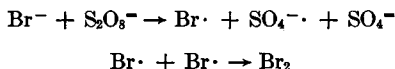


New Method for Graft Polymerization of Vinyl Monomers in Wool Fibers

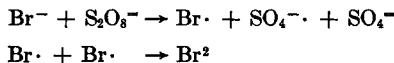
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Synopsis

When a small amount of persulfate is dissolved in a relatively concentrated aqueous solution of bromide salts, especially LiBr, liberation of Br₂ occurs to some extent. This system was utilized for the graft copolymerization of various acrylates in wool fibers using diethylene glycol monobutylether as monomer-solubilizer. The grafting was fairly well performed at a relatively low temperature (10–40°C.) and without homopolymerization while liberating Br₂. This new graft copolymerization has been attributed to the concerted action of the fiber-swelling power of bromide salts, the following redox system, and the mild bromination of some monomers by which the grafting will proceed without homopolymerization.



It is known that the bromides of alkali metals or ammonium are well absorbed by protein materials such as wool, silk, or gelatin accompanying its hydration, swelling, or contraction, more or less according to the lyotropic series of cations (Li⁺ > Na⁺ > K⁺ for wool or silk, Li⁺ > NH₄⁺ > Na⁺ > K⁺ for gelatin¹⁻³). When a small amount of persulfate, in the form of K₂S₂O₈ or (NH₄)₂S₂O₈, is dissolved in relatively concentrated aqueous solutions of these bromides, the liberation of Br₂ occurs to some extent. The mechanism of this reaction involves the following redox system:



The facility of Br₂ liberation was observed to be in the order K⁺ > NH₄⁺ ≥ Na⁺ > Li⁺ and decreased with increasing the degree of hydration of bromide.

Thus, we attempted to utilize the fiber-swelling action of these bromides and the redox system formed between Br⁻ and S₂O₈⁼ for the graft copolymerization of vinyl monomers in wool fibers. In order to solubilize vinyl monomers, especially water-insoluble monomers, in the aqueous solutions

containing bromide and persulfate, the addition of suitable organic solvent or surface-active agent in a proper quantity was required. The solubilizers must be well compatible with the salt solutions and the redox system. Screening studies indicated that the LiBr-monoalkyl ether of mono- or diethylene glycol, especially LiBr-diethylene glycol monobutyl ether (BC) system was favorable for the graft copolymerization. This may perhaps be due to the great water solubility of LiBr and the ability of BC to remove water from the hydrated LiBr, which appear to be responsible for the smooth progression of the redox system. Furthermore, it should be noted that the relatively mild liberation of Br₂ in the reaction medium is indispensable for the graft copolymerization without homopolymerization. Too vigorous liberation of Br₂ not only inhibits the formation of homopolymer, but decreases the rate of graft copolymerization because of a large consumption of monomers by bromination.

NH₄Br and NaBr were also quite efficient for the grafting, but the variable range of concentration was not so large as for LiBr because these salts are less water-soluble. The water solubility of KBr was too low to permit a homogeneous, stable, and effective reaction medium to be obtained. A comparison of LiCl, LiBr, and LiI for grafting showed that LiBr was distinctly superior, as evident in Table I. The decomposition of iodide may perhaps be too rapid to give free radicals.⁴

TABLE I
Comparison of LiCl, LiBr, and LiI for MMA Graft Copolymerization in Wool Fibers^a

LiX	Graft-on, %	Halogen liberation Observed	Formation of homopolymer in reaction medium
LiCl	10.7 ^b	None	Observed
LiBr	65.2	Observed	None
LiI	0	Observed, vigorous	None

^a Composition of reaction liquor (by weight): LiX, 22.5%; K₂S₂O₈, 0.2%; MMA, 2.0%; BC 35.3%; H₂O, 40.0%. Conditions of reaction: liquor ratio, 100:1; 30°C.; 5 hr.

^b Soxhlet-extracted with acetone.

Table II shows the effect of concentration of BC in the LiBr-BC system in grafting of MMA on wool fiber (Merino). The grafting was proceeded without homopolymerization. The liberation of Br₂ becomes more marked with increasing concentration of BC. It is noteworthy that the grafting is effective in the system in which there is mild liberation of Br₂. Table III shows the effect of concentration of LiBr on grafting of MMA on wool fibers. The maximum grafting appears at 25-28% LiBr, which is near the critical concentration both for the liberation of Br₂ and the formation of homopolymer. At a concentration of LiBr higher than this critical concentration, liberation of Br₂ becomes vigorous, and grafting tends to decrease. The MMA graft-on at varying concentrations of

TABLE II
Effect of Concentration of BC on MMA Graft-On for Wool Fibers^a

BC, %	H ₂ O, %	Graft-on, %	Br ₂ liberation observed
0 ^b	67.3	0.0	None
5 ^b	62.3	0.4, 1.3	None
12	55.3	111.8	Observed in the absence of wool and MMA
15	52.3	101.3	Observed
22.5	44.8	80.9	Observed
30	37.3	59.2	Observed

^a Composition of reaction liquor (by weight): LiBr, 27.5%; K₂S₂O₈, 0.2%; MMA, 5.0%; BC + H₂O, 67.3%. Conditions of reaction: liquor ratio, 100:1; 30°C.; 3 hr.

