# A New Physicochemical Technique for Studying Native and Modified Structures of Polymer Fibers: The Continuous Measurement of Length Variations, Under Tension, in a Swelling Medium of Continuously Variable Concentration

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## Synopsis

A device for linear variation of the concentration of a binary mixture in function of time is described. This device is used to study the dimensional variations of cotton yarns immersed in an aqueous caustic soda solution under a fixed tension while the concentration is increased from 0 to 10$N$. This method is very sensitive and seems of particular interest for the study of fibrous polymer structures.

## INTRODUCTION

Although many papers have been published on the changes produced in the length of polymeric fibers when treated with swelling media, the kinetic aspects of the process have been largely ignored and the behavior of such fibers in a continuously changing medium has not been studied. Therefore, while considerable information is available on the free retraction of synthetic fibers in various organic solvents[1] and on the swelling and retraction of natural[2] and regenerated cellulose fibers,[3] the information is almost invariably confined to the equilibrium conditions in liquid media whose composition remains unchanged throughout the experiment.

In recent years a new technique has been developed: thermomechanical analysis (TMA) can be applied to the problem of retraction of fibers. In this method a continuous recording is made of the variations in length of a single fiber (or a bundle of fibers) under a fixed external tension, while the temperature of the surrounding medium is modified according to a predetermined program, the method being a particular development of a DTA or DSC apparatus.[4]

We thought it would be useful to investigate the capabilities of a somewhat analogous method by which the length variations would be recorded under constant temperature and external tension in liquid media whose concentration was modified slowly. The present paper describes the experimental apparatus and gives some preliminary results for cotton threads immersed in aqueous caustic soda while the alkali concentration is progressively increased.

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## DESIGN OF ELECTRONIC DEVICE TO VARY
## NORMALITY OF A BINARY SOLUTION AT CONSTANT RATE

We made use of the following principle: If an amount of liquid, consisting initially of the pure solvent, is maintained at constant volume $V_0$ by adding a continuous flow, $dV/dt$, of a mother liquor consisting of the same solvent plus solute, and simultaneously extracting the increasingly concentrated solution at the same rate $dV/dt$, the concentration will increase linearly with time, provided that

$$\frac{dV}{dt} = \frac{aV_0}{(C_0 - at)} \tag{1}$$

where $a$ is the rate of increase of concentration with time, $C_0$ is the concentration of the mother liquor (expressed either in grams of solute per liter of solution or in volume of solute per liter of solution), and $t$ is the time.

We used peristaltic pumps (one for the addition of mother liquor and the other for the evacuation of the solution of treatment) for which there is a simple relationship between the flow and the rate of rotation:

$$dV/dt = kU \tag{2}$$

where $U$ is the electric voltage applied to the motor of the pump and $k$ is a constant essentially dependent on the diameter of the crushed tube.

Consider the circuit drawn on Figure 1: $E_0$ represents a reference voltage, $R$ is a linear potentiometer the contact arm of which is moved at uniform rate by a motor, and $R_1$ is a fixed resistance. One can write, at a given instant:

$$U = E_0R_1/(R_1 + R - x) = E_0R/(R_1 + R - KT) \tag{3}$$

where $K = R/T$ and $T$ is the time necessary for the contact arm to traverse the whole potentiometer. Since eqs. (1) and (2) have the same form, the various electrical constants can be adjusted by analogy, so that

$$a = C_0/T(1 + \delta)$$

$$V_0 = TkE_0\delta$$

where $T$ is the total time for the experiment, $a$ is the chosen concentration gradient, and $\delta = R_1/R$; $1/(1 + \delta)$ is thus the ratio of the concentration of the mother solution to the concentration of the solution at the end of the experiment.

This device enables the various parameters to be adjusted, particularly the gradient $a$ and the duration $T$ of the experiment.

We have constructed and used such a device for aqueous solutions of caustic soda; the volume $V_0$ is 100 or 150 cm³, and initially consists of pure water. The mother solution of caustic soda is $14N$, in which case the gradient $a$ can be adjusted between $0.03N$/min and $0.16N$/min; the linearity is maintained (with an error less than $\pm 2\%$) up to a concentration value of $12N$. It was found that the volume contraction due to the dilution
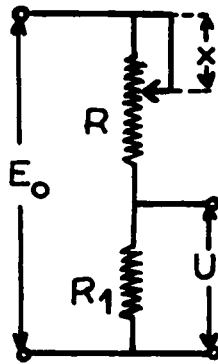
Fig. 1. Electronic diagram for the homographic function.

of mother liquor could be neglected. (Obviously, the maximum concentration obtained and the possible gradients will be proportional to the concentration of the mother solution.)

