

## **DMSO as solvent on the synthesis of flame-retardant polyether polyols**

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### **ABSTRACT**

Polyether polyols with flame-retardant properties are synthesized by using glycerol phosphate disodium salt as an initiator and dimethyl sulfoxide (DMSO) as a solvent. The molecular weight of the polyol decreased when higher solvent to initiator ratios were used, revealing that a larger amount of salt was activated. In addition, the larger the amount of activated salt was, the higher the percentage of phosphorous was in the final polyol. Glycerol phosphate disodium salt was still partially insoluble in the studied proportions of DMSO. Thus, the recovery and reuse of this part of the salt for the synthesis of new flame-retardant polyols were evaluated. The recovered salt promoted a shorter induction period because it presented a larger amount of deprotonated hydroxyl groups. In addition, there were no differences between both synthesized polyols, indicating that it is possible to use the recovered salt in the same way as it is used commercially with the advantage of a shorter induction period for polymerization.

### **INTRODUCTION**

Flame-retardants are materials or substances that help to prevent ignition or flame propagation and, thus, flashover. The term “flame-retardant” does not refer to a specific class of chemical;

rather, it describes the function of retarding a flame. In the 1970s, the introduction of halogenated flame-retardants solved potential safety problems related to fire hazards associated with polyurethanes. However, in the 1990s, it was discovered that halogenated products might affect human health and the environment. Currently, the substitution of these compounds is a scientific challenge. Flame-retardants are incorporated in different materials to reduce the risk of fire, either by providing increased resistance to ignition or by acting to slow down combustion and thereby delay the spread of flames.

The wide application of polyurethanes (PUs) requires a PU material design that allows the development of products with high thermal stability and flame retardance. The combustion of polyurethanes primarily depends on the thermal properties of the polymer, the presence of impurities and formulation residue in the polymer, as well as the supply of oxygen. An overview of a number of parameters that influence the flame retardance of the polyurethane and recent developments can be found in the literature, including parameters such as polyurethane structure, types of additives or the method of introducing flame retardants.<sup>1-6</sup>

Currently, more than 200 different types of flame retardants are known. As their composition is specific to their interaction with fire, the industry tends to classify them according to their chemical base.<sup>3,7</sup> Most are phosphorous compounds of a different nature and functionality. The addition of these compounds in the formulation of PUs is the most common method for the incorporation of flame retardant properties to PUs.<sup>8</sup> However, this direct addition may result in poor compatibility and leaching and can cause a reduction in the mechanical properties of the

obtained PU.<sup>9-11</sup> Therefore, there is increasing interest in the incorporation of phosphorous compounds as moieties on PU structures to overcome such drawbacks.<sup>12</sup>

The synthesis of reactive compounds and their flame retardance in PU has been investigated by multiple research groups. Studies by Youssef et al.<sup>13</sup>, Spirckel et al.<sup>14</sup>, Khatib et al.<sup>11</sup> and Celabi et al.<sup>15</sup> have been directed towards the production of polyurethanes with varying percentages of phosphorus from the synthesis of novel phosphonated diols as chain extenders. These studies incorporate phosphonated groups instead of phosphates. Those groups determine the process that is used to obtain low molecular weight diols (chain extenders). The diols have the disadvantage of requiring other commercial polyols for polyurethane foam synthesis but not for the synthesis of elastomers and similar materials. Schütz et al.<sup>16</sup> synthesized a phosphated catalyst which can be employed in polymerization, replacing the alkaline catalyst. However, it is not a polyol.

In previous studies, it has been demonstrated that the use of glycerol phosphate sodium salt as an initiator for polyol synthesis facilitates the development of polyols with phosphate groups in their structures that have not been previously described in the literature.<sup>17</sup> Some of the critical points for the use of glycerol phosphate salt are the lower reactivity of the salt and the necessity of a solvent (DMSO). Although the anionic polymerization mechanism of polyether formation is well known, it seems convenient to clarify the role that DMSO plays at the starting point of the polymerization process. First, the catalyst deprotonizes the hydroxyl groups of the initiator, resulting in the formation of two water molecules and glycerol phosphate alkoxide. This alkoxide, together with DMSO, must form a homogeneous mixture in which the initiator and the propylene

oxide (PO) are soluble enough to mutually interact. This is the role that DMSO plays because glycerol phosphate is a solid and favours the contact of the components in the reaction. In addition, it has been noted that only 40 wt.% of the salt used as initiator is activated, since the experimental phosphorous content in the final polyol was lower than the theoretical content. These two critical points, the low solubility of the salt and the use of a solvent, must be optimized because the salt and solvent removal are essential for developing high quality polyols.

In this work, the main goal is to determine the amount of solvent (DMSO) needed to obtain good solubility of the initiator salt (glycerol phosphate disodium salt). Additionally, a process for recovering the non-polymerized salt was developed to allow its reuse as an initiator in subsequent polymerization reactions.

## **EXPERIMENTAL**

### **Materials**

Propylene oxide (PO, 100%) was provided by Praxair. The chosen catalyst was caesium hydroxide monohydrate (99%) supplied by Chemetall GmbH (Germany).  $\beta$ -Glycerol phosphate disodium salt pentahydrate (98%) was used as an initiator and was purchased from Sigma-Aldrich. Dimethyl sulfoxide (DMSO, >99%) was used as a solvent and was supplied by Sigma-Aldrich. Amberlite 252 was used in the purification process and was purchased from Rohm and Haas Co.

