Solvent Effects on the Radiation Graft Copolymerizations onto Poly(Vinyl Alcohol)

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The radiation graft copolymerization of styrene or methyl methacrylate (MMA) onto poly(vinyl alcohol) films was carried out in the presence of swelling agents such as methanol and water. Basing on the variation of conversion, weight increase, and molecular weight of the polymer formed, effects of the swelling agents on the grafting were discussed. In addition the investigation was extended to the grafting systems containing a small amount of chain transfer agents. It was found that methanol has several effects on the heterogeneous grafting other than to accelerate the diffusion of monomers into the substrate matrix. In the grafting of styrene methanol caused an appreciable gel effect, while it behaved as a simple diluent in the grafting of MMA. The chain transfer agents reduced the yield as well as the length of the polymer molecules formed in the film, the chain transfer constant being in agreement with that in the conventional catalytic homopolymerization. The number of grafted branches was not affected by the presence of the chain transfer agent.

INTRODUCTION

Most of the radiation graft copolymerizations which proceed heterogeneously in a substrate matrix are performed with the use of solvents[1] (often named swelling agent). It is generally believed that they accelerate the diffusion of a monomer into the substrate matrix and hence increase the grafting extent. Surely this is the strongest reason why solvents are used for grafting. However, it should be also noted that they can affect grafting as a diluent of the monomer, a chain transfer agent and either a good solvent or non-solvent of growing polymer chains. This variety of the solvent effects may make the-kinetic study of the grafting much difficult.

The polymer adopted as a substrate in the present work is poly(vinyl alcohol) (PVAL), a typical hydrophilic polymer, and the monomers are methyl methacrylate (MMA) and styrene. The added solvent is mainly methanol. This is known to be a very effective swelling agent to promote the grafting not only onto PVAL,[2~4] but also cellulose,[5~11] nylon,[12~15] poly(ethylene terephthalate)[15,16] and other polymers.[13,17~20]

To study the solvent effects, the amount and the molecular weight of polymers formed in the polymer matrix must be determined. It was previously found that the separated branch of the true graft copolymer and the homopolymer formed in the polymer matrix have the same molecular weight.[16,21,22] Therefore, it is not necessary to distinguish between the grafted branch polymer and the non-grafted homopolymer, unless the chemical structure of the graft copolymer or the number of the true graft branches has to be determined. Therefore, a large amount of the homopolymer

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produced during the grafting in the matrix was not separated from the true graft copolymer in the present work unless otherwise mentioned, and the conversion of monomer or the weight increase was used as a measure of polymerization extent instead of the percent graft. Since chain transfer agents are known to behave peculiarly in the heterogeneous polymerizations,[23,24] the effects were also discussed in some detail.

EXPERIMENTAL

1. Graft Copolymerization

The graft copolymerizations onto PVAL films were carried out with both a mutual irradiation and a preirradiation method. In the latter grafting, dry films of 0.05-mm thickness were irradiated in the presence of air at room temperature with gamma-rays from a ^{60}Co source. The irradiated films were transferred into an ampoule, and then a sufficient amount of monomer–swelling agent mixture, in some cases containing a small amount of a chain transfer agent, was added to the ampoule to immerse the films. After the ampoule was degassed by freezing and thawing and sealed, the graft copolymerization was carried out under incessant rotation of the sealed ampoule in a water bath kept at 50°C unless otherwise mentioned.

The mutual irradiation grafting was carried out in the fashion similar to the pre-irradiation grafting except that dry or water-swollen films were irradiated simultaneously with the monomer solution in a degassed ampoule with gamma-rays.

2. Conventional Polymerization

Catalytic polymerization of styrene was carried out at 50°C in methanol solution in the presence of carbon tetrachloride (CCl$_4$) (styrene : methanol=40 : 60 by volume) by using α, α'-azobisisobutyronitrile (AIBN) as an initiator.

3. Removal of Homopolymers

The whole reaction products were placed in plenty of benzene at room temperature and the homopolymer formed in the outer solution and adsorbed on the surface of the films was removed. The weight increase was calculated from the weight difference of the original films and the reaction product. When the chain transfer agent was present in the monomer mixture, the reaction products were at first soaked in water to prevent the eventual cross-linking of PVAL by CCl$_4$ or trichloroethylene (TCE).[21,22]

In case to determine the number of truely grafted branches, the polystyrene homopolymer and the unreacted PVAL were alternately extracted with benzene and water–n-propanol (75 : 25) mixture at 80 and 95°C, respectively. The alternate extraction was continued till the amount of the polymers extracted decreased to a relatively low extent. Then the PVAL part in the residue was completely acetylated and further extraction was repeated for the polystyrene homopolymer with hot cyclohexane and for the poly(vinyl acetate) homopolymer with hot methanol to assure 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 reduced the extraction time to a considerable degree. When no more polymer was extracted with each solvent, the final residue was regarded as pure graft copolymer.

