

Radiation-Induced Graft Copolymerization of Methyl Methacrylate onto Poly(vinyl Alcohol) Film in the Presence of Chain Transfer Agents

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The grafting of methyl methacrylate onto poly(vinyl alcohol) by pre-irradiation technique was studied in the presence of various chain transfer agents such as *n*-butyl mercaptan, triethylamine and trichloroethylene. It was found that the length of grafted side-chain could be reduced by the use of these chain transfer agents. Chain transfer constants estimated from the change in degree of polymerization of homoPMMA formed during the grafting and PMMA obtained by the usual catalytic polymerization were in good agreement. Not only percent grafting and graft efficiency, but also overall rate of polymerization were decreased with increasing concentration of chain transfer agents. From the results it was concluded that the growing radicals on the grafted side-chain were transferred to the chain transfer agent and, that the radicals derived from chain transfer agent deactivated partially the active species for grafting besides re-initiation of the homopolymerization. The grafting was also carried out in the presence of *p*-benzoquinone which is known as a retarder, and some discussion was given on the result obtained.

INTRODUCTION

Lengths of the side-chains formed during heterogeneous grafting reaction are often found to be much longer than those of the substrate polymers. For instance, it has been shown by the previous study¹⁾ of the radiation-induced grafting of methyl methacrylate (MMA) onto poly(vinyl alcohol) (PVA) films that the graft copolymer has an extraordinarily long side-chain with degrees of polymerization (DP) from 20,000 to 60,000, whereas the DP's of the starting PVA range from 1,000 to 2,000.

However, in order to investigate general properties of the graft copolymer it is preferable to use samples having a balanced structure with respect to the length of the substrate and the side-chain polymer. One of the methods to prepare such a graft copolymer sample with relatively short side-chains would be to carry out the grafting in the presence of chain transfer agents. It is then expected that the growing radicals on the side-chains may be transferred to the added transfer agents, so that the length of resulting grafted side-chain will be reduced in accordance with the amount of transfer agents.

The purpose of the present work is to study the radiation-induced graft copolymerization in the presence of chain transfer agents and to compare the results

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with those of the conventional polymerization. A large number of studies up to date have concerned, in most cases, with an accelerating effect of various solvents and additives on the graft copolymerization. On the contrary, very little attention has been devoted to the graft copolymerization in the presence of chain transfer agents.^{2,3)}

EXPERIMENTAL

1. PVA Films

The sample of PVA used for the substrate was purified by alkaline re-saponification. Films of 0.1 mm thickness were prepared by casting 6% aqueous solution of the purified PVA. They were cut into strips of 6 cm×0.5 cm, and dried *in vacuo* at 50°C for 1 day.

2. Irradiation

Pre-irradiation of PVA films was carried out in the presence of air at room temperature with γ -rays from a Co-60 source. The dose rate and the total dose were 9.0×10^4 r/hr and 1.0×10^6 r, respectively. The DP of PVA was decreased from 1,140 to 960 upon irradiation.

3. Polymerization

The grafting was initiated immediately or at least within a few days after irradiation. The MMA monomer was distilled before use at a reduced pressure after removing the inhibitor from the commercial monomer. Chain transfer agents selected for the present study were *n*-butyl mercaptan (BM), triethylamine (TEA) and trichloroethylene (TCE). They were obtained from commercial sources and purified by distillation. About 100 mg of pre-irradiated films was put into ampules containing 10 ml of 40 : 60 MMA-methanol solution and various concentrations of chain transfer agents. The ampules were degassed by repeated freezing and thawing cycles, and then sealed. The graft copolymerization was carried out, rotating incessantly the sealed ampules in a water-bath kept at 50°C.

The conventional polymerization of MMA was carried out at 50°C in methanol solution (monomer : methanol = 40 : 60) using α , α' -azobisisobutyronitrile (AIBN) as an initiator.

4. Extraction of HomoPMMA

The homopolymer formed in the outer solution during the course of the grafting reaction was separated from the grafted films by pouring the reaction product in acetone and standing it over night at room temperature. Then the homoPMMA occluded inside the films was extracted with boiling acetone till no polymer was extracted. Although by the experiment⁴⁾ performed after this study it was confirmed that large amounts of homoPMMA still remained inside the film after this conventional extraction procedure, in the present study the percent grafting and the graft efficiency were calculated for convenience' sake from the following equations :

$$\text{Percent grafting (\%)} = \frac{\text{weight gain of films after extraction}}{\text{weight of starting films}} \times 100$$

$$\text{Graft efficiency (\%)} = \frac{\text{weight gain of films after extraction}}{\text{weight of total polymerized monomer}} \times 100$$

It should be noted here that these values are consequently only apparent ones.

