Polymerization of 1-Vinyl-2-methylimidazole Initiated by Carbon Tetrachloride, Water and Cellulose*

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In connection with a series of studies of the graft polymerizations of methyl methacrylate in the absence of radical initiators,$^{1)}$ we have found a new initiator system, consisting of carbon tetrachloride, water, and cellulose. This system is capable of vinyl polymerization, especially of 1-vinyl-2-methylimidazole.

Recently, Breitenbach and his co-workers have reported on the polymerization of *N*-vinylcarbazole in the presence of carbon tetrachloride.$^{2,3)}$ With reaction conditions similar to those described by them, the polymerization of 1-vinyl-2-methylimidazole was carried out at first in a carbon tetrachloride solution at 30°C for 5 hr. Contrary to the case of *N*-vinylcarbazole, no initiation of the polymerization could be observed in this case. However, a marked polymerization of 1-vinyl-2-methylimidazole was observed when water and cellulose were present along with carbon tetrachloride. Polymerization could not be initiated when the reaction system was devoid of even one factor among the three components: carbon tetrachloride, water and cellulose.

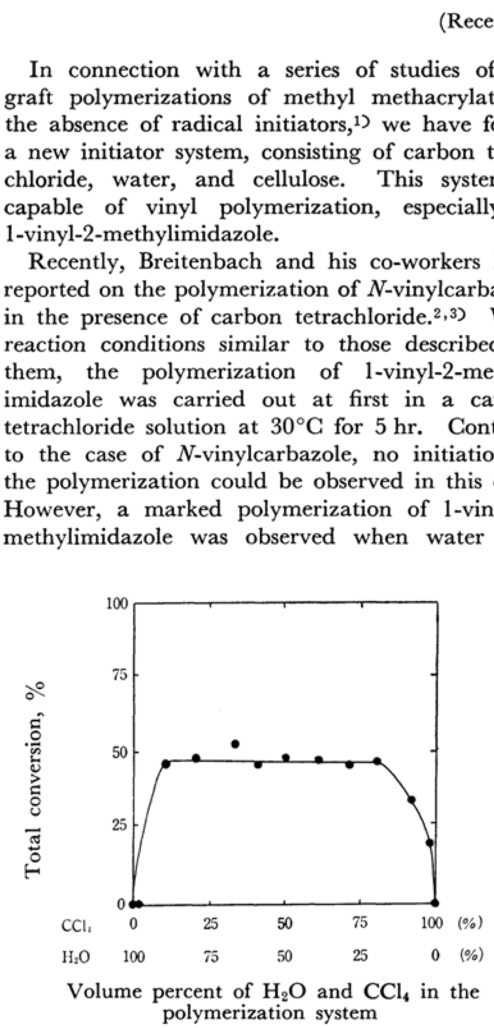

Fig. 1. Polymerzation of 1-vinyl-2-methylimidazole: 30°C, 5 hr in the dark: monomer 1.020 g, cellulose 0.1 g, H_2O+CCl_4 5.0 ml.

Figure 1 shows the results of the polymerization of 1-vinyl-2-methylimidazole initiated by this system. The total conversions amounted to *ca.* 50% in the presence of carbon tetrachloride, water, and cellulose.

Different from the previous cases,$^{1)}$ the polymer formed consisted mainly of homopolymers, the graft polymer of 1-vinyl-2-methylimidazole on cellulose resulted in a much smaller amount (see Table 1). The polymerization was inhibited by hydroquinone, which showed radical features for the initiation by this system. It was also found that the chlorine atom was incorporated in the polymer. Polymerization was not affected by the different grades of purification of the carbon tatrachloride used. As well as cellulose, silk and polyvinyl alcohol can also initiate the polymerization of 1-vinyl-2-methylimidazole, but chloroform and dichloromethane in place of carbon tetrachloride can not initiate the polymerization. At elevated temperatures, other vinyl monomers, including methyl methacrylate, and methyl acrylate, were similarly polymerized to give their homopolymers.

These experimental results suggest that the polymerization in the vinyl monomer - carbon tetrachloride - water - cellulose system is due to a specific interaction between these four components. Further study is now in progress.

Experimental

1-Vinyl-2-methylimidazole was purified by distillation three times in a nitrogen stream; bp 29.2°C/0.06 mmHg. Tissue paper (α-cellulose, 99.0%) was treated with hot water, and then with a benzene and methanol mixture (2 : 1) three times; it was then dried in a vacuum on calcium chloride at room temperature. Carbon tetrachloride was washed with a 5% aqueous sodium hydroxide solution and then thoroughly with water, dried on potassium carbonate, and then, in order to remove all acidic and oxidizing impurities, distilled under nitrogen in the dark through a condenser filled with active alumina.

Polymerizations were carried out in sealed tubes. 0.1 g of cellulose, 5 *ml* of a carbon tetrachloride - water

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Table 1. Polymerization of 1-vinyl-2-methylimidazole
(30°C, 5 hr Monomer 1.020 g, in the dark)

No.	Backbone polymer g	CCl_4 ml	H_2O ml	Result				
				Total yield g	Total conversion g	Backbonepolymer after extraction g	Polymer grafted g	Homo-polymer g
1	Cellulose 0.1000	1.0	2.0	0.5519	54.1	0.1134	0.0134	0.5385
2	Cellulose 0.1089	4.0	1.0	0.4851	49.5	0.1224	0.0135	0.4716
3	Cellulose 0.1066	2.0	3.0	0.4690	46.0	0.1184	0.0118	0.4572
4	Cellulose 0.1059	1.0	4.0	0.5207	51.0	0.1139	0.0080	0.5127
5	Cellulose 0.1130	0.5	4.5	0.4799	47.0	0.1119	0	0.4799 a)
6	Cellulose 0.1134	3.0	2.0	0.4938	48.4	0.1150	0.0016	0.4922
7	Cellulose 0.1013	1.0	2.0	0.5798	56.8	0.1192	0.0179	0.5619
8	Silk b) 0.1024	1.0	2.0	0.3031	30.3	0.1488	0.0464	0.2567
9	PVC c) 0.1039	1.0	2.0	0.5211	52.1	0.1783	0.0744	0.4467

a) N, 25.08% ; Cl, 1.0%. $[\eta]$ (30°C, in 0.1 N aqueous HCl solution)=3.3
b) Treated with 0.1 N aqueous $NaBH_4$ solution at purification.
c) Completely hydrolyzed. $\overline{P}=2400$

mixture, and 1.0 ml of 1-vinyl-2-methylimidazole were charged in a test tube, cooled in a dry ice - methanol bath, and sealed in a vacuum. The sealed tube was shaken in a thermostat maintained at 30°C for a given time. The contents were then poured into acetone to precipitate the polymer mixtures, which was then extracted with methanol for 30 hr, using a Soxhlet extractor. The methanol solution was poured into acetone to obtain the homopolymer.

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