CELLULOSE CHEMISTRY AND TECHNOLOGY

# GRAFTING OF SOME MONOMERS ONTO CELLULOSE BY ATOM TRANSFER RADICAL POLYMERIZATION. ELECTRICAL CONDUCTIVITY AND THERMAL PROPERTIES OF RESULTING COPOLYMERS

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The research team grafted N-cyclohexylacrylamide (NCHA), 4-vinylpyridine (4VP), diacetone acrylamide (DAAM) and diallylamine (DA) onto pulverized cellulose by atom transfer radical polymerization (ATRP). First, cellulose chloroacetate (Cell.ClAc) was prepared as a macroinitiator by reacting chloroacetyl chloride with primary alcoholic OH groups on powder cellulose, where CuCl and 2,2'-bipyridine were utilized as transition-metal compound and ligand, respectively. The graft copolymers were characterized by FT-IR, elemental and thermal analyses, as well as with regard to their electrical conductivity and optical parameters. The thermal stability of the graft copolymers was determined by the TGA method. The results indicated that all the grafting processes decreased the initial thermal stability of the cellulose. The electrical conductivity of the graft copolymers was measured as a function of temperature, and it was found that it increased with increasing temperature. This indicates that the studied copolymers exhibit semiconducting behavior.

***Keywords***: polymers, cellulose, semiconductors, atom transfer radical polymerization (ATRP), thermogravimetric analysis (TGA)

## INTRODUCTION

The demand for renewable materials in many industrial applications has increased in recent years due to environmental concerns. Cellulose, one of most abundant natural polymers, can be obtained primarily from plant cell walls, but also from microorganisms and animals. Due to its renewability, biodegradability and wide availability, increasing attention has been paid to cellulose-based materials.[1] Cellulose derivatives, containing polymeric side chains covalently linked to the oxygen of the glycoside unit, are usually named cellulose graft copolymers. Since 1950, various olefins have been grafted onto cellulose and starch in order to prepare novel products with peculiar properties.[2]

A number of methods are known for graft copolymerization of various monomers on the cellulose backbone, such as free radical polymerization[2,3] ring-opening polymerization,[4] nitroxide-mediated polymerization (NMP),[5] reversible addition–fragmentation chain transfer (RAFT) polymerization[6] and ATRP.[7-13] Among these methods, ATRP has been extensively studied for achieving graft copolymerization of monomers onto cellulose and cellulose derivatives in a living/controllable way.

Semiconducting polymers have come under the spotlight since they are promising materials for optoelectronic devices, such as light-emitting diodes, photovoltaic cells and nonlinear optical systems.[14-21]

In general, physical measurements, specifically with regard to electrical conductivity, are performed on synthetic polymers. In our present work, cellulose, a natural polymer, was turned into a semi-synthetic polymer, and then it was modified with synthetic constructs. The obtained graft copolymers were characterized chemically and physically, with regard to their thermal stability, electric and optical behaviors.

## EXPERIMENTAL

### Material and methods

Powdered cellulose, supplied by Aldrich, was washed with dilute NaOH, water, dilute acetic acid, methanol and acetone, and then dried under vacuum. Potassium tert-butoxide, chloroacetyl chloride and 2,2'-bipyridine (Aldrich), as well as cuprous (I) chloride (Sigma), were used as received. Diacetone acrylamide (Aldrich) monomer was purified by recrystallizing from chloroform. Cyclohexylamine (Fluka) was freshly distilled under vacuum prior to use. Diallylamine (Aldrich) was first rinsed with a dilute NaOH solution to extract the polymerization inhibitor, followed by rinsing with pure water, then dried and finally distilled under vacuum. 4-Vinylpyridine (Aldrich) was passed through a basic alumina column as diethyl ether solution with the same purpose, and then used after the ether was distilled off. All the other solvents used were of reagent grade and no further purification was performed.

### Synthesis of cellulose chloroacetate and graft copolymers by atom transfer radical polymerization

Cellulose chloroacetate (Cell.ClAc) was prepared by a method adapted from the literature.[2,3,7-10] Cellulose (0.02 moles repeating unit) was left to swell in acetonitrile (50 mL) at room temperature overnight and 0.06 mole solution of potassium-t-butoxide was added to 50 mL of acetonitrile. This mixture was stirred for 4 h at room temperature, and then 0.2 mole of chloroacetyl chloride in 50 mL of acetonitrile was added dropwise under continuous stirring. The reaction mixture was refluxed for 24 h, cooled and filtered. Cellulose chloroacetate was rinsed with water, acetonitrile, ethanol, acetone and diethyl ether, and finally dried under vacuum.

