

Kinetics of Graft Copolymerization of Methyl Methacrylate in Wool Fibers

MICHIHARU NEGISHI and KOZO ARAI, *Faculty of Technology, Gumma University, Kiryu, Japan*, and SADAYUKI OKADA, *Amaike Research Laboratory, Daido Worsted Ltd., Tokyo, Japan*

Synopsis

The graft copolymerization of methyl methacrylate in wool fibers was investigated in the aqueous LiBr-K₂S₂O₈ system without homopolymer. The rate of grafting and the degree of polymerization of graft polymer were determined on varying the extent of reduction of wool fibers and the concentration of monomer. From the graft copolymerization behavior observed at a given concentration of redox catalysts (LiBr and K₂S₂O₈), the thiol groups in wool fibers were considered to play a role as a sort of catalyst of polymerization, not as the chain transfer agent, and also to give the grafting sites. So, the initiation process of grafting was assumed to be started by $d[S\cdot]/dt = k_i[SH]_{eff}$, and the kinetic consideration was found to lead to the following expression in agreement with the experimental results: $1/\overline{DP} = (k_t/k_p^2[M]_{fib}^2)R_p$, where $d[S\cdot]/dt$ is the rate of formation of thiol radicals by radicalotropy to -SH from SO₄^{-·}, OH[·], or Br[·]; k_i , k_p , and k_t are the rate constants of initiation, propagation, and termination, respectively; $[SH]_{eff}$ and $[M]_{fib}$ are the concentration of the effective thiol groups and the MMA monomers within the wool fibers, respectively; \overline{DP} is the average degree of polymerization of graft polymers, and R_p the overall rate of grafting.

INTRODUCTION

In previous studies, we found that graft copolymerization of vinyl monomers occurs in wool fibers with the aqueous LiBr-K₂S₂O₈ system without homopolymer formation and reported that the thiol groups on wool could be considered to give predominantly the sites of grafting.¹⁻³ It is well known that the reduction of wool fibers facilitates the graft copolymerization or internal polymerization of vinyl monomers.

The purpose of the present investigation is to develop a quantitative kinetic consideration of this grafting mechanism in wool fibers. The graft copolymerization of methyl methacrylate was investigated in further detail, especially the rate of grafting and the degree of polymerization of graft polymer, on varying the extent of reduction of wool fibers and the concentration of monomer.

EXPERIMENTAL

Materials

The tops of Merino wool fibers were purified by Soxhlet extraction with acetone for about 24 hr., followed by washing with cold water and air drying.

Commercially available methyl methacrylate was washed with 5% NaOH solution and water, then dried with anhydrous sodium sulfate, and distilled under reduced pressure in a stream of nitrogen before use.

Lithium bromide, potassium persulfate, thioglycolic acid (TGA), and diethylene glycol monobutyl ether (BC) were of first or special reagent grade and used without further purification.

Reduction of Wool Fibers

The wool (0.5 g.) was treated for 24 hr. at 30°C. with 0.0282–0.500*N* solution of TGA adjusted to pH 4.8 (50 ml.), washed with water, ethanol, again with water, pressed out with filter paper, and then subjected to grafting.

The content of thiol group in the wool fibers was determined by Leach's polarographic method with methylmercury iodide.⁴ All the analyses were carried out twice or three times, and the average value was taken.

Graft Copolymerization

The preparation of the LiBr–K₂S₂O₈ system for grafting was carried out by the procedure reported in the previous report.²

As with the graft copolymerization to the wool fibers of various extent of reduction, the wool (0.5 g.) was treated with 50 g. of solution containing 27.5% LiBr, 0.2% K₂S₂O₈, 22.5% BC, 44.8% H₂O, and 5.0% monomer (MMA) (by weight). In the experiment in which the concentration of monomer was varied, a reaction mixture containing 13.75% LiBr, 0.1% K₂S₂O₈, 11.25% BC, 22.4% H₂O, and 0.5, 1.0, 2.5, or 5 g. MMA was used for 0.5 g. of wool fibers. The rates of graft copolymerization were determined at 30°C.

The grafting proceeded with almost no homopolymer formation, in the same manner as observed in the previous reports both for natural and reduced wool fibers. Therefore, after the reaction period, the wool fibers were only washed with water and dried without acetone extraction.

The extent of grafting was expressed as the weight-per cent increase based on the original weight of the wool fibers.

