The Mutual Irradiation Grafting of Styrene onto Poly(Vinyl Alcohol) and the Characterization of the Graft Copolymer

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Styrene was graft-copolymerized to poly(vinyl alcohol) (PVA) films in the presence of methanol by means of mutual irradiation. Methanol was found to promote the grafting, and to increase the molecular weight of polystyrene. The latter result was different from that found in the grafting of methyl methacrylate. The length of the branch was very high, but could be reduced by an addition of carbon tetrachloride to such an extent that the length of the branch became comparable with that of the backbone polymer. The graft copolymer was isolated from the grafting product by vigorous extraction of homopolystyrene and unreacted PVA. The G-value for the graft branch formation was found to be 1.3, which was comparable with the G_R-value for the radical formation of PVA. Isolation of the branch polystyrene from the backbone and determination of the number-average molecular weights enabled to deduce the conclusion that the graft copolymer consists of one mother PVA and one branch polystyrene.

INTRODUCTION

Concerning the radiation-induced graft copolymerization a large number of investigations have been carried out during the past decade. However, too little work has so far been reported on the true yield and the chemical structure of the graft copolymers. In our laboratory the radiation grafting of vinyl monomers such as styrene and methyl methacrylate onto poly(vinyl alcohol) (PVA) films has been widely investigated.[1-4] At present we have focussed our attention to the characterization of graft copolymers, because of its great importance to understand the radiation grafting in more detail.

Recently we have published some of characterization results on PVA-methyl methacrylate graft copolymers prepared by mutual and pre-irradiation method[5,6] and of PVA-styrene graft copolymer prepared by pre-irradiation method.[7] It was found in all cases that the isolated graft copolymers have one graft branch. In the present work we will report the results relating to mutual irradiation grafting of styrene onto PVA and the characterization of the graft copolymer obtained.

EXPERIMENTAL

1. Grafting

PVA films of 0.1 mm thickness were prepared by casting method from aqueous

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solutions of purified PVA with viscosity-average degree of polymerization of 2,400. Styrene monomer and other chemical reagents were purified by distillation. The detailed procedure of grafting has been described previously.[6] Dry or pre-swollen films were immersed in monomer mixture in glass ampoules, degassed by freezing and thawing, and then the ampoules were sealed under 10^{-4} mmHg. The sealed ampoules were put in a thermostat kept at 50° or 55°C and irradiated with gamma-rays from a Co-60 source at a dose rate of 6.0×10^3 or 1.0×10^4 R/hr for a given time.

2. Removal of Homopolymers

The whole graft products were immersed in plenty of benzene at room temperature and homopolystyrene formed in the outer solution was precipitated into methanol. When carbon tetrachloride (CCl_4) was present in the monomer mixture, the graft films were at first soaked in water to prevent the eventual crosslinking reaction between PVA molecules[6] and then subjected to the conventional extraction with boiling benzene to remove homopolystyrene occluded in the films. Apparent percent graft was calculated by the equation;

$$\text{apparent percent graft} = \frac{W_1 - W_0}{W_0} \times 100 \tag{1}$$

where W_0 is the weight of starting PVA and W_1 is the weight of the graft films after benzene extraction.

In order to make clear the chemical structure of graft copolymers, they should be free of both unreacted backbone and homopolymer formed. For this purpose, the unreacted PVA was extracted with water-n-propanol (75 : 25) mixture at 95°C. The alternate extraction with benzene and water-n-propanol was continued till amounts of polymer extracted were decreased to a relatively low extent. Then, the PVA part in the residue polymer was completely acetylated and further extraction was repeated for homopolystyrene with hot cyclohexane and for homopoly (vinyl acetate) with hot methanol to ensure the complete isolation of the graft copolymer. The residue was re-dissolved in benzene or dioxane and precipitated into n-hexane or water. This procedure was repeated several times. The acetylation enabled the extraction time to be greatly reduced. When no more polymer was extracted with either of the solvents, the final residue was regarded as pure graft copolymer. The true percent graft was calculated by the equation:

$$\text{true percent graft} = \frac{\text{total weight of graft branch}}{\text{weight of starting PVA films}} \times 100. \tag{2}$$