4. Determination of Molecular Weights and Chemical Compositions

The molecular weights of the homopolymers were estimated from the limiting viscosity numbers $[\eta]$ in benzene with the use of the equations,

$$[\eta]=1.13\times10^{-6}\bar{M}_v^{0.73} \qquad \text{(polystyrene, 25°C)}[25]$$
$$[\eta]=8.69\times10^{-5}\bar{M}_v^{0.76} \qquad \text{(PMMA, 30°C)}[26]$$

Osmotic pressure measurements were carried out with a High-Speed Membrane Osmometer (Hewlett Packard Co., 502-type) in toluene at 30°C for the mother PVAL, the isolated graft copolymer and the grafted branch polymer, after the hydroxyl groups in each polymer were completely acetylated in acetic anhydride–pyridine (1 : 2) mixture. The grafted branch was separated from the backbone by cleaving 1,2-glycol bonds in the hydrolyzed graft copolymer with sodium metaperiodate in dimethylformamide. The chemical composition of the graft copolymers was determined from the alkali-consumption at the hydrolysis of the acetylated graft copolymers in benzene–methanol (20 : 1) mixture with $N/4$ methanolic NaOH. More detailed procedures of the characterization were described in the previous papers.[21,22]

RESULTS AND DISCUSSION

1. Effects of Swelling Agents

Figures 1 and 2 show the influences of methanol on the graftings of styrene and Figs. 3, 4, and 5 on the grafting of MMA, respectively.
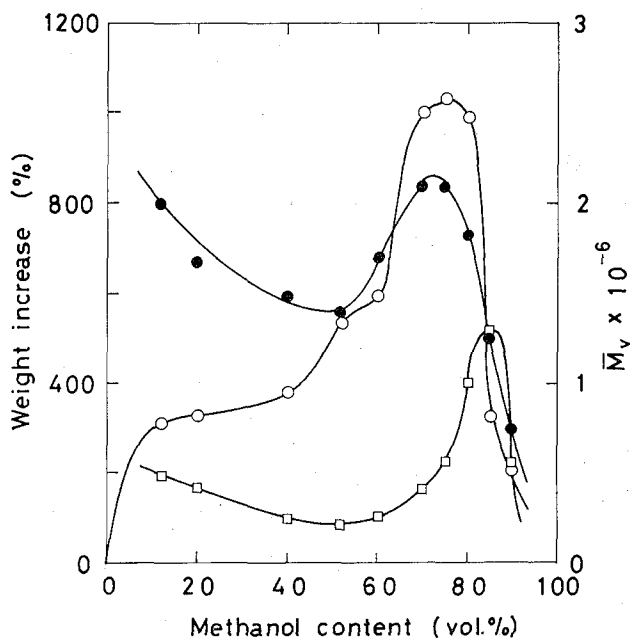

Fig. 1. Effect of methanol on the weight increase and $\bar{M}_v$ of the polystyrene homopolymer at the mutual grafting of styrene onto dry PVAL films: radiation dose=2.5×10^5 rad; temp.=55°C; (○) weight increase; (●) $\bar{M}_v$ of the polystyrene homopolymer formed in the interior of the films; (□) $\bar{M}_v$ of the polystyrene homopolymer formed in the outer solution.
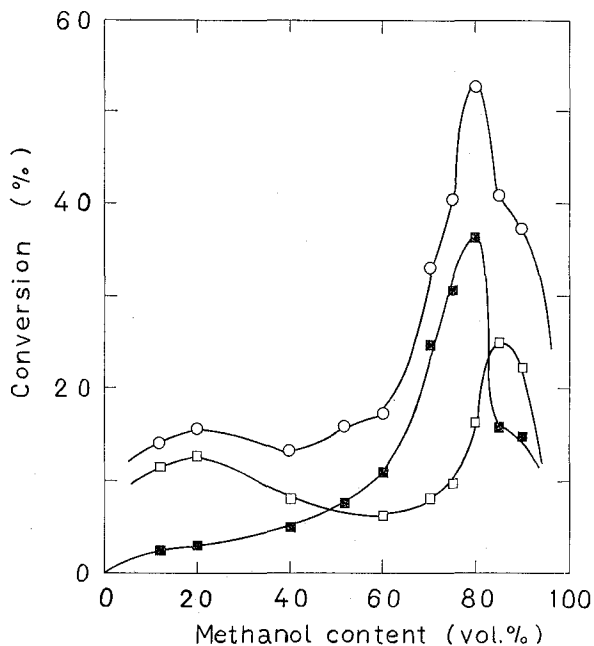
Fig. 2. Effect of methanol on the conversion of monomer at the mutual grafting of styrene onto dry PVAL films: radiation dose=2.5×10^5 rad; temp.=55°C; (◯) total conversion; (▢) conversion in the outer solution; (▧) conversion in the interior of the films.
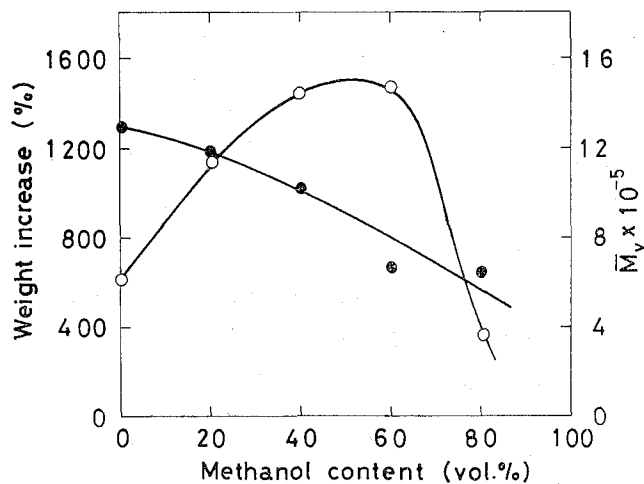
Fig. 3. Effect of methanol on the weight increase and $\bar{M}_v$ of PMMA homopolymer at the mutual grafting of MMA onto water-swollen PVAL films (DS=0.66): radiation dose=2.4×10^5 rad; (◯) weight increase; (●) $\bar{M}_v$ of PMMA homopolymer formed in the interior of the films.

