Synthesis and Physical Properties of Oligo(propylene oxide-block-ethylene oxide) Allyl Methyl Ether

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Abstract: Oligo(propylene oxide-block-ethylene oxide) allyl methyl ethers (Allyl oligo(PO-b-EO) Me) with varying chain lengths and EO/PO ratios were synthesized using methylation, and addition reaction. Allyl oligo(PO-b-EO) with the reactive allyl end group was prepared by adding PO and EO using allyl alcholate initiator ionized with KOH. Metalization was applied to the other hydroxy end using t-BuOK. Allyl oligo(PO-b-EO) Me was then synthesized by reacting this metallic anion with MeOTs of a good leaving group using Sn2. These mono- and bi-substituted oligomers were identified using FT-IR, 1H-NMR, and GPC. They were then studied for the thermal properties and aqueous solution phase behaviors.

Keywords: ethylene oxide, propylene oxide, allyl ether group, methylation, and phase transition behaviour

Introduction

Poly(ethylene oxide) (PEO) has numerous applications in the surfactant, biochemical, and polymeric industries due to its hydrophilic, nontoxic, and hydrolytic properties. Using the hydrophilic properties of PEO, the non-ionic surfactants that were synthesized by adding a hydrophobic group such as fatty alcohol, alkyl phenol, and alkyl amine are applied to a detergent, fiberic treatment, and emulsifier. Likewise, PEO block copolymers are utilized as proteolytic drug delivery system (DDS) using sol-gel transition behavior on aqueous solution as varying temperatures. They are also used by solid polymer electrolyte (SPE) according to solvation for cationic alkali metals. However, the lack of reactive group in the PEO copolymers' have an important in ethylene oxide units. Thus, synthesis of the polymers having reactive end groups has generated massive interest [1,2],

In the last few years, several researchers have studied on the synthetic focus of various functional end groups applied to the chemical industry of PEO. End groups allow control and adjustment of the physicochemical properties of the resulting materials. For example, hydrophilic/hydrophobic block-copolymers are obtained through copolymerization of PEO having a reactive end group with comonomer. The preparation of well-defined heterobifunctional PEOs is of great interest for the bioconjugation of these polymers with proteins or with liposomes [3-6].

Lee and coworkers [7] investigated the synthesized PEO with heterobifunctional end groups. Proteins or liposomes were found to be inadequate therapeutic agents because of their degradation by proteolytic enzymes, thermal instability, and immunogenicity. Nonetheless, forming a conjugate between the protein or liposome and the PEO reduced this problem. The conjugate can also be used in various applications as an end group.

Ito and coworkers [8,9] prepared amphiphilic PEO macromonomers with their hydrophilic/hydrophobic balance influenced by the end alkoxy group and the PEO chain length. Their study showed that reactivities of such PEO macromonomers for copolymerization reactions with styrene or benzyl methacrylate depended on the nature of end groups.

Cammas and coworkers [10] studied a polymeric micelle system that can be used as high-performance vehicles for drug delivery. These polymeric micelles were prepared through the anionic polymerization of ethylene oxide with allyl alcholate as initiator and addition of methyl iodide on the hydroxy function of this
prepolymer. The drug entrapped in the micelles core can be stabilized in the body and especially in the blood. Smith and coworkers [2] synthesized a PEO cross-linking agent with both allyl end groups for application to high-absorption polymer. They investigated the resulting physical properties of high-absorption gel according to this agent. The cross-linking agent was found to be effective in preparing high-absorption gel with low solubility. A low crosslinking density was evident on the initial polymerization step that caused the acrylate agent activity to be lower; however, the gel showed homogeneous density. Moreover, they reported that the reaction mechanism was identical with vinyl polymerization.

Wagner and coworkers [11-13] prepared PEO with various chain lengths to react with a siloxane having active hydrogen. Low molecular weight PEOs with allyl and methoxy end group were synthesized through condensation reaction, with narrowly distributed products obtained. However, this synthetic process involving several steps was complicated. It also had limited application in the chemical industry. Likewise, it showed less than surface active property for polydisperse PEO.

In this study, polydisperse oligo(PO-b-EO)s with allyl and methoxy end groups were synthesized through addition of EO and PO using allyl alcoholate as the initiator. They were prepared by varying hydrophilic/hydrophobic ratios chain lengths, and their physical properties in these structures studied.

