

Radiation-Induced Graft Copolymerization of Styrene onto Poly(Vinyl Alcohol) in the Presence of Carbon Tetrachloride

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The grafting of styrene onto poly(vinyl alcohol) (PVA) films by pre-irradiation technique was studied in the presence of carbon tetrachloride (CCl_4). It was found that lengths of the grafted branch could be lowered expectedly by the use of CCl_4 . The chain transfer constant, C_s , estimated from the change in degree of polymerization of the homopolymer formed in the interior of the films was 8.0×10^{-3} , and it was in good agreement with the C_s found for the conventional catalytic polymerization. Not only the percent grafting and the graft efficiency, but also the overall rate of polymerization were decreased with increasing concentration of CCl_4 , similarly in the case of PVA-methyl methacrylate graft copolymerization. In the present study the graft copolymer was carefully isolated from both the homopolymer and the ungrafted PVA, in order to make it possible to discuss the grafting mechanism in detail. As a result, it was concluded that the number of branch and the grafted PVA per unit weight of starting PVA films was decreased with increasing concentration of CCl_4 . However, when the calculation was made using the data obtained after the conventional, simple extraction of the homopolymer, the opposite conclusion was drawn that the number of branches was increased with CCl_4 . This finding suggests strongly that it is essential to isolate the pure graft copolymer, in order to obtain any definite conclusion on the mechanism of grafting and the chemical structure of graft copolymer.

INTRODUCTION

When the graft copolymerization is performed heterogeneously in the solid substrate matrix such as polymer films or fibers, the branch polymers are apt to grow so long that their correct molecular weights are not measurable by usual methods. Consequently, it becomes extremely difficult to characterize the graft copolymer precisely, unless the length of the branches is made shorter by some way. One of the most effective and simple means to reduce the branch length may be the use of chain transfer agents. However, no systematic study has been made, up to date, on the effects of chain transfer agents on the grafting¹⁻³⁾. In an earlier publication⁴⁾, we have studied the effects of chain transfer agents on the radiation-induced graft copolymerization of methyl methacrylate (MMA) onto poly(vinyl alcohol) (PVA). The study indicated that the chain length of branches became shorter expectedly with increasing concentration of chain transfer agents, and that the ordinary transfer agents such as *n*-butyl

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mercaptan decreased not only the percent grafting, but also the overall rate of polymerization. However, at that time, more detailed information could not be obtained, because the isolation of the graft copolymer was not carried out completely. For instance, it was not possible to confirm whether the number of grafted branches was increased or decreased by the presence of chain transfer agents.

It is interesting to examine whether the anomalous effects such as the decrease in the overall rate of polymerization by chain transfer agents are observed for other grafting systems. For this purpose and moreover to accumulate the knowledge about the effects of chain transfer agent, the graft copolymerization onto PVA was carried out, using styrene as a monomer and carbon tetrachloride (CCl_4) as a chain transfer agent. In the present investigation, attention was paid especially to the isolation of graft copolymers to enable the mechanism of graft copolymerization to be discussed in detail. Results of the characterization of the graft copolymer will be described in the subsequent paper.

EXPERIMENTAL

1. PVA films

Commercial PVA was purified by alkaline re-saponification and then by extraction with methanol. Films of 0.1 mm thickness were prepared by casting 6% aqueous solution of the purified PVA on glass plates at room temperature. They were cut into strips of 6 cm \times 0.5 cm, and dried *in vacuo* for 1 day at 50°C. The degree of polymerization (DP) of the starting PVA was 2,340.

2. Irradiation

Pre-irradiation of PVA films was carried out in the presence of air at 25°C with gamma-rays from a Co-60 source. The dose rate and the total dose were 8.4×10^4 R/hr and 1.0×10^6 R, respectively. The irradiated films were kept in a desiccator containing P_2O_5 at room temperature.

