Characterization of Star-shaped marcomole-cules with calix[8]arene core by Differential Scanning Calorimetry (DSC)

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This thesis was written to analysis thermal behavior of oligomer and their star-shaped macromolecules by Differential Scanning Calorimetry (DSC) and Polarized Optical Microscope (POM) methods. The thermal properties of these substances were detected by glass transition, endotherm or exotherm peaks. Amphiphilic oligomer, brij 58, and its star-shaped block copolymer showed glass transition at very low temperature and crystalline peak in heat flux curves. On the other hand, thermo-responsive oligomer, 2-isopropyl-2-oxazoline-$(CH_2)_{10}COOC_2H_5$, and its copolymer behaved as amorphous macromolecule which just displayed glass transition in DSC experimental curves. Then, all substances were observed by POM associated with a hot-stage component to detect crystalline in the studied substance.

This thesis was conducted at Laboratory of Polymer Chemistry of Department of Chemistry, University of Helsinki as a project work.

Keywords:	Differential scanning calorimetry, polarized optical microscope, crystalline, amphiphilic, thermo-responsive, glass transition, endotherm, exotherm.
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Glossary

Tg: Glass transition temperature

Tm: Melting temperature

DSC: Differential scanning calorimetry

SEC: Size exclusive chromaphy

NMR: Nuclear magnetic resonance

IsoPrOx: 2-isopropyl-2-oxazoline

LCTS: Lower critical solution temperature

PP: Polypropylene

POM: Polarized optical microscope

1 INTRODUCTION

1.1 Background

Differential scanning calorimetry is a technique which combines the ease of measurement of heating and cooling curves with the quantitative features of caloreimetry. The fundamentals of the method were first explored in the early 1960s in Perkin-Elemer calorimeters [11]. Recently, many articles related to DSC have been published. Together with X-ray diffraction, DSC has become the principal methods of studying and controlling the state of polymeric materials.

DSC is an analysis method that combines traditional equilibrium calorimetry with the dynamic analysis of thermal processes. Hence, DSC offers possibilities to determine both thermodynamic parameters of substances, i.e. heat capacity, its changes, temperature, enthalpy, entropy of phase transitions, and the kinetic characteristic of processes and relaxation transition under linear temperature change.

The macromolecules studied are star-shape block copolymers with calixarene core and eight block copolymer arms. The [1_n]metacyclophanes are known as calixarene exhibit unique properties in host-guest complex chemistry. In molecular scale, the conformation forms internal cavities of different size by a belt of phenyl ring. These cavities have the ability to accommodate guest molecules of a certain size. This feature helps calixarene to be considered in molecular recognition application [4]. On the other hand, due to the trend to form micelles with narrow molecular weight distribution, calixarene is a substance under intensive research in drug delivery.

The synthesized copolymers were prepared by Prof. A.V. Tenkovtsev's research group at the Institute of Macromolecular Compounds of Russian Academy of Science in Russia. Star-shaped macromolecules with calixarene core synthesized to neutral amphiphilic block copolymer arms, i.e. brij 58 and thermo-responsive poly(2-isopropyl-2-oxazoline) arms were two of the studied substances.

1.2 Statement of objective

The objective of this thesis is to characterizing thermal behavior of studied polymers. The experiments were conducted by Differential scanning calorimetry (Mettler Toledo DSC 822). The glass transition temperatures, melting point, enthalpy at phase transition are the main studied objectives.

1.3 Scopes and limitations

The DSC results are necessary values in order to be aware of thermal behavior of oligomer arms as well as star-shaped copolymers. The physical, mechanical properties of macromolecules are influenced by thermal condition and thermal history.

The limitation of this thesis is studying method just only focused on DSC, excluding other analysis methods such as NMR, TGA, etc.

2 LITERATURE REVIEW

2.1 Definition of terms

2.1.1 Glass transition temperature, T_g

Glass transition temperature, T_g, is temperature point where below it, materials behave like glassy material, hard and brittle, polymer chains are frozen. Above T_g, the amorphous segment of polymer chain network start to vibrate at certain degree, materials exhibit rubbery properties.

2.1.2 Melting point, T_m

The melting temperature, T_m, derived from crystalline segment in polymer network. When sample's temperature reach to T_m, small crystalline segment start to melt first, then as temperature increasing more, larger segment melt until largest one.

The melting temperature is characterized by the top of endotherm peak of experimental DSC curve. As observed polymer's temperature reach to melting point, the small crystals start to melt by absorbing thermal energy. Next, larger to largest crystals were also melting when thermal energy absorption grows up. This process was detected by heat flux curve drop down to forming endotherm peak. On the other hand, the crystal creation is an exothermic process which release energy from investigated system.

2.1.3 Enthalpy change, ΔH; maximum enthalpy change, ΔH_m^0

Enthalpy change, ΔH, is the change of energy transfer between investigated system and surrounding environment. If the system releases energy, it's called exothermic process. And if the system absorbs energy, it is called endothermic process. In DSC, the enthalpy is determined by the area of endotherm peaks or exothermic peaks.

Maximum enthalpy change, ΔH_m^0, is the maximum energy transfer of a specified pure crystal material which the crystallinity degree reaches to maximum point.

2.1.4 Surfactant

A substance is called surfactant when it contains both hydrophilic (aqueous soluble) and hydrophobic groups (oil soluble), i.e. amphiphilic, in its molecular structure. In aqueous solution, surfactants tend to create micelles, colloid in which hydrophobic groups form inner core and hydrophilic groups form outer layer. The micelles structure forms oppositely in inorganic solution.

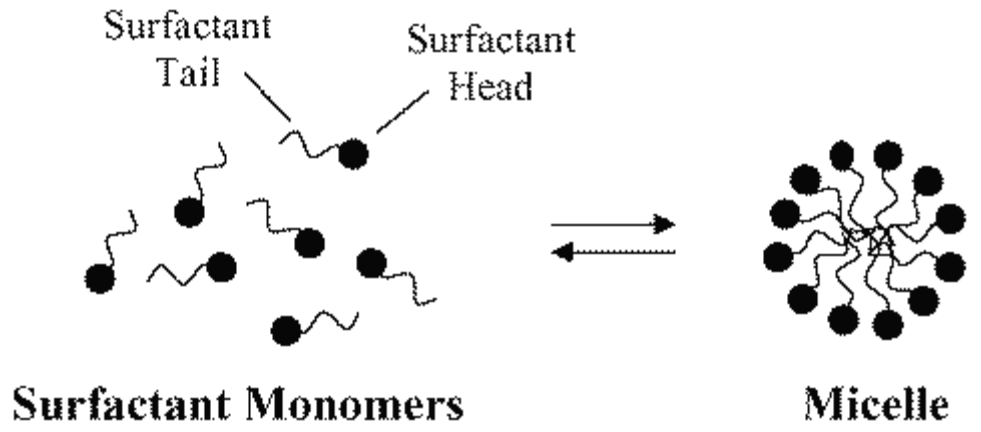


*Figure 1Micelles structure [**Carlota Oliveira Rangel-Yagui[1], Adalberto Pessoa Junior, Leoberto Costa Tavares**]*

2.1.5 Amorphous, crystalline, degree of crystallinity

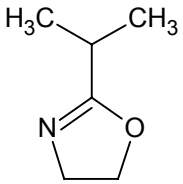
Solid macromolecules consist of two ordinary regions, crystals and amorphous region. In crystalline, polymer chains arrange in one direction. On the other hand, in amorphous regions, polymer chains are organized randomly. In practical, there are no 100% crystalline polymeric materials; most of them are semi-crystalline polymers.

The ratio of ΔH and ΔHm^0 determine the crystallinity degree (χ_{DSC}) of the investigated sample.

$$\chi \mathrm{DSC} = \left(\frac{\mathbf{\Delta Hm}}{\mathbf{\Delta H_m^0}}\right) * \mathbf{100}\%$$

2.1.6 Thermo-responsive polymer, poly(2-propyl-2-oxazoline)

Poly(2-isopropyl-2-oxazoline) is one of common thermo-responsive polymer. In aqueous solution, if the temperature below the LCST (~40 ^{0}C), the amide group of this polymer are dramatically hydrated resulting in macromolecules turn out to be hydrophilic. Above the LCST, the degree of hydration declines and intermolecular hydrogen forms a bond between amide fragments. The macromolecules transform to globular conformation resulting in hydrophobic and precipitate in aqueous solution [7].