The grafting of styrene was carried out by the mutual irradiation method onto dry PVAL films at 55°C. The dose rate and the total dose are 6.0×10^3 rad/hr and 2.5×10^5 rad, respectively. The mutual grafting of MMA was carried out onto dry or water-swollen films with a dose of 9.0×10^4 rad except for the film of DS=0.66 (2.4×10^5 rad). The
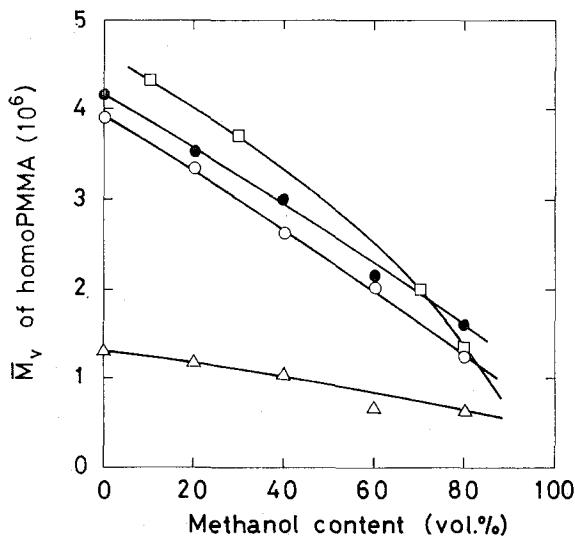
Fig. 4. Effect of methanol on $\bar{M}_v$ of PMMA homopolymer formed in the interior of the films at the mutual grafting of MMA onto water-swollen PVAL films: radiation dose=9.0×10^4 rad except for DS=0.66 (2.4×10^5 rad); (□) DS=0; (△) DS=0.66; (●) DS=1.2; (○) DS=2.3.

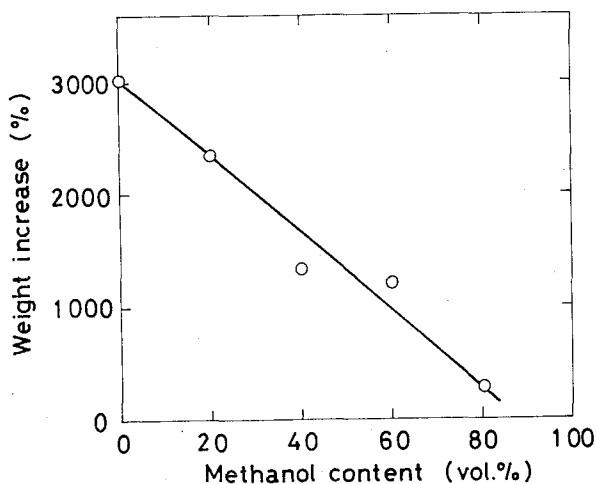Fig. 5. Effect of methanol on the weight increase at the mutual grafting of MMA onto highly water-swollen PVAL films (DS=2.3): radiation dose=9.0×10^4 rad.

degree of swelling (DS), defined as gram water contained in one gram PVAL film, varied from 0 to 2.3. As can be seen, methanol actually promoted the graftings in both cases, unless the DS of the films was high. However, comparison of Fig. 1 with Fig. 3 reveals clearly that there is a difference between styrene and MMA in the variation of the molecular weight as well as the weight increase with the methanol content. This indicates that the swelling agents have some effects other than to accelerate the diffusion of the monomers into the substrate matrix. As this penetration effect of solvents is a well-known fact, we will discuss other effects and clarify whether the weight increase is due mainly to the increase in the number or the length of the polymer chains formed.

