New aspects of graft copolymerization of styrene onto cellulose induced by gamma rays

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Graft products of styrene onto cellulose prepared by simultaneous gamma-ray irradiation under various conditions were acid-hydrolysed to recover polystyrene produced within the cellulose matrix. The polystyrene was subjected to gel permeation chromatography to determine the molecular weight (M) and further separated with a thin-layer chromatographic (t.l.c.) technique into two components, i.e. the true grafted side-chain polymer and attendant homopolymer. This t.l.c. experiment allowed an estimation of the true percentage grafting (Y). Influences of changing the reaction conditions upon the values of M and Y were thus investigated, and some newer aspects on vinyl polymerization occurring within the cellulose matrix are presented.

INTRODUCTION

Graft copolymerization of vinyl monomers onto cellulose may be regarded as one of the classical subjects in the field of polymer chemistry[1]. However, it seems fair to say that no definitive conclusion on the copolymerization has yet been drawn because a complete characterization of graft products has not yet been achieved. This arises from difficulty in isolating the component of true graft copolymer from a given graft product. Various authors have noted[2–5], that solid state graft copolymers may act to homogenize the two different homopolymer species, namely, the side chain and the mother polymer, which should, by nature, be incompatible with each other; in the liquid state, graft copolymers often may act as emulsifiers in reducing the incompatible nature of different polymer species. These effects make it hazardous to isolate true graft copolymer by the fractional precipitation technique, which has usually been applied.

Recently we have reported that thin-layer chromatography (t.l.c.) was applicable to separation problems in cellulose–styrene graft products prepared by irradiation with gamma-rays[6,7]. At the outset of the study the crude graft product was subjected to extraction with boiling benzene, followed by degradation of the cellulose backbone by acid hydrolysis to obtain the side chain polystyrene. T.l.c. was then used to analyse the polystyrene residue after hydrolysis. It was found that the sample was separated into two components: one involving some sugar residues at one chain end (regarded as the truely grafted side chain); the other, the attendant homopolymer. Thus, analysis of such a chromatogram made it possible to estimate the percentage grafting due to true grafting, which had never been determined in a satisfactory manner.

The success in polymer separation mentioned above motivated us to re-examine the process of simultaneous graft copolymerization of styrene onto cellulose induced by irradiation with gamma-rays. The experiments were carried out varying copolymerization conditions, such as the composition of reaction medium, the concentration of monomer and chain transfer agent, the total dosage and the dose rate. The influence of these factors upon the true percentage grafting and the molecular weight of the side chains was investigated. Our special concern was to elucidate the chemical yield of irradiation (G_s value) for cellulose, which is defined as the number of side chains produced by radiation energy of 100 eV. In this study we thus intended to study the progress of the radiation graft copolymerization by combining the G_s data with those for the true percentage grafting and the molecular weight of the side chains.

EXPERIMENTAL

Materials

Commercial viscose rayon fibres with a fineness of 5 denier were purified first by extraction using a hot binary solution of benzene + methanol (1:1 by volume) for 24 h to remove the additives. After washing with distilled water, the fibres were subjected to further extraction with boiling methanol for 7 h and then dried at 50°C under reduced pressure.

Styrene monomer was washed three times with a 10% caustic soda solution to remove the inhibitor, then several times with distilled water, and dried over calcium chloride over night. Before use, distillation was carried out twice under a nitrogen atmosphere. Other chemicals used were of reagent grade.

Irradiation experiments

To accelerate monomer diffusion into the cellulose substrate and to suppress the propagation reaction of the side chains, the graft copolymerization condition was chosen as follows: 1 g of the rayon sample was immersed in a mixture of styrene/methanol/water of 20 ml, to which an approp-

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riate amount of carbon tetrachloride was added as a transfer agent. Several polymerization runs were performed by varying the monomer content in the ternary mixture, the concentration of carbon tetrachloride, the total dose and the dose rate. Each reaction mixture was exposed to air in a ^{60}Co gamma ray source at a certain dose rate for several prescribed time intervals ranging from 4 to 24 h. The reaction temperature was kept below 20°C as much as possible. The dose rate was varied over the range from 7×10^2 to $\sim 5 \times 10^4$ rad h^{-1}. However, if not otherwise stated, all irradiation experiments were conducted at a dose rate of 4.4×10^4 rad h^{-1}.

Physical and chemical treatments of graft products

The reaction mixture was filtered to remove unreacted monomer after each irradiation run. The residue was washed several times with acetone to extract low molecular weight polystyrene fractions produced in the reaction mixture. From this crude graft product, attendant polystyrene was extracted with boiling benzene for 24 h and recovered by precipitation with methanol. After this extraction, the graft product was weighed to estimate the apparent weight increase (percentage grafting) of cellulose substrate, which is given by:

$$Y_a(\%) = \frac{(\text{Wt of graft product}) - (\text{Wt of cellulose})}{(\text{Wt of cellulose})} \times 100$$

The graft product treated in this way was further subjected to acid hydrolysis of the cellulose backbone to isolate the side chain polystyrene. The detail of the treatment has been reported elsewhere[6].