Separation of Graft Polymers and Molecular Weight Determination

The 72% H₂SO₄ digestion method to separate the graft polymers from the wool trunks, which was used in the previous studies,^{1,2} was too time consuming, especially in the purification of isolated graft polymers. Thus, in the present work, the following procedure of separating the graft polymers was found to be much more convenient.

The grafted wool fibers (0.5 g.) were digested in 35 ml. of 6*N* HCl for 24 hr. at 115°C. in a flask with a reflux condenser attached, washed to neutral, and dried. The insoluble residues could be isolated as they remained in the fiber state. From the weight decrease of the starting mate-

rials it was found that the wool trunks could be almost completely decomposed without the loss of graft polymers. Furthermore, the carboxyl content of the isolated poly(methyl methacrylate) was negligibly small (0.57 mole-%) and the polymer was completely soluble in acetone. The isolated products were purified by twice being dissolved in acetone, filtered off, and precipitated with water; the viscosity of the products was then measured in acetone solution.

When the amount or molecular weight of the sample was small, the single-point method as employed in the previous report was used to obtain the intrinsic viscosity.⁵ The average molecular weight of the isolated poly(methyl methacrylate) was calculated from the equation:⁶

$$[\eta]_{25^\circ\text{C.}} = 9.6 \times 10^{-5} \bar{M}^{0.69}$$

where $[\eta]$ is expressed in deciliters per gram.

On the other hand, the same acid treatment as used in the separation of the graft polymer was also carried out for the various methyl methacrylate homopolymers, which were in the form of fine powder and of various molecular weights. The experimental relation between the average molecular weights after and before acid treatment thus obtained are shown in Table I. From this result, it was found that poly(methyl methacrylate)

TABLE I
Changes of Average Molecular Weight of Poly(methyl Methacrylate)
Homopolymer on 6*N* HCl Treatment (24 hr., 115°C.)

\bar{M} before acid treatment $\times 10^{-4}$	\bar{M} after acid treatment $\times 10^{-4}$
8.91	7.25
33.1	29.9
47.9	40.8
132	95.5

was somewhat depolymerized on treatment with 6*N* HCl. The true molecular weight of the graft polymer from the grafted wool could thus be estimated graphically, being approximately 1.13 times the value obtained directly from the experiment at below $\bar{M} = 300,000$.

The number of grafting sites, in moles per 10⁵ g., was calculated from the extent of grafting and the average molecular weight of graft polymers, assuming one site of grafting for each molecule of graft polymer.

RESULTS AND DISCUSSION

Rate of Grafting

Concentration of Monomer. Figures 1 and 2 show the rates of grafting at varying concentrations of monomer for unreduced and 0.218*N* TGA-reduced wool fibers, respectively. As is clear from these results, the rates

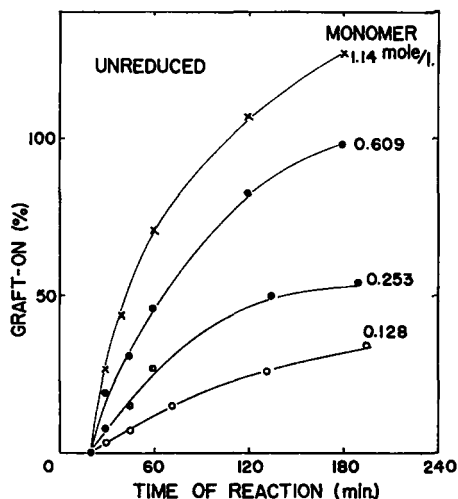


Fig. 1. Rate of grafting at varying monomer concentration for unreduced wool fibers.

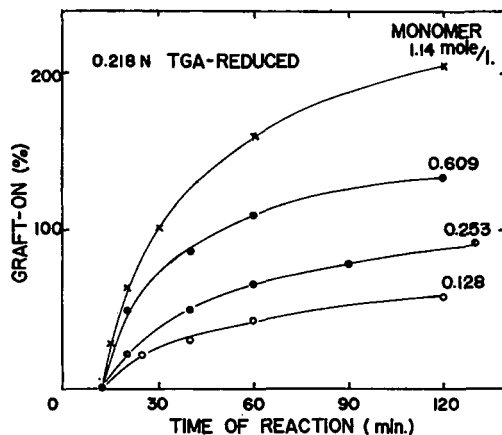


Fig. 2. Rate of grafting at varying monomer concentration for 0.218N TGA-reduced wool fibers.

of grafting increase with increasing concentration of monomer both for unreduced and reduced wool. The induction periods are only slightly affected by monomer concentration, being about 20 min. and 12 min. in unreduced and reduced wool, respectively.