3. Graft Copolymerization

The grafting reaction was initiated immediately, or at least within a few days, after the pre-irradiation. The St monomer, CCl_4 and methanol were purified by the conventional distillation, just before the start of graft copolymerization. The grafting was carried out at 50°C in the absence of air by immersing the pre-irradiated films in the 40:60 St-methanol mixture containing adequate amounts of CCl_4 . This ratio of monomer to methanol and the polymerization temperature are the same to the previous case of the grafting of MMA onto PVA⁹. The monomer solutions were added to the films so as to immerse them sufficiently. After the ampoules containing the films and the monomer solution were degassed and sealed, grafting was started, incessantly rotating the sealed ampoules in a water bath kept at 50°C.

For the comparison with the grafting, conventional polymerization of St was carried out at 50°C in methanol solution in the presence of CCl_4 (St: methanol = 40:60 vol. ratio) using α , α' -azobisisobutyronitrile (AIBN) as an initiator.

4. Extraction of Homopolymer

After the graft copolymerization, the whole content of the ampoules was poured into plenty of benzene containig *p*-benzoquinone to inhibit the further polymerization, and was allowed to stand overnight at room temperature. Thus, the homoPSt formed out of the films and occluded loosely in the vicinity of the film surface was separated from the grafted films. Then the homoPSt occluded in the interior of the films was extracted with benzene at 80°C, till no more polymer was extracted. As pointed out in the previous paper⁵, a large amount of homopolymers still remains in the interior of films, if only this conventional extraction is carried out. Therefore in the present study, the homoPSt was again extracted after the ungrafted PVA was extracted with the *n*-propanol-water (20 : 80) mixture at 95°C, which is known to be a better solvent than pure boiling water for PVA⁶. This extraction with benzene and *n*-propanol-water was alternately repeated, till no more extractable polymer was present. The extracted polymer was confirmed to be pure PSt or pure PVA by the infra-red spectroscopy.

5. Measurement of Chemical Composition and DP.

DP's of PSt were calculated from viscosities of benzene solutions at 30°C, using the equation $[\eta] = 2.8 \times 10^{-3} \times DP^{0.783}$ cited by Ewart *et al*⁷. The chemical compositions of the isolated graft copolymers were determined by the elementary analysis, the accuracy of which was so satisfactory that the total weight of carbon, oxygen and hydrogen was found to amount to $100 \pm 1\%$ in every case. The chemical compositions are mean values of three or four determinations.

RESULTS AND DISCUSSION

1. Effect of Chain Transfer Agent

According to the kinetic theory of vinyl polymerization, the rate of polymerization should be independent of the concentration of additives, if these behave as ideal chain transfer agent. As can be seen easily, in the case of grafting reaction, not the rate of grafting, but the overall rate of polymerization should be used as the kinetic rate of polymerization. The total conversion used to estimate the overall rate of polymerization is defined here as a weight ratio of total polymerized, that is, homopolymerized and graftpolymerized monomer to the initial monomer feeded in the grafting system. In the case of grafting of MMA onto the pre-irradiated PVA in the presence of various chain transfer agents, the overall rate of polymerization was decreased with increasing amount of chain transfer agents, although they were proved to act as ideal chain transfer agent at conventional polymerization initiated by AIBN.

Fig. 1 shows the result obtained in the case of graft copolymerization of St onto PVA films. The result demonstrates distinctly that the overall rate of polymerization is decreased, as the concentration of CCl_4 becomes higher. On the other hand, rates of conventional polymerization of St carried out using AIBN as an initiator are constant independently of the concentration of CCl_4 , as is

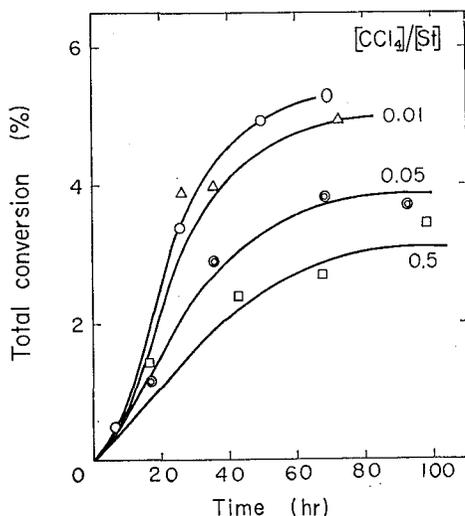


Fig. 1. Effect of CCl_4 on the overall rate of polymerization at the grafting.

