

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Radiation-Induced Reactions with Cellulose. XI. Comparison of Cellulose with Wool and Polyethylene as Trunk Polymers in Copolymerization

S. Dilli^{ab}; J. L. Garnett^{ab}; R. S. Kenyon^{ab}; E. C. Martin^{ab}; D. H. Phuoc^{ab}; Y. Yen^{ab}; J. D. Leeder^{ab}

^a School of Chemistry The University of New South Wales Kensington, NSW, Australia ^b Division of Textile Industry, CSIRO Geelong, Victoria, Australia

To cite this Article Dilli, S. , Garnett, J. L. , Kenyon, R. S. , Martin, E. C. , Phuoc, D. H. , Yen, Y. and Leeder, J. D.(1972) 'Radiation-Induced Reactions with Cellulose. XI. Comparison of Cellulose with Wool and Polyethylene as Trunk Polymers in Copolymerization', *Journal of Macromolecular Science, Part A*, 6: 4, 719 – 744

To link to this Article: DOI: 10.1080/10601327208056871

URL: <http://dx.doi.org/10.1080/10601327208056871>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

**Radiation-Induced Reactions with Cellulose.
XI. Comparison of Cellulose with Wool and
Polyethylene as Trunk Polymers in Copolymerization**

S. DILLI, J. L. GARNETT, R. S. KENYON, E. C. MARTIN,
D. H. PHUOC, Y. YEN, and J. D. LEEDER

School of Chemistry
The University of New South Wales
Kensington, NSW
Australia

and

Division of Textile Industry
CSIRO
Geelong, Victoria
Australia

SUMMARY

The effect of structure of trunk polymer on radiation copolymerization has been studied using cellulose, polyethylene, and wool as representative systems. Styrene, 4-vinylpyridine, and 5-methyl-2-vinylpyridine were used as monomers in a range of polar solvents. All grafting experiments were by the simultaneous method. For styrene in methanol system, cellulose and polyethylene exhibited Trommsdorff effects whereas wool did not. For the vinylpyridine monomers, gel effects were observed with both cellulose and wool. The results have been interpreted in terms of a charge-transfer theory for grafting.

The data show that the stability of radiation-induced radicals in wool is less than in cellulose or polyethylene, consistent with ESR studies. Significant post-irradiation grafting has been observed with all three trunk polymers. The kinetics of post-irradiation grafting to cellulose are reported.

INTRODUCTION

Extensive work on the radiation grafting of monomers to trunk polymers such as cellulose [1-5], wool [6], and polyethylene [7] has recently been published; however, little systematic data are available for comparing the grafting properties of these three trunk polymers under the same radiation conditions of dose and dose-rate. We now wish to report such data showing that certain radiation grafting phenomena are common to a wide variety of trunk polymers, although the conditions under which the phenomena are observed may vary depending on the structure of the trunk polymer. The particular aspects discussed in the present work will include the occurrence of the Trommsdorff effect or accelerated grafting [8] and post-irradiation grafting. Cellulose, wool, and polyethylene will be used as representative trunk polymers. The monomers studied in these reactions were styrene, 4-vinylpyridine, and 2-methyl-5-vinylpyridine. In this way it should be possible to separate radical and ionic copolymerization processes. All grafting experiments were performed by the simultaneous or mutual irradiation technique.

EXPERIMENTAL

Grafting by the Simultaneous Method

For the cellulose work, grafting was achieved by irradiating strips of paper in solutions of monomer in solvent using the technique previously described [1, 4]. The paper was Whatmans No. 41 double acid washed sheets for chromatography cut into strips 70×30 mm, the same batch of paper being used for all runs. After irradiation (see below), the strips of paper were removed from the irradiation vessels, extracted with benzene in a Soxhlet for 70 to 75 hr, dried, humidified to 65% r.h. at 20°C , and weighed. The increase in weight was calculated as a percentage of the conditioned weight of the original paper. Dilli and Garnett [1] have shown that this procedure is satisfactory for the complete extraction of the homopolymer and remaining monomer.

In the wool and polyethylene experiments, similar procedures to the above were adopted with the following modifications. The wool was a plain weave worsted fabric of 170 g/m^{-2} , made from virgin Merino 64-70s wool. Extraction and weighing procedures were as for cellulose. With polyethylene (low density, 0.002 in.), removal of homopolymer, particularly polystyrene, where necessary, was easily achieved by dusting off the powder from the surface of the grafted material.

For these experiments only two monomers were used: styrene and 4-vinylpyridine.

Post-Irradiation Studies

For this work, experiments were confined essentially to cellulose as trunk polymer with styrene and 2-methyl-5-vinylpyridine as monomers in methanol solvent. Cellulose was chosen because of the large amount of data on radiation grafting already reported, especially at low doses and dose-rates where the post-irradiation effect predominates [4]. 2-Methyl-5-vinylpyridine was selected as one of the monomers because, in radiation grafting, it is the most reactive of the three common commercially available vinylpyridines [9]. Styrene in methanol was also used because of the many studies of grafting to cellulose already reported with this system [2, 3]. In the actual experiments, 2-methyl-5-vinylpyridine in solvent methanol (1:1 by volume) was irradiated in contact with the cellulose. Irradiations were performed on two groups of six test tubes, each containing three strips of paper. The first group was irradiated for 5 hr (approximate total dose 0.45 Mrad), the second for 48 hr (4.3 Mrads). After completion of the irradiation, the tubes were allowed to stand at room temperature for logarithmically equal intervals of time over a period of from 15 min to 3 days. At the end of each time interval, one sample was removed and given a preliminary extraction sufficient to preclude further post-irradiation grafting. This was achieved by extracting five times with hot methanol. At the end of 3 days, the combined samples were completely extracted for 70-75 hr as described above.

For the styrene in methanol experiments, the same procedure as previously adopted [2] was used. After irradiation, tubes were allowed to stand for 170 hr at room temperature before extraction.

Irradiation Procedures

Three types of sources were utilized for the irradiations. The first was an 800 Ci ^{60}Co air source at The University of New South

Wales. The second was a large ^{60}Co pond facility at the Australian Atomic Energy Commission Research Establishment, while the third was a spent fuel element facility at the same establishment. Fricke dosimetry was used to calibrate all sources.

