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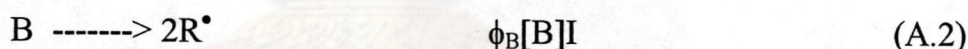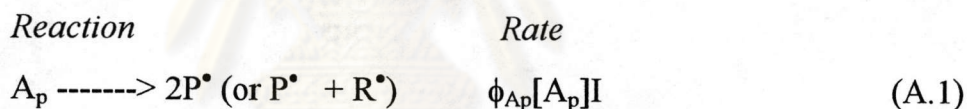
APPENDIX A

Relationship of the G-value to Radiation Grafting

In direct grafting method, radiation grafting involves the irradiation of a two-component system, i.e. a polymer A_p and a monomer B. Since free radicals arise under irradiation of both the polymer and the monomer, it is clear that the yield of grafting will increase under those experimental conditions which minimize the radiolysis of the monomer. The rates of the two radiation chemical events which lead to free radials are given by the following expression:

Reaction	*Rate*	
$A_p \text{-------} > 2P^\bullet \, (\text{or } P^\bullet + R^\bullet)$	$\phi_{Ap}[A_p]I$	(A.1)
$B \text{-------} > 2R^\bullet$	$\phi_B[B]I$	(A.2)

Here $P^\bullet$ is a polymeric free radical and $R^\bullet$ a low-molecular-weight radical or an atom; $\phi_{Ap}[A_p]$ and $\phi_B[B]$ represent the free radial yields pertaining to polymer A_p and monomer B respetively and I is the exposure dose-rate. Both yields $\phi_{Ap}[A_p]$ and $\phi_B[B]$ are expressed in moles of free radicals per litre per roentgen; they are directly related to the corresponding G_R values (e.g. to the free radical yields expressed in number of radicals per 100 eV absorbed in the irradiated medium).

It immediatedly follows from expressions (A.1) and (A.2) that grafting will be favoured with respect to homopolymerization

$$\text{(1) if } \phi_{Ap} \gg \phi_B \tag{A.3}$$

$$\text{(2) if } [A_p] \gg [B] \tag{A.4}$$

Consequently, the highest yields of grafting are expected in those polymer-monomer combinations in which the free radical yield of polymer A_p is much larger than that of monomer B, and, for a given polymer-monomer combination, the yield of grafting is greater the lower the concentration of the monomer. Fairly large yields of grafting can be obtained even if the free radical yield of the monomer is higher than that of the polymer, provided one irradiates polymer A_p slightly swollen with monomer B.

The free radical yield of the monomer can be directly derived from the kinetics of its radiation polymerization and from experiments with free radical scavengers (diphenylpicrylhydrazyl, DPPH). Typical G_R values of various monomers are listed in Table A-1.

On the other hand, only little information is available on the free radical yields of polymer. In most cases, these yields have to be estimated on the basis of the G_R values obtained for low-molecular weight model substances having a similar chemical structure or from the yields of other radiation-chemical processes involving the particular polymer, such as cross-linking, degradation, gas evolution, etc. The expected free radical yields of a number of common polymers are listed in Table A-2.

Table A-1 Free Radical Yields of Monomers Derived from Radiation
Polymerization Kinetics and from Scavenger Data

Monomer	Method	G_R
Butadiene	—	Presumably very low
Styrene	Kinetics and DPPH	0.69
Ethylene	Kinetics	≈ 4
Acrylonitrile	Kinetics	5.6
	DPPH	5.0
Methyl methacrylate	Kinetics	11.5
	DPPH	5.5-6
Methyl acrylate	DPPH	6.3
Vinyl acetate	Kinetics	12.0
	DPPH	9.6
Vinyl chloride	—	Presumably close to 10

Table A-2 Expected Free Radical Yields of Polymers Estimated from the
G_R Values of Model Substances

Polymer	Model substance	Expected G_R
Polybutadiene	Low-molecular-weight olefins	2-4
Polyisoprene		
Polystyrene	Isopropylbenzene, xylene	1.5-3.0
Polyethylene	Low-molecular-weight alkanes	6-8
Poly(methyl methacrylate)	Low-molecular-weight esters	6 or 12
Poly(vinyl acetate)		
Poly(methyl acrylate)		
Cellulose	Ethers and alcohols	10
Poly(vinyl alcohol)		
Poly(vinyl chloride)	Low-molecular-weight alkyl chlorides	10-15
Poly(vinylidene chloride)		
Polyamides		Unknown, presumably high
Fluorinated polymers		

The figures quoted in this table are only crude estimates and should not be considered as being definitely established. They are believed to be useful, however, in selecting a particular polymer-monomer combination for grafting by the direct radiation method (1).

