Synthesis of High Molecular Weight Nylon 6 by Anionic Polymerization of ε-Caprolactam

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ABSTRACT: To obtain high molecular weight nylon 6, the anionic polymerization of ε-caprolactam was investigated in terms of water content in monomer and concentration of catalyst (Grignard reagent; ethyl magnesium bromide) and chain initiator (monofunctional; N-acetyl-ε-caprolactam or bifunctional; N,N'-adipoyl-bis-ε-caprolactam). The weight average molecular weight, $M_w = 7.0 \times 10^5$ (the intrinsic viscosity; $[\eta] = 11.2$) was obtained using the monofunctional chain initiator, and $M_w = 9.5 \times 10^5$ ($[\eta] = 14.1$) was found using the bifunctional chain initiator under the following conditions: water content, 0.013 mol%; concentration of catalyst, 0.1 mol%; concentration of chain initiator, 0.03 mol% (monofunctional), 0.015 mol% (bifunctional); polymerization temperature, 150°C. In the present study, the molecular weight of the polymer is governed by quantities of active molecular chains. Since water mainly terminates the propagation of molecular chains, minimizing water content in ε-caprolactam is indispensable to maximizing the molecular weight of the polymer.
KEY WORDS High Molecular Weight / Nylon 6 / Anionic Polymerization / ε-Caprolactam / Water Content / Catalyst / Grignard Reagent / Chain Initiator

The anionic polymerization of ε-caprolactam has been extensively investigated because of the high yield and high rate of polymerization.[1-4] Fundamental characters such as various catalysts,[2,5,6] propagation mechanism[7-15] and kinetics[16-26] are well known. Sebenda *et al.*[7,16-22,27] studied the propagation mechanism and kinetics of the polymerization, and propose the free ion mechanism and side reaction mechanism. Recently, Stehlicek and Puffr reported that Grignard reagents as anionic catalysts gave much higher rates of the polymerization than sodium-ε-caprolactamate.[26] On the other hand, Puffr and Vladimirov synthesized the high molecular weight nylon 6 using potassium-ε-caprolactamate as the catalyst at 180°C.[6] The studies directed toward high molecular weight nylon 6, however, were not performed on the Grignard reagents. In addition, the influence of water content on polymerization was not investigated in spite of the general concept that water content is very important. In this paper, we describe the method for synthesizing high molecular weight nylon 6 by the anionic polymerization of ε-caprolactam. Discussed is the importance of water content and concentration of the catalyst (Grignard reagent) and mono- or bifunctional chain initiator.

EXPERIMENTAL

Materials

Industrial fiber grade ε-caprolactam as monomer, ethyl magnesium bromide (EtMgBr; Aldrich Chemical Co., Inc.) as catalyst in $3.0 \, \text{mol} \, l^{-1}$ diethyl ether solution or $1.0 \, \text{mol} \, l^{-1}$ tetrahydrofuran solution and N-acetyl-ε-caprolactam (Ac-CL; Tokyo Chemical Industry Co., Ltd.) as monofunctional chain initiator were used for the polymerization. N,N'-adipoyl-bis-ε-caprolactam (Ad-CL) as bifunctional chain initiator was prepared from ε-caprolactam and adipoyl-chloride (Aldrich Co., Inc.) in the presence of pyridine, and the product was purified by recrystallization.[28] 96% sulfuric acid (Ishizu Seiyaku Ltd.) as solvent for viscosity measurement and hexafluoro-2-propanol (HFIP; Ishizu Seiyaku Ltd.) as the mobile phase in gel permeation chromatography were of reagent grade and used without further purification.

Polymerization

Water in ε-caprolactam was removed to less than 0.013 mol% by bubbling dry argon gas for 5 h in a three-neck flask at 120°C. Water content was controlled by adding water to this ε-caprolactam and measured by Karl Fischer auto titration equipment (Hiranuma Industrial Co., AQV-5S). The chain initiator was injected into ε-caprolactam with controlled water content. The mixture of monomer and initiator was poured into a glass tube (inside diameter 20 mm, volume 20 ml) beforehand dried by heating above 100°C under 10 Pa of vacuum. The catalyst (EtMgBr) solution was injected into the tube *via* a syringe, and the tube was sealed after unnecessary solvent was evaporated at 10 Pa. Polymerization was carried out with shaking in an oil bath at 130—190°C (thermostated at ±1.0°C).