T.l.c. experiments

The polystyrene residue recovered after hydrolysis was separated by t.l.c. into two spots on the solvent front and starting level: these were identified with the attendant homopolymer and the true side chain, respectively. The separation was made analytically as well as preparatively, and the procedure was almost the same as reported previously[6], but with some modifications: (i) benzene was used as developer; (ii) for analysis, the sample size was reduced to 0.6 μg or less, and (iii) quantification of chromatograms was made by a method, similar to that proposed by Padley[8], which may be called 'thin layer-*FID* chromatography'. The separation was carried out on a quartz rod of 0.90 mm diameter and 148 mm length, coated with silica gel of 75 μm thickness, available from Yatron Co. Ltd, Tokyo. After the development procedure, the rod was brought for quantification into an apparatus equipped with a flame ionization detector (*FID*) (Yatron Thinchrography Model TFG-10). The procedure has been described elsewhere[9]. By this analysis we evaluated a quantity, P_g, which is defined by:

$$P_g = \frac{R_2}{R_1 + R_2}$$

where R_1 and R_2 are the *FID* responses due to the attendant homopolystyrene and the side chain polystyrene, respectively. P_g may be regarded as a graft effeciency within the cellulose matrix and may be applied to estimate the true percentage grafting, $Y (= Y_a \times P_g)$.

T.l.c. separation effected in the above evaluation of P_g was based on the difference in the chain-ends possessed by the truely grafted and attendant polystyrene[6,10]. When carbon tetrachloride is added to the reaction system and its chain-transfer action occurs in the normal manner, it is clear that the polystyrene chains generated carry chlorine and/or CCl_3 residues at their chain ends. Such end-groups might exhibit an adsorption behaviour of the stationary phase, which is similar to that of some sugar residues attached to the grafted polystyrene chain. However, it was found by separate experiments that this was not the case.

In addition to the above, a Shimadzu TLC-UV-Scanner Model CS-900[11] (Shimadzu Seisakushyo Co. Ltd, Kyoto) was applied to qualitative analyses of chromatograms which were obtained with the usual chromotoplate. We adopted light of wavelength 210 nm as the sample beam.

Molecular weight determination

Polystyrene samples derived from different sources were subjected to gel permeation chromatography (g.p.c.) to determine the molecular weight and molecular weight distribution. A Shimadzu GPC Model 1-A furnished with a series arrangement of four columns having upper porosity ratings, 10^6, $10^5 \times 2$, 10^4 expressed on a molecular weight scale was used at room temperature. The eluent was THF, and the flow rate was adjusted to ~1 ml min^{-1}. The molecular weight was estimated with the aid of a calibration curve established with narrow-distribution polystyrene samples having known molecular weights.

RESULTS AND DISCUSSION

Influence of monomer content in reaction medium

A series of graft copolymerization experiments (Series A) were carried out with variation in the monomer (styrene) content in the reaction medium. Throughout this series of experiments, the volume ratio $[MeOH]/[H_2O]$ and the mole ratio $[CCl_4]/[Styrene]$ were adjusted to 10:1 and 5:100, respectively, and the total irradiation dosage was kept constant at 3.8×10^5 rad. The results are summarized in *Table 1*, in which the amounts of polystyrene produced in the reaction medium (F–PS) and within the cellulose matrix (B–PS) and the apparent percentage grafting, Y_a, are given. *Table 2* contains characterization data for polystyrenes recovered as the hydrolysis residue of graft products and also the value of P_g estimated by t.l.c., the true percent grafting Y, the number-average molecular weight M_n determined by g.p.c.

First the molecular weights of F–PS were of the order of 10^3 and apparently lower than those of B–PS due to the absence of the so-called gel effect (see *Table 2*). In *Table 1*

Table 1 Radiation graft copolymerization data (Series A) obtained under variation of St content

Sample code	St/MeOH/H_2O (by vol)	Produced PS (g)		
		F–PS[a]	B–PS[b]	(wt%)
G05	0.5/10/1	0.020	0.050	5.0
G1	1/10/1	0.058	0.075	7.5
G5	5/10/1	0.072	0.247	24.7
G7	7.3/10/1	0.136	0.281	28.1
G10[c]	10/10/1	0.183	0.231	23.1

[a] Polystyrene produced in reaction medium
[b] Polystyrene produced within cellulose matrix
[c] Phase separation of reaction medium occurred

Table 2 Characterization results of graft products (series A) and polystyrenes recovered as hydrolysis residue

Sample code				G.p.c. results		
Graft product	PS	P_g	$(Y_a \times P_g)$	$M_n \times 10^{-4}$	M_w/M_n	G_s[a]
G05	PSh-05	0.49	2.5	3.2	2.0	2.2 (4.4)
G1	PSh-1	0.46	3.5	5.1	2.1	2.0 (4.3)
G5	PSh-5	0.44	10.8	13.6	4.9	2.2 (5.1)
G7	PSh-7	0.41	11.5	15.3	4.8	2.3 (5.4)
G10	PSh-10	0.48	11.1	11.5	2.9	2.8 –