RESULTS

Trommsdorff Effect

In previous radiation grafting studies with cellulose and a variety of monomers [1, 2], a peak in the copolymerization was observed for a particular concentration of monomer in solvent. This is obviously the well-known Trommsdorff or gel effect [8]. A brief summary of these earlier results relevant to the present data is shown in Fig. 1. This graph is reproduced here in order to assist

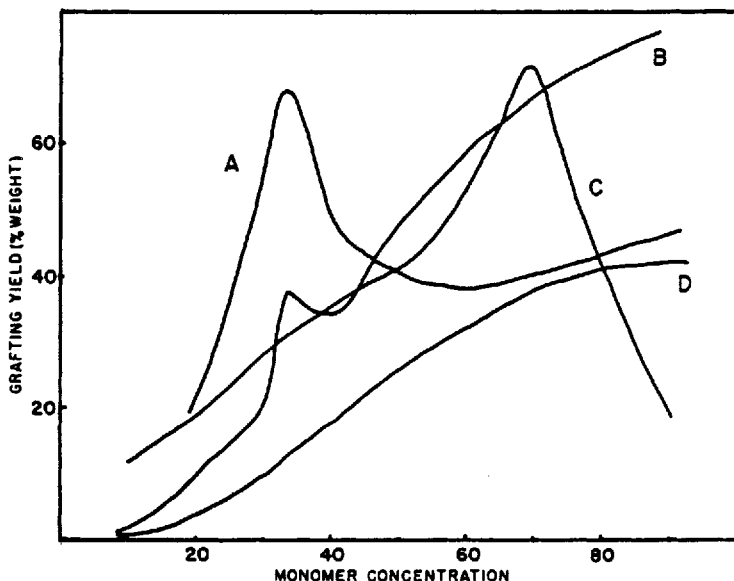


FIG. 1. Data showing maximum grafting rates for styrene and 4-vinylpyridine. (A) Styrene in methanol, 1 Mrad in air at 0.077 Mrad/hr. (B) Styrene in dimethylformamide, 1 Mrad in air at 0.077 Mrad/hr. (C) 4-Vinylpyridine in methanol, 1 Mrad in air at 0.081 Mrad/hr. (D) Styrene in dimethylformamide, 0.5 Mrad in air at 0.077 Mrad/hr.

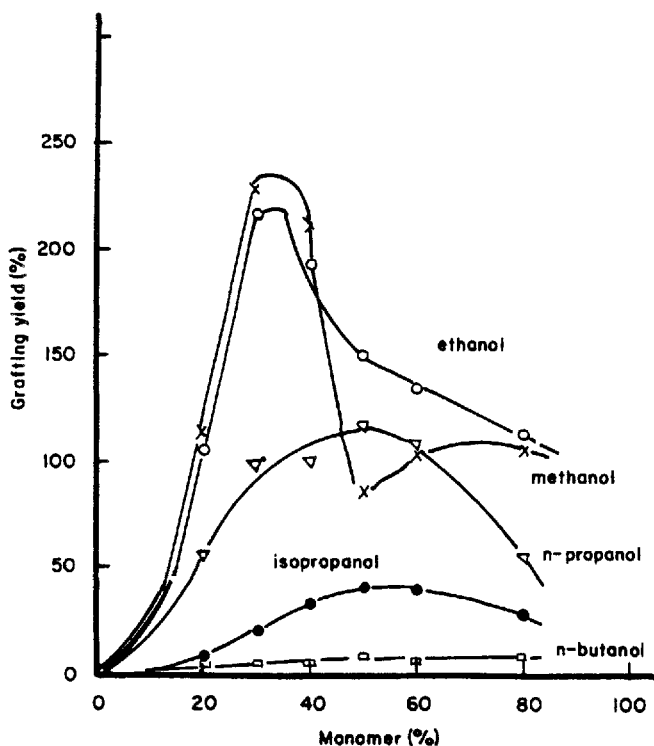


FIG. 2. Grafting of styrene in alcohols to cellulose. Dose rate: 8.32×10^3 rads/hr. Total dose: 0.20 Mrad.

with comparisons of data to be discussed later in the current paper.

In the present work involving the grafting of styrene to cellulose, the results show that the variables affecting the appearance of the Trommsdorff peak include solvent structure, particularly for the alcohols (Fig. 2), and radiation dose and dose-rate (Figs. 3 and 4). It is particularly significant that in Figs. 3 and 4 the position of the Trommsdorff peak shifts from the 28% monomer concentration at a graft of 120% to 40% monomer at a graft of 280%.

By contrast, when wool is used as trunk polymer with the styrene-methanol system under similar radiation dose and dose-rate conditions to those used above for cellulose, no Trommsdorff peak is observed, although styrene grafting is slightly more efficient with wool (Figs. 5-7, Tables 1-3).

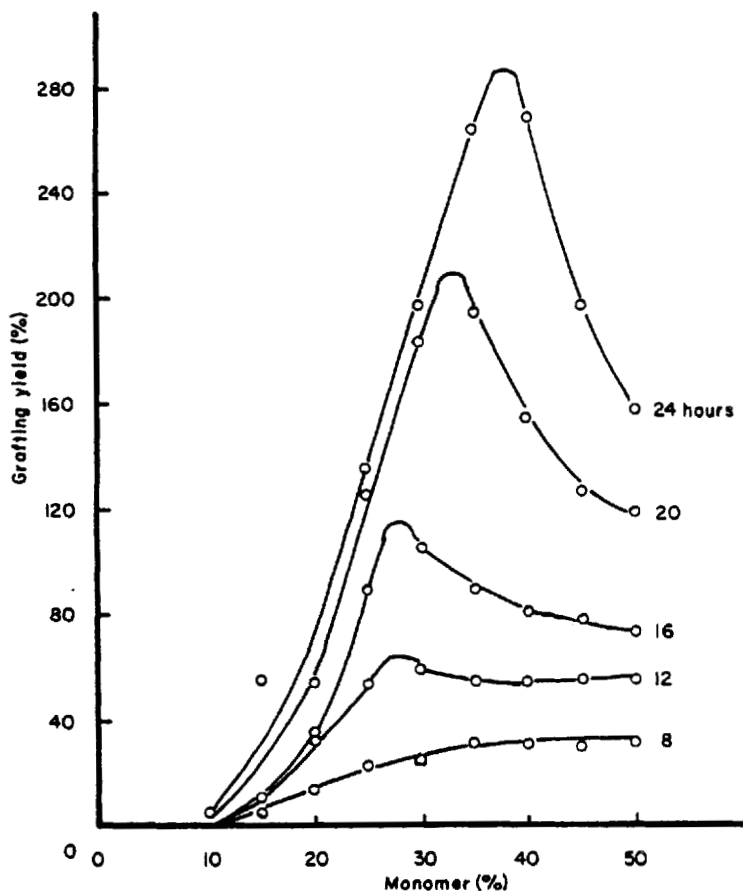


FIG. 3. Grafting of styrene in methanol to cellulose in air. Dose rate: 1.42×10^4 rads/hr. Exposure times: As shown on the curves.

When polyethylene is used as trunk polymer, the presence of a Trommsdorff peak at relatively low radiation doses and dose-rates for the grafting of styrene in methanol (Fig. 8, Table 4) indicates that polyethylene more closely resembles cellulose in styrene grafting properties than wool. Odian et al. [10] have previously observed a very slight gel effect when styrene in methanol is grafted to low-density polyethylene at 70,000 rads/hr. However, the total dose used by these authors was significantly lower than in the