3. Determination of Molecular Weights and Chemical Composition

The poly(vinyl acetate)-styrene graft copolymer was converted to PVA-styrene graft copolymer by hydrolysis of acetate groups, and then the graft branches were separated from the backbone by oxidative cleavage of PVA main chains with periodic acid.[2] The hydrolysis fragment of the backbone PVA which is linked to the end of a separated polystyrene molecule was re-acetylated to make this polymer soluble in common organic solvents such as benzene. Number-average molecular weights, $\bar{M}_n$, of the acetylated graft copolymer, the separated branch,

the acetylated mother PVA and the homopolystyrene were determined in all cases by osmotic pressure measurements in benzene at 30°C. The osmometer used was "501-type High Speed Membrane Osmometer" manufactured by Mechlolab. Inc. The viscosity-average molecular weights, $\bar{M}_v$, of homopolystyrene were calculated by means of the equation :[8]

$$[\eta] = 1.13 \times 10^{-6} \bar{M}_v{}^{0.73} \quad \text{(in benzene, 25°C).} \tag{3}$$

The chemical composition of the graft copolymer was determined in an almost similar way as to the case of poly(vinyl acetate)-methyl methacrylate graft copolymer[2] from the alkali-consumption by the alkaline hydrolysis of the acetylated graft copolymer. In the present case, the hydrolysis was performed in benzene–methanol (20 : 1) with N/4 methanolic NaOH at 30°C for 2 days followed by addition of water. Back titration was done in aqueous medium after evaporation of benzene.

RESULTS AND DISCUSSION

1. Factors Influencing Grafting Reaction

It is a well-known fact that some swelling agents such as water and methanol are necessary to promote the graft copolymerization of styrene onto PVA films.[1] Figures 1 and 2 show effects of methanol on the apparent percent grafts and molecular weights of homopolystyrenes formed in the interior of films. The grafting was carried out using dry films at 50°C (Fig. 1) and 55°C (Fig. 2). Several interesting trends can be seen from the figures. The first is that when methanol was added to the monomer the extent of grafting was increased first gradually, reached a maximum at methanol contents of about 60 to 80 % and then decreased rapidly. It is of interest to note that the maximum molecular weights of homopolystyrene formed in the interior of the films also is located at about the same methanol contents. Figure 2 demonstrates further that the methanol contents
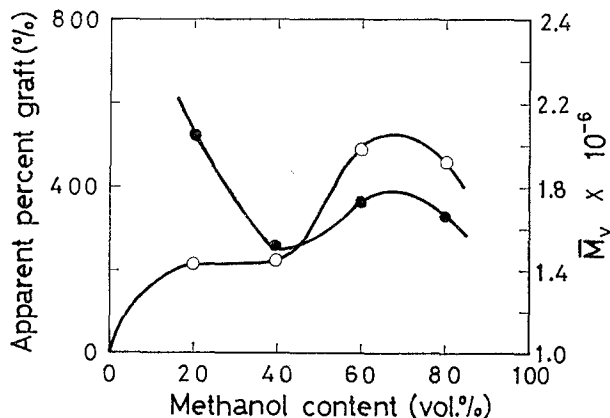

Fig. 1. Effects of methanol content in the styrene-methanol mixture on the apparent percent graft and $\bar{M}_v$ of homopolystyrene. (Radiation dose=9.0×10^4 R and temp.=50°C)
○ : apparent percent graft.
● : $\bar{M}_v$ of homopolystyrene formed in the interior of films.

where homopolymers have the maximum molecular weights are significantly different for the homopolystyrene formed in thefilms and that in the outer solution of films. This may be ascribed to the different methanol content in the films from that in the outer solution.
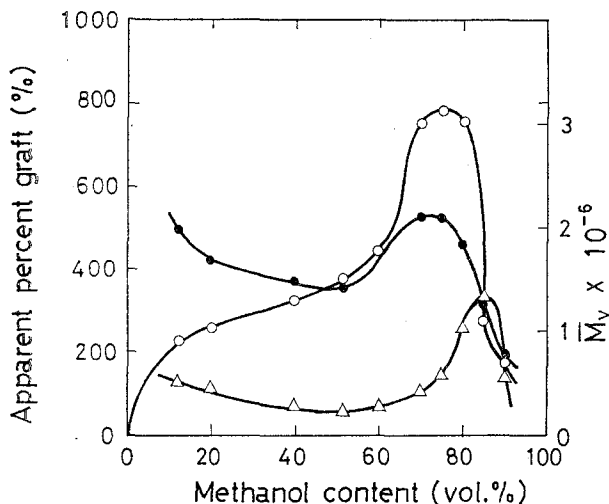

Fig. 2. Effects of methanol content in the styrene-methanol mixture on the apparent percent graft and $\bar{M}_v$ of homopolystyrene. (Radiation dose$=2.5\times10^5$ R and temp.$=55°$C)

○ : apparent percent graft.

