

Cellulose Acetate Deacetylation in Benzene/Acetic Acid/Water Systems

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ABSTRACT: An unconventional system for cellulose acetate hydrolysis, consisting of homogeneous mixtures of benzene/acetic acid/water of different compositions, was investigated from the perspective of kinetics and also with respect to the degradation of the cellulosic chains during the process. It was observed that the decrease of the degree of substitution of the polymer occurs with higher reaction rate than that in the reference system, free of benzene, and depends on the composition of the reaction medium. A pseudo-first-order kinetic law satisfactorily describes the deacetylation process performed in the presence of benzene. Also, the degradation of the polymeric chain during the

process is dependent on the presence of the hydrocarbon and on the composition of the reaction system used. A lower degradation rate was found to characterize the first period of the process, compared with that produced in a benzene-free system. These peculiarities were explained by the influence of benzene on the composition of solvent shell in the vicinity of macromolecules. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1965–1968, 2004

Key words: cellulose acetate; hydrolysis; kinetics (polym.); chain; degradation

INTRODUCTION

The conventional method used for obtaining soluble, partially substituted cellulose acetates still consists of the homogeneous hydrolysis of highly acetylated cellulose in aqueous acetic acid media and in the presence of a mineral acid as a catalyst.^{1,2} In this case, apart from the temperature and the reaction time, the composition of the reaction medium (e.g., the water : acetic acid ratio) is a very important factor controlling both the hydrolysis rate and some fundamental properties of the polymer: the distribution of substituents and the degree of polymerization (DP).

This procedure presents some drawbacks such as long reaction times, the necessity of addition of water during the process, and the difficult recovery of by-products. On the other hand, other organic solvents (e.g., benzene, toluene) are used in cellulose acetate synthesis³ or for the recovery of acetic acid from the reaction system.²

In previous experiments, we observed that the presence of toluene in the hydrolysis media remarkably decreased the time required for obtaining soluble far-hydrolyzed cellulose acetates, useful for further derivatization.^{4,5}

For these reasons, the present article deals with a study on the influence of the presence of benzene in the hydrolysis mixture on the evolution of deacetylation process, as well as on the degradation of the macromolecular chains of the hydrolyzed products.

EXPERIMENTAL

Cotton linters with DP 1000, activated overnight with glacial acetic acid, were acetylated in acetic acid medium with an excess of acetic anhydride using 10 wt % sulfuric acid (with respect to the starting cellulose) as a catalyst.⁶

The partial hydrolysis was performed without isolation of high-acetyl cellulose acetate. This product was first hydrolyzed to the degree of substitution (DS), about 2.80 in 90% aqueous acetic acid, at 40°C for 10 h. After this prehydrolysis stage, the corresponding amounts of benzene, acetic acid, and water were added to obtain the compositions of the reaction systems listed in Table I. An aliquot was removed from each reaction system for the determination of the initial DS, then the temperature was raised to 60°C and the hydrolysis was carried out under continuous stirring. Samples were removed after 8, 16, 24, and 32 h of reaction.

The hydrolyzed cellulose acetates were isolated by precipitation into water, then purified and stabilized, as described in the literature,⁶ and air-dried.

DS values were determined by the alkali saponification method.⁷

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TABLE I
Compositions of Benzene/Acetic Acid/Water Reaction
Systems for Cellulose Acetate Hydrolysis at 60°C

Reaction system	Composition (wt %)			Rate constant (h ⁻¹)
	Benzene	Water	Acetic acid	
BAC ₁	20	8	72	0.0157
BAC ₂	15	8	77	0.0128
BAC ₃	35	8	57	0.0213
BAC ₄	35	6	59	0.0193
BAC ₅	45	6	49	0.0267
BAC ₆	45	4	51	0.0264
AC	0	8	92	—

The reduced viscosity, η_{sp}/c , of solutions of cellulose acetates in glacial acetic acid was measured at 25°C using a Ubbelohde viscometer. For samples with DS = 2.70, a concentration of 0.0952 g/dL was chosen. For the other DS values, corrections of concentrations were necessary.