### **Polymerization Procedures**

The polymerization reactions were performed in a 2 L jacketed glass reactor (Büchi, Uster, Switzerland) with a digitally controlled stirring rate, temperature and pressure. The vacuum was

controlled using a Divatronic DT (Köln, Germany) digital vacuum indicator-controller acting on a solenoid valve. The initiator, glycerol phosphate disodium salt, was added to the reactor, together with caesium hydroxide as a catalyst. Then, the solvent (DMSO) was added to favour the starting step of the polymerization. This mixture was pressurized with nitrogen to achieve an inert atmosphere, and heated to 120°C. When this temperature was reached, the mixture was stirred under a high vacuum for 3 h to ensure that the initiator solution was free of water (<0.2% water). Subsequently, propylene oxide was fed into the reactor obtaining a pressure in the reactor of 3 bar (0.3 MPa). During this addition, the PO consumption rate was calculated by measuring the remaining PO in the feed at different times. After the final addition of PO, a certain post-synthesis time was needed so that a high vacuum in the reactor was reached. Finally, to eliminate residual monomers, the high vacuum (40 mbar) was applied for 2 h.

To perform process of salt recovery, a filtration process was used. The operation was developed at 4-5 atm. Subsequently, the retained salt was dried in an oven at 60°C and was washed with acetone before drying in the same filtering equipment.

### **Purification Procedures**

To obtain polyols of high quality and purity, purification processes were performed. Solvent removal was performed by desorption, and then the catalyst was removed by ion exchange. Desorption consists of solvent removal in the vapour phase by means of an inert gas (nitrogen). The nitrogen was fed into a glass-mixing vessel, which contained polyol and DMSO, through a lower inlet. Operation conditions were 100°C and 100 rpm for 4 h to assure maximum contact between the nitrogen and the solvent. Once the solvent was removed, ion exchange was

performed to eliminate the catalyst. A macroreticular sulfonated polystyrene-divinylbenzene resin, Amberlite 252, was used.<sup>17</sup> A quantity of Amberlite 252, previously wetted in methanol, was mixed with the polyol in a glass-mixing vessel. This process occurred at 100°C and 500 rpm for 2 h to favour mass transfer. Generally, less than 5 ppm of caesium ions and sulfur in the polyol were obtained after the purification process.

### **Characterization**

Gel Permeation Chromatography (GPC) was used to determine the molecular weight distribution of the polyols. Measurements were performed with a Viscotek chromatograph with two columns (Styragel HR2 and Styragel HR0.5) at 35°C with a flow of 1 mL min<sup>-1</sup> and THF as eluent. The calibration curves for GPC analysis were obtained with poly(ethylene glycol) standards (from Waters).

Infrared spectra (FT-IR) were recorded on a Varian 640-IR FT-IR spectrophotometer using KBr discs. The spectral data were acquired using Resolution Pro™ software with 35 scans per experiment at a resolution of 16 cm<sup>-1</sup> in the range of 4000 to 600 cm<sup>-1</sup>.

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry (MS) was performed using a Bruker Autoflex II TOF/TOF spectrometer (Bremen, Germany) and using dithranol (1,8,9-trihydroxyanthracene) as a matrix material. Samples that co-crystallized with the matrix in a ratio of 100:1 on the probe were ionized in positive reflector mode. External calibration was performed using the Peptide Calibration Standard II (covered mass range: 700–3200 Da) and Protein Calibration Standard I (covered mass range: 5000–17500 Da).

Thermogravimetric analysis (TGA) was performed with a TA instruments SDT Q600 Simultaneous DSC-TGA from room temperature to 600°C at a heating rate of 10°C min<sup>-1</sup> in a nitrogen atmosphere.

The phosphorus content in the polyol was measured by inductively coupled plasma emission spectroscopy (ICP spectroscopy) with a VARIAN 710-ES ICP Optical Emission Spectrometer at a wavelength of 213.618 nm, using xylene as a solvent.

## **RESULTS AND DISCUSSION**

DMSO plays an important role as a solvent in the polymerization of propylene oxide (PO) using glycerol phosphate disodium salt as initiator because it is able to solubilize all of the different reagents, allowing their interaction. When the catalyst deprotonates the hydroxyl groups of the initiator, two molecules of water and glycerol phosphate alkoxide are formed. The alkoxide and the DMSO must form a homogeneous mixture to allow interaction between PO and the initiator. This is the role that DMSO plays; because glycerol phosphate is a solid, it makes the different components of the reaction soluble.<sup>17</sup> Next, the nucleophilic attachment of the alkoxide occurs on the less substituted carbon of propylene oxide. Finally, the chain increases in length due to the continuous addition of monomers (Figure 1).

To study the influence of the solvent on the reaction rate, different reactions using different solvent/initiator ratios were performed. Figure 2 compares the reaction rate of PO consumption with time for different molar ratios of DMSO (solvent, S) to glycerol phosphate sodium salt (initiator, I): 9, 7 and 0.007 (namely, S/I-9, S/I-7 and S/I-0.007, respectively).

Previous studies have investigated the influence of the presence of DMSO on the PO consumption rate.<sup>17</sup> The polymerization rate of PO with DMSO as a solvent was higher than without it. In Figure 2, it is apparent that the presence of a larger amount of DMSO shortens the initiation step. In addition, the higher the DMSO/initiator molar ratio is, the higher the polymerization rate is, with slopes of the propagation step of  $13.8 \text{ g min}^{-1} (\text{S/I-9}) > 9.6 \text{ g min}^{-1} (\text{S/I-7}) > 0.66 \text{ g min}^{-1} (\text{S/I-0.007})$ .