5. Measurement of DP

DP of PMMA was calculated from viscosities of benzene solution at 30°C, using the equation $[\eta] = 1.71 \times 10^{-3} P^{0.76}$ reported by Cohn-Ginsberg *et al.*⁵⁾

RESULTS AND DISCUSSION

1. Change in the Length of PMMA

DP's of homoPMMA formed in the outer solution during the grafting in the presence of TCE are given in Fig. 1. It demonstrates that, as is usually observed in the case of conventional catalytic polymerization, DP's are constant all over the polymerization time. It can be also seen in Fig. 1 that DP of homoPMMA

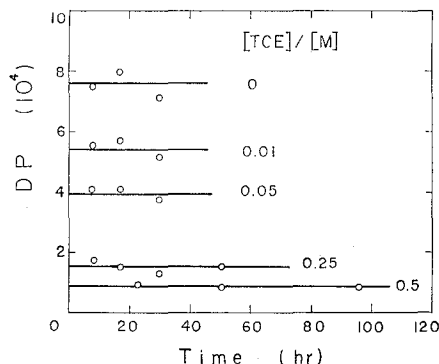


Fig. 1. DP of homoPMMA formed in outer solution during the grafting reaction.

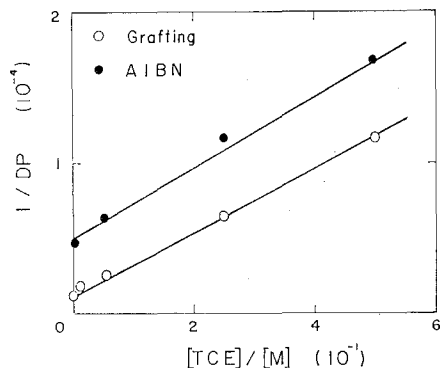


Fig. 2. Effect of trichloroethylene on DP of PMMA formed during the grafting reaction and by the conventional polymerization (AIBN = 5.0×10^{-4} mol/l).

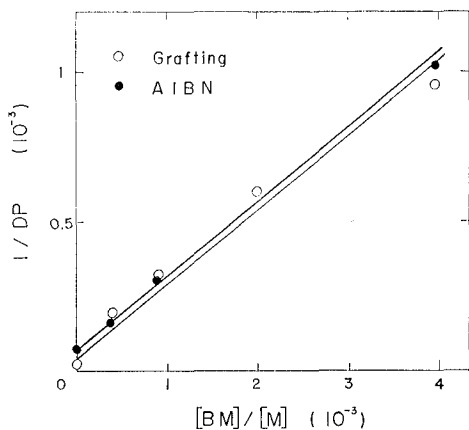


Fig. 3. Effect of *n*-butyl mercaptan on DP of PMMA formed during the grafting reaction and by the conventional polymerization (AIBN = 5.0×10^{-4} mol/l).

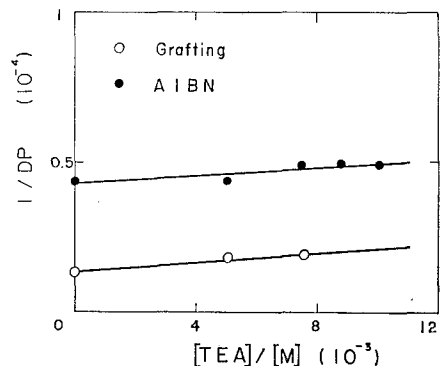


Fig. 4. Effect of triethylamine on DP of PMMA formed during the grafting reaction and by the conventional polymerization (AIBN = 5.0×10^{-4} mol/l).

is decreased expectedly with increasing concentration of TCE. Fig. 2, where reciprocals of DP of PMMA are plotted against the mole ratios of TCE to monomer, represents this tendency more explicitly. For comparison, in Fig. 2 are also shown DP's of PMMA obtained by the polymerization under the same condition as for the grafting reaction except that AIBN was used as an initiator instead of irradiated PVA. The latter can be regarded as a macroinitiator. The results obtained, when BM and TEA were used as chain transfer agents, are given in Figs. 3 and 4.

