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Radiation-Induced Copolymerization of Styrene and Cellulose at Low Dose Rates

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SUMMARY

A study has been made of the radiation-induced grafting of styrene to cellulose in the presence of cobalt-60 gamma irradiation at low total doses and dose rates. For copolymerization, Whatmans 41 filter paper was immersed in solutions of styrene in methanol at various monomer concentrations. The dose rates were varied from 140 to 3100 rads/hr while the total dose varied from 10^3 to 2×10^5 rads.

In the presence of oxygen the grafting results showed considerable scatter, but a statistical analysis revealed that at all concentrations a linear relationship existed between total dose and graft %. Three factors contributing to the variance about the regression line were examined. Residual oxygen in the solution, while not important at high dose rates, was shown markedly to contribute to the variance in the range examined. A linear dose-rate effect involving a decrease in graft with increasing dose rate was demonstrated. A LET effect also contributed to the over-all variance. Preliminary results indicate the presence of a maximum which may be a Trommsdorff effect.

INTRODUCTION

A number of reports have been published showing that styrene in solution may be heterogeneously grafted to cellulose under the influence of ionizing radiation [1-10]. In particular, Dilli and Garnett [11] have thoroughly investigated this copolymerization reaction at dose rates of 70 krads/hr and higher for total doses above 10 krads. Interesting phenomena, including a Trommsdorff effect, were observed at the lower dose rates by irradiation of a solution of the monomer in which the cellulose had been immersed. The purpose of this present paper is to report a study of the same grafting process at very low dose rates and at total doses varying from 1.2 to 164 krads.

EXPERIMENTAL

The grafting was effected by irradiating strips of paper in solutions of styrene in methanol. The styrene prepared from a commercial source by distillation under reduced pressure was mixed with freshly distilled methanol to obtain solutions of 10, 20, 30, 40, and 60% of monomer by volume. The methanol was purified by the magnesium-iodine technique. The paper was Whatmans No. 41 double acid washed sheets for chromatography cut into strips 70 X 30 mm, the same batch of paper being used for all runs. Each strip was weighed, then folded in alternate directions to give a crimped strip 30 mm long. Three strips were placed in each test tube, one above the other, each layer being positioned at 90° to the horizontal axis of the previous one. A constriction was drawn in the upper part of the test tube and, after cooling, the paper in the tube was covered completely with 15-16 ml of the monomer solution (see Fig. 1). Thus some space (2-3 cc) containing air was left above the solution and consequently the initial stages of the irradiation were done in the presence of some oxygen.

The irradiations were carried out using an 800 Curie ^{60}Co source in the University of New South Wales. Fricke dosimetry was used to calibrate the source and the different dose rates were achieved by setting the test tubes at distances varying from 60 to 200 cm from it. This gave a range of eleven dose rates whose approximate values were 150, 300, 450, 600, 750, 1100, 1500, 1900, 2200, 2700, and 3100 rads/hr.

For the linear energy transfer (LET) effect studies a set of irradiations was made at three dose rates, i.e., 2000, 1143, and 667 rads/hr, in aluminum canisters. This was paralleled by a set of irradiations run in test tubes at the same dose rates. The aluminum canisters were 75 mm in diameter internally and of 5 mm wall thickness. Paper strips, 50 X 50 mm, were arranged on a rack at 10 mm intervals so that, apart from the rack areas, they were at least 10 mm from all but the solutions (see Fig. 2). For both canisters and tubes containing the paper but no solution, oxygen was

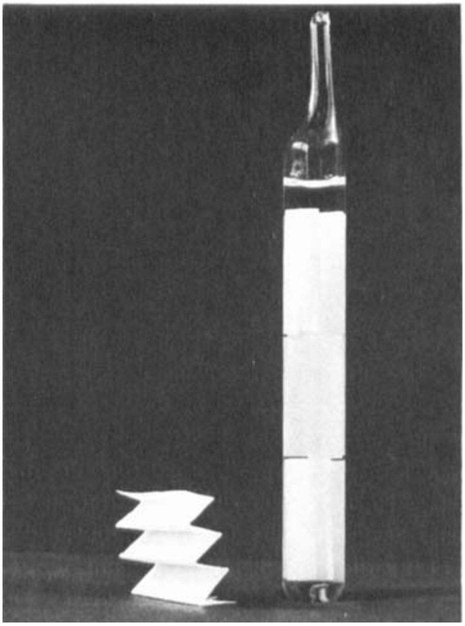

Fig. 1. Folded paper strip and sealed test tube with solvent and three paper strips.

