# X-Ray Diffraction Methods in the Study of the Effect of Microwave Heating on the Transformation of Cellulose I into Cellulose II During Mercerization

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**ABSTRACT:** X-ray diffraction (XRD) techniques were used in the study of the effect of microwave (MW) heating on the structural properties of cotton celluloses I and II and on the mercerization mechanism of cotton fibers. Samples of celluloses I and II were MW heated at 900 W for different times ranging from 10 to 40 min. The obtained data revealed that MW heating of cellulose II in opened glass tubes produces no significant effects on the resolution of its XRD patterns, whereas the most evident effects occur when cotton fibers (cellulose I) are heated in opened tubes at 900 W for 10 and 20 min. Also, mixtures of cotton fibers and aqueous solution of NaOH with different concentrations were exposed to MW radiation for different times and different powers. It was found that MW heating has no considerable effects on the mechanism of transformation of cellulose I into cellulose II during mercerization. On the other hand, MW heating of cotton fibers during mercerization reduces the values of concentration of NaOH in the aqueous solution and the time of treatment that are needed for the complete transformation of cellulose lattice type I into cellulose lattice type II without any heating. Also it was found that the magnitude of reductions depends on the applied power. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 2978–2983, 2007

**Key words:** X-ray diffraction (XRD); microwave heating; celluloses I and II

## INTRODUCTION

A lot of attention has been devoted in recent years to the application of microwave (MW) heating in polymer and textile fibers processing.[1–7] The MW heating is more effective than the conventional heating because it has a specific property, which is the equilibrium heating inside the matter. Typically, the MW energy is lost to the sample by two mechanisms, ionic conduction and dipole rotation. In many practical applications of microwave, ionic conduction and dipole rotation take place simultaneously. In conventional heating, heat can be transferred to the material by radiation, conduction, and convection. Therefore, in case of textile processing as in dye fixation, heating setting, or drying the product, the conventional heating means a slow process involving a number of stages in the transfer of the energy before the material to be heated reaches a uniform state of molecular activity and temperature. The property of MWs, which makes them attractive for dye fixations and other uses, is their ability and suitable conductions to produce rapid and uniform heating through out the material exposed to them. The study of the effect of conventional heating on the structure or properties of cotton cellulose has been a subject of interest for a number of researchers.[8–12] However, till the present time, the effect of MW heating on the structural properties of cotton celluloses I and II and on the mercerization mechanism has not yet been fully investigated. So, the main purpose of the present study is to apply X-ray diffraction (XRD) to investigate the MW heating induced changes in the structural properties of celluloses I and II and also the effect of MW energy on the mercerization mechanism of cotton fibers.

## EXPERIMENTAL

Cotton fibers of Giza 75 were used in the preparation of the samples investigated in the present study. The cellulose lattice type II was prepared by immersing cotton powders of particle size (180–120 μm in diameter) in 18% concentration (w/w) of NaOH solution at room temperature (25°C) for 8 min. The material liquor ratio was 1 : 50 (w/w). The fibers were washed with 1% acetic acid solution for 5 min. The fibers were again washed with distilled water and dried at 50°C. Samples (2 g/each) of cotton fibers (cellulose I and cellulose II) of the same particle size were heated in MW oven operating at the frequency 2450 MHz with an input power 900 W for different times namely (10, 20, 30, and 40 min) and at the MW power 900 W.

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Cellulose I was heated in closed and opened glass tubes, whereas cellulose II was heated in opened tubes only.

Mixtures of cotton powders and aqueous solutions of NaOH with different concentrations (6, 9, 12, 15, and 18%) were exposed to MW energy in closed vessels for different times (2, 4, 6 and 8 min) and at different powers 450 and 900 W. The powder was then filtered washed and dried in the same way as before.

The X-ray diffraction patterns were recorded on Diano difractometer (Cobalt source).