2.2 Differential Scanning Calorimetry

2.2.1 DSC principles

DSC belongs to physical and physcico-chemical methods of thermal analysis which are used to detecting thermal energy (enthalpy) changes in observed substances. Primarily, thermometry (temperature measuring method) includes differential thermal analysis (DTA).

DTA's principle is measuring the temperature difference between studied substance and reference sample during transition phase. The studied substance and reference are supplied with the same amount of thermal energy from heater and the temperature is recorded by thermal e.m.f of a thermocouple contacting the sample at one point. This is a weakness of DTA, and can be eliminated by accurate calorimetric measurement.

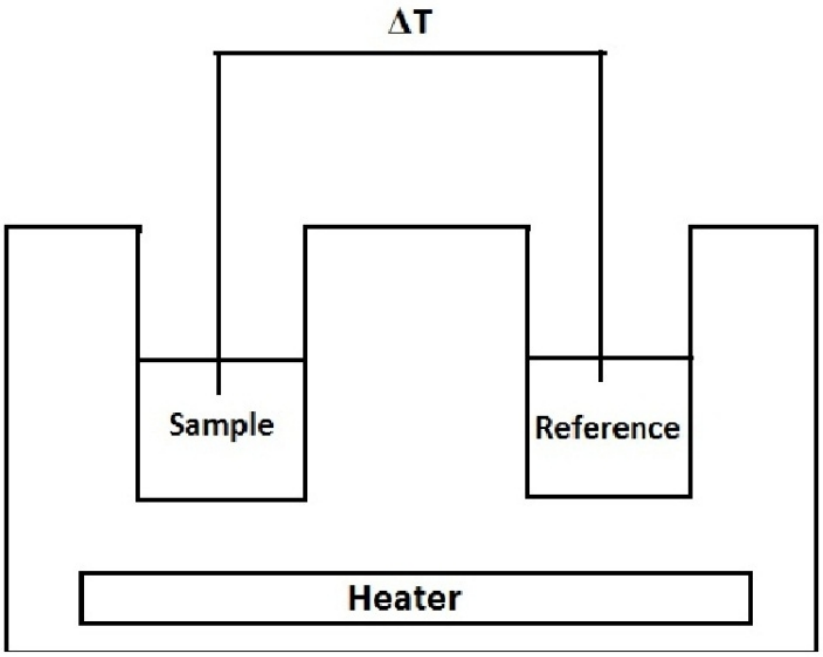


Figure 2 Diagrammatic view of calorimeter chambers in DTA

DSC is based on heating and, cooling one sample and one reference at a certain rate and measuring the compensating heat flux that keep the temperature of both substances the same. To keep the same temperature of sample and reference, two individual heaters are used to supply heat.

The experimental DSC curve shows the heat flux (mJ/s) or specific heat capacity Cp (J/gK) versus temperature. The compensating heat flux between the sample and the reference is directly proportional to the change in the internal energy (enthalpy). Consequently, when determining the internal energy, there is no need to convert recorded data by mathematic models as in quantitative DTA.

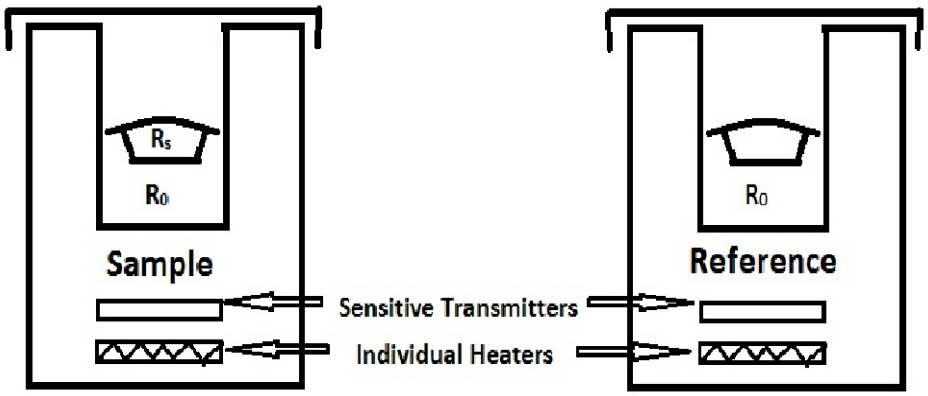


Figure 3 Diagrammatic view of calorimeter chambers in DSC

In both DTA and DSC, thermal resistance R includes R_s and R_0 component. Rs is thermal resistance detected by the sample itself and is influenced by thermal contact of the surface of the sample with its capsule (holder), i.e. the shape of the sample, and how it is manipulated and pressed into the capsule.

$$R = R_o + R_s$$

2.2.2 Component

Mainly, Mettler Toledo DSC 822 machine includes liquid nitrogen tanks, automatic furnace, and robot sample. DSC is controlled by an installed program,

DSC experiment is a series of heating and cooling processes in which electrical resistors respond to heating; and nitrogen liquid to cooling. To keep the temperature precisely following the programmed temperature rate, cooling work is conducted by two separate nitrogen liquid tanks. One main nitrogen tank may be refilled after several experiment runs. The other one just provides a small amount of nitrogen liquid when temperature almost reaches to ending temperature. This tank may be refilled only by an authorized person annually.

The function of a sample robot is to take the capsule from a sample dish to the furnace with reasonable force in the attempt to avoid over-force applying which may deform the capsule.

One essential accessory of DSC is a capsule press. The capsules include an aluminium pan and a cap which must be sealed together.

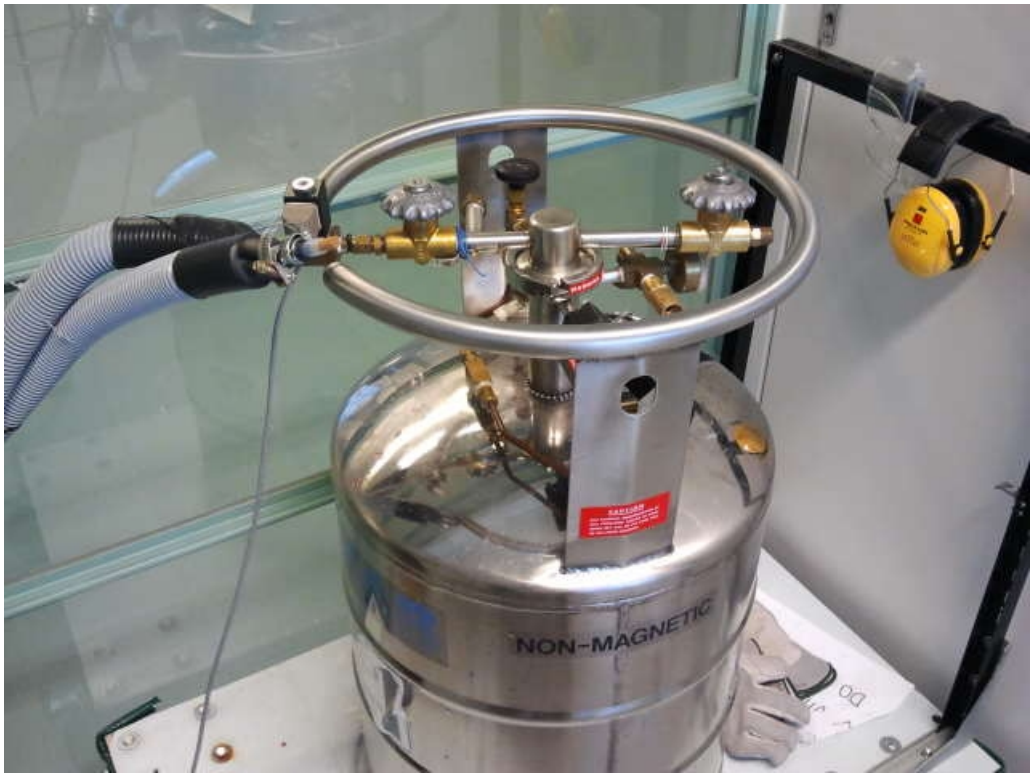


Figure 4 Nitrogen liquid tank

Figure 5 Capsule press and milligram scale.

