

## **Anionic Graft Polymerization of Vinyl Monomers on Cellulose and Polyvinyl Alcohol**

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### **Synopsis**

Graft polymers of acrylonitrile, methacrylonitrile and methyl methacrylate on polyhydroxy polymers such as cellulose and polyvinyl alcohol were prepared by anionic graft polymerization. The alkali alkoxide derivative of the polyhydroxy polymer backbone was used as initiator of polymerization. The graft polymerizations were carried out in liquid ammonia and other inert solvents at low temperature. Grafting was accompanied by considerable homopolymerization caused by chain transfer to monomer and to ammonia. The graft polymers were separated from homopolymers and unreacted polyhydroxy polymers by extraction with suitable solvents. The per cent of the grafted vinyl polymer increased with increase in the monomer and alkoxide concentrations. No crosslinking occurred during the anionic graft polymerization, and soluble graft polymers were obtained.

### **INTRODUCTION**

Free radical graft polymerization of vinyl monomers on polyhydroxy compounds has been extensively studied. Active free radical initiation centers on the polyhydroxy polymer backbone were produced by various radiation<sup>1-5</sup> and chemical<sup>6-10</sup> methods.

The anionic polymerization of some vinyl monomers by alkali metal alkoxides<sup>11</sup> was utilized for anionic graft polymerization.<sup>12</sup> Such anionic graft polymerization on polyhydroxy polymers has not been described elsewhere. Until very recently no mention has been made of anionic graft polymerization,<sup>13</sup> and only relatively few anionic graft polymerizations have been reported since.<sup>14</sup>

In the present work alkali metal alkoxide derivatives of cellulose, polyvinyl alcohol, cellulose acetate, and polyvinyl acetate were used as initiators for the anionic graft polymerization of acrylonitrile, methacrylonitrile, and methyl methacrylate.

### **Advantages of Anionic Graft Polymerization**

Anionic graft polymerization has certain advantages as compared to that by free radicals. Radical growing ends of grafted side chains may terminate by combination leading to crosslinked insoluble polymers, whereas in

ionic graft polymerization, due to electrostatic repulsion between the growing ends, such a combination is impossible. Strongly acidic monomers, such as nitroethylene and vinylidene cyanide, which are not sufficiently active in free radical polymerization, can be grafted anionically. Anionic polymerization is also fast and can be carried out at low temperature. Contrary to most free radical polymerizations on polyhydroxy polymers, the anionic active sites on the polymer backbone are defined and fixed, so that the number of grafted side chains can be controlled.

### Preparation of Alkoxide Derivatives of Polyhydroxy Polymers

Alkali metal alkoxide derivatives of cellulose and related compounds were prepared by reaction of the polyhydroxy compound with concentrated aqueous alkali hydroxide solutions, yielding cellulose alkoxide derivatives of known alkoxide content.<sup>15</sup> They were also prepared in anhydrous systems by reacting cellulose with an alkali metal alkoxide in the derived alcohol<sup>16</sup> or dispersed in an inert solvent.<sup>17</sup> However, these methods are unsuitable for anionic graft polymerization, as the presence of water or alcohol prevents polymerization. In addition, excess of alkali present with the alkoxide derivative will lead to a simultaneous homopolymerization of the vinyl monomer. Therefore we prepared the alkoxide derivative by reacting the polyhydroxy polymer with sodium or potassium dissolved in liquid ammonia,<sup>18</sup> which has already been used as a solvent for various anionic polymerizations.

## EXPERIMENTAL

### Materials

Alphacel, ground wood cellulose powder (NBC), consisting of 99.9%  $\alpha$ -cellulose was purified by refluxing 30 g. portions in absolute ethanol (150 ml.) for 5 hr., followed by a similar refluxing in ether. The purified cellulose was dried at 100°C. for 24 hr. and kept in vacuo over phosphorus pentoxide. Dried polyvinyl alcohol (BDH) containing less than 2% acetate groups and cellulose acetate containing 36.5% acetyl groups were used. Acrylonitrile,<sup>19</sup> methacrylonitrile (Fluka),<sup>19</sup> methyl methacrylate,<sup>20</sup> dimethylformamide (DMF),<sup>19</sup> tetrahydrofuran,<sup>20</sup> and petroleum ether<sup>20</sup> were purified and dried as previously described.

### Graft Polymerization Procedure

The polymerization vessel consisted of a three-necked flask equipped with a high-speed stirrer, a separatory funnel for introducing monomer, and a soda-lime guard tube. The polyhydroxy polymer was dispersed in dry liquid ammonia, cooled to the required temperature, and the alkali metal added in portions. A characteristic deep blue color was formed which disappeared slowly as the alkali metal reacted to give the alkoxide derivative. After addition of the alkali metal, monomer was added drop-

wise with strong stirring. The polymerization was very fast. At the end of the polymerization, the ammonia was left to evaporate, the residue was ground to a fine powder (80 mesh) and heated *in vacuo* at 40°C. to remove the ammonia. It was dried *in vacuo* over phosphorus pentoxide, and the yield of the crude product determined. This product was freed from alkali metal and any bound ammonia by acidification in the cold with hydrochloric acid. In the case of cellulose, 6% dilute aqueous hydrochloric acid was used, followed by washings with cold distilled water until the precipitate was free of chloride ion. In the case of polyvinyl alcohol a 10% methanolic solution of hydrochloric acid was used, followed by washings with 80% methanol, to prevent solution of the polyvinyl alcohol which is water-soluble. The product consisting of graft polymer, vinyl homopolymer, and ungrafted polyhydroxy polymer, was dried *in vacuo* over phosphorus pentoxide.

### Separation and Purification of the Graft Polymers

The crude polymerization products obtained were separated as follows.