## EXPERIMENTAL DEVICE AND MODE OF UTILIZATION

### Brief Description

Figure 2 shows a diagrammatic representation of the whole apparatus used for the experiments on yarns. It consists essentially of:

1. The device as described above for varying the concentration with two identical micropumps, $MP_1$ and $MP_2$, and controlling the circuits for the input of mother solution and the output of solution; the electronic unit EU; and a third pump CP with a relatively high flow for the mixing of the solution of variable concentration.
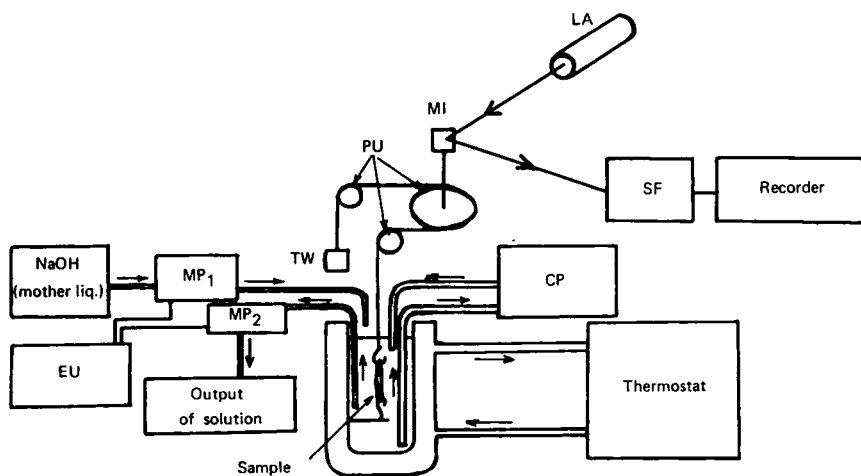


Fig. 2. Block diagram of apparatus for measuring length and concentration variations.

2.   A device for recording length variations by the Poggendorff method, with a mirror Ml, a lamp LA, and a photoelectric cell following the spot, SF.   The length variations of the sample immersed in the swelling medium (vessel VE with a thermostating jacket), and maintained under tension by the weight TW, are transformed into angular movements by means of flexible steel wire passing over a system of three low friction pulleys PU. Another similar device using the same principle but a much greater sensitivity has been built for tests on single fibers.

## Operation of the System

**Sample Preparation.**   In the case of yarns, experiments were conducted on single loop made with the help of a steel cylinder.   (It was possible to
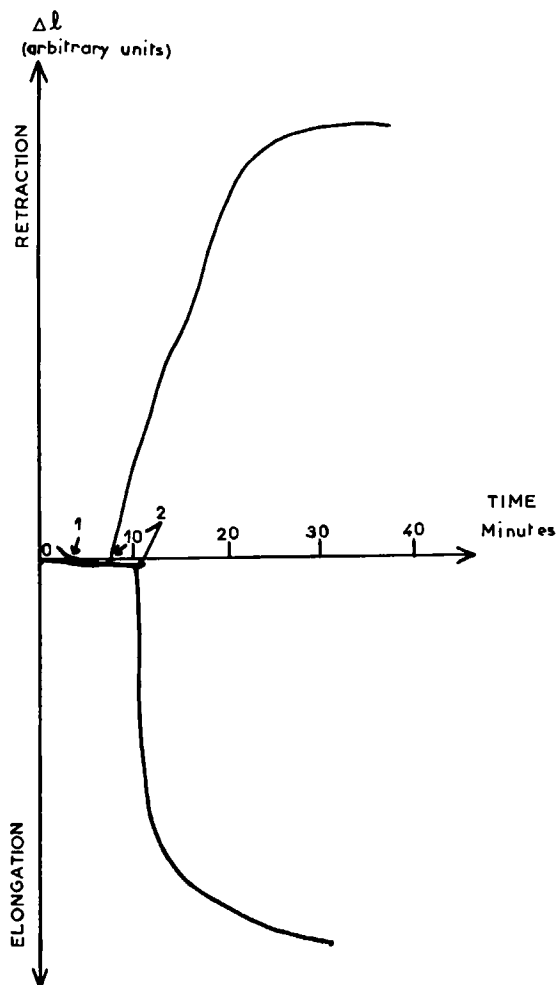
Fig. 3.   Typical kinetics curves:  (1→) equilibrium in air;  (2→) immersion time. Upper part: retraction in 22% NaOH (20°C, 0.37 g/tex);  lower part: elongation in 6% NaOH (20°C, 0.93 g/tex).

get, by this procedure, a reproducible initial length within the range of ±1%.) The loop was hung between a fixed hook and a moving hook. In the case of the fiber device, it was found better to use tweezers because of the difficulty of making a loop from a single fiber.

