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Viscoelastic Evaluation of Poly(trimethylene carbonate)s Bearing Oligoethylene glycol Units Which Shows Thermoresponsive Properties at Body Temperature

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((Optional Dedication))

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Abstract: Poly(trimethylene carbonate) (PTMC) derivatives have been extensively researched for use as low-toxicity biomaterials. Better biocompatibility and lower toxicity have been achieved by eliminating acid generation from the ester group at the side chains. In this study, thermosensitive PTMC derivatives bearing oligo(ethylene glycol) units were synthesized by ring-opening polymerization for the development of low-toxicity and thermosensitive soft materials. The viscoelastic properties of the obtained polymers were then investigated by rheometry to clarify the thermosensitive and molecular weight effects. Furthermore, thermosensitive behaviors and dynamics of these polymers were observed by UV-vis transmittance, DSC, and ^{1}H NMR spectra analysis. These data suggest a mechanism for the thermosensitive behavior where it was surmised that some kind of dehydration phenomena induced aggregation behavior in aqueous media above lower critical solution temperature (LCST). These thermosensitive behaviors provide an important road map for the development of thermosensitive soft materials using ester free PTMC derivatives by controlling the thermosensitive behaviors and bulk properties.

1. Introduction

Developments of biomaterials and medical materials are important to extend healthy life expectancy[1]. Among them, biodegradable materials have attracted attention and been developed for various applications, such as drug delivery systems[2-5] injectable gels,[6,7] artificial body parts,[8] scaffolds[9-12] and tissue engineering.[13-16] These applications require not only the biodegradable behavior but also other properties. For example, stimuli-responsive behavior is important for drug delivery systems and mechanical properties are important for artificial body parts. Thus, various biodegradable polymers, such as polyurethane[2,6,8,10] chitosan,[4,5,7,9] poly(lactic acid)[12,14,15] and poly(trimethylene carbonate)[3,11,16] (PTMC), have been researched for use as biomaterials. Above all, PTMC derivatives possess the unique property of having no acid generation from the polymer main chain during degradation.[17,18] Therefore, PTMC derivatives are expected to play an important role in the development of low-toxicity and low-inflammatory materials compared with other biodegradable polymers.

The structures of trimethylene carbonate (TMC) derivatives usually include a six-membered ring[19-21] and are polymerized by ring-opening polymerization[22] using organic,[23-25] inorganic[26] and enzyme catalysts.[27] Two side chains can be introduced into TMC. Actually, many kinds of TMC derivatives bearing functional side chains have been synthesized[19-21] for tunable properties[28-30] of biomaterials, such as drug/cell delivery systems[31] and vascular stents.[32] However, ester groups were introduced into the PTMC at the side chains. These change to carboxylic acid groups after degradation and have the potential to cause inflammation. Therefore, ester free PTMC derivatives bearing the side chain were designed in previous research by our group.[33-39]

PTMC derivatives bearing the ester free side chain were developed for low-toxicity biomaterials. Thus, the thermosensitive behavior, lower critical solution temperature (LCST), was introduced by controlling the balance between hydrophilicity and hydrophobicity for actual applications.[40] The ethylene glycol chains were introduced to TMC derivatives bearing the side chain as a hydrophilic part and then their monomers, 5-[2-{2-(2-

methoxyethoxy)ethoxy}ethoxymethyl]-5-methyl-[1,3]-dioxa-2-one (TMCM-MOE3OM) and 5-ethyl-5-(2,5,8,11,14-pentaoxapentadecyl)-1,3-dioxan-2-one (TMCE-MOE4OM), were polymerized with1,8-diazabicyclo[5.4.0]-7-undecene (DBU) as catalysts. The LCST of the synthesized polymers was 33ºC for poly(TMCM-MOE3OM) (PTMCM-MOE3OM) and 37ºC for poly(TCCE-MOE4OM) (PTMCE-MOE4OM), although their TMC derivatives were a viscous liquid.[34] Then, the block copolymers with PTMC derivatives bearing the ethylene glycol chain and poly(lactic acid) were synthesized using a macro initiator of PTMC derivatives to improve the mechanical strength. Their block copolymers were obtained as a solid although the ester group was converted to a carboxylic acid group during degradation[35,36] which induce the acid condition as a side effect compared with ester free PTMC derivatives.[39] Above all, the properties of PTMC bearing the ethylene glycol chain have not been widely studied although several properties were investigated such as, degradation behaviors[37] and photo- and thermo-sensitive behaviors.[38]