**Cellulose-Polyacrylonitrile Graft Polymer.** The yellow crude product was extracted with DMF in a Soxhlet apparatus *in vacuo* (98°C./45 mm.) under anhydrous conditions until the extract contained no solute. The extract was precipitated by ether and methanol or water and consisted of homopolyacrylonitrile and graft polymers having a relatively high polyacrylonitrile content. The undissolved material, consisting of graft polymer and unreacted cellulose, was stirred in the cold three times with fresh cuprammonium solution, each time for 5 hr.; this dissolved all free cellulose. The residue, which now consisted only of the pure graft polymer, was acidified with cold 5% hydrochloric acid and washed with water and methanol and dried.

**Cellulose-Polymethyl Methacrylate Graft Polymer.** The white crude polymer was extracted with benzene in a Soxhlet apparatus to remove polymethyl methacrylate homopolymer. The soluble fraction was precipitated and washed with methanol. The pure graft polymer was obtained on extraction of the unreacted cellulose as described before.

**Cellulose-Polymethacrylonitrile Graft Polymer.** The yellow crude polymer was extracted with dry acetone in a Soxhlet apparatus for 48 hr. to remove homopolymethacrylonitrile. The dissolved polymer was recovered on evaporation of the acetone *in vacuo*. The pure graft polymer remained after extraction of free cellulose.

**Polyvinyl Alcohol Graft Polymers.** The crude graft polymers of polyvinyl alcohol with polymethyl methacrylate and polymethacrylonitrile were purified from the latter homopolymers by extraction with benzene and acetone, respectively. Homopolyacrylonitrile was extracted from the crude polyvinyl alcohol-polyacrylonitrile graft polymer by stirring several times in the cold with DMF, as hot DMF dissolved also unreacted polyvinyl alcohol and part of the graft polymer in addition to the homopolyacrylonitrile. Then 1-g. portions of the insoluble fraction, consisting of

graft polymer and polyvinyl alcohol, were stirred three times with water (150 ml.) for 6 hr. to remove unreacted polyvinyl alcohol and obtain the pure graft polymers.

## RESULTS

### Graft Polymerization of Acrylonitrile on Cellulose

In the present heterogeneous graft polymerizations the amount of grafted polyacrylonitrile increased with increasing initial monomer concentration (compare experiments 6 and 7 with 8 and 9) (Table I) and with electropositivity of the alkali metal,  $K > Na$ . There were no significant differences in the yield of graft polymer on addition of the monomer dropwise or in one portion to the reaction mixture.

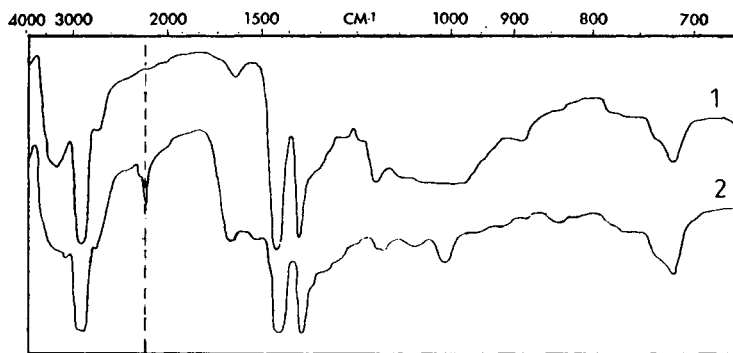


Fig. 1. Infrared spectrum of polyacrylonitrile-cellulose graft polymer: (1) cellulose; (2) graft polymer.

A considerable amount of homopolymer was also formed. The nitrogen content of the polyacrylonitrile extracted by DMF was much lower than the theoretical (26.4%) and its infrared spectra showed absorptions at 3300  $\text{cm}^{-1}$  (OH groups), and 1050–1150  $\text{cm}^{-1}$  (ether groups) in addition to those characteristic for polyacrylonitrile. This indicates that graft polymers having a high polyacrylonitrile content are soluble in DMF.

The fraction extracted with cuprammonium solution contained, besides unreacted cellulose, also graft polymers having a low polyacrylonitrile content, as shown from infrared spectra of these fractions and their nitrogen content. The pure graft polymers had a polyacrylonitrile content of about 70–80% and were soluble in hot 72% zinc chloride solution, which excludes the possibility of crosslinking. Their infrared spectra (Fig. 1) showed the characteristic absorptions of both cellulose and polyacrylonitrile.

The alkoxide derivative was isolated free from ammonia and dispersed in inert solvents for graft polymerization. The yield of the graft polymer was much lower than in the case of liquid ammonia (Table I). In petro-

TABLE I. Graft Polymerization of Acrylonitrile on Cellulose<sup>a</sup>

Expt. no.	Alkali metal	Equiv./ glucose unit	Time of addition of monomer, min.	Polymerization time, min.	Yield after acidification, g. <sup>b</sup>	Fraction insoluble in DMF		Fraction insoluble in cuprammonium		Fraction soluble in cuprammonium, %	Yield, g.	N, %	Poly-AN in graft polymer, %	Fraction soluble in DMF, N, %
						Yield, g.	N, %	Yield, g.	N, %					
1	Na	2.25	0.091	°	15	11.6	91	3.6	13.6	—	1.74	15.0	60.1	0.7
2	Na	2.25	0.091	45	0	11.5	84	3.4	13.0	23.3	1.13	11.0	76.4	0.8
3	Na	2.28	0.091	°	80	11.3	87	4.5	17.0	18.5	2.32	20.5	60.0	0.8
4	Na	2.23	0.091	150	5	12.8	88	4.2	16.0	18.5	2.15	19.0	61.2	0.6
5	Na	2.17	0.377	45	0	26.0	40	4.8	18.1	—	1.13	11.0	21.5	1.5
6	K	2.37	0.392	165	15	19.0	70	13.2	50.0	21.3	9.16	55.9	19.0	1.2
7	K	2.37	0.377	230	0	29.6	66	12.6	47.7	23.8	10.5	77.8	22.9	1.1
8	K	2.37	0.151	°	180	13.5	91	6.4	24.2	18.9	—	—	—	—
9	K	2.37	0.151	107	180	11.4	90	4.5	17.0	—	—	—	—	—
10 <sup>d</sup>	K	2.00	0.151	°	90	13.5	66	1.8	6.8	22.6	0.6	6.5	16.1	0.4
11 <sup>e</sup>	Na	2.30	0.388	180	10	29.5	33	1.4	5.3	23.1	0.5	5.1	5.7	0.5
12 <sup>f</sup>	Na	1.00	0.283	°	45	15.4	19	9.2	35.0	24.4	0.18	6.2	20.6	—
13 <sup>g</sup>	Na	2.00	0.151	°	110	11.8	82	1.4	5.3	21.3	0	—	—	1.2

<sup>a</sup> Experimental conditions: 10 g. cellulose; 200 ml. liquid ammonia; temperature of polymerization  $-78^{\circ}\text{C}$ .