1.1. Gel Effect. The steep rise in the weight increase owing to the presence of methanol is frequently ascribed to the so-called gel effect.[6,7,9,11,13,18,19] If this effect is actually predominant, the molecular weight of the polymer formed should be increased in proportion to the weight increase. This case is just seen in Fig. 1, where the results of the grafting of styrene in the presence of methanol are given. It is clear that the polystyrene homopolymer formed in the films has the highest molecular weight at the same methanol content where the weight increase becomes a maximum. Therefore, the steep rise in the weight increase around the methanol content of 75% is concluded to be principally due to the gel effect.

It is interesting to point out that the methanol content where the polystyrene homopolymer had the highest molecular weight is somewhat different between the homopolymer formed in the films and that in the outer solution of the films. One of the plausible reasons is that the methanol concentration in the films is different from that in the outer solution. However, even if it is true, the concentration difference seems not to be so large as that in the grafting of styrene onto polyethylene[19,20] or cellulose acetate.[10] On the other hand, the difference in molecular weight of the polystyrene homopolymers formed in each location might be also taken into account, since the precipitation of polystyrene depends not only on the methanol content but also on the molecular weight.

Another remarkable feature seen in Fig. 1 is that the molecular weight of the polystyrene homopolymer formed in the films is about twice larger than that formed in the outer solution. This result may be explained in terms of the matrix effect originating from the polymer substrate in which the mobility of polymer chains is strongly reduced. Since the gel effect is substantially caused by the decrease in the rate of the collision of mutual propagating polymer chains mainly because of high viscosity of the medium, the matrix effect can be regarded as a sort of the gel effect. Methanol may cause the propagating polystyrene chains to coil up, leading to the burying of the radicals, while the substrate matrix decreases the mobility of the propagating polymer chains through the gel-like property.

1.2. Diluent Effect. As can be seen in Fig. 4, the molecular weights of PMMA homopolymers formed in the PVAL films were decreased steadily with the increasing methanol content, in contrast with the grafting of styrene. Huang[7] also observed in a rayon–styrene grafting the monotonous decrease of the molecular weight of polystyrene branch with the increasing content of acetone, which is a non-solvent for polystyrene.

The reason of the different influence of the methanol content on the molecular weight change in the MMA and styrene graftings is not clear, but it seems probable that methanol coagulates polystyrene much stronger than PMMA, giving rise to the significant gel effect in the grafting of styrene. Anyhow, the above results suggest that the role of swelling agents in the heterogeneous grafting is not simple and should be discussed by taking various factors into consideration.

Two factors may be important for explaining the result that the molecular weight of the homopolymer was monotonously decreased with the methanol content. One is the dilution of the monomer with methanol and the other is the radical transfer to methanol. In the mutual grafting the indirect effect due to the methanol radicals formed directly by irradiation should be further taken into consideration similarly to the radiation-induced homopolymerization.[27] As a result of the indirect effect the rate of initiation R_i becomes

a complicated function of the concentration of the swelling agent. However, in the case of MMA–methanol mixture R_i may be regarded as independent of the concentration to a first approximation, since the G-value for radical formation is nearly the same for MMA ($G_R=27.5$) and for methanol ($G_R=24.0$).[28] On the contrary, it is known[27] that the transfer of excited energy takes place between styrene and methanol, resulting in the pronounced increase in the polymerization rate. The small maxima of the conversion in the outer solution and the total conversion observed at the methanol content of 20% (Fig. 2) may be explained in terms of this indirect effect. Here the conversions in the outer solution and in the interior of the films are defined as the fractions of the monomer polymerized in each location to the initial total monomer amount and the total conversion is the sum of them.

If the diluent and chain transfer effects are assumed to be the chief factors influencing the number-average degree of polymerization of the PMMA homopolymer, $\bar{P}_n$, it is given by

$$\frac{1}{\bar{P}_n}=C_M+C_S\frac{[S]}{[M]}+\frac{k_t^{1/2}}{k_p}\cdot\frac{R_i^{1/2}}{[M]} \tag{1}$$

where [S] and [M] are the concentrations of solvent and monomer in the film, C_M and C_S the chain transfer constants to monomer and solvent, k_t and k_p the rate constants of termination and propagation, respectively. If [M] and [S] are assumed to be proportional to those of the outer solution [M'] ($=k'$[M]) and [S']($=k''$[S]), the following equation is obtained

$$\frac{1}{\bar{P}_n}=C_M-\frac{\rho_S M_{0,M}}{\rho_M M_{0,S}}\cdot\frac{k''}{k'}\cdot C_S+\left(\frac{\rho_S M_{0,M}}{\rho_M M_{0,S}}\cdot k''C_S+\frac{k_t^{1/2}R_i^{1/2}}{k_p}\cdot\frac{M_{0,M}}{\rho_M}\right)\cdot\frac{1}{k'v'} \tag{2}$$