In this study, we synthesized ester free PTMC derivatives, PTMCM-MOE3OM and PTMCE-MOE4OM, by ring-opening polymerization using various catalysts, DBU and Zn complex, for the development of thermosensitive soft materials as low-toxicity biomaterials. The viscosity of the synthesized polymers was then investigated by rheometry to evaluate the effect of molecular weight and the effect of the side chain. In addition, thermosensitive behaviors of PTMC derivatives were researched by not only UV-vis transmittance but also differential scanning calorimetry (DSC) and ^{1}H NMR spectrum analysis in order to reveal the mechanisms of thermosensitive behaviors and effect of the side chain.

2. Result and Discussion

2.1. Polymer Synthesis

In order to examine the mechanical properties of thermosensitive biodegradable homopolymers, two monomers were synthesized **(Scheme 1)**, TMCM-MOE3OM (total yield 18%) and TMCE-MOE4OM (total yield 22%), following our previously reported methodology.[34,37] These monomers were then polymerized by ring-opening anionic polymerization with catalysts using synthesized monomers[34,37] **(Scheme 2)**. Table 1 shows the polymerization conditions and analysis data of the synthesized polymers, PTMCM-MOE3OM and PTMCE-MOE4OM, which were designed for two reasons. First, the ester free structure of trimethylene carbonates was designed to prevent any toxicity during degradation, due to no generation of carboxyl acid groups. Second, the different lengths of oligo(ethylene glycol) (OEG) units and a methyl or an ethyl group were designed in order to control their thermosensitive properties by altering the balance between hydrophilicity and hydrophobicity.

The molecular weights of each polymer did not agree with the theoretical molecular weight derived from calculation by the initial ratio between the monomer and the initiator. In addition, PTMCM-MOE3OM (*M*n 7,600 g/mol) **(Table 1, entry 1)** was analyzed by MALDI-TOF MS **(Figure S1)** and the spectra showed several fragment peaks due to different chain end groups. These results indicated that the polymerization mechanism was not only growing reactions of the main chain but also main chain exchange reactions and/or back-biting reactions, which have already been reported by other researchers.[33,41] The main reason for the side reactions was surmised to be the effect of steric hindrances of the side chain and/or the concentration effect of reduced monomers and the reactive end chain between the immediate start reaction and the end reactions. Moreover, the obtained polymers looked like viscous liquids and these were subsequently investigated by rheometry.

2.2. Viscoelastic Evaluation

Figure 1 shows the frequency dependence on the dynamic modulus of PTMCM-MOE3OM (Table 1, entry 1) and PTMCE-MOE4OM **(Table 1, entry 4)**. The values of dynamic modulus, storage modulus (G') and loss modulus (G"), for PTMCE-MOE4OM **(Figures 1a and b)** were higher than for PTMCM-MOE3OM **(Figures 1c and d)**. There were presumed that fewer intermolecular interactions for PTMCM-MOE3OM than PTMCE-MOE4OM because of the large amount of excluded volume effect at the long side chain of the former compared with the latter. In addition, the dynamic modulus of PTMCE-MOE4OM showed a phase transition following frequency increases from a liquid-like state (G'<G") to a solid-like state (G'>G") at around 8 Hz **(Figures 1c and d)**. This result surmised that molecular interactions were influenced by the effect of side chain tangle. As the side chain elongated, the values of dynamic modulus were increased. Above all, it was interesting that the slight change of chain lengths and alkyl groups were influenced, revealing that the monomer design of TMC derivatives could be one of the important approaches to control the physical properties.

