x 10 ⁹	13
OH + OH	\rightarrow	$O^- + H_2O$	3.6 x 10 ⁸	-
OH + H ₂ O ₂	→	HO ₂ +H ₂ O	4.5 x 10 ⁷	7
			1.2 x 10 ⁷	0.4-3
			2.25 x 10 ⁷	-
$O^{-} + HO_{2}^{-}$	\rightarrow	$O_2^- + OH^-$	7 x 10 ⁸	13
			2.74 x 10 ⁸	13
OH + H ₂	\rightarrow	$H + H_2O$	6 x 10 ⁷	7
			4.5 x 10 ⁷	7
O +H ₂	→	H + OH	8 x 10 ⁷	13
H ₃ O ⁺ + OH ⁻	\rightarrow	2H ₂ O	14.3 x 10 ¹⁰	-
			4.4 x 10 ^{10a}	-

^a Low value obtained in neutral solution with high-intensity pulses

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