**Experiments.** In the case of the measurements with variable concentration, the apparatus is run with pure water, recorded till a true equilibrium extension is reached so as to be sure that yielding phenomena can be neglected in the experiments; a vertical line on the records indicates the beginning of the addition of caustic soda. In the case of the kinetics studies, one obviously records the whole curve as soon as the immersion begins, after recording the equilibrium value in air.

## RESULTS

The results of experiments on cotton yarns swollen by aqueous caustic soda solutions are given below.

### Kinetic Experiments

A few preliminary experiments were made in order to evaluate the time required to reach equilibrium in various NaOH solutions (of constant concentration). These showed that this time lay between 2 and 10 min at 20°C according to the twist factor of the yarn and without any wetting agent. All the experiments with variable concentrations were made using an alkylaryl sulfonate-type surfactant agent.

Figure 3 shows some recordings of kinetics curves. Two recordings have been drawn on the same graph and correspond to different experiments, the first one with a retraction process, the second one with an elongation process.

### Results in NaOH Gradients

*Experiments with a "Standard" Yarn Spun From High Long-Staple Cotton*

Conditions were as follows: breaking strength, 13.3 g/tex; breaking elongation, 6%; twist factor, 105; count, 27 tex.

Figure 4 shows an example of the recording for an external tension of 0.37 g/tex and a concentration gradient of $0.045N$/min. A maximum elongation is observed at a normality of about $1.8N$ (i.e., approximately 6.7% by weight); moreover, there is small but definite retraction when the caustic soda is first added. Figure 5 shows the effect of a much higher concentration gradient ($0.16N$/min) on the same yarn and at the same external tension. The maximum elongation occurs, in this case, at a normality of $2.5N$ (ca. 9.5% by weight).

*Comparative Study of the Same Yarn Before and After "Crosslinking" by Formaldehyde*

Figure 6 shows the results obtained by using the present method on two yarns with the following characteristics: control sample, warp yarn
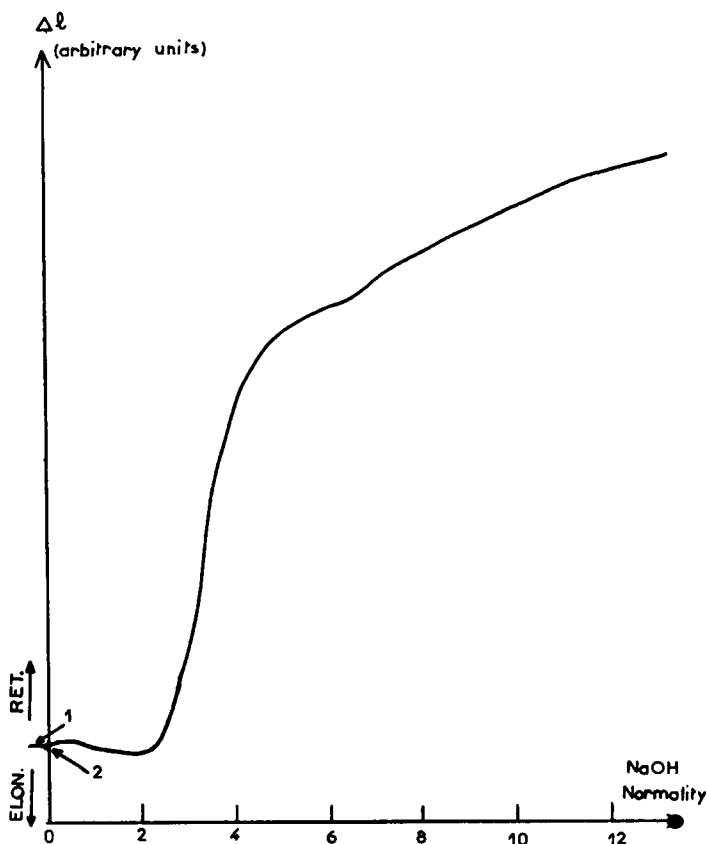
Fig. 4. Dimensional curve for cotton yarn (0.37 g/tex, 20°C) in aqueous NaOH gradient of 0.045$N$/min: (1→) equilibrium in pure water (1 min = 0.5 mm); (2→) NaOH addition.

(26.8 tex) from a scoured cotton fabric (different from the yarn considered previously); treated sample, warp yarn from the same fabric having been subjected to a crosslinking treatment with formaldehyde according to Chance et al.[5] after a preswelling by pure water, and the stress being developed toward warp direction during the crosslinking treatment.

