**Journal of Macromolecular Science, Part A**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

# The Polymerization of Free Enols with Electron-Deficient Comonomers

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**To cite this Article** Novak, Bruce M. and Cederstav, Anna K.(1997) 'The Polymerization of Free Enols with Electron-Deficient Comonomers', Journal of Macromolecular Science, Part A, 34: 10, 1815 — 1825
**To link to this Article: DOI:** 10.1080/10601329708010310
**URL:** http://dx.doi.org/10.1080/10601329708010310

J.M.S.—PURE APPL. CHEM., A34(10), pp. 1815–1825 (1997)

# THE POLYMERIZATION OF FREE ENOLS WITH ELECTRON-DEFICIENT COMONOMERS

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## ABSTRACT

The balance between kinetics and thermodynamics is illustrated herein by the first direct polymerization of vinyl alcohol, the thermodynamically unstable tautomer of acetaldehyde, at a rate faster than it can tautomerize. Vinyl alcohol was formed through the acid catalyzed hydrolysis of ketene methyl vinyl acetal. With excess water present, the kinetics of tautomerization first order dependence upon vinyl alcohol ($k_{obs} = 2.73 \times 10^{-4}\ s^{-1}$). Under water starved conditions, however, the kinetics now show a zero order dependence upon the concentration of vinyl alcohol ($k_{obs} = 3.5 \times 10^{-6}$ M/s). Under these latter conditions, the half life of vinyl alcohol is nearly 24 hours at room temperature. Although cationic and homo free radical polymerization of vinyl alcohol failed, we found that this meta-stable species could be quantitatively polymerized in a copolymerization (AIBN, hυ, -10 to 25°C) with maleic anhydride. The $k_{obs}$ for copolymerization was found to be $4.41 \times 10^{-4}\ sec^{-1}$ at -10°C. Since the rate of polymerization is far greater than that of tautomerization under these conditions (*ca.* 30 times faster at -10°C), there is no significant increase in acetaldehyde concentration during polymerization.

## INTRODUCTION

Macromolecules with hydroxyl substituents range from biomaterials that are essential to life processes to synthetic polymers of vast commercial utility. The high dipole moment and propensity of the O-H bond to participate in hydrogen bonding impart attractive features such as water solubility and the potential to form supramolecular structures to many of these materials. The amphoteric nature and high reactivity of the alcohol moiety also allow for facile reactions of hydroxy substituted polymers with a variety of species.

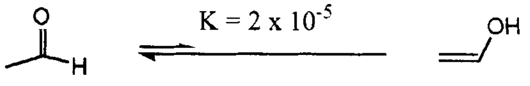
Of the synthetic polyalcohols, poly(vinyl alcohol) (PVOH) is the largest volume material produced in the world. PVOH is synthesized through the hydrolysis of ester precursor polymers. The discovery of PVOH dates back to 1924 when researchers Herrman and Haehnel, working for the German "Consortium für Elektrochemische Industrie," dropped alkali into an alcoholic solution of poly(vinyl acetate) (PVAc) and observed formation of an ivory precipitate [1]. A provisionary patent was published in 1924, [2] but it was not until three years later that the discovery of PVOH was reported in the literature. At this time, Herrman and Haehnel published the synthesis of PVOH from PVAc both via saponification and transesterification, and also predicted some of the applications of PVOH (in fibers, as protective colloids, and as a precursor for polyvinyl acetals) that have since proven to be immensely profitable [3]. Shortly thereafter, Staudinger reported the macromolecular structure as deduced from the reversible transformation between PVOH and PVAc [4].

Large-scale production of PVAc is complex and is accomplished with continuous flow reactors [5]. Monomer and initiator solutions are combined and the reaction mixture is passed through a number of polymerization chambers. The reaction is carried out in refluxing alcohol solution and cooled to maintain the desired temperature (polymerization temperatures range from 45-130°C). After polymerization (2-4 hours), residual VAc is removed in a stripping column to yield PVAc solutions contaminated by less than one percent monomer. Elements of the reactor design such as feed rates, concentrations, residence times, and the exact temperature determine product molecular weights.

