Vinyl Polymerization. LXIV. Graft Copolymerization of Vinyl Monomers to Starch*

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Many authors have reported on the synthesis of graft copolymers of starch. The methods described were chain transfer reaction$^{1,2)}$, high energy radiation$^{3)}$, oxidation with ozone$^{4)}$, oxidation with ceric salt$^{5)}$, and polymer blend$^{6)}$. In order to obtain a graft copolymer of starch with high efficiency, we used the method of the polymerization of the monomer in the presence of oxidized starch. Kargin et al. peroxidized starch with ozone and initiated vinyl polymerization with it to obtain a graft

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* LXIII of this series: M. Kinoshita, *Chem. High Polymers, Japan.*, in press.

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1) Brit. Pat. 715194 (1959).

2) Brit. Pat. 809745 (1959).

3) A. Mishina, *J. Agr. Chem. Soc. Japan*, 35, 40 (1961).

4) V. A. Kargin, P. V. Kozlov, N. A. Plate and I. I. Konoreva, *Vysokomol. Soed.*, 1, 114 (1959); V. A. Kargin, N. A. Plate and E. P. Rebinder, ibid., 1, 1547 (1959).

5) S. Kimura and M. Imoto, *Makromol. Chem.*, 42, 140 (1960).

6) R. F. Ceresa, IUPAC Simposium (1960); A. A. Berlin, Je. A. Penskaja and G. I. Wolkova; IUPAC Simposium (1960).

copolymer. They obtained grafted starch with polymethyl methacrylate or polystyrene. However, the efficiency of their reaction was not stated4).

The present paper concerns the stability of ozone-oxidized starch, the graft copolymerization of methyl methacrylate, acrylonitrile or vinyl chloride with the oxidized starch, and the fractionations of the grafted copolymer and their properties.

Experimental

Oxidation of Starch.—Starch was purified by re-precipitation from an aqueous solution with ethanol. It was charged into a four-necked flask which contained water or carbon tetrachloride. Ozonized oxygen generated by an ozonizer of the Japan Ozonizer Co. (Type 03-5-2) was introduced at the velocity of 6 l./hr. at room temperature while the mixture was vigorously stirred. A stirrer, as shown in Fig. 1, was made from a glass-tube; it had two gas-outlets, of which one opened near the bottom in the liquid layer and the other just above the liquid surface. After a definite time, the reaction mixture was filtered in order to obtain oxidized starch.

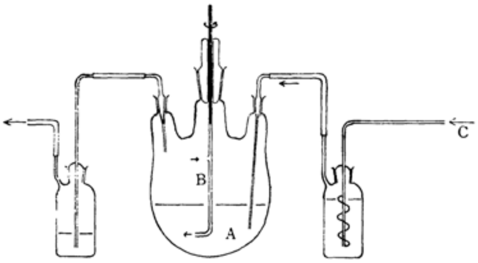

Fig. 1. Equipment for the ozonization of starch.

A Suspension of starch
B A glass-tube stirrer
C O_3 (in O_2)

Determination of the Content of the Peroxide Group in Oxidized Starch.—The content of the peroxide group in the oxidized starch was determined as follows. A definite quantity of the oxidized starch was immersed in a 10% aqueous solution of potassium iodide for 10 min. at room temperature (29°C) or for 3 min. at 70 and 100°C. The content of the peroxide group was expressed by the number of peroxide groups per anhydroglucose unit (AGU) of starch. The quantity of starch in the filtrate was estimated on the basis of the amount of glucose which was liberated by hydrolysis in 1.0 N hydrochloric acid at 95°C for 3 hr. The determination of the glucose was made by Somogyi's method.

Polymerization Procedure.—The polymerization of methyl methacrylate (MMA), acrylonitrile (AN), and vinyl chloride (VC) was carried out under the conditions described in Table I.