Experiments

Materials

Allyl alcohol (AIOH, Acros Chemical Co.), ethylene oxide (EO), and propylene oxide (PO) were used after distilling under the vacuum to remove moisture moieties. Potassium hydroxide (KOH, Aldrich Chemical Co.) acted as the catalyst while acetic anhydride (AA, Aldrich Chemical Co.) as the neutralizer for the product; the two chemical were used without further purification.

For methylation reaction of allyl oligo(PO-b-EO) Me, potassium tert-butoxide (t-BuOK, Aldrich Chemical Co.) and methyl p-toluenesulfonate (MeOTs, Aldrich Chemical Co.) were used as received. Tetrahydrofuran (THF, Aldrich Chemical Co.) distilled with Na2SO4 and dehumidified for a week using 4 Å molecular sieves was used as the reaction solvent.

Synthesis of Allyl Oligo(PO-b-EO)

For the synthesis of allyl oligo(PO-b-EO), a 2000 mL stainless steel highpressure reactor was set up with a gas inlet, gas outlet, pressure gauge and a thermocouple (Figure 1). AIOH and KOH (Table 1) were placed in the reactor. Nitrogen gas was then injected to remove moisture and oxygen from reaction mixture and reduce the pressure. EO and PO were injected into the reactor using 10 atm nitrogen gas, with the reaction condition maintained under 5 atm at 130°C. The pressure was

Table 1. The Notation and Recipe of Allyl Oligo(PO-b-EO)

<table>
<thead>
<tr>
<th>Notation</th>
<th>AIOH (mol)</th>
<th>Additive Unit</th>
<th>KOH (mmol)</th>
<th>Yield (%)</th>
<th>Mw Theor.</th>
<th>Mw GPC</th>
</tr>
</thead>
<tbody>
<tr>
<td>A04</td>
<td>1</td>
<td>-</td>
<td>5.2</td>
<td>98.4</td>
<td>234.29</td>
<td>248.38</td>
</tr>
<tr>
<td>A05</td>
<td>1</td>
<td>-</td>
<td>5.2</td>
<td>97.9</td>
<td>278.34</td>
<td>286.26</td>
</tr>
<tr>
<td>A06</td>
<td>1</td>
<td>-</td>
<td>5.2</td>
<td>98.4</td>
<td>322.40</td>
<td>321.06</td>
</tr>
<tr>
<td>A07</td>
<td>1</td>
<td>-</td>
<td>5.2</td>
<td>97.9</td>
<td>366.45</td>
<td>353.66</td>
</tr>
<tr>
<td>A16</td>
<td>1</td>
<td>1</td>
<td>5.2</td>
<td>96.6</td>
<td>380.48</td>
<td>-</td>
</tr>
<tr>
<td>A25</td>
<td>1</td>
<td>2</td>
<td>5.2</td>
<td>91.3</td>
<td>394.50</td>
<td>-</td>
</tr>
<tr>
<td>A34</td>
<td>1</td>
<td>3</td>
<td>5.2</td>
<td>95.8</td>
<td>408.53</td>
<td>-</td>
</tr>
</tbody>
</table>
stirred for 30 min at 15°C to remove moisture. To ionize the hydroxy end group, t-BuOK/THF solution was dropped under argon at 15–20°C. When t-BuOK was added, the mixture was observed to change from a clear to a pale yellow solution of metalated oligo(PO-b-EO). After stirring for 30 min, the MeOTs/THF solution was added to substitute the anion to methoxy group at 15–20°C under an inert argon environment. Yellowish white salts was observed during the substitution reaction at 20°C. Allyl oligo(PO-b-EO) Me was purified as extracting with D.D.I. water and chloroform to remove salts. Allyl oligo(PO-b-EO) Me was then distilled by evaporation under vacuum for a day [14]. Table 2 shows the feed compositions of allyl oligo(PO-b-EO) Me.

