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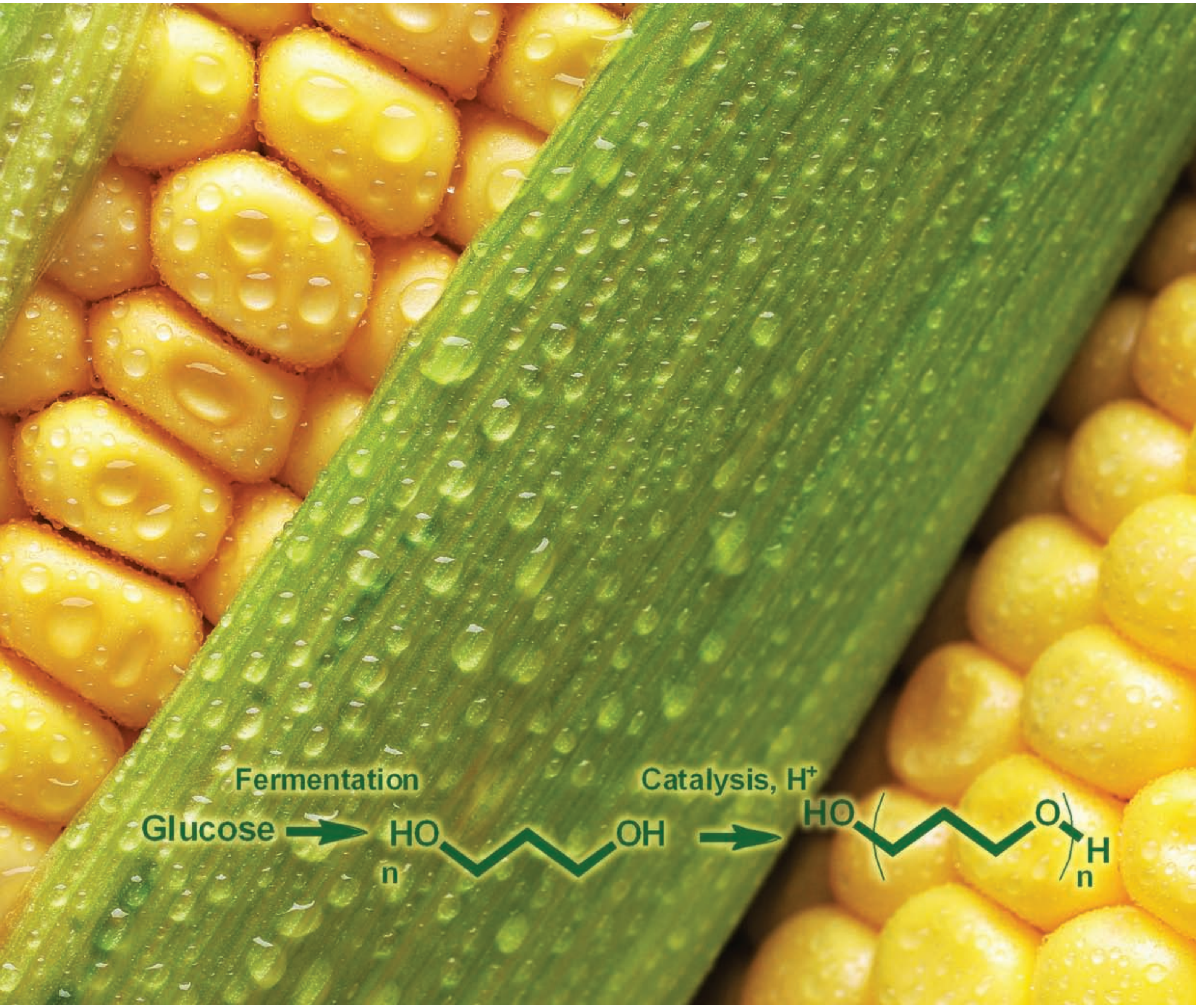

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Renewably sourced polytrimethylene ether glycol by superacid catalyzed condensation of 1,3-propanediol

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In this paper we describe the synthesis of a new 100% renewably sourced polymer, polytrimethylene ether glycol (polyol). This is an alternative to petroleum-sourced polytetramethylene ether glycol (PTMEG) and polypropylene glycol (PPG) and adds to the slowly expanding list of polymers from renewables, such as polylactic acid. The polymer is based upon a renewably sourced monomer, 1,3-propanediol (PDO), which itself has a lower environmental footprint compared to the chemically derived monomer, with both lower amount of green house gas emissions and energy use, during formation. Herein we discuss the development of polymerization conditions to provide polytrimethylene ether glycol with low color and low unsaturated end groups using the superacid tetrafluoroethane sulfonic acid (TFESA, b.p. 212 °C). The initial high color (brown) and high unsaturated impurities of the polymer, has been overcome by careful control of the processing conditions, leading to a new class of 100% renewably-sourced polymers. Preliminary kinetic analyses are also reported.