<sup>b</sup> The yields before neutralization were approximately quantitative. Part of the product dissolved during acidification (see Table II).

<sup>c</sup> Monomer added in one portion.

<sup>d</sup> Polymerization carried out in petroleum ether.

<sup>e</sup> Polymerization carried out in dimethylformamide.

<sup>f</sup> Polymerization carried out in a solution of 75 g. sodium thiocyanate in 400 ml. liquid ammonia; 1.9 g. cellulose was used.

<sup>g</sup> Polymerization carried out in tetrahydrofuran.

leum ether the fraction insoluble in DMF contained 7% grafted polyacrylonitrile, and in DMF this fraction contained 5% grafted polyacrylonitrile.

A solution of sodium thiocyanate in liquid ammonia is a good solvent for cellulose. Graft polymerization was carried out in this solvent (experiment 12) (Table I) with the expectation of better results. But on addition of a solution of metallic sodium in liquid ammonia to the dissolved cellulose, the alkoxide derivative precipitated out as a gel, and the graft polymerization was subsequently carried out in a heterogeneous condition. The results were similar to those obtained with liquid ammonia.

TABLE II

Graft Polymerization of Acrylonitrile on Cellulose and Acidification of the Crude Polymerization Mixture<sup>a</sup>

Expt. no.	Yield before acidification, g. <sup>b</sup>	Fraction insoluble on acidification		Fraction soluble on acidification	
		Yield, g.	N, %	Yield, <sup>c</sup> %	N, %
5	29.9	26.0	15.8	13	—
3	16.5	13.0	5.7	21	17.9
4	15.9	12.8	4.9	20	19.2
8	19.5	11.7	—	30	14.2
13	19.2	11.8	—	38	16.7

<sup>a</sup> Experimental conditions for polymerization: see Table I.

<sup>b</sup> Calculated from the weight of the crude polymer obtained less the weight of alkali metal introduced.

<sup>c</sup> Calculated from the difference between the yields before and after acidification. The soluble fraction was not collected completely, and the per cent of nitrogen reported is of the fraction collected.

During acidification of the crude product, obtained after evaporation of the ammonia, by cold 6% aqueous hydrochloric acid, about 10–40% of the product dissolved (Table II), which partially precipitated on addition of the aqueous washings and on standing. These fractions contained a high nitrogen content (14–20%), and their infrared spectra showed absorptions of nitrile groups and of cellulose. Cyanoethyl cellulose having a degree of substitution (D.S.) of 0.7–1 is soluble in acidic, neutral, and basic aqueous solutions, and that of D.S. > 1 is partially soluble.<sup>21</sup> It may therefore be that these soluble fractions are cyanoethyl cellulose and low grafted cyanoethyl cellulose. It was shown<sup>22</sup> that cyanoethylation of alcohol occurred during the heterogeneous polymerization of acrylonitrile by alcoholic solutions of alkoxides.

### Graft Polymerization of Acrylonitrile on Polyvinyl Alcohol

Polyvinyl alcohol is soluble in liquid ammonia but the alkoxide derivative is insoluble. Much homopolymer was formed, and this was extracted

TABLE III  
Graft Polymerization of Acrylonitrile on Polyvinyl Alcohol<sup>a</sup>

Expt. no.	Equiv. Na/OH group	Monomer, mole	Yield after acidification, g.	Fraction insoluble in DMF		Grafted poly-AN, %	Fraction soluble in DMF, N, %	Fraction insoluble in water <sup>b</sup>		Fraction soluble in water, N, %
				Yield, g.	%			Yield, %	N, %	
14	0.9	0.091	7.7	4.25	55	8.1	18.5	32	6.0	7.8
15	0.9	0.091	7.8 <sup>c</sup>	3.6	48	7.3	18.3	28	5.2	6.4
16	0.5	0.091	—	—	37	2.8	19.2	—	—	—
17	0.5	0.091	—	—	46	4.0	18.7	—	—	—
18	0.9	0.182	12.4	10.7	85	12.8	19.8	35	9.0	13
19	0.9	0.182	12.5	10.9	87	11.0	20.2	35	6.4	14.1
20	0.5	0.182	—	—	30	5.6	19.2	—	—	—
21	0.5	0.182	—	—	29	7.0	18.7	—	—	—
22	0.9	0.272	17.6 <sup>d</sup>	5.3	33	—	—	—	—	—
23	0.9	0.272	17.4 <sup>e</sup>	5.3	34	5.5	16.4 <sup>f</sup>	30	4.1	5.1
24	0.9	0.151	10.8	6.7	62	11.8	18.8	—	—	—

<sup>a</sup> Experimental conditions: 3 g. polyvinyl alcohol; 250 ml. liquid ammonia; sodium metal was used; monomer was added during 10 min.; temperature of polymerization  $-60^{\circ}\text{C}$ ., time of polymerization 2 hr.

<sup>b</sup> The fraction insoluble in DMF was extracted with water.

<sup>c</sup> Extraction with hot DMF: yield, 33%; N, 5.3%; grafted poly-AN, 20.1%.

<sup>d</sup> Extraction with hot DMF: yield, 17%; N, 1.6%; grafted poly-AN, 6.0%.

<sup>e</sup> Extraction with hot DMF: yield, 17%; N, 2.0%; grafted poly-AN, 7.6%.