Figure 3 shows the role of the solvent (DMSO) in the polymerization based on its interaction with the ions. The high polarity of the solvent allows for separating the ion pairs, solvating the cation ( $\text{Cs}^+$ ) and making the anion more accessible to the monomer to polymerize it. The rate of anionic polymerization depends strongly on the interactions of the active anionic species with the surrounding molecules and cation-anion associations, as well as the nature of the solvent.<sup>18,19</sup> The initiator and propagating anion can exist in different forms, such as aggregated ion-pairs, contact ion-pairs, solvent-separated ion pairs and free ions in a polar solvent.<sup>18-21</sup> Depending on the concentration, the solvent-separated ion pairs can dissociate into free ions. The reactivity of free ions is very high when compared to that of solvent-separated ions, and their participation in propagation increases the reaction rate tremendously.<sup>18-21</sup> Considering all of this, according to our results, the high polarity of DMSO improves both the initiation step, making the initiation step shorter, and the propagation step, increasing the propagation rate.

Once the polyols were obtained, their main properties were determined. Table 1 summarizes the average molecular weight ( $M_n$ ), the polydispersity index (PI) and the phosphorous content (wt.%) of the polyols obtained with the different ratios of initiator to DMSO.



Because the molecular weight of the polyol decreased when higher ratios of solvent to initiator were used, this indicates that a larger amount of salt was activated. The molecular weight decreased because the number of monomeric units per initiator molecule was lower. For the same reason, as more initiator salt is activated, more phosphate molecules react and the weight percentage of phosphorous in the final polyol chain increases (see Table 1).

To obtain a thorough knowledge of the influence of the DMSO on the polyol composition, they were analysed by FT-IR. Figure 4 shows the FT-IR spectra of the polyols obtained with different amounts of DMSO. Differences were observed between different polyol samples because of the increase in the DMSO/initiator ratio. For example, at approximately  $1700\text{ cm}^{-1}$ , there is an increase in carbonyl groups derived from the oxidation of hydroxyl groups. Therefore, it can be interpreted that an increase in the DMSO to initiator ratio involves an increase in carbonyl groups.<sup>22</sup>

Unfortunately, glycerol phosphate disodium salt was still partially insoluble in DMSO, forming aggregates for more than  $0.113\text{ g mL}^{-1}$  of DMSO at  $120^{\circ}\text{C}$ . In addition, only 40 wt.% of the salt used as initiator is activated, since the experimental phosphorous content (Table 1) in the final polyol was lower than the theoretical one (1.5%). The high price of the salt (50-55 USD/kg) and the necessity to purify the final polyol of the rest of the salt that has not been reacted make the recovery and reuse of the salt a suitable process to improve the economic benefits of flame-retardant polyol production.

Once the un-reacted salt was recovered, several analyses were performed to test for the possibility of reusing the salt as a polymerization initiator. FT-IR spectra of the commercial and

recovered salt, shown in Figure 5, reveal that both maintain the same characteristic bands of C-OH stretching vibrations at  $3240\text{ cm}^{-1}$ ; C-O stretching vibrations at  $1108\text{-}1110\text{ cm}^{-1}$ ; and P=O stretching vibrations at  $960\text{ cm}^{-1}$ . It is apparent that stretching vibrations at  $1970\text{-}2169\text{ cm}^{-1}$  in the commercial salt, corresponding to  $\text{CO}_2$  and air humidity impurities, disappeared in the recovered salt spectrum.

A polymerization reaction with the recovered salt was performed and compared to the polymerization that was performed with the same reaction conditions (catalyst/initiator molar ratio of 4, solvent/initiator molar ratio of 9) but using fresh salt as an initiator. Figure 6 compares the reaction rate in terms of consumption of PO with time for both cases.

The rate of addition of propylene oxide for the recovered salt was exactly the same as that for the commercial salt since the slope of the propagation step is the same for both reactions. However, the recovered salt promoted a shorter induction period. This is attributed to the fact that the recovered glycerol phosphate sodium salt presents more deprotonated hydroxyl groups because an initiation step has already been performed; therefore, the reaction activation time is shorter.

FT-IR spectra of the polyols obtained using both commercial and recovered salt (Figure 7) revealed that both have the same framework.

The average molecular weight ( $M_n$ ) and the polydispersity index of the polyols were  $1568\text{ g mol}^{-1}$  and 1.39, respectively, for the polyol based on commercial salt and  $1565\text{ g mol}^{-1}$  and 1.37, respectively, for the polyol based on recovered salt. Hence, the reuse of the glycerol phosphate

sodium salt did not affect to the final molecular weight and polydispersity of the synthesized polyols.

