NOTES

Grafting of Cellulose Copolymers with Water-Insoluble Monomers with Redox System Cellulose Xanthogenate–Hydrogen Peroxide

INTRODUCTION

The redox system cellulose xanthogenate–hydrogen peroxide is one of the most promising means for initiating grafting copolymerization in the formation of viscous fibers. The formation of a homopolymer outside the fiber mass can be avoided when using this redox system in the flow-like process.[1,2] Of particular importance is a two-bath method for the grafting of acrylonitrile (AN), characterized by the initiation of copolymerization in an aqueous solution of the monomer (first bath) and an increase of the grafted chains in a pure monomer medium (second bath).

The aim of this study is to establish whether it is possible to graft monomers insoluble in water as well as their mixtures with acrylonitrile.

EXPERIMENTAL

All the experiments were made with freshly formed viscous fibers with a linear specific mass of 1.5 denier. The fibers were taken after a coagulation bath and just before a plastification bath. The specimen was treated for 5 min in a solution of sodium bicarbonate at a concentration of 60g/l. at 20°C, so as to prevent a further saponification of the xanthogenic groups; the fibers were washed for 2 min with distilled water at 20°C. The fibers thus prepared with a residual degree of esterification γ-5-6 were steeped in the first bath, containing a 7% aqueous solution of AN and a certain quantity of hydrogen peroxide at pH 2 and 20°C for 20 sec. They were then pressed to a 1:3.5 degree of pressing and steeped in the second bath containing styrene (St) or methyl methacrylate (MMA) or their mixtures with AN.

The quantity of grafted copolymer was determined gravimetrically as a residue after hydrolysis with 72% sulfuric acid of the cellulose component in the copolymer graft. When grafting the monomer mixture with AN, the content of the bound AN was determined by measuring the nitrogen content by Kjeldahl's accelerated method[3] and the content of the other monomer, by the difference between the total quantity of grafted polymer and the quantity of bound AN.

The presence or absence of a homopolymer in the second bath was established by diluting part of it with acetone. The monomers were purified by means of double distillation.

The sodium bicarbonate was chemically pure, while the remaining chemicals used were of A.R. grade.

RESULTS AND INTERPRETATION

The first bath, in which the graft copolymerization was initiated and the growth of the grafted chains began, contained 7% AN in all cases. AN was chosen for the following reasons: good polymerizability and ability to easily copolymerize with most of the known vinyl monomers.

First, the effect of the hydrogen peroxide concentration in the first bath was traced, using St as a medium in the second bath. The results obtained (Table I) confirmed the assumption that the two-bath method can be used in grafting water-insoluble monomers (in the case of St). The quantity of the grafted monomer was not considerable, although the second bath consisted of pure St. The main cause of this is probably the fact that its contact with the growing macroradicals has to be realized through the water carried by the wet fibers after treatment in the first bath.

With an increase in hydrogen peroxide concentration to 0.5%, the quantity of the bound St also

TABLE I
Effect of Hydrogen Peroxide Concentration in First bath on Quantity
of Bound Styrene[a]

Hydrogen peroxide concn, %	0.05	0.10	0.20	0.30	0.40	0.50
Bound St, %	0.9	1.3	3.1	5.7	6.0	7.6

[a] First bath: 7% AN; pH 2; temp. 20°C; M 1:10; duration 20 sec. Second bath: 100% St; temp. 50°C; M 1:10; duration 15 min. Content of bound AN in ready specimens, 0.2%. $M = \dfrac{\text{mass of fiber}}{\text{mass of liquid}}$

TABLE II
Effect of Temperature of Second Bath on the Quantity of Bound Styrene[a]

Temp. of second bath, °C	40	50	60	70	80	90
Bound St, %	6.0	7.9	9.6	12.4	19.2	24.8

[a] First bath: 7% AN, 0.5% hydrogen peroxide, pH 2, temp. 20°C, M 1:10, duration 20 sec. Second bath: 100% St, duration 15 min, M 1:10. Bound AN content in ready specimens, 0.2%.

TABLE III
Effect of Treatment Duration in Second Bath on Quantity of Bound Styrene[a]

Duration, min.	1	5	10	15	20	30
Bound St, %	2.2	4.3	6.5	7.8	9.8	10.7

[a] First bath: 7% AN, 0.5% hydrogen peroxide, pH 2, temp. 20°C, M 1:10, duration 20 sec. Second bath: 100% St, temperature 50°C, M 1:10.

increases. It was not considered expedient to seek an optimal concentration about 0.5%, because the use of higher concentrations would render the method much more expensive and would considerably restrict its applicability. The subsequent investigations were made, therefore, with the 0.5% concentration of the hydrogen peroxide in the first bath.

The diffusion of the monomer in an aqueous layer depends strongly on the temperature in the second bath. This probably explains why, with a rise in temperature from 40 to 90°C, the quantity of bound St more than quadruples (Table II).