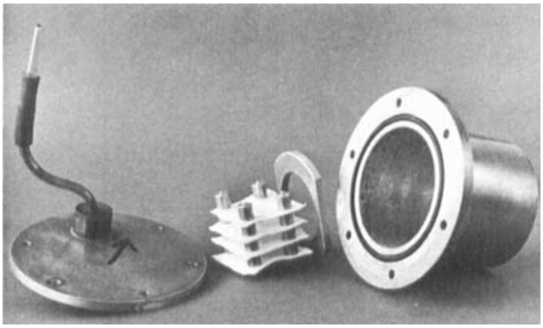

Fig. 2. Lid, rack with paper strips and spreaders in place, and aluminum canister.

removed by alternatively evacuating and filling with moist nitrogen; this was repeated several times. The solutions were then made up from freshly prepared reagents. The methanol was purged with dry nitrogen for 10 min

Table 1. Grafting of Styrene to Cellulose in Methanol under Differing Conditions of Radiation Dose, Dose Rate and Monomer Concentration in the Presence of Oxygen

Dose (rads) $\times 10^{-3}$	Dose rate (rads/hr)	Graft (% w/w) $\times 10$	Dose (rads) $\times 10^{-3}$	Dose rate (rads/hr)	Graft (% w/w) $\times 10$
Part (a) 10% Monomer					
2	148	11	35	735	18
3	140	24	35	1470	28
5	135	25	35	2220	18
5	304	9	38	1050	56
7	143	6	42	1730	36
7	290	23	42	2680	13
7	455	10	48	3060	20
10	280	22	51	1410	87
10	430	24	51	2090	40
10	608	9	54	1120	93
12	750	22	61	1700	89
14	300	14	62	2550	46
14	580	26	64	148	315
15	415	23	71	2930	63

17	720	27	72	2010	87
18	1140	10	72	1500	119
20	560	27	84	1750	164
21	442	14	89	2460	117
24	1520	12	101	2110	187
25	700	34	101	2800	127
26	1090	27	125	2610	139
29	595	30	131	304	452
29	1870	15	144	3000	203
Part (b) 20% Monomer					
2	148	0	27	1140	45
4	148	8	29	595	300
5	135	19	29	1870	73
5	304	7	35	2220	104
6	298	14	36	750	453
7	148	15	36	1520	297
7	285	25	38	1050	256
7	455	7	41	1700	78

(continued)

Table 1 (continued)

Dose (rads) $\times 10^{-3}$	Dose rate (rads/hr)	Graft (% w/w) $\times 10$	Dose (rads) $\times 10^{-3}$	Dose rate (rads/hr)	Graft (% w/w) $\times 10$
10	280	14	42	2680	125
10	608	7	45	1870	144
11	455	75	48	3060	118
12	750	11	49	2040	368
14	570	47	51	1410	348
14	575	62	55	1140	152
15	304	15	61	1700	282
15	415	35	64	2680	344
18	750	141	68	2840	393
18	1140	37	72	2010	322
20	560	45	73	3060	402
22	455	236	89	2460	416
24	1520	43	90	1870	550
25	700	79	101	2800	409
26	1070	78	107	2220	601
26	1070	196	147	3060	616

Part (c) 30% Monomer

1	138	4	20	413	890
2	148	27	20	560	205
2	288	4	21	2900	390
2	705	30	24	1520	197
3	140	54	25	700	298
3	413	5	25	1049	173
4	575	7	26	1090	446
5	135	16	28	575	831
5	304	14	29	1870	245
5	705	9	34	705	1195
6	262	11	34	1401	218
7	138	286	34	1430	607
7	140	455	35	2220	301
7	290	177	38	1050	450
7	455	42	41	2510	296
10	430	217	42	1730	730
10	608	33	42	2680	315

(continued)

Table 1 (continued)