In Experiments I, III, V and VI, a mixture of a monomer, starch and solvent was charged in a test tube, cooled in a dry ice-methanol bath, and sealed in vacuum. The sealed tube was shaken at 90°C in a thermostat for a given time; the contents were then poured into methanol to precipitate the polymer mixtures. In Experiments II and IV, the mixture was charged into a three-necked flask, and nitrogen was then introduced into it at room temperature for 15 min. Then, the mixture was heated while being stirred. After a given time, the contents were poured into methanol to precipitate all the polymers.

Fractionation of Polymerization Products.—*Copolymerization Product with Methyl Methacrylate.*—Copolymerization product with MMA was extracted with benzene for 30 hr., using a Soxlhet extractor. The benzene solution was poured into methanol to precipitate polymer I. The residue of the extraction was dissolved or swelled in dimethyl sulfoxide. It was then poured into warm water (about 50°C) to precipitate polymer II. As will be discussed below, it was assumed that polymer I was pure PMMA and that polymer II was a starch-PMMA graft copolymer.

The grafting efficiency and grafting ratio were computed as follows:

$$\text{Grafting efficiency} = \frac{\text{Wt. of vinyl polymer in grafts}}{\text{Total wt. of vinyl polymer formed}} \times 100$$

$$\text{Grafting ratio} = \frac{\text{Wt. of vinyl polymer in grafts}}{\text{Wt. of starch in grafts}}$$

The intrinsic voiscosities of PMMA and hydrolyzed graft copolymer were measured in benzene at 30°C.

Copolymerization Product with Vinyl Chloride.—Copolymerization product with vinyl chloride was

TABLE I. POLYMERIZATION PROCEDURE

Exp. No.	Oxi-starch g.	Monomer	ml.	Water ml.	Emulsifier* g.	Procedure
I	1	MMA	15	0	0	In sealed tube
II	1	MMA	5	60	0.15	In flask, under N_2 atmosphere
III	0.2**	MMA	3	15	0.08	In sealed tube
IV	1	AN	9	90	0	In flask, under N_2 atmosphere
V	1	VC	10	0	0	In sealed tube
VI	1	VC	4	15	0.1	In sealed tube

* "Emulgen-120", polyoxymethylene deriv.
** Starch deriv. See Table IX

extracted with tetrahydrofuran for 30 hr., using a Soxlhet extractor. The solution was poured into methanol to precipitate polymer III. The residue of the extraction was dissolved in dimethylsulfoxide and poured into warm water (about 50°C) to precipitate polymer IV. Polymers III and IV were assumed to be pure polyvinyl chloride and its graft copolymer respectively. The grafting efficiency and grafting ratio were computed according to the above equations. The intrinsic viscosities of polymer III and hydrolysed polymer IV were measured in a tetrahydrofuran solution at 30°C.

Acetylation of Graft Copolymer.—The acetylation of the graft copolymer of starch was carried out with acetic anhydride in pyridine, according to Pacsu's method[7]. The pyridine solution was poured into methanol to obtain the acetylated polymer. The infrared spectra of the resulting acetate no longer showed hydroxyl band.

Melting Points of Polymers.—An apparatus with a hot plate and a microscope (Shimadzu Seisakusho) was used for the measurement of the melting points of polymers.

Results and Discussion

Oxidation of Starch with Ozone.—During the oxidation with ozone in water, the oxidized starch was separated into water-soluble and water-insoluble parts. Figures 2 and 3 show the relationships between the contents of the peroxide group and the oxidation durations. The insoluble oxidized starch in water (abbr. as insoluble "oxi-starch-W") was used for syntheses of graft copolymers.

Oxi-starch-W was colored red purple with an iodine solution. Since the coloration of non-oxidized starch is blue, it was assumed that partial hydrolysis occured in the course of oxidation.

However, when ozonization was carried out in carbon tetrachloride, starch remained insoluble in the medium and was not hydrolyzed. This was abbreviated in "oxi-starch-C". Figure 4 shows the relationship between the contents of the peroxide group of oxi-starch-C and the oxidation time.

