Retardation effect in acetalization of poly(vinyl alcohol) with butyraldehyde

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ABSTRACT

The condensation reaction of butyraldehyde with poly(vinyl alcohol) at various degrees of polymer conversion was studied from the kinetic point of view. The reaction was carried out at 20–50 °C. On the basis of the effective rate constants calculated from the kinetic investigations, it was inferred that the reaction proceeded with retardation as the degree of acetalization increased. The anomalous retardation was observed in dilute polymer solutions (1 wt.%). The retardation effect thus revealed was explained in terms of the conformation of the polymer chains and possible side reactions.

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1. Introduction

Acetals of poly(vinyl alcohol) (PVA) are important industrial products that find application in the aviation and automobile industries. One such polymer is poly(vinyl butyral) (PVB). PVB is extensively used in laminated safety glasses, binders, paints, and adhesives [1,2]. The HCl-catalyzed reaction of PVA with butyraldehyde produces a copolymer containing residual hydroxyl groups (x) and acetal rings (y) (Scheme 1).

Previous studies revealed some peculiarities in the kinetics of the acetalization reaction of pure PVA with various aldehydes. In the kinetic investigation of the acid-catalyzed formation of PVA formal in aqueous media at 70 °C [3], it was found that the rate of the reaction was proportional to the stoichiometric concentrations of both formaldehyde and hydroxyl groups of PVA. Studies of the hydrolysis kinetics of the acetalization of pure PVA with acetaldehyde in water–dioxane solutions at different temperatures [4] indicated that (i) the rate of the hydrolysis decreases with increasing acetal concentration and (ii) for copolymers of various compositions, but at the same acetal concentration, the hydrolysis proceeds most rapidly for the copolymers with the highest hydroxyl group content. The rate constants derived from kinetic investigations of the acid-catalyzed acetalization with different aldehydes in homogenous media using water as the solvent [5] indicated that the formation of *hemi*-acetal is the rate-determining step. The reaction of stereoisomers of pentane-2,4-diol and heptane-2,4,6-triol with formaldehyde has also been investigated as a model for the formalization reaction of PVA [6]. That study indicated that the (*meso*) diol portion reacted with formaldehyde several times faster than did the optically active diol portion at 30–80 °C. The rates of hydrolysis of the obtained formals of the diols were compared with those of the triols to evaluate the effect of a hydroxyl group adjacent to the forming ring on the reaction. No appreciable rate differences were observed, and it was deduced that the increase in the rate of hydro-

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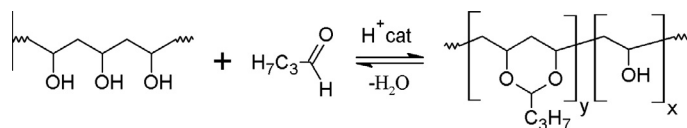
Scheme 1.

lysis of polyvinyl formal with an increase in the number of hydroxyl groups could be attributed to polymeric effects.

The reactivity of the functional groups of the polymer chain may be affected by a number of factors including the neighbouring-group effect [7], configurational and conformational effects [8], and preferential solvent effect [9]. It is also necessary to take into account the fact that the kinetics of acetalization involving PVA might be complicated due to the specific peculiarities of this reagent such as strong inter- and intra-molecular association of the hydroxyl groups. Compositional and structural modification of the macromolecules occurs during the acetalization of PVA, which influences the character of the aforementioned effects and thus influences the kinetics. Therefore, our motivation was to clarify the kinetic differences between acetalization of pure PVA and partially modified PVA by varying the ratio of acetal and hydroxyl groups.