## RESULTS AND DISCUSSION

The XRD patterns of both cotton celluloses I and II are shown in Figure 1(a,b) respectively. The diffractograms of these samples show (101, $10\bar{1}$) and (002) at

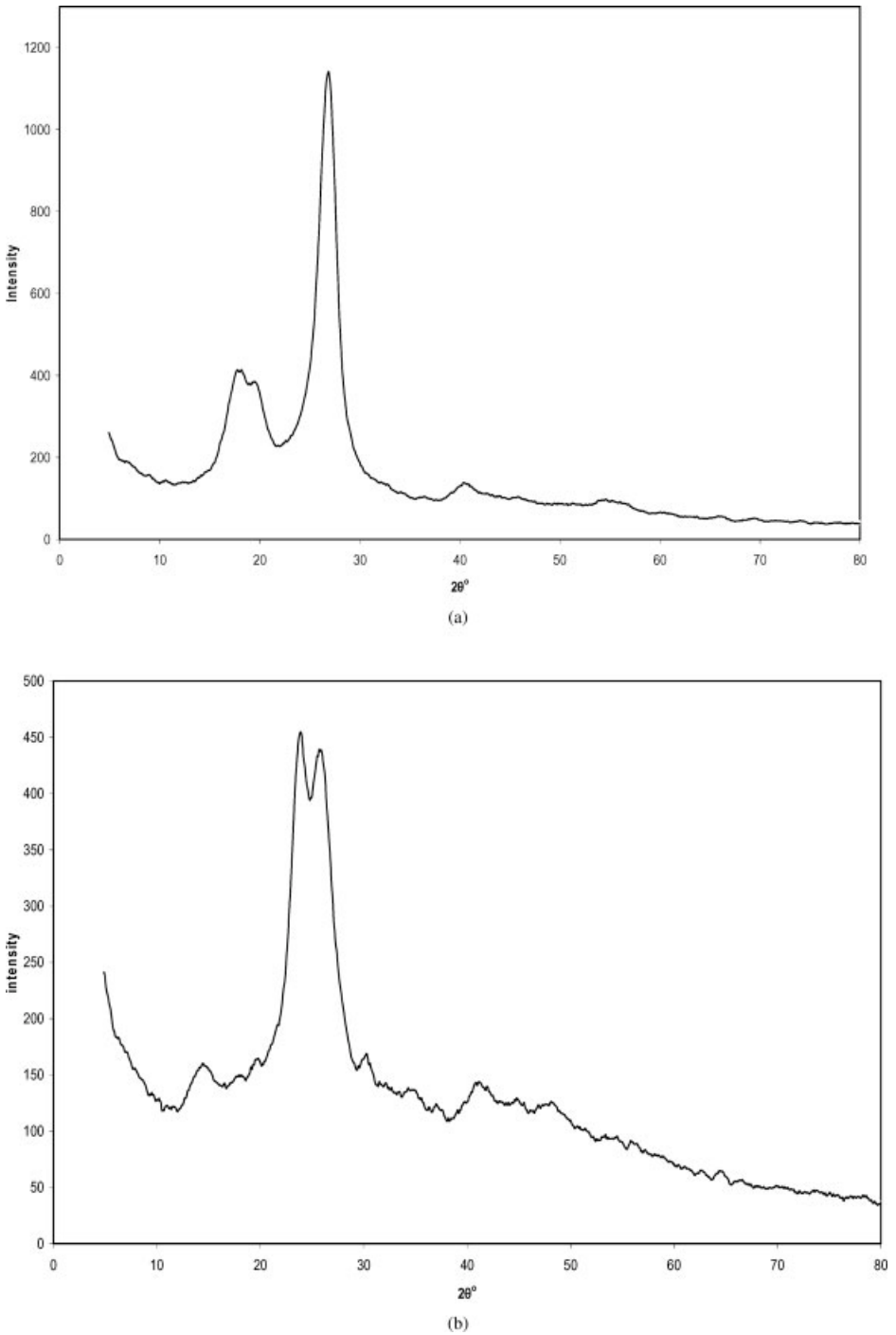


**Figure 1** (a) X-ray diffraction pattern of cellulose I. (b) X-ray diffraction pattern of cellulose II.

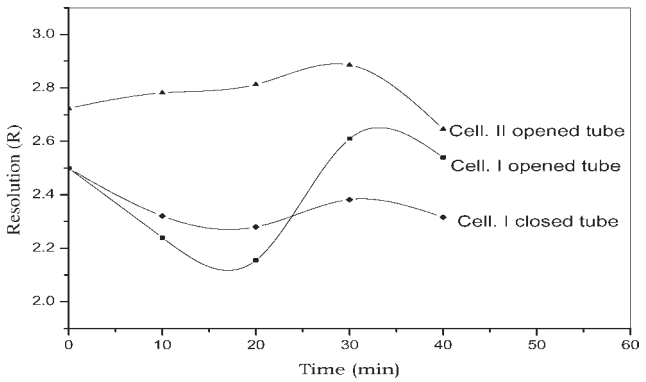


**Figure 2** The relationship between the resolution ($R$) and the MW heating time.

diffraction peaks 2θ = 14.8°, 16.25°, and 22.60° for cellulose I respectively, and 2θ = 12.0°, 20.2°, 21.8° for cellulose II respectively.

The resolution ($R$) of the (101) and (10$\bar{1}$) peaks of XRD scan of cellulose I and that of (10$\bar{1}$) and (002) peaks of cellulose II were calculated from the relation (Ref. 12).

$$R = h1 + h3/h2$$

where $h1$, $h2$, and $h3$ are the heights at $2\theta = 16.5°$, 15.8°, and 14.8° for cellulose I, respectively, above the background line connecting the points on the scan at $2\theta = 10°$ and 18. 0°. $h1$, $h2$ and $h3$ are the heights for cellulose II at $2\theta = 21.8°$, 20.9°, and 20.2° respectively, above a background line connecting two points at $2\theta = 14.3°$ and 25.2°.

Samples of cotton powder of the same particle size (180–125 μm diameter) for both cellulose I and cellulose II were heated in a MW oven for different heating times at the same power of MW 900 W. Cellulose I was heated in closed and opened tubes, whereas cellulose II was heated in opened tubes. The resolution ($R$) values of raw and MW heated samples (cellulose I and cellulose II) at 900 W are represented graphically against the heating time in Figure 2.

It is apparent from Figure 2 that MW heating of cellulose II in an opened glass tubes at 900 W causes no significant effects on the resolution of its XRD. The most evident effect occurs when cotton fibers are MW heated in opened tubes at 900 W for 10 and 20 min. The induced changes in the resolution values of the XRD pattern of cotton cellulose, brought about by MW heating may be attributed to the liberation of