The PVAc is then converted into PVOH by either hydrolysis or alcoholysis (the latter being more common in commercial production) [5]. For alcoholysis, strong base, alcohol, and PVAc solutions are combined in a high intensity mixer, and the resulting gel is transported by belt or screw conveyors to a tank where the polymer is ground, washed, and concentrated. Alternatively, the saponified mixture can be passed through stirred tank reactors where VAc and solvent are removed via distillation until PVOH precipitates. However, the latter method is not suited for making partially hydrolyzed PVOH resins with narrow hydrolysis distributions [5].

A variety of vinyl precursor polymers have been explored as potential sources of PVOH [6]. The traditional free radical polymerization of VAc yields polymer with broad molecular weight distributions, and PVAc is not suited for polymerization by conventional living cationic and anionic methods. Other precursor polymers have been explored in the hope that they would afford vinyl alcohol polymers with both improved properties and more narrow molecular weight distributions than those presently available. Though these methods yield PVOH resins with interesting structures and properties, all the above methods are fundamentally similar to the traditional PVOH synthesis in that the alcohol functionality is obtained from modification of a precursor polymer. This circuitous approach necessarily increases the production cost of these resins. A more efficient means of making vinyl alcohol polymers would be the direct polymerization of a substrate that does not require modification after polymerization.

The chemistry literature is replete with references asserting that simple enols are species which, although important intermediates in many organic reactions, do not persist for any appreciable amount of time. This conventional wisdom regarding vinyl alcohol (VA) stems from the extremely small fraction of enol tautomer that is present at equilibrium (Equation 1) [7].



(1)

Although much work in which transient simple aliphatic enols have been generated in the gas phase, complexed to transition metals, [9] or made in low-temperature solution by photochemical methods [10] has been reported since the 1960s, this work reinforced the idea that simple enols are not stable.

The proposal to make PVA from acetaldehyde dates back to the early work with PVA by Staudinger [4] and remains an elusive goal today. If the perfectly linear aldol condensation of acetaldehyde could be achieved, PVA would be formed. Unfortunately, aldol condensations are not clean enough for this to be possible. Both dehydration to form unsaturated species and mixed aldol reactions that yield branched products are characteristic side reactions that lead to complex mixtures of products [11]. It has been asserted that linear PVA oligomers were generated by reaction of a Na/Hg amalgam and acetaldehyde at high temperatures and pressures [12]. However, further scrutiny of this work showed that the product oligomers from this reaction are spectroscopically identical to non-linear ones from acetaldehyde condensations catalyzed by $K_2CO_3$ [13].

Finally, the radical polymerization of preformed enolate anions also affords materials that become hydroxy-functionalized upon acidification [14]. However, homopolymerization of enolates [15] only proceeds to chain lengths of less than ten monomer units, and even radical copolymerization with electron-deficient substrates affords polymers with low molecular weights [14]. The failure of enolates to copolymerize to high polymer was attributed to excessive buildup of charge on the polymer chain [14]. In addition, since enolates are also good initiators for anionic polymerizations, they can only be polymerized with selected comonomers.

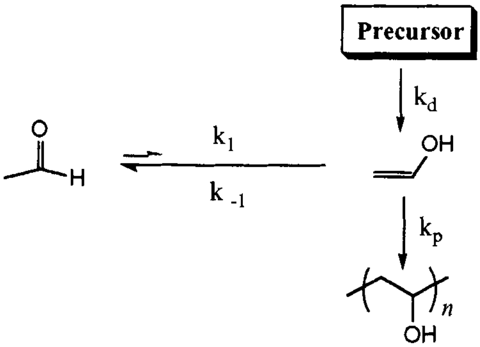
Recent discoveries have shown that simple enols are not nearly as unstable as was previously believed [16, 17]. In light of this new information, the question comes to mind once again whether alcohol functionalized polymers in general, and ultimately PVA itself, can be obtained from the direct polymerization of these species. If such polymerizations were possible and cost-efficient syntheses of simple enols could be developed, the implications for the price and usage of the environmentally benign hydroxy-functionalized resins would be enormous. Herein, we describe our efforts in the direct polymerizations of simple enols.