It is seen that the present method shows a large difference between the two samples. (In each case, the curve represents the mean of 10 tests.) The maximum elongation is much smaller and is shifted toward higher concentrations for the treated sample; moreover, the retraction, occurring at high alkali concentration, is less for the control sample.

## DISCUSSION

### "Standard Sample"

Our observations are in good agreement with much earlier results obtained by the "static" method (loc. cit.). According to these results, at an external tension of 50 mg per fiber, maximum elongation was observed

at a concentration zone between 4.5 and 6% by weight (at a temperature of 20°C).  In our experiments, the yarn consists of about 180 fibers per cross section so that a tension of 10 g (20 g for the loop, i.e., for two threads)
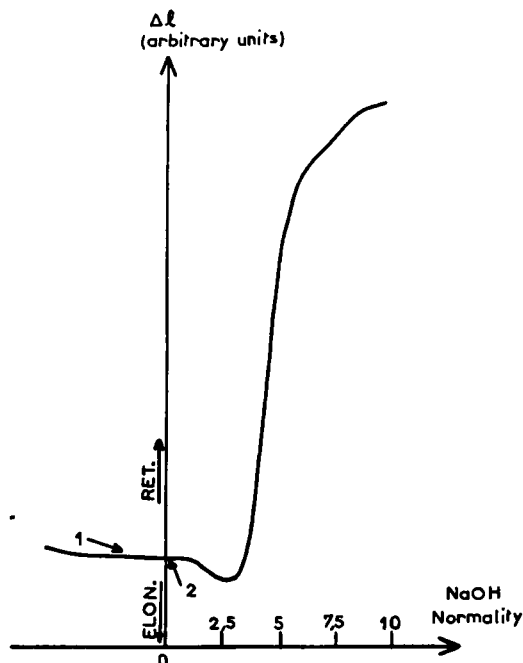
Fig. 5. Dimensional curve for cotton yarn (0.37 g/tex, 20°C) in aqueous NaOH gradient of 0.160$N$/min:  (1→) equilibrium in pure water (1 min = 0.5 mm);  (2→) NaOH addition.
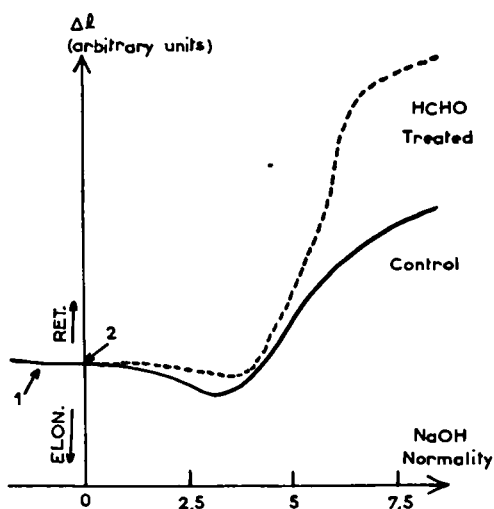
Fig. 6. Comparison of the curves for a yarn treated with formaldehyde and control (0.93 g/tex, 0.045$N$/min, 20°C):  (1→) equilibrium in pure water (1 min = 0.5 mm); (2→) NaOH addition.

corresponds approximately to a mean tension of 55 mg per fiber; we observed a maximum elongation at a concentration of 6.7% by weight caustic soda at 20°C when the concentration gradient is sufficiently low. At higher concentration gradients, the sample can no longer "follow" the variations of the swelling medium, and this leads to a shifting of the maximum toward higher concentrations (Figs. 4 and 5). The use of a higher external tension results in the same retarding effect.

## Treated Samples

The high sensitivity of the test method is seen in the study of crosslinked samples. The higher tension required to "reveal" the elongation maximum, and the fact that this extremum occurs for higher concentrations than for the "standard" yarn, are probably due to the high twist factor of the yarn. As far as the differences in behavior between the control and treated samples are concerned, the following interpretation can be suggested: At low concentrations, the penetration of water is limited to the *interfibrillar* level and is retarded by crosslinking because the latter has essentially occurred in the same region. Conversely, when the ionic strength of the solution becomes sufficient to allow an *intrafibrillar* swelling, the "cooperative" effect of the fibrils, being crosslinked, is higher, which leads to a greater shrinking effect. It is likely that in the case of the crosslinked samples there is also an acceleration of the swelling, which might account for reaching the equilibrium length more rapidly in experiments with a concentration gradient.

## CONCLUSIONS

We believe that the device for linear variation of the concentration of a binary mixture would be suitable for many problems besides that of retraction and related phenomena (in general, every phenomenon sensitive to the concentration). In addition, the technique described in the present paper seems of interest in providing useful information, particularly for the study of interactions between synthetic polymer fibers and swelling organic solvents.

## References

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