N-cyclohexylacrylamide (NCHA) was synthesized by a method adapted from the literature.[9] Graft copolymers were prepared by a method described in earlier studies.[2,3,7-10] 2,2'-Bipyridine (ligand) and CuCl were added to a polymerization tube and stirred under argon for about 15 min. Cellulose chloroacetate (macroinitiator) and the respective monomer (NCHA, 4VP, DAAM and DA) in 10 ml N,N-dimethylformamide (DMF) were added and argon was passed through for 15 min. The polymerization tube was sealed and the grafting reaction of the monomer onto cellulose was allowed to proceed at 130 ºC for 24 h. Cell.ClAc, CuCl, 2,2'-bipyridine and each separate monomer were used at a mole ratio of 1:1:3:100, respectively. After the mixture was filtered, it was washed with acetonitrile, DMF, chloroform, a mixture of water-ethanol-HCl, pure water, ethanol, acetone and diethyl ether to eliminate oligomers and homopolymers formed as by-products in the reaction. The obtained graft copolymers were then dried under vacuum.

### Instrumental measurements

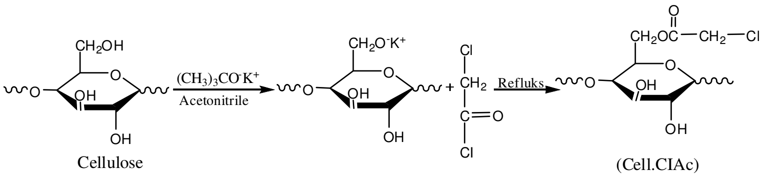
FT-IR spectra were recorded using a Perkin Elmer Spectrum One FT-IR spectrophotometer on solid samples as KBr pellets. Thermal analysis was performed with a Shimadzu thermobalance TGA-50 at a heating rate of 10 ºC min$^{-1}$ under nitrogen flow of 10 ml min$^{-1}$. A Leco CHNS-932 apparatus was used for elemental analysis. Absorbance spectra of the copolymers were measured using a Shimadzu 3600 UV-VIR-NIR spectrophotometer. The electrical conductivity measurements were performed using a Keithley 6517A electrometer.

## RESULTS AND DISCUSSION

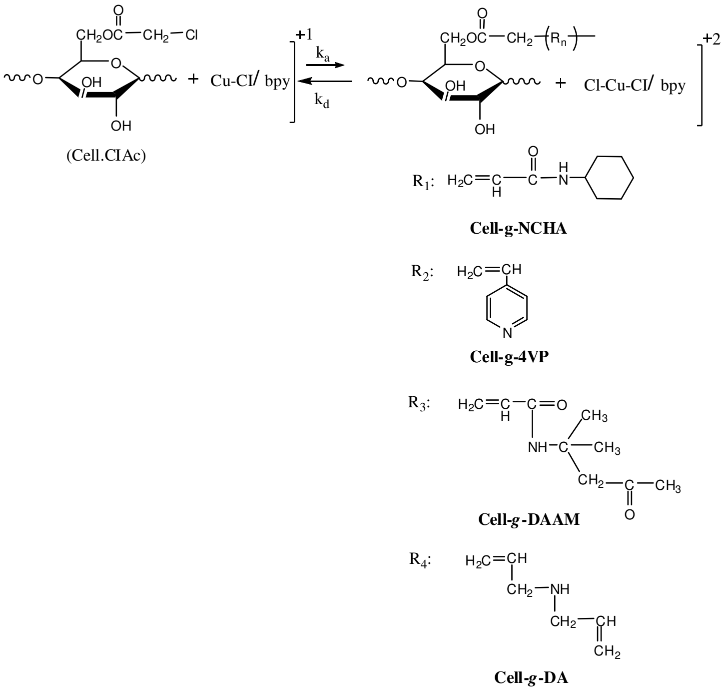
### Preparation and characterization of graft copolymers

The chloroacetyl group is an effective initiator for ATRP.[7-10] As mentioned above, in order to achieve the grafting of cellulose, cellulose chloroacetate was first obtained, as indicated in Scheme 1, and then a series of grafting experiments onto cellulose were carried out by utilizing Cu(I)/2,2'-bipyridine complex as a catalyst of ATRP graft copolymerization. Scheme 2 shows the reactions of grafting on cellulose. Chloroacetate groups act as a macroinitiator under these conditions.