Introduction

The production of renewably-sourced chemicals and polymers such as polylactic acid and polyglycolide is an active area of interest.[1–4] Polyhydroxyalkanoate (PHA) polymers are polymers produced within the bacterial cell wall.[5] Interestingly, PHA can also be extracted from cellulosics such as switchgrass. PHA and PLA (polylactic acic) are considered excellent bio-based product substitutions for PET (polyethylene terephthalate), and both show a wide variety of thermoplastic properties. Examples of applications include molded goods, non-woven fabrics, adhesives, films and polymer performance additives. Biodegradable PLA can be found in everyday use such as in plastic drink containers. PHBV, or poly(3-hydroxybutyrate-co-3hydroxyvalerate), is a PHA polymer which has been used in commercial production of plastic bottles and coated paper. If economically produced, PHA could capture a significant portion of the plastics market.

1,3-propanediol is produced by a large scale industrial fermentation process (over 100 million pounds per year) and is used as a component in the recently commercialized polymer Sorona®. A detailed account of this is described by the pioneering work of Kurian.[6] Another polymer polybutylene succinate (PBS), traditionally made *via* the petrochemicals route, has also been developed using biobased succinic acid.[7] The resultant polymer is also biodegradable. The use of a low cost biobased succinic acid is the key to renewable, high performance biobased PBS that may compete with the petrochemical based plastics. The general trend is therefore very clear, polymers have been successfully developed using both partially bioderived to 100% renewably sourced materials. With improvements in both fermentation technology and extraction technology, the improved chemical process is paving the way for these new, renewably sourced plastics to take the place of some of the traditional based polymers.

Recently, a new family of polyethers derived from 1,3-propanediol (PDO) have been commercialized by DuPont.[8] As the 1,3-propanediol monomer is produced from a glucose fermentation process (Bio-PDO™), the resulting polytrimethylene ether glycol (PO3G) is 100% renewably-sourced. Amongst other uses, the polymer can be used as a key ingredient in a variety of elastomeric products such as spandex fibers, thermoplastic polyurethanes (TPU), copolyester elastomers (COPE) and copolyamide elastomers (COPA). These polymers are also starting to find a range of uses as lubricants, coatings, oils, clothing, and additives in other polymer systems.

Other polymers of this type, from petroleum, include polytetramethylene ether glycol (PTMEG)[9,10] or poly propylene glycol[11] (PPG) derived from tetrahydrofuran (THF) or propylene oxide respectively. The poly trimethylene ether glycol polymer is based upon the renewable monomer 1,3-propanediol (Bio-PDO™). This monomer provides the benefit of a reduced environmental footprint including reduced fossil energy consumption and reduced greenhouse gas emissions when compared to the chemically prepared PDO. Polytrimethylene ether glycols have been found to be useful as additives to enhance the performance of various products, for example, in polyurethane coating products for automotive refinish and industrial coatings applications. These polyols have also been found to provide improvement in chip resistance without loss of other important properties such as adhesion or productivity.

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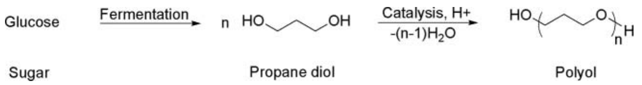
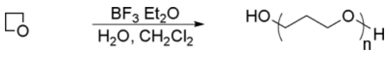
Polytrimethylene ether glycols are made in the acid-catalyzed polycondensation reaction of 1,3-propanediol (below)and yields water as a byproduct which needs to be removed during the reaction in order to build polymer of sufficient molecular weight. The reaction has reasonably high atom efficiency and with a selectivity of 100%, about 1.3 kilograms of Bio-PDO™ are consumed per kilogram of polymer produced.



The homopolymer ($M_n = 500$) when tested under the modified Zahn–Wellens test, biodegraded more than 90% in 28 days indicating its ultimate biodegradability. Typical molecular weights range from about 250 to 3000 g mol^{-1} with a polydispersity range from 1.5 to 1.9. Key challenges of the process include the comparably slow reaction kinetics, the formation of a brown color which has to be overcome and the formation of high levels of unsaturated polymer end groups ($–CH_2CH=CH_2$). High product color or high levels of unsaturation are not acceptable for use in many elastomer and other end-use applications.

Both homogenous and heterogeneous acid catalysts can be used to make polytrimethylene ether glycol. However, the utility of a wide variety of solid acid catalysts (Nafion®, alumino silicates, zeolites, ion exchange resins such as Amberlyst 70®, sulfated zirconia) have been found to be limited as they yield very high color, low molecular weight products, and have a low catalyst life at the reaction temperatures used. Suitable homogenous acid catalysts include sulfuric acid, some sulfonic acids, and so-called superacids. This paper focuses on the use of homogenous superacid catalysts[12] as, unlike sulfuric acid, they do not react with the polymer product to form esters.[13] The absence of ester formation provides key process advantages such as (i) reducing the required reaction time, and (ii) eliminating a subsequent ester hydrolysis step.