[a] Values in parentheses were calculated on the basis of Y_a

Table 3 Graft copolymerization data (Series B) obtained under variation of total dosage

	Irradiation		Produced PS (g)			
				B-PS[a]		
Sample code	(h)	(rad x 10^{-5})	F–PS	(I)	(II)	(wt %)
G5-04	4	1.8	0.036	~0	0.133	13.3
G5-08	8	3.5	0.080	~0	0.247	24.7
G5-16	16	7.0	0.234	0.019	0.629	62.9
G5-20	20	8.8	0.407	0.053	1.051	105
G5-24	24	10.5	0.473	0.049	1.436	144

[A] B–PS (I) and (II) refer to extractable and unextractable polystyrene from graft product, respectively

we find that the values of Y_a exhibit a maximum when plotted against the styrene (St) content. Similar observations have been reported by other authors[12–14]. In this connection it should be stated that the reaction medium having a composition, 10/10/1 (St/MeOH/H_2)), was separated into two phases even in the presence of the sample fibre. Hence the decrease in Y_a may be attributed to a lowering of effective St content caused by the phase separation.

The result summarized in *Table 2* makes it clear in which way the grafting of styrene onto cellulose took place. From the table it is seen that the graft efficiency defined within the cellulose matrix (P_g) remains approximately constant independent of the St content, and the values of Y and M_n increase almost linearly with the St content, except for at the highest St contents. This implies that the propagation step of side chains may be described in terms of normal radical polymerization kinetics. A more interesting feature is shown in a plot of Y against M_n, which is approximated by a straight line. This linearity suggests that the increase in Y was caused uniquely by the propagation of each side chain. Thus it may be concluded that the number of primary radicals on cellulose, which initiate the grafting, is kept constant during each graft copolymerization. This situation will be closely related to the P_g values (see *Table 2*).

To confirm the above conclusion, we have estimated the chemical yield of irradiation for cellulose, G_s, which is given by:

$$G_s = \frac{Y \times N_A}{M_n^s \times R \times A}$$

where M_n^s is the number-average molecular weight of side chains, N_A is the Avogadro number, R is the total dosage (rad), and A is the energy conversion factor, 5.8×10^{13} [eV $(\mathrm{g\ rad})^{-1}$], which is derived by assuming that the radiation energy yield for cellulose of unit weight is the same for water, namely 0.973. As seen from the last column in *Table 2*, the values of G_s thus evaluated are regarded as being independent of the St content and having a value of 2.1 ± 0.1. It is clear that a constant value endorses the conclusion mentioned above. The order of magnitude of G_s will be discussed later in comparison with reported by other authors. It is emphasized that the present evaluation of G_s was made on the basis of Y not Y_a. Values of G_s thus calculated are listed in parentheses in *Table 2;* the values are much larger than 2.1 and scattered in an irregular manner.

Influence of total dosage

The influence of changing the total irradiation dosage (irradiation time) under a constant dose rate was investigated by keeping the other conditions constant. The composition of the reaction medium and the ratio $[\mathrm{CCl_4}]/[\mathrm{St}]$ were adjusted to 5/10/1 (St/MeOH/H_2O) and 0.05, respectively, and the dosage was varied from 1.9×10^5 (4 h) to 11×10^5 rads (24 h). This series of experiments will be coded as 'Series-B'. The copolymerization results are summarized in *Table 3*; characterization of polystyrenes recovered as a hydrolysis residue are reported in *Table 4.*

In *Table 3* it is found that the values of Y_a first increase almost linearly with the irradiation time and then steeply in a range of longer irradiation times. In contrast to this observation, the graft efficiency within the matrix (P_g) tends to decrease with increasing time, and consequently the values of Y level off in the range where Y_a just begins to increase steeply, as seen from *Table 4.* This means that attendant poly styrene was predominantly produced by larger dosages, and may be interpreted in terms of the diffusion-controlled nature of graft copolymerization in heterogeneous systems: i.e., the local concentration of styrene monomer around the cellulose primary radicals becomes lower when polymerization proceeds.

More interesting data are seen in *Table 4.* The values of M_n for side-chain polystyrenes are practically independent of the total dosage. This allows us to conclude that the number of side chains having nearly the same length increased with increased dose so that the value of Y was enhanced. This conclusion may further be endorsed by inspecting values of G_s found in this series of experiments. As seen in the last column of *Table 4*, G_s values range from 1.9 to 2.3 and may be regarded as a constant (2.1 ± 0.2), indicating that a constant number of side chains having nearly the same length was generated by unit irradiation energy.