Figure 6 Automatic furnace

Figure 7 Automatic Robot hand and samples dish.

2.2.3 Calibration

Calibration is an essential requirement for every thermal analytical study. Calibration is the establishment of a defined relationship between a value of a quantity indicated by measuring instrument and the true value (E. Gmelin, St.M. Sarge). Indium is the most common calibration substance in DSC due to its well identified heat of fusion and melting point.

2.3 Techniques

2.3.1 Blank curve subtraction

In practical, it is not possible to obtain perfect zero-line heat flux curve even between empty sample system and empty reference system over entire temperature range. To obtain the real heat flow rate into the sample, the blank curve is essentially subtracted

from the actually measured curve. Initially, the blank curve is detected by two empty capsules at reference and sample positions.

Each experimental method has a specific temperature range, cycle, rate which makes its blank curve become unique. Hence, when changing to a new experimental method, new blank curve must be determined.

2.3.2 Temperature rate

Obviously, temperature rate influences experimental DSC curves. At low rate, the studied substance has more time to re-arrange network structure which may alter initial state of substance, resulting in high crystallization degree. On the other hand, accurate results might be achieved at high temperature rate, however if thermal conducting coefficient of studied substance was high, unequal temperature at different layers could affect final results.

2.3.3 Sample weight

Normally the sample's weight for DSC varies from 2 mg to 4 mg. If the sample was too little, less than 1mg, the enthalpy change would also be very small, it's difficult for DSC detect. On the other hand, too much sample is neither good due to thermal gradient. The temperature is not homogenous at every point, the deepest point where contact to pan is hotter than others. If the sample has high thermal resistance, it takes more time to transfer heat from outer surface to inner area.

2.3.4 Self-nucleation

The crystals rise up from pre-existing nuclei, left over by the prior small crystals in prior, incomplete melting or dissolution is called self-nucleation (B. Wunderlich, et al). In self-nucleation, crystallinity degree increase due to more amorphous chains involving in nucleation process.

For instance, Polypropylene (PP) is measured by two different methods to study thermal history effect of polymeric materials. In first measurement method, PP is heated over melting temperature without any interruption, the crystallinity from 32.35% to 38.25%.

However, at the same heating rate of 10 ^{0}C/min, the second method with interruption at 160^{0}C obtains a significantly higher degree of crystallinity, i.e. 49.23%. PP is heated to 160^{0}C, then cooled down to room temperature before heated up again over melting point.

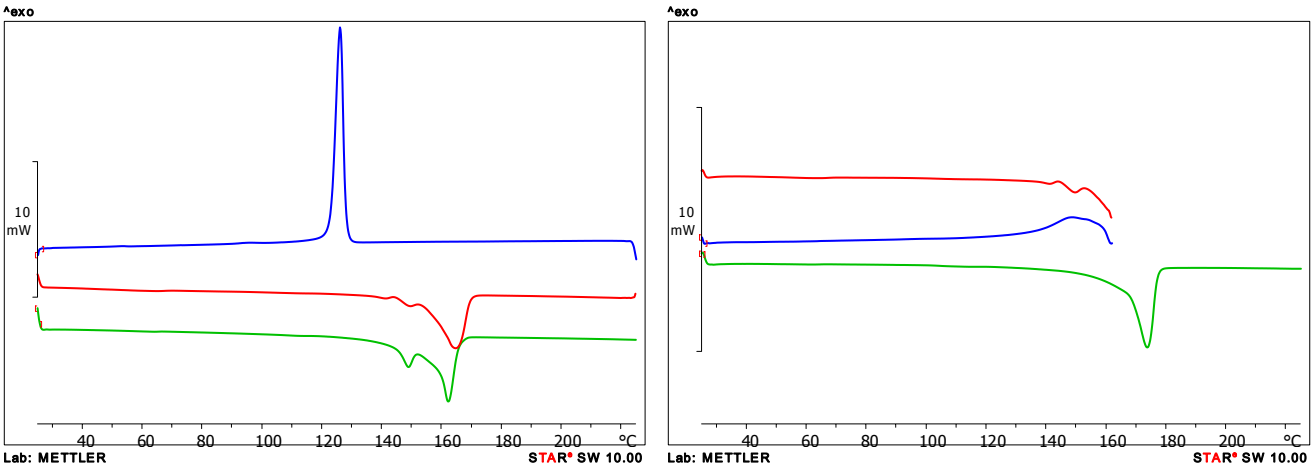


Figure 8 DSC curves of Polypropylene. With self-nucleation effect (right). Without self-nucleation effect (left)

3 Method

3.1 Materials

3.1.1 Brij 58 and Brij 58 star-shaped polymer.

Brij 58 is a trademark name of polyoxyethylene-20-cetyl-ether, a non-ionic surfactant which is commonly used in biochemical applications. In brij 58 molecular structure, there are both water soluble (polyoxyethylene) and organic soluble (alkyl chain) segments.

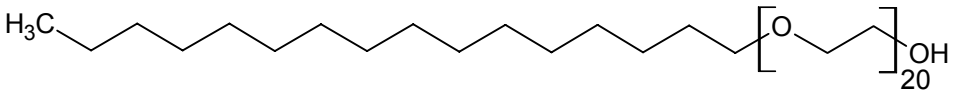


Figure 9 Brij 58 molecular structure

The following synthesis process was presented by A.V Tenkovtsev, et al [***]

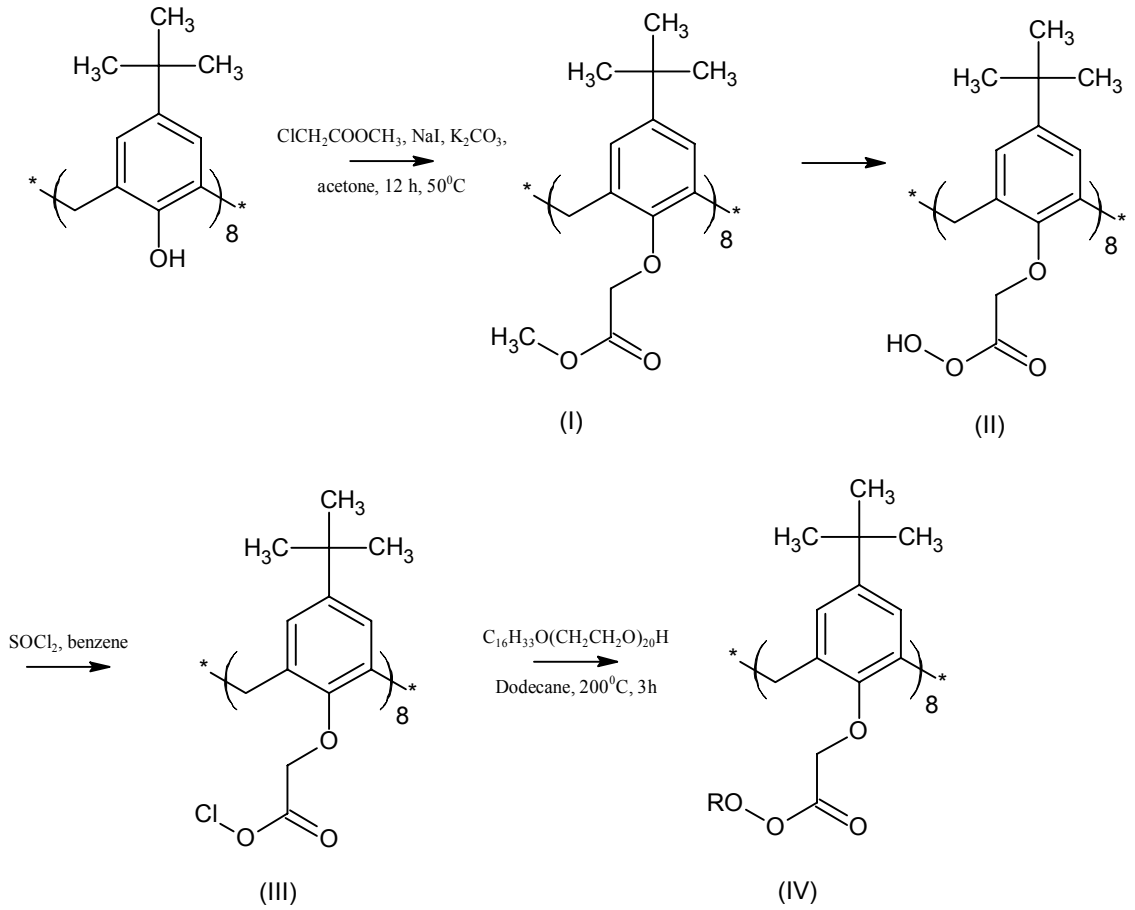


Figure 10 the synthetic route to star-shape block copolymer with brij 58 arms

5,11,17,23,35,41,47-Octa-tert-butyl-9,50,51,52,53,54,55,56-octakis(carbomethoxy)calix[8]arene octamethyl ester (I)