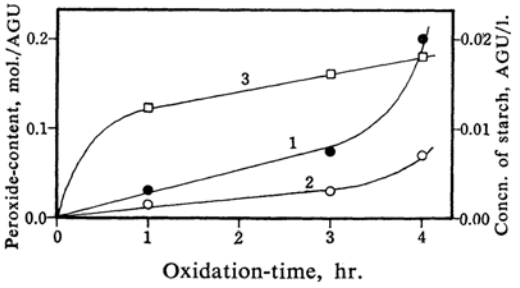

Fig. 2. Peroxide-content of soluble oxi-starch-W.

1 Determination by treating with KI solution at room temp. for 10 min.
2 Determination by treating with KI solution at 100°C for 3 min.
3 Concentration of starch

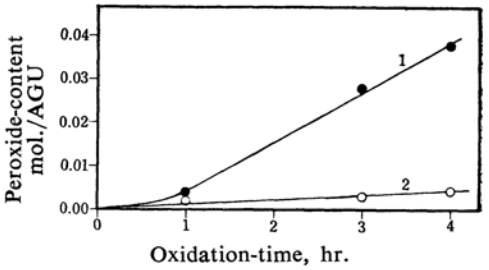

Fig. 3. Peroxide-content of insoluble oxi-starch-W.

1 Determination by treating with KI solution at room temp. for 10 min.
2 Determination by treating with KI solution at 70°C for 3 min.

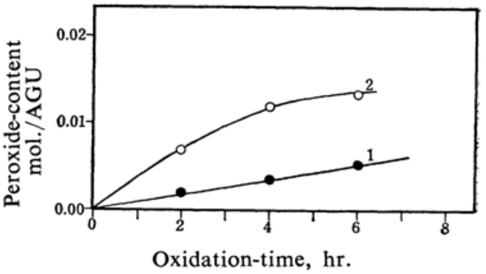

Fig. 4. Peroxide-content of oxi-starch-C.

1 Determination by treating at room temp. for 10 min.
2 Determination by treating at 100°C for 3 min.

The figures for the contents of the peroxide group of oxi-starch-W, as determined by treating it at room temperature for 10 min., were higher than those determined by treating it at 70°C for 3 min. Conversely, the figures for the contents of the peroxide group of oxi-starch-C, as determined by treating it at room temperature for 10 min., were lower than those determined at 100°C for 3 min. During the oxidation, starch particles swelled in water but not in carbon tetrachloride. Accordingly, it was assumed that the swelled particles were oxidized more uniformly, and that the unswelled particles were oxidized only on the surface. The differences in the contents of peroxide group according to the temperature of determination may be explained by the consideration that the peroxide groups located within the strach particles were inactivated at a higher temperature, before potassium iodide molecules diffused to the reaction centers. The following determination of the peroxide group of oxi-starch was

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[7] E. Pacsu and W. Mullen, *Ind. Eng. Chem.*, **34**, 1209 (1942).

TABLE II. BULK POLYMERIZATION OF MMA IN THE PRESENCE OF OXI-STARCH

Exp. No.	Polymerization: Oxi-starch: Type	Polymerization: Oxi-starch: Peroxy-content mol./AGU	Polymerization: Polymn. temp. °C	Polymerization: Polymn. time hr.	Polymers: Total yield g.	Polymers: Conversion %	Polymers: Homopolymer: Yield g.	Polymers: Homopolymer: [η]	Polymers: Graft: Yield g.	Polymers: Graft: Starch-cont. %	Polymers: Graft: [η]	Graft eff. %	Graft ratio
I-1	W	0.002	90	4	1.2631	5.6	0.3384		0.0060				
I-2	W	0.014	90	4	1.7521	16.0	0.9418		0.0069				
I-3	W	0.019	90	4	1.2958	6.3	0.3096		0.0070				
I-4	—	—	90	4	0.3638	7.7	0.3638						
I-5	C	0.0040	60	1	2.7593	37.4	1.6302	2.43	0.1374	2.9	2.43	7.5	33.4
I-6	C	0.0050	60	1	3.0026	42.6	1.9601	2.43	0.1028	2.9	2.43	4.9	33.4
I-7	—	—	60	1	0.0778	1.7	0.0778						
I-8	C	0.0040	60	2	3.7493	58.7	2.5737	3.17	0.1431	2.8	3.10	5.0	34.7
I-9	C	0.0050	60	2	3.8076	59.8	2.7858	2.57	0.0774	3.1	2.57	3.0	31.3
I-10	—	—	60	2	0.1230	2.6	0.1230						