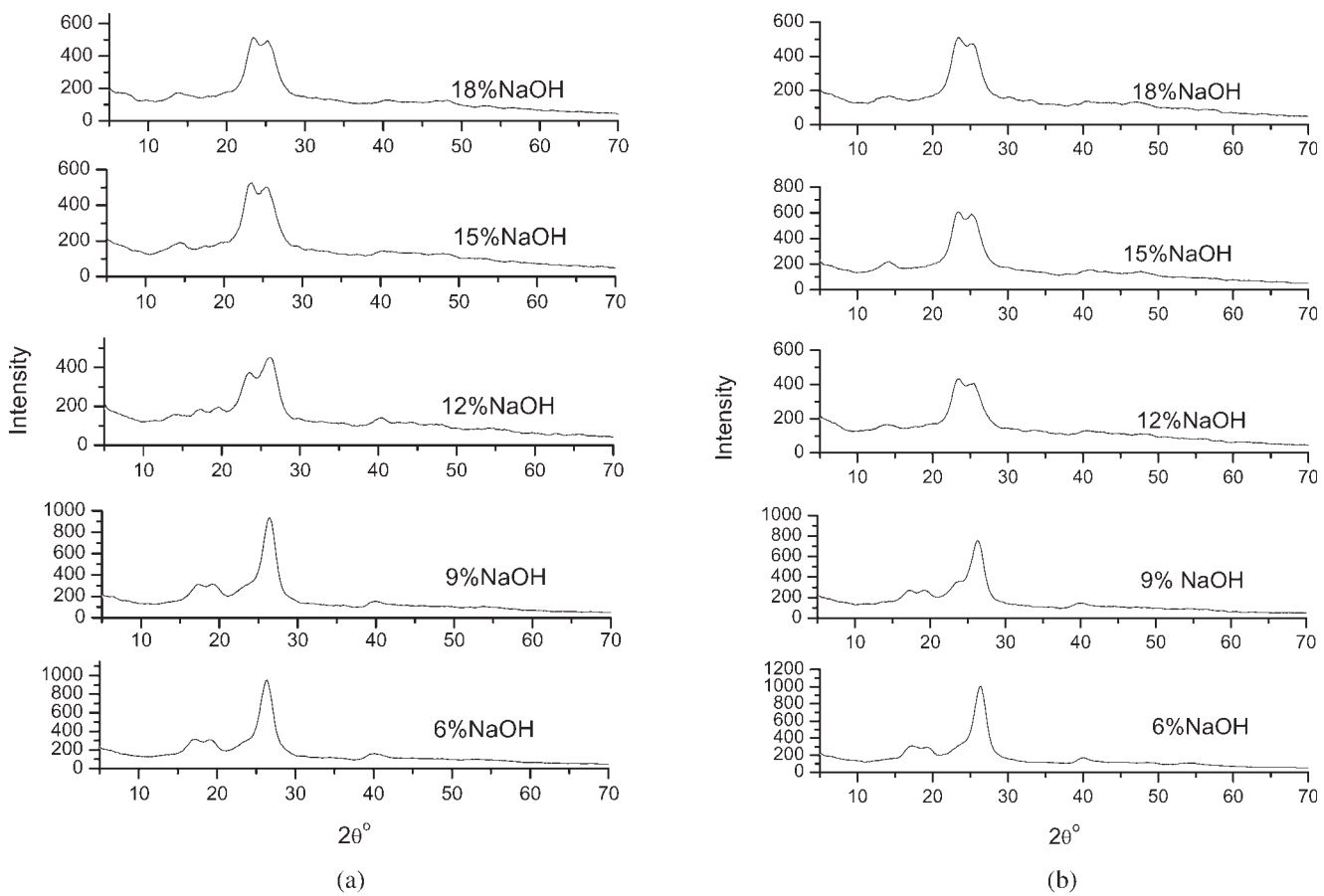


**Figure 3** (a) X-ray diffraction patterns of cotton samples treated with various concentrations of NaOH at 450 W (b) X-ray diffraction patterns of cotton samples treated with various concentrations of NaOH at 900 W.

**TABLE I**
**The Table Contains the Resolution (*R*) of XRD Peaks of Cotton Fibers Treated With Different NaOH Concentrations and Heated at Different Powers**

| Type of cellulose | Samples | *R*1 of 450 W microwave | *R*1 of 900 W microwave |
|---|---|---|---|
| Cellulose I | Raw sample | 2.5 | 2.5 |
| | 6% NaOH | 2.587 | 2.591 |
| | 9% NaOH | 2.688 | 3.072 |
| Type of cellulose | Samples | *R*2 of 450 W microwave | *R*2 of 900 W microwave |
| Cellulose II | 12% NaOH | 3.11 | 2.494 |
| | 15% NaOH | 2.62 | 2.568 |
| | 18% NaOH | 2.552 | 2.265 |