Poly trimethylene ether glycol can also be formed from oxetane. Oxetane is produced initially from 1,3-propanediol but that process involves more than one step with poor yields.



Oxetane is a highly flammable hazardous material (flash point = –20 °C), volatile (boiling point = 47–49 °C), difficult to transport and store (storage temperature = 2–8 °C), toxic and unstable. In contrast, 1,3-propanediol has low-volatility (b.p. = 214 °C), low flammability (flash point = 129 °C), and is easier to handle, store and transport, with low toxicity and is also biodegradable. In addition, most of the ring opening polymerization processes require high-pressure reactors, and the reactions are exothermic.

In summary, we report on the formation of a new class of renewably-sourced polymers, an important addition to other bio-based polymers, such as polylactic acid. We reveal how careful control of the chemistry leads to high quality polymer at commercially acceptable rates. The new process follows many of the principles of Green Chemistry, being safer, fewer side products, high yield, based upon a renewably-sourced monomer, with the final product showing biodegradability.

Results and discussion

Herein we discuss the acid catalyzed polymerization of 1,3-propanediol using the superacid, tetrafluoroethane sulfonic acid[14] (TFESA, bp 212 °C). Similar results were also obtained using the more commonly available triflic acid (TA, bp 162 °C), although TFESA is generally preferred due to the lower volatility which results in virtually no loss of acid even as the water is removed under a nitrogen purge. As mentioned above, this reaction can also be carried out using sulfuric acid (1–2 wt%) however a significant drawback is in the formation of sulfate esters (esterification of the $–CH_2OH$ leading to $–CH_2OSO_3H$). The sulfate ester has to be removed after the product has formed *via* an additional water hydrolysis step. This leads to a reduction in yield and also adds to the processing time, which translates to a lower energy use in production. No such esters are formed using superacids due to the non-coordinating character of the acids (or more specifically the anion). In a typical synthesis, a homogeneous solution of 1,3-propanediol and TFESA was heated at 170 °C under a nitrogen purge. The water evolved as the polymerization took place, was collected in a condenser. Fig. 1, shows an example of the initial polymer formed using 1 wt% TFESA acid, heated at 170 °C for about 7 h, under a nitrogen purge to remove the water evolved. The M_n is around 2000, and the polymer has an oil like viscosity. Although the molecular weight readily builds up the polymer had significant coloration, which is undesirable in terms of applications.

Fig. 1 Polytrimethylene glycol formed at 170 °C, using 1 wt% TFESA, after 7 h.

A subsequent series of reactions were investigated to measure the rate of number average molecular weight (M_n) increase as a function of both time and reaction temperature. As the polymerization progressed, the viscosity increased and polymer samples were taken at 1 h intervals to track the increase in the number average molecular weight (M_n) as determined by ^{1}H-NMR spectral integration (see Experimental). The progression of the reaction can be easily followed *via* NMR, as shown in Fig. 2. The unreacted propane diol (I) has peaks at approximately 4.5 (4H) and 2.2 (2H) ppm, respectively, which gradually shift to the polyol (II) at approximately 3.5 (4H) and 1.9 (2H), respectively. These spectral changes are due to the gradual increase in ether content (and subsequently decreasing terminal –OH) as the polymerization proceeds and are a convenient means by which to monitor reaction progress (as described in detail in the Experimental, ^{1}H-NMR also provides a convenient measure of degree of polymerization (DP) and associated unsaturated end groups (meq kg_{-1})).

