Structure Relaxation Disruption on Temperature-dependence of Polymerization of HTPB-based Polyurethane

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Abstract

The temperature-dependence of polymerization rate of hydroxyl-terminated polybutadiene (HTPB)-based polyurethane can be disrupted by a structure relaxation of polymer. The objective of the study is to investigate the disruption on the polyurethane (PU) formed of various molecular weights of HTPB. The study was carried out by applying temperatures of 50, 60 and 70 °C in measuring viscosity until 80 minutes of reaction. The sample that was used is HTPB with various molecular weights and Toluene diisocyanate (TDI). Based on decreasing value of viscosity, it is obtained that relaxation temperature of HTPB-based PU is around 60 – 70 °C. By applying The Eyring equation of flow, it is found that the relaxation of structure causes the existence of relaxation dominant-time (RDT). RDT is the reaction time at which molar volume reaches the maximum value. Furthermore, by determining activation entropy, the RDT was revealed to be a borderline between two types of polymerization. The linear reaction occurs before RDT, while cross-link reaction occurs after RDT. From a structure point of view, The PU-polymerization type of HTPB with low molecular weight tends to be more sensitive towards structure relaxation which is originated from the hard segment.

Keywords: Polymerization, Polyurethane, Relaxation temperature, Temperature effect.

1. Introduction

Having an exceptional purpose, a space vehicle requires materials possessing a lightweight as well as excellent mechanical and thermal properties. The requirements are reported to be sufficiently fulfilled by the use of a thermosetting polymeric composite material which is an assembly of polymer and particles, especially those with polyurethane as the matrix (Hsissou et al., 2021). Moreover, polyurethane with hydroxyl-terminated polybutadiene (HTPB) as the polyol is preferable because of its wide possibility in structure design by providing cis, trans, vinyl isomers as well as stereoisomers which are atactic, syndiotactic, and isotactic (Dey et al., 2017).

In addition, to determine mechanical and thermal properties of the composites, the matrix also has a crucial role in the fabrication process and thus, on the perfection of the composite structure (Rueda et al., 2017). The viscosity of matrix has to be not too low and not too high. A high viscosity matrix is an obstacle to castability. While, low viscosity matrix tends to cause agglomeration of particles (Restasari & Abdillah, 2017; Rueda et al., 2017). The problem becomes significant for composite solid propellant, a rocket fuel, which is advised to have a high solid content as around 88% or above, with 25% of aluminum (Kakavas-Papaniaros, 2020).

Involving polymerization reaction between isocyanate (NCO) group and hydroxyl (OH) group under certain temperature and mixing speed, viscosity of polyurethane can be designed chemically and physically. Physical modification, such as temperature adjustment, promises a modest application over chemical modification such as varying ratio of NCO:OH and plasticizer (Restasari et al., 2020; Rosita, 2016). Bogdan Florczak reported anomalous viscosity changes towards temperature on polyurethane with HTPB R45M from 0 – 80 minutes of reaction time regardless of the not deep investigation about the origin (Florczak, 2014). It is hypothesized to be originated from a long and complicated hydrocarbon chain of HTPB. Because of the characteristics of the chain,

increasing temperature can increase (positive effect) and decrease (negative effect) viscosity of HTPB-based polyurethane.

The positive effect is originated from increased polymerization rate. Increasing concentration of polyurethane as a product of polymerization (*M*) level up the viscosity (Billmeyer, 1962). While, the negative effect is possible to be originated from structure relaxation of polymer. Based on linear viscoelasticity of polymers, temperature affects both of elastic modulus (*G'*) and loss modulus (*G"*). Relaxation temperature is signed as a peak of tan δ = *G"/G'*, where loss modulus or viscous flow dominates elastic modulus. On this temperature, based on Equation 1-1 and 1-2, *G** or complex modulus become lower. As the result, complex viscosity (η^*) on Equation 1-3 is also lower. Value of η^* is connected to steady shear viscosity (η) through Cox-Merz rule as long as the polymer is Newtonian and the shear rate is very low (Hsissou et al., 2022; Ueda, 2019). Therefore, in relaxation temperature, viscosity of polymer reaches the minimum value of η^* and its temperature-dependent viscosity tend to exhibit non-Arrhenius behavior (Rosa Junior et al., 2019).