All the results shown above indicate that the length of homoPMMA is reduced by addition of chain transfer agents to the grafting system. However, the final aim of the addition of chain transfer agents is to make the grafted side-chain shorter. Therefore, in order to ascertain whether lengths of the side-chain are surely reduced or not, it is necessary to measure directly the change in lengths of side-chain.

In Fig. 5 are shown the measured DP's of various sorts of PMMA. The grafted side-chains were separated by cleaving the backbone of PVA; details of the experimental condition for the measurement of the length of side-chains and its separation will be reported in the future paper together with the method of isolation of pure graft copolymer. The side-chain length of graft copolymer prepared in the absence of any chain transfer agent has already been reported elsewhere.¹⁾ Fig. 5 denotes clearly that the lengths of homoPMMA formed inside the film are practically identical with those of separated side-chains, demonstrating the same influence of TCE on the length of both side-chains and homopolymers. In Fig. 5 it can be seen, further, that DP's of homoPMMA formed inside the film are somewhat shorter than those of homoPMMA formed in outer solution, presumably because of the difference in the concentration of reacting species between outside and inside the film.

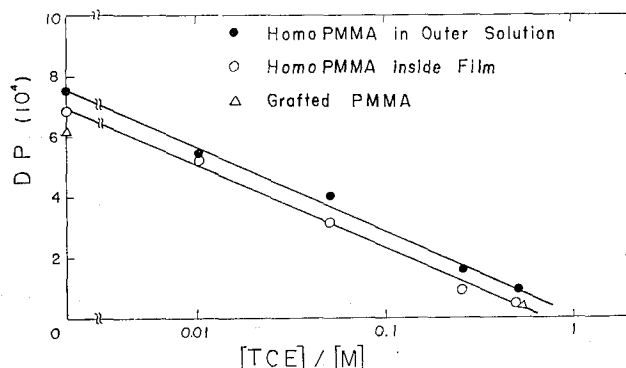


Fig. 5. Change in DP of various PMMA's with the concentration of trichloroethylene.

The results obtained lead to the conclusion that the growing radicals are transferred to added chain transfer agents, which results in reduction of the length of both grafted side-chains and homopolymers. The ability of a growing radical to capture an atom from an additive can be indicated quantitatively by the chain transfer constant C_s , which is calculated from slopes of the linear

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Table 1. Chain transfer constants calculated from results of the grafting and the conventional polymerization (50°C).

	<i>n</i> -butyl mercaptan	triethylamine	trichloroethylene
Grafting	0.25	6.8×10^{-4}	2.1×10^{-4}
Conventional polymerization	0.25	6.8×10^{-4}	2.2×10^{-4}

curves in Figs. 2, 3 and 4. The calculated transfer constants are summarized in Table 1, where also chain transfer constants calculated from DP of PMMA obtained by the conventional catalytic polymerization are given. As is obvious from Table 1, the two values of C_s are in excellent agreement. This result confirms again the conclusion that the role of chain transfer agent at the grafting reaction is essentially identical with that at the conventional polymerization. The difference in DP between two PMMA's may be ascribed to the difference in the concentration of initiator for the grafting and the catalytic polymerization.

2. Percent Grafting

The effect of various chain transfer agents, i. e. BM, TEA and TCE, on the percent grafting is shown in Figs. 6, 7 and 8, respectively. As is obvious from these results, in all cases the percent grafting is decreased remarkably with even relatively small amounts of transfer agents and no induction period is observed. The decrease in percent grafting by addition of these transfer agents is not surprising, since, as shown above, the length of grafted side-chain was reduced with increasing concentration of transfer agents. As one of the other reasons for the

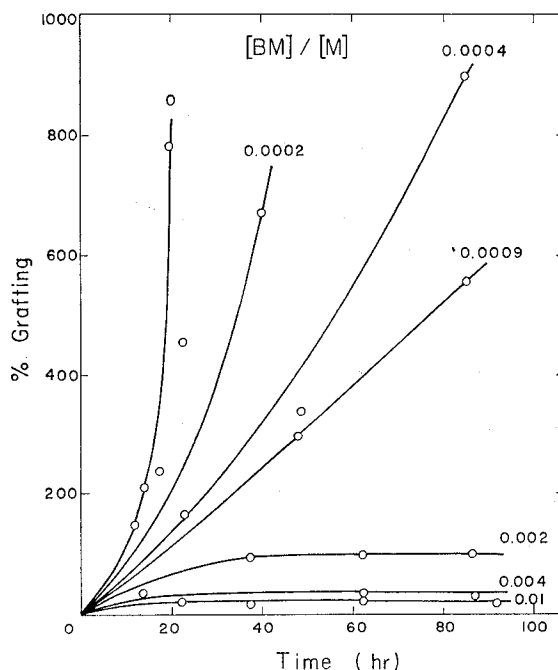


Fig. 6. Grafting of MMA onto PVA in the presence of *n*-butyl mercaptan.