N.B. The value of (*R*) for the sample treated with 18% aqueous solution of NaOH at room temperature for 8 min is 2.724 (as a reference).

water molecules from the fibers. This result is in agreement with that reported by Sidiras et al.[13] who used X-rays diffraction patterns in the study of the effects of various treatments on the crystallinity of purified commercial celluloses and concluded that the drying of cellulose decreases its degree of crystallinity. Dobb and Safain[8] applied the method of multipeak resolution and computation of background scatter in X-ray diffraction from fibers for the investigation of the effect of the time of heating for native and mercerized cotton fibers at 220°C on the crystallographic order. They concluded that thermally induced structural modifications are time dependent and that dissimilar mechanisms operate in the two specimens examined. For example, it appeared that an initial recrystallization occurs in native fibers, whereas in mercerized specimens degradation of order increases continuously with the time of heating.

However, it could be concluded that the differences in the behavior of rates of changes of the resolution *R* for celluloses I and II, which are brought about by MW heating may be attributed to the differences in the internal forces in the unit cells on changes of lattice type I into lattice type II.

Samples of cotton powder of the same particle size (180–125 μm in diameter) of cellulose I were immersed in aqueous solution of NaOH with various concentrations namely 6, 9, 12, 15, and 18% (w/w) and then immediately heated for 8 min at MW heating powers 450 and 900 W.

The XRD of these samples are shown in Figure 3(a) for samples MW-heated at 450 W and Figure 3(b) for samples MW-heated at 900 W. It can be seen from Figure 3(a,b) that the samples treated with 6% aqueous solution of NaOH during MW heating at 450 and 900 W and the samples treated with 9% aqueous solution of NaOH during MW heating at 450 W indicate the presence of cellulose I in addition to a small fraction of cellulose II whose content increases with the increase of MW heating power and the concentration of NaOH in the aqueous solution. The presence of cellulose II is indicated by the presence of very weak shoulder on the left side of the peak (002 at $2\theta = 22.60^\circ$) of cellulose I. The peaks in the X-ray diffraction patterns of the samples treated with 9% aqueous solution of NaOH during MW heating at 900 W and 12% aqueous solution of NaOH during MW heating at 450 W indicate that these samples are mixtures of cellulose lattice types I and II, and a part of cellulose II increases with the increase of MW heating power and the concentration of NaOH in the aqueous solution. The samples treated with 12% aqueous solution of NaOH during MW heating at 900 W and the samples treated with 15 and 18% aqueous solution of NaOH during MW heating at 450 and 900 W converted completely into cellulose lattice type II, as indicated by the absence of the peaks characteristic for cellulose I.

Table I illustrates the NaOH concentrations dependence of *R* values for samples MW heated at 450 and 900 W for 8 min.

It is apparent from the table that, the *R*1 value of cellulose I heated at 450 W increases gradually with the treatment of 6 and 9% aqueous solution of NaOH, whereas, in the case of the sample heated at 900 W, *R*1 assumes an initial slight increase followed by sharp increase with the increase of NaOH concentration. Also the value of *R*1 for the sample treated with 9% and heated at 900 W is higher than its corresponding value of the sample treated with the same concentration at 450 W.

The resolution *R*2 of cellulose II of the samples treated with 12, 15, and 18% NaOH solution and heated at 450 W shows initial sharp decrease followed by slow decrease with the increase of NaOH concentration, whereas in the case of heating at 900 W the *R*2 value suggests slight increase after treatment with 15% compared with its value for the sample treated with 12% and then shows sharp decrease with the increase of concentration. It could be noticed from the table that, for any given concentration (12, 15, and