$$G^* = G' + i\ G''$$ (1-1)

$$|\ G^*\ | = ((G')^2 + (G'')^2)^{1/2}$$ (1-2)

$$\eta^* = G^* / \omega$$ (1-3)

Considering that relaxation temperature is originated from structure relaxation (Restasari et al., 2021), polyurethane (PU) which has two segments, hard and soft, should has at least two kinds of relaxation temperature which is also reported for the other polymer with two segments (Kida et al., 2020). The two temperatures can be α and β. It is reported that PU formed of poly(2-hydroxypropyl methacrylate) (PHPMA) has three relaxation temperatures named α, β, γ respectively based on its ecreasing alue. The α-relaxation temperature is around 50 - 70 oC (Dupenne et al., 2017). Molecular weight of soft segments is reported to determine the value of α-relaxation temperature of diethylene glycol-based PU (Zajac et al., 2017). While for HTPB-based PU, value of relaxation temperature depends on the composition. PU consists of HTPB, PTHF, IPDI shows relaxation temperature on around ˗60 and 27 oC (Kohga, 2012). While, PU with complete composition of HTPB, IPDI, antioxidant, bonding agent and plasticizer exhibits relaxation temperatures on -73 and -20 oC (Brzić et al., 2014). PU formed by HTPB, PDI, dibutyltin dilaurate shows a relaxation temperature at -60 oC (Sikder & Jana, 2018). However, report that only observed one kind of relaxation temperature of PU can be considered as having lack of data due to measurement limitation, such as short temperature range. Moreover, most of those reports investigate solid PU and not monitores relaxation temperature of PU during polymerization, from liquid-like to gel-like. Thus, understanding of the effect of temperature on viscosity of PU, especially PU formed of HTPB and TDI, during polymerization is still needed to be developed.

$$Ln\ \eta = ln\ (Nh/V^*) + (\Delta F/RT)$$ (1-4)

$$Ln(k/T) = -(\Delta H^*/RT) + ln\ (R/Nh) + (\Delta S^*/R)$$ (1-5)

This work aims to investigate structure relaxation disruption on temperature-dependences of polymerization on HTPB-based PU. This work uses thermodynamics approach by using The Eyring equation focusing on movement-related parameter. The Eyring equation for flow is described on Equation 1-4 where *N* is Avogadro number (6.02 x 10^{23}), *h* is Planck constant (6.62 x 10^{-34}), ΔF^* is the difference of free energy before and after movement or activation free energy and *V* is molar molecular volume (Muraki, 2013). While, for reaction, Equation 1-5 of the Eyring relationship can be applied where *k, ΔH^*, ΔS^** are reaction rate, activation enthalpy and activation entropy, respectively (Espenson, 2002). In addition, to shape understanding of structural origin, several HTPB with different molecular weight are used in this work.

2. Methodology

In this study, three types of HTPBs were used, named HTPB A, B and C with weight averaged molecular weight (M_w) of 4536, 7234, 8160 g/mol and M_w/M_n of 1.1, 1.06, 1.2, respectively. HTPB A is produced by Hanwha Co Ltd. While, HTPB C is produced by Dalian Chlorate Ltd. HTPB B was made by mixing both HTPBs. Specifications related to polymerization include hydroxyl number of HTPBs of 47 mg KOH/g, Toluene diisocyanate (TDI) with isomer 2,4-TDI of 80.5% and isomer 2,6-TDI of 19.5% as well as weight ratio of HTPB:TDI 14:1.

IKA Mechanica Stirrer RW 20 digital with double helix impeller was used to ensure a well distribution of low viscosity TDI into high viscosity of HTPB. Effort to obtain this well distribution was also conducted by heating HTPB at 40 °C and mixing at speed of 60 rpm for 5 minutes prior to a mixing with TDI. In mixing process, one-shot method, speed of 100 rpm for 30 minutes were used.