● : $\bar{M}_v$ of homopolystyrene formed in the interior of films.

△ : $\bar{M}_v$ of homopolystyrene formed in the outer solution of films.

The fact that the maximum apparent percent graft and the maximum molecular weight of homopolystyrene occurred at the same methanol content may indicate that the Trommsdorff effect must be predominant in this methanol content range, as has been pointed out frequently in the heterogeneous graftings. It should be mentioned here that the molecular weight of homopolymer was, on the contrary, decreased steadily with increasing methanol content in the case of graft copolymerization of methyl methacrylate onto dry PVA films.[9] The main reason may be due to different ability of methanol to coagulate polystyrene and poly(methyl methacrylate). Anyway it is noteworthy that the role of swelling agents in the heterogeneous grafting is rather complicated and should be discussed taking various factors into consideration.

As Figs. 1 and 2 show, the molecular weights of homopolystyrene and hence of branch polystyrene also are extraodinarily high in comparison with molecular weight of the parent PVA. Accordingly it seems very difficult to characterize the graft copolymers with accuracy. For the purpose to reduce the molecular weight of the polystyrene branch to such a low value that the determination of the molecular weight by osmometry is more accurate, the grafting was done with an addition of CCl₄ which behaves as a chain transfer agent. In this case the PVA films which were pre-swollen with a water-methanol mixture were used instead of dry ones. When graft copolymerization was carried out onto dry films in the

presence of CCl₄, the graft films were colored light-yellowish. On the other hand, such coloration did not appear, when water-swollen films were used. Viscosity-average molecular weights of homopolystyrenes formed in the films were plotted in Fig. 3 as a function of CCl₄ concentration. From this result the apparent

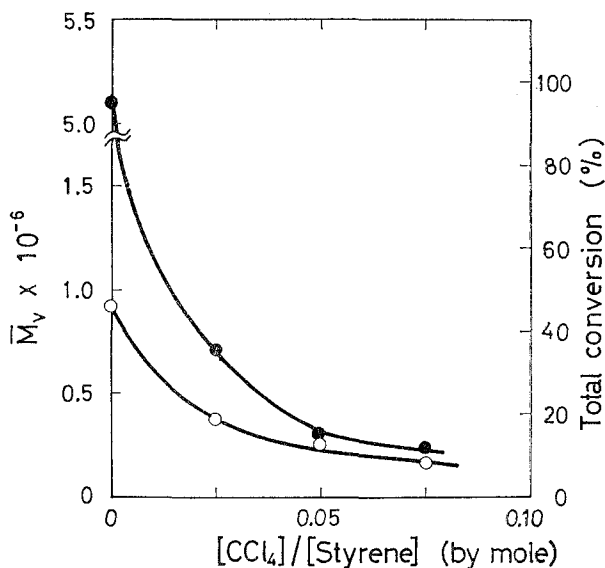Fig. 3. Effects of CCl₄ concentration in the monomer mixture on the $\bar{M}_v$ of homopolystyrene formed in the interior of films and the total conversion of monomer. (Methanol content=80 vol.%, radiation dose =1.44×10⁵ R, and temp.=50°C)
○: $\bar{M}_v$ of homopolystyrene.
●: total conversion.

chain transfer constant of CCl₄ was calculated to be 6.0×10^{-3}, which is nearly equal to that found in the pre-irradiation grafting of styrene onto PVA films.[4] In both cases the total conversion of monomer was decreased with increasing CCl₄ concentration, presumably because the polymerization proceeds in a heterogeneous system.[10]

2. Yield of Graft Copolymer

Table 1 gives grafting conditions to prepare the graft sample to be subjected to the characterization study. Isolation of the graft copolymer from the graft films and separation of branches from the backbone were performed in such a fashion as described in the EXPERIMENTAL section. It is of interest to note that benzene solutions of the branch polystyrene separated from the backbone PVA gave turbid appearance before acetylation. When the grafting has taken place, the separated branch polystyrene should have a PVA fragment with a degree of polymerization of 50 to 100 at the end of the branch, since the oxidative cleavage of C-C bonds in PVA backbone occurred solely at 1, 2-glycol bonds which are contained in PVA by 1 to 2 mole%. It is quite likely that the separated branch polystyrene molecules associate with each other in benzene through PVA fragments.

Table 1. Conditions of grafting reaction.