<sup>f</sup> The relatively low nitrogen content indicates solubility of graft polymer in DMF.

with cold DMF. The extract contained also graft polymers having a relatively high polyacrylonitrile content, which was evident from the low nitrogen analyses, 17–20% (theoretical 26.4%), and from the infrared spectra.

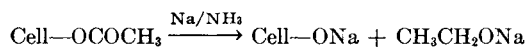
The amount of grafted polyacrylonitrile in the fraction insoluble in DMF increased both with increase in the alkoxide and monomer concentrations (compare experiments 14,15 with 16,17 in Table III, and experiments 14,15 with 18,19 or 16,17 with 20,21). But with relatively high monomer concentration (experiment 23), the amount of grafted polyacrylonitrile decreased. However, the fraction soluble in DMF contained in this case an exceptionally low nitrogen content (16.4%) and must have incorporated with the homopolymer a relatively large amount of graft polymer rich in polyacrylonitrile which is soluble in DMF. Such graft polymers could have been formed as a result of the relatively large monomer concentration used.

On extraction of the crude polymer with hot DMF, an insoluble residue remained which contained 6–20% grafted polyacrylonitrile; this provides a good proof for the formation of graft polymers on polyvinyl alcohol. About 30% of the DMF-insoluble fraction was insoluble in water, providing also a good proof for the formation of graft polymers. The water-soluble fractions had a high nitrogen content, and their infrared spectra showed the presence of polyacrylonitrile and polyvinyl alcohol. It may be that these water-soluble fractions contained besides unreacted polyvinyl alcohol, partially cyanoethylated polyvinyl alcohol, low grafted cyanoethyl polyvinyl alcohol, and certain graft polymers on polyvinyl alcohol as was found in the case of cellulose.

Infrared spectra of the pure graft polymers showed the absorptions for polyacrylonitrile and polyvinyl alcohol (Fig. 2).

### Graft Polymerization of Acrylonitrile on Cellulose Acetate

On addition of alkali metal to a solution of cellulose acetate in liquid ammonia, a white precipitate formed which on neutralization and isolation was found from its infrared spectrum (Fig. 3) to be pure cellulose. This cellulose was formed by reduction of the cellulose acetate by the alkali metal in the same way as esters are reduced to the corresponding alcohols:<sup>23</sup>



The infrared spectra of the graft polymers obtained were identical to those of cellulose–polyacrylonitrile graft polymers. In the preparation of these graft polymers starting from cellulose acetate, there is the advantage that the cellulose alkoxide is formed as a fine precipitate having a large surface area which increases the extent of the heterogeneous graft polymerization. On the other hand the simultaneous formation of the alkali ethoxide is a great disadvantage, as it leads to homopolymerization of the vinyl monomer.



TABLE IV  
Graft Polymerization of Acrylonitrile on Cellulose Acetate<sup>a</sup>

Expt. no.	Alkali metal	Equiv./glucose unit	Monomer, mole	Yield after acidification, g. <sup>b</sup>	Fraction insoluble in DMF			Fraction insoluble in cuprammonium				
					Yield g.	N, %	Grafted poly-AN, %	Yield g.	N, %	Poly-AN in graft polymer, %		
25 <sup>c</sup>	Na	2.0	0.302	14.3	2.4	17	6.6	25	0.36	14.8	13.5	51.0
26 <sup>d</sup>	K	1.43	0.377	21.7	5.3	24	7.0	26.5	—	—	—	—

<sup>a</sup> Experimental conditions: 200 ml. liquid ammonia; monomer added during 2 hr.; polymerization time after addition of monomer 15 min.; polymerization temperature  $-78^{\circ}\text{C}$ .

<sup>b</sup> Yield before acidification was quantitative.

<sup>c</sup> A 5-g. portion of cellulose acetate was used.

<sup>d</sup> A 10-g. portion of cellulose acetate was used.

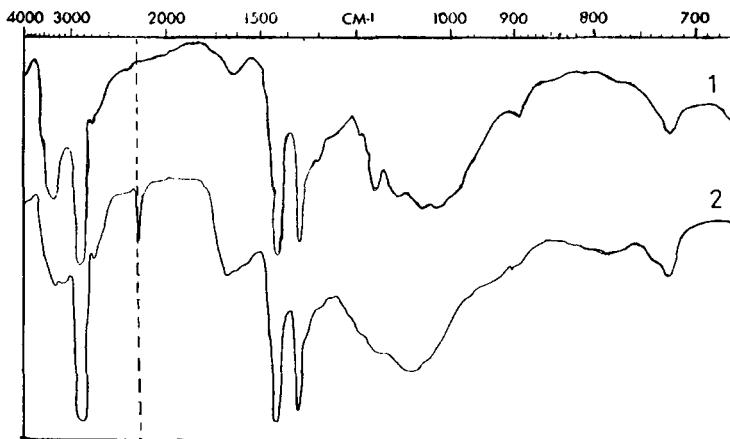


Fig. 2. Infrared spectrum of polyacrylonitrile-polyvinyl-alcohol graft polymer: (1) polyvinyl alcohol; (2) graft polymer.

Actually there was no advantage in starting with cellulose acetate for the preparation of cellulose-polyacrylonitrile graft polymers (Table IV).

#### Graft Polymerization of Acrylonitrile on Polyvinyl Acetate

Polyvinyl acetate dissolved in liquid ammonia was partially reduced and precipitated by alkali metal (1 equiv.) as in the case of cellulose acetate. The reduced product contained no nitrogen, and its infrared spectrum showed the absorptions typical of both polyvinyl alcohol and polyvinyl acetate. It was soluble in benzene.

Polyvinyl acetate (5 g.) was dissolved in liquid ammonia (250 ml.) at  $-60^{\circ}\text{C}$ . and 1 equiv. of sodium metal was added followed by acrylonitrile (180 mmole), and the graft polymerization was carried out as usual.