Viscosity of each polymer (A, B, C) was measured at 50; 60; and 70 °C using Rheometer Brookfield DV-III with HA-04 spindle at 4 rpm, low shear rate, every 20 minutes until 80 minutes. Temperature was set using hotplate and inserted digital thermometer.

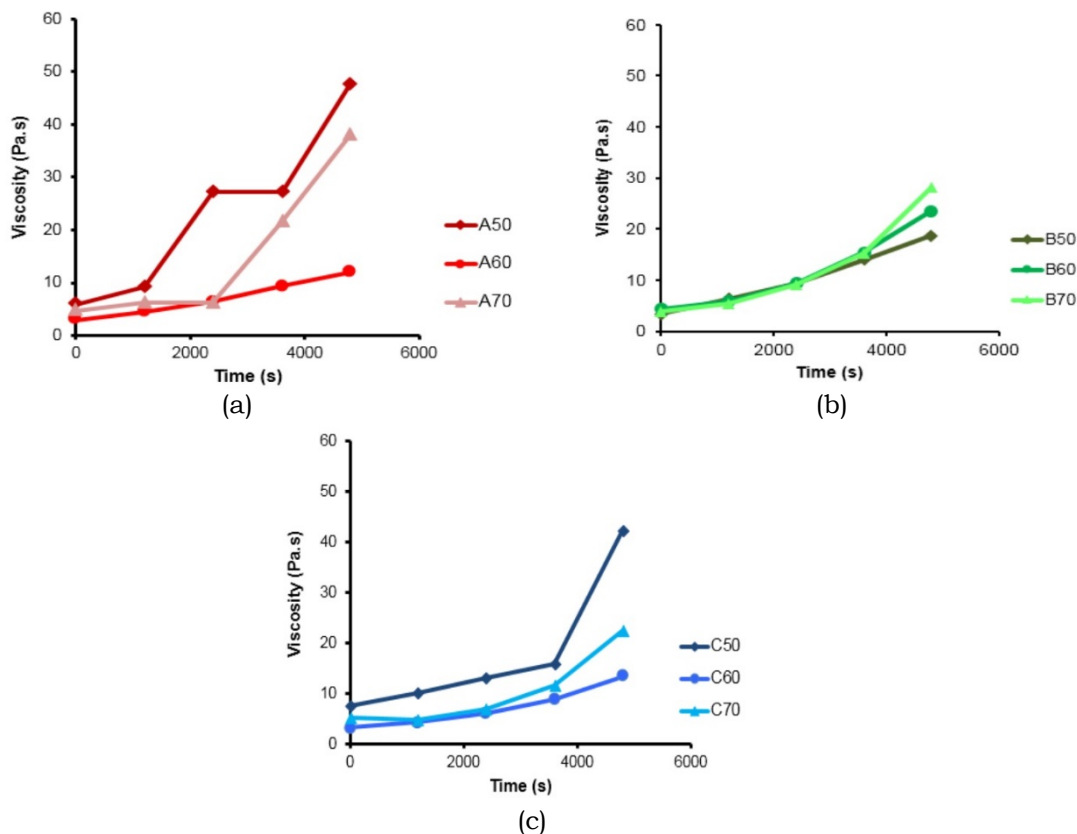## 3. Result and Analysis

Figure 3-1: Viscosity build-up of PU-A (a), PU-B (b) and PU-C (c).

In PU polymerization, hydroxyl group from HTPB reacts with isocyanate group from TDI to form urethane bond. Some urethane bond are attached to each other, forming hard segments (Cheikh et al., 2019). The progress of polymerization process can be monitored by viscosity value (Billmeyer, 1962). For chemical reaction, increasing temperature leads to increase reaction rate. It should be that the higher reaction rate, the higher the viscosity. However, because of structure relaxation of long chain of HTPB, temperature effect of PU polymerization can be varied.