The initial rates of grafting, dG_0/dt obtained graphically are shown in Tables II and III. On plotting dG_0/dt logarithmically against the logarithm of the initial monomer concentration $[M]_0$, linear relationships are obtained as expressed by the eqs. (1) and (2) for unreduced wool and for 0.218N TGA-reduced wool, respectively.

$$dG_0/dt = 2.46[M]_0^{0.72} \quad (1)$$

$$dG_0/dt = 6.92[M]_0^{0.69} \quad (2)$$

TABLE II
Effect of Monomer Concentration on Initial Rate of Grafting
and Molecular Weight of Graft Polymer in Initial Stage of Grafting

Initial concentration of monomer $[M]_0$ mole/l.	Initial rate of grafting dG_0/dt , %/min.		Molecular weight of graft polymer in initial stage, $\bar{M}_0 \times 10^{-4}$	
	Un-reduced	0.218N TGA-reduced	Un-reduced	0.218N TGA-reduced
0.253	0.90	2.7	21.0	2.0
0.609	1.70	4.9	35.0	3.0
1.14	2.75	7.7	55.0	5.1

TABLE III
Effect of Extent of Reduction on Initial Rate of Grafting and
Molecular Weight of Graft Polymer in Initial Stage of Grafting

Concentration of TGA, N	Content of $-SH$ in wool, $[SH]$, mole/ 10^5 g.	Initial rate of grafting dG_0/dt , %/min.	Molecular weight of graft polymer in initial stage $\bar{M}_0 \times 10^{-4}$
Unreduced	4.1	1.52	39.0
0.0282	6.3	1.64	12.0
0.0565	8.4	2.10	8.0
0.0948	11.5	4.12	6.3
0.218	18.5	5.50	3.95
0.500	30.2	8.10	3.20

It is noteworthy that the powers of $[M]_0$ give approximately the same values both for unreduced and reduced wool fibers.

Extent of Reduction. Figure 3 shows the rate of grafting at varying extents of reduction. It is evident that the rates increase with increasing extent of reduction and the induction period is also shortened. The initial rates of grafting obtained graphically are shown in Table III. Extrapolation of the plot curve of dG_0/dt versus $[SH]$ to the $[SH]$ axis as seen in Figure 4 shows about 3.5 moles of thiol groups per 10^5 g. wool appear to have been shielded from the reaction of grafting or to be unequivalent to other thiol groups, which corresponds to 85% of the total content of thiol groups in unreduced wool. These thiol groups may perhaps exist mainly in the paracortex structure which is considered to have a greater content of cystine linkages and is subject more to diffusion control of reagents. Then, a log-log plot of dG_0/dt against $([SH] - 3.5)$ yields the nearly linear relationship expressed by eq. (3),

$$dG_0/dt = 1.33 [SH]_{\text{eff}}^{0.52} \quad (3)$$

where $[SH]_{\text{eff}} = [SH] - 3.5$ designates the effective content of thiol groups. The existence of shielded thiol groups for grafting has been also observed in the grafting system of $K_2S_2O_8$ alone as described in detail elsewhere.⁷

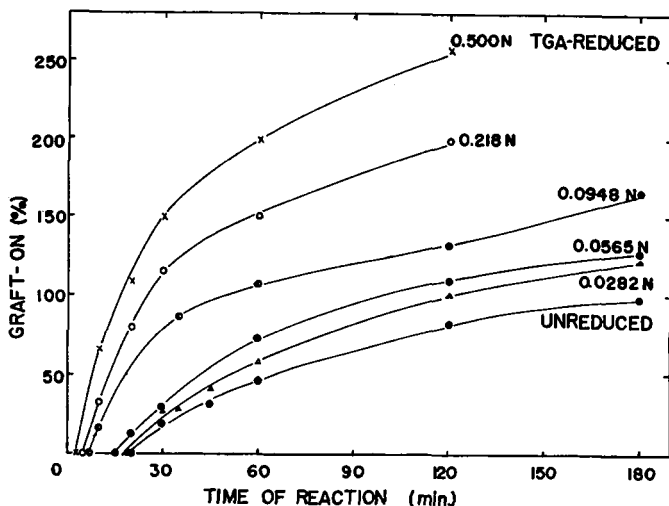


Fig. 3. Rate of grafting at varying extent of reduction of wool fibers.