where v' is the volume fraction of the monomer in the outer solution, $M_{0,M}$ and $M_{0,S}$ the molecular weights of monomer and solvent, and ρ_M and ρ_S the densities of monomer
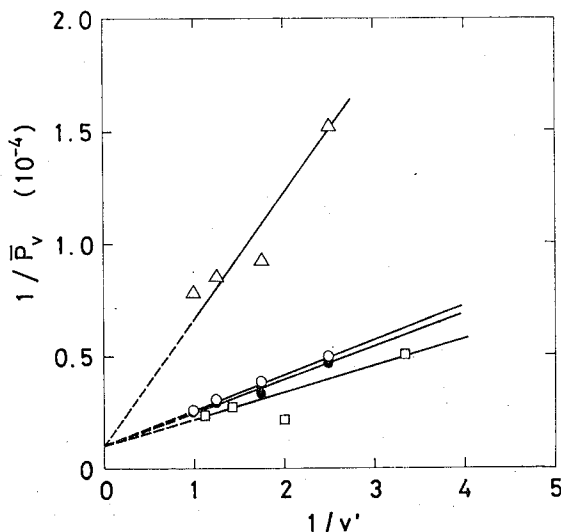

Fig. 6. Plots of $1/\bar{P}_v$ versus $1/v'$ according to Eq. (2): (□) DS=0; (△) DS=0.66; (●) DS=1.2; (○) DS=2.3.

and solvent (g/ml), respectively. In this equation the concentration is expressed by mole/ml. Therefore, the value of $C_M - (\rho_S M_{0,M}/\rho_M M_{0,S}) \cdot (k''/k') C_S$ can be determined as the intercept of a plot of $1/\bar{P}_n$ against $1/v'$. The plot is shown in Fig. 6, where it is seen that the intercepts are 1.0×10^{-5} regardless of the DS of the film. As C_M is 1.0×10^{-5} according to the literature,[29] C_S is found to be zero. It is, therefore, concluded that the decrease in the length of the homopolymer molecule is attributed to the dilution effect of methanol.

Consequently the change of the weight increase seen in Fig. 3 should be explained in terms of the penetrating effect of methanol. The resulting increase in the number of branches with the methanol content was already pointed out in the previous paper.[3] The monotonous decrease in the weight increase with the methanol content (Fig. 5) maybe due to deswelling of water-swollen films by methanol which is a poorer swelling agent than water for PVAL.

2. Chain Transfer Agent Effect

As is demonstrated above and in other works,[7,11,16,19,30] the polymer chains formed during the heterogeneous graftings have an extremely long length compared with those of the backbone polymer. Actually the polymer chain appears to be able to grow almost to the upper limiting length that is determined by C_M, the radical chain transfer constant to monomer. This is probably due to the matrix effect of the substrate polymer hindering the mutual collision of the growing chain ends.

One of the features of heterogeneous polymerizations is known to be the decrease in the total conversion of monomer with the increasing concentration of a chain transfer agent, even if it is not a degradative one.[23,24] We found a similar result also in a heterogeneous grafting.[31] Figure 7 shows the result of the preirradiation grafting of styrene onto PVAL in the presence of CCl$_4$, a strong chain transfer agent for styrene.
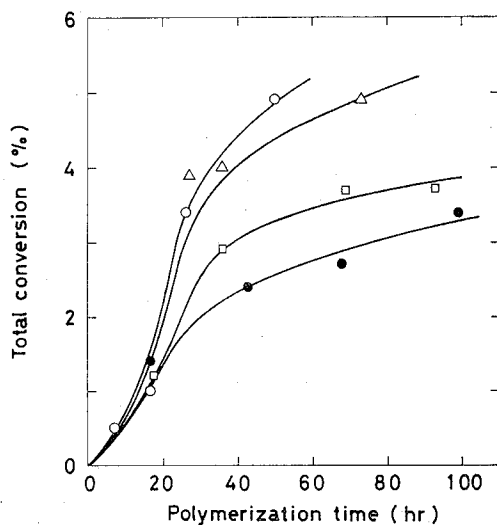