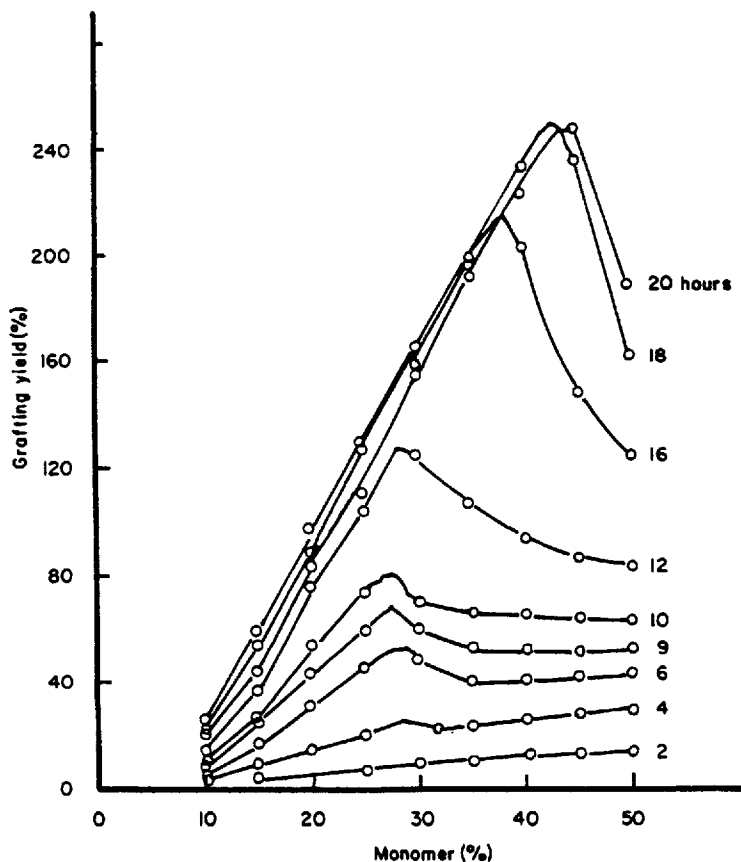


FIG. 4. Grafting of styrene in methanol to cellulose in air. Dose rate: 6.70×10^4 rads/hr. Exposure times: As shown on the curves.

present work, thus these experiments need to be repeated for comparison purposes with wool and cellulose under similar conditions. They also observed the peak at 30% styrene in methanol, whereas in Fig. 8 the peak is very much stronger than in Odian's work and also occurs at approximately 50% monomer concentration. This result is consistent with the previous data for cellulose [11] which show that the position of the peak is total dose dependent and can also shift with monomer concentration if the total dose is varied.

The similarity in styrene radiation grafting properties between cellulose and polyethylene is further accentuated when DMF is used

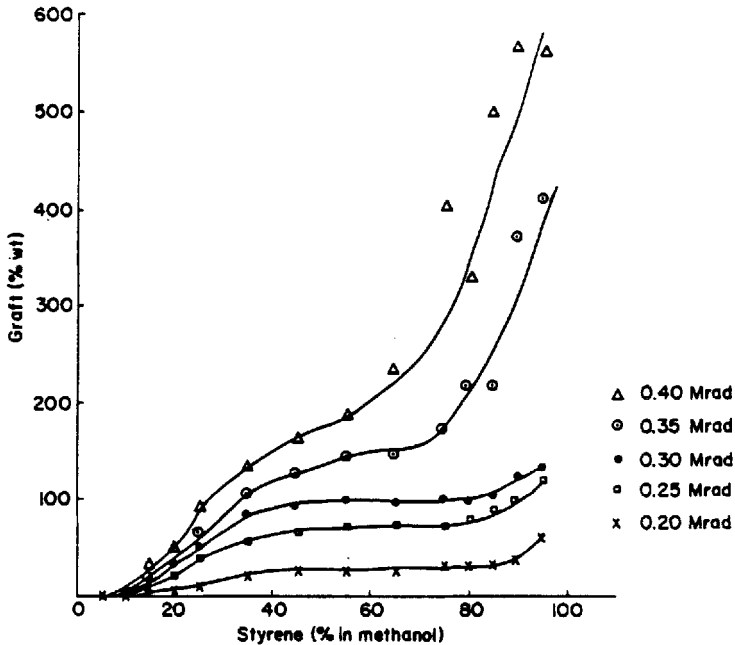


FIG. 5. Grafting of styrene to wool. Dose rate: 0.025 Mrad/hr.

as solvent for the monomer. DMF is almost as good as methanol (Figs. 1 and 8), the Trommsdorff peak occurring with polyethylene at 70% monomer concentration and a total dose of 0.5 Mrad. With cellulose (Fig. 1), the peak occurs at 30% monomer (1 Mrad); however, no peak is observed at 0.5 Mrad.

If 4-vinylpyridine is used instead of styrene as monomer, the grafting properties of cellulose and wool are similar. Both trunk polymers give a Trommsdorff peak with 4-vinylpyridine in methanol (Figs. 1 and 9, Table 5), although cellulose gives slightly higher grafts under approximately comparable radiation conditions. At 1 Mrad and dose rates of 80,000-100,000 rads/hr, the peak with cellulose occurs at 70% monomer concentration whereas with wool it is observed at 60% with radiation doses of 1 and 4 Mrads.

With respect to dose-rate effects on grafting, both cellulose and wool react similarly for the styrene-methanol system (Fig. 10) in that grafting decreases with increasing dose-rate at constant total dose. However, compared with the previous dose-rate effects reported for cellulose [1, 2], the corresponding data for wool (Fig. 10) show an even greater decrease in grafting rate with

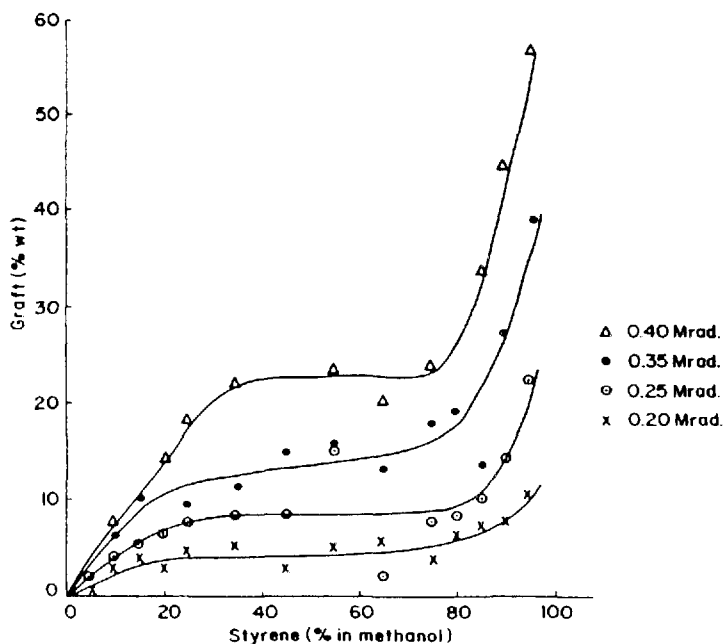


FIG. 6. Grafting of styrene to wool. Dose rate: 0.1 Mrad/hr.

increase in total dose-rate from 25,000 to 250,000 rads/hr. This dose-rate effect with wool is even more pronounced when the total dose is increased from 0.2 to 0.3 Mrad.

Post-Irradiation Effects

The observation of a post-irradiation effect is of importance in the possible utilization of radiation grafting for commercial processing. In preliminary studies of the styrene-methanol system at one total dose, Dilli and Garnett [1] found a significant post-irradiation effect. If their results are now plotted (Fig. 11) such that only the post-irradiation effect is now considered, it is obvious that a Trommsdorff effect is also associated with post-irradiation.