Figure 2 shows molecular weights of PTMCM-MOE3OM to be *M*n 3,800 g/mol **(Figures 2a and b)**, *M*n 4,900 g/mol (Figures 2 c and d) and 7,600 *M*n g/mol (Figures 2e and f). The G' values decreased as the molecular weight was reduced but the G" values increased under the same conditions. One of the reasons why was suggested to be the side chain effects of low molecular weight polymers, such as hydrogen bonding at the ethylene glycol chain, which were increased compared with high molecular weight polymers. In addition, phase change transitions from a liquid-like state (G'<G") to a solid-like state (G'>G"), were observed at 3 Hz **(Figures 2c and d)** and 8 Hz (Figures 2a and b). These behaviors were not only for the reasons stated above but also molecular mobility and intermolecular and/or inner molecular interactions which were important factors for clarification of the phase change properties. Taking the wide polydistribution index (PDI) into account, it might not be possible to identify the difference of between *M*n 3,800 and *M*n 4,900, that chain end moieties still influence on the

polymer properties, as well as LCST.[34] We therefore selected *M*n 7,600 for the subsequent evaluation.

Since both of the polymers were known to have temperature responsive properties in aqueous solution, we next investigated the temperature effect. **Figure 3** also shows the frequency dependence of the dynamic modulus of PTMCM-MOE3OM at various temperatures; 0 ºC, **(Figures 3a and b)** 25 ºC **(Figures 3c and d)** and 37 ºC **(Figures 3e and f)**. The dynamic modulus values increased at higher frequencies at every temperature. They showed low values at high temperature, probably due to the molecular mobility even though PTMCM-MOE3OM was in a liquid-like state (G'<G"). This tendency seems to be in good agreement with their temperature responsive properties at around body temperature.

Figure 4 shows the share rate dependence of share viscosity of PTMCM-MOE3OM at 0ºC **(Figure 4a)**, 25 ºC **(Figure 4b)**, and 37 ºC **(Figure 4c)**. The share viscosity values were not dependent on the share rate and were almost constant at each temperature however their values decreased depending on the temperature increase. The cause of this behavior was probably the molecular mobility of polymers which was the same as the variations of dynamic modulus (Figure 3). The temperature dependence light transmittance of PTMCM-MOE3OM and PTMCE-MOE4OM. The LCST were observed at 33ºC and at 37ºC, indicating that LCST could be controlled by the balance between the hydrophilicity and the hydrophobicity at the side chain, a methyl or an ethyl group and length of an ethylene glycol chain.

2.2. Thermosensitive Behavior

Thermosensitive behaviors were also observed by DSC curves of PTMCM-MOE3OM **(Figure 5a)** and PTMCE-MOE4OM **(Figure 5b)** with water. The endothermic peaks were registered at 30.1 ^{o}C (Figure 5a, $\triangle$H = -3.56 J/g) and 31.4 ^{o}C (Figure 5b, $\triangle$H = -3.18 J/g) and enthalpy changes ($\triangle$H) and their dynamics were in almost the same state. Therefore, the

mechanism of thermosensitive properties of PTMCM-MOE3OM and PTMCE-MOE4OM was suggested by the dehydration properties.

Since the thermoresponsive properties have not been closely examined in previous reports, PTMCM-MOE3OM was analyzed by ^{1}H NMR spectral analysis. At each temperature, 5 ºC, 15 ºC, 25 ºC, 35 ºC, 37 ºC, and 45 ºC there are integral intensity values at each peak, peak a (4.1~4.3 ppm), peak b (0.9~1.1 ppm) and peak c (3.4~3.7 ppm) **(Figure 6)**, where the spectral pattern changed, depending on temperature specifically under or above the LCST (33 ºC) **(Figure S2)**. In low temperature conditions (5 ºC ~ 25 ºC), the reason for the difference in integral intensity values was suggested to be the solubility of polymers which was decreased at a low temperature and that these values were influenced by the solvation behavior derived from the hydrophobic interaction and/or hydrogen bonding. On the other hand, in high temperature conditions (25 ºC ~ 45 ºC), the ratio of integral intensity values between peak c (3.4~3.7 ppm), at the ethylene glycol group, and peak a (4.1~4.3 ppm), at the main chain, was increased above LCST (33 ºC) **(Figure S2 a)**. The range was greater than that for the other, i.e. the ratio between peak c (3.4~3.7 ppm) and peak b (0.9~1.1 ppm), the methyl group at the side chain **(Figure S2 b)**. Thus, the integral intensity value of peak a (4.1~4.3 ppm), the methylene group at the main chain, was decreased compared with the value of peak b (0.9~1.1 ppm), the methyl group at the side chain. This result suggested that some kind of dehydration phenomena induced aggregation behavior in aqueous media above LCST.