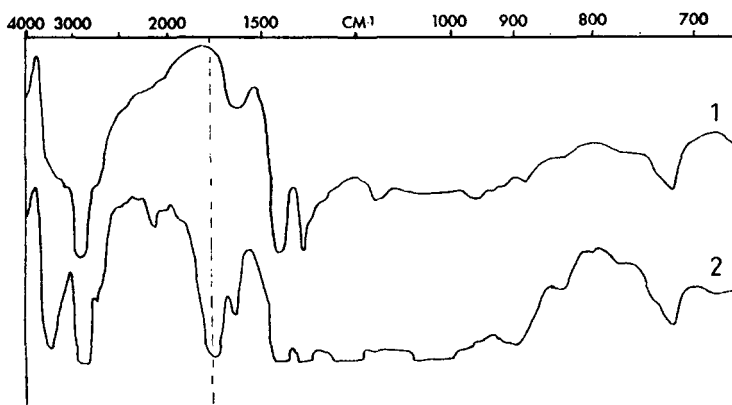


Fig. 3. Infrared spectrum of cellulose acetate after treatment with sodium in liquid ammonia: (1) treated polymer; (2) untreated polymer.

TABLE V

No. of fraction	Weight of fraction, g.	N, %
1*	0.2	5.2
2	0.25	9.2
3	0.1	16.6
4	0.2	19.8
5	0.2	19.9

\* Fraction that was insoluble in DMF.

The product was neutralized, dried, and extracted with benzene and with methanol. The residue was dissolved in DMF (1 g./100 ml.) and a rough fractionation was carried out by addition of 90% methanol as precipitant at 23°C. Five fractions were precipitated (Table V).

The variation in the nitrogen content indicates the formation of graft polymers having varying degrees of grafting.

#### Graft Polymerization of Methyl Methacrylate on Cellulose

The anionic polymerization of methyl methacrylate by sodium methoxide has been mentioned.<sup>24</sup> It was polymerized easily by the alkoxide derivative of cellulose and polyvinyl alcohol in liquid ammonia.

The yield of the graft polymers in the fraction insoluble in benzene, was relatively low (Table VI). The yield of the fraction insoluble in cuprammonium solution, consisting of the pure graft polymer, was also small. The fraction dissolved in cuprammonium solution contained about 4-8% grafted polymethyl methacrylate.

The benzene-soluble fraction contained, besides homopolymethyl methacrylate, some graft polymers rich in polymethyl methacrylate. In one experiment five fractions were precipitated with petroleum ether from the benzene extract, and their methoxyl content was determined. The first fraction contained 25.5% methoxyl, the second 27.0%, and the fifth 29.2%, as compared to 31% for the pure homopolymer. The infrared spectrum of the first fraction showed absorption bands for both polymethyl methacrylate and cellulose, while the fifth fraction was almost pure polymethyl methacrylate (Fig. 4).

#### Graft Polymerization of Methyl Methacrylate on Polyvinyl Alcohol

For a relatively high monomer concentration, the fraction insoluble in benzene contained less grafted polymethyl methacrylate than that obtained with lower monomer concentration (Table VII). The fraction insoluble in benzene was extracted with water, and about 10% of the polymer dissolved, the rest being the pure graft polymer.

#### Graft Polymerization of Methacrylonitrile on Polyvinyl Alcohol

The yield of graft polymer increased with amount of added monomer in the range of 0.059-0.118 mole under the specified experimental conditions

TABLE VI  
Graft Polymerization of Methyl Methacrylate on Cellulose<sup>a</sup>

Expt. no.	Monomer, mole	Poly-mer-ization time, min.	Yield before acidifica-tion, g. <sup>b</sup>	Yield after acidifica-tion, g.	Fraction insoluble in benzene		Fraction insoluble in cuprammonium		Grafted poly-MMA, %	Poly-MMA in graft polymer, %	Fraction soluble in benzene, OCH <sub>3</sub> , %		Fraction soluble in cuprammonium	
					Yield g.	%	Yield g.	%			Yield g.	%	Yield g.	%
27 <sup>c</sup>	0.35	120 <sup>d</sup>	45.1	—	12	38	9.4	4	0.5	80	30.0	1.5	4.8	
28 <sup>c</sup>	0.30	50	38.4	35.1	10.2	34	9.3	11	1.15	44.2	27.0	2.4	7.7	
29 <sup>e</sup>	0.23	30	34.3	29.6	8.5	37	10.0	8	0.65	43.2	27.5	1.4	4.5	
30 <sup>e</sup>	0.25	30	—	26.7	8.2	31	10.6	10	0.85	41.0	28.9	1.2	3.9	

<sup>a</sup> Experimental conditions: 10 g. cellulose; 200 ml. liquid ammonia; monomer added in one portion; temperature of polymerization -78°C.

<sup>b</sup> Calculated from total weight of product less the weight of alkali metal introduced.

<sup>c</sup> Sodium metal, 2.23 equiv./glucose unit was used.

<sup>d</sup> Monomer added during 30 min.

<sup>e</sup> Potassium metal, 2.37 equiv./glucose unit was used.

TABLE VII  
Graft Polymerization of Methyl Methacrylate on Polyvinyl Alcohol<sup>a</sup>

Expt. no.	Metal	Equiv./OH group	Monomer, mole	Yield after acidification		OCH <sub>3</sub> after acidification, %	Fraction insoluble in benzene			
				g.	%		Yield	Grafted poly-MMA, %		
31	Na	1.00	0.047	6.7	87	15.5	2.7	40	5.4	17.4
32	K	1.39	0.094	9.7	78	12.8	5.4	56	3.6	11.6

<sup>a</sup> Experimental conditions: 3 g. polyvinylalcohol, 200 ml. liquid ammonia, monomer added dropwise during 10 min., temperature of polymerization -60°C., polymerization time 2 hr.