The present additional work with the post-irradiation effect on cellulose (Table 6, Fig. 12) shows that 1) monomers such as 2-methyl-5-vinylpyridine are also active, 2) the magnitude of the polymerization is total dose dependent, and 3) after 3 hr at room temperature the post-irradiation grafting reaches a plateau. In preliminary studies [12]

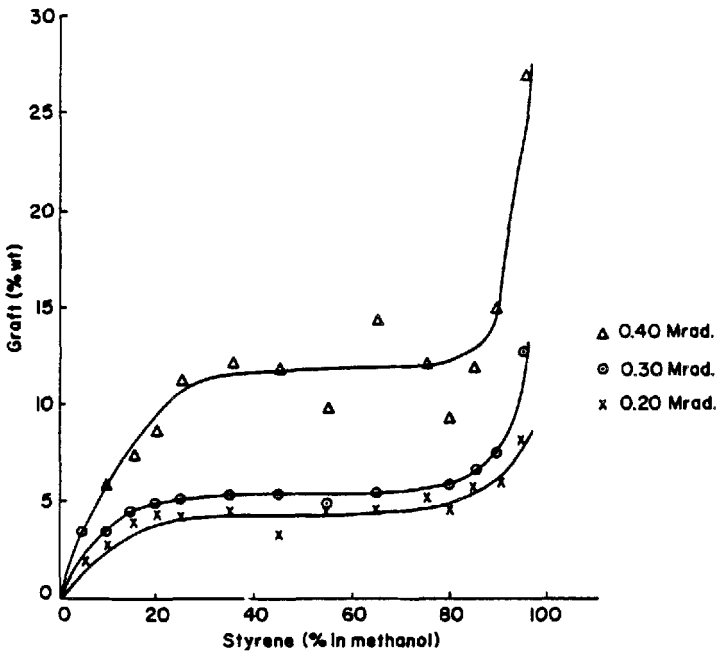


FIG. 7. Grafting of styrene to wool. Dose rate: 0.25 Mrad/hr.

it has also been found that analogous post-irradiation effects occur with both wool and polyethylene, so the effect is a general phenomenon with all three trunk polymers.

DISCUSSION

Trommsdorff Effect

The appearance of a Trommsdorff or gel effect in radiation copolymerization is valuable both mechanistically and also for commercial exploitation of the grafting reaction since, if grafting is performed at the monomer concentration which gives the peak, relatively low radiation doses only are needed for significant copolymerization. The importance of the Trommsdorff effect in grafting to cellulose has previously been discussed in detail [1, 2],

TABLE 1. Grafting of Styrene to Wool at 25,000 rads/hr

% Styrene in methanol	Graft % at total dose (Mrad) of						
	0.20	0.25	0.30	0.35	0.40	0.45	0.50
5	Nil	Nil	Nil	Nil	Nil	0.7	3.0
10	Nil	1.2	4	4.3	5.1	10.2	8.5
15	5.7	12	11	25	33	42	54
20	8.6	23	36	29	50	63	76
25	13	42	51	65	96	-	116
35	26	58	88	109	136	142	162
45	28	67	91	127	162	144	188
55	29	74	100	146	184	188	-
65	27	75	97	147	232	215	235
75	33	76	99	175	400	-	-
80	33	79	97	215	328	142	-
85	32	89	104	218	500	-	560
90	38	100	124	370	570	219	-
95	61	124	130	410	560	-	-
100	0.7	0.8	0.7	Nil	1.2	0.7	Nil

TABLE 2. Grafting of Styrene to Wool at 100,000 rads/hr

% Styrene in methanol	Graft % at total dose (Mrad) of				
	0.20	0.25	0.30	0.35	0.40
5	0.8	2.2	3.6	3.8	2.4
10	2.7	4.2	8.1	6.5	7.7
15	3.5	5.5	10.8	10.2	9.7
20	3.0	6.8	14.8	6.6	14.3
25	4.5	7.9	19.8	9.6	18.2
35	5.1	8.4	21.0	11.2	22.0
45	2.9	8.3	22.1	15.0	-
55	4.9	15.2	24.6	15.4	23.5
65	5.9	2.1	16.6	13.0	20.5
75	4.0	7.8	22.6	18.0	24.6
80	6.3	8.2	17.7	19.3	23.3
85	7.5	10.2	30.5	13.8	33.7
90	7.8	14.4	32.0	27.3	44.5
95	10.3	22.5	30.0	39.1	56.5

TABLE 3. Grafting of Styrene to Wool at 250,000 rads/hr

% Styrene in methanol	Graft % at total dose (Mrad) of		
	0.20	0.30	0.40
5	2.0	3.5	3.5
10	2.6	3.5	5.8
15	4.0	4.6	7.4
20	4.4	4.9	8.6
25	4.0	5.2	11.3
35	4.3	5.4	12.0
45	3.3	5.3	11.7
55	4.6	4.7	9.8
65	4.6	5.5	14.4
75	5.2	4.7	12.1
80	4.6	5.7	9.2
85	5.6	6.6	11.9
90	6.2	7.5	14.8
95	8.1	12.6	27.0

thus only those aspects of the theory which will assist the interpretation of the present data, particularly the wool and polyethylene work, will be briefly summarized here.

The Trommsdorff effect has been observed for a wide range of monomers and solvents. It is associated with a change in the viscosity of the medium, thus at higher viscosities, bimolecular chain termination of the radical chains is hindered. By contrast, other steps in the polymerization, e.g., initiation, chain propagation, and radical transfer, are not affected to the same degree by an increase in viscosity since the molecules involved are smaller and more mobile. The Trommsdorff effect is thus responsible for the rapid consumption of monomer and the production of high molecular weights. It is also further accentuated in grafting because the mobility of the polymer chains is restricted to varying degrees depending on the structure of the particular trunk polymer. When grafting commences, the fiber of the trunk polymer swells, thus assisting the diffusion of monomer to the growing chains and active sites on the trunk polymer. From preliminary studies (Fig. 1) with cellulose, the important variables determining the position of the Trommsdorff peak are radiation dose and dose-rate, concentration of monomer in solvent, and structure of both monomer and solvent.

Further additional work in the present paper (Figs. 2-4) supports the earlier conclusions summarized above, especially with respect