## RESULTS AND DISCUSSION

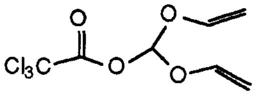
Although the enol tautomer is highly disfavored based on energetics, we were interested in determining whether this potential monomer could be polymerized by approaching this problem from a kinetic, rather than a thermodynamic perspective. Our kinetic approach involves hydrolyzing, decomposing or isomerizing a precursor to liberate vinyl alcohol, and then polymerizing the vinyl alcohol at a rate faster than it can tautomerize (i.e., identify kinetic conditions in which $k_p >>> k_{-1}$) (Scheme I).

Following the work of Capon, we synthesized a variety of precursor molecules that liberate vinyl alcohol as a kinetic product under hydrolytic conditions.

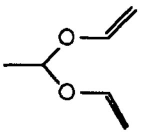
Of these various precursors, the orthoester, **I**, and the ketene acetals, **III** and **IV**, have rates of hydrolysis fast enough for implementation into our scheme (Equation 2).



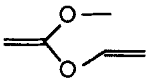
Scheme I



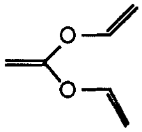
I



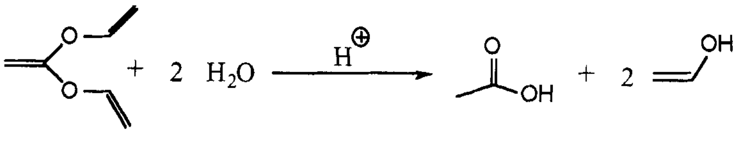
II



III

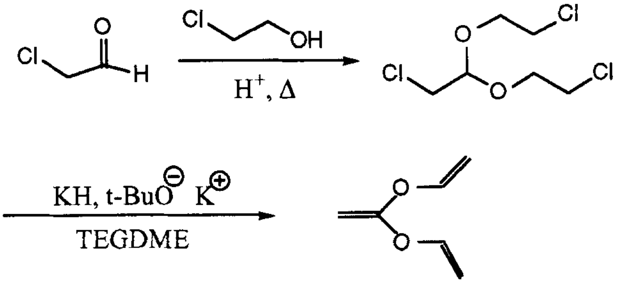


IV



(2)

Reported syntheses of **III** [17] used combinations of sodium hydride, sodium *t*-butoxide and *t*-butanol in solvents such as DME and diethylene glycol diethyl ether to effect the dehydrohalogenation of chloroacetaldehyde 2-chloroethyl methyl acetal. We found that when sodium hydride was employed, reaction times were long (2 days), the yield was low (25%), and the reaction was quite temperature sensitive. Only one of the two dehydro-halogenations occurred at temperatures below 90°C, but decomposition of the product set in above 94°C (i.e., a 4° reaction window). It was also cumbersome to remove all *t*-butanol and solvent from the product. We chose instead to employ an excess of pure potassium hydride and a catalytic amount of preformed potassium *t*-butoxide for the dehydrohalogenation. With the stronger base, the reaction was complete in less than one hour at room temperature. Also, use of tetraethylene glycol dimethyl ether, a higher boiling solvent, allowed for facile separation of pure precursor in higher yield (85%) via vacuum-transfer from the reaction mixture. The same methodology was used to synthesize (**IV**) from chloroacetaldehyde bis(2-chloroethyl) acetal (Scheme II). Extreme care



IV

Scheme II

needs to be taken as these reactions are quite exothermic and rapidly generate large volumes of hydrogen gas.

Previous kinetic studies of VA tautomerization had been carried out in aqueous solution but not in organic solvents [18]. Since water had been implicated as a ketonization catalyst and polymerizations were to be carried out in acetone, kinetic studies in acetone solutions containing minimum amounts of water were performed. The addition of water is required for ketene acetal hydrolysis and VA could not be isolated in our hands; therefore, it was not possible to follow the ketonization in completely anhydrous solvents. However, VA was generated in good yield through reaction with only a small excess of water such that when one equivalent of water had been consumed, solutions were 0.31 M in VA and only 0.16 M in $D_2O$. To increase $[D_2O]$ without altering other conditions, degassed $D_2O$ was added after completion of precursor hydrolysis. The change in concentration of VA over time was monitored via NMR spectroscopy by integration of the methylene proton *cis* to the alcohol ($\delta$4.14).

