Radiation-Chemical Yield of Graft Copolymers in Radiation Grafting

Yoshito Ikada,* Fumitaka Horii, Yasuko Nishizaki, Tomoe Kawahara, and Hiroshi Uehara

Department of Polymer Chemistry, Faculty of Engineering, Kyoto University, Kyoto, 606, Japan.

Received September 4, 1974

ABSTRACT: Experimental results which have already been published on radiation graft copolymerizations allowed us to calculate the G value for the formation of graft branches, G_b, which is defined as the number of branches per 100 eV of energy absorbed in the substrate polymer. G_b was found to be comparable with G value for the radical formation on the substrate polymer, G_R. Combining this result with a statistical calculation it may be predicted that the average number of branches per graft copolymer molecule does not exceed two, at least when the starting substrate polymer having a $\bar{M}_n$ of about 10^5 is grafted with a radiation dose below 10^6 rads. Experimental results support this prediction. Also, the fraction of the substrate polymer grafted was discussed in correlation with the G_b. Observed ratios of the number-average molecular weight of the backbone of the graft copolymer to that of the starting substrate polymer also agreed with theoretical values, *i.e.*, close to two for unfractionated starting substrate polymers and nearly unity for fractionated ones.

There are numerous publications on the application of high-energy radiation to synthesize graft copolymers.[1-4] It is generally believed that the radiation graft copolymerization is initiated by active species such as radical and peroxide produced on the substrate polymer upon irradiation. In spite of a large number of studies on the graft copolymerization, no researcher has discussed the yield of the graft copolymer in terms of the amount of active species produced except for Stannett and coworkers.[5] We have been engaged in the studies of radiation graft copolymerizations,[6-18] especially focussing attention on the true yield and the chemical structure of the graft copolymers. Based on the experimental results it is possible to calculate the radiation-chemical yield, *i.e.*, G value for the formation of branches, G_b, which is defined as the number of branches formed per 100 eV of energy absorbed. In the present article calculated G_b values will be compared with G_R values, *i.e.*, G values for the radical formation on substrate polymers.

The number of branches per graft copolymer molecule and the molecular weight ratio of the backbone of the graft copolymer to the starting substrate polymer will also be discussed in correlation with the G_b value.

Results and Discussion

(1) Calculation of G Value of Branch Formation (G_b). The G_b value can be calculated in the following manner, provided that the grafting takes place uniformly throughout the films or fibers employed for the experiment. The total number of branches formed per gram of substrate polymer is $RAG_b/100$, since 1 g of substrate polymer absorbs an energy of RA, where R is the radiation dose and A is an energy conversion factor ($=6.243 \times 10^{13}$ eV/(rad g)). Therefore, the per cent graft Y is given by

$$Y = \frac{RAG_b}{100}\,\frac{\overline{M}_b}{N_A} \times 100 \qquad (1)$$

where M_b is the number-average molecular weight of the branch and N_A is Avogadro's number. By rearrangement of eq 1, we get

$$G_b = YN_A/RA\overline{M}_b \qquad (2)$$

Thus, G_b values can be calculated, if Y and $\bar{M}_b$ are available. Those Y's and $\bar{M}_b$'s which were obtained in the radiation graft copolymerization of styrene (St) and methyl methacrylate (MMA) onto poly(vinyl alcohol) (PVAL),[6-13] cellulose,[14-16] nylon,[17] and poly(ethylene terephthalate) (PET)[17] were employed for the calculation.

Conditions and results of the grafting are briefly given in Tables I, II, and III. The definitions of the terms in Table II are:

$$\text{total conversion of monomer} = \frac{\text{wt of total polymer formed}}{\text{wt of monomer employed}} \times 100$$

$$\text{per cent graft} = \frac{\text{wt of graft branches}}{\text{wt of substrate polymer}} \times 100$$

$$\text{graft efficiency} = \frac{\text{wt of graft branches}}{\text{wt of total polymer formed}} \times 100$$

$$\text{wt fraction of substrate polymer grafted} = \frac{\text{wt of substrate polymer participating in grafting}}{\text{wt of substrate polymer}}$$

Details of the grafting were described in the previous papers. Those grafting conditions were chosen in every case so that the per cent graft may become as high as possible. In the range of these radiation doses both cross-linking and scission of the substrate polymers do not take place to a significant extent.