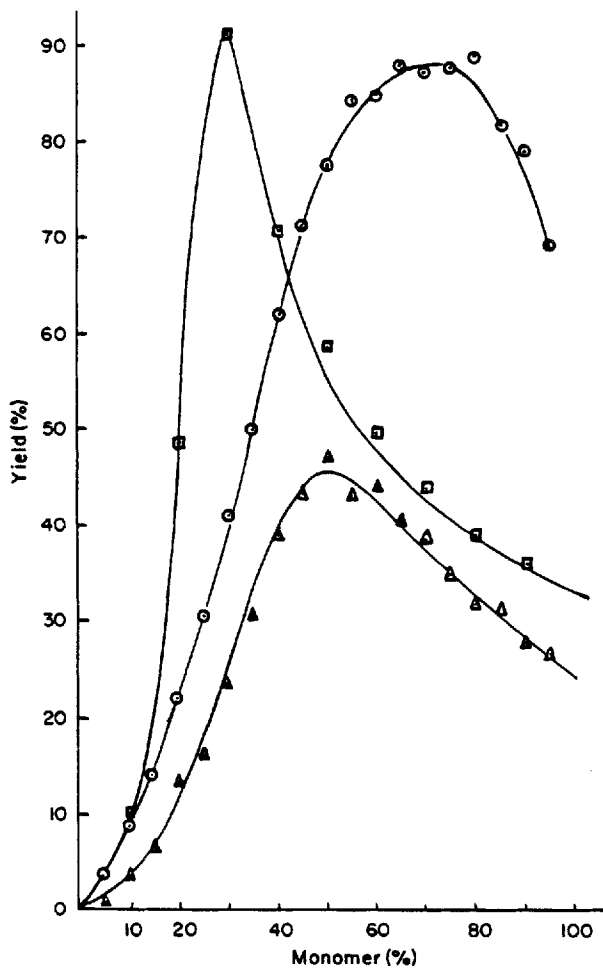


FIG. 8. Effect of solvent on grafting of styrene to polyethylene. (□) Methanol, 0.2 Mrad, 40,000 rads/hr. (○) Dimethylformamide, 0.5 Mrad, 80,000 rads/hr. (△) Methanol, 0.2 Mrad, 80,000 rads/hr.

to solvent structure, dose, and dose-rate, and also illustrates a further important aspect of the total dose effect at grafts above 120% (Figs. 3 and 4). From Fig. 4 particularly, the position of the Trommsdorff peak has moved to styrene concentrations of 45%. This probably reflects two important features of the gel effect in this

TABLE 4. Radiation-Induced Grafting of Styrene in Methanol and DMF to Polyethylene

% Styrene (by volume)	Grafting yield (%)	
	In DMF at ^a 0.5 Mrad	In methanol at ^b 0.2 Mrad
5	3.7	0.2
10	8.7	3.5
15	14.0	6.6
20	21.8	13.0
25	30.7	15.7
30	40.5	23.3
35	49.6	30.5
40	62.0	39.5
45	70.8	43.3
50	77.1	46.9
55	83.9	42.8
60	84.5	43.9
65	87.5	40.0
70	86.9	38.4
75	87.1	34.3
80	88.3	31.6
85	81.6	31.0
90	78.7	27.5
95	68.4	26.1
100	38.6	19.1

^a Dose rate = 80,000 rads/hr.

^b Dose rate = 77,500 rads/hr.

region; namely, that above 120% graft, 1) the fraction of grafting sites left in the cellulose is severely diminished, and 2) grafting now occurs predominantly to styrene already copolymerized rather than to bare cellulose sites. This latter observation also suggests a refinement in the actual grafting mechanism since cellulose with its hydroxyl groups is more polar than polystyrene, thus the shift in the positions of the Trommsdorff peak with magnitude of graft may indicate the degree to which ionic processes contribute to the grafting reaction.

Grafting to Wool and Polyethylene

Compared with cellulose, the grafting of styrene in methanol to wool (Figs. 5-7, Tables 1-3) and polyethylene (Fig. 8, Table 4) by

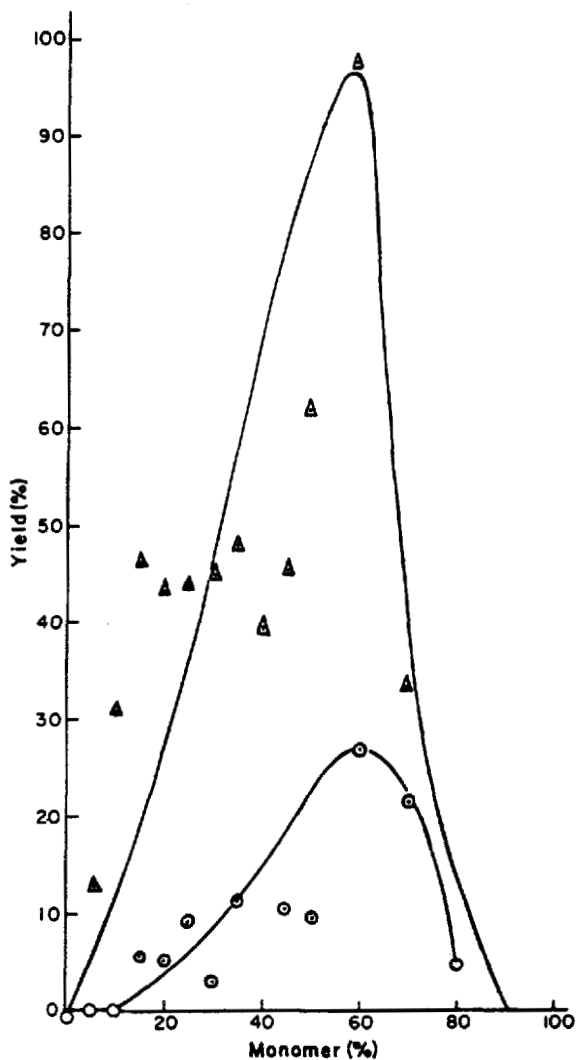


FIG. 9. Grafting of 4-vinylpyridine in methanol to wool (100,000 rads/hr in air). (Δ) 4 Mrads dose. (\odot) 1 Mrad dose.

the simultaneous procedure is different in terms of the occurrence of the Trommsdorff effect. Even at the comparatively low dose-rate of 25,000 rads/hr at total doses of 0.2 to 0.4 Mrad, wool does not exhibit a Trommsdorff effect at any concentration of styrene in methanol,

TABLE 5. Grafting of 4-Vinylpyridine to Wool^a

% 4-VP in Methanol	Graft (%) at dose of	
	1 Mrad	4 Mrads
5	Nil	13.4
10	Nil	31.2
15	6.0	46.4
20	5.5	43.3
25	9.9	43.9
30	3.1	44.8
35	11.9	48.1
40	2.9	39.6
45	10.6	47.4
50	10.3	62.1
60	27.8	97.4
70	22.7	33.6
80	4.9	Gelled
90	Gelled	Nil
100	Nil	Nil

^a Dose rate = 100,000 rads/hr.

only a plateau being generally observed in the 20-80% concentration region.

With polyethylene, however, the grafting behavior with styrene-methanol resembles that of cellulose since a small Trommsdorff effect is observed at 30% styrene in methanol at low dose-rates and low total doses. As the dose-rate and total dose (or graft) increase (Fig. 8), the position of the Trommsdorff peak gradually moves to 45% styrene in methanol (46% graft) and 60% monomer concentration at 88% graft.