3. Conclusion

We evaluated the viscoelastic properties of PTMCM-MOE3OM and PTMCE-MOE4OM by rheometry and the data indicated that the dynamic modulus of PTMC derivatives were influenced by various conditions. PTMCE-MOE4OM was in a gel-like state (G'>G") at the high frequency region, probably due to the entanglement with the longer 4 units of OEG and ethyl groups units than that of PTMCM-MOE3OM. G' and G" were higher under low

temperature conditions, although the *M*n effect was not clearly observed below 5,000 g/mol. Thermosensitive mechanisms of PTMCM-MOE3OM and PTMCE-MOE4OM were hypothesized to be the same because enthalpy changes (△H) and their dynamics were in almost the same state. The ^{1}H NMR spectra of PTMCM-MOE3OM suggested that some kind of dehydration phenomena induced aggregation behavior in aqueous media above LCST.These results show thermosensitive behaviors and bulk properties of ester free PTMC derivatives could be controlled by molecular weight and the side chain length for applications.

4. Experimental Section

4.1. Materials

Benzyl alcohol and 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) were purchased from Tokyo Chemical Industry (TCI), Japan. Dichloromethane (CH_2Cl_2), hexane, tetrahydrofuran (THF) and isopropanol were purchased from AZBIO CORP., Japan. Calcium hydride (CaH_2) was purchased from Nacalai Tesque Inc., Japan. Benzyl alcohol and DBU were distilled before use. Anhydrous THF and CH_2Cl_2 for monomer synthesis and purification were used and distilled with calcium hydride (CaH_2) before use. Unless otherwise mentioned, all materials were used as received without further purification.

4.2. Apparatus

^{1}H NMR spectra were measured by a JEOL JNM-ECX400 system. The interferograms were co-added 64 times and Fourier-transformed at a resolution of 4 cm^{-1}. The number average molecular weights and their distribution were measured by gel permeation chromatography. ChromNAV system (JASCO Corporation, Japan) using AS-2055 and RI-2031 was employed with PS standards at 40 °C. Two commercial columns (TSKgel SuperH3000 and TSKgel GMHXL) were connected in series and THF was used as an eluent. MALDI-TOF/MS was measured with a BRUKER auto flex II. DSC was performed using a Hitachi DSC6200 under

nitrogen flow. The samples were heated using a second heating cycle from −100 to 95 °C at a rate of 10 °C/min. UV-2600 spectrophotometry was performed using a Shimadzu S-1700 at 500 nm wavelength. LCST were determined by transmission changes by UV–Vis spectrometer at 50% transmission. Low temperature incubation was performed using a FMU-263I (FUKUSHIMA INDUSTRIES CORP., Japan). Rheometry was performed using a KNS2100 (Kinexus, Japan).

4.3. Polymerization

The monomers, TMCM-MOE3OM and TMCE-MOE4OM were synthesized as described in our previous research.[34] Obtained monomers were polymerized by typical ring-opening polymerization following previous research.[34] The standard procedure was selected for the ring-opening polymerization of TMCM-MOE3OM. In a three-necked flask, 3 g of TMCM-MOE3OM (10.3 mmol) was dissolved in about 20 mL of anhydrous CH_2Cl_2 with CaH_2 for stirring overnight. Using a cannula with a glass filter to remove CaH_2, the monomer solution was transferred to another flask with a three-way cock and the solvent CH_2Cl_2 was evaporated under reduced pressure. Then, the required amount of anhydrous CH_2Cl_2 under a nitrogen atmosphere was introduced. Into the monomer solution, 0.6 mL of benzyl alcohol (0.052 mmol) solution in CH_2Cl_2 as an initiator and 6 mL of DBU (1.3 mmol) solution in CH_2Cl_2 as a catalyst was added to start the polymerization at room temperature for 8 h. The reaction was stopped by adding a small amount of acetic acid, then the reaction mixture was poured into a large amount of hexane/2-propanol (9/1, v/v). The product was recovered by decantation and centrifugation and dried under vacuum (77% yield).