A mixture of dried sodium iodide (3 g, 20 mmol) and methyl chloroacetate (2 g, 18 mmol) in 50 ml of dry acetone was stirred for 20 min, and then NaCl was filtered off. A suspension of potassium carbonate (5 g, 36 mmol) and octa-tert-butylcalix[8]arene (1.3 g, 1 mmol) in 100 ml of acetone solvent was added to stirred filtrate. Whole mixture was heated up for 6 hour and was recrystallized from ethanol.

5,11,17,23,29,35,41,47-OCta-tert-butyl-9,50,51,52,53,54,55,56-octakis(carboxymethoxy)calix[8]arene (II)

A 30 ml of 5% NaOH (ethanol/water 1/1 v/v solution) and 0.9 g (0.48 mmol) of (I) was boiled for 2 hour. The precipitate formed was filtered off, dried, and recrystallized by methanol.

5,11,17,23,29,35,41,47-OCta-tert-butyl-9,50,51,52,53,54,55,56-octakis(chlorocarbonloxymethoxy)calix[8]arene (III)

A suspension of (II) (0.42 g, 0.24 mmol), $SOCl_2$ (5 ml) and bezene (20 ml) was stirred under reflux for 2 hour. And then the suspension was dried and recrystallized by hexane.

5,11,17,23,29,35,41,47-OCta-tert-butyl-9,50,51,52,53,54,55,56-octakis(carboxymethoxy)calix[8]arene octa(eicosaethylene glycol hexadecyl ether) ester (IV)

A solution of α-cetyl-ω-hydroxyoligoethylene oxide (Mw=1000 g/mol, Brij 58) and (III) (0.27 g, 0.14 mmol) in 2 ml of dodecane was heated at 180 ^{o}C during 2 h under argon atmosphere. Methylene chloride (1 ml) and hexane (50 ml) were used to recrystallize solution.

3.1.2 Thermo-responsive oligomner 2-isopropyl-2-oxazoline and its star-shaped polymer.

The thermo-responsive oligomer and its polymer were synthesized by A.V. Tenkovtsev, et al. The synthesis processes was published at Polymer Science in 2011.

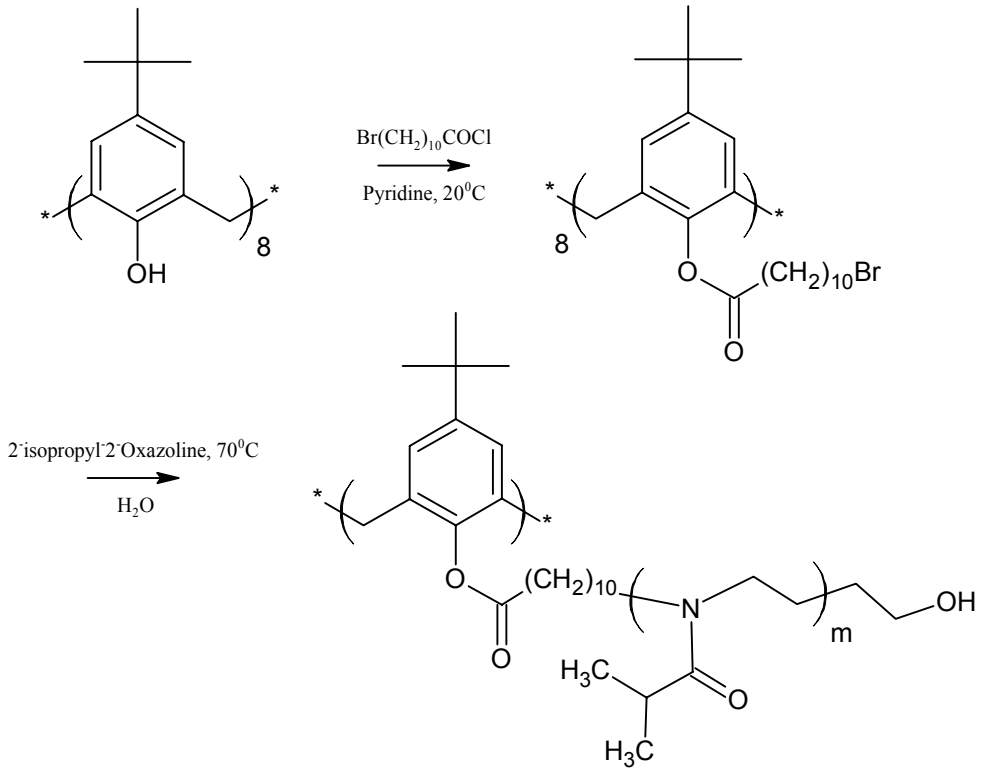


Figure 11 the synthetic route to star-shape block copolymer with thermo-reponsive oligomer arms

A solution of octa-tert-butylcalix[8]arene (1 g, 0.77 mmol) and anhydrous pyridine (1 mL) was prepared and cooled to 0 ^{0}C. A solution of ω-bromoalkanoic chloride(3.5 g) was adder under intense stirring. After 3 three day staying at room temperature, the mixture was washed with 0.1 M hydrochloric acid, a saturated solution of sodium bicarbonate, and water. The precipitated layer was dyried under vacuum condition and magnesium sulfate.

Polymerization of 2-isopropyl-2-oxazoline initiated by octa-ter-butylcalix[8]arene octa(11-bromoindecanoate)

A desired amount of initiator and mixture of 2-isopropyl-2-oxazoline and octa-ter-butylcalix[8]arene octa(11-bromoindecanoate) was frozen to -196 ^{0}C in an ampoule in an atmosphere of argon. And then, the ampoule was sealed and heated at 70 ^{0}C for a certain time. After heating period, aqueous ethanol (1 ML, 50 %) was added to ampoule and stay at room temperature for 24 hour. The solvent and the unreacted monomer were removed by heating (100 ^{0}C) in vacuum. Last, the polymer was dissolved in water, dialyzed against water for 24 hour, and lyophilized.

3.2 Experimental

A tiny amount of observed sample, 2-4 milligrams, was weighted by milligram scale. Tolerance was to be accurate up to 0.01 milligram. Then the capsule was sealed by sample press, and placed on a sample dish. One empty capsule also was prepared to measure the blank curve.

Before preparing sample capsules, the liquid nitrogen tank had to be filled to ensure that there was enough liquid nitrogen during the whole measurement.

The sample capsules were put into a furnace automatically by a robot hand. The measurement was started when initial temperature had been reached. Usually, the initial temperature is set at room temperature.

As mentioned above, the temperature rate is a vital parameter which influences the DSC results. In this study, the heating rate may differ from cooling rate in order to save experimental time.

3.2.1 Brij 58

The experimental method for brij 58 and its polymers had five segments. The temperature range is from -150 ^{0}C to 50 0C with 20 ^{0}C/min or 10 ^{0}C/min rate.

Table 1 DSC method for brij 58 and its polymer

Order	Temperature range (^{0}C)	Temperature rate (^{0}C/min)
1	25 …-150	-20
2	-150…50	10
3	50…-150	-20
4	-150…50	10
5	50..25	-20

3.2.2 Thermo-responsive polymer

For thermo-responsive polymer, temperature rate remained at one certain temperature rate. If the rate changed, the studied polymers responded another way. These substances were studied under two separate methods with 10 0C/min and 20 0C/min temperature rates.