From these results with cellulose, wool, and polyethylene, it is obvious that the grafting efficiency depends markedly on the structure of the trunk polymer. The reason why wool alone of the three trunk polymers does not exhibit a Trommsdorff peak under the present radiolysis conditions requires comment. From previous work [5] it has been suggested that the predominant mechanism of the Trommsdorff effect in styrene-methanol systems involves hydrogen atoms produced radiolytically. These atoms, essentially from solvent molecules, are able to abstract H atoms from the trunk polymer and thus provide sites for the graft reaction. It is known from ESR studies with wool, [13, 14] that the trapped radicals

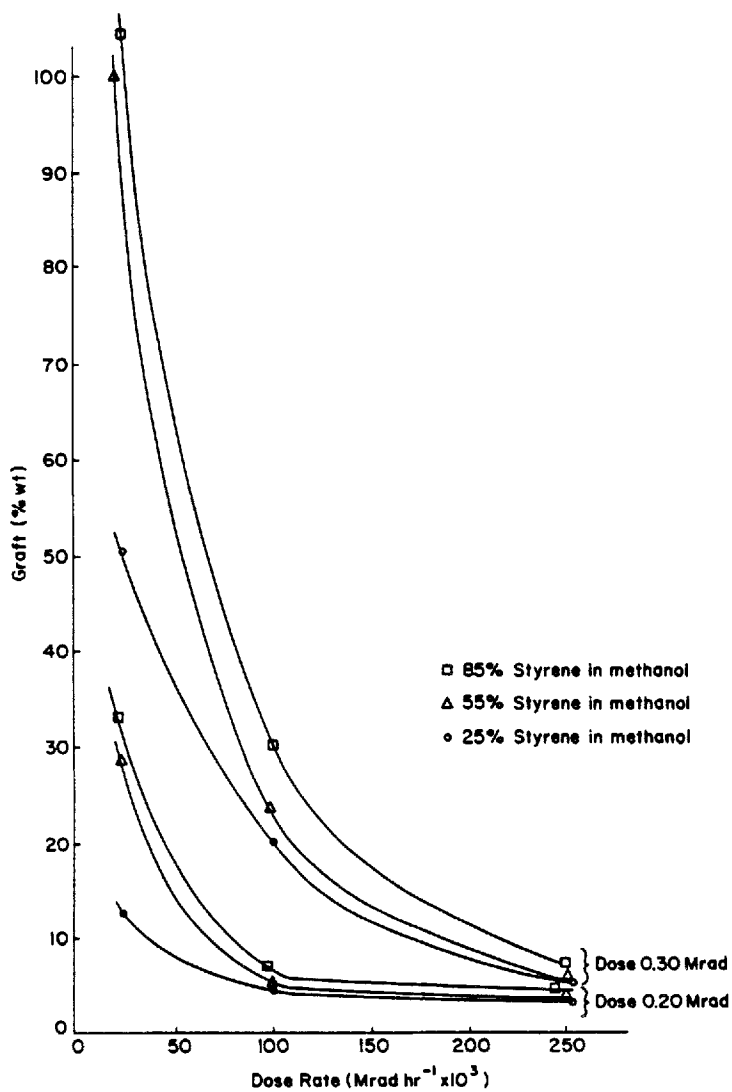


FIG. 10. Effect of dose rate on grafting of styrene to wool.

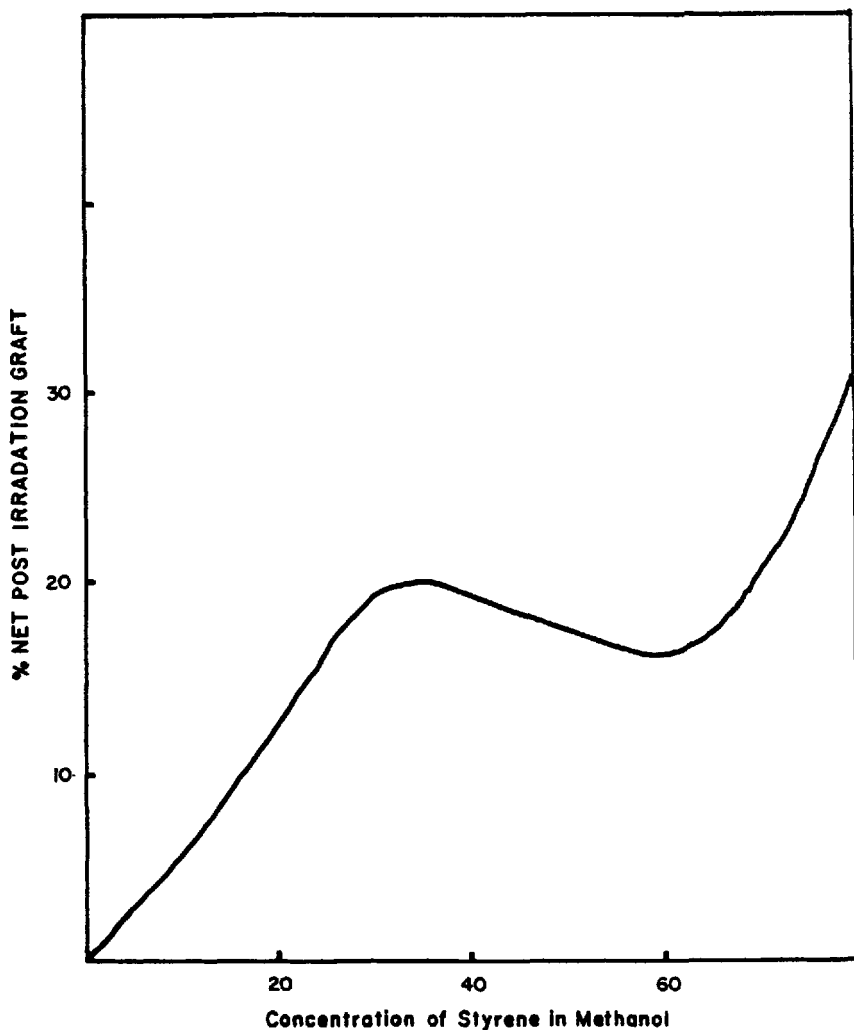


FIG. 11. Post-irradiation grafting of styrene in methanol to cellulose. Dose: 1.5 Mrads in air at 145,000 rads/hr. Tubes stood at room temperature for 170 hr after irradiation. Data are for post-irradiation graft only.

generally have a much shorter lifetime than in cellulose, i.e., these trapped radicals in wool are more reactive. Thus it is plausible to suggest that the radicals in wool are more accessible to the monomer

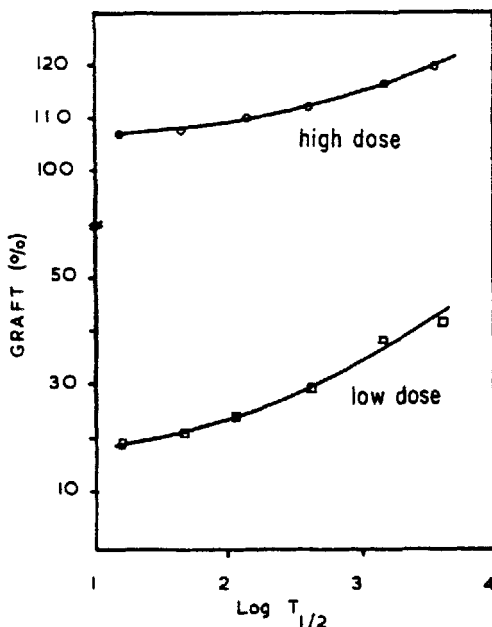


FIG. 12. Post-irradiation grafting of 2-methyl-5-vinylpyridine in methanol to cellulose (Eq. 1). High dose: 4.3 Mrads. Low dose: 0.45 Mrad at dose rate of 90,000 rads/hr.