TABLE VIII  
Graft Polymerization of Methacrylonitrile on Polyvinyl Alcohol<sup>a</sup>

Expt. no.	Metal	Monomer, mole <sup>b</sup>	N in residue after acidification, %	Fraction insoluble in acetone		Grafted poly-MAN, %	Fraction soluble in acetone, N, %	Fraction insoluble in water		Grafted poly-MAN, %	Fraction soluble in water
				Yield g.	%			N, %	Poly-MAN in graft polymer, %		
33	Na	0.059	12.8	1.8	26	14.8	19.2	—	—	—	—
34	Na	0.118	13.0	6.2	56	34.4	19.4	9.5	45.6	1.1	5.2
35	K	0.118	13.6	4.4	40	38.3	19.0	10.2	49.0	1.3	6.3
36	K	0.118	13.3	5.7	52	37.5	18.9	10.8	51.9	0.8	3.8
37	K	0.177	—	6.9	46	39.4	13.1	11.1	53.3	1.2	5.8
38 <sup>c</sup>	K	0.059	—	1.7	34	34.4	18.8	—	—	—	—
39 <sup>c</sup>	K	0.059	—	1.6	32	35.4	19.4	—	—	—	—

<sup>a</sup> Experimental conditions: 3 g. polyvinyl alcohol, 250 ml. liquid ammonia, 1 equiv. alkali metal/OH group was used; monomer added during 10 min., temperature of polymerization  $-60^{\circ}\text{C}$ ., time of polymerization 2 hr.

<sup>b</sup> The yield was quantitative.

<sup>c</sup> Polyvinyl alcohol (1 g.) was stirred for 1 hr. in tetrahydrofuran (50 ml.) under nitrogen and potassium naphthalene in tetrahydrofuran (0.5 equiv./OH group) added at room temperature. After color of reagent disappeared, monomer was added. Time of polymerization 1 hr.

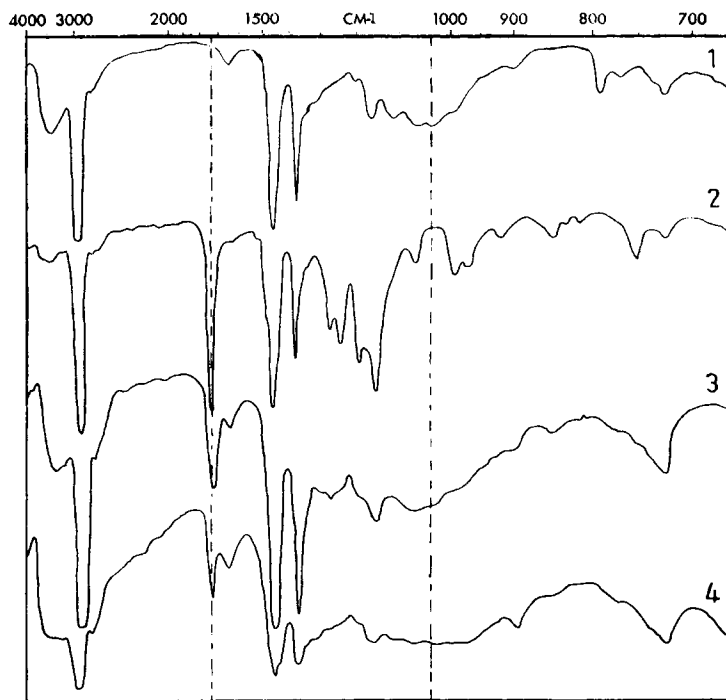


Fig. 4. Infrared spectra of polymethyl methacrylate-cellulose graft polymers: (1) cellulose; (2) homopolymethyl methacrylate; (3) graft polymer (containing 13.7% methoxyl); (4) graft polymer precipitated from the benzene extraction (fraction containing 25.5% methoxyl).

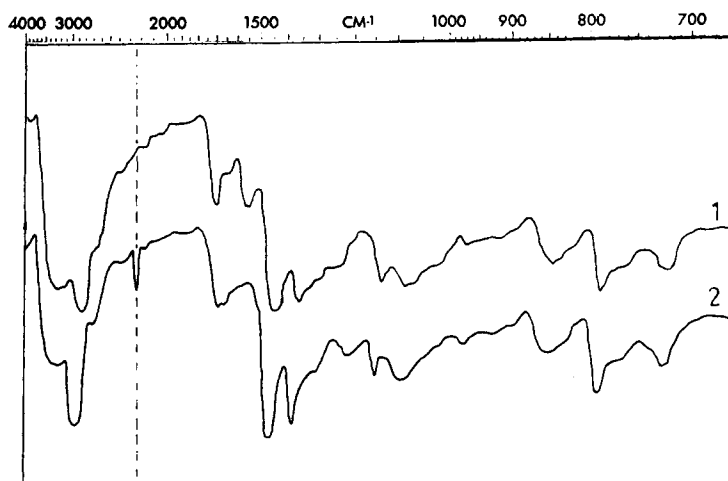


Fig. 5. Infrared spectrum of polymethacrylonitrile-polyvinyl alcohol graft polymer: (1) polyvinyl alcohol; (2) graft polymer.

TABLE IX  
Graft Polymerization of Methacrylonitrile on Cellulose<sup>a</sup>

Expt. no.	Monomer, mole	Product after acidification		Fraction insoluble in acetone		Grafted poly-MAN, %		Fraction soluble in acetone, N, %		Fraction insoluble in acetone and in cuprammonium	
		Yield, g.	N, %	Yield, g.	N, %	Yield, %	N, %	Yield, %	N, %	Yield, %	N, %
39	0.118	13.0	12.5	4.9	37.5	2.2	10.5	15.7	34	3.7	17.7
40	0.177	16.9	13.5	5.1	30	3.2	15.3	17.6	25	4.1	19.7

<sup>a</sup> Experimental conditions: 5 g. cellulose; 250 ml. liquid ammonia; monomer added dropwise during 10 min.; 1.7 equiv. of K/glucose unit was used; temperature  $-60^{\circ}\text{C}$ .; polymerization time 2 hr.