Measurement

Fourier transform infrared spectra (FT-IR) were recorded with a Biorad® FTS-7 spectrometer. 1H-nuclear magnetic resonance spectroscopy (1H-NMR) of reactants and products dissolved in CDCl3 were recorded at ambient temperature using a Varian® Mercury 300 model. The chemical shift was reported as ppm downfield from tetramethyl silane (TMS). Gel permeation chromatography analyses (GPC, Waters Co.) were run in THF on a Waters® Syragel™ HR4 column using RI detector at 35°C. The flow rate was 1.0 mL/min. Polystyrene standards were employed for molecular weight calibration. Gas chromatography analyses (GC) were carried out on an Agilent Technologies HP 6890 GC series using a 30-m DB-5 capillary column with 0.25 mm diameter, modified with 0.1 μm crosslinked polystyrene (temperature program: 5 min at 40°C; afterwards 40–320°C, heating rate of 10°C/min; finally 17 min at 320°C, FID) [16]. Thermogravimetric analyses (TGA, Shimadzu TGA-50) were carried out in the range of room temperature up to 600°C at the heating rate of 20°C/min under a nitrogen atmosphere.

Phase transition temperature (T_p) of HMTS-Oligo (PO-b-EO) through hydrosilylation was determined using the thermo-optical analyzer (TOA) equipped with Mettler® FP82HT hot stage, Mettler® FP 90 central processor, and Olympus® BX50 optical polarized microscope [17]. A 10.0 wt% aqueous solution of wetting agents was prepared then stored at 30°C for 24 hs. A capillary tube (I.D. 3 mm, length 50 mm) that

Table 2. The Notation and Recipe of Allyl Oligo(PO-b-EO) Me

<table>
<thead>
<tr>
<th>Notation</th>
<th>Allyl Oligo(PO-b-EO) (mol)</th>
<th>t-BuOK (mol)</th>
<th>MeOTs (mol)</th>
<th>Mw Theor.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A04M</td>
<td>1</td>
<td>1.2</td>
<td>1.2</td>
<td>248.32</td>
</tr>
<tr>
<td>A05M</td>
<td>1</td>
<td>1.2</td>
<td>1.2</td>
<td>292.37</td>
</tr>
<tr>
<td>A06M</td>
<td>1</td>
<td>1.2</td>
<td>1.2</td>
<td>336.42</td>
</tr>
<tr>
<td>A07M</td>
<td>1</td>
<td>1.2</td>
<td>1.2</td>
<td>380.48</td>
</tr>
<tr>
<td>A16M</td>
<td>1</td>
<td>1.2</td>
<td>1.2</td>
<td>394.50</td>
</tr>
<tr>
<td>A25M</td>
<td>1</td>
<td>1.2</td>
<td>1.2</td>
<td>408.53</td>
</tr>
<tr>
<td>A34M</td>
<td>1</td>
<td>1.2</td>
<td>1.2</td>
<td>422.56</td>
</tr>
</tbody>
</table>
was sealed on one side was injected with these solutions, after which the other side was also sealed. The tube was sonicated for 5 min to remove foam from solution. TOA was then carried out in the range of room temperature up to 150°C at the heating rate of 5.0°C/min under nitrogen atmosphere. Tp was set as the midpoint of the phase transition temperature region in the TOA thermograms.

Results and Discussions

Addition Reaction
As shown in Scheme 1, alkyl oxide oligomers with reactive alkyl group were synthesized through the addition reaction of PO and EO for ALOH. Allyl alcohol was ionized while reacting with ALOH and KOH. Allyl oligo(PO-b-EO)s were then prepared by adding PO and EO to this anion.

Figure 2 shows the FT-IR spectra for allyl oligo (PO-b-EO) synthesized with the reactive alkyl end group. Absorption band at 1660 cm⁻¹ corresponding to C=O stretching vibration peak was observed in whole products, with addition completion with alkyl group identified from this peak.

Figure 3 shows the variable details of characteristic peaks as chain length of PO and EO for these oligomers. Absorption bands at 2968, 2930, 1373, and 1297 cm⁻¹ corresponding to -CH₂- peaks for A04, A05, A06, and A07 increased with increasing EO chain length. Bands at 2968, 2930, 1373, and 1297 cm⁻¹ corresponding to CH₂ peaks for A07, A16, A25, and A34 with same chain length increased with increasing PO ratios.

The reaction and purification for allyl oligo(PO-b-EO) were investigated using ¹H-NMR. Figure 4(a) shows ¹H-NMR spectrum for A07. The allyl group in oligomer was identified as characteristic peaks (CH₂=CH₂-CH₂-) at 5.2, 5.9, and 4.0 ppm. Addition reaction and chain length were confirmed as ethylene peaks (-CH₂-CH₂-O-) at 3.5 ppm. Likewise, KOH acting as the catalyst was removed while AA serving as the neutralizer after purifying was certificated.