FT-IR spectra of cellulose, Cell.ClAc and all the graft copolymers (Cell-*g*-NCHA, Cell-*g*-4VP, Cell-*g*-DAAM, and Cell-*g*-DA) are presented in Figure 1. Two new bands at 1745 cm$^{-1}$ (C=O stretching) and at 790 cm$^{-1}$ (C-Cl stretching) in the spectrum of Cell.ClAc show that the chloroacetyl group has attached to cellulose. Meanwhile, there are no such bands in the spectrum of the control cellulose sample.



Scheme 1: Synthesis of cellulose chloroacetate as macroinitiator



Scheme 2: Grafting of cellulose with some monomers by ATRP

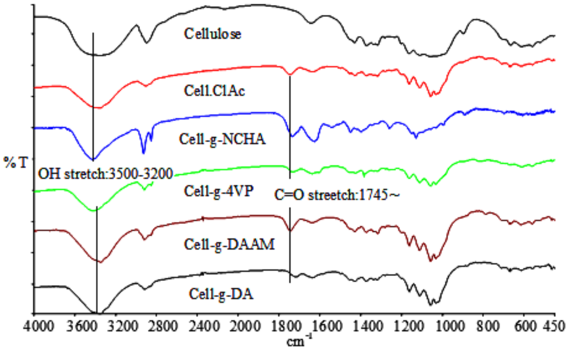


Figure 1: FT-IR spectra of the graft polymers

The presence of the bands at 1660 cm$^{-1}$ (C=O in the amide group) for Cell-*g*-NCHA, at 1660 cm$^{-1}$ (C=O in the amide group) and 1730 cm$^{-1}$ (C=O increase in the ester group) for Cell-*g*-DAAM, as well as at 1600 cm$^{-1}$ (as a shoulder, pyridine ring N stretching) for Cell-*g*-4VP, is the most important evidence of grafting. For Cell-*g*-DA, the band of N-H at 3300 cm$^{-1}$ and the stretching band of cellulose's OH groups between 3500-3200 cm$^{-1}$ have overlapped.

The substitution degree (%) in the glucose units of cellulose was calculated as 36.5% by mole from the percentage of carbon, as described in the literature.[2,3,7-10] This result indicated that the substitution on the –$CH_2OH$ groups in cellulose was achieved to a high extent.

The elemental analysis results for all the polymers and the % mole quantities of the monomers and Cell.ClAc in the graft copolymers (%n) are presented in Table 1. The average molecular weight of Cell.ClAc and unsubstituted cellulosic unit were calculated as follows:

$$\bar{M} = y \cdot M_{Cell.ClAc} + (1-y) \cdot M_{Cellulose} = 189.9 \qquad (1)$$

The copolymer composition was calculated from the nitrogen content of the graft copolymer. Mole quantities (n) of each monomer grafted onto cellulose were calculated from the following relationship:

$\%A = a \cdot M_{m1} / M_e$ $\quad \%B = 100 - \%A$

$n_1 = A / M_{m1}$ $\quad n_2 = B / M_{m2}$

$\%n_1 = n_1 / (n_1 + n_2) \cdot 100$ $\quad \%n_2 = n_2 / (n_1 + n_2) \cdot 100$

where A is the nitrogen content in the monomer, B is Cell.ClAc; %A and %B are the corresponding mass in the copolymer; $M_{m1}$ is the molecular mass of the monomer; $M_e$ is the atomic mass of the element analyzed; $n_1$ and $n_2$ indicate the number of moles in 100 g copolymer. Thus, $\%n_1$ shows the mole% of monomer in the copolymer, $\%n_2$ shows the mole% of substituted Cell.ClAc in the copolymer.[22]