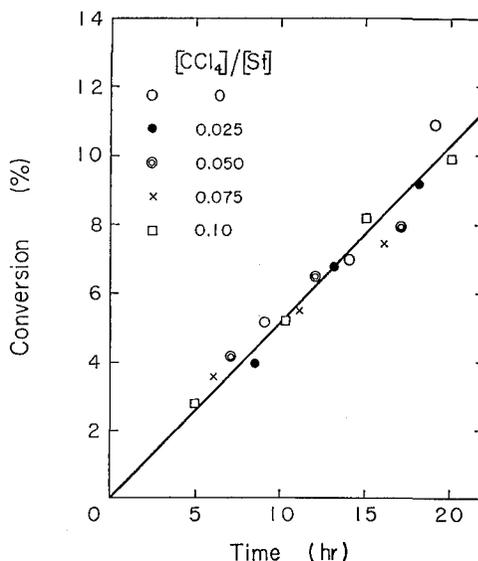


Fig. 2. Effect of CCl_4 on the rate of polymerization at the catalytic polymerization ($\text{AIBN} = 1.0 \times 10^{-2} \text{ mol/l}$).

clear from Fig. 2. These results are identical to those found in the previous work⁴). Therefore one may conclude that the abnormal feature of the overall rate of polymerization is common for the grafting, at least, onto the pre-irradiated PVA, and this may be explained by the previous assumption that radicals from chain transfer agent molecules deactivate the active species of the grafting at least partially in a mechanism to give radicals which do not grow. The effects of chain transfer agents on the radiation-induced mutual grafting onto PVA are now being carried out.

As mentioned above, the main purpose of addition of the chain transfer agent to the grafting system is to reduce the length of branches. Therefore, in order to ascertain whether the branches become really shorter, it is necessary to measure directly the change in chain length of the grafted branches. However, as the previous work⁵) confirmed that lengths of homopolymer can be regarded to be nearly equal to those of branches, merely DP's of the homoPSt were measured in the present case. In Figs. 3 and 4, reciprocals of DP's of the homoPSt and the PSt obtained by the conventional polymerization, are plotted against the mole ratios of CCl_4 to monomer, respectively. As can be seen from Fig. 3, the DP of homoPSt is decreased expectedly with increasing concentration of CCl_4 . The chain transfer constants, C_s , calculated from slopes of the linear curves in Figs. 3 and 4 are 8.0×10^{-3} for the grafting and 7.4×10^{-3} for the conventional polymerization. Also in the case of MMA, the two values of C_s obtained from the different polymerization results were found to be in good agreement⁴). These results indicate that the ratio of CCl_4 to monomer in the vicinity of the growing chain ends in the films is nearly equal to that for the growing chains at the conventional polymerization.

Radiation-Induced Graft Copolymerization

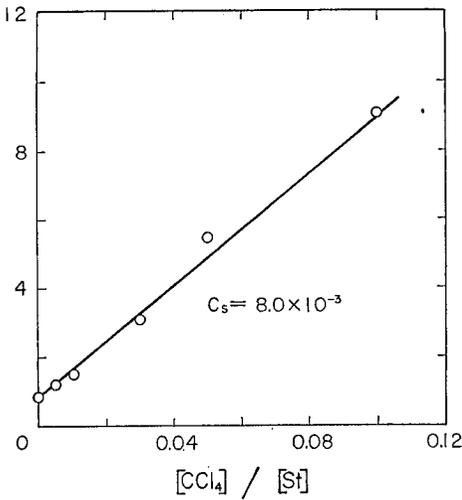


Fig. 3. Effect of CCl₄ on the DP of the homo-PSt formed during the grafting.