The G_b values calculated with eq 2 using the per cent graft in Table II and the $\bar{M}_b$ value in Table III are given in Table IV, where G_R values in the literatures are also shown for comparison. It is apparent that G_b is in every case lower in the preirradiation grafting than in the simultaneous irradiation. This low efficiency of the preirradiation grafting is ascribed to partial disappearance of radicals prior to the initiation of graft copolymerization. In addition, it should be noted that the preirradiation grafting is restricted to the film and fiber surface because of insufficient diffusion of the monomer, in contrast with the simultaneous grafting with swelling agents.

If the radiation graft copolymerization actually starts from radicals or peroxides produced by irradiation on the polymer molecules, a correlation should be found between the amount of active sites and that of branches. The most relevant measure relating directly to the amount of active sites may be the G_R value. As can be seen from Table IV, the G_b values are almost equivalent to G_R at least in order of magnitude. This is not due to the presence of chain transfer agent used to regulate the length of branch, because the G_b was recently found not to be affected by the chain transfer agent.[18] The extremely low G_b found in the grafting onto PET is attributed undoubtedly to the low G_R, in other words, to an extraordinarily high stability of PET against radiation. Comparison of G_b with G_R leads to the

Table I
Conditions of Graft Copolymerizations

	Polymer								
	PVAL				Cellulose	PET		Nylon	
	Monomer								
	MMA			St	St	St		St	
Grafting method	Simul[a] irrad	Pre-irrad	Without[b] irrad	Simul[a] irrad	Simul irrad	Simul irrad	Pre-irrad	Simul irrad	Pre-irrad
[Monomer]/[MeOH], vol	20/80	40/60	40/60	20/80	20/72[c]	50/50	50/50	50/50	50/50
[Chain transfer agent[d]]/[monomer], mol	0.5	0.5	0.5	0.05	0.05	0.05	0.05	0.05	0.05
Dose rate × 10^{-4}, rad/hr	0.61	6.6		1.0	1.0	1.0	17	0.83	17
Dose, Mrad	0.30	1.0		0.46	0.20	0.50	14	0.39	2.4
Polym temp, deg C	50	50	60	50	50	50	50	50	20

[a] Preswollen with H_2O-MeOH (40–60) to a degree of swelling of 1.64. [b] Preswollen with H_2O to a degree of swelling of 2.69. [c] H_2O was added by such an amount as [monomer]/[MeOH]/[H_2O] = 20/72/8. [d] Trichloroethylene for MMA and carbon tetrachloride for St.

Table II
Results of Grafting

	Polymer								
	PVAL				Cellulose	PET		Nylon	
	Monomer								
	MMA			St	St	St		St	
Grafting method	Simul irrad	Pre-irrad	Without irrad	Simul irrad	Simul irrad	Simul irrad	Pre-irrad	Simul irrad	Pre-irrad
Total conversion of monomer, %	93.5	18.4	14.8	~100	34.3	~100	15.4	~100	27.1
Per cent graft, %	16.5	18.1	1.9	11.1	11.1	0.47	3.4	6.2	14.6
Graft efficiency, %	4.0	10.2	1.8	2.0	6.4	0.14	10.3	1.7	27.3
Wt fraction of substrate polymer grafted (10^{-2})	8.9	4.3	0.46	6.4	5.0	0.043	0.56	0.54	1.4

Table III
Number-Average Molecular Weights ($\bar{M}_n$) and Chemical Compositions of Graft Copolymers

	Polymer								
	PVAL[a]				Cellulose[a]	PET		Nylon	
	Monomer								
	MMA			St	St	St		St	
Grafting method	Simul irrad	Pre-irrad	Without irrad	Simul irrad	Simul irrad	Simul irrad	Pre-irrad	Simul irrad	Pre-irrad
MMA or St content of graft copolymer, wt %	39.5	61.4	68.8	63.5	55.8	91.5	85.9	91.9	91.4
$\bar{M}_n \times 10^{-5}$									
Graft copolymer	3.95	6.65	6.88	3.90	3.06	2.20	1.90	2.89	3.87
Substrate	1.15	1.15[b]	1.15[b]	1.15[b]	0.724	0.197	0.197	0.153	0.153
Separated branch	1.56	4.42	5.32	1.88	1.87	2.03	2.00	2.37	3.71
Homopolymer formed	0.76	4.63		2.44	1.95	2.11	1.77	2.16	3.90
$\bar{M}_v \times 10^{-5}$ [c]	40	80		20	14	60			14

[a] Hydroxyl groups in the polymers were completely acetylated. [b] The $\bar{M}_n$ values given in ref 11 and 13 should be corrected. [c] Viscosity-average molecular weights of homopolymers formed in the substrate matrix in the absence of chain transfer agents.