Concentration effects of transfer agent

The foregoing two series of experiments were conducted at a fixed ratio $[\mathrm{CCl_4}]/[\mathrm{St}]$. This series (Series C) was aimed

Table 4 Characterization results of graft products (Series B) and polystyrene recovered as hydrolysis residue

			G.p.c. results		
Sample code	P_g	Y (wt %)	$M_n \times 10^{-4}$	M_w/M_n	G_s
PSh5-04	0.38	5.1	13.9	3.1	2.1
PSh5-08	0.44	10.8	13.6	4.1	2.3
PSh5-16	0.35	22.0	15.5	4.8	2.1
PSh5-20	0.31	32.6	16.8	4.5	2.3
PSh5-24	0.23	33.0	16.6	4.2	1.9

Table 5 Graft copolymerization data (Series C) obtained under variation of transfer agent concentration

Sample code	$[CCl_4]/[St]$ (mol ratio)	PS produced (g) F–PS	PS produced (g) B–PS	conversion (wt %)	Y_a (wt %)
G5 (00)	0	0.084	0.520	10.7	52.0
G5 (02)	0.02	0.092	0.332	7.5	33.2
G5 (05)	0.05	0.080	0.274	5.8	24.7
G5 (10)	0.10	0.079	0.204	5.0	20.4

Table 6 Characterization results of graft products (Series C) and polystyrenes recovered as hydrolysis residue

Sample code	P_g	(wt %)	$(Y_a - Y)$	$M_n \times 10^{-4}$	M_w/M_n	G_s[a]
PSh5-(00)	0.71	36.9	15.1	40.2	3.7	2.8[b] (3.6)
PSh5-(02)	0.54	17.9	15.3	20.2	4.1	2.6 (4.5)
PSh5-(05)	0.44	10.8	13.9	13.6	4.9	2.2 (4.8)
PSh5-(10)	0.13		17.7	8.4	5.9	1.0 (6.8)

[a] Values in parentheses were calculated on the basis of Y_a

[b] Calculated by identifying M_n of the side-chain PS with that of the attendant PS. For the detail, see text

at investigating concentration effects of transfer agent, CCl_4. For this purpose we adjusted both the reaction medium composition and irradiation dose to 5/10/1 ($St/MeOH/H_2O$) and 3.5×10^5 rads, respectively, and varied the mole ratio $[CCl_4]/[St]$ from zero to 0.1. Results of this series are summarized in *Tables 5* and *6*.

The total conversion of monomer to polymer decreases sharply by enhancing the mole ratio of CCl_4 to styrene (*Table 5*). On the other hand, the amount of polystyrene produced in the reaction medium (F–PS) may be regarded independent of the CCl_4 concentration. In this connection it must be mentioned that no detectable amount of polystyrene was recovered by the extraction procedure for graft products. Consequently, the decrease in the total conversion is directly related to the yield of polystyrene formed within the cellulose matrix (B–PS). Thus, the distinct decrease in Y_a values suggests that the polymerization, which took place within the matrix, cannot be described by the normal chain transfer mechanism of radical polymerization kinetics, in contrast to that in the reaction medium. Results similar to ours have already been reported by Sakurada *et al.* for graft copolymerization of methyl methacrylate and styrene onto the poly(vinyl alcohol) film[15], but no interpretation has yet been given.

In order to discuss this problem, we will inspect the changes in Y_a and Y with CCl_4 concentration. It is interesting to note that if the difference ($Y_a - Y$) for each CCl_4 concentration is calculated, these values do not depend on the CCl_4 concentration, as shown in the fourth column of *Table 6*. Since this difference is identified with the conversion for the homopolymer, the above finding may suggest that the normal scheme for the chain transfer mechanism holds for the attendant polystyrene despite the fact that it was formed within the matrix. To test this theory, we plotted the reciprocals of number-average degree of polymerization of polystyrene formed within the matrix, DP_n, against the mole ratio $[CCl_4]/[St]$. As seen in *Figure 2*, the plot was well approximated by a straight line and its slope yielded 9.5×10^{-3} for the chain-transfer constant, which is in good agreement with those reported for homogeneous radical polymerization of styrene in the presence of CCl_4 [16], namely, $\sim 1 \times 10^{-2}$. These two findings allow us to conclude that the same CCl_4 chain transfer mechanism has been established for the homogeneous polymerization of styrene even within such a heterogenous system. In addition, this conclusion may suggest that small radicals derived from CCl_4 by radiolysis do not play any significant role in this polymerization, although CCl_4 has a high G value for radical formation[17].

The problem to be discussed is thus focussed into a discussion of the Y value, i.e. the conversion of the side-chain polymer, which decreases with CCl_4 concentration. It is possible that the side-chain polymer radicals are terminated by $Cl\cdot$ and $\cdot CCl_3$ radicals, which will be formed by radiolysis of CCl_4. However, it is inconceivable that such small radicals can distinguish side-chain polymer radicals from attendant homopolymer radicals. We have confirmed that the normal chain transfer mechanism holds quantitatively for the atten-