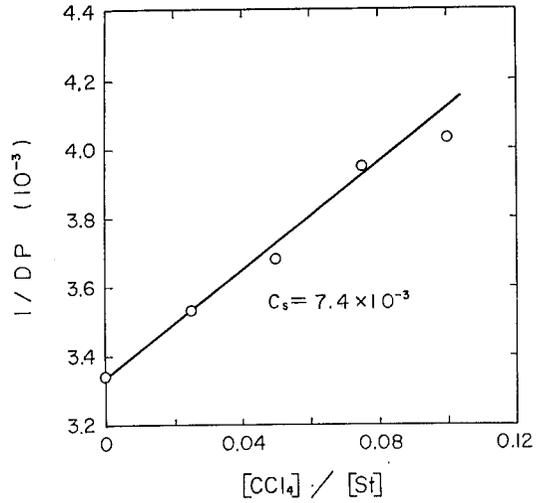


Fig. 4. Effect of CCl₄ on the DP of the PSt obtained by the catalytic polymerization (AIBN = 1.0 × 10⁻² mol/l).

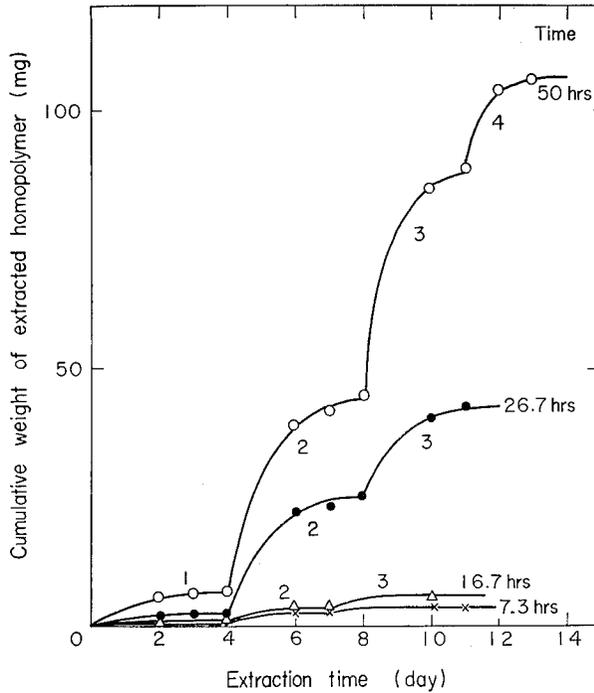


Fig. 5. Typical extraction curves for homoPSt extracted with benzene from grafted films.

2. Percent Grafting and Graft Efficiency

In the previous case of grafting of MMA onto PVA, the mechanism of grafting could not be discussed in detail, since the graft copolymer was contaminated with a large amount of both the homoPMMA and the ungrafted PVA. Therefore, in the present work, both polymers were extracted from the graft copolymer as much as possible. Recently we have demonstrated that the alternate extraction is a highly effective method to remove the occluded homopolymer from the grafted films. Fig. 5 shows an example of such alternate extraction which was carried out for the reaction product of the grafting at a concentration of $[\text{CCl}_4]/[\text{St}] = 0.001$. The numbers by the curves denote the order of benzene extraction. The result of extraction of PVA is omitted in Fig. 5, which was performed between each benzene extraction. The result in Fig. 5 shows clearly that a large amount of homoPSt is extracted after the extraction of the ungrafted PVA.

Generally the percent grafting is calculated from the data obtained after the conventional, that is, first extraction of homopolymer alone. Therefore, the conventional percent grafting is merely an apparent value. The percent graftings calculated after the conventional extraction and the complete, alternate extraction are shown in Figs. 6 and 7, respectively. As is apparent from the comparison of Figs. 6 and 7, the percent grafting after the alternate extraction is markedly lower than that of the conventional one. In order to demonstrate the difference more clearly, the leveling-off percent grafting is given in Table 1. It can be seen that the difference between two values of percent grafting become more predominant as the concentration of CCl_4 is increased. This may be