## Thermal stability of copolymers

The effect of grafting on the thermal stability of cellulose was studied using thermogravimetric analysis as a characterization technique. Figure 2 shows the TG curves of the grafted celluloses (Cell-*g*-NCHA, Cell-*g*-4VP, Cell-*g*-DAAM and Cell-*g*-DA) with different monomers, of the ungrafted one and the substituted one (Cell.ClAc) and of the control cellulose. If initial decomposition temperature (IDT) and the temperature where the weight loss reached 50% are taken as a measure of thermal stability, the data given in Table 2 show that all the grafting processes have decreased the thermal stability of cellulose. While the IDT of the control cellulose is around 290 ºC, all the graft copolymers show lower values, including Cell.ClAc, which exhibits an IDP of about 265 ºC. Cellulose decomposes in a narrower temperature interval, whereas the others have a wider interval. All the graft copolymers show a breaking point at a definite temperature after some weight loss. This means that the graft copolymers have two stages of decomposition, while cellulose degraded in only one stage. Similar thermal behaviors have been identified in the case of cellulose fibers partially esterified with some long-chain organic acids[23] and of methyl acrylate, methyl methacrylate and 2-hydroxyethyl methacrylate grafted celluloses.[24]

Table 1
Elemental analysis and grafting of cellulose with some monomers

| Polymer | C (%) | H (%) | N (%) | % mole quantities of monomer in graft copolymer ($\%n_1$) | % mole quantities of Cell.ClAc in graft copolymer ($\%n_2$) |
|---|---|---|---|---|---|
| Cellulose | 42.03 | 5.55 | - | | |
| Cell.ClAc | 40.11 | 5.34 | - | | |
| Cell-*g*-NCHA | 44.01 | 6.06 | 2.16 | 27.70 | 72.30 |
| Cell-*g*-4VP | 43.43 | 6.56 | 2.54 | 29.82 | 70.18 |
| Cell-*g*-DAAM | 47.31 | 6.60 | 1.24 | 16.57 | 83.43 |
| Cell-*g*-DA | 46.19 | 7.50 | 1.08 | 13.65 | 86.35 |

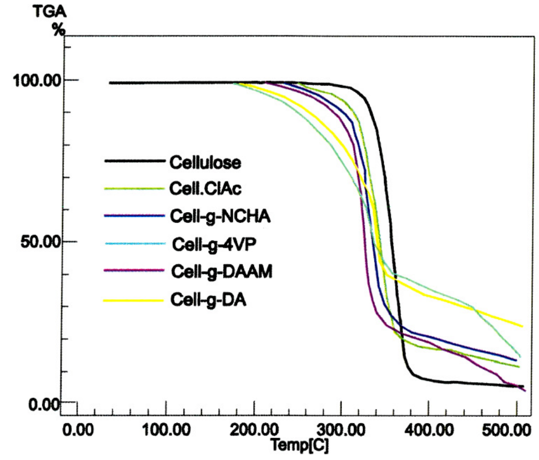


Figure 2: TGA curves of the graft polymers

Table 2
Thermal stabilities of cellulose, substituted cellulose and its graft copolymers

| Polymer | (%) Initial decomposition temperature (ºC) | Temperature of 50% weight loss (ºC ) | Residue (%) at 500 ºC |
|---|---|---|---|
| Cellulose | 290 | 370 | 6.0 |
| Cell.ClAc | 265 | 355 | 15.8 |
| Cell.ClAc-*g*-NCHA | 221 | 344 | 12.5 |
| Cell.ClAc-*g*-4VP | 180 | 333 | 13.9 |
| Cell.ClAc-*g*-DAAM | 209 | 323 | 2.8 |
| Cell-ClAc-*g*-DA | 184 | 337 | 19.9 |

## Electrical conductivity and optical parameters of copolymers

The electrical conductivities and optical parameters of the initial polymer and the modified ones were evaluated. Figure 3 shows the plots of σ versus T for the control cellulose and the modified polymers and it may be observed that electrical conductivity increases with increasing temperature. The electrical conductivity of the copolymers changes when the amide monomers are grafted. The cellulose grafted with the NCHA monomer exhibits the lowest conductivity, whereas the Cell-*g*-4VP copolymer has the highest conductivity at room temperature. However, with an increase in temperature, the conductivity deviated from linearity – beyond 350 K, it decreased and then increased again. This behavior is related to the chemical structure of the grafted monomer.