Finally, to confirm the polymer structure and evaluate the degree of incorporation of the phosphate group, the polyol based on the recovered salt was also characterized using MALDI-TOF (Figure 8). MALDI-TOF allows the characterization of the polymer structure and identification of the initiator, the end group and the repeat unit, as well as other polymer chains from side reactions.<sup>23-25</sup>

Two molecular weight Gaussian distributions are identified in the spectrum. The spacing between the main peak series of each distribution was 58.08 Da, characteristic of the PO repeat unit.<sup>26</sup> In contrast, the space between both distribution peaks is 44 Da, which means that these distributions correspond to two types of polymers that differ by two sodium atoms in the initiator structure. In this way, the main distribution corresponds to a polyol with a  $M_n=1087.2 \text{ g mol}^{-1}$ , which corresponds to a polyol that contains 13 PO units, the glycerol phosphate disodium salt with both sodium atoms and two terminal PO units with a proton in each one ( $M_n = 13 \cdot 58.08 + 214 + 2 \cdot 59.08 = 1087.2$ ). The second distribution corresponds to a polyol with a  $M_n=1914.4 \text{ g mol}^{-1}$ , indicating that it contains 28 PO units and the glycerol phosphate disodium salt, but both sodium atoms are replaced by protons and two terminal PO units with a proton in each one ( $M_n = 28 \cdot 58.08 + 170 + 2 \cdot 59.08 = 1914.4$ ) [17]. The different polymer structures are shown in Figure 9.

Finally, thermogravimetric analysis (TGA) was used to investigate the effect of the recovered glycerol phosphate salt on the thermal stability of the polyol. Figure 10 shows the TGA and the DTG curves of the phosphorylated polyols that were obtained with the commercial and

recovered salt in a nitrogen atmosphere. The decomposition temperatures of both polyols were very similar (378.1 and 377.2°C, respectively).

There is a direct relationship between char formation during the combustion of a polymer and its flame retardance, and the char percentage that is measured with TGA is accepted as an indirect way of measuring this property.<sup>27,28</sup> In this case, the char percentage was 7% for phosphorylated polyol based on both the commercial and recovered salt. Because of this, we interpret the flame-retardant property was not modified by using the recovered salt since the phosphate group still exists in the salt as an effective char-promoter.

According to these results, we conclude that it is possible to use recovered glycerol phosphate disodium salt in the same way that commercial salt is used, with the added advantage of a shorter induction period of polymerization.

## **CONCLUSIONS**

The addition rate of PO using glycerol phosphate sodium salt increases when using DMSO as a solvent, and it also shortens the initiation step. For the investigated ratios, the higher the DMSO/initiator ratios are, the higher the polymerization rate is and the shorter the induction period is. In addition, the molecular weight of the polyol decreased with the solvent/initiator ratio because a larger amount of salt was activated, initiating more chains of shorter lengths. For the same reason, the more that salt was activated, the more that phosphate molecules reacted and the higher the amount of phosphorous in the final polyol. This final phosphorous content was lower than the theoretical content because only a percentage of salt was activated. The non-

incorporated salt can be recovered and reused as an initiator for further polymerizations. In this case, the rate of addition of PO remains the same, but a shorter induction period is observed because the recovered salt presents a larger amount of deprotonated hydroxyl groups than that of the commercial salt. The main properties of the polyols obtained with the recovered and commercial salts were similar, without differences in molecular weight, polydispersity index or framework (FT-IR). Finally, TGA analysis revealed that the flame-retardant properties are similar in both polymers. Thus, the recovered glycerol phosphate disodium salt can be used in the same way as the commercial salt, with the advantage of the shorter induction period of the polymerization.

#### ACKNOWLEDGEMENTS

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### Figure captions

**Fig. 1** Synthesis of polyether polyol.

**Fig. 2** Propylene oxide consumption rate for phosphorylated polyols using different DMSO to initiator molar ratios (9, 7 and 0.007). The initiator to catalyst molar ratio is 6.

**Fig. 3** Effect of the solvent (DMSO) on the polymerization.

**Fig. 4** FT-IR spectra of phosphorylated polyols using different DMSO/initiator molar ratios.

**Fig. 5** FT-IR spectra of commercial and recovered salts.

**Fig. 6** Propylene oxide consumption rate for phosphorylated polyols using recovered and commercial salts. The initiator to catalyst molar ratio is 4.