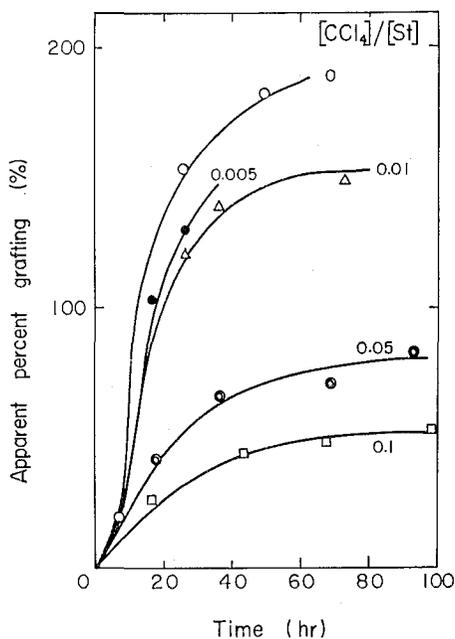


Fig. 6. Percent grafting calculated after the conventional extraction.

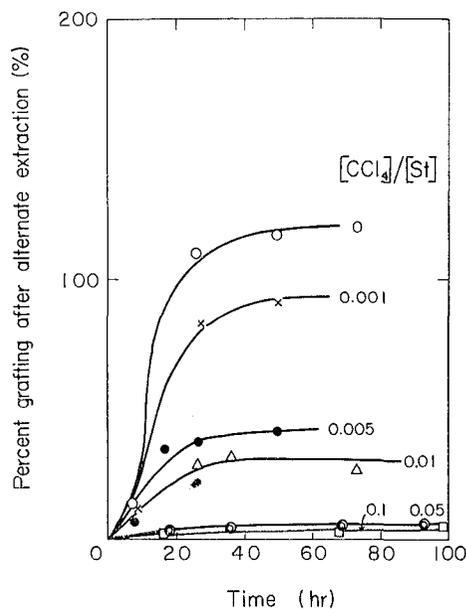


Fig. 7. Percent grafting calculated after the complete alternate extraction.

Radiation-Induced Graft Copolymerization

Table 1. Leveling-off Percent Grafting after Conventional Extraction, G_c , and Alternate Extraction, G_a .

$[\text{CCl}_4]/[\text{St}]$	0	0.005	0.01	0.05	0.1
G_c	190	(170)	150	85	50
G_a	135	75	45	20	6
G_c/G_a	1.4	(2.3)	3.3	4.3	8.3

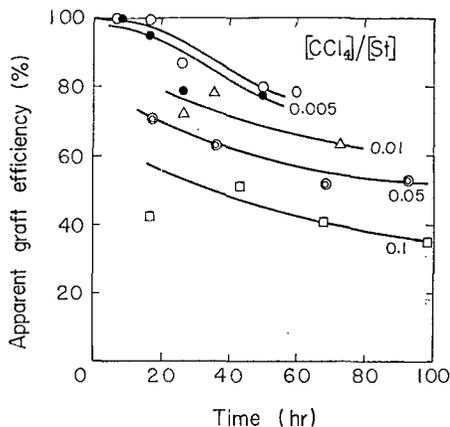


Fig. 8. Graft efficiency calculated after the conventional extraction.

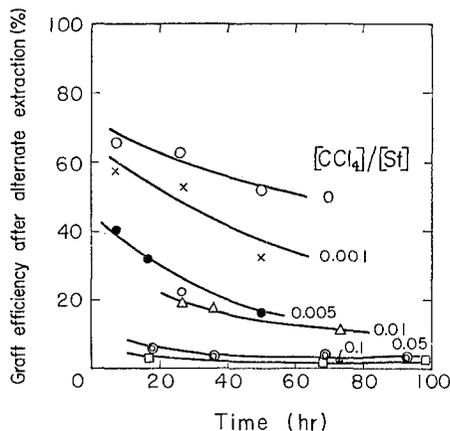


Fig. 9. Graft efficiency calculated after the complete alternate extraction.

attributed to the fact that the homopolymer is produced much more easily with increasing concentration of CCl_4 . The effect of CCl_4 can be seen distinctly also in the graft efficiencies, which are shown in Fig. 8. The apparent graft efficiency is given in Fig. 9. As is clear, the conventional graft efficiencies are considerably high even at the concentration of $[\text{CCl}_4]/[\text{St}]=0.1$, but the graft efficiencies calculated after the alternate extraction are quite low.