Table IV
G Values of Branch Formation (G_b) and Radical Formation (G_R)

	Polymer								
	PVAL				Cellulose	PET		Nylon	
	Monomer								
	MMA			St	St	St		St	
Grafting method	Simul irrad	Pre-irrad	Without irrad	Simul irrad	Simul irrad	Simul irrad	Pre-irrad	Simul irrad	Pre-irrad
G_b	3.4	0.4		1.2	2.8	0.04	0.01	0.65	0.22
G_R		1–6, 11.3			2.88, 2.9	0.025		0.7	
Ref		19 20			21 22	23		24	

Table V
Number N_g of Branches per Graft Copolymer Molecule and Molecular Weight Ratio $\bar{M}_B/\bar{M}_{B,0}$ of Backbone of the Graft Copolymer to Starting Substrate Polymer

	Polymer								
	PVAL				Cellulose	PET		Nylon	
	Monomer								
	MMA			St	St	St		St	
Grafting method	Simul irrad	Pre-irrad	Without irrad	Simul irrad	Simul irrad	Simul irrad	Pre-irrad	Simul irrad	Pre-irrad
N_g	1.00	0.93	0.89	0.97	0.92	0.99	0.82	1.12	0.95
$\bar{M}_B/\bar{M}_{B,0}$	2.07	2.23	1.87	1.80	1.87	0.95	1.36	1.56	2.22

Table VI
Molecular Weight Ratio $\bar{M}_B/\bar{M}_{B,0}$ of Backbone to Starting Substrate Polymer for the Graft Copolymers Prepared from Fractionated and Unfractionated PVAL's as Substrate

	Code No.						
	M1M[c]	C1M[a,c]	M3M[d]	M3S[d]	M8S[d]	M9S[d]	M10S[d]
Monomer	MMA	MMA	MMA	St	St	St	St
$\bar{M}_{B,0} \times 10^{-5}$[b]	1.84	1.99	0.664	1.15	0.664	1.15	1.15
$\bar{M}_B/\bar{M}_{B,0}$	1.20	1.10	1.69	1.94	2.09	2.05	2.54
Ref	11	11		18	18		18

[a] Only in this case grafting was carried out by a chemical method with potassium persulfate as initiator. [b] Hydroxyl groups were completely acetylated. [c] Fractionated. [d] Unfractionated.

important conclusion that the number of branches formed by radiation grafting is closely related to the number of active sites formed on the polymer substrate upon irradiation. Although one should not place too much emphasis on the absolute G_R value because of its dependence on the irradiation conditions and the history of the polymer specimen, it may be concluded that the maximum per cent graft can be predicted from the G_R value.

It should be mentioned here that Stannett and coworkers[5] have obtained a similar result; the G_b values for both simultaneous irradiation and preirradiation grafting of styrene onto cellulose acetate compare reasonably with the G_R value.

(2) Fraction of the Substrate Polymer Grafted. The probability α of a monomer unit of the substrate polymer to be effectively grafted is related to G_b by the following equation

$$\alpha = \frac{RAG_b}{100}\frac{M_{0,S}}{N_A} \tag{3}$$

where $M_{0,S}$ is the molecular weight of the monomer unit of the substrate polymer. As shown in the previous work,[25] when the substrate polymer has initially the most probable molecular weight distribution, the weight fraction w of the substrate polymer effectively grafted is given by

$$w = \alpha\bar{P}_{B,0}(2 + \alpha\bar{P}_{B,0})/(1 + \alpha\bar{P}_{B,0})^2 \tag{4}$$

where $\bar{P}_{B,0}$ is the number-average degree of polymerization of the starting substrate polymer. Since the G_R, which is comparable with G_b as mentioned above, ranges from 0.1 to 10 for most of the polymers[26] and the dose R employed in the usual radiation grafting is 10^4 to 10^6 rads, it follows from eq 3 that α ranges from 10^{-7} to 10^{-3}. If α and $\bar{P}_{B,0}$ are, say, 10^{-5} and 1000, respectively, w is calculated from eq 4 to be 2×10^{-2}. Thus it is very reasonable that the fraction of the substrate polymer grafted is quite low as seen in Table II.