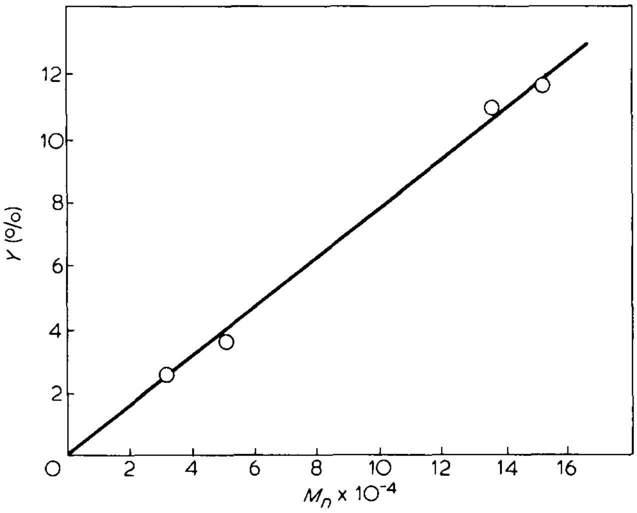

Figure 1 Relation between the true percent grafting (Y) and the molecular weight of side chain found in Series A

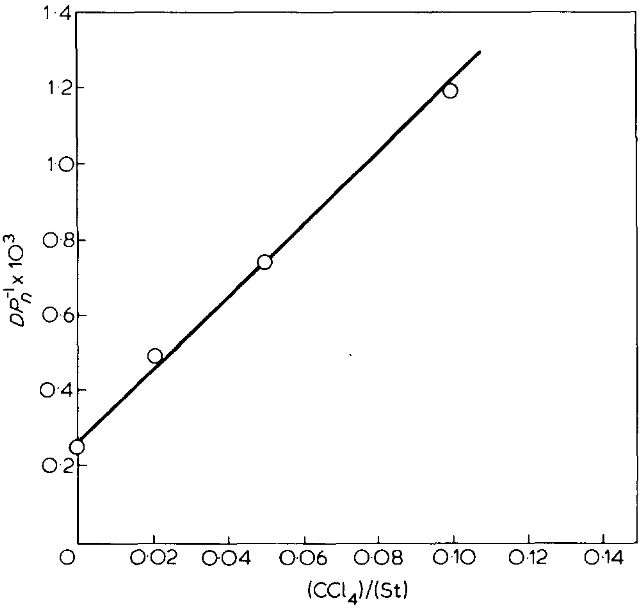

Figure 2 Plot of the reciprocals of number-average degree of polymerization against the mole ratio $[CCl_4]/[St]$

dant homopolymer. Therefore we must look for another mechanism. A number of investigators have reported that the effective rate coefficients for propagation, transfer and termination could be reduced by occlusion of the radicals, which occurs due to precipitation (coiling) of polymers during growth[18,19]. In addition, it has been shown by Bamford and White that the rate of polymerization decreased with an increase in the concentration of transfer agent when polymer precipitation took place during the polymerization[20]. These phenomena might be related to the decrease in the Y value, as will be discussed below.

A localized medium just surrounding each cellulose molecule is first considered. It is reasonable to assume that the water content in this medium will be significantly higher than that in a medium far enough away from cellulose molecules as a consequence of selective absorption of water by cellulose: i.e., the cellulose matrix, if seen microscopically, consists of two kinds of microphase, coded as α- and β-phase, which refer to the localized medium adjacent to and apart from each cellulose molecule, respectively. Thus the α- and β-phase are generally specified by a poor and a fairly good dissolving power towards polystyrene, respectively. Polymerization within the β-phase will proceed normally since a large enough quantity of monomer should be present to dissolve or at least to swell polymers thus produced. Polymers produced in the α-phase, i.e. side-chain polymers, will be tightly coiled during growth so that the occlusion effect could be operative on the propagating free radicals. As suggested by Bamford and Jenkins[20,21] the effect of mild degrees of occulsion is to reduce the effective rate coefficient for termination. We observed that in the absence of CCl_4, the molecular weights of the side-chain polymers produced was distinctly higher than those of attendant homopolymers.

In the presence of CCl_4, transfer of the propagating side-chain radicals with CCl_4 will take place, but the small radicals thus generated will be trapped within the coiled chain and then deactivated by recombination with primary radicals generated on cellulose molecules. Evidence to support this supposition may be seen in the decrease of G_s value with the CCl_4 concentration as shown in *Table 6*. A discussion on the G_s values will be made later. We will now summarize our speculations for the decrease of Y values as follows: this decrease may be attributed to: (i) reduction of the effective rate coefficient for propagation of the side-chain due to the occulsion effect; and (ii) the chain transfer action of CCl_4, but with the reservation that small radicals from CCl_4 are immobilized within the domain of coiled polymer chain and deactivated by recombination with primary radicals on cellulose molecule.

Finally, we will compare our relation between G_s and CCl_4 concentration with those reported by other authors. Huang reported that the G_s value of cellulose (rayon yarn) increased with an increase in the CCl_4 concentration, and explained this trend by assuming that a secondary action of radiolysed CCl_4 is operative[22]. Such an action was confirmed experimentally by Chapiro[23] and Manabe *et al.*[24] for the homogeneous systems styrene and CCl_4 or CBr_4. However, this speculation may not be plausible for heterogenous systems, as discussed previously in this section. Our findings deny the secondary action of radiolysed CCl_4. Recently, Ikada *et al.* indicated that the G_s value for poly(vinyl alcohol) (film) was independent of the CCl_4 concentration, and attributed Huang's result to overestimate of the true percentage grafting caused by incomplete removal of attendant homopolymer[25]. In agreement with this, we also found an increasing trend in the G_s–CCl_4 concentration relation when our Y_a values were employed, as shown in the last column of *Table 6*. At present we feel it is difficult to explain the decrease in Y if the G_s-value does not decrease with the concentration of transfer agent.