Dose (rads) $\times 10^{-3}$	Dose rate (rads/hr)	Graft (rads/hr) $\times 10$	Dose (rads) $\times 10^{-3}$	Dose rate (rads/hr)	Graft (% w/w) $\times 10$
12	753	106	44	1834	389
13	531	78	45	3060	354
14	288	684	51	1410	610
14	580	234	51	2090	832
15	415	130	61	1700	848
15	624	60	62	2550	923
15	2050	24	71	2930	959
17	720	331	72	2010	921
18	742	112	101	2800	829
18	1140	143	120	2505	1332
18	2510	53			
Part (d) 40% Monomer					
1	138	0	24	1520	256
2	148	10	25	700	496
2	288	4	26	700	100

2	305	248	26	1070	364
3	413	3	26	1080	388
4	148	7	29	610	501
4	575	7	29	1870	284
5	135	122	34	1430	423
5	304	57	34	1430	424
5	705	23	35	2220	337
			35	1440	505
7	148	92	36	750	647
7	304	66	36	1520	107
7	455	108	38	1050	660
8	1070	34	41	1707	483
9	575	186	41	2500	553
10	280	253	42	2680	310
10	608	121	48	3060	368
10	1440	49	48	2050	646
11	455	105	51	1410	758
12	753	149	59	2510	595
12	1720	78	60	2500	537
15	415	206	60	2505	671

(continued)

Table 1 (continued)

Dose (rads) $\times 10^{-3}$	Dose rate (rads/hr)	Graft (% w/w) $\times 10$	Dose (rads) $\times 10^{-3}$	Dose rate (rads/hr)	Graft (% w/w) $\times 10$
15	608	199	61	1700	849
15	2050	81	68	2840	675
16	148	644	70	2900	720
17	700	269	72	2010	951
18	750	210	73	1520	1133
18	1140	234	73	3060	477
18	2510	135	89	2460	1043
20	560	438	101	2800	1099
21	2900	144	147	3060	2021
			164	1520	2410
Part (e) 60% Monomer					
1	148	10	21	1140	363
2	148	15	21	3060	132
2	304	12	22	455	362
3	138	63	23	1440	305

3	455	16	24	1520	195
4	148	32	26	1070	360
4	608	21	26	1080	312
5	304	58	28	1720	269
5	753	29	29	595	394
7	148	152	29	1870	257
7	285	166	33	304	468
7	288	144	34	1430	396
7	288	170	34	2050	270
7	304	109	35	1490	421
7	413	102	35	2220	299
7	413	186	36	750	501
7	455	58	40	1720	438
8	1140	65	40	2505	391
9	575	134	41	1705	445
10	413	154	42	2680	293
10	413	213	45	1870	437
10	608	127	47	2900	340
10	1520	57	48	2050	485

(continued)

Table 1 (continued)

Dose (rads) $\times 10^{-3}$	Dose rate (rads/hr)	Graft (% w/w) $\times 10$	Dose (rads) $\times 10^{-3}$	Dose rate (rads/hr)	Graft (% w/w) $\times 10$
12	705	191	48	3060	295
12	750	152	49	2050	465
13	1870	95	60	2500	442
14	570	255	60	2500	454
14	575	231	60	2505	365
14	575	251			
15	610	64	68	2840	514
15	2220	110	70	2900	511
16	148	70	73	1520	705
17	705	219	73	3060	422
17	707	236	107	2220	845
17	1080	257	128	2670	833
18	1140	163	147	3060	942
18	2680	117			

prior to mixing. Sakurada [2] and co-workers used a similar technique. For the test-tube irradiations the dose rate was determined as above. For the experiments in the canisters, however, in order to allow for the increased absorption of the impinging radiation by the aluminum, dosimetry was carried out within the canister itself. The canisters were found to absorb 15% of the radiation and allowance was made for this in calculating the distances from the source at which they were placed for dose-rates equivalent to those received by the solutions in the test tubes.

After irradiation, the strips of paper were removed from their containers, extracted with benzene in a Soxhlet extractor for 70 to 75 hr, dried, humidified, and weighed. The increase in weight was calculated as a percentage of the weight of the original paper. Dilli and Garnett [11] have shown this to be sufficient for complete extraction of the homopolymer and remaining monomer.