The results of these studies showed a significant correlation between water concentration and rate, and ultimately the mechanism of tautomerization. At higher $[D_2O]$ (22 mol equiv.), a first order dependence ($k_{obs} = 2.73 \times 10^{-4}\ s^{-1}$) of the ketonization rate on [VA] was observed. However, when only a small excess of $D_2O$ (0.5 mol equiv.) was present in solution with VA, the rate of tautomerization had a zero order dependence ($k_{obs} = 3.4 \times 10^{-6}$ M/s) (Figure 1).

This change in kinetics has a dramatic effect on the longevity of VA; under first order conditions a 0.25 M sample of VA completely tautomerizes in 3 hours, while under zero order conditions the same tautomerization process takes 20 hours.

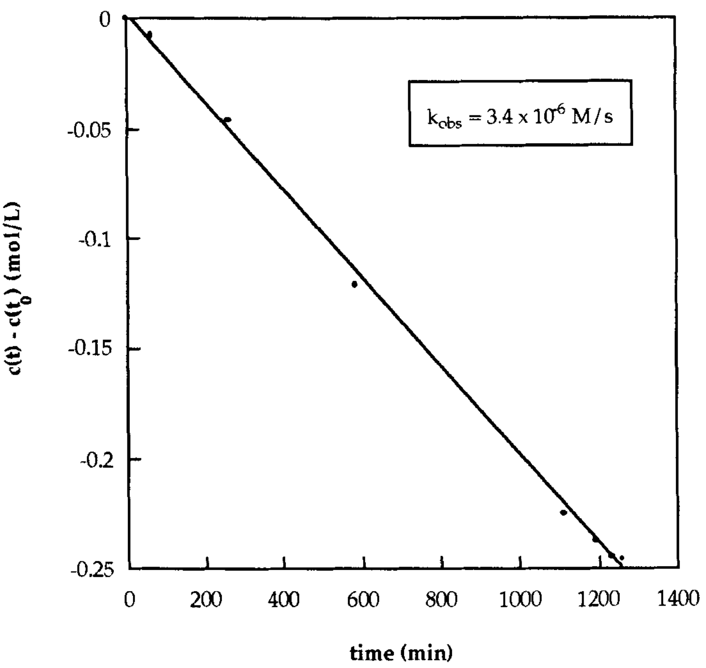


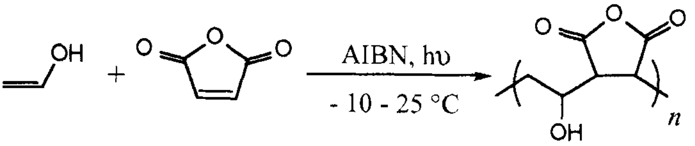
**Figure 1.** VA tautomerization kinetics have a zero order dependence on [VA]. $[VA]_0 = 0.31$ M, $[D_2O]_0 = 0.16$ M.

Hence, we were successful in identifying reaction conditions that would allow us to form meta-stable solutions of VA.

Having developed the methodology to make persistent solutions of VA, we began to probe the polymerization reactivity of this new simple monomer. We initially chose to focus on the study of more traditional radical initiated polymerizations. Since enols and vinyl ethers are isoelectronic, their reactivities toward radical polymerization should be similar. Unfortunately, vinyl ethers do not readily homopolymerize via radical initiation because the electron donating alkoxy group stabilizes the propagating radical. An analogous interaction would be expected to occur in VA radicals, and indeed attempts to homopolymerize VA via radical methods failed. Vinyl ethers do homopolymerize slowly under extreme conditions to form low molecular weight materials, [19] but VA could neither be generated in the large concentrations nor heated to the high temperatures required for such polymerizations.

On the other hand, radical initiated alternating copolymerizations of vinyl ethers are favored. Many classes of comonomers, including but not limited to olefins, acrylates, acrylonitrile, maleic anhydride, fumarates, vinyl pyrrole, and vinyl carbazole, have been copolymerized with vinyl ethers to make interesting materials. [19]. Therefore, we endeavored to carry out the analogous copolymerization of VA using electron-deficient maleic anhydride (MA) as the comonomer.