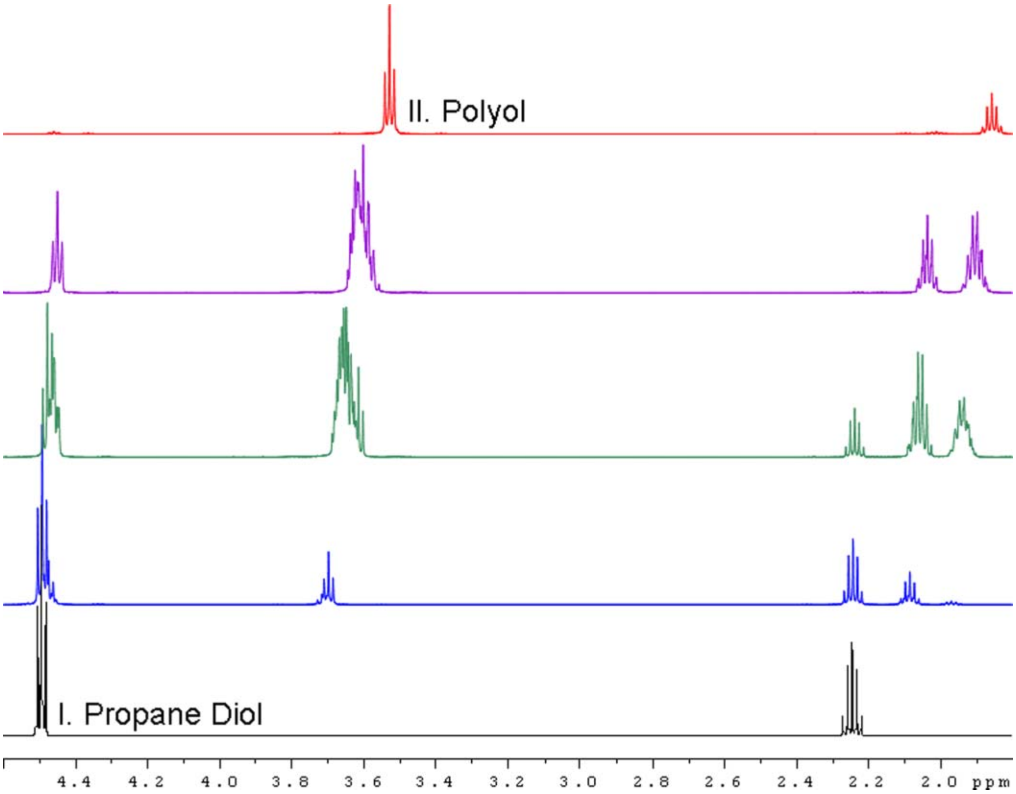


Fig. 2 ^{1}H-NMR spectra during the conversion of propane diol (I) to polyol (II), showing the formation of oligomers to the extended polymer.

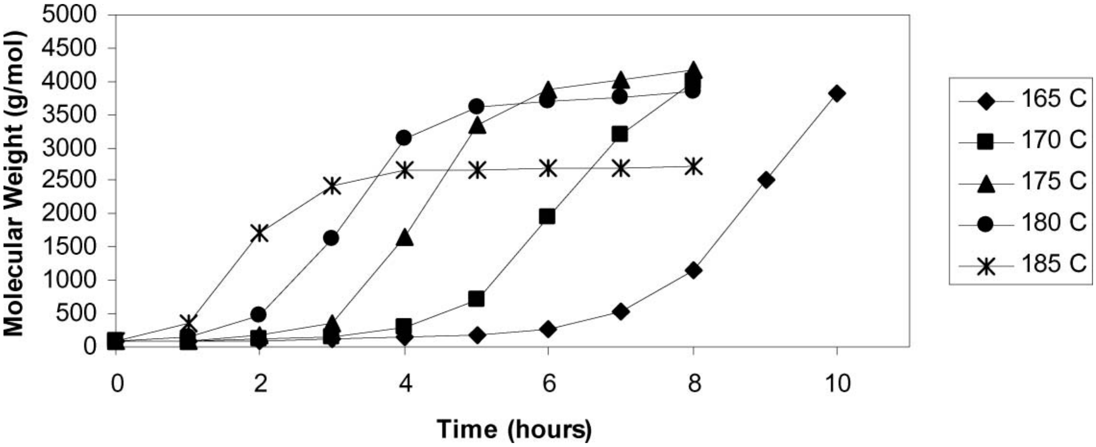


Fig. 3 Formation of polytrimethylene ether glycol as a function of reaction time at different temperatures (1 wt% acid).

At the end of the reaction the superacid catalyst is readily removed by absorption on basic alumina or Boehmite (BASF G250) followed by filtration. The catalyst itself can be recycled by adding sulfuric acid to the TFESA adsorbed catalyst, followed by heating to distill off the pure acid. Thus, sulfuric acid can be added to the TFESA on alumina and the TFESA can be purified *via* distillation. The recovered catalyst is identical (from NMR) to the initial catalyst and when used again showed the same reaction rate as the original TFESA.

A series of reactions at 1 wt% TFESA catalyst loading were carried out at different reaction temperatures and the results are shown in Fig. 3, showing the variation of number average molecular weight.