RESULTS

The results of the tests run in the general experiment are reported in Table 1. The values given for graft % are the means of each set of three results from each test tube. The values for each concentration were analyzed statistically to obtain constants for the regression lines representing the relationship between dose and percentage graft for each monomer.

The analysis was made according to the method described by Brownlee [12] and based on standard procedures. The data were processed by an IBM 360 computer. The constants for the regression lines, correlation coefficients, and residual variance about the regression line are reported in Table 2. The results of the dose-rate effect study are given in Table 3 while Table 4 shows the comparison of tests with and without oxygen. The LET results are given in Table 5.

DISCUSSION

Statistical Analysis

It is clear from the results of the statistical analysis (Table 2 and Fig. 3) that the relationship between graft and total radiation dose is linear within the limits of the experiment. The data fit Eq. (1):

$$\Gamma = mcd + \Gamma' \tag{1}$$

Table 2. Results of Statistical Analysis of Data in Table 1 Calculated to Fit Eq. (1) ($\Gamma = mcd + \Gamma'$)

c% (% v/v)[a]	m X 10^5	Γ'(%)	n[a]	r[a]
10	1.85	-1.4	46	0.781
20	2.48	-0.6	48	0.887
30	3.74	4.8	57	0.797
40	3.24	-1.6	65	0.940
60	1.09	8.2	72	0.920

[a]c represents the monomer % in solution, n the number of sets of results, and r the correlation coefficients. For comparison the value of r at the 0.001 level of significance lies between 0.380 (n = 70) and 0.456 (n = 45).

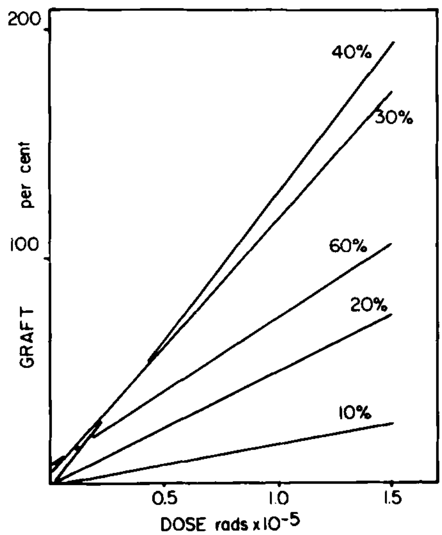

Fig. 3. Plot of graft % vs dose (rads). The constants given in Table 2 were used with Eq. (1) ($\Gamma = mcd + \Gamma'$).

Table 3. Dose-Rate Effect

(Constants for regression equation $\Gamma\% = acd - bcd_r + \Gamma''$. Dose in rads and dose rate in rads/hr)

Monomer % (% v/v)	a X 10^5	b X 10^4	Γ''	Variance ratio	Level of significance (%)
10	2.91	6.25	1.9	82.6	0.1
20	2.96	1.99	0.9	3.1	10
20[a]	11.05	6.74	-55.0	24.7	0.1
30	4.78	3.77	9.5	6.3	2.5
40	3.91	3.63	8.6	51.5	0.1
60	1.26	0.68	10.7	8.6	0.5

[a] Obtained under conditions of minimum LET effect and oxygen replacement with nitrogen.

Table 4. Effect of Adsorbed Oxygen

[Comparison of irradiations done in test tubes with (a) adsorbed O_2 and (b) adsorbed N_2 on cellulose. Dose 48,000 rads][a]

Dose rate (rads/hr)	20% Monomer		30% Monomer	
	a	b	a	b
2000	21.4	44.7	55.7	63.3
1143	24.8	58.6	65.4	129.0
667	26.7	73.8	70.8	183.1

[a] The values in the columns headed a were calculated from data in Table 2, i.e., with adsorbed oxygen corresponding to partial pressure of oxygen in air. Those in columns headed b were determined after repeated outgassing and simple replacement of air with moist nitrogen.

where Γ represents the increase in weight per 100 g paper when irradiated to dose d with a ^{60}Co source while immersed in a solution containing methanol and styrene (c%). The values of the constants m and Γ′ vary with conditions and are apparently the repository of such parameters as dose-rate effect, oxygen content of the system, LET effect, and general experimental error. Equation (1) is derived from the expression for the regression line and there is evidence that some of the effects contribute to both constants. Further, the effects appear to be interlinked but there is insufficient evidence to quantify this idea.

