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Graft Copolymerization onto Cellulose in Dimethyl Sulfoxide by Means of a Ceric Salt Containing Lauryl Sulfuric Ions

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Styrene was polymerized in dimethyl sulfoxide by alcohol-ceric salt containing lauryl sulfuric ions. The rate of polymerization increased with the amount of ethyl alcohol added. A deuterium isotope effect was observed when tetradeuteromethyl alcohol was used as an initiator. Accordingly, the generation of radicals by the elimination of the hydrogen atom from the alcohol molecule was concluded. When styrene was polymerized in the presence of cellulose, graft copolymer was obtained. The grafting efficiency amounted to about 70%.

Many workers have reported the graft copolymerization of vinyl monomers onto cellulose.[1] Previous investigations have, however, dealt almost exclusively with polymerizations in aqueous systems. On the other hand, some reactive monomers react with water rather than graft. No radical initiator which initiates graft copolymerization onto cellulose in an inert organic solvent is yet known.

The author has been studying the polymerization by ceric ions in an organic solvent.[2,3] Ceric salt containing lauryl sulfuric ions (hereafter refered to as CLS) was found to be an effective initiator. As our purpose is to show the effectiveness of CLS in grafting vinyl monomers onto cellulose, the present paper will deal with the polymerization of styrene.

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[1] For example, M. Imoto and K. Takemoto, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **70**, 1851 (1967).

[2] K. Kaeriyama, This Bulletin, **41**, 722 (1968).

[3] K. Kaeriyama, *Polymer* (*London*), **10**, 11 (1969).

Experimental

Material. The styrene, ethyl alcohol, dimethyl sulfoxide (DMSO), and dimethylformamide (DMF) were distilled under reduced pressure just prior to use. The tetradeuteromethyl alcohol was of commercial origin (E. Merck AG.).

The CLS was generally prepared according to the following procedure.4) To a solution of 32 g of ceric ammonium nitrate in 70 m*l* of water, there was added a solution of 12 g of sodium laurylsulfate in 50 m*l* of water. The slurry was poured into 800 m*l* of water, and the precipitate thus separated was collected on a sintered filter and dried *in vacuo*. The yield was 14.8 g. The CLS thus obtained was not soluble in any of the organic solvents examined except DMSO and DMF. The ceric ion content in CLS was 23.00% by weight.

The cellulose used was 40/1 cotton cloth which had been desized and scoured according to the usual procedure.

Polymerization Procedure. In a glass tube with a capacity of 25 m*l* there was placed a 20 m*l* portion of the polymerizing mixture. After the tube had been degassed by the freeze-thaw-method, it was sealed off. After the tube had then been maintained at 60°C for a given time, the contents were poured into methyl alcohol containing a small amount of benzoquinone. The polystyrene thus precipitated was collected on a sintered filter and dried *in vacuo* to a constant weight.

The grafted cellulose was extracted with benzene until no further polymers could be extracted.

Molecular Weight. The viscometry was carried out at 30°C in a benzene solution. The molecular weight was calculated from the intrinsic viscosity based on the equation:5)

$$\log[\eta] = -4.013 + 0.74 \log M_n$$

Definitions. In this paper, the polymer yield, the grafting, and the grafting efficiency are defined as follows:

Polymer yield (mol/*l*)

$$= \frac{\text{weight of polymer produced per liter}}{\text{molecular weight of the polymer produced}}$$

Grafting (%)

$$= \frac{\text{weight increase of cellulose after extraction}}{\text{weight of original cellulose}} \times 100$$

Grafting efficiency (%)

$$= \frac{\text{weight increase of cellulose after extraction}}{\text{weight of polymerized styrene}} \times 100$$

Results and Discussion

Polymerization in DMF. Polymerization was carried out in DMF, in which CLS was soluble. The results are shown in Table 1. Polymerization is not initiated by the ethyl alcohol - CLS system in DMF. The conversion is much lower than that of similar runs in DMSO, which will be described below. In view of the above results, the polymerization was thereafter carried out in DMSO.

TABLE 1. POLYMERIZATION IN DIMETHYL FORMAMIDE

Ethyl alcohol (mol/*l*)	Conversion (%)
1.73	2.46
0.606	2.33
0.173	2.85
0.0346	2.69
0.00692	2.74

[Styrene] = 2.18 mol/*l*; [CLS] = 8.21×10^{-3} mol/*l*
Solvent: dimethyl formamide
Polymerization: at 60°C for 48 hr

Polymerization in DMSO. Polymerization was carried out in DMSO. It can be seen from Table 2 that polymerization is initiated by the ethyl alcohol - CLS system in DMSO.

TABLE 2. EFFECTS OF THE CONCENTRATION OF ETHYL ALCOHOL

Ethyl alcohol (mol/*l*)	Conversion (%)	M_n $\times 10^{-5}$	Polymer yield (mol/*l*) $\times 10^4$
1.73	22.5	2.4	2.1
0.606	18.9	3.4	1.3
0.173	15.8	3.7	0.97
0.0173	14.7	5.6	0.60
0.00173	10.4	5.7	0.41

[Styrene] = 2.18 mol/*l*; [CLS] = 8.21×10^{-3} mol/*l*
Solvent: DMSO
Polymerization: at 60°C for 48 hr

Because the polymer yield increases with the amount of ethyl alcohol added, the latter is concluded to participate in the initiation reaction of polymerization. This suggests that a graft copolymerization of styrene onto cellulose may be possible in DMSO.