Molecular weights of truely grafted side chains

To test the hypothesis of microscopic environments for graft and homopolymerization within the cellulose matrix, we carried out a series of experiments on graft copolymerization, varying the additives in the reaction mixture in the presence or absence of CCl_4 (Series D). The basic experimental procedures were the same as described in the previous section. This series of experiments was conducted at 4.1×10^4 rad h^{-1}. The results are shown in *Table 7*.

Series-D aimed to show whether or not the molecular weight of the side-chain polymer is the same as that of the attendant polymer simultaneously produced within the matrix. To this end, polystyrene, recovered as the hydrolysis residue of each graft product, was subjected to conventional t.l.c. on a preparative scale. Each stock solution involving ~10 mg of the polystyrene was applied in a band to a silica-gel layer 0.5 mm thick, precoated on a glass plate 20×20 cm^2 T.l.c. separation was made continuously in a sandwich vessel for 48 h using benzene as developer. The sample was separated into two components on the solvent front and starting level, and each component was then extracted with dioxane from the corresponding silica-gel layer, as previously[6]. The same separation experiment was performed several times to obtain a sufficient amount of samples for subsequent studies.

Number-average molecular weights of the side-chain and attendant polystyrenes thus separated were estimated by g.p.c. and are presented in *Table 8* together with those for polystyrenes recovered as the hydrolysis residue of graft products. As seen in the Table, the molecular weights of side-chain polystyrenes derived from graft products, which were prepared commonly in the absence of CCl_4 but in a different reaction medium, are distinctly higher than those of the attendant homopolystyrenes, except for the case of a sample PSh–DW(O) (a discussion of this sample will be given later). In sharp contrast to this result, the difference in the molecular weights disappeared completely for the case of graft products prepared in the presence of CCl_4.

The above observation gives strong support to our hypothesis of localized media for graft and homopolymerization within the cellulose matrix. As discussed in above, the propagation of side-chain radicals will proceed in the α phase in which polymer chains tend to be tightly coiled (precipitated), and the effective rate coefficient for termination will be reduced by the occlusion effect proposed by Bamford *et al.*[18,19,20]. In the presence of CCl_4, these species will be able to penetrate into the domain of the coiled polymer chain in the α phase and will terminate the propagation in the same manner as in the β phase; thus the molecular weight difference is no longer evident. This picture may explain the difference in molecular weight.

This consideration is based primarily on the supposition that the α phase would be different from the β phase in its dissolving power for polystyrene. Thus we may expect no molecular weight difference when both the α and β phases possess good dissolution powers for polystyrene. This is the case for sample PSh–DW(O), derived from a graft product which was prepared in a reaction medium containing dioxane. This reaction medium will behave as a fairly good solvent

Table 7 Graft copolymerization data for Series D and characterization results of polystyrenes recovered as hydrolysis residue

Sample code	Reaction medium[a] (by vol)	$[CCl_4]/[St]$	Dosage (rad x 10^{-5})	Y_a (wt %)	PS[b] recovered	M_n 10^{-4}	$M_n(g)/M_n(a)$
G-MW(0)	St/Me/W (5/10/1)	0	8.2	258	PSh-MW(0)	41.1	3.4
					–(a)	31.4	
					–(g)	108	
G-MW(5)	St/Me/W (5/10/1)	0.05	8.2	122	PSh-MW(5)	14.5	1.0
					–(a)	13.3	
					–(g)	13.5	
G-AW(0)	St/Ac/W (5/10/1)	0	8.2	64.9	PSh-AW(0)	12.1	2.6
					–(a)	8.2	
					–(g)	21.4	
G-AW(5)		0.05	8.2	36.2	PSh-AW(5)	7.1	1.0
					–(a)	7.0	
					–(g)	7.2	
G-MO(0)	St/Me (33/67)	0	9.8	134	PSh-MO(0)	23.2	1.8
					–(a)	17.6	
					–(g)	31.0	
G-WO(0)	St/W (95/5)	0	9.8	229	PSh-WO(0)	28.8	2.2
					–(a)	20.3	
					–(g)	44.1	
G-DW(0)	St/D/W (30/68/2)	0	22.0	12.6	PSh-Dw(0)	3.3	1.1
					–(a)	3.0	
					–(g)	3.5	

[a] Abbreviations used are: Me (methanol), W (water), Ac (Acetone) and D (dioxane).
[b] –(a) and –(g) refer to the attendant and side-chain polystyrene, respectively

Table 8 Graft copolymerization data (Series E) obtained under variation of dose rate