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APPENDIX B

Monomer Reactivity Ratios

The monomer reactivity ratios for many of the more common monomers in radical copolymerization are shown in Table B-1. These data are useful for study of the relation between structure and reactivity in radical addition reactions. The reactivity of a monomer toward a radical depends on the reactivities of both the monomer and the radical. The relative reactivities of monomers and their corresponding radicals can be obtained from an analysis of the monomer reactivity ratio data. The reactivity of a monomer can be seen by considering the inverse of the monomer reactivity ratio (1/r). Table B-2 shows 1/r values calculated from the data in Table B-1. The data in each vertical column show the monomer reactivities of a series of different monomers toward the same reference polymer radical. Thus the first coumn shows the reactivities of the monomers toward the butadiene radical, the second column shows the monmer reactivities toward the styrene radical, and so on. It is important to note that the data in each horizontal row in Table B-2 cannot be compared; the data can only be compared in each vertical column (1).

Table B-1 Typical Monomer Reactivity Ratios

Monomer 1	Monomer 2	r_1	r_2	$T(^oC)$
Acrylonitrile	1,3-Butadiene	0.02	0.3	40
	Methyl methacrylate	0.15	1.22	80
	Styrene	0.04	0.40	60
	Vinyl acetate	4.2	0.05	50
	Vinyl chloride	2.7	0.04	60
1,3-Butadiene	Methyl methacrylate	0.75	0.25	90
	Styrene	1.35	0.58	50
	Vinyl chloride	8.8	0.035	50
Methyl methacrylate	Styrene	0.46	0.52	60
	Vinyl acetate	20	0.015	60
	Vinyl chloride	10	0.1	68
Styrene	Vinyl acetate	55	0.01	60
	Vinyl chloride	17	0.02	60
Vinyl acetate	Vinyl chloride	0.23	1.68	60

Table B-2 Relative Reactivities (1/r) of Monomers with Various Polymer Radicals

Monomer	Butadiene	Styrene	Vinyl Acetate	Vinyl Chloride	Methyl Methacrylate	Methyl Acrylate	Acrylonitrile
Butadiene		1.7		29	4	20	50
Styrene	0.7		100	50	2.2	5.0	25
Methyl methacrylate	1.3	1.9	67	10		2	6.7
Methyl vinyl ketone		3.4	20	10			1.7
Acrylonitrile	3.3	2.5	20	25	0.82	1.2	
Methyl acrylate	1.3	1.3	10	17	0.52		0.67
Vinylidene chloride		0.54	10		0.39		1.1
Vinyl chloride	0.11	0.059	4.4		0.10	0.25	0.37
Vinyl acetate		0.019		0.59	0.050	0.11	0.24

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APPENDIX C

Viscosities of Products before and after Irradiation

Viscosities of gelatinized starch and products after irradiation in each of total dose are shown in Table C-1.

Table C-1 Viscosities of gelatinized starch and products after irradiation

Total dose (kgy)	Viscosity of gelatinized starch[a] (cps)	Viscosity of products after irradiation[b] (cps)	
		5 rpm	10 rpm
2	810	54,000	32,000
2.5	799	59,000	34,000
3	779	68,000	42,000
3.5	872	78,000	55,000
4	855	76,000	53,000
5	891	81,000	73,000

[a] Viscosities were determined by BROOKFIELD Viscometer Model DV-III with a No. LV 62 spindle at a shear rate of 34 rpm.

[b] Viscosities were determined by BROOKFIELD Viscometer with a No. RV 6 spindle

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