As mentioned above, a large amount of homopolymer is still occluded in grafted films after the conventional extraction only. Moreover, also the ungrafted substrate polymer is not separated in most cases, especially at studies on heterogeneous grafting onto films and fibers. The present study suggests strongly that it needs careful attention to deduce any conclusion concerning the grafting mechanism and the chemical structure of graft copolymers, only from the result obtained after the conventional, simple extraction of homopolymers.

3. Number of Branches

Although it is important in the investigation of the graft copolymerization to estimate the number of grafted branch, only few studies have dealt with this problem in the field of radiation-induced grafting. This may be due to the fact that the isolation of pure graft copolymers, which is essential to determine the number of branches, has not been done owing to its tediousness. As stated above, also in the previous works it was impossible to examine whether chain transfer agents changed the number of branches, because the data necessary for the

calculation were insufficient.

The number of branches per unit weight of the starting PVA films is given by $G \cdot N_L / 100 \cdot P \cdot M_m$, where G is the percent grafting, *i.e.*, percent weight increase based on the weight of the starting film, P and M_m are the DP of the branch and the molecular weight of MMA monomer, respectively, and N_L is the Avogadro's Number. Figs. 10 and 11 show the relative values of G/P , which were calculated from the result obtained after the conventional and the alternate extraction, respectively, assuming DP's of homopolymer to be equal to DP of the branch.

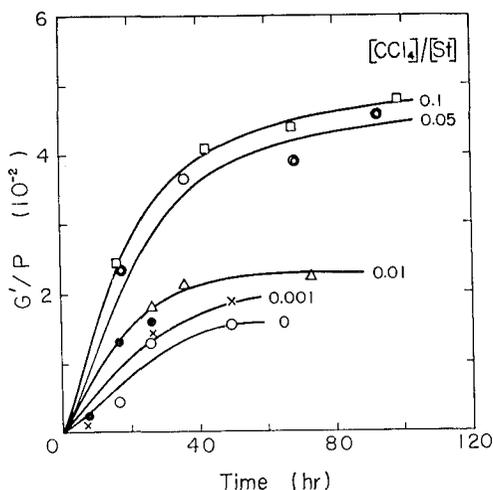


Fig. 10. Effect of CCl_4 on G'/P . G' = percent grafting calculated after the conventional extraction.

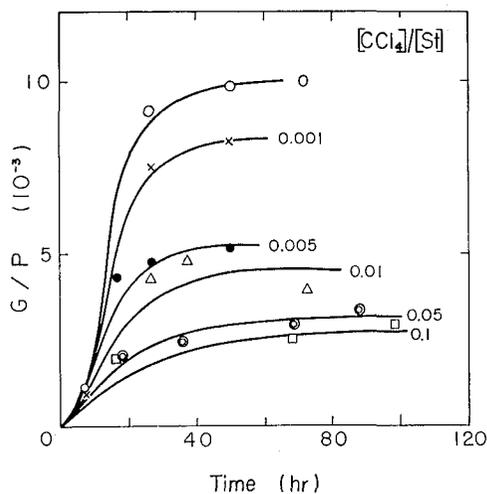


Fig. 11. Effect of CCl_4 on G/P . G = percent grafting calculated after the complete alternate extraction.

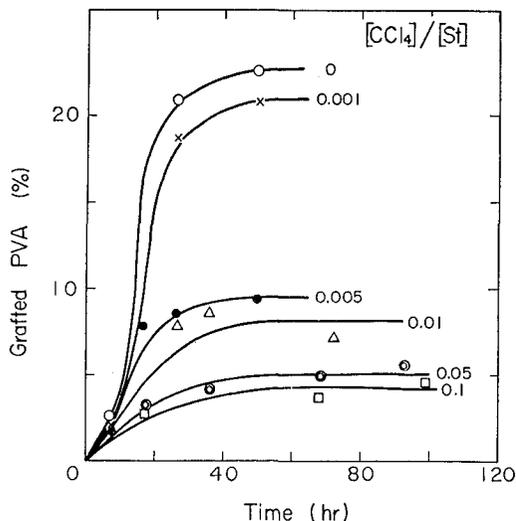


Fig. 12. Effect of CCl_4 on the fraction of PVA participated in the grafting reaction.