Sample code	Dose rate (rad h^{-1} x 10^{-3})	Produced PS (g)			Total conversion (wt %)	Y_a (wt %)
		F–PS	B–PS (I)	B–PS (II)		
G-07R	0.7	0.289	4.506	0.368	91.8	36.8
G-2R	2.2	0.184	4.590	0.527	94.2	52.7
G-5R	5.0	0.282	2.255	1.779	76.2	178
G-12R	12	0.192	0.105	1.460	31.2	146
G-20R	20	0.273	0.139	0.585	15.5	58.5
G-41R	41	0.137	0.013	0.440	10.5	44.0

Table 9 Characterization results of graft produces (Series E) and polystyrenes recovered as hydrolysis residue

Sample code	P_g	(wt %)	G.p.c. results M_n x 10^{-4}	G.p.c. results M_w/M_n	G_s
PSh-07R	0.88	32.4	18.0	4.5	5.6
PSh-2R	0.79	41.6	22.2	4.3	5.8
¼Sh-5R	0.27	48.0	25.1	4.1	6.0
PSh-12R	0.21	30.7	17.3	4.7	5.5
PSh-20R	0.21	12.3	13.3	5.0	2.9
PSh-41R	0.21	9.2	13.4	4.7	2.2

for polystyrene up to an appreciably high water concentration, and this may be the reason why no molecular weight difference was observed for the case of PSh–DW(O) even in the absence of transfer agent.

Dose rate effects

The effects of dose rate on the graft copolymerization were examined by varying it from 0.7 x 10^3 to 41 x 10^3 rad h^{-1} while keeping the other conditions constant. The composition of the reaction medium was fixed at 5/10/1 ($St/MeOH/H_2O$), the mole ratio $[CCl_4]/[St]$ at 0.05 and the total dosage was adjusted to 3.3 x 10^5 rad. This series of experiments is coded as Series E, and the results are summarized in *Tables 8* and *9*.

Firstly, we will mention that the visible states of the graft products obtained at lower dose rates were much different from those at higher dose rates. The former can no longer be regarded as fibre and takes on a flake-like form. A similar observation has been made for graft products in Series B, i.e. G5-20 and G5-24, which were prepared at 4.4 x 10^5 rad h^{-1} but with much higher dosages, namely, 8.8 x 10^5 and 10.5 x 10^5, respectively. The change in the visible state of graft products is indicative of a degradation of the cellulose backbone, induced by irradiation. The degradation loosens the fine structure of the rayon fibre, and, as a result, it may be expected that homopolystyrene produced within the fibre can more easily be extracted with boiling benzene. The amount of B–PS(I) recovered by the extraction was larger for lower dose rates and decreased steeply with an increase in the dose rate, as seen in *Table 8*. In this connection it is interesting to note that appreciable amounts of B-PS(I) were extracted from the products G5-20 and G5-24 whose visible state was in a flake-like form (see *Table 3*).

The lowering of the dose rate brings about another problem, i.e. degradation of the cellulose backbone. Thus, it seems no easier to elucidate the effect of dose rate on the graft copolymerization. For example, values of Y_a exhibit a maximum in the range between 5 x 10^3 and 8 x 10^3 rad h^{-1}, as shown in *Figure 3*. It is clear that the appearance of this

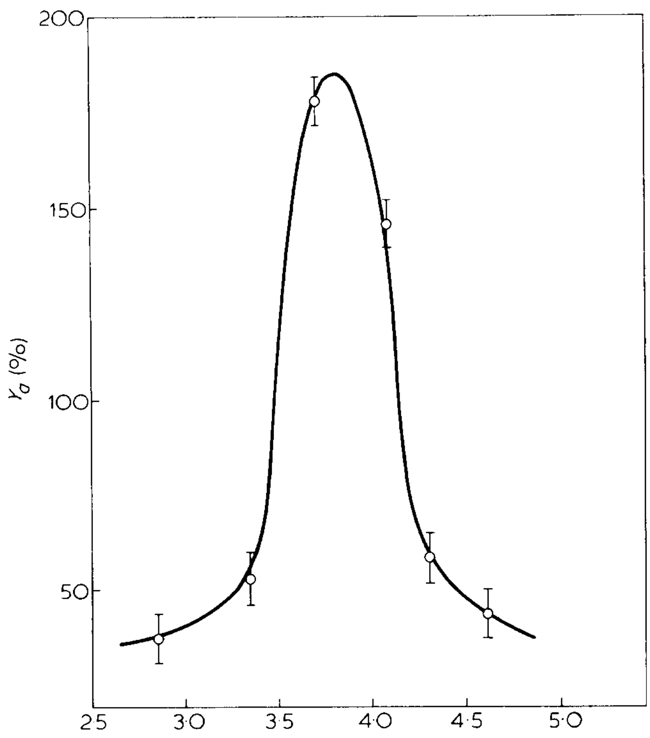

Figure 3 Plot of the apparent percent grafting (Y_a) against the logarithm of dose rate found in Series E

maximum cannot be explained solely in terms of the dose rate effect for homogeneous vinyl polymerization systems[26], which may be identified with the concentration effect of the initiators. Further discussion of this result would be meaningless, since our experiments were not designed for obtaining kinetic data, especially time–conversion data.