Fig. 7. Effect of CCl$_4$ on the total conversion of monomer at the preirradiation grafting of styrene onto dry PVAL films: methanol/styrene=60/40; (○) [CCl$_4$]/[styrene]=0; (△) [CCl$_4$]/[styrene]=0.01; (□) [CCl$_4$]/[styrene]=0.05; (●) [CCl$_4$]/[styrene]=0.10.
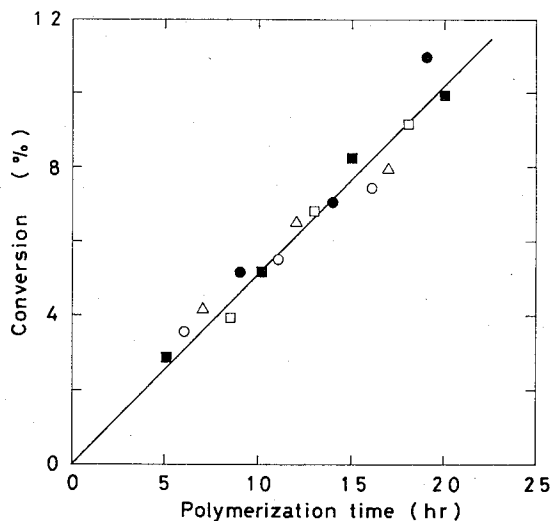
Fig. 8. Effect of CCl₄ on the conversion of monomer at the catalytic polymerization of styrene: AIBN=1.0×10⁻² mole/l; methanol/styrene=60/40; (●) [CCl₄]/[styrene]=0; (□) [CCl₄]/[styrene]=0.025; (△) [CCl₄]/[styrene]=0.050; (○) [CCl₄]/[styrene]=0.075; (■) [CCl₄]/[styrene]=0.10.
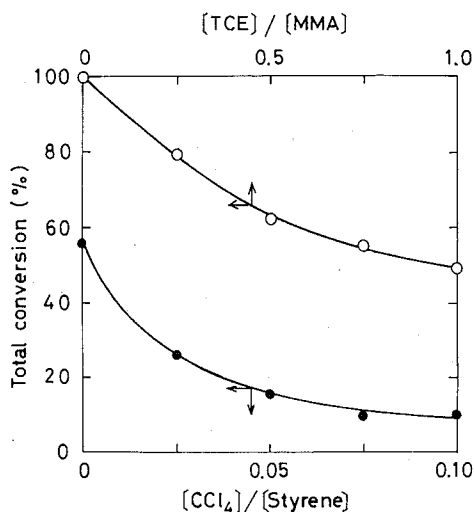

Fig. 9. Effect of chain transfer agents on the total conversion at the mutual graftings: (○) PVAL–MMA–TCE system, methanol/MMA=60/40, radiation dose=9.0×10⁴ rad, and DS=2.3; (●) PVAL–styrene–CCl₄ system, methanol/styrene=80/20, radiation dose=1.44×10⁵ rad, and DS=0.66.

The dry PVAL films were preirradiated to a dose of 1.0×10^6 rad at a dose rate of 8.4×10^4 rad/hr and then immersed in styrene–methanol (40 : 60) mixture containing CCl₄ for grafting. As is observed in Fig. 8, this agent did not cause any reduction of the conversion in the catalytic solution polymerization of styrene with the use of 1.0×10^{-2} mole/l AIBN. As is seen in Fig. 9, the similar results were observed also in the mutual graftings of styrene and MMA, where CCl₄ and TCE were used as chain transfer agents.

2.1. **Change of the Number of Branches by Chain Transfer Agent.** In the study of the effects of chain transfer agents on the graftings, it is important first of all to know whether the added chain transfer agent deactivates the initiating sites for the grafting on the substrate polymer. For this purpose, the mutual grafting of styrene onto PVAL films was carried out in the presence of a small amount of CCl_4 and the chemical structure of the graft copolymer formed was determined after complete removal of the polystyrene homopolymer and the unreacted PVAL. The grafting results are tabulated in Table I together with the reaction conditions.

Table I. Mutual Grafting of Styrene onto Water-Swollen PVAL Films (DS= 0.66) in the Presence of CCl_4: Dose Rate$=1.0 \times 10^4$ rad/hr, Radiation Dose$=4.6 \times 10^5$ rad, and Temp.$=50°C$.

		M3S	M4S	M8S	M10S
Wt. of PVAL film	(g)	34.13[a]	20.07[a]	23.37[b]	14.64[a]
Styrene	(ml)	234	119	119	120
Methanol	(ml)	940	476	476	478
[CCl₄]/[Styrene] (mole ratio)		0.13	0.05	0.05	0.025
Total conv. of monomer (%)		69	100	93	89
Wt. of true graft copolymer (g)		2.976	3.523	2.124	3.323
Styrene content of the graft copolymer (wt. %)		53.3	63.5	67.7	67.6
True percent graft[c] (%)		4.6	11.1	6.2	15.3
True grafting efficiency[d] (%)		1.1	2.2	1.5	2.0
Wt. frac. of reacted PVAL		0.041	0.064	0.029	0.073
G-value for branch formation		1.0	1.3	1.0	1.2

a) $\bar{M}_n = 5.89 \times 10^4$. b) $\bar{M}_n = 3.40 \times 10^4$.
c) (Wt. of the true graft branch/wt. of mother polymer) $\times 100$.
d) (Wt. of the true graft branch/wt. of total polymer formed) $\times 100$.

Table II summarizes the data of characterization.

Table II. Chemical Structures of PVAL–Styrene Graft Copolymers

Sample	VAC cont. of acetylated graft copolymer (wt%)	$\bar{M}_n \times 10^{-5}$				Number of branches in a graft copolymer molecule	$\dfrac{\bar{M}_B[b]}{\bar{M}_{B,0}[c]}$
		Acetylated graft copolymer	Backbone[a] PVAC	Branch[a] PS	Separated branch		
M3S	63.1	3.54	2.23	1.31	1.04	1.26	1.94
M4S	53.0	3.90	2.07	1.83	1.88	0.97	1.80
M8S	48.2	2.89	1.39	1.50	1.41	1.06	2.09
M10S	48.4	6.03	2.92	3.11	2.71	1.15	2.54

a) Calculated from the composition and $\bar{M}_n$ of graft copolymer.
b) $\bar{M}_n$ of backbone PVAC. c) $\bar{M}_n$ of mother PVAC.