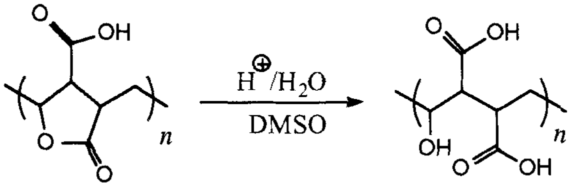
Though VA had been found to be relatively stable at 25°C, the rate of ketonization would clearly increase with temperature. We, therefore, desired to perform all copolymerizations at low temperatures using the photolysis of AIBN as the initiator. Under these conditions, we found that meta-stable solutions of VA could be quantitatively copolymerized with maleic anhydride (Equation 3).



(3)

Poly(MA-*co*-VA) was initially soluble in acetone, but with reprecipitation into benzene became progressively less soluble. This change in solubility led us to believe that MA units were being partially hydrolyzed during work-up. In fact, as no polymer was ever isolated without having undergone some MA hydrolysis, the reaction might begin during polymerization. Elemental analysis of a polymer sample which had been precipitated out of and lyophilized from dry benzene and then exposed to diffusion-pump vacuum for 48 hours was found to be consistent with a 1:1 alternating polymer containing approximately two wt% $H_2O$. Later evidence showed that substantial intramolecular lactonization occurs during the synthesis of this polymer to yield a material with lactone units.

Lactonization appears to be exclusively intramolecular based on the solubility of the polymer. The cyclic lactones can be reopened by treating the polymer with acid in wet DMSO (Equation 4).



poly(*h*-MA-*co*-VA)

(4)

Spectral data of poly(*h*-MA-*co*-VA) was also consistent with a polymer containing a combination of carboxylic acid, alcohol, and anhydride functionalities. $^1$H NMR spectra of poly(*h*-MA-*co*-VA) in DMSO-$d_6$ showed broad carboxylic acid and alcohol proton resonances at $\delta$ 11.5 and 4.4, respectively, as well as polymer backbone proton peaks at $\delta$ 2.9-1.3. The residual aldehyde resonances decrease with time as hydrolysis becomes complete. Poly(*h*-MA-*co*-VA) is fully soluble in MeOH and can be dissolved in $H_2O$. Once dry, the polymer is highly hydroscopic, in fact, deliquescent, as it will absorb sufficient moisture to become a gel in less than 10 minutes at atmospheric exposure. For characterization purposes, poly(*h*-MA-*co*-VA) was converted to its methyl ester derivative by treatment with diazomethane. The resulting polymer, which structurally corresponds to the perfectly alternating copolymer of vinyl alcohol and methacylate. Once esterified, the polymer was no longer deliquescent or water-soluble. Molecular weight anal-ysis using GPC (THF, polystyrene standards) yielded $M_n$ and $M_{w\ \mathrm{values}}$ of 55,800 and 183,600, respectively, for this polymer. These experiments proved that high molecular weight polymer results from the copolymerization of VA with MA.

## CONCLUSION

We have advanced the methodology for generating vinyl alcohol solutions in anhydrous acetone. Through our refinements, the solution half-life of this, the simplest of enols, has been extended from ten minutes to many hours at room temperature. The kinetics of VA tautomerization were studied and the results show that the presence of small amounts of water has a critical effect on enol stability. In the presence of excess water, VA tautomerization shows a first order rate dependence on enol concentration. In solutions containing less than one equivalent of water, the tautomerization rate is independent of the substrate concentration. It is this zero order tautomerization that significantly prolongs the viability of vinyl alcohol solutions.

Vinyl alcohol has been copolymerized with maleic anhydride via free radical methods. To our knowledge, this is the first time that metastable solutions of vinyl alcohol have been used as reagents for chemical transformations. It is also the first time that an enol has been employed as a monomer for direct incorporation into polymeric materials. The copolymerization proceeds rapidly and in good yield to form highly alternating copolymers. These high molecular weight ($M_n$ = 55,800) materials have been modified by hydrolysis and esterification reactions to yield highly functionalized, water-soluble polymers.

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