TABLE 6. Post-Irradiation Grafting of Methyl Vinylpyridine to Cellulose^a

Time of standing (min)	Graft % at total dose of	
	0.45 Mrad	4.3 Mrads
15	18.9	107.3
45	20.6	107.4
110	23.9	
135		110.3
405	29.0	111.8
1410	38.2	
1470		116.5
3645		119.4
4050	41.6	

^a Dose rate = 90,000 rads/hr; temperature = 25°C.

and thus chain termination becomes more effective and there is no opportunity to build up chain length to the point where the Trommsdorff effect occurs. Unfortunately, there are no comparable ESR data for the lifetimes of radiolytically-produced radicals in polyethylene. However, on structural considerations, the accessibility of the radicals in polyethylene would be expected to more closely resemble cellulose than wool, and this is consistent with the grafting observations.

Grafting with 4-Vinylpyridine

With both wool and cellulose, the 4-vinylpyridine in methanol exhibits a Trommsdorff effect during grafting (Figs. 1 and 9); however, the grafting of this monomer to cellulose is more efficient than with wool. The reason why 4-vinylpyridine and not styrene gives a Trommsdorff effect with both wool and cellulose is obscure; however, 4-vinylpyridine is more polar than styrene and the results may reflect the contribution of an additional ionic mechanism to the Trommsdorff effect. Ions as well as radicals are known to be produced during irradiation with ^{60}Co and such ions, especially H^+ , would protonate the heterocyclic nitrogen of the vinylpyridine.

Dose-Rate Effect

For the styrene-methanol systems, wool again exhibits more marked effects than either cellulose or polyethylene when the dose-rate is considered (Fig. 10). Both cellulose and polyethylene show a decrease in graft with increasing dose-rate in the 25,000 to 100,000 rads/hr region.

Post-Irradiation Effects

In previous preliminary studies with the grafting of styrene in methanol to cellulose [1], a post-irradiation effect was observed. Other authors have been conscious of post-irradiation effects in grafting [3]; however, few systematic studies of the phenomenon have been made. If the original data of Dilli and Garnett [1] are plotted (Fig. 11), then a small Trommsdorff effect is observed at 35% styrene in methanol. These data are thus consistent with the suggestion that the post-irradiation grafting is due to trapped radical formation in the trunk polymer. In this respect the effect

is similar to grafting by the pre-irradiation procedure [2] which is attributed to radiolytically produced trapped radicals. It is also significant that small Trommsdorff effects have been observed in the pre-irradiation grafting [2].

From the systematic study of the post-irradiation effect with 2-methyl-5-vinylpyridine grafting (Fig. 12, Table 6), it is obvious that the phenomenon is much more marked at a total dose of 0.45 Mrad than at 4.3 Mrads. At the lower dose, an increase of approximately 120% by weight of grafting cellulose is observed after approximately 16 days standing at room temperature, whereas at the higher dose the increase is 11% after approximately the same time.

In Fig. 12, the data are shown for both low and high dose experiments, a logarithmic scale being used for the time of standing after irradiation had ceased. Figures were read from the curves drawn through the values obtained in this kinetic treatment and used to calculate the rate of grafting $[\delta y/\delta T]$. From these, straight lines were obtained (Fig. 13) when $\log [\delta y/\delta T]$ was plotted against $\log T_{\frac{1}{2}}$. The parameter $T_{\frac{1}{2}}$ was taken as the period after irradiation to the point midway between successive measurements of graft. Thus the change in rate of grafting with passage of time is obtained. These values show that the relationship (Eq. 1), a condition common to

$$\delta y/\delta T = kc^n \quad (1)$$

heterogeneous reactions, is followed for a particular concentration. Ideally "n" would be unity but the change in concentration of monomer, c, with time would produce a variation in k with time. This presumably is related to the slope of the lines obtained.

Dilli and Garnett [15] have explained the grafting of monomer to cellulose on the basis of a reaction activated by trapped radicals in the cellulose. Such an explanation fits the present situation and explains the decreasing rate of grafting with time as the removal of trapped radicals by the grafting process. The lower rate of grafting with the high dose samples may be due to a lower concentration of trapped radicals in grafted vinylpyridine together with a shielding of the cellulose trapped radicals by grafted monomer.

The observation of the conditions under which the post-irradiation effect is found is important for two reasons. First, the procedure may be of value commercially for increasing the magnitude of the graft without further additional radiation processing, and second, the results show that care should be exercised in fundamental studies of the grafting reaction such that a minimum of time should elapse before grafted samples are extracted to reduce the post-irradiation phenomenon.

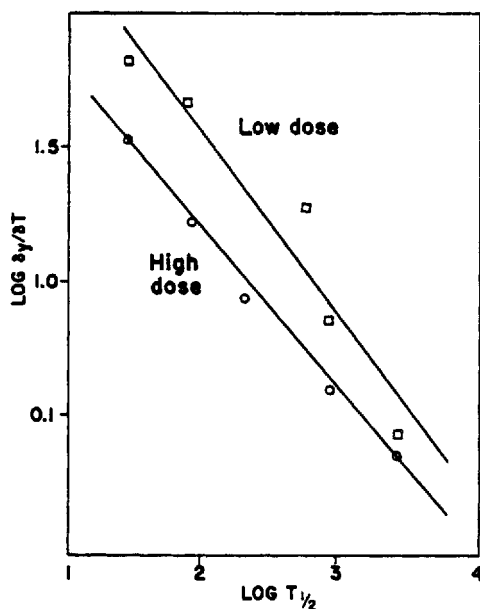


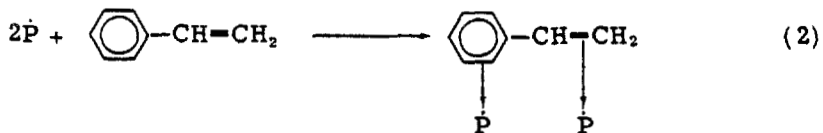
FIG. 13. Post-irradiation grafting of 2-methyl-5-vinylpyridine in methanol to cellulose. Conditions as in Fig. 12. Axes defined in Eq. (1).

Mechanism of Grafting Reaction

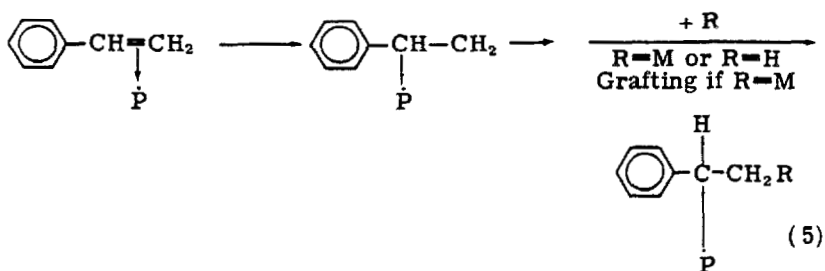
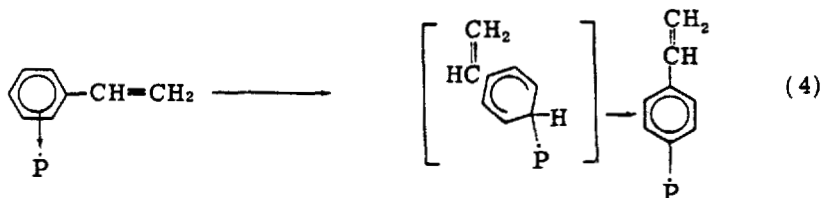
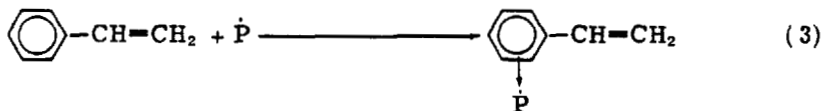
Because many aspects of the simultaneous radiation grafting of monomers to the three trunk polymers, cellulose, wool, and polyethylene, are common, it is probable that one general mechanism is applicable to all systems. A charge-transfer theory has already been proposed [15] and discussed in detail for the grafting of a wide range of monomers to trunk polymers, particularly cellulose. Recently, Gaylord [16] has also discussed a theory involving charge-transfer bonded species in grafting reactions. Gaylord's theory [16] and the original charge-transfer proposal [15] are very similar in many respects.