Apparently, two opposite conclusions are drawn from the results ; when the conventional percent grafting was used for the calculation, the number of branches was found to be increased with increasing concentration of CCl_4 . On the other hand, when the values of G/P were calculated using the percent grafting after the alternate extraction, it is concluded that CCl_4 reduces the number of branches. This is a good example to indicate how the apparent values lead to a deceptive conclusion.

One more conclusive evidence for the reduction of the number of branches by CCl_4 are obtained from the results given in Fig. 12, where the ratios of grafted PVA to the initial PVA are shown to be decreased with increasing concentration of CCl_4 . This result demonstrates clearly that the chain transfer agent deactivates the active sites for the grafting at least partially in a mechanism to give radicals which do not grow. This deactivation of the active sites should lead to the decrease in the overall rate of polymerization by CCl_4 as shown above. As one of the other reasons for the reduction of branch numbers, it might be thought that CCl_4 hinders the penetration of the monomer into the interior of PVA films. However, this effect is probably quite insignificant, because the concentration of CCl_4 in the monomer solution is extremely low in the present case. As a conclusion, it can be said from the results given above that there is no evidence to indicate the possible attack of the transfer agent radicals on the PVA molecules resulting in formation of new active sites for the initiation of grafting, which would cause the increase in the number of branches.

4. Chemical Structure of Graft Copolymer

If the length of the backbone polymer is known, it is possible to estimate the number of branches per each graft copolymer from the results shown above.

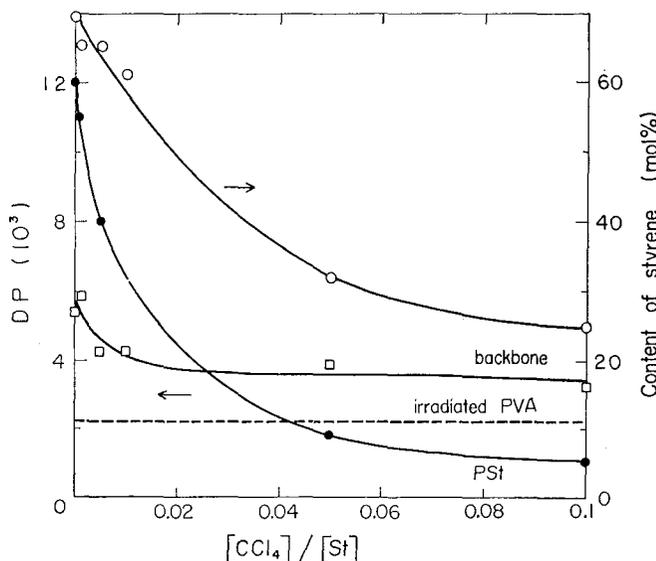


Fig. 13. DP of the backbone and the homoPSt, and the chemical composition of the isolated graft copolymers.

As we have made clear previously, the length of the backbone polymer is not necessarily equal to that of the starting substrate polymer. But it is highly probable that the graft copolymer has only one branch, as in the case of PVA-MMA graft copolymer. Therefore, if the number of branch per each graft copolymer molecule is assumed to be one, the length of the backbone polymer can be calculated from the chemical composition of the graft copolymer and the DP of the branch. In Fig. 13 are shown the lengths of the backbone thus calculated, together with the chemical compositions and the DP's of homopolymers. The lengths of the backbones were calculated here under an assumption that the branch lengths were equal to the viscosity-average DP's of the homopolymers, and hence they must be taken to be only qualitative ones. The chemical composition of the graft copolymers obtained at the constant ratio of $[\text{CCl}_4]/[\text{St}]$ was found to remain unchanged irrespectively of the polymerization time. As can be seen from Fig. 13, the DP's of the backbone polymers are considerably higher than that of the starting PVA. This is the same conclusion obtained in the case of PVA-MMA graft copolymer. More detailed discussion on the chemical structure of this graft copolymer will be given in the next paper.

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