Table 2 DSC method for thermo-responsive oligomer and its polymers. Temperature rate 10 ^{0}C/min

Order	Temperature range (^{0}C)	Temperature rate (^{0}C/min)
1	25 …-50	-10
2	-50…250	10
3	250	0 (*)
4	250…-50	-10
5	-50…250	10
6	250	0 (*)
7	250…25	-10

(*) Isothermal segments, i.e. temperature remained at 250 ^{0}C for 10 min.

Table 3 DSC method for thermo-responsive oligomer and its polymers. Temperature rate 20 ^{0}C/min

Order	Temperature range (0C)	Temperature rate (0C/min)
1	25 …280	10
2	280…25	-10
3	25…280	10
4	280…25	-10

4 RESULTS AND DISCUSSION

4.1 Brij 58

Brij 58 was purchased from Sigma-Aldrich, has homogeneous length with narrow molecular weight distribution, polymer dispersion (PD), 1.087. According to *Fig. 12*, glass transition temperature was observed at -137 ^{0}C in the second heating run.

The first and second heating-cooling cycle gave quite similar heat flux curves, hence the second cycle was chosen to analyse. From 37 ^{0}C, sample absorbed heat to melt crystal regions, experimental DSC curve create endotherm melting peak. The area of melting peak determines directly the enthalpy of melting of the polymer, ΔH_m, i.e. 147 J/g.

In cooling turn, a clear exothermal peak formed at 23 ^{0}C with correlative enthalpy released, 150 J/g. The polymer sample release heat energy to form crystal regions.

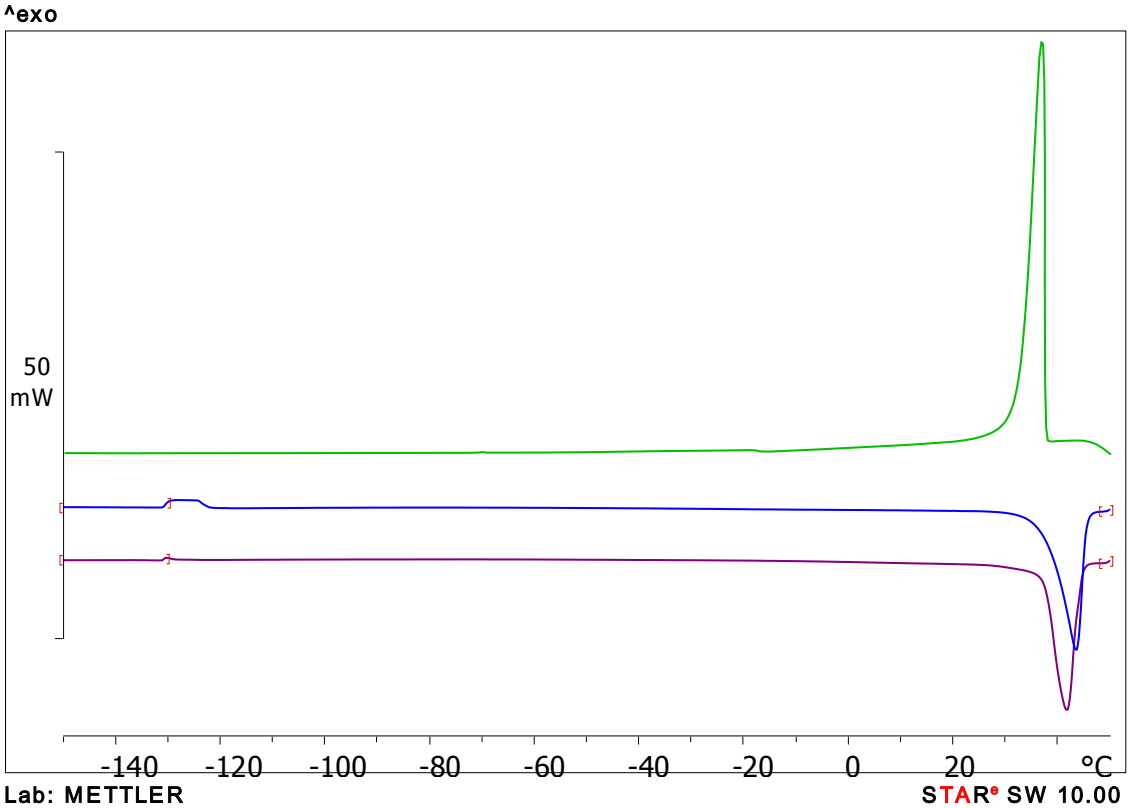


Figure 12 DSC curves of brij 58. Cooling curve (top), first heating curve (middle), second heating curve (bottom).

4.2 Brij 58 star-shaped polymer

The synthesized Brij 58 star-shaped polymer displayed multi-melting peaks in the first cycle. The multiplicity of endotherm melting peaks could be caused by various reasons. For instance, reorganization of metastable crystals from folded chains; recrystallization of folded chain crystals; phase transition in solid polymers preceding melting; melting and isotropization of liquid-crystalline polymers; the appearance of inter- and intermolecular melting steps in a highly oriented polymer, etc[11]. However, there are two remarkable possibilities, the presence of crystal with two or more sizes, and the presence of crystal varying in structure in polymer.

Star-shaped polymerization was a complex process with many reactions and purification steps resulting in several average molecular weights of synthesized polymers. According to SEC results, there were two major molar mass peaks, one had Mw 10 049 g/mol, another had 1 899 g/mol. Those with different molar mass formed different size crystal leading to multiplicity in observed DSC curves.

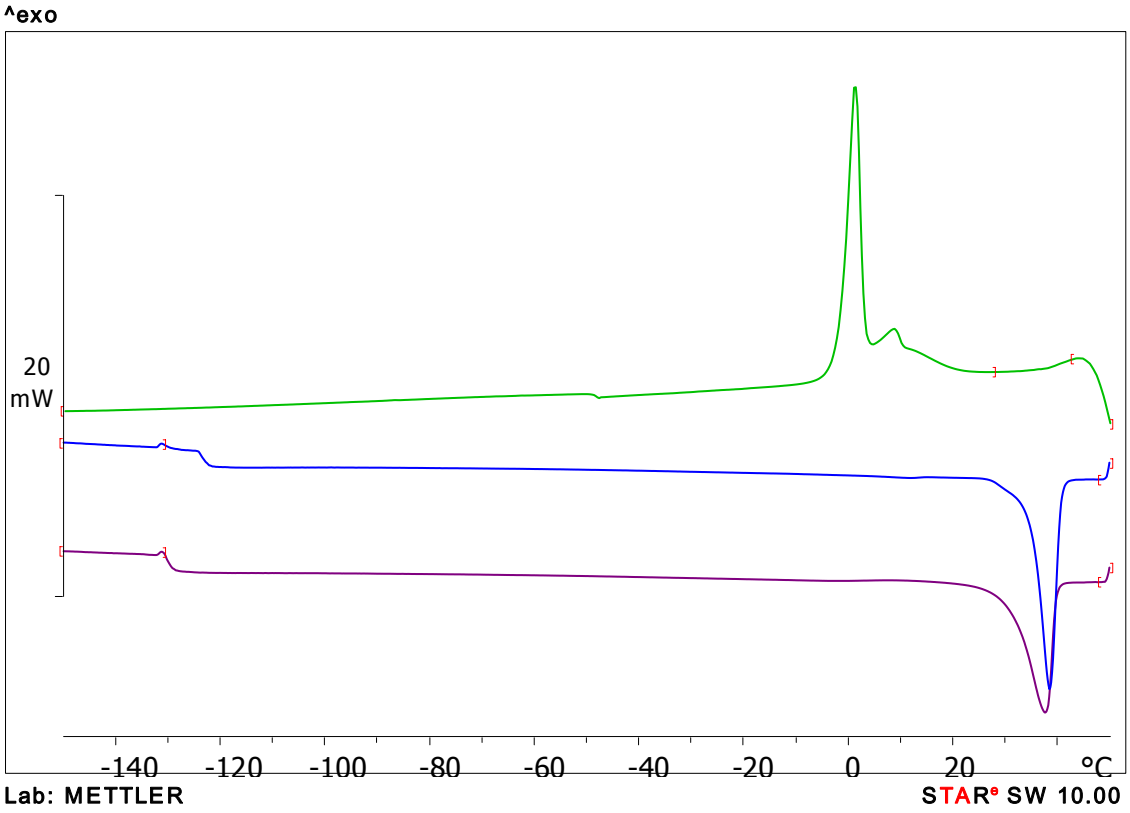


Figure 13 DSC curves of star-shape block copolymer with calixaren core and Brij 58 arms. Cooling curve (top), first heating curve (middle), second heating curve (bottom).