Polymerization mixture: 1 g. of oxi-starch, and 15 ml. of MMA

TABLE III. EMULSION POLYMERIZATION OF PMMA IN THE PRESENCE OF OXI-STARCH

Exp. No.	Polymerization: Starch: Type	Polymerization: Starch: Peroxy-content mol./AGU	Polymerization: Polymn. temp. °C	Polymerization: Polymn. time hr.	Polymers: Yield g.	Polymers: Conversion %	Polymers: Homopolymer: Yield g.	Polymers: Homopolymer: [η]	Polymers: Graft copolymer: Yield	Polymers: Graft copolymer: Starch content %	Polymers: Graft copolymer: [η]	Polymers: Free starch %	Graft eff. %	Graft ratio
II-1	C	0.0024	90	3	4.877	82.3	1.712	2.60	1.960	6.0	2.90	87.0	57.0	15.7
II-2	C	0.0024	60	3	1.237	5.0	0.323	3.70	0.368	31.0	3.06	81.6	47.9	2.2
II-3	C	0.0024	30	3	0.992	0								
II-4	W	0.0016	90	3	5.121	87.7	1.299	3.45	2.590	4.0	4.75	88.5	68.5	24.0
II-5	W	0.0016	60	3	1.136	2.8	0.180							
II-6	W	0.0016	30	3	0.956	0								
II-7	N	—	90	3	1.7817	16.6	0.4746	5.10	1.110	63.7	6.20	29.2	39.3	0.6
II-8	N	—	60	3	1.0288	0.6								
II-9	N	—	30	3	0.9820	0								
II-10	—	—	90	3	0.4128	8.9	0.4128							
II-11	—	—	60	3	0.1630	3.5	0.1630							
II-12	—	—	30	3	0									

Polymerization mixture: Type of starch, C, W and N mean oxi-starch-C, oxi-starch-W and non oxidized starch, respectively.
5 ml. of MMA, 60 ml. of water, 0.15 g. of emulsifier and 1 g. of starch or the derivatives,
In Expt. No. II-10, 11 and 12, starch was absent,

TABLE IV. SOLUBILITY OF ACETYLATED STARCH-PMMA GRAFT COPOLYMER

Solvent	Polymer			
	Starch	Acetyl-starch	PMMA	Acetyl-starch-PMMA graft
Tetrachloroethane	ins	s	ins	s
Pyridine	sw	s	ins	vs
Chloroform	ins	ss	s	vs
Dioxane	ins	ss	s	s
Dimethylsulfoxide	s	ss	ins	s
Acetone	ins	sw	s	vs
Tetrahydrofuran	ins	sw	s	s
Ethyl Acetate	ins	sw	s	s
Dimethy formamide	ins	sw	s	ss
Benzene	ins	sw	s	s
Methanol	ins	ins	ins	ins
Water	ss	ins	ins	ins

vs: very soluble; ss: slightly soluble; ins: insoluble; sw: swell

carried out by treating it at room temperature.

Figure 4 shows that oxi-starch was decomposed during the preservation at a different temperature. Oxi-starch-W was more stable than oxi-starch-C. The half life of oxi-starch-W was 4 and 12 days at 29 and 5°C respectively. That of oxi-starch-C was 4 days at 29°C.

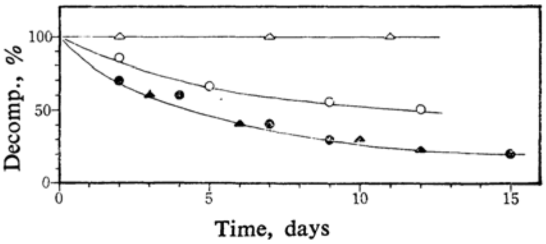

Fig. 5. Decomposition of peroxide group of oxi-starch.