^b A homogeneous phase was barely maintained by the forced stirring.

K₂S₂O₈ is shown in Table IV. The formation of homopolymer did not occur. Liberation of Br₂ and a leveling off of grafting are observed at more than 0.2% K₂S₂O₈.

The effect of temperature on the rate of MMA grafting is shown in

TABLE III
Effect of Concentration of LiBr on MMA Graft-On for Wool Fibers^a

LiBr, %	H ₂ O, %	Graft-on, %	Br ₂ liberation observed	Formation of homopolymer in reaction medium
0	72.3	0	None	None
15.0	57.3	9.3	None	Observed
20.0	52.3	48.9	None	Observed
22.5	49.8	69.2	None	None
25.0	47.3	81.8	Observed	None
27.5	44.8	80.9	Observed	None
30.0	42.3	66.4	Observed	None

^a Composition of reaction liquor (by weight): K₂S₂O₈, 0.2%; MMA, 5.0%; BC, 22.5%; LiBr + H₂O, 72.3%. Conditions of reaction: liquor ratio, 100:1; 30°C.; 3 hr.

TABLE IV
Effect of Persulfate Concentration on MMA Graft-On for Wool Fibers^a

K ₂ S ₂ O ₈ , %	Graft-on, %	Br ₂ liberation observed
0	(-0.3)	None
0.05	0.0	None
0.1	45.7	None
0.2	87.2	Observed
0.3	97.0	Observed
0.5	93.6	Observed

^a Composition of reaction liquor (by weight): LiBr, 27.5%; MMA, 11.0%; BC, 22.5%; H₂O, 39.0-38.5%; K₂S₂O₈, 0-0.5%. Conditions of reactions: liquor ratio, 100:1; 30°C.; 3 hr.

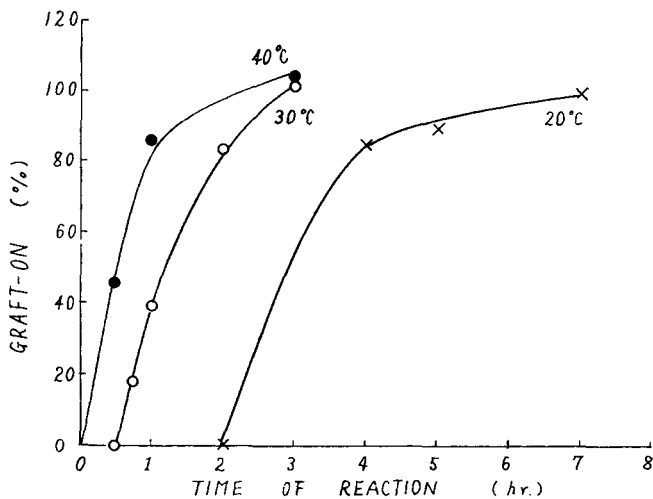


Fig. 1. Rate of MMA grafting in wool fibers at varying of reaction temperature. LiBr, 27.5%; $K_2S_2O_8$, 0.2%; MMA, 5.0%; BC, 15.0%; H_2O , 52.3%. Liquor ratio, 100:1.

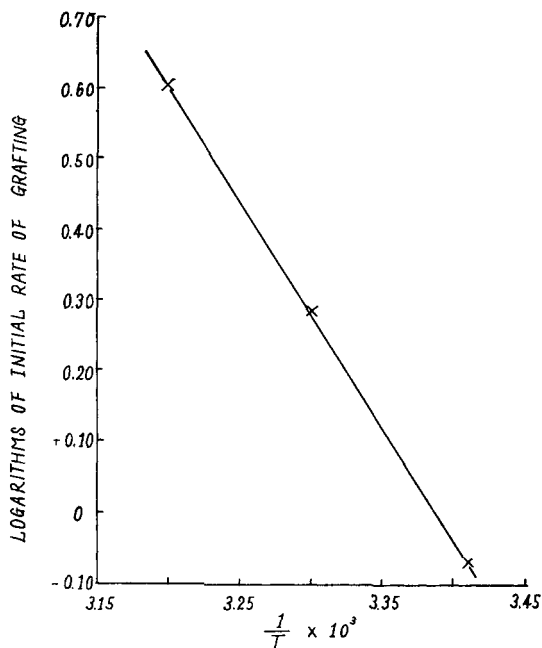


Fig. 2. Logarithms of initial rate of MMA grafting vs. $1/T$ for wool fibers.