From these results one can calculate the G-value for branch formation, defined as the number of branches formed per 100 eV radiation energy. (Detailed discussion on the chemical structure such as $\bar{M}_B/\bar{M}_{B,0}$ was given elsewhere.[32]) It was found from the calculation that the G-values do not scatter virtually from the average value of 1.0 in the

range of [CCl₄]/[styrene] from 0.025 to 0.13. Thus an important conclusion is obtained that the chain transfer agent does not affect the number of branches. On the contrary, Hayakawa *et al.*[33] and Huang[7] reported that the number of branches increased with addition of CCl₄ in the graftings of styrene onto cellulose acetate and rayon, respectively. In these cases it is, however, questionable whether the polystyrene homopolymer formed within the fibers was completely removed.

2.2. Chain Transfer Constant in the Grafting.   In Fig. 10, $1/\bar{P}_v$ was plotted against the initial concentration ratio of CCl₄ to styrene to estimate the chain transfer constant C_s.
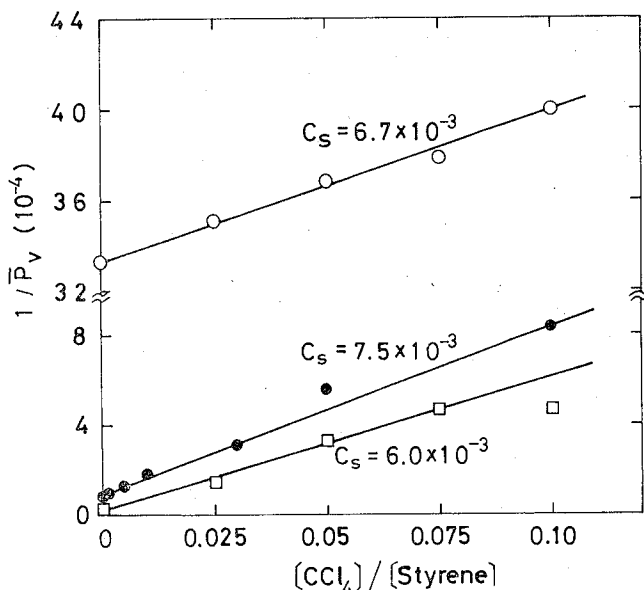

Fig. 10.   Effect of CCl₄ on $\bar{P}_v$ of polystyrene homopolymers formed at various
polymerizations: (○) catalytic polymerization (AIBN=1.0×10⁻² mole/l);
(●) preirradiation grafting; (□) mutual grafting.

The C_s values calculated from the slopes of the straight lines are 6.0×10^{-3} for the mutual irradiation grafting, 7.5×10^{-3} for the preirradiation grafting, and 6.7×10^{-3} for the conventional polymerization with AIBN.   Also in the graftings of MMA onto PVAL[34] and styrene onto cellulose acetate,[33] the two values of C_s obtained from the grafting and the catalytic polymerization were in good agreement with each other.   These results suggest that the concentration ratio of the chain transfer agent to the monomer in the vicinity of the growing chain ends in the film is nearly equal to that for the growing chains at the conventional polymerization and in addition the rate constants of polymerization (k_p) and of chain transfer (k_{tr}) in the heterogeneous grafting are the same as in the catalytic polymerization.

2.3. Decrease in the Total Conversion.   The above experiments denote that the chain transfer agent neither deactivates the primary radicals on the substrate polymers, nor behaves abnormally, at least, with respect to the change of the polymer chain length. However, it decreases greatly not only the percent graft,[35] but also the total conversion of monomer, as shown in Figs. 7 and 9.   To gain a deep insight on the mechanism, we
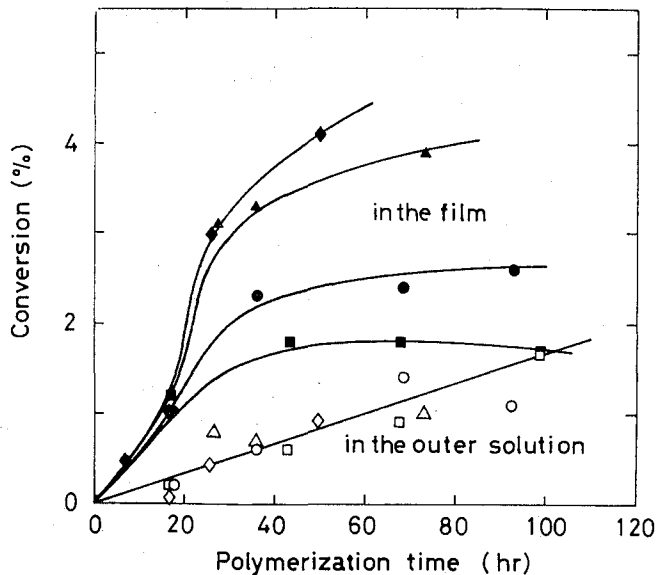
Fig. 11. Effect of CCl₄ on the conversion of monomer in the interior of
the film and in the outer solution at the preirradiation grafting of
styrene onto PVAL films: methanol/styrene=60/40; (◇, ◆) [CCl₄]/
[styrene]=0; (△, ▲) [CCl₄]/[styrene]=0.01; (○, ●) [CCl₄]/[styrene]
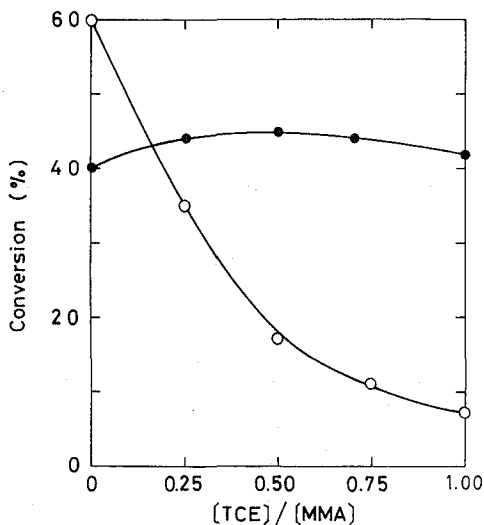=0.05; (□, ■) [CCl₄]/[styrene]=0.10.