Weight of PVA films	(g)	20.07
Degree of swelling[a] of pre-swollen[b] films		1.64
Styrene	(ml)	120
Methanol	(ml)	480
[CCl$_4$]/[styrene] (mole ratio)		0.05
Dose rate	(R/hr)	1.0×10^4
Radiation dose	(R)	4.6×10^5
Temperature	(°C)	50

a) (weight of swollen film)/(weight of dry film) -1
b) immersed in methanol-water (6 : 4) mixture at 50°C for 24 hrs.

The results of the grafting reaction were summarized in Table 2. The true percent graft and the fraction of the reacted PVA were calculated under an assumption that no graft copolymer formed was lost during the isolation procedure.

Table 2. Results of grafting reaction.

Total conversion of monomer	(%)	ca. 100
Weight of graft copolymer	(g)	3.523
Mole fraction of styrene part		0.423
Weight ,, ,,		0.635
True percent graft	(%)	11.1
True grafting efficiency	(%)	2.0
Fraction of reacted PVA		0.064
G_b-value for branch formation		1.3

From the yield of graft copolymer, it is possible to estimate G_b-value for the graft branch formation. As the G_b is the number of graft branches formed per 100 eV, it is given simply by

$$G_b = \frac{100}{DA} \cdot \frac{Y}{100} \cdot \frac{N_L}{\bar{M}_b} \tag{4}$$

where D is the radiation dose in Röntgen unit, A is an energy conversion factor ($=5.8 \times 10^{13}$ eV/g·R), Y is the true percent graft ($=$ the amount of branches formed in 100 g of the backbone polymer), $\bar{M}_b$ is the number-average molecular weight of the branch polymer molecule, and N_L is Avogadro's number. In the present case $\bar{M}_b$ is 1.88×10^5, as will be shown later. Consequently the G_b was found to be 1.3 from the above equation. An unpublished ESR work done in our laboratory showed the G_R-value for radical formation of PVA, that is, the number of PVA radicals formed per 100 eV to range from 1 to 6. The G_R would be expected to vary considerably with the irradiation condition and the history of the irradiated sample. Nevertheless, the finding that the G_b compares favorably with the G_R, suggests that most of the free radicals formed on PVA molecules by irradiation and detected by the ESR experiment are able to initiate effectively the graft copolymerization of styrene.

3. Chemical Structure of Graft Copolymer

To estimate the number and the length of the graft branches, it is necessary

to measure the number-average molecular weights of the graft branch besides that of the graft copolymer. The observed molecular weights were presented in Table 3 together with those of acetylated mother PVA and homopolystyrene formed in the interior of the films. The molecular weights of the graft copolymer and the separated branch polystyrene were determined by osmometry in benzene after the PVA part of the graft copolymer was completely acetylated. The sum of molecular weight of branch and backbone part in one molecule of graft copolymer can be calculated by multiplying the molecular weight of the graft copolymer by the weight fraction of branch and backbone part, respectively, and was given in the table as calculated molecular weight.

The number of graft branches and mother PVA molecules in one graft copolymer molecule is able to be calculated directly by dividing the calculated molecular weights by the observed ones. The numbers calculated in this way were given in the last column of Table 3. The result leads to the important

Table 3. $\bar{M}_n$ of the graft copolymer and other polymers, and the number of branch and mother PVA in one molecule of graft copolymer.

Polymer	$\bar{M}_n \times 10^{-5}$		Number per graft copolymer molecule
	Observed	Calculated	
Mother polymer[a]	1.72	2.07	1.2
Branch polystyrene	1.88	1.83	1.0
Graft copolymer[a]	3.90	——	——
Substrate+Branch	4.04	——	——
Homopolystyrene[b]	2.24	——	——

a) Hydroxyl groups were completely acetylated.
b) Homopolymer formed in the interior of films.

conclusion that the graft copolymer molecule consists of one mother PVA and one branch polystyrene on the average, and that the length of the branch is approximately equal to that of the homopolymer formed in the interior of the films. The similar conclusion was also deduced for the PVA-methyl methacrylate graft copolymers prepared by the radiation grafting.[5,6] It is quite reasonable that the isolated graft copolymers have in any case only one branch molecule, if the magnitude of the G_R-value for radical formation of backbone polymer, the radiation dose and the molecular weight of mother backbone polymer are properly taken into consideration. The characterization of graft copolymers synthesized by radiation methods from various substrate polymers is currently being studied in our laboratory.

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