Supporting Information ((delete if not applicable))
Supporting Information is available from the Wiley Online Library or from the author.

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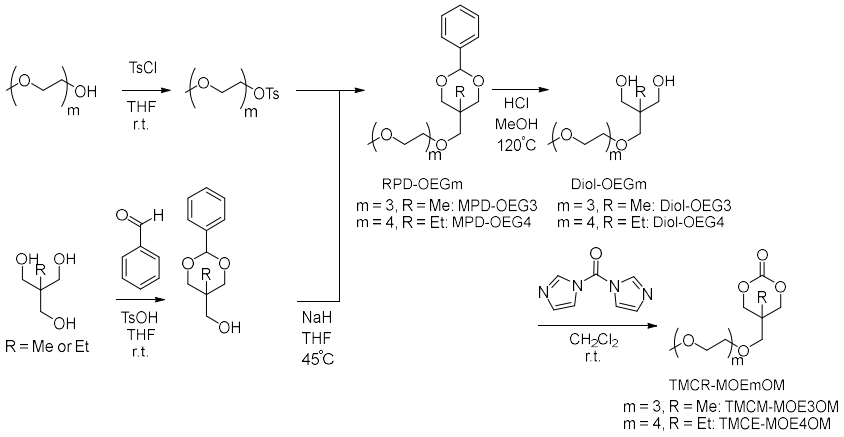
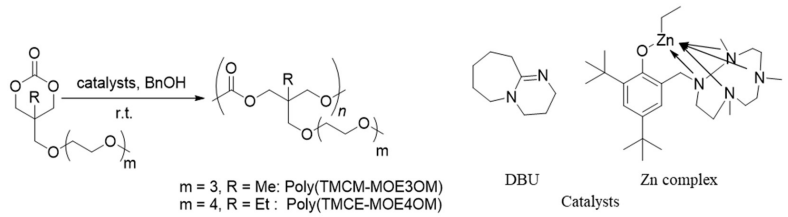


Scheme 1. Synthesis of trimethylene carbonate derivatives.



Scheme 2. Synthesis of poly(TMCR-MOEmOM).

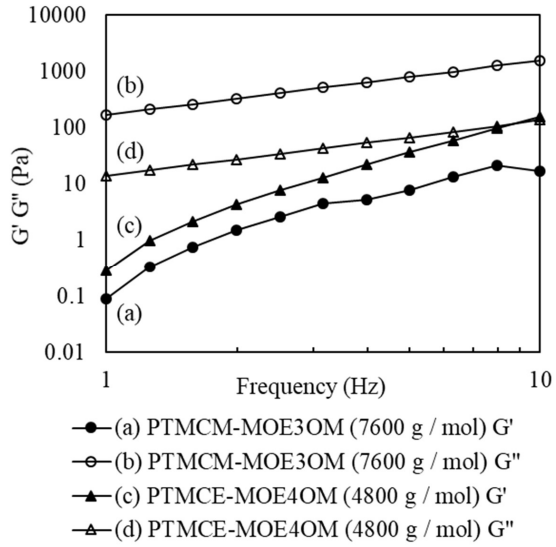


Figure 1. The analysis data of rheometer measurement of PTMCM-MOE3OM and PTMCE-MOE4OM. The viscoelastic character *vs* frequency storage modulus (a) and loss modulus (b) of PTMCM-MOE3OM and storage modulus (c) and loss modulus (d) of PTMCE-MOE4OM at 25 ℃.