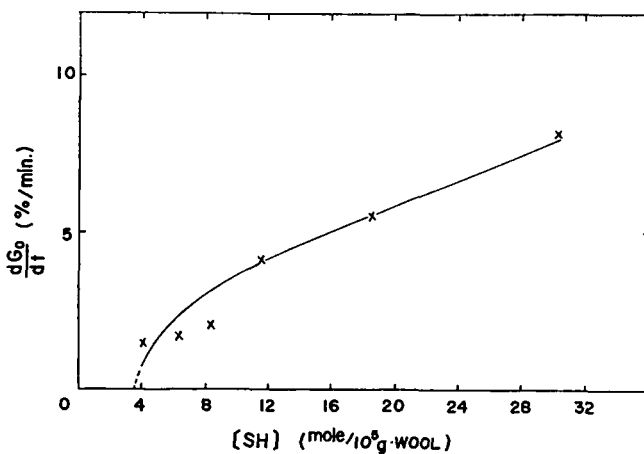


Fig. 4. dG_0/dt vs. $[SH]$ for unreduced and reduced wool fibers.

Average Molecular Weight of Graft Polymer

Concentration of Monomer. Figure 5 shows the average molecular weight of graft polymers \bar{M} versus graft-on at varying concentration of monomer for unreduced and 0.218N TGA-reduced wool fibers. It is seen that \bar{M} of graft polymers generally increases with increasing concentration of monomer, but exhibits a maximum value which tends to shift in position to the side of greater graft-on with increasing concentration of monomer in unreduced wool fibers.

Extent of Reduction. As with the wool reduced to various extents, the relations of \bar{M} versus graft-on obtained in grafting at 5% monomer concentration are shown in Figure 6. It is found that \bar{M} of graft polymers

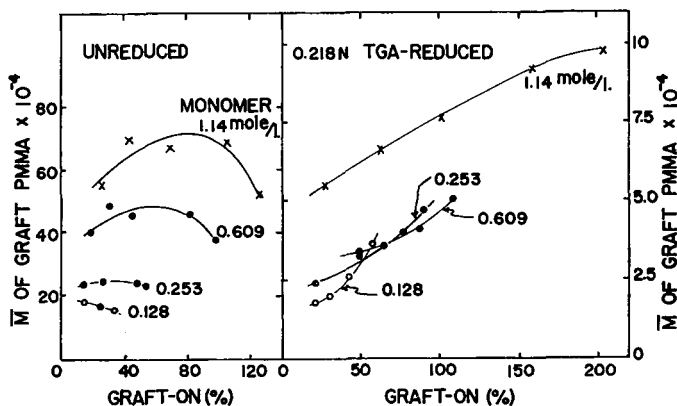


Fig. 5. Average molecular weight of graft polymer vs. graft-on at varying monomer concentration for unreduced and 0.218N TGA-reduced wool fibers.

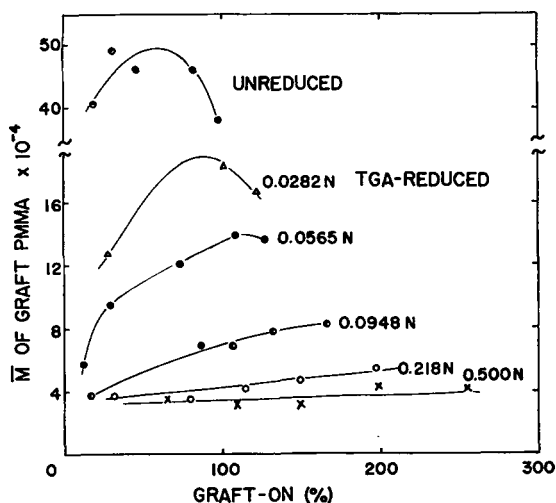


Fig. 6. Average molecular weight of graft polymer vs. graft-on for wool fibers reduced to various extents.

decreases distinctly with an increase of extent of reduction and gives a maximum value which tends to shift to the side of greater graft-on with increasing extent of reduction.