Considering the values of P_g, the graft efficiency within the matrix, and the values of G_s, it is shown in *Table 9*, that P_g-values are close to unity at the lowest dose rates and that they decrease steeply with further increases in the dose rate. Despite this decreasing trend in P_g, the G_s values remain almost constant (5.7 ± 0.3) up to about 1×10^5 rad h^{-1} but then fall drastically to 2.2 at 4.1×10^5 rad h^{-1}, as shown in *Figure 4*. The latter G_s-value is, of course, in agreement with those found at 4.4×10^5 rad h^{-1} (1.9 ~ 2.3) in the other series of experiments (see *Tables 2* and *4*).

For the purpose of interpreting the drastic change in G_s values between the lower and higher range of dose rates it will be sufficient to look at two factors, namely, the Y and M_n-values, since the experiments were carried out for the same total dosage. As seen in *Table 9*, the values of M_n may be regarded as decreasing monotonically with increasing dose rate (although the value found for G–07R is somewhat too low), and this trend is qualitatively in agreement with the dose rate effect[26] which may be identified with the concentration effect of the initiator in radical polymerization kinetics. Thus the cause of the drastic change in G_s at the higher dose rates should be attributed to the large values of Y. These Y values may be related to the rate of monomer diffusion. When the dose rate is low, the rate of radical formation on the cellulose will also be low so that the monomer molecules will be able to react with them. This may be the reason why higher G_s values were found for lower dose rates.

Finally, a comment should be made about G_s values which lie around 5.7. Considering this graft copolymerization to be diffusion-controlled, it is safely said that these high G_s values are due to the lower dose rates. G_s-values for cellulose reported so far by other authors[22,27,28] range from 1 to 3. It should be remembered however, that these values were found for graft products prepared at higher dose rates than 1×10^4 rad h^{-1}, and are really in agreement with our values (1.9 ~ 2.3) found at $4.1 \sim 4.4 \times 10^4$ rad h^{-1}. In this connection the radio-chemical yield of cellulose, i.e. the G_R value, must be considered. The values reported by Florin and Wall[29] and Guthrie *et al.*[30] were those close to 3, but these data cannot explain our high G_s values. On the other hand, Chapiro presumed $G_R = 10$ for cellulose after an e.s.r. measurement on a model analogue of cellulose[31]. Thus our present opinion is that an appreciable portion of the primary radicals generated on cellulose chains will decay spontaneously and some portion of the active radicals will decay without reacting with monomer molecules, depending on the balance between the rate of radical formation on cellulose and the rate of diffusion of monomer molecules.

CONCLUSIONS

(i) The increase in true percentage grafting (Y) with monomer concentration in the reaction mixture is caused uniquely by the increase in molecular weight of each side chain.

(ii) The increase in Y with total dosage is caused uniquely by an increase in the number of side chains having nearly the same molecular weight.

(iii) Normal chain-transfer effects for CCl_4 are operative for homopolymerization even within the cellulose matrix, but not for graft copolymerization. In the latter case, the conversion of monomer to polymer prominently decreases with CCl_4 concentration and this may be related to the recombination of small radicals with primary radicals on cellulose.

(iv) No significant effects of radiolysed CCl_4 radicals upon graft homopolymerization seem operative.

(v) In the absence of CCl_4, the molecular weight of the side chains is much larger than that of the attendant homo-

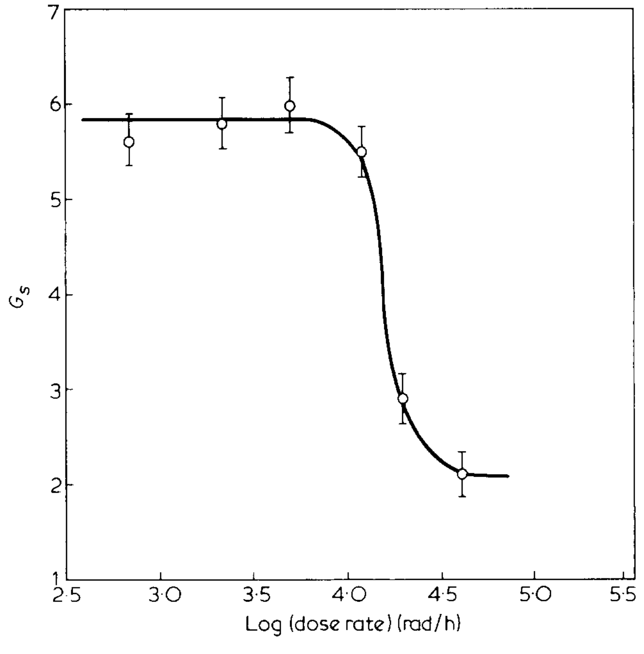

Figure 4 Plot of the G_s against the logarithm of dose rate

polymer chains simultaneously produced within the matrix; the presence of CCl_4 eliminates such a difference. The phenomena may be interpreted in terms of the occlusion theory proposed by Bamford *et al.*

(vi) The G_s values for cellulose are within a range from 1 to 3 for dose rates higher than 1×10^5 rad h^{-1} but tend to increase drastically with a decrease in the dose rate.

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