

## Anionic Graft Polymerization of Acrylonitrile and Methacrylonitrile on Cellulose Acetate

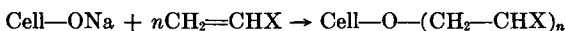
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### Synopsis

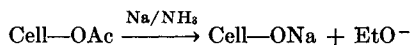
The anionic graft polymerization of AN and MAN on cellulose acetate alkoxide derivative (Li, Na, K) was investigated in THF, DMF, and DMSO. Although the yield of the polymerization was high the extent of grafting of acrylonitrile was low (1.4-5.3% in DMF and DMSO and 20% in THF) due to homopolymerization caused by chain transfer to monomer. With methacrylonitrile which has no acidic  $\alpha$ -hydrogen the amount of grafted monomer was higher (37-72%).

### INTRODUCTION

The alkali metal alkoxide derivatives of cellulose and poly(vinyl alcohol) were recently used as initiators of the anionic graft polymerization of vinyl monomers,<sup>1</sup> e.g.,

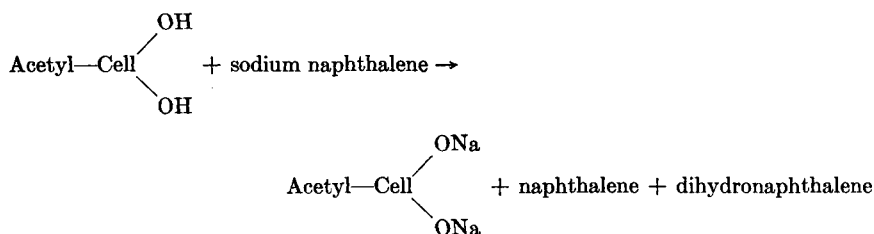


The alkoxide derivatives of the polyhydroxy polymers were prepared in liquid ammonia, in which solvent the subsequent graft polymerization was carried out. The graft polymerization was accompanied by considerable homopolymerization caused by chain transfer to monomer and to ammonia. Soluble graft polymers were obtained. Preparation of the alkoxide derivative of cellulose acetate by the same procedure and subsequent graft polymerization led to degradation of the cellulose acetate and formation of graft polymers of cellulose, the ester groups being reduced<sup>2</sup> by Na/NH<sub>3</sub> to the cellulose alkoxide derivative which initiates graft polymerization.



The presence of the ethoxide anions also leads to homopolymerization of the vinyl monomers.

Since no method is known for the formation of alkoxide derivatives of cellulose acetate without accompanying degradation, we have developed in the course of the present work a new method for the formation of alkoxide derivatives of cellulose acetate,<sup>3</sup> using the reaction of alkali metal naphthalenes with cellulose acetate in an inert solvent:



The corresponding reaction with simple alcohols is well known.<sup>4</sup> This method was found to be efficient for the preparation of the alkali metal alkoxide derivative of cellulose acetate and also for subsequent graft polymerization, since the side products do not interfere; also no degradation occurred.<sup>3</sup>

## RESULTS AND DISCUSSION

We have investigated the yield of the polymerization of acrylonitrile (AN) and methacrylonitrile (MAN) initiated by the Li, Na, and K alkoxide derivatives of cellulose acetate, in tetrahydrofuran (THF), dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) (Table I). Acrylonitrile was found to be more reactive than MAN, as known from ordinary anionic polymerization. The yield of the polymerization was dependent on the electropositivity of the alkali metal counterion, the lithium alkoxide being the weaker initiator. With lithium alkoxide under the conditions investi-

TABLE I  
Graft Polymerization of Acrylonitrile and Methacrylonitrile on Cellulose Acetate<sup>a</sup>

Run no.	Alkali metal alkoxide	Monomer	Solvent	[Alkoxide] × 10 <sup>2</sup> , mole/l.	[Mono-mer], mole/l.	Crude yield, % <sup>b</sup>
14C	Li	AN	THF	8.0	0.92	0
15C	Li	AN	DMF	8.0	0.92	30
16C	Li	AN	DMSO	8.0	0.92	90
23C	Li	MAN	DMSO	8.0	0.71	0
1C	Na	AN	THF	9.0	0.51	100
5C	Na	AN	DMF	7.0	1.84	67
10C	Na	AN	DMSO	7.6	0.92	69
11C	Na	AN	DMSO	4.8	0.92	58
2C	Na	MAN	THF	9.0	0.51	35
6C	Na	MAN	DMF	7.0	1.19	75
18C	K	AN	DMF	7.5	0.92	60
19C	K	AN	DMSO	7.5	0.92	90
2D	K	MAN	THF	7.0	0.95	63
25C	K	MAN	DMF	7.5	0.71	58
24C	K	MAN	DMSO	9.0	0.71	88

<sup>a</sup> Experimental conditions: cellulose acetate (36.8% acetyl) (1 g.) was dissolved in 50 ml. solvent and reacted with a solution of alkali naphthalene to form the alkoxide derivative. Monomer was added in one portion.