After all, the smaller the thiol content in the wool fibers and the lower the monomer concentration in the reaction bath become, the lower tends to become the graft-on at which the maximum \bar{M} of graft polymers appears. Although this behavior may be complicated, it should be considered to be explicable to some extent at least on the basis of diffusion of monomer into fibers, that is, a sort of change of monomer concentration within the fibers. When the grafting proceeds to some extent, an open structure of fibers will be formed which facilitates penetration of monomer into fibers, the

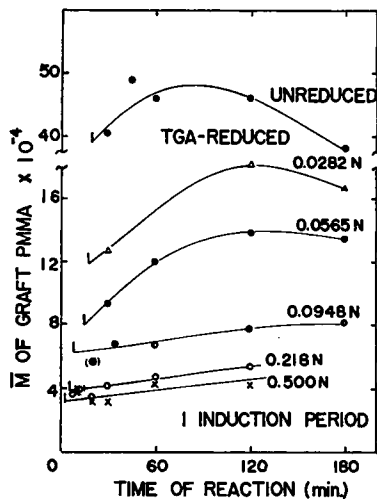


Fig. 7. Average molecular weight of graft polymer vs. time of reaction for wool fibers reduced to various extents.

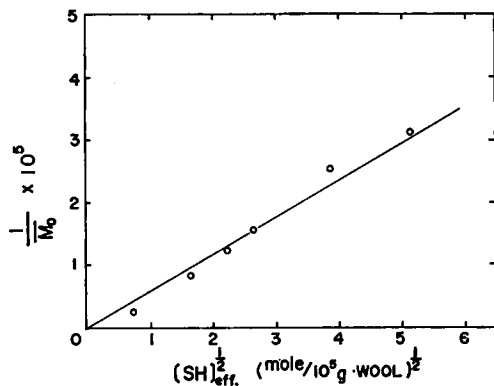


Fig. 8. $1/\bar{M}_0$ vs. $[\text{SH}]_{\text{eff}}^{1/2}$ for wool fibers reduced to various extents.

affinity between monomer and graft polymer also being in part responsible. Thus, the concentration of monomer in the wool fibers should become greater, contributing to an increase of \bar{M} of the graft polymers. The more the wool fibers become cystine-rich, the tighter the internal networks, and the lower the monomer concentration in the reaction bath, the earlier the above effects appear in grafting. On the other hand, the graft polymers formed within the wool fibers will be gradually separated from the polymerization system, especially at lower concentrations of monomer, and the monomer diffusion from the reaction bath tends to decrease. The above competitive behavior is considered to give a maximum value for \bar{M} of graft polymer at some graft-on.

To avoid the complexity involved in this diffusion-controlled behavior, the plot of \bar{M} against reaction time was extrapolated to the starting time of

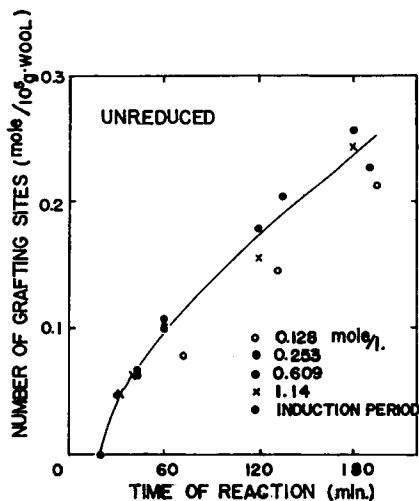


Fig. 9. Number of grafting sites vs. time of reaction at varying monomer concentration for unreduced wool fibers.

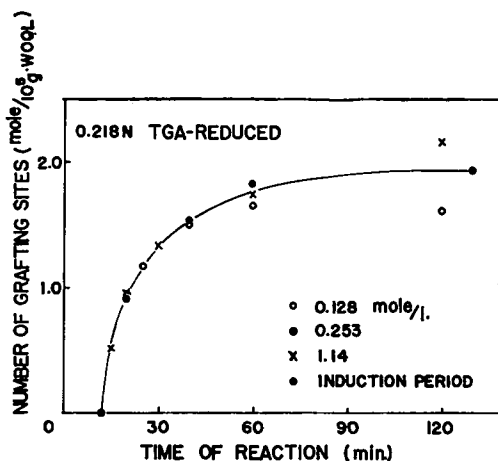


Fig. 10. Number of grafting sites vs. time of reaction at varying monomer concentration for 0.218N TGA-reduced wool fibers.

reaction (induction period) referring to the relation of \bar{M} versus graft-on; the molecular weight of graft polymers in the initial step of polymerization, \bar{M}_0 , was thus estimated as shown in Figure 7. The results are shown in Tables II and III. From the linear relationships obtained between $\log \bar{M}_0$ and $\log [M]_0$, \bar{M}_0 is found to be expressed as shown in eqs. (4) and (5) for unreduced wool and 0.218N TGA-reduced wool, respectively.