One implication of the linearity of the relationship of graft and dose is that the rate of diffusion of styrene to the surface of the cellulose must be greater than the rate of grafting and further, small changes in the concentration of monomer do not greatly effect the amount of graft. The highest graft recorded in this series was 240% which amounts to about 16% of the total styrene present. Most grafting results were less than half of this amount. The possibility exists that the grafting species is not limited exclusively to monomer (though this may be the main source of styrene) but includes dimers and higher groups and may even include solvent. The observed linearity of the graft with dose supports the work of Huang [13] with purified viscose where linear relationships up to 300% graft were obtained.

Table 5. Linear Energy Transfer Effect

(Comparison of data from irradiations in aluminum canisters with irridations in test tubes. 20% monomer solution and nitrogen adsorption on cellulose in both cases).

Dose rate (rads/hr)	Total dose (rads)	Graft (%)	
		Test tube	Canister
2040	48960		26.2
2000	48000	44.7	23.4
1870	44880		22.5
1793	43090		20.5
1155	48520		36.8
1143	48000	58.6	33.2
1082	45430		29.7
1047	43990		26.2
669	48140		46.8
667	48000	73.8	46.2
636	45780		38.1
620	44670		32.7

Dose-rate Effect

Dilli and Garnett [14] have shown the existence of a dose-rate effect in the radiation-induced grafting of styrene to paper at dose rates of 10^4 to 10^6 rads/hr. When considered in terms of graft for a given dose at various dose rates from 10^5 to 10^6 rads/hr, the relationship appeared hyperbolic in form, with the graft decreasing with increased dose rate. Over the small range considered in the present experiments, i.e., 140 to 3100 rads/hr, the possibility that the grafting effect might be linear with dose rate was examined. The data in Table 1 were therefore tested by using a form of statistical analysis [12] for multiple correlation considering both independent variables, dose and dose rate, to have linear relationships with the amount of grafting. The results of this analysis are given in Table 3 where a, b, and Γ'' refer to Eq. (2). It will be observed that two new constants, a (for dose) and b (for dose rate), have been introduced in Eq. (2). This is because m in Eq. (1) depends upon both dose and dose rate, and these two variables should be separated if possible.

$$\Gamma = acd - bcd_r + \Gamma'' \tag{2}$$

Here d and d_r refer to dose and dose rate, respectively, Γ and c are as for Eq. (1), and a, b, and Γ″ are constants. The variance ratio due to the effects of dose and dose rate was highly significant in the case of 10, 40, and 60% solutions and of some doubt in 20 and 30% solutions. However, all data were in agreement with Dilli and Garnett's work in regard to the sign of the effect, i.e., a decrease in graft occurs with increased dose rate. Even in the doubtful cases (20 and 30% solutions) the effect is considered to be real (see below) but is masked by the magnitude of the experimental error.

The examples of grafting at very low oxygen contents (after nitrogen replacement of oxygen) reported in Table 4 confirm the existence of a dose-rate effect in the 20 and 30% solutions. The fact that this effect is extensive when the oxygen concentration is low illustrates the dependence of dose rate on the oxygen content of the system. This result is in contrast to the work of Dilli and Garnett who found that oxygen had little effect at higher (70 to 140 krads/hr) dose rates.

Concentration Effect

Equations (1) and (2) demonstrate the dependence of graft on both radiation dose and concentration. The nature of the constants m and a is not so clear since the numerical values of these constants depend on a number of effects. In general terms the constants represent the slopes of the lines connecting graft and dose (Fig. 3) and vary in an interesting way. Plotted as in Fig. 4, the values of a are represented as falling on one or other of two curves of similar characteristics but of opposite sense, one representing the increasing concentration of monomer and the other the increasing concentration of solvent. The interaction of these curves represents the concentration that should give the greatest response in terms of graft for a given dose.