Figure 3-1 shows viscosity build-up for each PU at each temperature. Remarkably, viscosity of all type of PU decrease when viscosity is higher than 50 °C. The decrease is also reported on PU with HTPB R45M (Florczak, 2014). It suggests that relaxation temperature of PU is around 60 - 70 °C. The temperature are also reported as *a-*

relaxation temperature for PHPMA-based PU (Dupenne et al., 2017). However, a further research is needed at temperature higher than 70 °C. On the other side, exceptional pattern of viscosity build-up is observed on PU-B. It shows similar pattern for all temperature. It can be caused by its narrow M_w/M_n. It means that PU-B has more homogenous chain length so that the effect of structure relaxation is less diverse (Billmeyer, 1962).
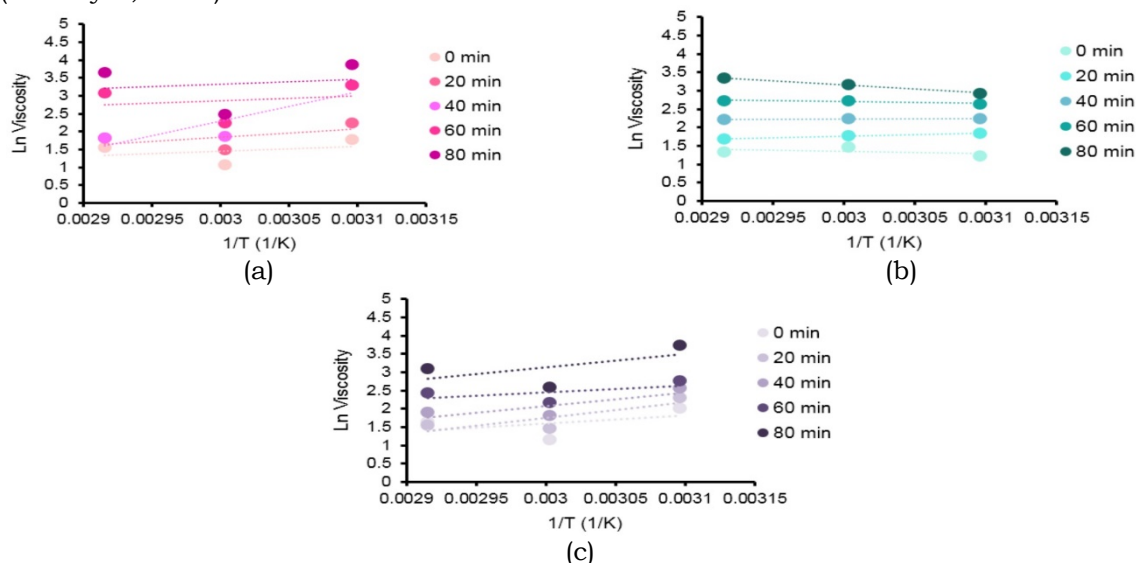

(a)

(b)

(c)

Figure 3-2: *Ln* viscosity *vs* 1/T to obtain value of molar molecular volume of PU-A (a), PU-B (b) and PU-C (c).