The glass transition of star-shaped copolymer was also determined at very low temperature, i.e. -136 ^{0}C, as same as polymer arms. The melting point was similar to brij 58, 36 ^{0}C. Nevertheless, the enthalpy of star-shape polymer (83 J/g) was much smaller than arm polymer, brij 58, (147 J/g). The star-shaped molecular structure may influence crystallinity of brij 58, prevent brij 58 to form crystals. The arms were grown up from calixarene core, hence arms were not able to orientate in one direction to form crystals.

4.3 Oligomer 2-isopropyl-2-oxazoline-$(CH_2)_{10}COOC_2H_5$

Obviously, thermal history, also called prehistory, of oligomer sample influenced the first experimental cycle curve. The glass transition was not detected well in the first cycle.

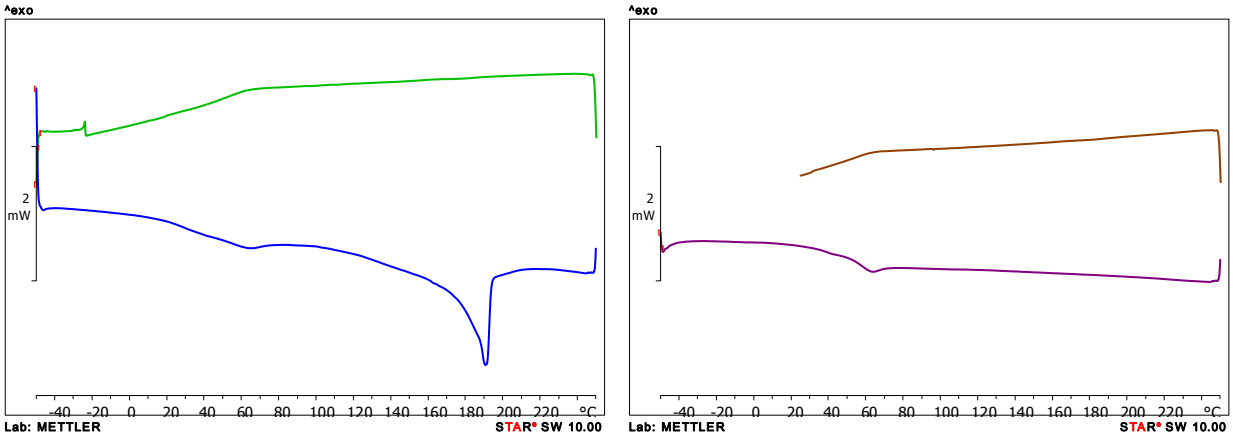


Figure 14 DSC curves of thermo-responsive oligomer. Temperature rate 10 0C/min. First cycle run (left). Second cycle run (right)

A remarkable difference between the first and second cycle was endotherm peak appeared only on the first heating segment. The endotherm peak may correspond to crystal melting or polymer degradation. In case of degradation, the glass transition was supported to disappear from the second heating cycle, since the material was already "burned off". However, glass transition temperature was clearly determined at 56 ^{0}C. Thus endotherm peak could only represent for residual degradation. Some residuals may remain in product after synthesis processes.

On the other hand, endotherm peak may be raised by crystal melting, and was irreversible. The crystals were formed in synthesis processes as crystal melted by heat, they cannot be recrystallized again. In POM's observation, there was no crystalline in both oligomer and polymer at room temperature (Appendix).

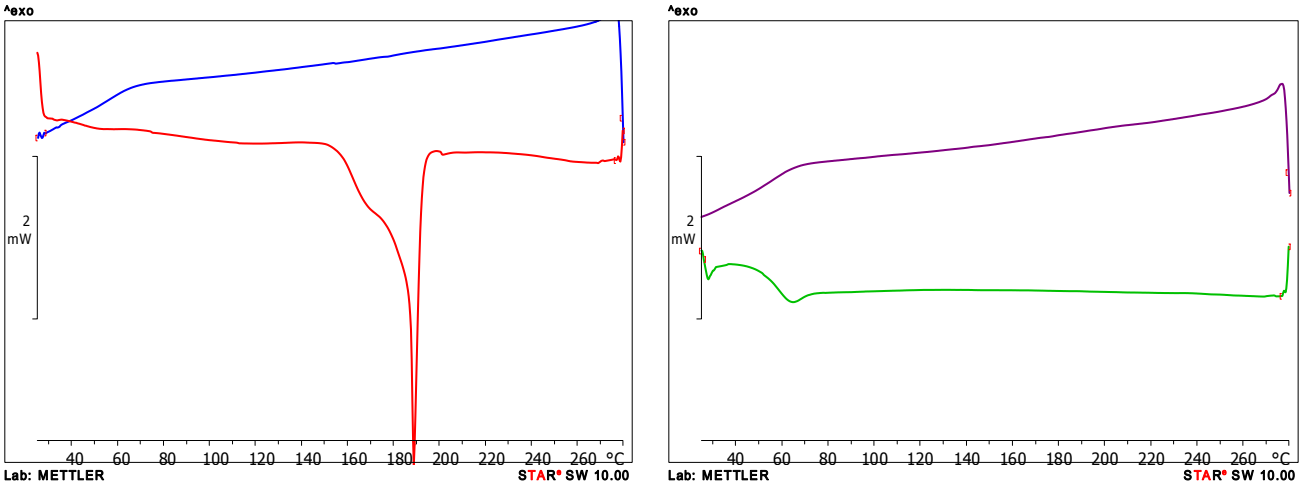


Figure 15 DSC curves of oligomer 2-isopropyl-2-oxazoline-(CH2)10COOC2H5. Temperature rate at 20 0C/min. First cycle run (left). Second cycle run (right)

The phenomenon of reversible glass transition and irreversible recrystallization were repeated in heating rate of 20 ^{0}C experiment.

4.4 Thermo-responsive star-shaped block copolymer

Star-shaped copolymer with thermo-responsive arms gave a similar glass transition temperature, 58 ^{0}C, 60 ^{0}C for 10 ^{0}C/min and 20 ^{0}C/min heating rate, respectively. However, during the first heating run, endotherm peak was not seen.

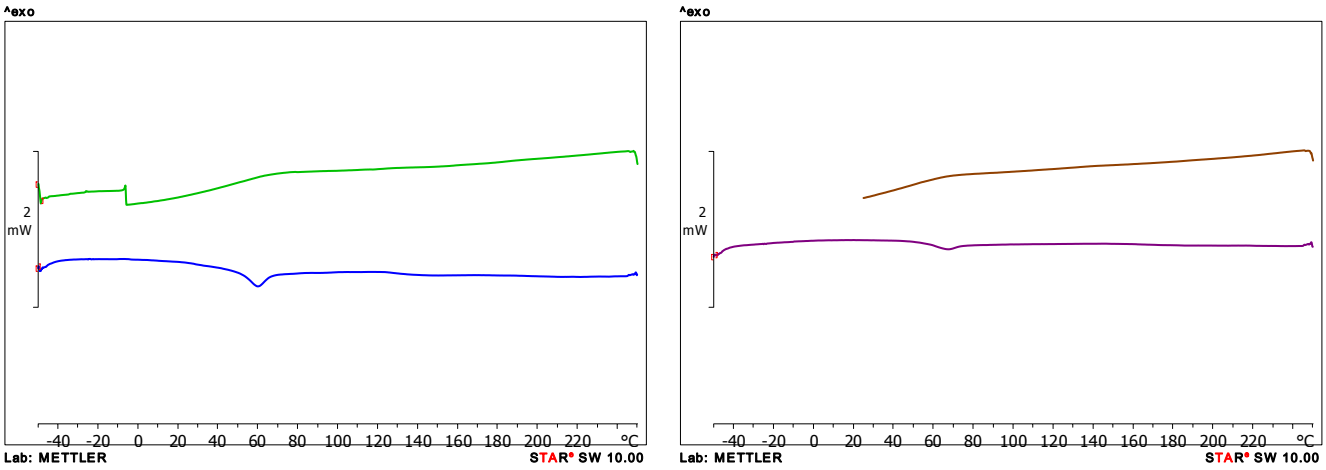


Figure 16 DSC curves of thermo-responsive star-shaped block copolymer. Temperature rate at 10 0C/min. First cycle run (left). Second cycle run (right)