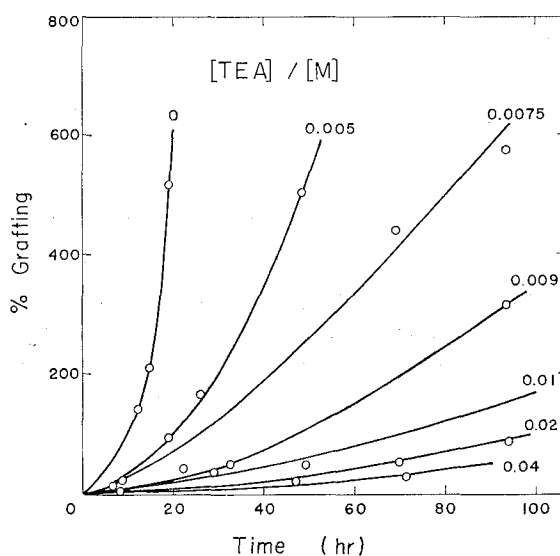


Fig. 7. Grafting of MMA onto PVA in the presence of triethylamine.

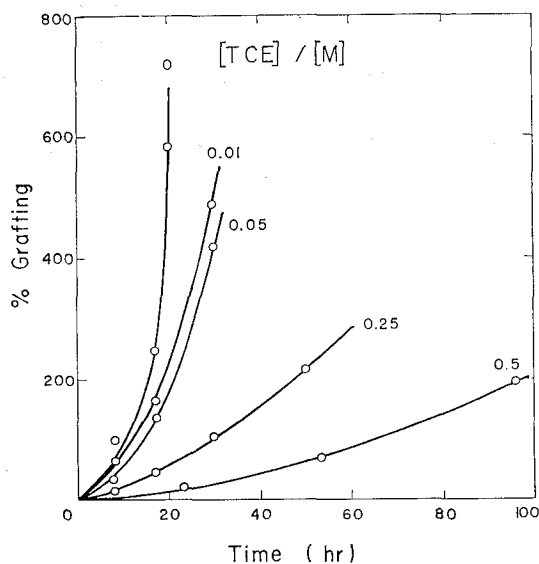


Fig. 8. Grafting of MMA onto PVA in the presence of trichloroethylene.

decrease in percent grafting, it is also probable that the number of side-chain per graft copolymer was decreased by the added chain transfer agent. At the present study it is, however, not possible to check this possibility, since the percent grafting given in Figs. 6, 7 and 8 are apparent values as pointed out above. This problem will be discussed in detail when the graft copolymer contaminated with no amount of homopolymer is isolated.

3. Graft Efficiency

If the role of the transfer agent is to transfer the growing radicals on the

grafted side-chain to themselves and hence to stop the further growth of side-chains, a large amount of homopolymer will be formed as a result of re-initiation reaction by radicals from transfer agents. The influence of chain transfer agents on the graft efficiency is shown in Fig. 9, where one can see that the graft efficiency is decreased expectedly as the amount of chain transfer agent becomes large for TEA. In other words, the more transfer agents are used, the more the homoPMMA is produced. It should be added that homopolymer was not formed practically at the grafting in the absence of transfer agent. Again, this finding supports the conclusion that the additives used here act as normal chain transfer agent. It is noteworthy that, in the case of TEA, the graft efficiency is nearly constant independently of its amount. On this point we will discuss later in this report.