<sup>b</sup> The yield is based on the polymerized monomer.

TABLE II  
Yield of the Graft Polymerization of Acrylonitriles<sup>a</sup>

Run no. <sup>b</sup>	Alkali metal alkoxide	[Monomer] [Alkoxide]	Solvent	Crude yield, %	Graft polymerization yield, % <sup>c</sup>	N in graft polymer, %	Grafted monomer, % <sup>d</sup>	$[\eta]$ of homo-polymer, dl./g. <sup>e</sup>
15C	Li	11.3	DMF	30	1.3	1.2	4.3	0.023
16C	Li	11.3	DMSO	90	0.9	0.9	1.0	0.095
1C	Na	5.7	THF	100	20.0	7.6	20.0	0.165
5C	Na	26.0	DMF	67	1.8	3.0	2.7	0.042
18C	K	12.1	DMF	60	3.2	2.7	5.3	0.031
19C	K	12.1	DMSO	90	1.3	1.2	1.4	0.138

<sup>a</sup> Experimental conditions as in Table I.

<sup>b</sup> The numbering is as in Table I.

<sup>c</sup> Calculated from the nitrogen content of the graft polymers, poly-AN-cellulose, obtained on hydrolysis of the crude poly-AN-cellulose acetate graft polymers and extraction of homopoly-AN by DMF.

<sup>d</sup> Based on the total monomer that polymerized.

<sup>e</sup> Intrinsic viscosity was measured in DMF at 25°C. The N content of the homopolymers was  $25.0 \pm 0.5\%$  (authentic polyacrylonitrile gave similar N analysis).

TABLE III  
 Yield of the Graft Polymerization of Methacrylonitrile<sup>a</sup>

Run no.	[Alkoxide] × 10 <sup>2</sup> , mole/l.	$\frac{[\text{Monomer}]}{[\text{Alkoxide}]}$	Solvent	Crude yield, % <sup>b</sup>	Graft poly- merization yield, % <sup>c</sup>	N in graft polymer, % <sup>d</sup>	Grafted monomer, % <sup>e</sup>
2D	14	13.6	THF	63	23	10.2	37
30D	14	3.4	DMF	75	54	7.8	72
31D	14	5.1	DMF	76	55	9.9	73
32D	14	8.5	DMF	88	37	10.4	42
33D	14	10.2	DMF	75	28	9.8	37
21D	13	10.9	DMSO	61	29	9.9	48
20D	9	13.4	DMSO	80	40	10.8	50

<sup>a</sup> Experimental conditions: cellulose acetate (36.8% acetyl) (2 g.) dissolved in 50 ml. solvent was converted to the potassium alkoxide derivative by reaction with potassium naphthalene and reacted with the monomer.

<sup>b</sup> The yield is based on the polymerized monomer.

<sup>c</sup> Calculated from N content of the graft polymers, poly-MAN-cellulose, obtained on hydrolysis of the crude cellulose acetate-poly-MAN graft polymers and extraction of homopoly-MAN by acetone.

<sup>d</sup> N content in homopolymers extracted by acetone was between  $19 \pm 0.5\%$ .

<sup>e</sup> Based on the total monomer that polymerized.

gated no polymerization occurred in THF both with acrylonitrile and methacrylonitrile. In DMF and DMSO polymerization occurred with acrylonitrile but not with methacrylonitrile, which is the less active monomer.

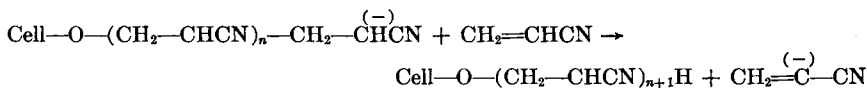
In all cases the graft polymerization was accompanied by homopolymerization. To remove the homopolymer fraction by selective extraction by solvents such as DMF (in the case of AN) and acetone (in the case of MAN) and to determine the yield of the graft polymerization of poly-AN it was found best to convert the graft polymers of poly-AN and poly-MAN on cellulose acetate to the corresponding insoluble cellulose graft polymers, by removal of the acetyl groups. The mixture of homopolymer and graft polymer obtained was treated with 15% of aqueous ammonia, according to a procedure which is known to remove the acetyl groups,<sup>5</sup> and was extracted with DMF (in the case of AN) or with acetone (in the case of MAN) to remove the vinyl homopolymer. The extracted polymers were essentially pure homopolymers, as seen from infrared spectra and nitrogen analyses.

In the case of AN it is seen that the graft polymerization yields were low (Table II). In DMF and DMSO with the use of Li, Na, and K alkoxides the yields were in the range of 1.3–3.2%. In spite of the fact that the yield of the polymerization was high, only 1.4–5.3% of the monomer polymerized was incorporated in the graft polymer. Using the sodium alkoxide derivative in THF (heterogeneous polymerization) the per cent of the monomer polymerized, that was incorporated in the graft polymer was higher, 20%.

In the case of MAN and with the potassium alkoxide derivative (Table III), the yield of the graft polymerization was 23–55% in DMF, DMSO, and THF; 37–72% of the monomer polymerized was incorporated in the graft polymer.