The yield and number average molecular weight (Mn) of allyl oligo(PO-b-EO) were measured using GC

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Figure 2. FT-IR spectra of allyl oligo(PO-b-EO) and characteristic peaks of allyl group; (a) A04, (b) A05, (c) A06, (d) A07, (e) A16, (f) A25, and (g) A34.

Figure 3. FT-IR spectra of allyl oligo(PO-b-EO) and characteristic peaks of alkyl group; (a) A04, (b) A05, (c) A06, (d) A07, (e) A16, (f) A25, and (g) A34.

Figure 4. ¹H-NMR (CDCl₃, 300 MHz) spectra of (a) allyl oligo(PO-b-EO) and (b) allyl oligo(PO-b-EO) Me.
More than 90%, even reaching 98%, yield of allyl oligo(EO)s were obtained as shown in Table 1. The measured $M_n$ was comparable to the calculated value. Byproducts such as PEG were not detected.

Figure 5 presents the molecular weights and distributions for allyl oligo(PO-b-EO) with GPC chromatograms. The molecular weights of these oligomers were observed to increase with increasing chain length of PO and EO. They also had similar retention time of polyethylene glycol 400 (PEG 400, Samchun Co., $M_w = 400$ g/mol). The oligomers showed molecular weight distribution of 2.0 − 2.5.

**Methylation Reaction**

As shown in Scheme 1, methylation for allyl oligo(PO-b-EO) was synthesized in a two-step reaction: the metalation of ionizing hydroxy end group of oligomer using t-BuOK as strong base and substitution (Sn2) to react with MeOTs as good leaving group [2,14].

Figure 6 illustrates the FT-IR spectra for allyl oligo(PO-b-EO) before and after methylation. The reaction completion of methylation was identified from the methoxy peak that appeared at 1199 cm$^{-1}$ and the hydroxy peak that dissapeard at 3485 cm$^{-1}$. Figure 4 (b) shows the $^1$H-NMR spectrum for allyl oligo (PO-b-EO) Me. The methoxy group (-OCH$_3$) of allyl oligo(PO-b-EO) at 3.4 ppm appeared as expected after methylation. A large quantity of salts was confirmed to have resulted from methylation; however, this was removed by purification.

![Figure 5. GPC chromatograms of allyl oligo(PO-b-EO).](image)

![Figure 6. FT-IR spectra of allyl oligo(PO-b-EO) Me and characteristic peaks of methoxy group; (a) A07 and (b) A07M.](image)

![Figure 7. TGA thermograms of (a) allyl oligo(EO) and (b) allyl oligo(PO-b-EO) as a function of temperature.](image)

**Thermal Properties**

The weight loss changes of allyl oligo(PO-b-EO) and allyl oligo(PO-b-EO) Me due to increasing temperature were investigated using TG analyzer under nitrogen condition. The TGA measurement revealed that the thermal behavior of oligomers is influenced by chain length and EO/PO ratio of oligo(PO-b-EO) and by methylation.

Figure 7 (a) shows TGA curves for allyl oligo(EO)s according to EO chain length of 4−7 moles. Weight loss tendency for allyl oligo(PO-b-EO)s was observed within the temperature range of 200−400°C. The weight loss temperature of allyl oligo(EO)s increased with increasing EO chain length that resulted in increased molecular weight.

Figure 7 (b) illustrates TGA curves for allyl oligo (PO-b-EO)s having a chain length of 7 moles in varying EO/PO ratios. As PO chain length of the oligomer increased, weight loss behavior slightly differed. The initial weight loss was recorded at a lower temperature and lower slope. In general, thermal behavior for the PO block of the oligomer was similar to the EO block.

Figure 8 shows the TGA curves of allyl oligo (PO-b-EO) and allyl oligo(PO-b-EO) Me according to
their thermal behavior during methylation. The thermal behavior for allyl oligo(PO-b-EO) Me with increasing temperature was similar to that of allyl oligo(PO-b-EO) with the hydroxy end group. The methoxy group within the oligomers seemed to have little influence in the thermal behavior of ether units.