As is shown, additives such as BM and TCE are those which act as a good chain transfer agent, so that a large amount of homoPMMA was formed during the grafting reaction as a result of radical transfer from growing radicals on the side-chain to the transfer agents. However, if the transfer agent is used only to

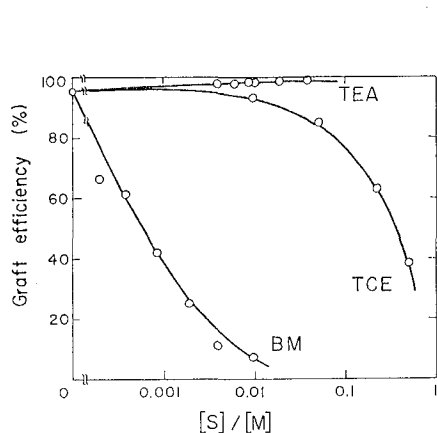


Fig. 9. Relation between the graft efficiency and the concentration of various chain transfer agents.

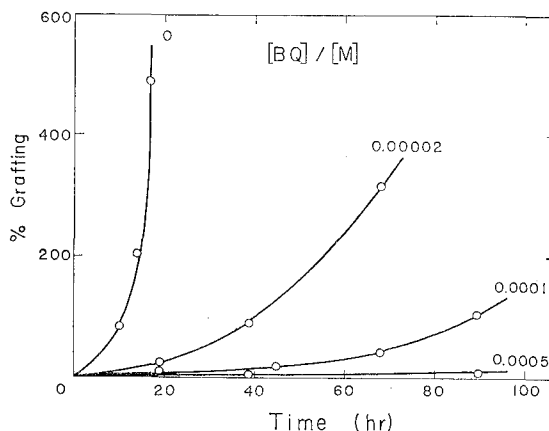


Fig. 10. Grafting of MMA onto PVA in the presence of *p*-benzoquinone.

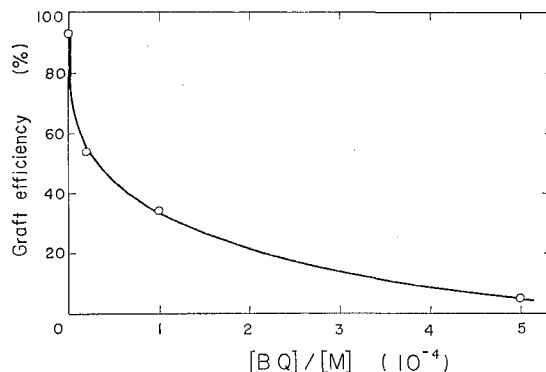


Fig. 11. Relation between the graft efficiency and the concentration of *p*-benzoquinone.

make the length of grafted side-chain shorter, it may be more effective to use a retarder rather than a normal chain transfer agent, since homopolymer may be formed only to a negligible extent during the grafting in the presence of retarder. To check this effect of retarder, the grafting was carried out in the presence of *p*-benzoquinone (BQ), which was reported to act as a retarder for the polymerization of MMA.⁶⁾ The result is presented in Figs. 10 and 11. The graft efficiency is decreased evidently with increasing amount of BQ, suggesting that BQ behaves as a chain transfer agent rather than as a retarder. The reason why the present result is inconsistent with that of conventional catalytic polymerization is at present not clear to us.

4. Overall Rate of Polymerization

According to the kinetic theory of vinyl polymerization, the rate of polymerization should be independent of the concentration of additive, if this acts as a good 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 corresponds to the rate of polymerization mentioned above. 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 fed in the grafting system. In Figs. 12, 13 and 14 the overall rates of polymerization calculated in this way are presented, the concentration of transfer agents being varied over the wide range. The results show distinctly that in all cases the overall rate of

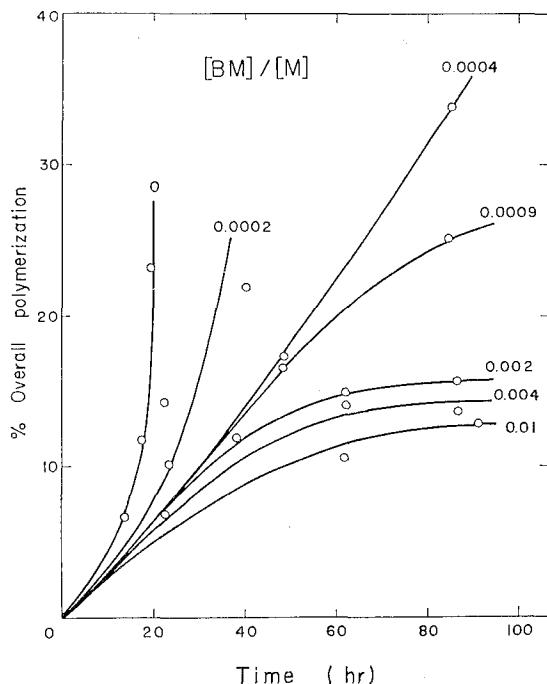


Fig. 12. Effect of *n*-butyl mercaptan on the overall rate of polymerization in the case of grafting.