To reveal the role of structure relaxation on temperature-dependence of polymerization, thermodynamic of flow is applied. When structure is relaxed, it is easier to move or flow and it can be monitored by molar molecular volume (*V*). It is a volume per mole that molecule occupy. The higher the *V*, the easier the flow (Muraki, 2013). It can be obtained by applying Eyring equation for flow, Equation 1-4, by plotting *ln* viscosity towards 1/*T*, shown on Figure 3-2.
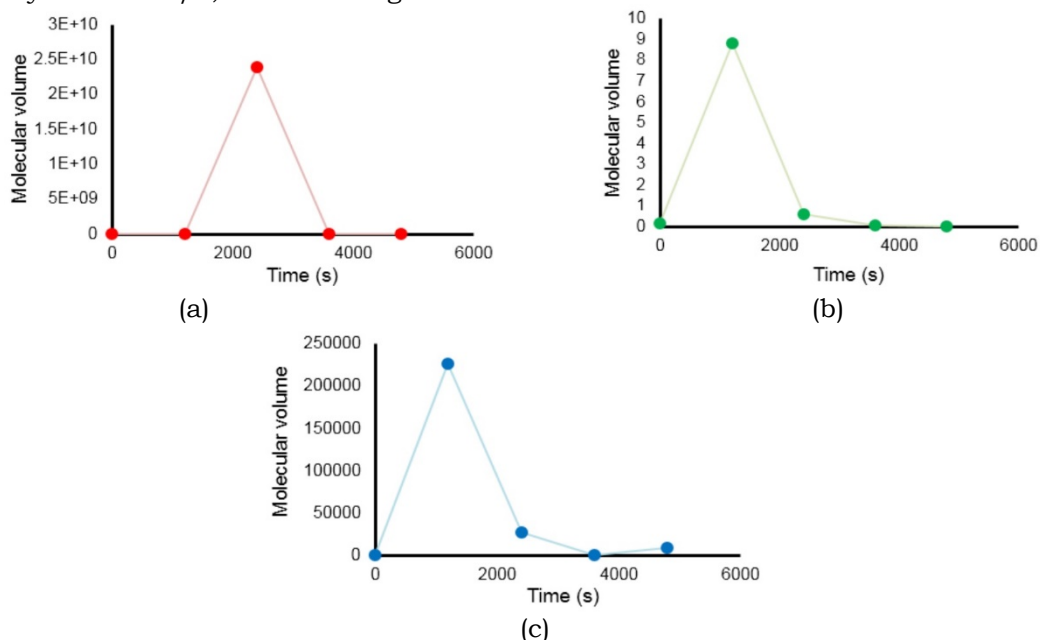

(a)

(b)

(c)

Figure 3-3: Time-dependent molar molecular volume of PU-A (a), PU-B (b) and PU-C (c).

Figure 3-3 shows fluctuative *V* for all PU during polymerization. Notably. all PU exhibits peak of *V*. It is called as a relaxation dominant-time (RDT). It is worthed to point out that RDT of PU A is at 40th minute which is more delayed than other PUs (RDT =