△▲ Oxi-starch-C, peroxide-content 0.0023 mol./AGU
○● Oxi-starch-W, peroxide-content 0.0038 mol./AGU
△○ Preservation at 5°C
▲● Preservation at 29°C

Bulk Polymerization of MMA in the Presence of Oxi-Starch. — The results of the bulk copolymerization of MMA with oxi-starch, and of the fractionation of the products, are summarized in Table II. Polymer I was not colored by the iodine solution and was so assumed to be pure PMMA. Polymer II contained starch and was insoluble in most organic solvents. However, after hydrolysis in an acidic medium, the product dissolved in benzene. Polymer II was therefore assumed to be a starch-PMMA graft copolymer.

The polymerization of MMA initiated with oxi-starch gave a large amount of the homopolymer of PMMA and a small amount of grafted PMMA.

From this table, it can be seen that the intrinsic viscosities of grafted PMMA were slightly higher than those of free PMMA.

Emulsion Polymerization of MMA in the Presence of Oxi-Starch or Non-oxidized Starch. —The polymerization of MMA in the presence of oxi-starch was carried out in an aqueous emulsion. The results of the polymerization and of the fractionation of the products are summarized in Table III. At 90°C, the polymerization proceeded smoothly. The grafting efficiency and the grafting ratio were quite high. At 60°C, the graft copolymer was obtained.

The graft copolymer was insoluble in most organic solvents, but the acetylated graft copolymer dissolved in some solvents, as is shown in Table IV. It was also shown that its solubility lay between PMMA and starch triacetate. From this solubility, it was assumed that polymer II is a starch-PMMA graft copolymer.

The differences between the cases of oxi-starch-W and of oxi-starch-C were only with difficulty observed with regard to the conversion of MMA and the free starch content of the products. The degrees of polymerization of free PMMA and of grafted PMMA were the same. However, the grafting efficiency with oxi-starch-C was slightly higher than that with oxi-starch-W.

Unexpectedly, non-oxidized starch could initiate the polymerization of MMA to yield a graft copolymer in an aqueous emulsion state. It is clear from Table III that the initiation of polymerization is not due to the heat. However, in the absence of water, no initiation by starch itself as is shown in Table II, was observed. The results of the interesting

TABLE V. EMULSION POLYMERIZATION OF MMA IN THE PRESENCE OF STARCH OR THE DERIVATIVES

Exp. No.	Polymerization		Polymer				Graft. eff. %
	Starch or the deriv.	Polymn. time hr.	Total yield g.	Conversion %	Fractionation		
					PMMA g.	Graft and starch deriv.	
III-1	—	3	0.1480	5.3			
III-2	—	3	0.2533	9.0			
III-3	—	3	0.2713	9.7			
III-4	—	4	0.3577	12.7			
III-5	Starch[a]	3	2.2760	73.9	1.0910	1.1850	47.4
III-6	Starch[a]	3	1.4670	45.1			
III-7	Starch refined[b]	3	1.2733	38.2			
III-8	Starch refined[b]	3	1.5469	48.0			
III-9	Soluble starch[c]	3	1.1164	32.6			
III-10	Soluble starch[c]	3	0.9475	26.6			
III-11	Starch-KI[d]	3	2.1924	71.0			
III-12	Heated starch[e]	3	0.9191	25.5	0.2597	0.6594	63.9
III-13	Heated starch[e]	3	0.8866	24.5			
III-14	Dialdehyde starch[f]	3	2.9438	97.7			
III-15	Maltose[g]	3	0.1762	6.3			
III-16	Maltose[h]	3	2.0099	64.2			
III-17	Maltose[h]	3	1.9693	70.0			
III-18	Maltose[i]	3	1.5056	53.8			
III-19	Maltose[j]	3	1.8149	64.8			
III-20	Sucrose[k]	3	0.1025	3.7			
III-21	Sucrose[k]	3	0.1132	4.0			
III-22	Glucose[l]	3	0.0723	2.6			
III-23	Glucose[l]	4	0.2381	8.5			