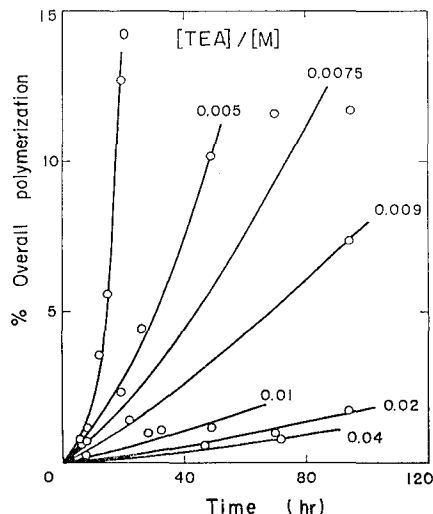


Fig. 13. Effect of triethylamine on the overall rate of polymerization in the case of grafting.

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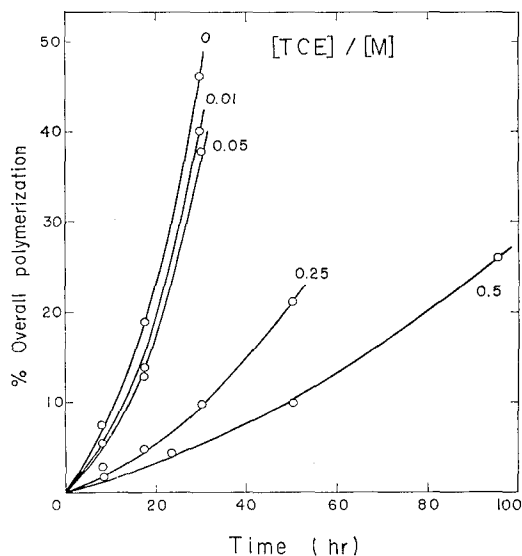


Fig. 14. Effect of trichloroethylene on the overall rate of polymerization in the case of grafting.

polymerization is decreased as the concentration of transfer agent becomes higher. This is apparently inconsistent with the theory of usual vinyl polymerization. As pointed out, the net effect of transfer agent on the grafting is thought only to transfer the location of free radical sites from the grafting phase to the homopolymerization phase. However, if these additives are not ideal but degradative chain transfer agents or retarders, the overall rate of polymerization would be

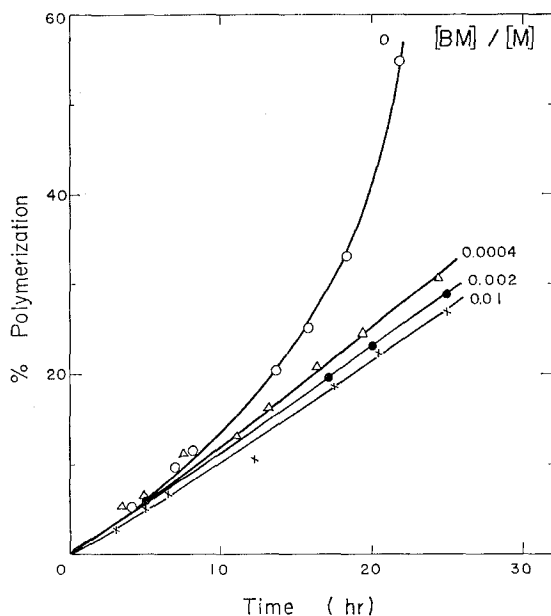


Fig. 15. Effect of *n*-butyl mercaptan on the rate of polymerization in the case of conventional polymerization ($AIBN=5.0 \times 10^{-4} \text{ mol/l}$).