Deuterium Isotope Effect. Ethyl alcohol participates in the initiation reaction, as is evident from the above results. However, it is not yet clear whether or not the radical is formed by the cleavage of the covalent bond in the alcohol molecule. In order to see how the radical is formed, styrene was polymerized by the CLS - tetradeuteromethyl alcohol system.

In the initiation step, if the reaction involves a rupture of the C–H bond, the rate of the reaction of the deuterated alcohol should be lower than that of the ordinary alcohol because of the difference in

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4) S. Kaizerman, N. Plainfield and G. Mino, U. S. Pat. 2922801.

5) R. H. Ewart and H. C. Tingey, Abstracts of Papers Presented at the 111th Meeting of American Chemical Society, Atlantic City, N. J. (1947).

6) K. B. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

TABLE 3. DEUTERIUM ISOTOPE EFFECT IN POLYMERIZATION CATALYZED BY METHYL ALCOHOL-CLS SYSTEM

Polymerization time (hr)	Without alcohol			CH_3OH			CD_3OD			
	Conversion (%)	$M_n \times 10^{-5}$	Polymer yield $\times 10^5$ (mol/l) A	Conversion (%)	$M_n \times 10^{-5}$	Polymer yield $\times 10^5$ (mol/l) B	Conversion (%)	$M_n \times 10^{-5}$	Polymer yield $\times 10^5$ (mol/l) C	Ratio (B−A)/(C−A)
5	2.43	1.6	3.5	3.79	1.2	7.2	3.30	1.3	5.8	1.6
10	3.61	2.2	3.7	7.34	1.4	12	6.42	1.7	8.6	1.7
15	4.91	2.9	3.8	10.2	1.7	14	8.26	1.9	9.9	1.7
20	5.41	3.3	3.7	12.3	1.9	15	11.0	2.1	12	1.4
30	7.11	3.6	4.5	16.1	1.9	19	13.3	2.4	13	1.7

[Styrene]=2.18 mol/l; [CLS]=8.21×10^{-3} mol/l; [methyl alcohol]=1.85 mol/l
Solvent: DMSO
Polymerization: at 60°C

TABLE 4. GRAFT COPOLYMERIZATION ONTO CELLULOSE

Cellulose* (g)	CLS 10^3 (mol/l)	Polymerization time (hr)	Total conversion (%)	Grafting (%)	Graft efficiency (%)
1.634	8.21	5	11.4	21.5	67.8
1.672	8.21	10	18.3	35.8	71.8
1.633	8.21	17	24.2	48.8	72.5
1.611	8.21	21	29.5	62.6	75.1
1.652	8.21	26	33.8	70.8	76.3
1.593	8.21	40	37.8	79.8	74.1
1.667	8.21	48	40.0	78.0	71.8
1.712	1.64	48	8.3	9.3	41.7
1.683	4.92	48	16.3	22.6	51.4
1.685	13.9	48	49.0	90.8	68.7
1.705	20.5	48	49.0	87.9	67.3

Styrene: 5 ml; DMSO: 15 ml
Polymerization: at 60°C
* Cotton cloth

zero-point energy and mass effect.⁶⁾ If the step is rate-determining, the difference in rates may actually be observed. In fact, the isotope effect has been observed in the radical oxidation of various alcohols.[7,8]

The results of polymerization in the presence of CH_3OH and CD_3OD and in the absence of any alcohol are shown in Table 3. Styrene was polymerized without any alcohol because of the initiation of polymerization by the CLS-DMSO system and thermal polymerization. In order to observe the effect of the methyl alcohol-CLS system, it is necessary to deduct the moles of polymer produced in the absence of alcohol from the total moles of the polymer produced. Ratios of the moles of the polymers produced by ordinary methyl alcohol to those produced by tetradeuteromethyl alcohol are shown in the last column. The mean value of the ratios is 1.6. This value suggests that a radical is formed by the elimination of a hydrogen atom from methyl alcohol in the rate-determining step; therefore, it may be concluded that it is possible to prepare graft copolymers by the initiator system.

Graft Copolymerization onto Cellulose. The results of graft copolymerization onto cellulose are shown in Table 4. The data show that styrene was graft-copolymerized onto cellulose. The grafting efficiency is high. The percentage of grafting increases with the polymerization time for 40 hr and in the range of the CLS concentration below 13.9×10^{-3} mol/l. The grafting efficiency reaches its maximum at the CLS concentration of 8.21×10^{-3} mol/l and at the polymerization time of 26 hr.

The method developed in this paper will be useful for preparing graft copolymers with functional side chains.

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7) F. H. Westheimer and N. Nicolaides, *J. Am. Chem. Soc.*, **71**, 25 (1949).

8) L. Kaplan, *ibid.*, **76**, 4645 (1954); **77**, 5469 (1955); **80**, 2639 (1958).