**Fig. 7** FT-IR spectra of polyether polyols obtained from commercial and recovered salts.

**Fig. 8** MALDI-TOF MS spectrum of recovered polyol.

**Fig. 9** Structures of polyether polyols.

**Fig. 10** Thermogravimetric analysis of commercial and recovered polyols in a nitrogen atmosphere.

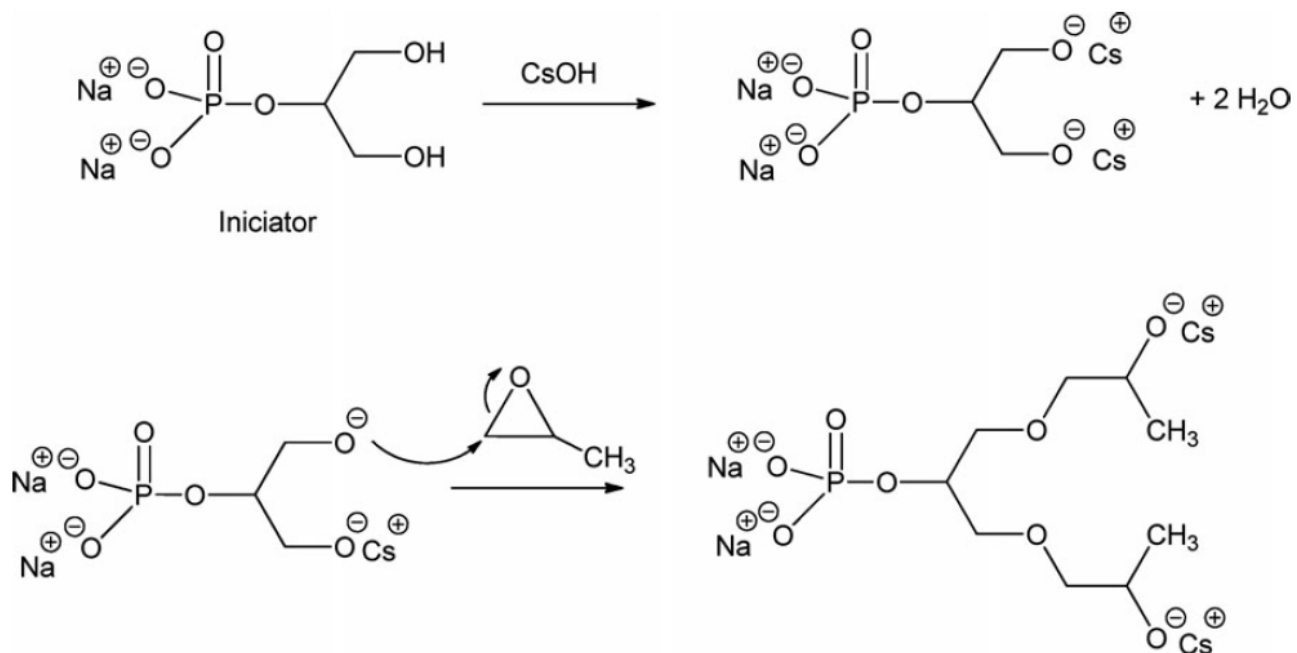


Figure 1



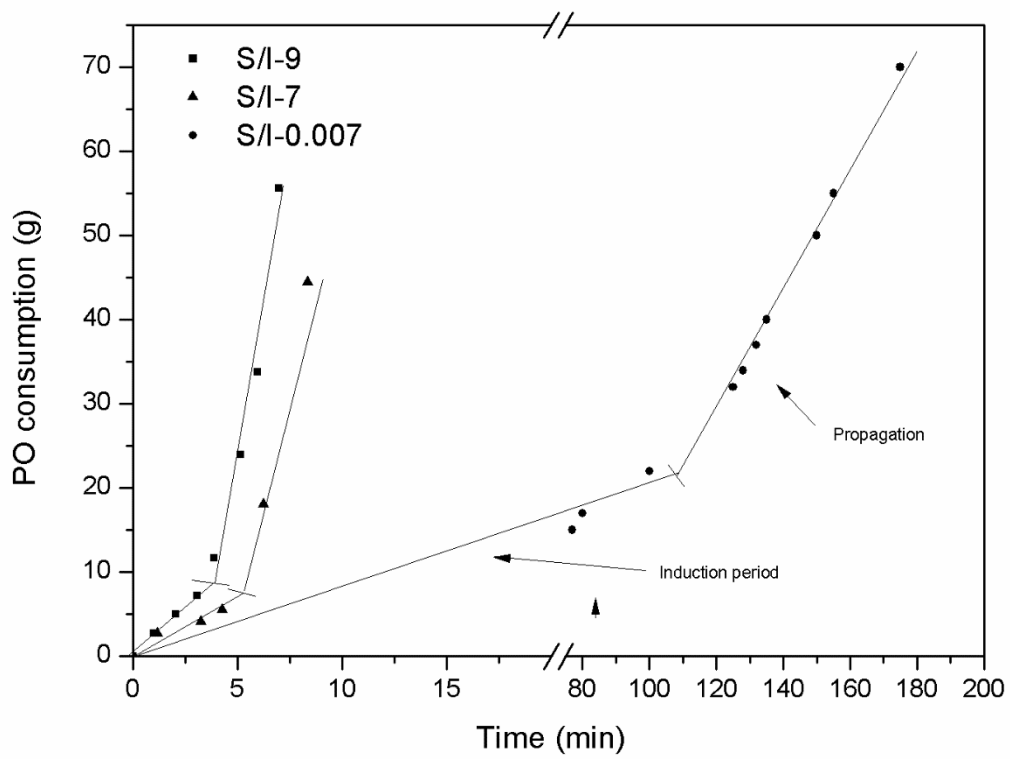


Figure 2

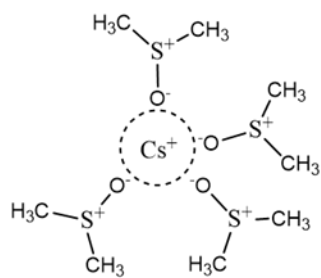
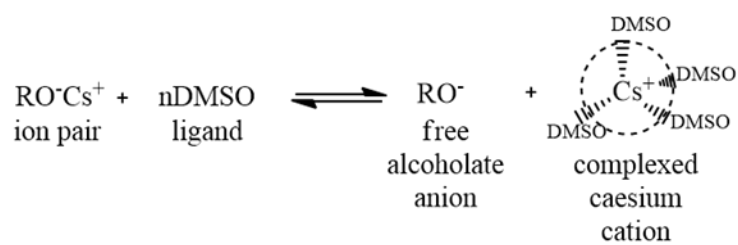