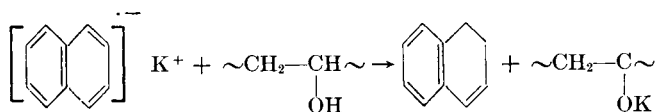


(Table VIII). At still higher amounts of monomer (0.177 mole), the per cent of grafted polymethacrylonitrile in the acetone-insoluble fraction did not increase further; on the other hand, graft polymer of relatively high polymethacrylonitrile content dissolved in the acetone extract together with the homopolymer. This is seen from the exceptionally low nitrogen analyses of this fraction (experiment 37).

On extraction with water, about 15% of the fraction insoluble in acetone dissolved; this fraction consisted of unreacted polyvinyl alcohol and low graft polymers having about 5% grafted polymethacrylonitrile.

The residue insoluble in both acetone and water, which is the pure graft polymer, was soluble completely in DMF (1 g. in 50 ml.). This provides evidence that no crosslinking occurred during the graft polymerization. The infrared spectrum (Fig. 5) showed the absorptions of both polymethacrylonitrile and polyvinyl alcohol.

Tetrahydrofuran was also used as solvent for the graft polymerization. The potassium alkoxide derivative of the polyvinyl alcohol was prepared by metallation with potassium naphthalene:<sup>25</sup>



From the results (Table VIII) it is seen that the fraction insoluble in acetone contained about 35% grafted polymethacrylonitrile.

#### Graft Polymerization of Methacrylonitrile on Cellulose

Graft polymers of relatively low polymethacrylonitrile content were obtained (Table IX). The fraction soluble in acetone contained besides homopolymethacrylonitrile also graft polymers rich in polymethacrylonitrile (Fig. 6).

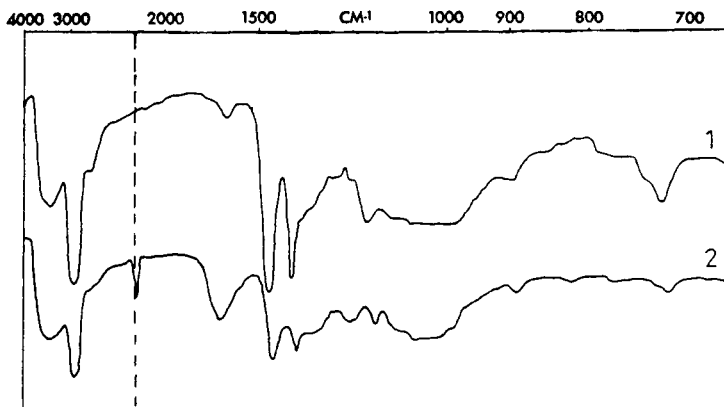
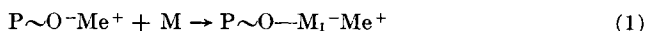


Fig. 6. Infrared spectrum of polymethacrylonitrile-cellulose graft polymer: (1) cellulose; (2) graft polymer.

### Mechanism of the Graft Polymerization

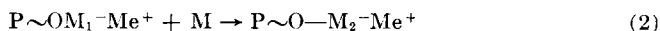
The formation of graft polymers is in accordance with the scheme shown in eqs. (1)–(5).

Initiation:

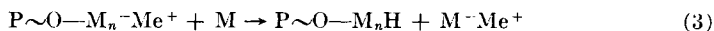


P = polyhydroxy polymer; M = vinyl monomer; Me = alkali metal.

Propagation:

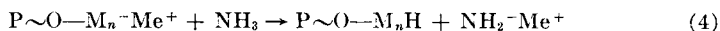


Termination: (a) Chain transfer to monomer:



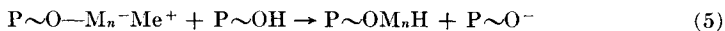
(In the case of acrylonitrile  $M^{-}$  is  $CH_2=\bar{C}-CN$ .)

(b) Chain transfer to the solvent:



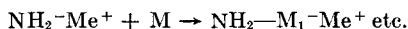
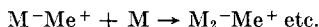
Such a termination occurred, for example, in the anionic polymerization of styrene in liquid ammonia.<sup>26</sup>

(c) Transfer to the free hydroxyl hydrogen of the polyhydroxy polymer:



Termination according to eq. (5) leads only to formation of new initiation centers on the polyhydroxy polymer. In the heterogeneous polymerization of acrylonitrile by alcoholic solutions of alkali metal alkoxides, termination was by transfer to the alcohol.<sup>22</sup> In the present case, however, termination according to eq. (5) must be of minor importance, as the free hydroxyl groups are attached to an insoluble polymer.

The homopolymers were formed by initiation either by the active carbanion  $M^{-}$ , formed in eq. (3)<sup>27</sup> or by the amide anion formed in reaction (4) as follows:



Accordingly, in the infrared spectrum the homopolymers of acrylonitrile showed absorptions for a double bond conjugated to a nitrile group at 2200  $cm^{-1}$ .<sup>28</sup>

In the case of methacrylonitrile and methyl methacrylate, which have no acidic  $\alpha$ -hydrogen, termination by transfer to monomer is impossible, and the formation of homopolymer was due to initiation by  $NH_2^{-}$  formed in eq. (4). Support for this is the fact that the homopolymethyl methacrylates extracted by benzene and containing about 30% methoxyl groups (i.e., pure homopolymers) contained 0.15–0.3% nitrogen. Based on the assumption that each polymer chain has one amino endgroup, the molecular weights of the polymers were in the range  $5-9 \times 10^3$ . Such an order of

molecular weights has been obtained in the anionic polymerization of methyl methacrylate by sodamide in liquid ammonia.<sup>29</sup>