The formation of polytrimethylene ether glycol, as shown in Fig. 3, has a number of interesting features. At 165 °C the rate of molecular weight build is initially slow but increases rapidly after 6 h. This initial reaction rate can be greatly accelerated by increasing the reaction temperature but with increased temperature we observe an apparent equilibrium behavior. This effect is highly pronounced at 185 °C where the polymerization reaches an M_n of 2500 after 3 h but levels off at about 2600 M_n. This equilibrium is believed to be due to the balance of reduced polymerization rates at higher molecular weight coupled with increased hydrolysis from the residual water in the polymer. Karl Fischer water analysis indicated that the polymer from this experiment contained 0.1 wt% water despite

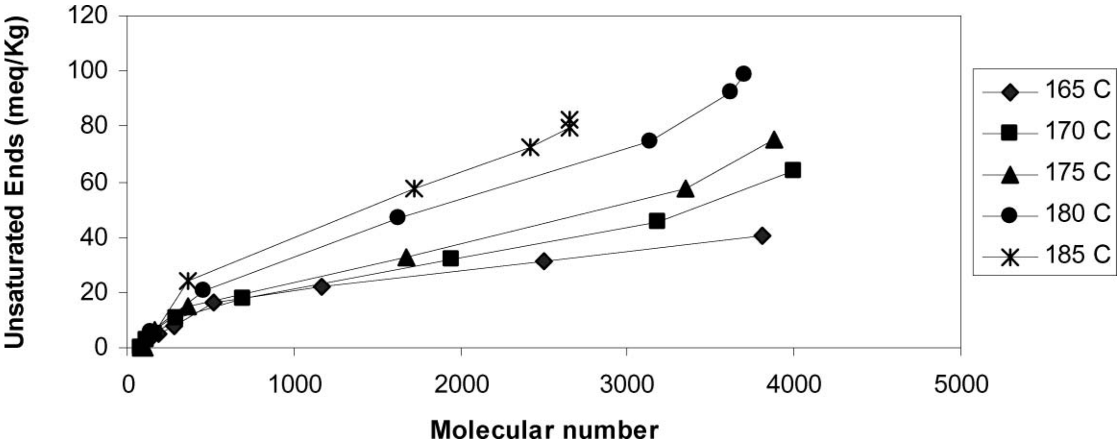


Fig. 4 Variation of unsaturated polymer ends as a function of M_n.

the nitrogen purge. Interestingly, the equilibrium M_n increases with decreasing temperature. Thus, by lowering the reaction temperature to 170 °C, an M_n exceeding 4000 can be obtained after 7 h.

As mentioned above, key challenges of the process include the formation of unsaturated polymer end groups and the formation of an off-brown color. Unsaturated polymer end groups in excess of 20 meq/kg negatively impact reactivity of PO3G for subsequent isocyanate reactions for polyurethane applications. The –$CH_2CH_2CH_2OH$ will react and crosslink, however the –$CH_2CH{=}CH_2$ will not, essentially acting as polymeric 'dead ends' which lead to poorer polymeric properties. Fig. 4 shows values of the unsaturated polymer end groups determined by ^{1}H-NMR spectral integration as a function of polymer molecular weight formed at different temperatures (Fig. 4).

There are several clear trends in this data. Firstly, as the molecular weight increases, the number of unsaturates increases. Secondly, as the temperature increases, the number of unsaturates increases (for a given M_n), for example the number of unsaturates for an M_n of around 1800 is about 27 (reaction T of 175 °C) compared to about 58 (reaction T of 185 °C). This effect is consistent with the competition between ether formation and alcohol dehydration (to the unsaturated end). Olah *et al.*[9] investigated the dehydration of alcohols over Nafion-H and found the ratio of % alkene (dehydration) to % ether increased as a function of temperature. In the case of isopropanol, 100% ether is formed at 100 °C, and at 130 °C, 45% ether and 55% alkene, and finally at 160 °C 100% of the alkene is formed. Dehydration reactions tend to be more demanding than etherifications, and thus the higher temperature favors dehydration. In order to control the desired polymer properties, we found careful control of the temperature profile led to suitable polymer in reaction times less than 12 h. We essentially developed an inverse temperature ramp, where the reaction starts at a higher temperature (175 °C) and polymerization occurs rapidly (say, to an M_n between 500 to 1000) and then the temperature is reduced (160 °C) and the reaction is allowed to continue. At this lower temperature, although the polymerization continues, the unsaturates do not increase and polymer can be produced up to around 2000 M_n with unsaturates less then 20 g mol^{-1}. This kind of simple temperature profile allows for polymer formation at reasonable reaction rates (*i.e.* commercially viable) whilst maintaining the desired polymer properties. Fig. 5, plots the number of unsaturates as a function of polymer M_n. The reaction ramp was held (180 °C) for 5 h, and then the temperature was reduced to 160 °C; note the unsaturates level off at this point although the polymer molecular weight still increases.

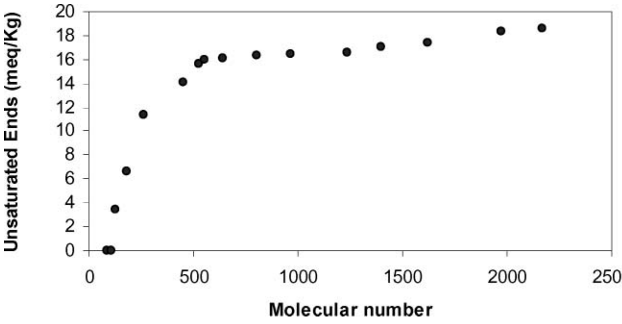


Fig. 5 Control of product polymer degree of unsaturation as a function of M_n.