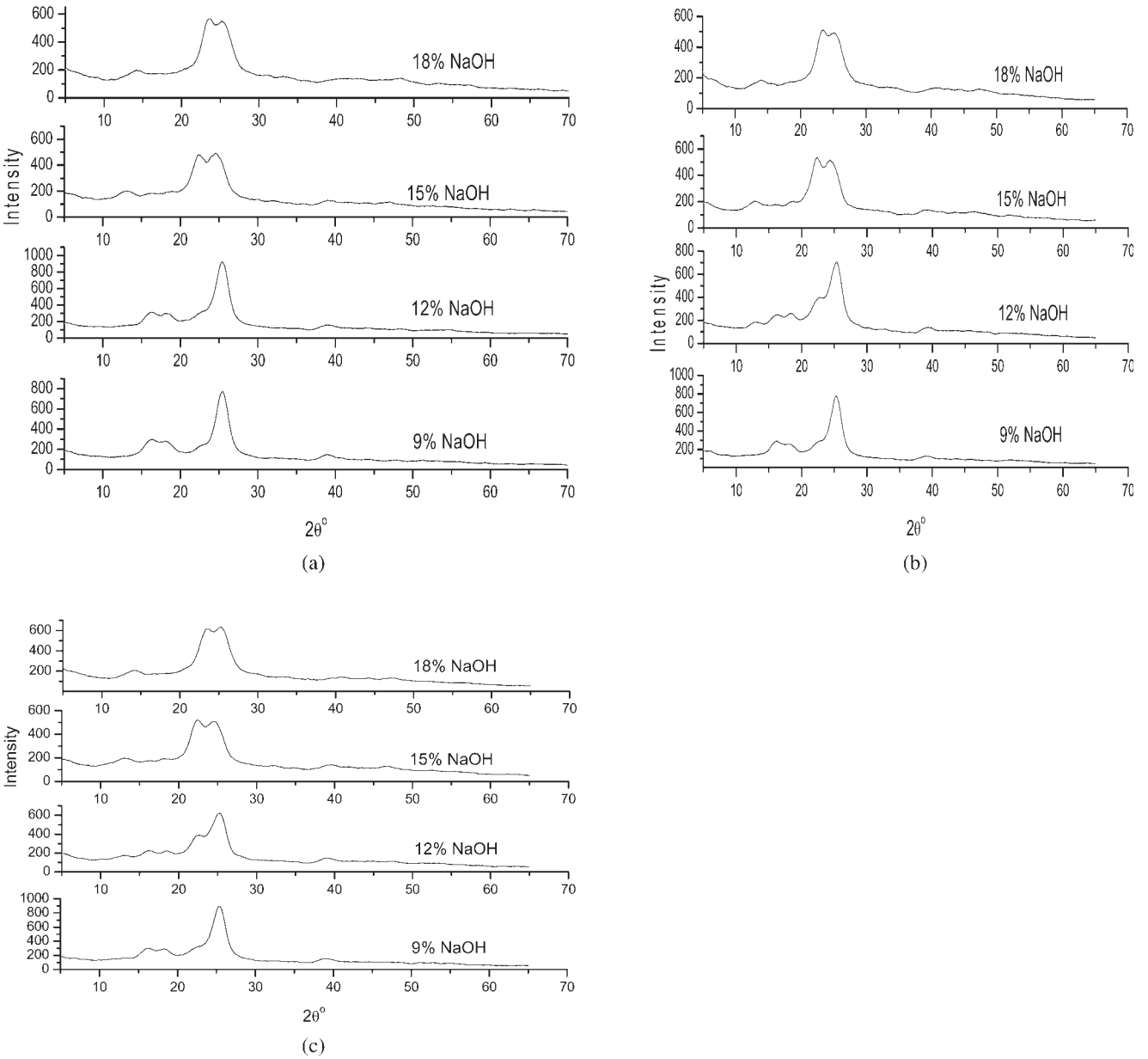


**Figure 4** (a) X-ray diffraction patterns of cotton samples treated with various concentrations of NaOH for 2 min at 900 W. (b) X-ray diffraction patterns of cotton samples treated with various concentrations of NaOH for 4 min at 900 W (c) X-ray diffraction patterns of cotton samples treated with various concentrations of NaOH for 6 min at 900 W.