$$\bar{M}_0 = 5.01 \times 10^5 [M]_0^{0.61} \quad (4)$$

$$\bar{M}_0 = 4.68 \times 10^4 [M]_0^{0.64} \quad (5)$$

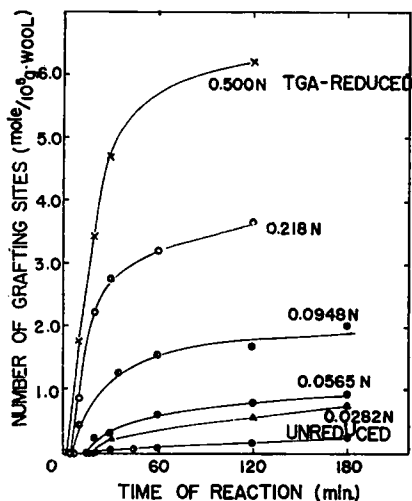


Fig. 11. Number of grafting sites vs. time of reaction for reduced wool fibers to various extent of reduction.

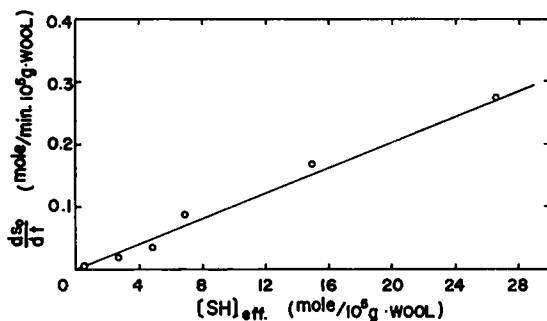


Fig. 12. ds_0/dt vs. $[SH]_{\text{eff}}$ for wool fibers reduced to various extents.

It is interesting that the powers of $[M]_0$ give approximately the same values as the relation of dG_0/dt versus $[M]_0$ obtained above.

Furthermore, a linear relation is obtained between $1/\bar{M}_0$ and $[SH]_{\text{eff}}^{1/2}$ as shown in Figure 8; this relation is expressed by the eq. (6):

$$1/\bar{M}_0 = 5.9 \times 10^{-6} [SH]_{\text{eff}}^{1/2} \quad (6)$$

Comparison of eqs. (3) and (6) shows significant similarity.

Grafting Sites

dG_0/dt divided by \bar{M}_0 should give the formation rate of grafting sites, ds_0/dt in the initial step of grafting. By using eqs. (1) and (4) or (2) and (5), ds_0/dt can be calculated for the unreduced or 0.218N TGA-reduced wool fibers, respectively. However, since the powers of $[M]_0$ in these equations give almost the same values, ds_0/dt is likely to be independent of $[M]_0$.

The relations of the number of grafting sites against time of reaction at varying monomer concentration are shown in Figures 9 and 10 for the unreduced and 0.218*N* TGA-reduced wool fibers, respectively. These results indicate that the number of grafting sites shows an increase with the time of reaction almost independent of the concentration of monomer, not only in the initial step but over the whole range of polymerization.

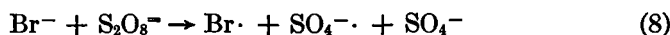
The relations of the number of grafting sites versus time of reaction at $[MMA] = 0.609$ mole/l. for reduced wool fibers to various extents of reduction are shown in Figure 11. The number of grafting sites increases with increasing the extent of reduction. From eqs. (3) and (6), it is natural that ds_0/dt is increased in direct proportion to $[SH]_{eff}$. Even by using the values of ds_0/dt obtained graphically from the initial slope of the curves in Figure 11, the above is clear as shown in Figure 12 and expressed approximately by the eq. (7)

$$ds_0/dt = 10^{-2}[SH]_{eff} \quad (7)$$

From these results, it is concluded that the rate of formation of grafting sites on the polypeptide chains of wool is independent of the concentration of monomer and determined by the content of thiol groups in wool fibers over the whole range of grafting reaction. These facts seem to be important in the kinetics of graft copolymerization.

Kinetics of Graft Copolymerization

As reported previously, in the LiBr-K₂S₂O₈ redox system, various kinds of free radicals have been presumed to be formed by the reactions (8)–(11).



Also, the initiation of graft copolymerization has been considered to be due mainly to the radicalotropy to thiol groups on wool from $SO_4^{\cdot-}$, $OH\cdot$, or $Br\cdot$. Furthermore, the inhibition of formation of homopolymers has been assumed to be caused mainly by the bromination of monomers by Br_2 .