Figure 3

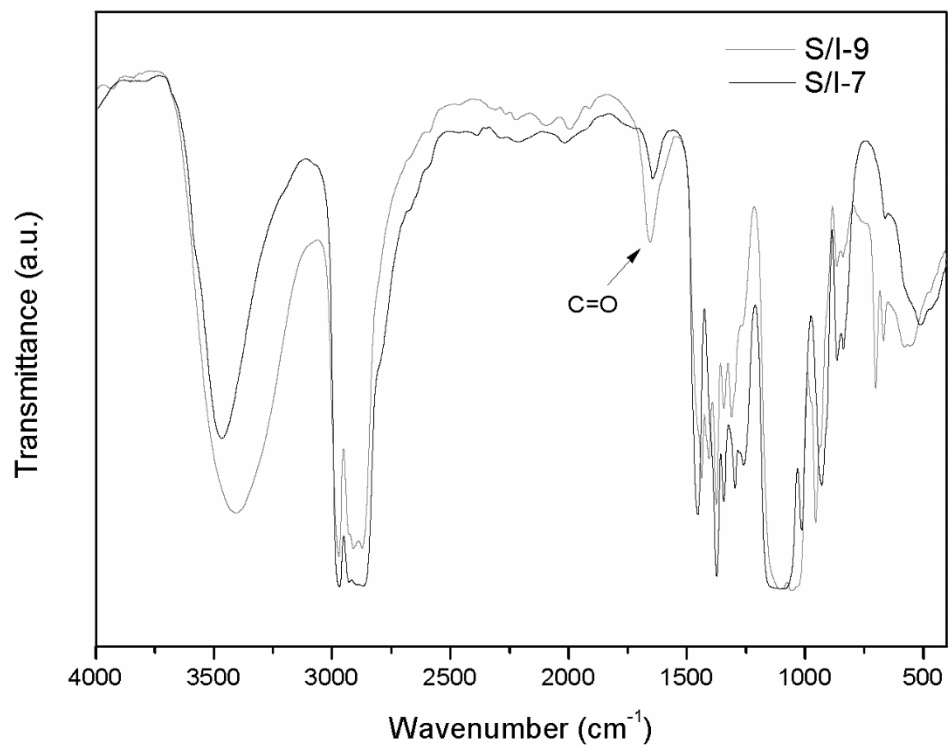


Figure 4

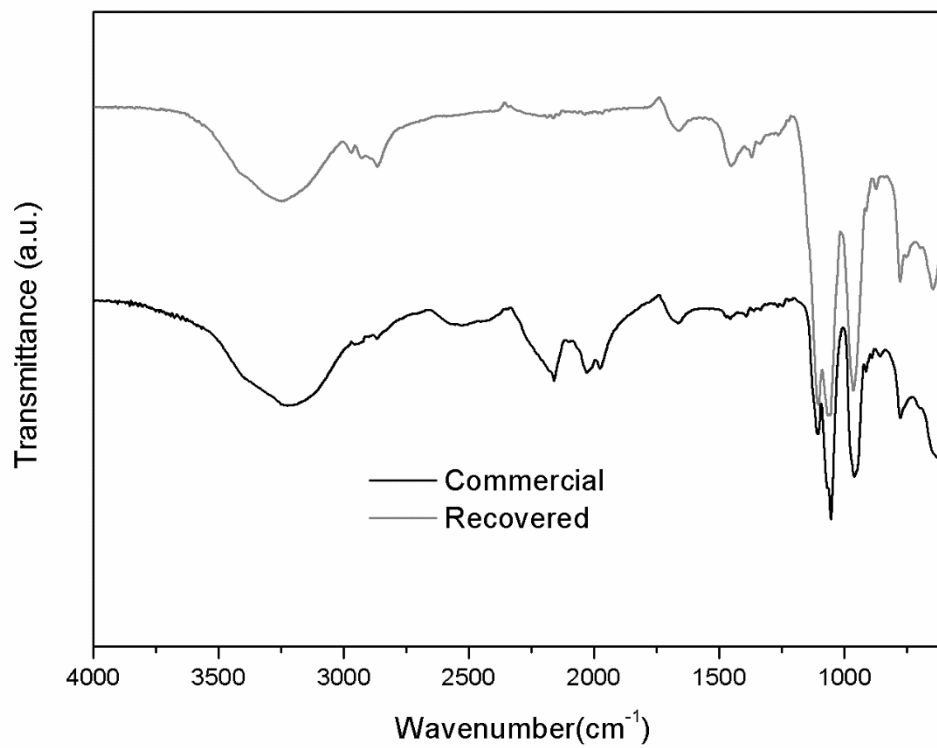


Figure 5

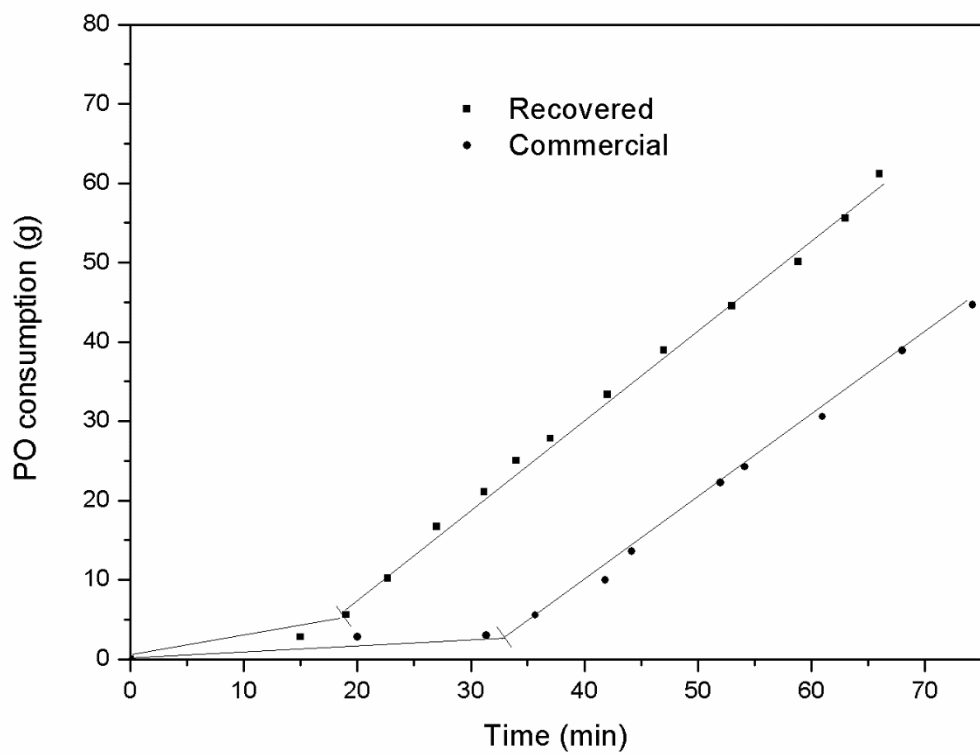


Figure 6

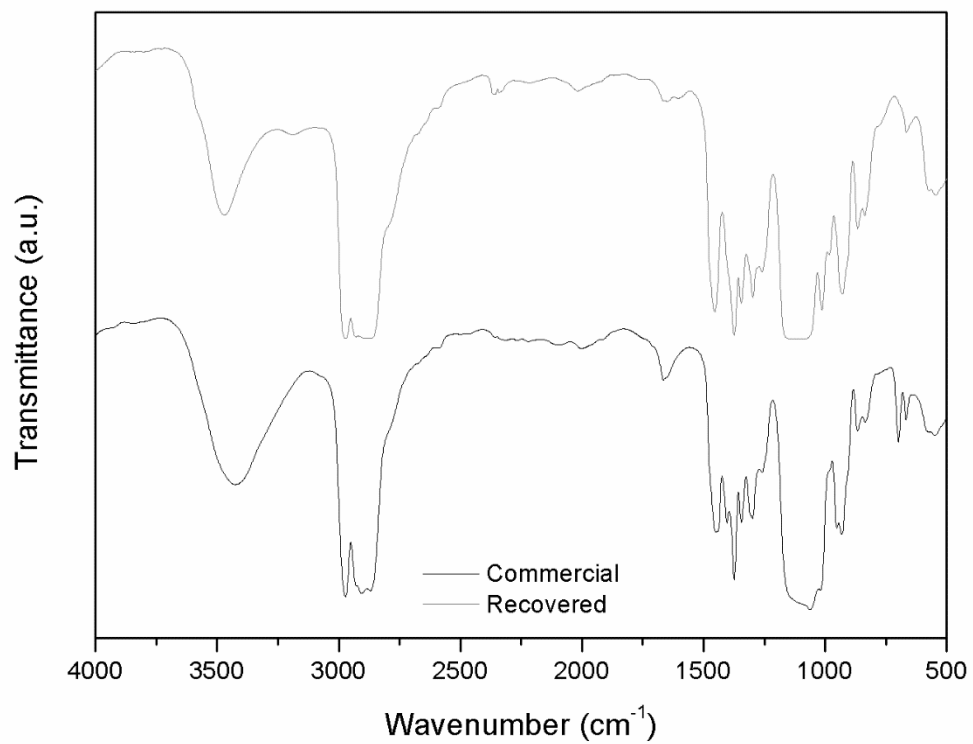


Figure 7

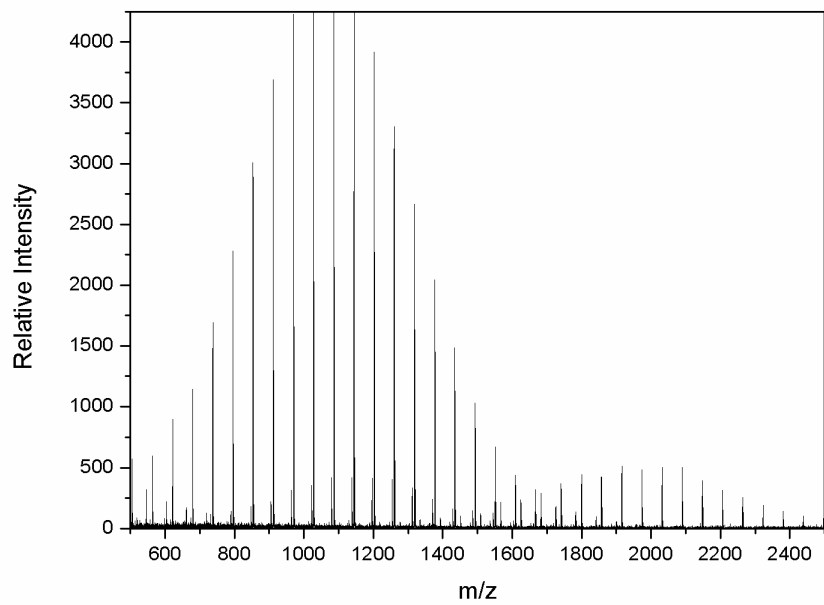


Figure 8