It is thus important to summarize the salient features of the earlier charge-transfer theory [15] developed for cellulose and to apply these to wool and polyethylene systems. The basic concept of the theory is that radiation-induced trapped radicals are available for bonding in the trunk polymer. Those radicals in the trunk

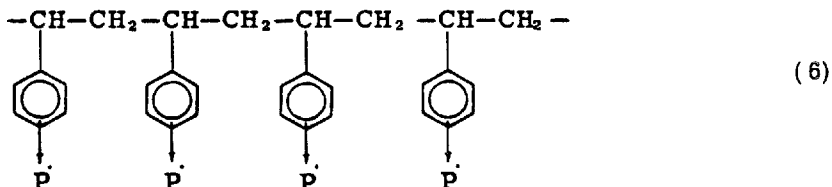
polymer which are readily accessible may form σ -bonds with the monomer to give graft, whereas "inaccessible" radical sites may also contribute to bonding if charge-transfer interactions are invoked. Using styrene and irradiated cellulose as representative model, the type of complex initially formed is depicted in Eq. (2) showing delocalized π -bonding between styrene and the free valencies of the irradiated cellulose. From this intermediate charge-transfer



complex, a number of specific grafting mechanisms are possible. For radical sites that are easily accessible at the surface, the π -complex may react further by a π - σ conversion with either the ring (Eqs. 3 and 4) or side chain (Eq. 5) positions to give a σ -bonded species.

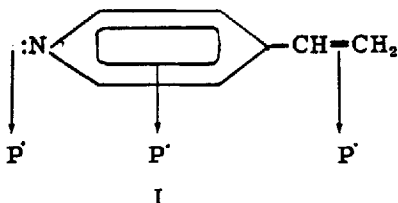


Where the mobility of the polystyrene chains and radicals is impeded, π - σ conversion processes are restricted; however, grafting could still occur through charge-transfer bonding of the type shown in Eq. (6). Such bonding would keep homopolymer locked between the chains as "graft" and could explain the apparent



anomalies observed when homopolymer is extracted from copolymerized celluloses. The theory is also applicable to grafting by uv and ceric ions.

When applied to monomers other than styrene, especially those with additional functional groups such as the vinylpyridines used in the present work, the theory can be modified to show that the functional group could act as donor as well as the conventional π -bonds, to give species such as I, where P denotes trapped radical in the polymer. The position of the heterocyclic nitrogen relative



to the vinyl group will determine the relative contributions of the line-pair and ring π -electrons in the formation of the initial complex.

Application of Theory to Wool and Polyethylene Grafting

The essential difference between cellulose and the other two trunk polymers, wool and polyethylene, in the application of this charge-transfer theory to grafting is the nature of the trapped radicals in each polymer. For example, in irradiated cellulose, ESR studies [14] show that two types of species (singlet and triplet in ESR) are predominantly

present, one of these being the alkoxyl radical. With polyethylene and more particularly wool, the structure of the equivalent radicals and their physical environment is quite different from cellulose. In wool the radicals generally have shorter lifetimes [13] than in the other two trunk polymers, i.e., the radicals are more "accessible" and more reactive. Thus, mechanistically, this would explain the generally higher grafting achieved with wool and would also suggest that, with this trunk polymer, processes depicted by Eqs. (3)-(5) contribute more to the ultimate graft than processes shown in Eq. (6).

In the preceding discussion it is emphasized that the present authors do not wish to imply that grafting occurs exclusively by charge-transfer processes involving radicals only. Present evidence suggests that such processes predominate in the grafting reaction; however, there are other mechanisms such as ionic and energy transfer processes which certainly contribute to grafting. In alcohols, especially, solvated electrons do participate actively in the fundamental radiolysis pathway and thus they will also be expected to influence radiation grafting processes using the simultaneous technique. For post-irradiation grafting, however, the copolymerization appears to occur exclusively by a radical process.

ACKNOWLEDGMENTS

The authors wish to express their thanks to Mr. J. Gray of the AAEC for dosimetry, the Australian Institute of Nuclear Science and Engineering for financing the irradiations at Lucas Heights, and the Australian Research Grants Committee and Australian Wool Board for continued support.

REFERENCES

- [1] S. Dilli and J. L. Garnett, J. Appl. Polym. Sci., **11**, 839-858 (1967); **11**, 859-870 (1967).
- [2] S. Dilli and J. L. Garnett, Aust. J. Chem., **24**, 981-987 (1971) and references therein.
- [3] H. A. Krassig and V. Stannett, Advan. Polym. Sci., **4**, 111-156 (1963).
- [4] J. L. Garnett and E. C. Martin, J. Macromol. Sci—Chem., **A4**(5), 1193-1214 (1970).
- [5] S. Dilli, J. L. Garnett, E. C. Martin and D. H. Phuoc, Proceedings of the Graft Polymerization onto Cellulose Symposium, 161st Meeting American Chemical Society, Los Angeles, March 1971, In Press.

- [6] J. A. Gervasi and V. Stannett, J. Appl. Polym. Sci., 10, 1217-1225 (1966).
- [7] G. S. Odian and B. S. Bernstein, Nucleonics, 21(1), 80-81 (1962).
- [8] E. Trommsdorff, H. Kohle, and P. Lagally, Makromol. Chem., 1, 169 (1948).
- [9] J. L. Garnett and E. C. Martin, Unpublished Data.
- [10] G. Odian, M. Sobel, A. Rossi, and R. Klein, J. Polym. Sci., 55, 663-673 (1961).
- [11] S. Dilli, J. L. Garnett, and D. H. Phuoc, Unpublished Data.
- [12] J. L. Garnett, Y. Yen, and E. C. Martin, Unpublished Data.
- [13] J. L. Garnett, R. S. Kenyon, J. D. Leeder, and G. S. Murty, Unpublished Data.
- [14] S. Dilli, I. T. Ernst, and J. L. Garnett, Aust. J. Chem., 20, 911-927 (1967).
- [15] S. Dilli and J. L. Garnett, J. Polym. Sci., Part A-1, 4, 2323 (1966).
- [16] N. G. Gaylord, Proceedings of the Graft Polymerization on to Cellulose Symposium, 161st Meeting American Chemical Society, Los Angeles, March 1971, In Press.

Received for publication February 7, 1972