In addition, the termination of the shorter and more movable polymers ($M_x\cdot$) by HBr or primary radicals such as $Br\cdot$ may occur, as shown in eqs. (13) and (14):



In a recent study by Saha et al.,⁸ when $Br\cdot$ was liberated in the reaction system of MMA polymerization the polymer obtained was of very low

molecular weight and the yield also very low. This suggests that the above termination may also occur to some extent in our LiBr-K₂S₂O₈ system.

The present experimental results indicate that the rate of formation of grafting sites is independent of the concentration of monomer and determined by the content of effective thiol groups in the wool fibers at a given concentration of LiBr and K₂S₂O₈. Hence, the initiation step in the grafting process may be represented simply by the reaction scheme for initiation by radicalotropy from SO₄⁻·, OH· or Br· shown in eqs. (15) and (16):



where -SH denotes the thiol groups on wool, M the monomer, and -S· and -SM· the corresponding radicals. k_i and k'_i are the rate constants of initiation reactions (15) and (16), respectively. On neglecting the formation of homopolymers because of its minute amount, the propagation, chain transfer, and termination steps are given as shown in eqs. (17)–(19).

Propagation:



Chain transfer to -SH:



Termination (termination by primary radicals ignored):



Here, k_p , k_{tr} , and k_t are the rate constants of propagation, chain transfer, and termination, respectively.

Assuming steady-state kinetics for the above reaction scheme we have

$$d[\text{S}\cdot]/dt = k_t[\text{SH}]_{\text{eff}} = k'_i[\text{S}\cdot][\text{M}]_{\text{fib}} = k_i[\text{SM}_x\cdot]^2 \quad (20)$$

where $[\text{M}]_{\text{fib}}$ is the concentration of monomer within wool fibers, and the overall rate of graft copolymerization R_p and the reciprocal average degree of polymerization of graft polymers $1/\overline{\text{DP}}$ are theoretically expressed by eqs. (21) and (22), respectively, the concentration of redox catalysts being taken as constant.

$$R_p = (k_t^{1/2} k_p/k_i^{1/2}) [\text{M}]_{\text{fib}} [\text{SH}]_{\text{eff}}^{1/2} \quad (21)$$

$$\frac{1}{\overline{\text{DP}}} = \frac{k_i^{1/2} k_{tr}^{1/2} [\text{SH}]_{\text{eff}}^{1/2}}{k_p [\text{M}]_{\text{fib}}} + \frac{k_{tr} [\text{SH}]_{\text{eff}}}{k_p [\text{M}]_{\text{fib}}} \quad (22)$$

Provided that k_{tr} can be ignored as very small (which is considered to be probable because the thiol group residue is the much greater polypeptide

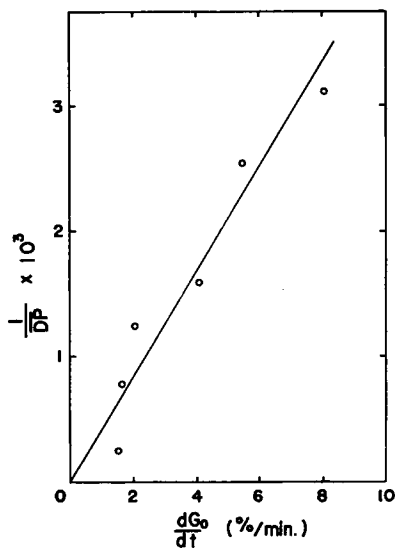


Fig. 13. $1/\overline{DP}$ vs. R_p for wool fibers reduced to various extents.

chain^{9,10}), the second term in eq. (22) may be omitted. Thus, from eqs. (21) and (22), the eq. (23) is obtained:

$$1/\overline{DP} = (k_t/k_p^2[M]_{\text{fib}}^2)R_p \quad (23)$$

Taking \overline{M}_0 and dG_0/dt obtained above as the values in the initial stage of reaction to correspond to \overline{DP} and R_p , respectively, we obtain a nearly linear relation passing through the origin, as shown in Figure 13. Furthermore, as recognized experimentally above, dG_0/dt or $1/\overline{M}_0$ is proportional to $[\text{SH}]_{\text{eff}}^{1/2}$ in agreement with the eqs. (21) and (22) if the second term is omitted. Thus, it is clear that the above reaction kinetics could be well applicable. This indicates that the thiol groups in wool fibers play a role in catalysis of polymerization, not in chain transfer agent as is usual in polymerization.