Figure 1. The leveling off of the rate might be influenced by the degree of fiber swelling. An induction period, during which the liberation of Br_2 is almost nil, exists at a relatively low temperature (20–30°C.). At over 60°C., graft copolymerization occurs only with difficulty because of too rapid liberation of Br_2 . When the logarithms of the initial slope of the

TABLE V
n-Butyl Acrylate Grafting for Wool Fibers with the LiBr-(NH₄)₂S₂O₈ System*

Reaction time, hr.	Graft-on, %
24	70.0
48	106.0
96	118.5

* Composition of reaction liquor (by weight): LiBr, 16.0% (NH₄)₂S₂O₈, 1.0%; *n*-BA, 5.0%; BC, 40.0%; H₂O, 38.0%. Conditions of reactions: liquor ratio, 100:1; 10°C.; 24-96 hr.

curve in Figure 1 are plotted against $1/T$, a straight line is obtained, as shown in Figure 2. The apparent energy of activation calculated from the slope of the line is about 6.5 kcal./mole, which is of the same order as that obtained for the usual redox polymerization.

At a relatively high concentration of (NH₄)₂S₂O₈ as catalyst at a low temperature, grafting with *n*-butyl acrylate was also possible. The results are shown in Table V. Mild liberation of Br₂ continued throughout the reaction, without the formation of homopolymer. The grafting of methyl or ethyl acrylate was much the same.

Although the graft-on was generally determined through water washing of the grafted wool alone, some determinations of Soxhlet-extraction loss were carried out. Extraction loss was very slight, in agreement with the fact that formation of homopolymer is not observed. For example, acetone, chloroform, and benzene extraction performed successively, each for 50 hr., of wool with 133.8% MMA add-on resulted in the loss of only about 3% of the original weight.

The decomposition of wool was carried out by using a digestion method with 72% H₂SO₄.⁵ The molecular weight of the isolated and purified graft polymer (PMMA) was determined to be about 372,000 by the viscosity method. On the other hand, the homopolymer formed in the same reaction system after cessation of Br₂ liberation was found to have a molecular weight of 109,000.

Despite the liberation of Br₂ in the reaction process, the Allwörden bubble reaction of wool fiber was not observed, and oxidative damage was slight.

This new grafting procedure was most effective for reduced wool, good for silk fibroin, less effective for brominated wool or silk, and almost ineffective for cellulose or conventional nylon fibers.

The initiation of grafting might involve hydrogen abstraction by Br; not only from cysteine —SH but also from tyrosine —OH groups on polypeptide chains, rather than the chain transfer to —SH groups, which has been accepted in most cases.⁶ However it appears that this graft copolymerization is attributable to the concerted action of the fiber-swelling power of bromide salts, the redox reaction between Br⁻ and S₂O₈⁼, and the mild bromination of monomers.

References

1. Crewther, W. G., and L. M. Dowling, *Textile Res. J.*, **29**, 541 (1959).
2. Docking, A. R., and E. Heyman, *J. Phys. Chem.*, **43**, 513 (1939).
3. Murase, R., in *Structure of Natural Silk*, T. Ito, Ed., Chikumakai, Ueda, Japan, 1957, p. 145.
4. Urakawa, N., and S. Okamura, *Kobunshi Kagaku*, **7**, 350 (1950).
5. Ide, F., *Kogyo Kagaku Zasshi*, **64**, 1489 (1961).
6. Madaras, G. W., and J. B. Speakman, *J. Soc. Dyers Colourists*, **70**, 112 (1954).

Résumé

Quand une petite quantité de persulfate est dissoute dans une solution aqueuse relativement concentrée de bromures, spécialement LiBr, la libération du Br₂ s'effectue dans une certaine proportion. Ce système est utilisé pour la copolymérisation greffée de divers acrylates dans des fibres de laines en utilisant le diéthylène glycol monobutyléther comme solvant du monomère. Ce greffage se fait parfaitement à une température relativement basse (de 10 à 40°C) et sans homopolymérisation lors de la libération de Br₂. Cette nouvelle copolymérisation greffée est attribuée à l'action simultanée du pouvoir de gonflement des fibres par les bromures et au système rédox indiqué dans le résumé en langue anglaise et à la bromuration douce de certains monomères par lequel le greffage s'effectuerait sans homopolymérisation.

Zusammenfassung

Bei Auflösung einer kleinen Menge von Persulfat in einer verhältnismässig konzentrierten wässrigen Lösung von Bromiden, besonders LiBr, tritt in einem gewissen Ausmass eine Freisetzung von Br₂ auf. Dieses System wurde zur Pfropfcopolymerisation verschiedener Acrylate in Wollfasern mit Diäthylenglykolmonobutyläther zur Solubilisierung des Monomeren verwendet. Die Aufpfropfung vollzog sich befriedigend bei verhältnismässig niedriger Temperatur (10–40°C) und ohne Homopolymerisation, solange Br₂ in Freiheit gesetzt wurde. Diese neue Pfropfcopolymerisation wurde auf die gemeinsame Wirkung der Faserquellung durch die Bromide, des Redoxsystems (s. englische Zusammenfassung) und die milde Bromierung gewisser Monomere, wodurch die Aufpfropfung ohne Homopolymerisation vor sich geht, zurückgeführt.

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