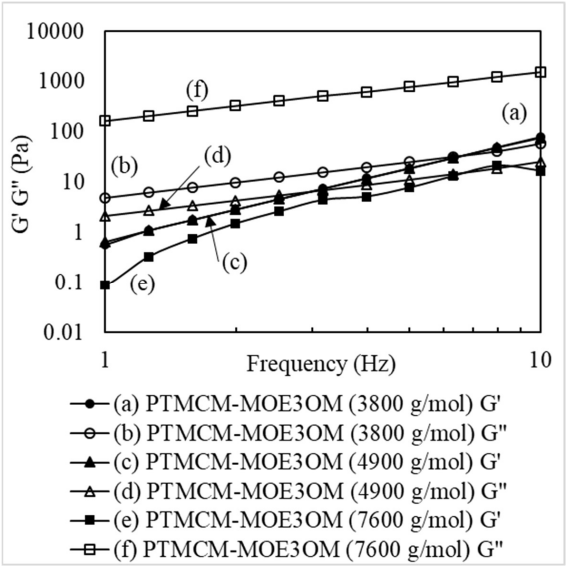


Figure 2. The viscoelastic character of PTMCM-MOE3OM *vs* frequency in each molecular weight. (a) Storage modulus of 3800 g/mol, (b) loss modulus of 3800 g/mol, (c) storage modulus of 4900 g/mol, (d) loss modulus of 4900 g/mol, (e) storage modulus of 7600 g/mol, and (f) loss modulus of 7600 g/mol.

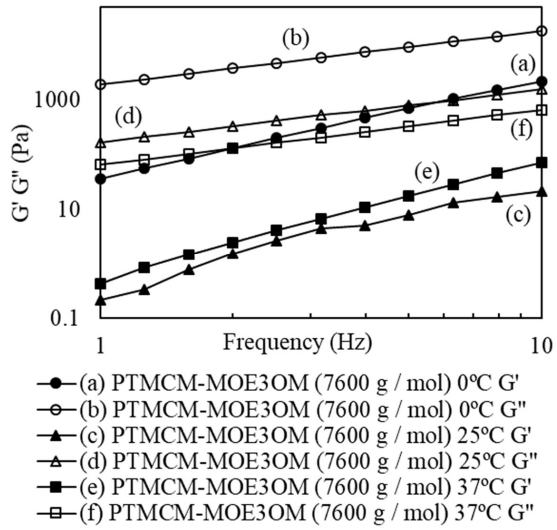


Figure 3. The viscoelastic character of PTMCM-MOE3OM *vs* frequency in each temperature. (a) Storage modulus at 0 ℃, (b) loss modulus at 0 ℃, (c) storage modulus at 25 ℃, (d) loss modulus at 25 ℃, (e) storage modulus at 37 ℃, and (f) loss modulus at 37 ℃.

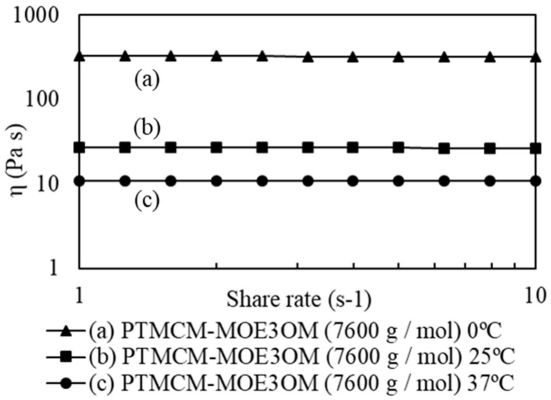


Figure 4. The viscosity character of PTMCM-MOE3OM *vs* shere rate at 0 ℃ (a), 25 ℃ (b), and 37 ℃ (c).