The action of thiol groups as a sort of catalyst also might contribute much more than the monomer-diffusion behavior mentioned above to increase the molecular weight of graft polymers with increasing graft-on or reaction time, as the thiol groups decreased as the reaction progresses. Also, if it is supposed that the relation of the concentration of monomer within the wool fibers to the external reaction bath concentration with which it is in equilibrium is expressed by the Freundlich equation,^{11,12} the eq. (24) may hold, at least in the initial stage of reaction,

$$[M]_{\text{fib}} = K[M]_0^\alpha \quad (24)$$

where K and α are constants.

As seen in eqs. (1), (2), (4), and (5), the powers of $[M]_0$ in the relation of dG_0/dt or \overline{M}_0 versus $[M]_0$ give almost the same values. These facts

seem also to indicate that the initiation process of grafting follows the above kinetics, as is clear from eqs. (21) and (22).

The results above suggest that all termination takes place by the disproportionation mechanism, that is, there is no crosslinkage by poly-(methyl methacrylate) between polypeptide chains.

The result of the graft copolymerization in $K_2S_2O_8$ alone will be reported in the near future.⁷

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Résumé

La copolymérisation greffée du méthacrylate de méthyle au sein des fibres de laine a été étudiée dans le système aqueux LiBr- $K_2S_2O_8$ sans homopolymère. La vitesse de greffage et le degré de polymérisation du polymère greffé ont été déterminés en variant le degré de réduction des fibres de laine et la concentration en monomères. Au départ des comportements de copolymérisation greffée observés à une concentration déterminée du catalyseur rédox (LiBr et $K_2S_2O_8$), les groupes thiols de la fibre de laine ont été considérés comme jouant un rôle de catalyseur de polymérisation et non de transfert de chaîne et fournissent ainsi des sites de greffage. Ainsi, le processus d'initiation de greffage est supposé démarrer par $d[S\cdot]/dt = k_i(SH)_{eff}$, et les considérations cinétiques amenaient à l'expression suivante, en accord avec les résultats expérimentaux: $1/\overline{DP} = (k_t/k_p^2[M]^2)_{fib}R_p$, où $d[S\cdot]/dt$ est la vitesse de formation de radicaux thiols par radicalotropie de -SH au départ de SO_4 , OH ou Br, k_i , k_p et k_t sont les constantes de vitesse d'initiation, de propagation et de terminaison, respectivement, $(SH)_{eff}$ et $(M)_{fib}$ sont les concentrations des groupes thiols effectifs et de monomères MMA au sein de la fibre de laine respectivement, \overline{DP} est le degré de polymérisation moyen des polymères greffés et R_p est la vitesse de greffage globale.

Zusammenfassung

Die Pfropfcopolymerisation von Methylmethacrylat in Wollfasern wurde im wässrigen LiBr- $K_2S_2O_8$ -System ohne Homopolymeres untersucht. Die Pfropfgeschwindigkeit und der Polymerisationsgrad des Pfropfpolymeren wurden bei Variation des Reduktionsausmasses der Wollfasern und der Monomerkonzentration bestimmt. Aus dem Verhalten der Pfropfcopolymerisation bei einer gegebenen Konzentration des Redoxkatalysators (LiBr und $K_2S_2O_8$) wurde geschlossen, dass die Thiolgruppen der Wollfasern eine Rolle als eine Art von Polymerisationskatalysator, nicht als Kettenüberträger spielen und auch die Pfropfstellen liefern. Es wurde daher angenommen, dass der Startprozess der Pfropfung nach $d[S\cdot]/dt = k_i[SH]_{eff}$ verläuft und das kinetische Schema lieferte folgenden, mit den Versuchsergebnissen übereinstimmenden Ausdruck $1/\overline{DP}$

$= (k_t R_p / k_p^2 [M]_{\text{Fas}}) R_p$. $d[S\cdot]/dt$ ist die Bildungsgeschwindigkeit der Thiolradikale aus $-SH$ mit $SO_4^{\cdot-}$, $OH\cdot$ oder $Br\cdot$; k_i , k_p und k_t sind die Geschwindigkeitskonstanten für Start, Wachstum und Abbruch; $[SH]_{\text{eff}}$ und $[M]_{\text{Fas}}$ sind die Effektivkonzentrationen von Thiolgruppen und monomerem MMA in den Wollfasern; \overline{DP} ist der mittlere Polymerisationsgrad des Pfropfpolymeren und R_p die Brutttopfropfgeschwindigkeit.

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