In addition to controlling molecular weight, the color also has to remain low (less than about 50 APHA, which typically is a very pale yellow on a litre sample). We discovered that color formation was very dependent upon polymer moisture content, and maintaining an elevated water content (either by purging the nitrogen through a water bubbler or a very slow direct addition of water with use of a syringe pump) assists in controlling color formation. A 30 g sample of polymer (M_n around 2000) using 0.5 wt% of catalyst and purged with dry nitrogen was light yellow in color (150 APHA), although when the reaction was repeated using nitrogen sparged through water, the polymer was visibly colorless (<20 APHA). The combination of the above two processing steps are critical in forming high quality polymer.

A typical summary of the optimum conditions is as follows. The following is an example of the optimized reaction conditions. 0.25 wt% TFESA is added to 800 g of PDO. The system is purged at 200 cm^3 per minute with nitrogen. Water is also added at 10 mL h^{-1} to control the color formation. Polymerization is carried out at 183 °C for six hours, followed by 165 °C for an additional 6 h. The reaction is then cooled and the acid removed. The resulting polymer has a molecular weight of 1400 with an APHA color of 20 and 16 meq/kg of unsaturated ends, Fig. 6. This material is well within the range for subsequent applications.

Below we propose a mechanism for the formation of the polymer, and include a scheme for the formation of the byproducts, such as the unsaturated ends. As discussed earlier, since the formation of Cerenol® is a condensation polymerization, water is formed as a byproduct during the reaction and if this water is not removed, the overall reaction progress is slowed or even reversed. The removal of water from this condensation reaction, therefore, requires the balancing of the water requirements needed to maintain low color and unsaturates with the potential reduction in overall reaction rate. One simplifying factor with this particular chemistry is the fact that while water is miscible with the Bio-PDO™ and low-molecular weight oligomers formed early in the reaction, as the reaction progresses and the polymer chain length is increased, the water becomes less miscible with the contents of the reaction vessel and is more easily driven off. This decreasing water solubility with increasing molecular weight is a fortunate effect since the rate of molecular weight build appears to be more sensitive to excess water concentrations at higher molecular weight. The reaction mechanism in Fig. 7 has been proposed to provide further rationale for these observations.

Fig. 6 Polytrimethylene ether glycol formed under optimum conditions, with low color. On larger scale, water is injected at a known addition rate to prevent color formation.

It is hypothesized that the production of polytrimethylene ether glycol from 1,3-propanediol proceeds *via* both S_n1 and S_n2 substitution reactions. However, early in the reaction, when there are a large number of reactive –OH groups due to a large number of alcohol ends and a high water content, the reaction is believed to be more strongly influenced by the S_n2 pathway. As water is stripped from reaction at higher molecular weights, and the availability of –OH groups decreases, the subsequent reaction is subject to a greater influence from the S_n1 pathway. Although the S_n1 pathway may in part lead to desired product, it likely also leads to the formation of unsaturated ends. Additionally, as rearrangement occurs, cross-condensation products are likely and further explain the observation that significant color is formed late in the reaction without a certain water content present in the liquid phase. In addition to attenuating the acidity of the acid catalyst, the elevated water content may also function to partly suppress the S_n1 pathway and unfavorable condensation reactions that lead to polyunsaturated "color forming" species.