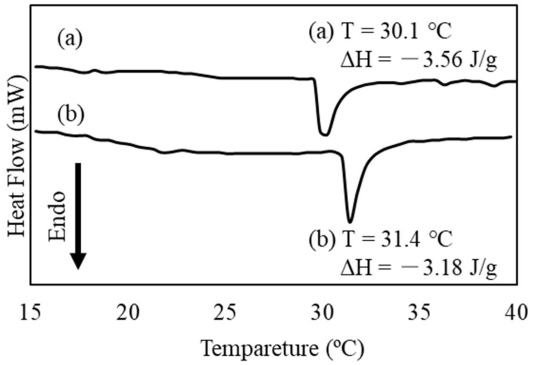


Figure 5. The analysis data of thermosensitive properties of PTMCM-MOE3OM and PTMCE-MOE4OM. DSC curves of PTMCM-MOE3OM (a) and PTMCE-MOE4OM (b) solutions in water at 0.5 mg/mL during second heating (heating rate 2.0 ℃/min).

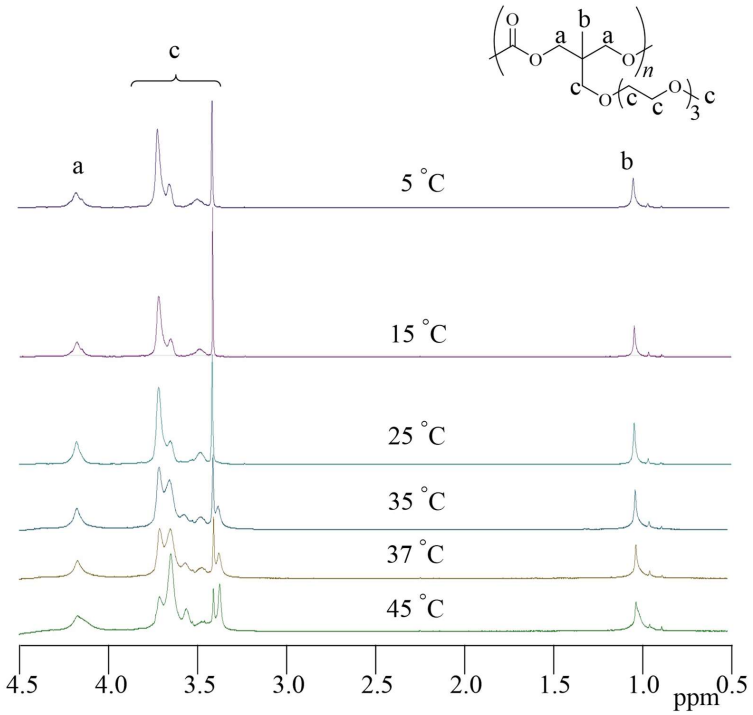


Figure 6. The analysis data of thermosensitive properties of PTMCM-MOE3OM. ^{1}H NMR spectrum at thermosensitive of PTMCM-MOE3OM in D_2O by variable temperature measurement.

Short summary

Thermosensitive PTMC derivatives bearing oligo(ethylene glycol) units were synthesized by ring-opening polymerization for the development of low-toxicity and thermosensitive soft materials. Thermosensitive viscosity and properties of these polymers were observed, which provide an important road map for the development of thermosensitive soft materials using ester free PTMC derivatives by controlling the thermosensitive behaviors and bulk properties.

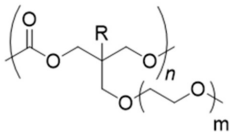
Table 2-2-1. Polymerization of TMCM-MOE3OM and TMCE-MOE4OM by using various catalysts.

Entry	Monomer	Catalyst	M/I	M/C	Yield[b]	M_n($\times 10^3$ g/mol)[c]	PDI[c]
1	TMCM-MOE3OM	DBU	200[a]	10	77	7.6	1.7
2	TMCE-MOE4OM	DBU	200[a]	10	50	4.8	1.4
3	TMCM-MOE3OM	Zn complex	100[a]	500	39	4.9	1.5
4	TMCM-MOE3OM	Zn complex	50[a]	50	64	3.8	1.6

[a]Initiator = benzyl alcohol (CH_2Cl_2 = 1.0 M). [b]Hexane : 2-propanol = 9 : 1 (v : v) insoluble part. [c]Determined by SEC by polystyrene (PS) standard in THF.

コメントの追加 [o1]: Figure 3 では、4900 となっていますが？
5000 出会っていますか？

Viscosity Evaluation as Thermosensitive Polymers



m = 3, R = Me
m = 4, R = Et