This substantial increase can be due only to summing the favorable effects of a higher diffusion and addition rate of the monomer molecules with the growing macroradicals.
Naturally, the effect of diffusability and, hence, of temperature will depend on the thickness of the aqueous layer, i.e., on the concrete degree of fiber squeezing out during the transfer from the first to the second bath.

With a rise in temperature, the diffusability of the water in St also increases. Since the aqueous layer contains a certain quantity of hydroxyl radicals, this will also increase the possibility of obtaining a homopolymer in the second bath. In our experiments, a certain quantity of homopolymer was formed at 90°C. Our subsequent experiments were made at 50°C.

The study of the effect of the treatment duration in the second bath on the quantity of bound St (Table III) shows a dependence typical of this type of process, i.e., an initial quick increase followed by an attenuation of the process.

The use of a St and AN monomer mixture in the second bath substantially modifies the conditions of graft copolymerization. To begin with, an effect is produced by the fact that one of the monomers (AN) has an even, though limited, water solubility and that its diffusion rate through the aqueous layer will far exceed the diffusion rate of the water-insoluble monomer (St). Along with this, the presence of the water-soluble monomer may be expected to increase the similarity of water with St and hence to increase the degree of its grafting. The known synergistic effect during the copolymerization of AN and St[4,5] acts in a similar manner.

TABLE IV

Effect of St:AN Ratio on the Quantity of the Two Monomers Bound
in the Graft Copolymer[a]

Ratio St:AN	0/100	10/90	20/80	30/70	40/60	50/50	60/40	70/30	80/20	90/10	100/0
Bound St, %	0.0	1.2	3.5	4.0	4.1	5.1	6.0	7.0	7.9	8.3	7.5
Bound AN, %	48.3	45.6	45.0	41.8	38.1	33.9	19.1	14.9	6.8	1.6	0.0

[a] First bath: 7% AN, 0.5% hydrogen peroxide, pH 2, temp. 20°C, M 1:10, duration 20 sec. Second bath: temperature 50°C, M 1:10, duration 15 min.

TABLE V

Effect of MMA:AN Ratio on the Quantity of the Two monomers Bound
in the Graft Copolymer[a]

MMA:AN ratio, %	0/100	10/90	20/80	30/70	40/60	50/50	60/40	70/30	80/20	90/10	100/0
Bound MMA, %	0.0	0.9	3.6	3.9	4.1	7.4	8.9	10.9	11.7	12.9	11.0
Bound AN, %	47.9	46.2	44.3	40.2	37.0	32.1	22.4	18.7	7.8	4.4	0.0

[a] First bath: 7% AN, 0.5% hydrogen peroxide, pH 2, duration 20 sec, M 1:10, temp. 20°C. Second bath: temp. 50°C, M 1:10, duration 15 min.

As can be seen from Table IV, at a 100:0 ratio, i.e., pure St, the quantity of bound St is less than the bound quantity of St at a 90:10 ratio. This confirms the positive effect of the mentioned factors on St grafting in the presence of AN. Up to a ratio of 70:30 St:AN, the quantity of bound AN still exceeds that of St. This we ascribe mainly to the water solubility of AN.

Analogous results were obtained when working with a MMA:AN mixture (Table V). Here, too, a maximal binding of the monomer not soluble in water is observed at a 90:10 MMA:AN ratio, while at a 100:0 MMA:AN ratio (i.e., pure MMA) the quantity of bound MMA decreases noticeably. In the free-radical copolymerization of MMA and AN, the two monomers are known to have similar copolymerization constants, and the greater quantity of bound AN at an MMA:AN ratio up to 70:20 is likewise explained by the water solubility of AN.

CONCLUSIONS

The possibility of grafting water-insoluble monomers and their mixtures with acrylonitrile to cellulose by initiating copolymerization with a redox system of cellulose xanthogenate–hydrogen peroxide has been demonstrated. This considerably broadens the applicability of this redox system to the production of grafted cellulose copolymers. The effect of some of the basic parameters on the graft copolymerization has been established.

References

1. P. Pavlov, K. Dinov, N. Simeonov, and D. Dimitrov, *Das Papier,* in press.
2. P. Pavlov, K. Dimov, N. Simeonov, and D. Dimitrov, *Himiya i Industriya,* in press.
3. *Spravochnik po mekhovoi i ovchinno shubnoi promishlenosti,* Vol. 1, Gislegprom, Moscow, 1964, p. 293.
4. G. I. Stanchenko, R. M. Livshitz, and Z. A. Rogovin: *High Mole. Comp.,* **B-10,** 715 (1968).
5. B. V. Kokta and J. L. Valade, *Tappi,* 3, 366 (1972).

P. PAVLOV
K. DIMOV
N. SIMEONOV

Chemico-Technological Institute Sofia 56, Bulgaria