RESULTS AND DISCUSSION

Figure 1 provides evidence of the decrease of DS of cellulose acetate during the hydrolysis performed in systems containing benzene, which is more pronounced than that produced in the absence of this hydrocarbon. This decrease is also dependent on the proportion of benzene. Thus, products with DS about 2.00 could be obtained after only 16 h in reaction media containing 35% benzene, compared with the 32 h necessary for the same DS in the reference system AC. Also, 35% benzene could provide a DS of about 1.70 (useful for further derivatization) after 24 h in the studied conditions. With 45% benzene, which implies a water content lower than 8%, the effect is more

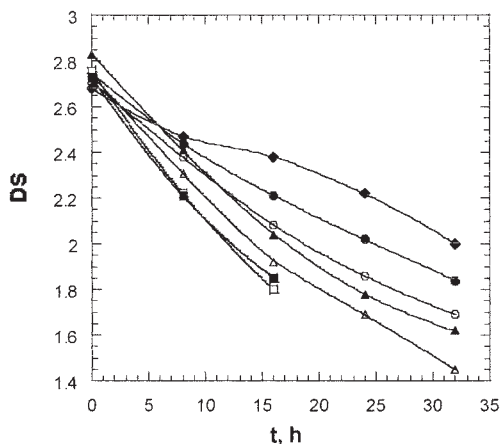


Figure 1 Hydrolysis of cellulose acetate in the reaction systems: \blacklozenge , AC; \bullet , BAC₂; \circ , BAC₁; \blacktriangle , BAC₄; \triangle , BAC₃; \blacksquare , BAC₆; \square , BAC₅.

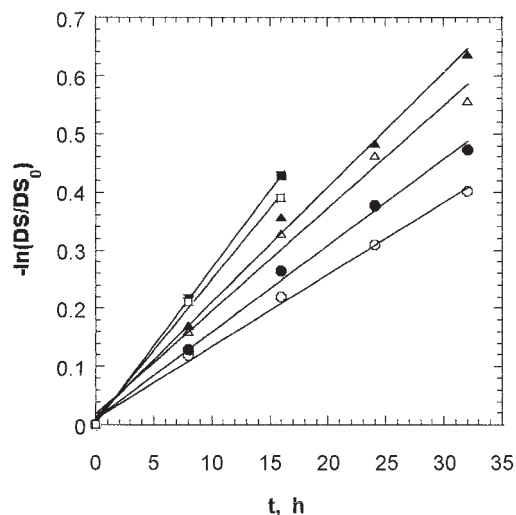


Figure 2 Kinetic plots for the reaction systems: \blacksquare , BAC₆; \square , BAC₅; \blacktriangle , BAC₂; \triangle , BAC₁; \bullet , BAC₄; \circ , BAC₃.

pronounced, although after 16 h of reaction, because of the high degradation and a partial precipitation of the polymer, the samples could hardly be isolated and purified.

As established from the literature,⁸ cellulose acetate hydrolysis performed in the conventional acetic acid/water system consists of two simultaneous and reversible second-order reactions. The position of acetyl (or hydroxyl) groups within the anhydroglucose unit (AGU) also influences the rate of deacetylation.

In contrast with this conventional system, the process in the benzene/acetic acid/water system follows an irreversible pseudo-first-order kinetic law [eq. (1)]; for higher proportions of benzene (systems BAC₅ and BAC₆), we may assume a similar behavior just for the first 16 h of the process.

In these conditions, the studied reaction systems can be described by the kinetic equation

$$\ln DS/DS_0 = -kt \quad (1)$$

where DS_0 and DS are the degrees of substitution of cellulose acetate at zero time and at time t , respectively.

The dependencies of $\ln DS/DS_0$ on the hydrolysis time are plotted in Figures 2 and 3, for systems containing benzene and for the reference system, respectively. A good linearity is observed just for the unconventional benzene/acetic acid/water system (Fig. 2).

The reaction rate constants k (Table I) are correlated with the system composition by means of the following regression equation:

$$y = 0.012906 + 0.000370x_1 - 0.000075x_2 \quad (2)$$

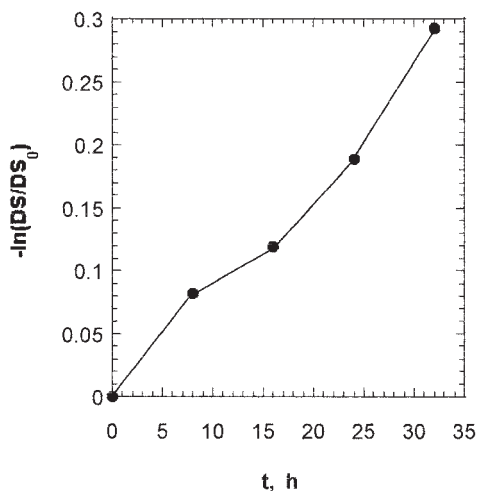


Figure 3 Kinetic plots for the reaction system AC.

where y is the rate constant and x_1 and x_2 are the proportions of benzene and acetic acid, respectively, in the hydrolysis medium (Table I).