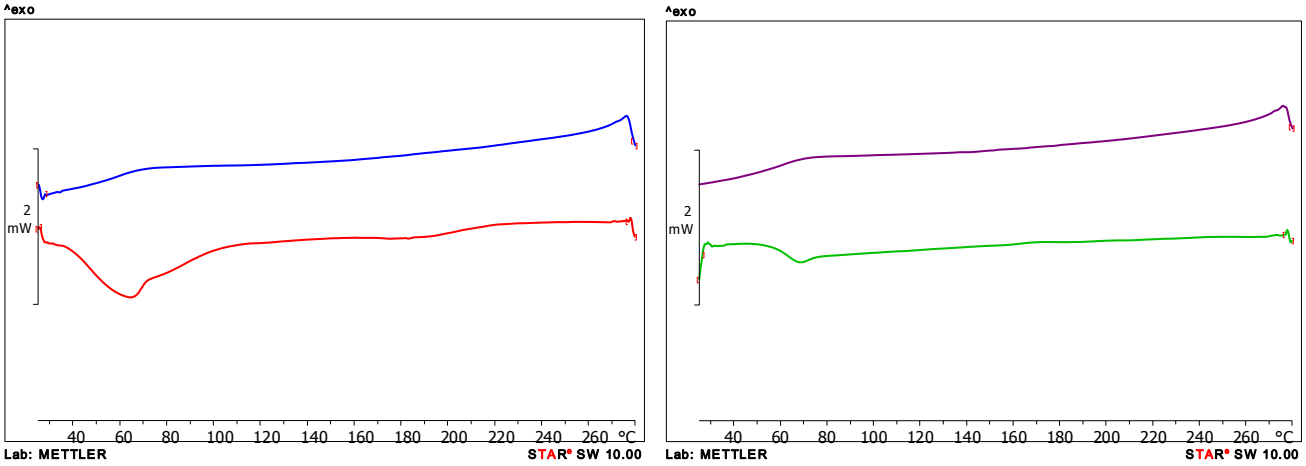


Figure 17 DSC curves of thermo-responsive star-shaped block copolymer. Temperature rate at 20 0C/min. First cycle run (left). Second cycle run (right)

5 CONCLUSION

Each of the studied substances gave different thermal behaviors when they were measured by DSC. Their nature were the primary factors that shaped the results, followed by experimental parameters such as temperature rate, sample weight, sample form, and thermal history, etc.

Generally, all substances show repeated DSC results at different temperature rates. Brij 58 oligomer and its polymer are semi-crystalline material which showed glass transition and endotherm peak in DSC curves. Thermo-responsive oligomer was quite special when it showed endotherm peak at the first heating run. However, the similar glass transition temperatures were determined in both oligomer and polymer.

To understand fully the behaviour of these substances, further analysis method must be conducted. For instance, Nuclear magnetic resonance is a powerful method to study molecular structure in order to detect residuals in the samples.

APPENDIX

Polarized optical microscope (POM)

Polarized optical microscope is designed to observe specimens that are visible primarily due to their optically anisotropic property. As illustrated in Figure 18, incident light from source comes through the first polarizer which transforms incident light to one plane polarized light. Since polarized light passes through birefringent specimen, two individual wave components (ordinary and extraordinary rays) are separately polarized in mutually perpendicular planes, are produced. Then the light components are recombined with constructive and destructive interference when they pass through the analyser.

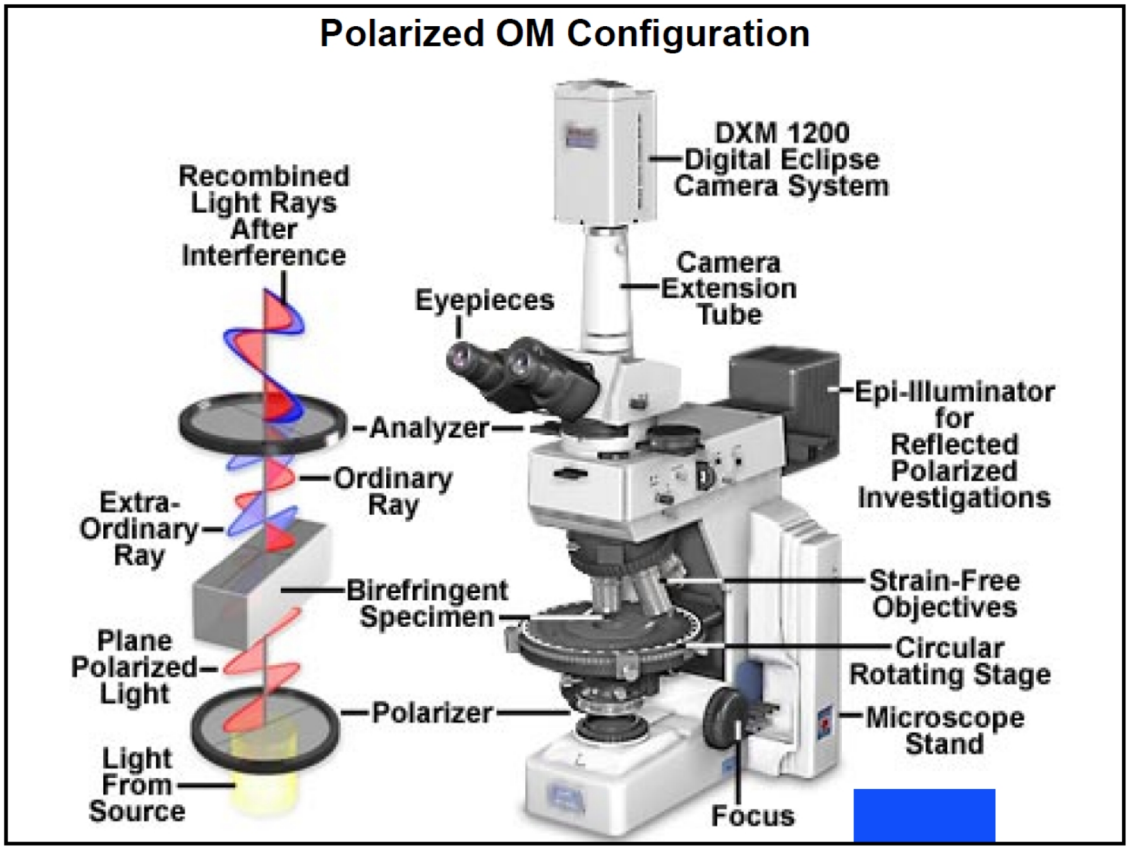


Figure 18 Schematic of the principle of polarized optical microscopy. [Nikon]

Polarized optical microscope is able to study several parameters such as absorption colour, optical path boundaries between minerals of differing refractive indices, in a manner similar to bright-field illumination, and also distinguish between crystalline and amorphous macromolecules.

A supplementary of POM is hot-stage component which supplies heat to substance during observation. Oligomer brij 58 and its star-shaped polymer were observed under heat providing condition. The temperature rate was adjust at slow rate, 1 ^{0}C/min, due to melting process was taken very quickly. The magnification of lens was chosen at 2 mm width.