20th minute). The hard segment in PU-A is suggested to be the origin. It is because motion of chain between urethane groups are reported to cause the existence of *a*-relaxation temperature (Zajac et al., 2017). HTPB A with low molecular weight has less diffusion hindrance so that it forms hard segment faster (Deylami & Kebritchi, 2020). As the results, it has more hard segments that need more time to reach optimum chain motion.
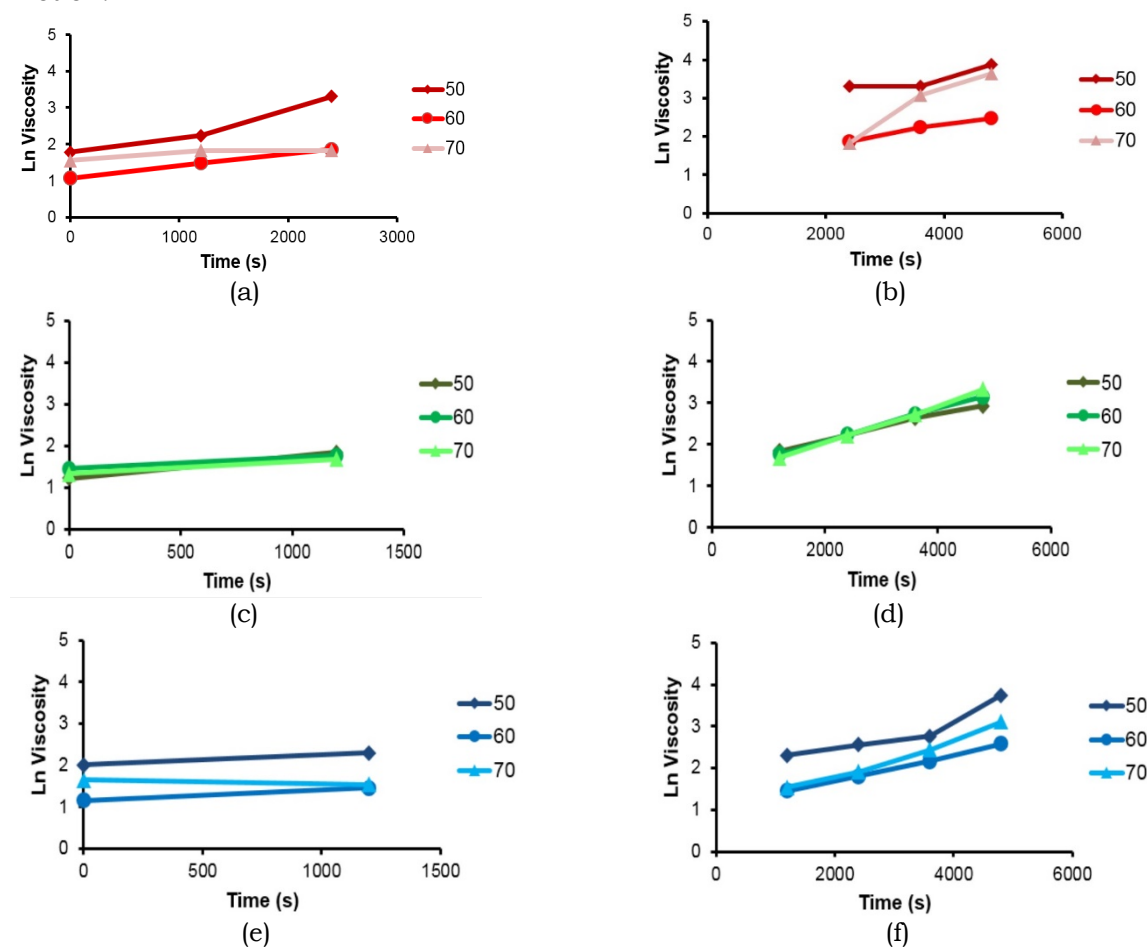

Figure 3-4 : *Ln* viscosity at all temperatures for PU-A before RDT (a), after RDT (b), PU-B before RDT (c), after RDT (d), PU-C before RDT (e), after RDT (f).

Increasing *V* before RDT and decreasing *V* after RDT inspires that type of polymerization before RDT can be different from those after RDT. Therefore, here, polymerization is divided into two parts which are step 1 (before RDT) and step 2 (after RDT) and the viscosity build up is shown on Figure 3-4. This division is obviously different from usual division of polymerization which is based on the level of rate constant, *k* (Deylami & Kebritchi, 2020; Guo et al., 2018; Wibowo et al., 2019). Graphs on Figure 3-4 are processed by using Equation 1-5 to obtain activation entropy as a basic to determine the type of polymerization.

Activation entropy (ΔS^*) represents freedom for structure to move. When two smaller compounds react and form one bigger compound as intermediate structure, such as in condensation reaction of PU, negative ΔS^* is obtained (Cheikh et al., 2019; Espenson, 2002). Figure 3-5 shows that all PU has negative ΔS^*. It underlines a successful PU polymerization reaction. In this work, the value of ΔS^* is similar to -154.512 J K^{-1} mol^{-1} as reported by Ashgar *et al* (Ashgar et al., 2019). Moreover, it is notably on Figure 3-5 that step 1 for all PU has more negative ΔS^* than step 2. It indicates the easier formation of intermediate structure in step 1 than step 2 (Espenson, 2002). It has been reported that formation of cross-linked PU is harder than linear PU (Cheikh et al., 2019; Malczewska & Biczyński, 2017; Ou et al., 2018). Therefore, conceivably, reaction before RDT was a linear polymerization, while after RDT was a cross-linking reaction. It can be caused by different reactivity of two isocyanate groups in 2,4-TDI. There, reactivity of ortho-isocyanate group is 8.3 times lower than para-isocyanate group. In the