All the grafted samples exhibit the same behavior. This confirms an interaction between the cellulose and the monomers. The Cell-*g*-4VP copolymer exhibits the highest conductivity due to the conjugation of 4VP. The potential difference and heat applied will shift an electron from one atomic site to another; therefore the π-electrons on the chain of the polymer will be delocalized. The conductivity increase of Cell-*g*-4VP occurs due to the heat and voltage applied.[25] The obtained results indicate that all the copolymers exhibit semiconducting behavior, but only sample Cell-*g*-4VP can be used as an organic semiconductor. Also, it can be said that the oscillation that is noted in curve 5 around 330 K (Fig. 3) is caused by tunneling and thermionic oscillation.

The plots of absorbance *versus* wavelength for the control polymer and the modified ones are shown in Figure 4. The absorbance of the copolymers varies as a function of the grafted monomer. The sudden increase in the absorbance of the copolymers is called an absorption edge. At this stage, the electrons move from the valence band to the conduction band. As may be noted in the figure, the Cell-*g*-4VP sample has the lowest absorption edge. This suggests that this sample has the lowest optical band. A low optical band is associated with high conductivity. This result in very good agreement with the conductivity results of the copolymers, which indicate that Cell-*g*-4VP has the highest conductivity.

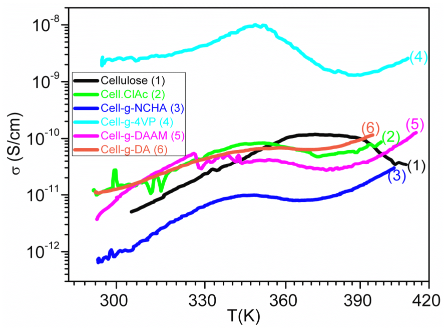


Figure 3: Plots of σ *versus* T for the polymers

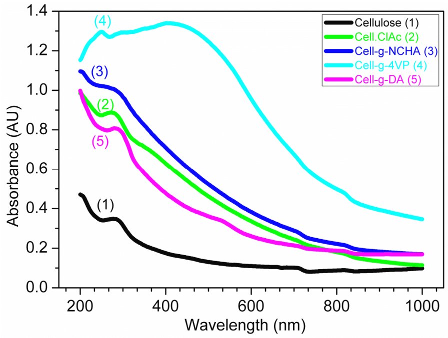


Figure 4: Plots of absorbance *versus* wavelength for the polymers

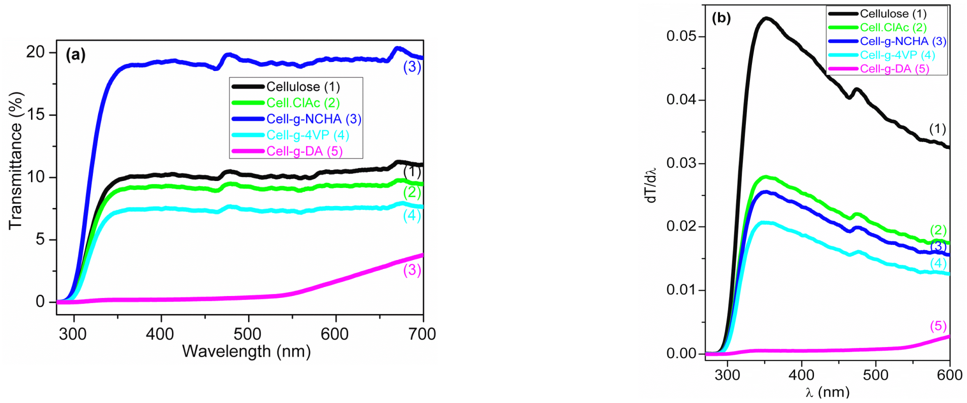


Figure 5: Plots of (a) transmittance *versus* wavelength and (b) dT/dλ *versus* λ for the polymers