(3) Number of Branches. The number N_t of branches per starting substrate polymer molecule is given by

$$N_t = (Y/\bar{M}_b)/(100/\bar{M}_{B,0}) \tag{5}$$

where $\bar{M}_{B,0}$ is the number-average molecular weight of the starting substrate polymer. Substitution of eq 1 into eq 5 gives

$$N_t = \frac{RAG_b}{100N_A}\bar{M}_{B,0} \tag{6}$$

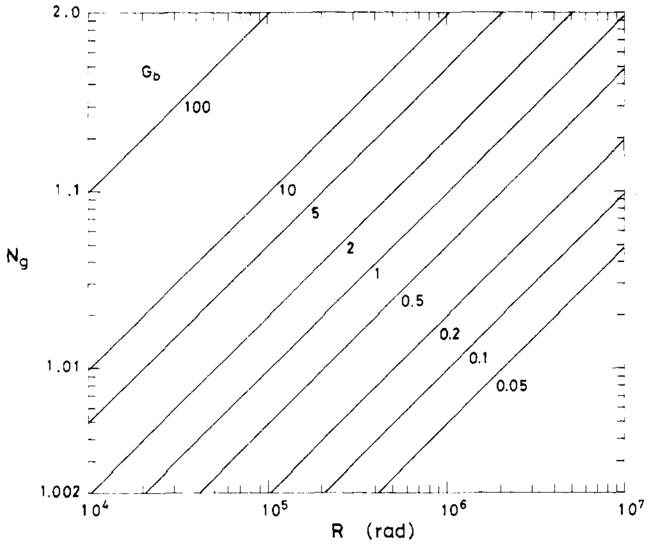

Figure 1. Relationship between radiation dose R, in rad, and average number N_g of branches formed per graft copolymer molecule. $\bar{M}_{B,0}$ is assumed to be 10^5.

N_t is also obtained as the product of α and $\bar{P}_{B,0}$. As demonstrated in the previous paper,[25] the number N_g of branches formed per graft copolymer is equal to $(1 + N_t)$ if the molecular weight distribution of the starting substrate polymer is most probable. Thus we get

$$N_g = 1 + \frac{RAG_b}{100N_A}\overline{M}_{B,0} \tag{7}$$

The relationship between N_g and R is shown in Figure 1 for various G_b values and a fixed $\bar{M}_{B,0}$ of 10^5. It is apparent that N_g would not exceed two in the usual radiation grafting.

In fact, the value of N_g, given in Table V, is in all cases about unity, in accord with the expectation from eq 7. Of course, the value of N_g may be increased to a value higher than two, if the substrate polymer has initially a much high molecular weight as several millions or carries such pendant groups that are readily attacked by radicals, for instance, sulfide group in wool.

(4) Molecular Weight of Backbone of Graft Copolymer. If the initial molecular weight distribution of a substrate polymer is uniform, the molecular weight of the backbone of the graft copolymer should be equal to that of the starting substrate polymer. However, if a substrate polymer having a broad molecular weight distribution is subjected to grafting, n-times longer molecules must have n-times greater chance to be grafted. In this connection we made a statistical calculation about the molecular weight $\bar{M}_B$ of the backbone of the graft copolymer.[25] According to this, the $\bar{M}_B/\bar{M}_{B,0}$ ratio should be close to two for the polymer having initially the most probable molecular weight distribution, so far as N_g is very close to unity, whereas it should be unity for the uniform distribution. For the former case we have already pointed out that the observed ratio is consistent with the theoretical one. This ratio is again given in Table V. As is seen, it is in the vicinity of two except for the graft copolymers from PET.

To present a further evidence to support the theoretical prediction, results on the fractionated PVAL are given in Table VI, together with those on the unfractionated PVAL. It can be clearly seen that the ratio is close to unity.

The fact that $\bar{M}_B/\bar{M}_{B,0}$ is about two in the case of graft copolymers prepared from the unfractionated substrate polymer is obviously attributed to the low probability of grafting reaction in the graft copolymerization.

The good agreement between the experimental and theoretical results shows that the synthesized copolymers are not block but graft type. If the end of substrate polymer is preferentially activated to form a block copolymer, $\bar{M}_B/\bar{M}_{B,0}$ should not be equal to two but unity regardless of the N_t value and the initial molecular weight distribution.