### Mechanism of the Graft Polymerization

The initiation consists of a direct addition of the polymeric alkoxide to the monomer.<sup>1</sup> The low yields obtained with AN are due to a chain transfer termination of the growing ends with the  $\alpha$ -acidic hydrogen of the monomer leading to the formation of homopolymers.



With MAN the yields were much higher due to the absence of an  $\alpha$  hydrogen available for chain transfer.

## EXPERIMENTAL

### Materials

Acrylonitrile, methacrylonitrile, dimethylformamide, and tetrahydrofuran were purified as previously described.<sup>1</sup> Dimethyl sulfoxide was purified in the same way as DMF. Cellulose acetate (BDH) containing 36.8% acetyl groups was dried *in vacuo* over phosphorus pentoxide. Stock

solutions of cellulose acetate in DMF and DMSO were further dried by azeotropic distillation with benzene. Solutions of alkali metal naphthalenes in tetrahydrofuran were prepared as previously described<sup>6</sup> and standardized by titration with 0.1*N* HCl. All liquid reagents were kept under argon in flasks fitted with self-sealing rubber caps.

### Graft Polymerization Procedure

The addition of reagents and the polymerization were carried out under argon. The graft polymerization was carried out in a three-necked flask fitted with a high-speed stirrer, a gas adapter for introducing argon, a thermometer, and an outlet fitted with a self-sealing rubber cap. The apparatus was dried by flaming *in vacuo* and cooled under nitrogen. A solution of cellulose acetate in a suitable solvent was introduced, followed by the required amount of alkali metal naphthalene. The color of the alkali metal naphthalene disappeared almost immediately, and the viscosity of the reaction mixture increased due to formation of the alkoxide derivative. Monomer was added at room temperature and the polymerization mixture was stirred for 2 hr. The crude graft polymer was precipitated with ethanol-petroleum ether (1:5) (500 ml.) filtered, washed with alcohol, and dried *in vacuo* over phosphorus pentoxide.

### Hydrolysis of the Acetyl Groups from the Crude Graft Polymers

Crude graft polymer (2 g.) was kept in 15% of aqueous ammonia for 3 days, filtered, and washed with water (to neutrality) and alcohol, and dried.

### Extraction of Vinyl Homopolymers

Crude graft polymer (1 g.) that was previously treated with aqueous ammonia was extracted at room temperature for 2 days with DMF (50 ml.) in the case of polyacrylonitrile and acetone (50 ml.) in the case of homopoly-methacrylonitrile. The graft polymer was filtered, washed with DMF or acetone and with alcohol, and dried. Polyacrylonitrile was recovered on precipitation with water, and polymethacrylonitrile on evaporation of the acetone.

### References

1. Feit, B. A., A. Bar-Nun, M. Lahav, and A. Zilkha, *J. Polymer Sci.*, **A2**, 4743 (1964).
2. Audieth, L. F., and J. Kleinberg, *Non-Aqueous Solvents*, Wiley, New York, 1953, p. 111.
3. Zilkha, A., and Y. Avny, Israel Pat. Appl. 19379 (June 1963).
4. Paul, D. E., D. Lipkin, and S. I. Weissmann, *J. Am. Chem. Soc.*, **78**, 116 (1956).
5. Ott, E., H. M. Spurlin, and M. W. Grafflin, *Cellulose*, Vol. II, 2nd Ed., Interscience, New York, 1954, p. 751.
6. Zilkha, A., and Y. Avny, *J. Polymer Sci.*, **A1**, 549 (1963).

### Résumé

Le greffage anionique de l'acrylonitrile et du méthacrylonitrile à l'alcoolate de l'acétate de cellulose (Li, Na, K) a été étudié dans le tétrahydrofurane (THF), le diméthylformamide (DMF) et le diméthylsulfoxyde (DMSO). Bien que le rendement de la polymérisation soit élevé, le pourcent d'acrylonitrile greffé était faible (1.4–5.3% dans DMF et DMSO et 20% dans THF) par suite de l'homopolymérisation due au transfert de chaîne sur monomère. Avec le méthacrylonitrile, qui n'a pas d'hydrogène  $\alpha$ -acide, le pourcent de monomère greffé était plus élevé (37–72%).

### Zusammenfassung

Die anionische Pfropfpolymerisation von AN und MAN auf das Zelluloseacetataalkoxyderivat (Li, Na, K) wurde in THF, DMF und DMSO untersucht. Obgleich eine hohe Polymerisationsausbeute erreicht wurde, war der prozentuelle Anteil in aufgepfropftem Acrylnitril wegen der durch Kettenübertragung zum Polymeren verursachten Homopolymerisation niedrig (1,4–5,3% in DMF und DMSO und 20% in THF). Bei Methacrylnitril, welches keinen sauren  $\alpha$ -Wasserstoff besitzt, war der prozentuelle Anteil an aufgepfropftem Monomeren höher (37–72%).

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