polymerization, para-isocyanate will react first with hydroxyl group from HTPB to form a linear para-urethane group. After that, at the same TDI structure, ortho-isocyanate will react so that 1 TDI can build 2 urethane bonds. It is called as a crosslinked polyurethane (Szycher, 2013). More detail on molecular weight effect, two patterns has been significantly observed on Figure 3-5. On step 1, the higher the M_w, the higher ΔS^*. It indicates, the higher the M_w, the more difficult for linear polymerization to occur. Opposite effect is observed on step 2. However, based on the slope, reaction easiness in step 1 was more sensitive towards M_w than step 2. It is also notably that ΔS^* of PU with high M_w of HTPB is same for step 1 and 2. It indicates that RDT or structure relaxation has no effect on type of reaction along polymerization.
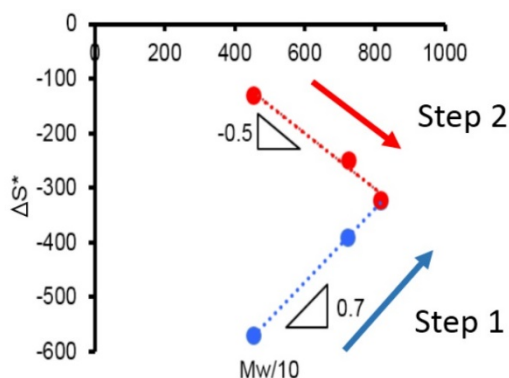

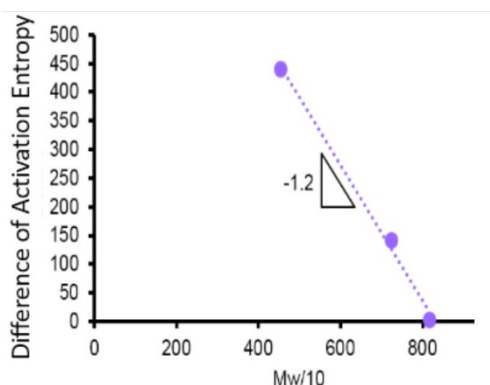Figure 3-5 : Correlation between molecular weight of HTPB and entropy activation for each step.

Figure 3-6: Effect of M_w of HTPB on difference of ΔS^* between step 1 and 2.

As a simple indicator to describe an easiness difference of polymerization between step 1 and 2, difference of ΔS^* are used. Based on Figure 3-6, PU-A with the smallest value of M_w of HTPB has large difference in reaction easiness. In step1, linear polymerization, PU-A has the easiest route of all kinds of PU. While, in step 2, cross-link polymerization, PU-A has the hardest route of all kinds of PU. Since PU-A has more hard segments than the others PU, it is suggested that the hard segment makes the structure of PU-A more rigid and less flexible to propagate polymerization (Young & Bowman, 1999).

4. Conclusions

Structure relaxation disruption on temperature-dependence of polymerization was explored towards HTPB-based PU with various M_w of HTPB by measuring viscosity at various temperature during polymerization. Based on decreasing value of viscosity, it is obtained that a-relaxation temperature of HTPB-based PU is around 60 – 70 ᵒC which is similar to the report of Dupenne *et al* (2017) on PHPMA-PU. By applying Eyring equation of flow, it was found that relaxation of structure causes the existence of relaxation dominant-time (RDT). Furthermore, by determining activation entropy, the RDT was revealed to be a borderline between two type of polymerization. Linear reaction occurs

before RDT, while cross-link reaction occurs after RDT. From structure point of view, PU-polymerization type of HTPB with low molecular weight tend to be more sensitive towards structure relaxation originated from hard segment.

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Contributorship Statement

AR[1] is the main contributor. AR[1] conceptualization, methodology, resources. AR[1], AS and RS investigation. AR[1] and NH data analysis. AR[1] writing original draft preparation. AR[1], LM and AR[3] writing review and editing. Note: AR[1] is Afni Restasari and AR[3] is Andi Rusnaenah.

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