The high value of the square multiple correlation coefficient, $R^2 = 0.959$, shows that a high fraction of the sum of squares of deviations of y from its mean is attributable to this regression.

Equation (2) shows the increase of the hydrolysis rate when increasing the proportion of benzene in the reaction bath.

This particular kinetic behavior of the deacetylation process performed in benzene-containing media, compared with those in benzene-free ones, can be explained by taking into account the observation of Kamide et al.⁹ that the contact of cellulose acetate with the solvent occurs especially by means of polar moieties of the solvent and *O*-acetyl and hydroxyl groups of the macromolecules, as well as the fact that benzene has a better compatibility with acetic acid than with water. Thus, the presence of benzene in the hydrolysis bath produces a decrease of acetic acid content and a corresponding increase of water content in the solvation shell, which accelerates the deacetylation and diminishes the reesterification process. Overall, the hydrolysis appears to be an irreversible process governed by a first-order kinetic law.

Besides this effect, we may also take into consideration the influence of the benzene upon the compatibility of the catalyst (sulfuric acid or its hydrates) with the solvent system containing a hydrocarbon. Our previous data, related to the partition of sulfuric acid in such solvent systems containing cellulose,⁴ showed that the amount of catalyst retained on cellulose increased with increasing hydrocarbon content. Therefore, this compatibility is lower in such systems compared with the reference system, free of benzene, suggesting that the concentration of the catalyst is

increased in the solvation shell, which accelerates the deacetylation process.

Another important property of cellulose acetate significantly influenced by the hydrolysis medium is the degree of polymerization that can be modified by both acetolysis and hydrolysis. As we have already shown,⁵ the reduced viscosities, η_{sp}/c , of cellulose acetate samples in glacial acetic acid are suitable to describe the macromolecular chain degradation during the process. Thus, a linear relationship was found between η_{sp}/c and the intrinsic viscosity in a "cuen" solution for cellulose regenerated from the corresponding cellulose acetate sample.⁵

The data plotted in Figure 4, for the degradation of cellulose acetates in different reaction media, show that, in systems containing benzene, the chain degradation in the first period of hydrolysis is lower and in the last one is higher than that in the benzene-free system.

These observations are also consistent with the above explanation regarding the composition of the solvation shell. Indeed, because of the better compatibility of benzene with acetic acid than with water, the vicinity of macromolecules is poorer in acetic acid and thus the chain degradation by acetolysis is significantly reduced. This effect seems to be more pronounced for higher DS values and so the degradation is diminished at the beginning of the process. When reducing DS (in the last part of hydrolysis), the higher polarity of the polymer determines lower quantities of benzene and, correspondingly, higher amounts of acetic acid and water in the solvation shell, which favor a higher degradation rate by acetolysis and hydrolysis, compared with the reference system, free of benzene. For this higher polarity, in a system not containing

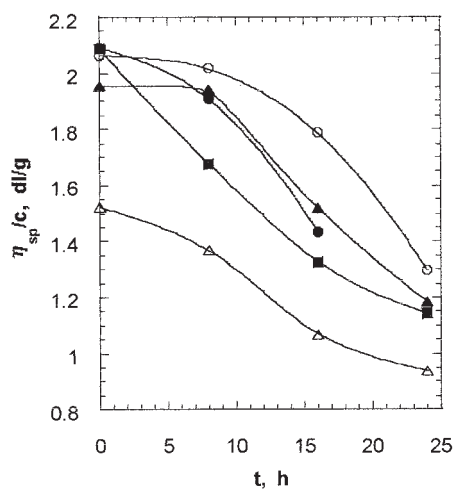


Figure 4 Reduced viscosity (η_{sp}/c) versus time (t) for the reaction systems: ○, BAC₂; ▲, BAC₃; ■, AC; ●, BAC₁; △, BAC₄.

benzene the concentration of the catalyst in the vicinity of macromolecules is lower than that in the case of using a hydrocarbon in the reaction medium; therefore, this system seems to provide a better protection of macromolecular chain from this perspective.⁴

CONCLUSIONS

1. The presence of benzene remarkably increases the rate of hydrolysis of cellulose acetate in homogeneous media benzene/acetic acid/water with an acid catalyst.
2. The hydrolysis process follows an irreversible pseudo-first-order kinetic law.
3. The chain degradation is slower in the first period of reaction and higher in the last one, compared with that produced in a benzene-free system.

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