Polymerization mixture: 0.2 g. of starch or its deriv., 3 ml. of MMA, 15 ml. of water and 0.08 g. of emulsifier

a Potato starch, from Japanese Pharmacopeia
b Purified starch by reprecipitation from aqueous solution of starch (a) with ethanol
c Soluble starch from Merck Co.
d Starch (a) was immersed in 20% solution of KI for a day, and was filtered, washed and dried.
e Starch (a) was treated by heat in air at 150°C for 5 hr.
f Oxidized starch by $NaIO_4$
g Maltose, from Difco Co.
h Maltose, from Wako Pure Chemicals Co.
i Recrystallized maltose of maltose (h)
j Solid substance from mother liquor of the recrystallization of maltose (h)
k Cane sugar, commercial pure, purity 99.9%
l Glucose, from Wako Pure Chemicals Co.

TABLE VI. MELTING POINTS OF STARCH-PMMA GRAFT COPOLYMER

Exp. No.	Graft copolymer			Hydrolysates* M. p. °C	Homopolymer		Acetates** M. p. °C
	Starch content %	[η]	M. p. °C		[η]	M. p. °C	
II-4	4.0	4.75	230∼274	230∼255	3.45	250∼264	150∼240
II-1	6.0	2.90	240∼278	241∼259	2.60	233∼264	
II-2	31.0	3.06	265∼280	235∼255	3.70	235∼255	
II-7	63.7	6.20	260∼281		5.20	240∼283	

Hydrolysates*: Hydrolysis product of the graft copolymer
Acetates** : Acetylation product of the graft copolymer

TABLE VII. POLYMERIZATION OF AN IN THE PRESENCE OF OXI-STARCH

Exp. No.	Polymerization				Polymerization product				Acetylated polymer			
	Starch		AN ml.	H_2O ml.	Total yield g.	Conversion %	Starch-content %	[η] of hydrolysates	Insoluble in pyridine		Soluble in pyridine	
	Type[a]	Peroxy-content mol./AGU							Yield g.	Starch-content %	Yield g.	Starch-content %
IV-1	C	0.0031	9	90	2.0230	17.1	39.3	5.10	1.468	20.3	0.554	89.5
IV-2	N	—	9	90	0.9100	0.0						
IV-3	—	—	9	90	0.0	0.0						

Polymerization mixture: 9 ml. of AN, 90 ml. of water and 1 g. of starch
Polymerization temp., 90°C; Time, 1 hr.
a. C: Oxi-starch-C, N: Non oxidized starch

TABLE VIII. SOLUBILITY OF ACETYLATED STARCH-PAN GRAFT COPOLYMER

Solvent	Polymer			
	Starch triacetate	Acetate*		PAN
		Soluble part	Insoluble part	
Tetrachloroethane	s	s	sw	ins
Pyridine	s	s	sw	ins
Chloroform	ss	ss	sw	ins
Dioxane	ss	sw	sw	ins
Dimethylsulfoxide	ss	sw	s	s
Acetone	sw	sw	sw	ins
Tetrahydrofuran	sw	sw	sw	ins
Ethyl acetate	sw	sw	sw	ins
Dimethylformamide	sw	sw	s	s
Benzene	sw	sw	sw	ins
Methanol	ins	ins	ins	ins
Water	ins	ins	ins	ins

* "Acetates" were separated to soluble and insoluble parts in pyridine.
s: soluble, ss: slightly soluble, sw: swell, ins: insoluble

graft-copolymerizations are tabulated in Table V.

Even starch treated with a solution of potassium iodide could initiate the polymerization of MMA. In this case, it is clear that starch had no peroxide group.

Dialdehyde starch, which was prepared by the oxidization of starch with periodic acid, could initiate the polymerization of MMA at a greatly increased rate. When starch was preheated, the rate of polymerization decreased. Glucose and purified maltose had no abilities to initiate the polymerization. However, when impure maltose was used, the polymerization of MMA started. Accordingly, the polymerization was initiated by some impurities existing in starch. The exact process still remains unexplained.