Conclusions

In conclusion it can be stated that the present work has quantitatively verified the generally accepted assumption in the radiation-induced graft copolymerization; the grafting starts from the active species produced on the substrate polymer by irradiation, resulting in the formation of branches. The reason is that the G value for branch formation is in every case found to be in the vicinity of the G value for the radical formation on substrate polymer. Clearly, the present findings that the fraction of the substrate polymer carrying graft branches is far less than unity and that the number of branches per graft copolymer molecule ranges from unity to two are to be extended to the grafting reactions conducted under the conventional condition onto other substrate polymers with medium G_R values.

Acknowledgment. The authors are indebted to Professor Ichiro Sakurada for advice and encouragement throughout the course of this investigation.

References and Notes

(1) H. A. J. Battaerd and G. W. Tregear, "Graft Copolymers," "Polymer Reviews," Vol. 16, Interscience, New York, N. Y., 1967.
(2) W. J. Burlant and A. S. Hoffman, "Block and Graft Polymers," Reinhold, New York, N. Y., 1960.
(3) R. J. Ceresa, "Block and Graft Copolymers," Butterworths, London, 1962.
(4) A. Chapiro, "Radiation Chemistry of Polymeric Systems," "High Polymer Series," Vol. 15, Interscience, New York, N. Y., 1962.
(5) J. D. Wellons, A. Schindler, and V. Stannett, *Polymer*, **5**, 499 (1964); H. A. Krässig and V. Stannett, *Advan. Polym. Sci.*, **4**, 111 (1965); D. Campbell, J. L. Williams, and V. Stannett, *J. Polym. Sci., Part A-1*, **7**, 429 (1969).
(6) I. Sakurada, Y. Ikada, and T. Yamaoka, *Bull. Inst. Chem. Res., Kyoto Univ.*, **45**, 1 (1967).
(7) I. Sakurada, Y. Ikada, T. Yamaoka, and F. Horii, *Bull. Inst. Chem. Res., Kyoto Univ.*, **46**, 13 (1968).
(8) I. Sakurada, Y. Ikada, and Y. Uesaki, *Bull. Inst. Chem. Res., Kyoto Univ.*, **47**, 49 (1969).
(9) I. Sakurada, Y. Ikada, and F. Horii, *Bull. Inst. Chem. Res., Kyoto Univ.*, **47**, 58 (1969).
(10) I. Sakurada, Y. Ikada, and F. Horii, *Makromol. Chem.*, **139**, 171 (1970).
(11) I. Sakurada, Y. Ikada, H. Uehara, Y. Nishizaki, and F. Horii, *Makromol. Chem.*, **139**, 183 (1970).
(12) Y. Ikada, Y. Nishizaki, and I. Sakurada, *Bull. Inst. Chem. Res., Kyoto Univ.*, **49**, 1 (1971).
(13) Y. Ikada, F. Horii, and I. Sakurada, *Bull. Inst. Chem. Res., Kyoto Univ.* **49**, 6 (1971).
(14) Y. Ikada, Y. Nishizaki, and I. Sakurada, *Bull. Inst. Chem. Res., Kyoto Univ.*, **50**, 20 (1972).
(15) I. Sakurada, T. Okada, and Y. Ikada, *Cellul. Chem. Technol.*, **6**, 35 (1972).
(16) I. Sakurada, Y. Ikada, and Y. Nishizaki, *J. Polym. Sci., Part C*, **37**, 265 (1972).
(17) I. Sakurada, Y. Ikada, and T. Kawahara, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 2329 (1973).
(18) Y. Ikada, F. Horii, and I. Sakurada, *Bull. Inst. Chem. Res., Kyoto Univ.*, **52**, 440 (1974).
(19) F. Kimura-Yeh, private communication.
(20) I. Nitta, S. Ohnishi, Y. Ikeda, and S. Sugimoto, *Annu. Rep. J. Assoc. Radiation Res. Polym.*, **2**, 219 (1960).
(21) R. E. Florin and L. A. Wall, *J. Polym. Sci., Part A*, **1**, 1163 (1963).
(22) J. T. Guthrie, M. B. Huglin, and G. O. Phillips, *J. Polym. Sci., Part C*, **37**, 205 (1972).
(23) D. Campbell and D. T. Turner, *J. Polym. Sci., Part A-1*, **5**, 2199 (1967).
(24) C. T. Graves and M. G. Ormerod, *Polymer*, **4**, 81 (1963).
(25) Y. Ikada and F. Horii, *Makromol. Chem.*, **175**, 227 (1974).
(26) D. Campbell, *J. Polym. Sci., Part D*, **4**, 91 (1970).