### References

1. Restaino, A. J., in *Effects of Radiation on Materials*, Reinhold, New York, 1958, p. 287.
2. Magat, E. E., and D. Tanner, Belg. Pat. 546,817 (1955).
3. Usmanov, Kh., B. I. Aikhodzhaev, and U. Azizov, *J. Polymer Sci.*, **53**, 87 (1961).
4. Tsuji, W., R. Kitamura, T. Ichiba, and Y. C. Kado, *Kogyo Kagaku Zasshi*, **63**, 1527 (1960).
5. Geacintov, N., V. Stannett, and E. W. Abrahamson, *Makromol. Chem.*, **36**, 52 (1959); N. Geacintov, V. Stannett, E. W. Abrahamson, and J. J. Hermans, *J. Appl. Polymer Sci.*, **3**, 54 (1960).
6. Bridgeford, D. J., *Ind. Eng. Prod. Res. Develop.*, **1**, 45 (1962).
7. Mino, G., and S. Kaizerman, *J. Polymer Sci.*, **31**, 242 (1958).
8. Sankalia, S. M., D. K. R. Chaudhuri, and J. J. Hermans, *Can. J. Chem.*, **40**, 2249 (1962).
9. Kimora, S., and M. Imoto, *Makromol. Chem.*, **42**, 140 (1960).
10. Kargin, V. A., and B. I. Khodshev, *Vysokomol. Soedin.*, **1**, 149 (1959).
11. Zilkha, A., B. A. Feit, and M. Frankel, *Proc. Chem. Soc.*, **1958**, 225; *J. Chem. Soc.*, **1959**, 928.
12. Zilkha, A., B. A. Feit, and A. Bar-Nun, Israel Pat. 15,962 (August 30, 1961).
13. Smets, G., and R. Hart, *Fortschr. Hochpolym. Forsch.*, **2**, 173 (1960).
14. Zilkha, A., A. Eisenstadt, and A. Ottolenghi, *Bull. Res. Council Israel*, **11A3**, 159 (1962); G. Greber and G. Egle, *Makromol. Chem.*, **64**, 207 (1963) and previous papers of this series; A. Dondos and P. Rempp, *Bull. Soc. Chim. France*, **1962**, 2313; D. Braun and I. Loflund, *Makromol. Chem.*, **53**, 219 (1962); J. Gole, G. Goutiere, and P. Rempp, *Compt. Rend.*, **254**, 3867 (1962).
15. Gaver, K. M., E. P. Lasure, and D. V. Tieszen, U. S. Pat. 2,572,923 (Oct. 30, 1951).
16. Schwenker, R. F., and T. Kinoshita, *J. Polymer Sci.*, **51**, 185 (1961).
17. Deriviskaya, V., M. Prokofeva, and Z. Rogovin, *Zh. Obshch. Khim.*, **28**, 1368 (1958).
18. Scherer, P. C., and R. E. Hussey, *J. Am. Chem. Soc.*, **53**, 2344 (1931); I. E. Muskat, *J. Am. Chem. Soc.*, **56**, 693, 2449 (1934).
19. Zilkha, A., B. A. Feit, and M. Frankel, *J. Polymer Sci.*, **49**, 231 (1961).
20. Zilkha, A., S. Barzakay, and A. Ottolenghi, *J. Polymer Sci.*, **A1**, 1813 (1963).
21. Ott, E., and H. M. Sperlin, *Cellulose*, Interscience, New York, 1954, p. 956.
22. Zilkha, A., and B. A. Feit, *J. Appl. Polymer Sci.*, **5**, 251 (1961).
23. Audrieth, L. F., and J. Kleinberg, *Non-Aqueous Solvents*, Wiley, New York, 1953, p. 111.
24. Schildknecht, C. E., *Ind. Eng. Chem.*, **50**, 107 (1958).
25. Zilkha, A., and Y. Avni, Israel Pat. Appl. 19379 (June 1963).
26. Higginson, W. C. E., and N. S. Wooding, *J. Chem. Soc.*, **1952**, 760.
27. Feit, B. A., and A. Zilkha, *J. Appl. Polymer Sci.*, **7**, 287 (1963).
28. Bellamy, L. J., *The Infrared Spectra of Complex Molecules*, 2nd Ed., Methuen, London, 1958, p. 264.
29. Goode, W. E., W. H. Snyder, and R. C. Fettes, *J. Polymer Sci.*, **42**, 367 (1960).

### Résumé

On a préparé des polymères greffés d'acrylonitrile de méthacrylonitrile et de méthacrylate de méthyle sur des polymères polyhydroxylés, tels la cellulose et l'alcool polyvinyle, par polymérisation anionique greffée. L'initiateur de polymérisation était

constitué par le dérivé alcoolate alcalin de la chaîne polyhydroxylée principale. Les polymérisations greffées ont été effectuées dans l'ammoniac liquide et dans d'autres solvants inertes à basse température. En plus du greffage, il y a une homopolymérisation considérable causée par un transfert de chaîne sur le monomère et sur l'ammoniac. On a séparé les polymères greffés des homopolymères et des polymères polyhydroxylés non modifiés par extraction au moyen de solvants adéquats. Le pourcentage de polymère vinylique greffé augmente avec la concentration en monomère et en groupements alcoolates. Il ne se produit pas de pontage pendant la polymérisation anionique greffée et les polymères greffés obtenus sont solubles.

### Zusammenfassung

Pfropfpolymeren von Acrylnitril, Methacrylnitril und Methylmethacrylat auf Polyhydroxypolymeren wie Cellulose und Polyvinylalkohol wurden durch anionische Pfropfpolymerisation hergestellt. Das Alkalialkoxyderivat der Polyhydroxypolymerkette wurde als Polymerisationsstarter verwendet. Die Pfropfpolymerisation wurde in flüssigem Ammoniak und anderen inerten Lösungsmitteln bei niedriger Temperatur ausgeführt. Während der Aufpfropfung erfolgte durch Kettenübertragung zum Monomeren und zu Ammoniak eine beträchtliche Homopolymerisation. Die Pfropfpolymeren wurden von den Homopolymeren und den nichtumgesetzten Polyhydroxypolymeren durch Extraktion mit geeigneten Lösungsmitteln getrennt. Der Prozentsatz an aufgepfropftem Vinylpolymeren nahm mit steigender Monomer- und Alkoxydkonzentration zu. Während der anionischen Pfropfpolymerisation trat keine Vernetzung auf und es wurden lösliche Pfropfpolymeren erhalten.

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