The melting points of starch-PMMA graft copolymers are shown in Table VI. They are slightly higher than the values of the homopolymer.

Polymerization of AN in the Presence of Oxi-Starch. — The polymerization of AN in the presence of oxi-starch was carried out in an aqueous suspension at 90°C. The results are shown in Table VII. The polymerization product dissolved with difficulty in most organic solvents. After its hydrolysis with 1 N hydrochloric acid at 95°C for 3 hr., a polymer soluble in dimethyl formamide was obtained. It contained no free starch.

After the acetylation of the polymerization product, it was separable into two parts: soluble and insoluble polymers in pyridine. The former was 89.5% starch, and the latter, 20.3% starch. It was assumed that the former was a mixture of PAN and starch acetate-PAN graft copolymers and that the latter was a mixture of starch acetate and a small number of the graft copolymers. The isolation of the graft copolymer was too difficult to accomplish. The solubilities of these polymers are shown in Table VIII.

No polymerization of AN by non-oxidized starch in an aqueous suspension was observed.

Polymerization of Vinyl Chloride (VC) in the Presence of Oxi-Starch. — The polymerization of VC in the presence of oxi-starch was carried out in bulk or in an aqueous

TABLE IX. POLYMERIZATION OF VC IN THE PRESENCE OF OXI-STARCH

Exp. No.	Polymerization						Polymer	
	Starch		VC ml.	H_2O ml.	Emulsifier g.	Time hr.	Total yield g.	Conversion %
	Type	Peroxy-content mol./AGU						
V-1	C	0.0031	10	0	0	7	1.0145	0.2
V-2	C	0.0031	10	0	0	7	1.0050	0.1
V-3	N	—	10	0	0	7	0.9710	0
V-4	N	—	10	0	0	7	0.9580	0
V-5	—	—	10	0	0	7	0.0000	0
V-6	C	0.0031	4	15	0.1	2	1.6123	17.1
V-7	C	0.0031	4	15	0.1	2	1.6075	16.1
V-8	N	—	4	15	0.1	2	1.0483	0.9
V-9	—	—	4	15	0.1	2	0.0000	0

Exp. No.	Polymerization					Grafting eff. %	Grafting ratio
	Homopolymer		Graft copolymer		Free starch %		
	Yield g.	[η]	Yield g.	Starch-content %			
V-6	0.520	0.49	0.321	67.6	78.0	23.5	0.5

Polymerization temp.: 60°C

emulsion, as is shown in Table IX. Only in aqueous emulsion was the polymerization observed. Polymer III did not contain starch and was assumed to be PVC. Polymer IV was 67.6% starch and was soluble in dimethyl sulfoxide. It was considered to be a starch-PVC graft copolymer. The degree of polymerization of PVC was lower. The grafting efficiency and the grafting ratio were lower than in the case of PMMA. The solubility of the graft copolymer is shown in Table X.

TABLE X. SOLUBILITY OF STARCH-PVC GRAFT COPOLYMER

Solvent	Polymer		
	Starch	Graft	PVC
Dimethylformamide	ins	sw	vs
Acetone	ins	sw	sw
Dimethylsulfoxide	s	s	s
Tetrahydrofuran	ins	ins	vs
Chloroform	ins	ins	ins
Dioxane	ins	ins	ins
Benzene	ins	ins	ins

vs: very soluble, s: soluble, sw: swell, ins: insoluble

Summary

1) Starch was oxidized with ozone in a medium of water or carbon tetrachloride to yield per-oxidized starch (abbreviated as oxi-starch-W or oxi-starch-C).

2) The stabilities of the peroxide-group of oxi-starchs were measured.

3) In the present of oxi-starch, polymerizations of methyl methacrylate (MMA), acrylonitrile (AN) and vinyl chloride were carried out. Graft copolymers of starch with vinyl polymers were obtained. Their properties were described.

4) It was confirmed that commercial starch, dialdehyde starch oxidized with periodic acid, starch treated with potassium iodide, and commercial maltose could also initiate the polymerization of methyl acrylate, yielding graft copolymers and vinyl homo-polymers.

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