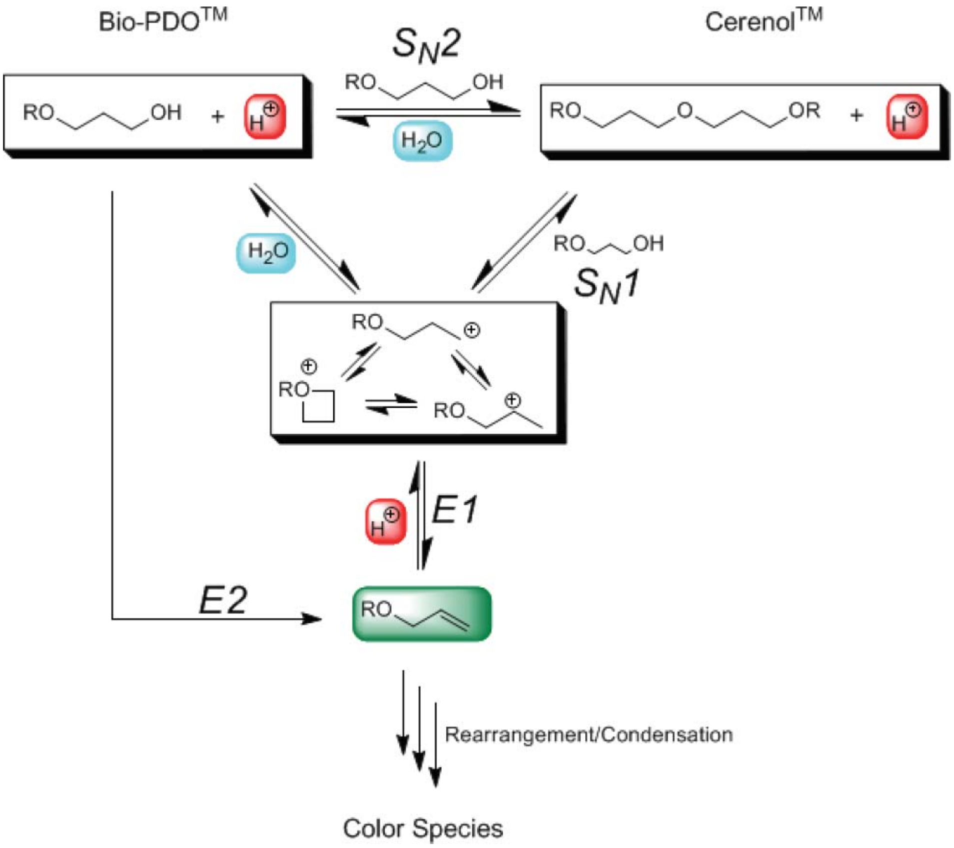


Fig. 7 Expected superacid catalyzed reaction mechanism.

The process controls described previously must, however, be carefully optimized as reverse temperature ramping and the addition of water to the reaction mixture also have the adverse effect of slowing down the overall reaction rate. Fully leveraging such improvements to provide the desired product in the shortest required reaction time while maintaining specification requires a comprehensive understanding of the interactions of reaction temperature, acid concentration, and water content on the product specifications of molecular weight, unsaturated ends, and color.

Preliminary kinetic data for this process was obtained through a Box–Behnken designed series of experiments. The effects of reaction temperature, TFESA catalyst concentration, and water addition rate were studied over the first 6 h of the reaction at 50 g scale. In addition to collecting data for a response surface analysis between the process variables, the experiments were structured to collect data useful for the creation of kinetic models to test the proposed mechanism. Fig. 8 plots the first (ln[ROH]) and second order integrands (1/[ROH]) corresponding to the expected kinetic expressions for the S_n2 and S_n1 reactions for the condensation of terminal alcohol ends. Neither first nor second order kinetics fully describe the behavior observed however we do observe a reaction rate-order shift from approximately 2 in the early reaction phase to greater than 1 for the later reaction phase. This order shift is consistent with the proposed reaction mechanism where a 2nd order S_n2 pathway would dominate when high concentrations of alcohol ends are available with ever increasing contributions from the 1st order S_n1 pathway as those ends react away. Subsequently, a more rigorous kinetic analysis to account for each of the known oligomer/polymer species has been completed and a model has been developed in MATLAB® and FORTRAN. This model, which will be reported separately, agrees well with experimental data over an extended range of reaction conditions and is supportive of the proposed reaction scheme for the condensation polymerization of Bio-PDO™.[15]

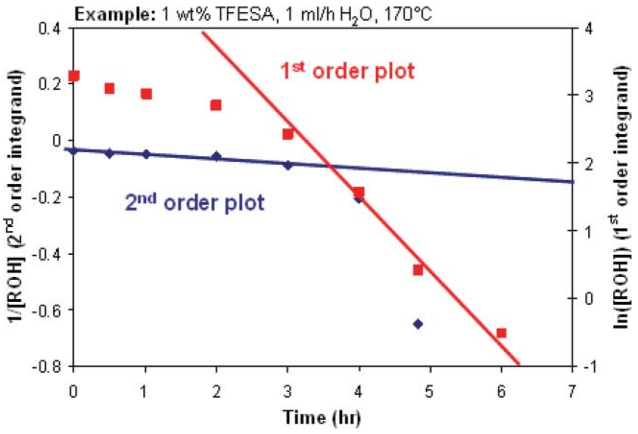


Fig. 8 Reaction order shift in superacid catalyzed reactions.

Conclusions

Polytrimethylene ether glycol (DuPont™ Cerenol™) opens a way to a new class of renewably sourced and high performance polyurethanes. These polyols can potentially be used to replace current petroleum based polyether polyols in several commercial products. Tetrafluoroethane sulfonic acid was found to be an effective catalyst for the condensation polymerization of 1,3-propanediol. Careful control of the reaction temperature and polymer water content during synthesis were found to be critical for the production of polymer with low color and low unsaturated ends. Preliminary kinetic analysis is consistent with the proposed mechanism of S_n2 substitution dominating the early stages of the polymerization with increasing contributions from S_n1 and dehydration reactions as total alcohol ends decline.