Since m in Eq. (1) is a function of both dose and dose rate, separate constants a and b have been used in Eq. (2) in connection with dose and dose rate, respectively. Thus plotting a vs concentration gives a value for the maximum sensitivity of the solution to grafting uninfluenced by the dose-rate effect as would be the case if m were plotted. The fact that a peak is obtained suggests that the system may exhibit a Trommsdorff effect [15]. It is worth noting that the peak occurs at a molar ratio

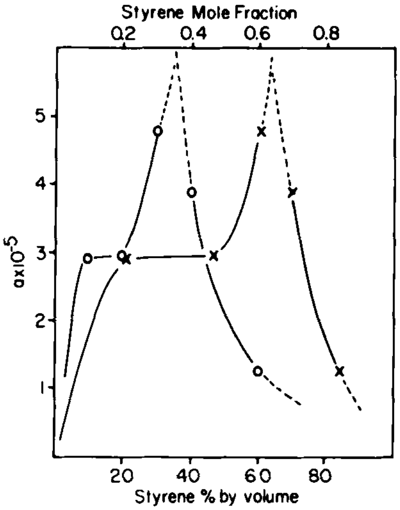

Fig. 4. Plot of slope of line representing graft % dose corrected for dose rate effect. The constant a of Table 3 is plotted against solvent concentration. Volume % (o) and (X) mole fraction of styrene.

(2:1) of styrene (S) to methanol (M). The system might then be considered as a solution of the complex S_2M in either styrene or methanol. The possibility that this complex is itself grafted might be studied more fully. The significance of the plateau in Fig. 4, between 10 and 20% styrene, has yet to be explained.

The advantages of correcting the graft percentage for the effects of dose rate and using a standard dose rate are obvious for the comparison of results between different groups. It is suggested that zero dose rate be used, an idea analogous to the infinite dilution concept.

Oxygen Effect

This effect is well known and is associated with an induction period or delay in the onset of grafting. The usual method of avoiding the effect is to outgas the sample solution by repeated freeze-pump-thaw cycles; however, this process can possess difficulties [16]. In an attempt to overcome this problem the technique described above for replacement of O_2 with N_2 was used with the 20 and 30% solutions. Tests were run parallel with those done in aluminum canisters. The replacement of gas on the surface of the cellulose would appear to have been accomplished easily, without seriously changing the quantity of water bound to the cellulose. The greatly increased grafting achieved compared with that obtained when limited oxygen was present (Table 4) amply illustrates the importance of removing oxygen from the surface of the cellulose and from the solution. The method is a simple alternative to the freeze-thaw procedure.

Linear Energy Transfer Effects

Evidence is now accumulating to show that the process of grafting in methanol depends on the formation and reaction of solvated electrons [17]. The electrons, arising from the interaction of γ photons with the atoms of container, paper, and solvent, will be solvated by the methanolic solution. The lifetime of these electrons is such that they can travel only relatively short distances before reaction. The ideal situation of measuring the graft caused by the electrons arising only from the atoms of the solution on the unfolded strip of paper has been almost achieved using the apparatus shown in Fig. 2. Here the paper is oriented perpendicular to the gamma irradiation from the source and over 10 mm from the inside surface of the canister. The supporting arms of the racks are the only foreign sources of electrons and these latter apparently are low in number. The 10 mm minimum distance for complete absorption of electrons is suggested by Trump and Van de Graaff [18]. Orientation of the paper parallel to the gamma radiation produced very little graft.

Table 5 gives the results for irradiations within canisters at the same dose rates as for the test-tube samples. The very considerable differences are considered to be largely due to LET effects.

The data obtained from these tests were also computerized to obtain a regression line relating the dose-rate effect to the graft % and dose. Despite the fact that the data were obtained from individual samples, each differing by only 2 to 5% in dose rate from its neighbor, a significant result was obtained for the existence and extent of the dose-rate effect. The constants for the regression line are reported in Table 3. The large value of the constant, however, suggests that extrapolation below 660 rads/hr. dose rate should lead to considerable error.

General Experimental Error

The manipulation errors involved in the experiments (e.g., weighing and measuring volumes) were small (~1%), yet the variation between triplicates within each test tube was at least 5% and repeated experiments at times produced even larger errors. The larger errors are attributed to two main sources, LET effects and oxygen effects. The removal of these as in the experiments reported in Tables 4 and 5 resulted in a variation between samples which approached the level of the manipulation errors outlined above. The reliability of the data, when compared with the regression line, is between 2 and 5%, better than the usual dosimetry errors.

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