Fig. 12. Effect of TCE on the conversion of monomer in the interior of
the films and in the outer solution at the mutual grafting of MMA onto
PVAL films: methanol/MMA=60/40; (○) in the film; (●) in the
outer solution.

measured the weight of the homopolymer formed in the interior of the film and in the
outer solution as well as the molecular weight of both polymers. The yield of the homo-
polymer, expressed here as conversion, is given in Figs. 11 and 12 and Table III. It
is seen in each case that the conversion in the film is decreased with the increasing

Table III. Effect of CCl₄ on the Mutual Grafting of Styrene onto Water-Swollen PVAL Films (DS=0.66): Methanol/Styrene=80/20, Radiation Dose=1.44× 10⁵ rad, and Temp.=50°C.

		S 75	S 76	S 77	S 78	S 79
[CCl₄]/[Styrene]	(mole ratio)	0	0.025	0.050	0.075	0.10
Conv. in the outer solution	(%)	14.6	15.1	11.2	7.3	8.0
Conv. in the interior of the PVAL films	(%)	40.8	7.7	4.5	2.5	2.0
Total conversion	(%)	55.4	22.8	15.7	9.8	10.0
$\bar{M}_v$ of polystyrene homopolymer	(10⁵)	51.0	7.07	3.12	2.24	2.24
Number of polystyrene molecules formed in PVAL films[a]	(10⁷)	1.05	1.42	1.86	1.42	1.17

a) (Wt. of the homopolymer formed in the films/$\bar{M}_v$ of the homopolymer)×Avogadro's number.

concentration of the chain transfer agent, whereas that in the outer solution changed rather insignificantly. The indirect effect due to CCl₄ can be neglected, because the similar decrease in the polymer yield is observed also in the heterogeneous preirradiation grafting. It is noteworthy that, as is seen in Table III, the number of the polymer molecules formed in the film seems to remain constant regardless of the CCl₄ concentration within the experimental error. It follows that the CCl₄ radicals produced as a result of radical transfer from the growing chain disappear rapidly from the substrate matrix. Referring to the fact that the yield of the homopolymer in the outer solution is constant or rather decreased with the chain transfer agent concentration, it seems probable that the radicals from the chain transfer agents disappear in the film as a result of their recombination.

CONCLUSION

1) The presence of methanol in a monomer enhances the diffusion of the monomer into the substrate film, resulting in an increase of the number of polymer chains formed in the film.

2) The monomer diffusion into the film is more largely enhanced by water than by methanol whose affinity for PVAL is much lower than water.

3) Grafting of styrene in methanol gives rise to the gel effect in the methanol content near 75% to a considerable extent. As a result the length of polymer chains becomes very long and hence the weight increase is increased in proportion to the chain length.

4) In contrast with the grafting of styrene, methanol in the grafting of MMA does not cause any gel effect, but acts merely as a simple diluent. The chain length is decreased with methanol content as predicted from the normal polymerization kinetics.

5) The total conversion as well as the percent graft are decreased significantly when the heterogeneous graftings of styrene and MMA are carried out in the presence of CCl₄ and TCE, though they are not degradative chain transfer agents in the conventional catalytic polymerizations. This may be a reflection of the heterogeneous polymerization process by which the graftings proceed.

6) The chain transfer constant to CCl₄ calculated from the variation of the molecular

weight of the polystyrene homopolymer formed in the film is in good agreement with that found in the conventional homopolymerization.

7) The characterization of the graft copolymers freed from the homopolymers exhibits that the number of truely grafted branches is neither increased nor decreased by the presence of CCl_4.

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