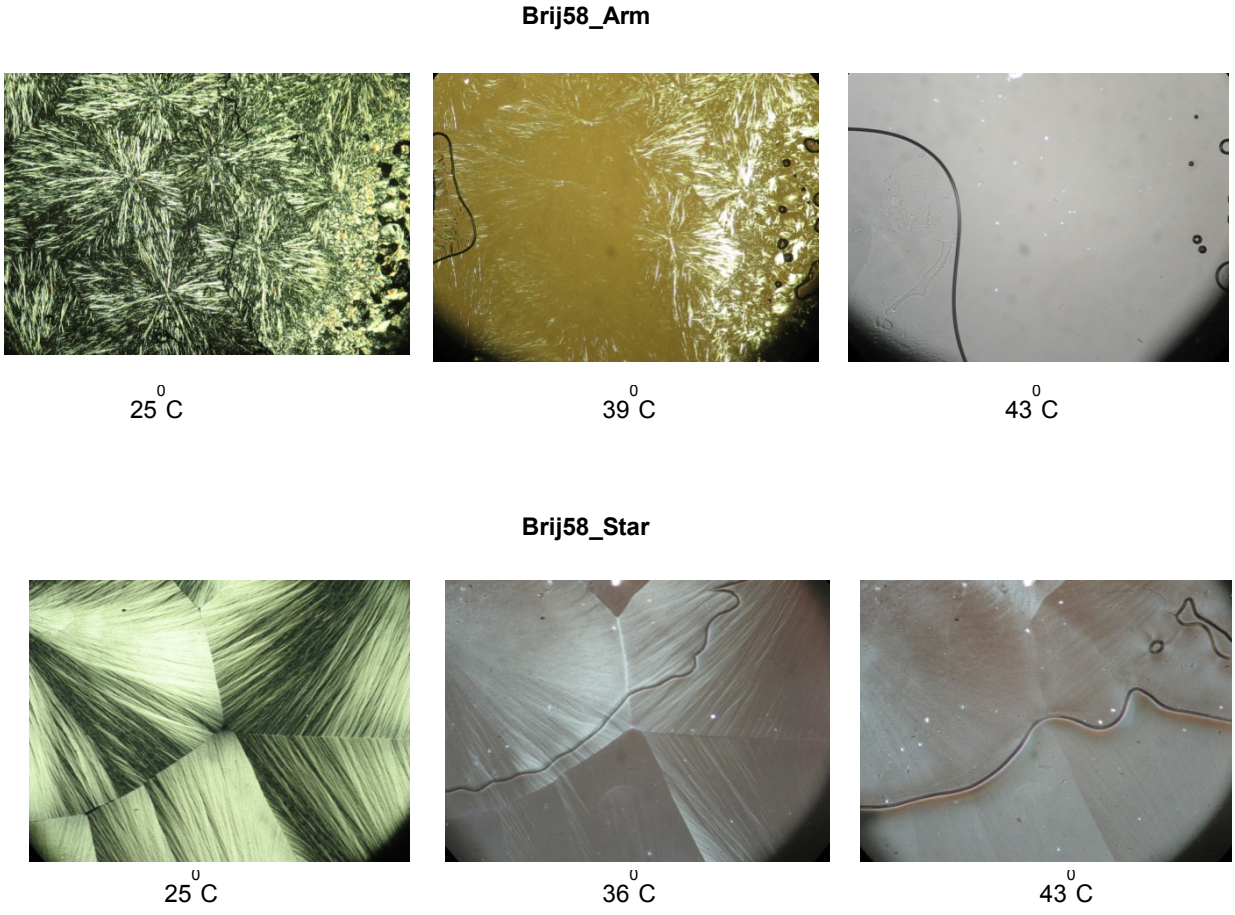


Figure 19 Photos from POM of oligomer brij 58 and its star-shaped polymer at various temperatures.

At room temperature, both oligomer and polymer of brij 58 were detected with crystalline. The nature of crystals was different, which could be further studied to figure out their characteristics.

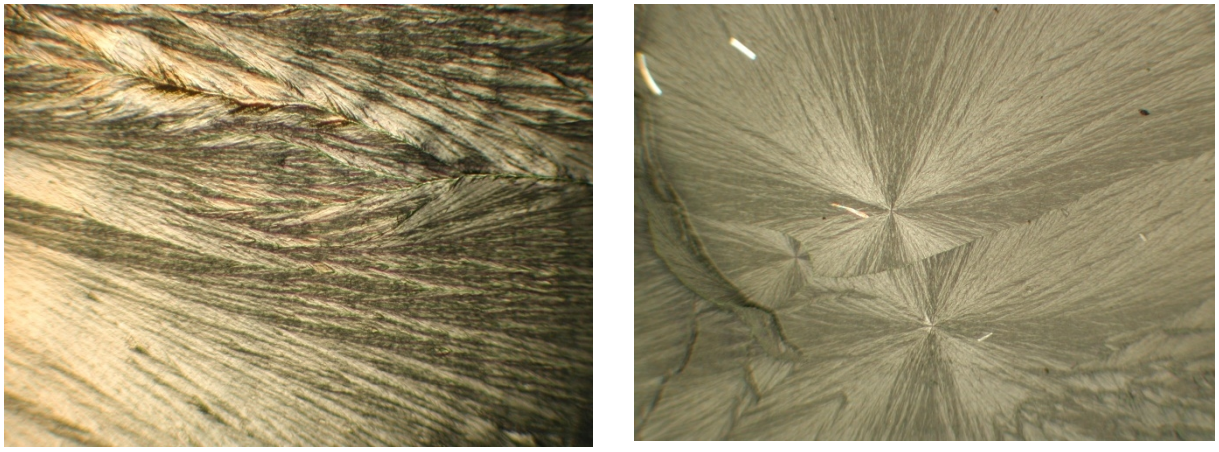


Figure 20 Photos from POM of oligomer brij 58 and its star-shaped polymer at room temperature after cooling. Brij 58 oligomer on the left. Brij 58 star-shaped polymer on the right.

After cooling to room temperature, crystalline also were detected in both oligomer and polymer. However, because when samples were at molten stage, they were moved to be taken out from POM, the profile of imagine changed.

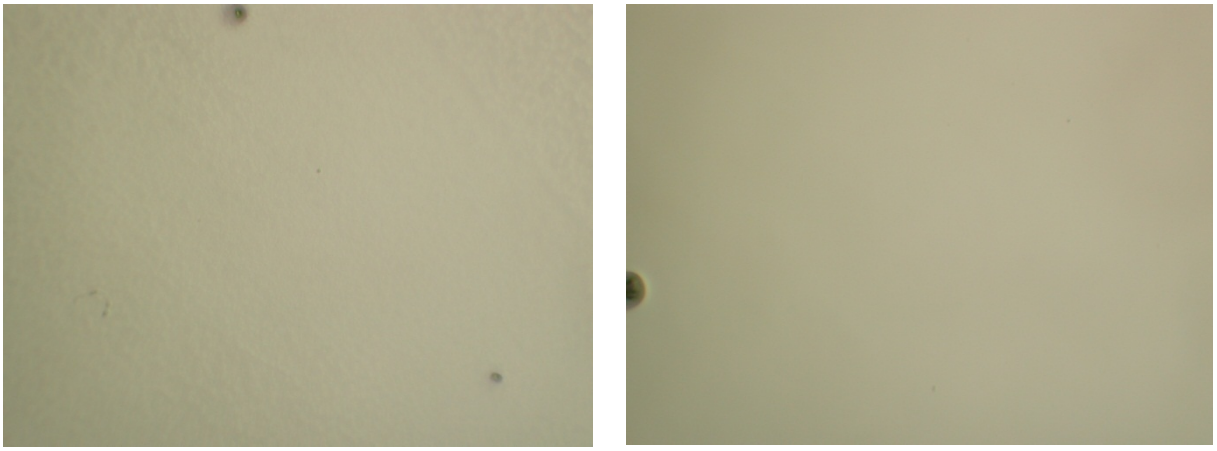


Figure 21 Photos from POM of thermo-responsive oligomer and its star-shaped polymer at room temperature. Oligomer on the left. Polymer on the rieght.

On the other hand, thermo-responsive oligomer and its polymer did not give any crystalline in POM.

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