2. Experimental

Commercial atactic PVA with an average polymerization degree of 1130 and saponification degree above 99% was used (see ^{13}C NMR spectra in the Supporting information). Butyraldehyde (BU), ⩾98.0% (GC) (Fluka) and 2,4-pentanediol, meso (±), 99% (Alfa Aesar) were used without further purification. Commercial dimethyl sulfoxide (DMSO) was purified by recrystallization before use. Hydrochloric acid (ACS grade, 37%) was used as a catalyst. To investigate the reactivity of PVB at various conversions, polymers containing varying amounts of acetal groups, obtained by the acetalization of PVA, were used as substrates. Water and DMSO were selected as solvents.

BU was added to a solution of PVA in water or DMSO. The mixture was stirred for 0.5 h, after which the HCl catalyst was added. After a defined interval of time, the products were isolated by precipitation in acetone. The polymer was purified by repeated precipitations from water or DMSO solution by addition into acetone, and the product was finally dried under reduced pressure at 50 °C. The initial concentrations of BU and hydrochloric acid were 0.007–0.12 and 0.02 M, respectively, for all experiments. The homogeneity of all systems examined herein was carefully maintained. BU concentrations were determined by gas chromatography using a Chromos GC-1000 chromatograph equipped with a VertiBond AqWAX capillary column (nitroterephthalic acid-modified polyethylene glycol stationary phase, length: 60 m, I.D.: 0.32 mm, film: 0.50 μm). The degree of acetalization was determined by ^{1}H NMR spectroscopy [10,11] and according to a previously described method [12]. The ^{1}H NMR spectra were obtained at 400 MHz using a Bruker AV-400 spectrometer and were recorded in methanol-d$_4$ and DMSO-d$_6$ with tetramethylsilane (TMS) as the internal standard.

The effective rate constants were calculated according to [13], using the following equation:

$$kt = \frac{1}{\left(c_p^0 - 2c_a^0\right)} \ln\left(\frac{1-\alpha_p}{1-\alpha_a}\right), \tag{1}$$

where c_p^0 is the PVA initial concentration (M); c_a^0 is the aldehyde initial concentration (M); $\alpha_a = (c_a^0 - c_a)/c_a^0$ is the aldehyde consumption; $\alpha_p = \left(c_p^0 - c_p\right)/c_p^0$ is the hydroxyl conversion.

The values of kt, calculated from Eq. (1), were plotted against reaction time t. For all experiments, linear plots were obtained and the effective rate constant, k_{eff}, was calculated from the slope of each line (the examples of the $kt = f(t)$ plots are given in the Supporting information for this article).

In order to study the viscosity change during the course of the reaction the prepared solutions were gently filtered through a synthetic filter and their viscosities were measured with falling ball (Höppler B3) viscometer.

FT-IR spectra were recorded at a resolution of 1 cm^{-1} on a Shimadzu IRAffinity-1 spectrometer and 25 scans were accumulated. The spectra of the mixtures were measured in a KRS-5 (Thallium Bromoiodide) cell of 0.1 mm thickness.

All calculations of quantum mechanics were performed using the Gaussian-03 [14] program. The geometries of the monomers and dimers were fully optimized using density functional theory (DFT) [15,16] of the B3LYP [17–19] hybrid exchange functional with the 6-31+G* basis set. The vibrational frequencies were evaluated at the same level of theory and scaled by a constant factor equal to 0.9614 [20] for zero-point energy (ZPE) corrections. The frequencies were assigned with respect to normal mode vibrations. The complexation energies (En) of all clusters were calculated using the same methodology. The change in binding energy, ΔE, of each complex was calculated as follows:

$$\Delta E = E_{\text{complex}} - \{E_1 + E_2\}, \tag{2}$$

Here, E_{complex}, represents total energy of any considered complex, formed by individual molecules, with total energies E_1 and E_2 respectively.

3. Results and discussion

As mentioned above, PVA contains highly polar hydroxyl groups that tend to form inter- and intra-molecular associations *via* H-bonding. The participation of hydroxyl groups in hydrogen bonding is mainly due to the large electronegativity difference between oxygen and hydrogen, resulting in partial net negative and positive charges on the respective atoms in the alcohols. The partial positive