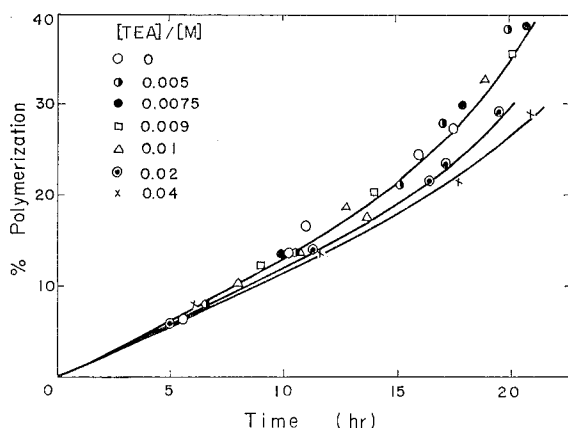


Fig. 16. Effect of triethylamine on the rate of polymerization in the case of conventional polymerization ($\text{AIBN} = 5.0 \times 10^{-4} \text{ mol/l}$).

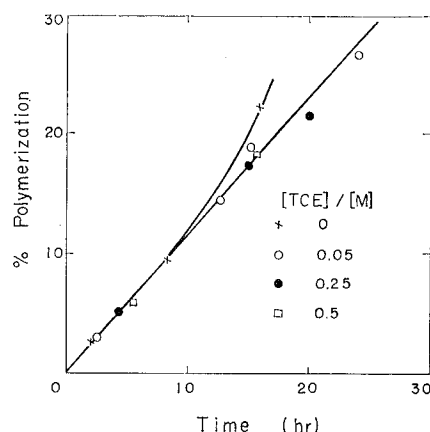


Fig. 17. Effect of trichloroethylene on the rate of polymerization in the case of conventional polymerization ($\text{AIBN} = 5.0 \times 10^{-4} \text{ mol/l}$).

necessarily decreased in the presence of these additives. This supposition is, however, denied from the results shown in Figs. 15, 16 and 17, where data of polymerization of MMA carried out using AIBN as an initiator are given. As is obvious from the figures, in any cases the rates of polymerization are nearly constant independently of the concentration of additives, when it becomes relatively high. A little higher rate of polymerization observed at very low concentrations of additives and at the later stage of polymerization may be due to a Trommsdorff effect, which probably appears at such range, since the polymerization system became cloudy during the polymerization reaction.

The abnormal feature of the overall rate of polymerization must be ascribed to peculiarities which are observed only at the grafting reaction. The main characteristics distinguishing the grafting from the usual polymerization are only two; active species for the initiation of grafting and the matrix where the grafting reaction proceeds heterogeneously. It is highly probable that, when the grafting takes place in the matrix, both the distribution and the reactivity of reactants, especially, the rate of termination may become different from those at the normal polymerization. For instance, the rate of termination between polymer radicals may be slow down in the matrix (Trommsdorff effect), but when the polymer radicals are transferred to the transfer agent, the overall rate of polymerization may be decreased with increasing concentration of transfer agent, as the rate of termination between small radicals derived from the transfer agents would be high, independently of the place where the reaction proceeds. In the present case, however, the change in the rate of termination seems not so predominant as to cause such a remarkable decrease in the overall rate of polymerization in the presence of very small amounts of chain transfer agent. On the contrary, the abnormal result can be explained more reasonably by the assumption that the radicals from transfer agents deactivate partially the active species for the grafting. Further confirmatory evidence for this assumption is the fact that in the case of TEA the graft efficiency is always constant independently of the amount

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of TEA, while the overall rate of polymerization is decreased remarkably. It, therefore, appears that TEA behaves like an inhibitor for this grafting. If this explanation is correct, it may be possible to obtain some information about the nature of active species for grafting by studying the effect of various additives on the graft efficiency and the overall rate of polymerization.

REFERENCES

- (1) I. Sakurada, S. Matsuzawa and Y. Kubota, *Makromol. Chem.*, **69**, 115 (1963).
- (2) A. J. Restaino and W. N. Reed, *J. Polym. Sci.*, **36**, 449 (1959).
- (3) K. Hayakawa, K. Kawase and T. Matsuda, *Chem. High Polym.*, **20**, 609 (1963).
- (4) Y. Ikada and Y. Uesaki, Int. Symp. Macromol. Chem. (Tokyo-Kyoto 1966), p. III-78.
- (5) E. Cohn-Ginsberg T. G. Fox and H. F. Mason, *Polymer*, **3**, 97 (1962).
- (6) J. C. Bevington, N. A. Ghanem and H. W. Melville, *Trans. Faraday Soc.*, **51**, 964 (1955) ; B. L. Funt and F. D. Williams, *J. Polym. Sci.*, **46**, 139 (1960).
- (7) J. C. Bevington, "Radical Polymerization," Academic Press, Inc., New York, N. Y., 1961, p. 130.