**LCST Behavior for PO/EO Chain Length and End Group Effect**

Non-ionic surfactant with hydrophilic and hydrophobic groups such as EO and PO in a molecular could exhibit lower critical solution temperature (LCST) behavior as a variable effect of EO/PO ratio and chain length [17,20,21]. An aqueous solution of these surfactants appeared as a clear phases composed of hydrogen bond between water and the EO group below the phase transition temperature. However solutions appeared as turbid phases separated between surfactants and water above this temperature, because hydrophobic-hydrophobic intermolecular interactions between PO groups are more than hydrogen bond.

Figure 9(a) and (b) show a relative light intensity of allyl oligo(PO-b-EO) and allyl oligo(PO-b-EO) Me with increasing temperature using TOA on 10.0 wt% aqueous solution. \( T_p \) for each oligomer were set as the midpoint of the phase transition temperature region through extrapolation in the TOA thermogram.

The oligomers with EO addition group like A04, A05, A06, and A07 did not show phase transition behavior within the temperature range measured. It seemed that phase transition behavior was not observed because the hydrophobicity of allyl group was smaller than the hydrophilicity of EO group [17,20,21]. However, Figure 9(a) shows that A25 and A34 having PO units with chain length of 7 moles had a rapidly decreasing light intensity. \( T_p \) for A16 with EO chain length of 1 mole was not showed. \( T_p \) of allyl oligo(PO-b-EO) decreased with increasing PO chain length, as in A25 and A34. Interactions between hydrophobic groups intensified as PO increased with increasing PO length. Likewise, they were more than hydrogen bonds at lower temperature.

As showed in Figure 9(b), the phase transition temperature for allyl oligo(PO-b-EO) Me appeared on lower region. A04M, A05M, A06M, and A07M did not show phase transition behavior on measured range because of the smaller hydrophobic group, i.e., the allyl and methoxy group. \( T_p \) increased with increasing PO chain length. Similarly, it seemed that there were more hydrophobic interactions than hydrogen bonds.

\( T_p \) for aqueous solution of the oligomers are shown in Table 3. The phase transition behavior for allyl oligo(PO-b-EO) Me appeared on lower temperature than allyl oligo(PO-b-EO). It seemed that this lower \( T_p \) as methylation was closely connected with the decrease of the hydroxy group than the increase of the methoxy group. The hydrogen bonds between water and hydroxy group decreased by methylation. They were also less than hydrophobic interactions [22].

**Figure 8.** TGA thermograms showing: changing weight loss through methylation.

**Figure 9.** TOA thermograms of (a) allyl oligo(PO-b-EO) and (b) allyl oligo(PO-b-EO) Me.

**Table 3.** \( T_p \) of Allyl Oligo(PO-b-EO) and Allyl Oligo (PO-b-EO) Me

<table>
<thead>
<tr>
<th>Sample</th>
<th>( T_p ) (°C)</th>
<th>Sample</th>
<th>( T_p ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A07</td>
<td>109.0</td>
<td>M07</td>
<td>-</td>
</tr>
<tr>
<td>A16</td>
<td>102.2</td>
<td>M16</td>
<td>68.7</td>
</tr>
<tr>
<td>A25</td>
<td>40.2</td>
<td>M25</td>
<td>40.2</td>
</tr>
<tr>
<td>A34</td>
<td>67.9</td>
<td>M34</td>
<td>67.9</td>
</tr>
</tbody>
</table>

\( a^1 \) \( T_p \): phase transition temperature in aqueous solution (10 wt%). \( b^2 \) Not detected.
Conclusions

Heterobifunctional oligomers such as allyl oligo (PO-b-EO) and allyl oligo(PO-b-EO) Me having allyl and methoxy end groups were synthesized through addition and methylation reaction with varying hydrophilic/hydrophobic ratios and chain length. Polydisperse oligomers were prepared through the addition of EO and PO with allyl alcololate. Any side-reactions and chain degradation during chemical modifications of end groups were inhibited.

TG analysis of oligomers showed that the weight loss temperature increased with increasing oligomer chain length. Likewise, it was hardly affected by PO moieties and end methoxy group.

Oligomer aqueous solution having EO moieties was almost visibly clear above phase transition temperature. However, the others having PO moieties or methoxy end group exhibited phase transition behavior. Tgs increased with increasing PO moieties and with the presence of methoxy end group.

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References