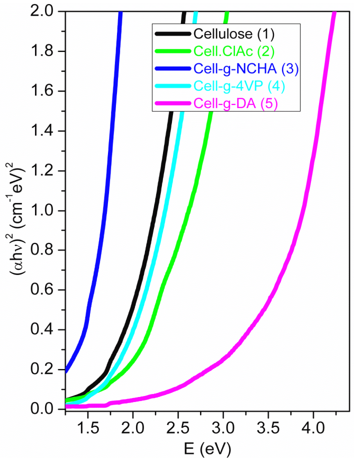


Figure 6: Plot of $(\alpha h\nu)^2$ *versus* E for the polymers

Table 3
Maximum peak position ($\lambda_{max}$), absorption band edge ($E_{g\text{-}Abs}$) and optical band gap ($E_g$) parameters of the polymers

| Polymer | $\lambda_{max}$ (nm) | $E_{g\text{-}Abs}$ (eV) | $E_g$ (eV) |
|---|---|---|---|
| Cellulose (1) | 352 | 3.523 | 1.936 |
| Cell.ClAc (2) | 352 | 3.5237 | 2.125 |
| Cell-g-NCHA (3) | 352 | 3.523 | 1.58 |
| Cell-g-4VP (4) | 349 | 3.553 | 1.981 |
| Cell-g-DA (5) | - | - | 3.375 |

The transmittance (T) spectra of the initial polymer and the modified ones are shown in Figure 5a. The transmittance values of all the samples increase sharply between 290 and 350 nm, then become almost constant at higher wavelengths. Also, the T values of Cell-g-NCHA (3) are the highest, while the T values of Cell-g-DA (5) are the lowest. The obtained results suggest that the transmittance values of the polymer can be controlled by the choice of the appropriate graft monomer.

We calculated the absorption band edge ($E_{g\text{-}Abs}$) values of all the samples from the first derivative (see Fig. 5b) of optical transmittance.[26,27] The $E_{g\text{-}Abs}$ values were obtained from the maximum peak position ($\lambda_{max}$). However, the $\lambda_{max}$ was not observed for Cell-g-DA (5). The obtained values for $\lambda_{max}$ and $E_{g\text{-}Abs}$

are given in Table 3. As may be seen in Table 3, the $\lambda_{max}$ value of cellulose (1), Cell.ClAc (2) and Cell-g-NCHA (3) is at 352 nm, while the $\lambda_{max}$ value of Cell-g-4VP (4) is at 349 nm. These results suggest that the $E_{g\text{-}Abs}$ value of the control cellulose (1), Cell.ClAc (2) and Cell-g-NCHA (3) is 3.523 eV, while that of the Cell-g-4VP (4) is 3.553 eV.

The optical band gap ($E_g$) is fundamental for optical parameters and is of great importance for optoelectronic applications. The $E_g$ values of the initial polymer and the modified ones can be obtained from the Tauc relation:[27-30]

$$(\alpha h\upsilon) = B(h\nu - E_g)^n \tag{3}$$

where B is a constant, hν is the photon energy, and n is the parameter measuring the type of band gaps.

The $E_g$ values of all the samples were obtained from Figure 6 (plot of $(\alpha h\nu)^2$ *vs.* E) and are given in Table 3. As seen in Table 3, the $E_g$ value (1.580 eV) of Cell-g-NCHA (3) is the lowest, while the $E_g$ value (3.375 eV) of Cell-g-DA (5) is the highest. The obtained results suggest that the initial polymer and the modified ones exhibit semiconducting behavior due to their optical band gap values.

## CONCLUSION

Cellulose chloroacetate was prepared by esterification of primary alcoholic OH groups on raw powdered cellulose and the yield was of 36.5%. Cellulose was first esterified with chloroacetyl chloride, yielding cellulose chloroacetate, which behaves as a macroinitiator due to the chloroacetyl groups on it. Graft copolymers of cellulose and some monomers, such as N-cyclohexylacrylamide, 4-vinylpyridine, diacetone acrylamide and diallylamine, were prepared by atom transfer radical polymerization. As expected, no homopolymer was formed during the grafting, because of ATRP.[7-14] The graft copolymers were characterized by FT-IR, elemental and thermal analyses, as well as with regard to their electrical conductivity and optical parameters. The thermal stability of the graft copolymers was determined by the TGA method and revealed that all the grafting processes decreased the thermal stability of the initial cellulose. The electrical conductivity of the graft copolymers was measured as a function of temperature and it was noted that it increased with increasing temperature. This indicates that the studied copolymers exhibit semiconducting behavior. The electrical and optical parameters of all the copolymers varied with the grafting monomer used. Cellulose exhibits the highest conductivity and lowest optical absorption edge when grafted with the 4VP monomer.

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