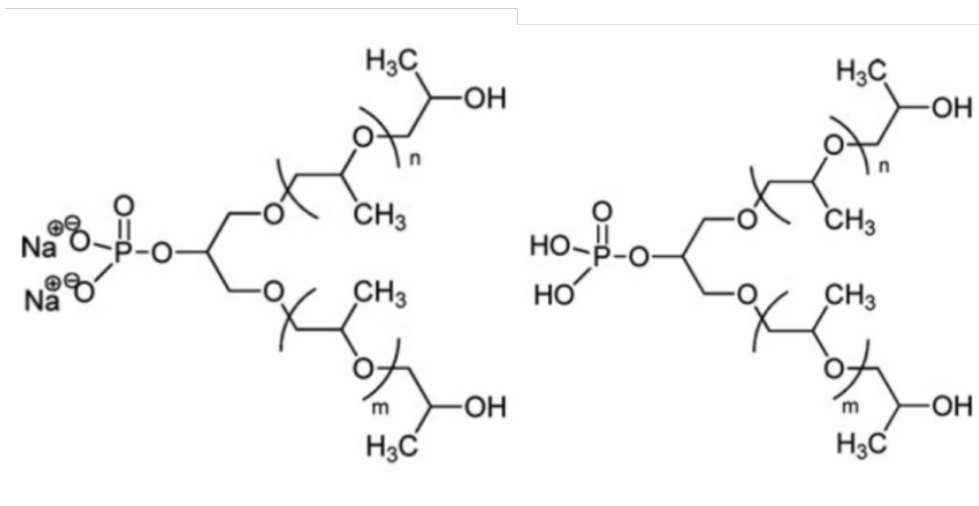


Figure 9



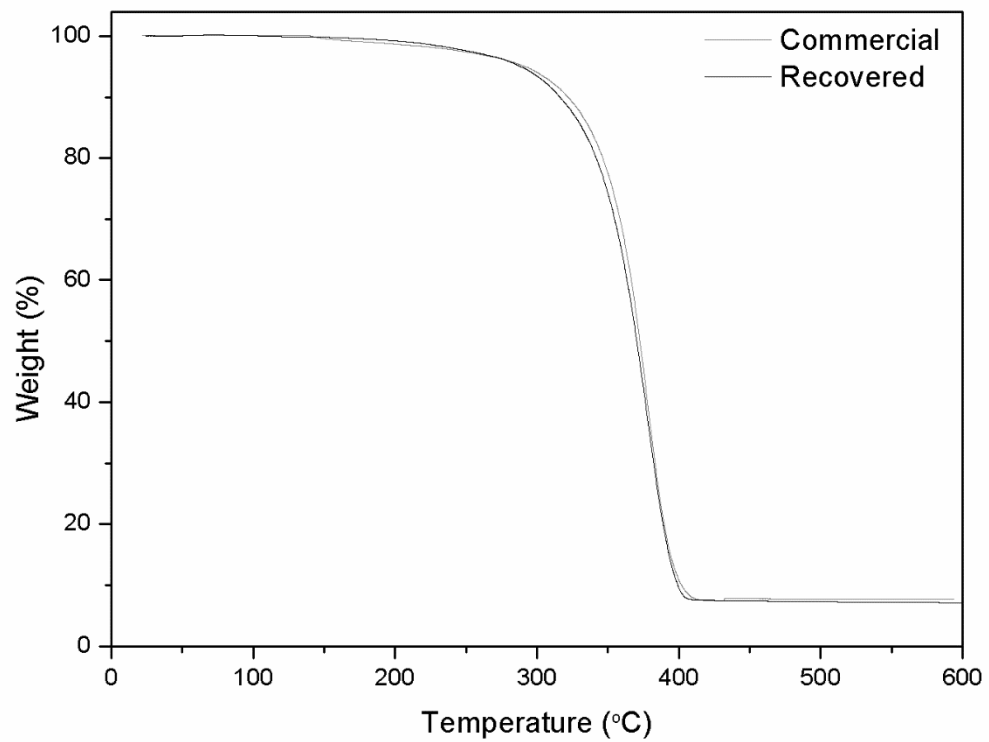


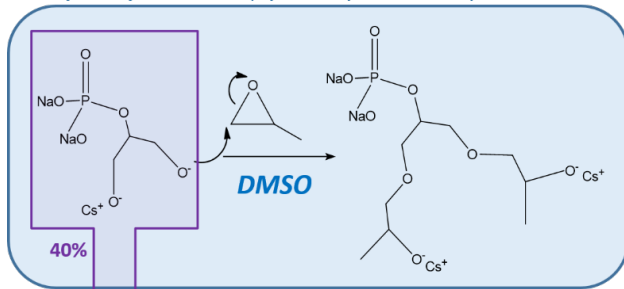
Figure 10

**Table 1. Main properties of phosphorylated polyols using different DMSO/initiator ratios**

<b>Polyol</b>	<b>DMSO/Initiator (molar)</b>	<b>Mn (g mol<sup>-1</sup>)</b>	<b>PI</b>	<b>P (wt.%)</b>
<b>S/I-9</b>	9	1164	1.28	0.63
<b>S/I-7</b>	7	1737	1.26	0.58
<b>S/I-0.007</b>	0.007	5263	1.76	0.50

## GRAPHICAL ABSTRACT

*Influence of DMSO/initiator (Glycerol Phosphate sodium salt) molar ratio*



*Polymerization of recovered initiator salt*