18%) for the samples heated at 900 W, $R2$ is always lower than the corresponding values for the samples heated at 450 W.

Powder samples of raw cotton of the same particle size (180–125 μm in diameter) were immersed in an aqueous solution of NaOH with concentrations 9, 12, 15, and 18% for 2, 4, and 6 min during MW heating at 900 W.

The XRD patterns of these samples are shown in Figure 4(a–c) for samples MW heated for 2, 4, and 6 min, respectively. Careful examination of Figure 4(a–c) revealed that the MW heating for 2 min at 900 W causes no observable changes in the XRD pattern of cotton sample treated with 9% aqueous solution of NaOH. Treatment with aqueous solution of 12% NaOH and heating for the same time results in appearance of trace amount of cellulose II, whereas a complete transformation of cellulose I to cellulose II takes place on treatment with 15 and 18% NaOH in aqueous solution. This transformation is indicated by the presence of two peaks at 2θ, 20.2° and 21.8°, which are characteristic of cellulose II and absence of the characteristic peaks of cellulose I. The treatment of cellulose I with 15 and 18% NaOH for 4 and 6 min at the same power 900 W results also in complete transformation of cellulose I to cellulose II, whereas treat-

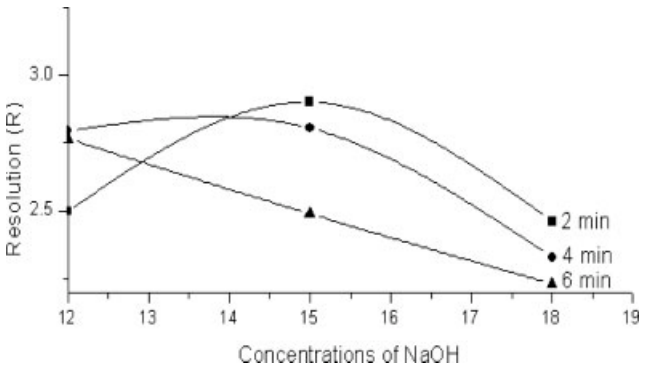


**Figure 5** The relationship between resolution ($R$) and the concentration of NaOH for different times of MW heating.

ment with 12% for the same periods results in partial transformation of cellulose I to cellulose II, which is indicated by the presence of the characteristic peaks of both cellulose I and cellulose II. Moreover, the treatment with 9% NaOH for 4 and 6 min gives weak evidence for the presence of cellulose II, which is indicated by appearance of very small shoulder on the lower side of the peak at $2\theta = 22.60^{\circ}$. Figure 5 illustrates the concentration dependence of the resolution $R2$ for different times.

## CONCLUSIONS

It is well known that mercerization is the swelling of cotton fibers in aqueous solution of sodium hydroxide. This swelling results in reorganization of the cellulose fiber, which becomes cellulose II when the swelling agent is removed. The swelling in sodium hydroxide breaks hydrogen bonds and weak van der Waal's forces between the cellulose chain molecules. Once the forces are broken between chains during swelling, the chains are freed to rearrange, expand, and reorient. When the sodium hydroxide is removed, these chains will form new bonds in this reorganized state.

Based on the foregoing data, it could be concluded that MW heating that causes molecular motions by migration of ions and rotations of the dipoles produces no considerable effects on the mechanism of mercerization but only reduces the concentration of NaOH in the solution and the time of treatment which are needed for the complete transformation of cellulose lattice type I into cellulose lattice type II without any heating. Moreover, it was found that the magnitude of reductions depends on the applied power.

Also, the obtained data lead to the conclusion that drying of cellulose causes slight changes in its crystallinity. The difference in the behavior of the changes in $R$ values of cellulose II compared with the changes in that values for cellulose I is an evidence of differences in internal forces in the unit cell on changes of lattice type I to type II.

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