Experimental

The synthesis of TFESA has recently been described.[14] For TFESA: ^{19}F NMR (CD$_3$OD) δ −125.2 ((dt, $^3J_{FH} = 6$ Hz, $^3J_{FF} = 8$ Hz, 2F); −137.6 (dt, $^2J_{FH} = 53$ Hz, 2F). ^{1}H NMR (CD$_3$OD) δ 6.3 (tt, $^3J_{FH} = 6$ Hz, $^2J_{FH} = 53$ Hz, 1H). Trifluormethane sulfonic acid was obtained from Aldrich Chemical Company.

Polyol formation (etherification)

A typical synthesis is described as follows. 1,3-Propanediol (30 g) was placed in a three-neck round-bottom flask. To this was added TFESA (1 wt% in the final solution). The homogeneous solution was heated using an oil bath between 125–175 °C under a nitrogen atmosphere, using a range of times. Water slowly evolved and was collected in a condenser. The polymerized product was followed *via* ^{1}H NMR spectroscopy. In some cases the nitrogen was purged through water to maintain minimum water content within the reactor. The flow rate of nitrogen was typically 200 sccm.

Characterization of polytrimethylene ether glycol by ^{1}H NMR spectroscopy

A comparison of relative integral values by ^{1}H NMR allows for the characterization of both crude and purified polytrimethylene ether glycol polymers. Although the method can be applied to NEAT samples, derivatization of reactive end groups with trifluoroacetic anhydride (TFAA) is normally used. In a typical preparation, 30 mg of polymer is dissolved in 650 µl CDCl$_3$ followed by careful addition of 200 µl TFAA. Fig. 9 shows a typical proton spectra for the crude trifluoroacetylated reaction mixture.

The ^{1}H NMR spectra is used to determine the relative amount of unreacted OH ends (I), ethers (II), and unsaturated end groups (III):

I: F3COCO–(C**H**2CH2CH2O)$_n$–COCF3 (t, 4H, 4.40–4.47 ppm)

II: F3COCO–(CH2CH2C**H**2O)$_n$–COCF3 (m, 4H, 3.45–3.65 ppm)

IIIa: **H**2CCHCH2(OCH2CH2CH2)$_n$–OCOCF3 (dd, 2H, 5.15–5.29 ppm)

IIIb: H2CC**H**CH2(OCH2CH2CH2)$_n$–OCOCF3 (m, 1H, 5.83–5.94 ppm)

These relative integral values are used for the subsequent determination of degree of polymerization (DP), molecular weight average (M_n), and unsaturated end groups as shown below:

The degree of polymerization (DP) is determined by the following:

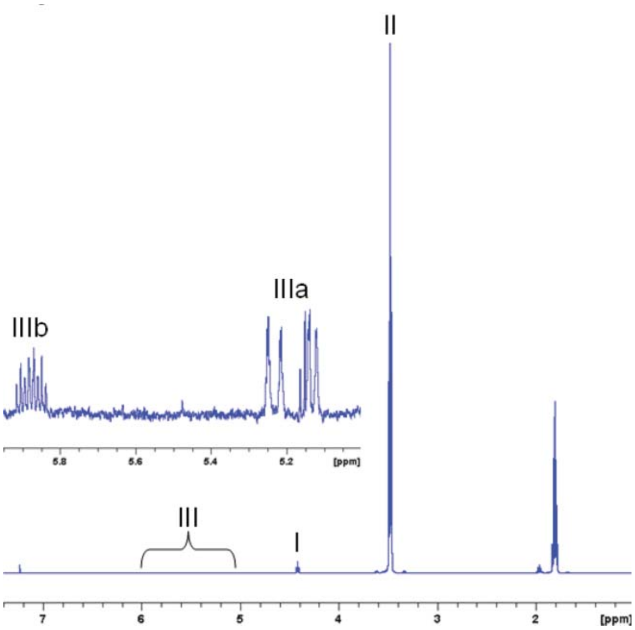


Fig. 9 Representative ^{1}H NMR of derivatized crude reaction mixture.

$$\mathrm{DP} = (\text{area of I} + \text{area of II} + 2 \times \text{area IIIb})/(\text{area of I} + 2 \times \text{area IIIb})$$

The molecular weight average (M_n) is determined by the following:

$$M_n = \mathrm{DP} \times 58.08 + 18.02$$

The total end groups (meq/kg) are determined by the following:

$$\text{Total end groups (meq/kg)} = 2 \times 1 \times 10^6/M_n$$

The total unsaturated end groups (meq/kg) are determined by the following:

$$\text{Unsaturated end groups (meq/kg)} = \text{total ends} \times (2 \times \text{area of IIIb})/(2 \times \text{area of IIIb} + \text{area of I})$$

Acknowledgements

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