As the polymerization of ε-caprolactam proceeded, the viscosity of the system increased, and fluidity disappeared. We called this point the solidification point, when the fluidity of the system disappeared, with glass tube in tilted position. We define the time from the beginning of the polymerization to the solidification point as the solidification time. Since it was confirmed that conversion almost reached 20% at the solidification time, this time was conveniently used for estimation of reaction rate. The polymerization was stopped at 2.5 times (using 0.5 mol% EtMgBr) or 6 times (using 0.1 mol% EtMgBr) of the solidification time. It was confirmed that at that time conversion was about 100%. Termination of the polymerization was carried out by quenching to dry ice/methanol temperature (−78°C). The product was shaved with a boring machine and analyzed. Monomer and oligomer in the polymer were extracted by
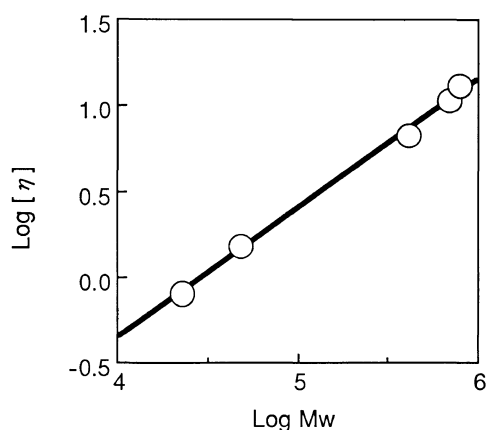
Figure 1. Relation between $\log[\eta]$ and $\log M_w$. $[\eta]$ was determined with polymer concentration below $0.2\,g\,dl^{-1}$ (5 points) using H_2SO_4 at 25°C. M_w was measured by LS using HFIP at 30°C.

boiling water in a flask for 5 h. The monomer content in the extract was measured by liquid chromatography (Column; Waters C18 Purecil, mobile phase; 0.1 M $NaH_2PO_4 + H_3PO_4$, pH 3.0), and conversion was calculated from change in monomer content before and after polymerization.

Molecular Weight Determination

The molecular weight of the polymers was conventionally evaluated by intrinsic viscosity measurement ($[\eta]$; 96% sulfuric acid, at 25°C). The concentration for this measurement was below $0.2\,g\,dL^{-1}$ because of non-Newtonian behavior in the ordinary concentration of the measurement (less than $0.5\,g\,dL^{-1}$).[29] Light scattering (LS; Wyatt LTD., DAWN-F) measurements for the polymer with various $[\eta]$ were carried out in HFIP to obtain weight average molecular weight (M_w).

Figure 1 shows the relation between $[\eta]$ and M_w of the polymer in this study. Linear regression analysis was applied to the data and coefficients of Mark–Houwink–Sakurada equation were determined as follows:

$$M_w = 2.81 \times 10^4 \times [\eta]^{1.35} \tag{1}$$

M_w of the polymers under various polymerization conditions were calculated by eq 1 using observed $[\eta]$.

Gel permeation chromatography (GPC; TSK gel GMH-H + G7000H) measurements were carried out with HFIP as the mobile phase. In general, GPC measurements give M_w, the number average molecular weight (M_n) and polydispersity ($P = M_w/M_n$). Calibration of the column could not be carried out, since we had no sample of standard nylon 6 with monodispersed molecular weight. Therefore, only P reliably obtained from GPC measurement was used. Details of the analysis will be published elsewhere.[30]

RESULTS AND DISCUSSION

Influence of Water Content

The influence of water content on anionic polymerization is demonstrated in Figures 2 and 3. Here in Figure 2 the experimental results of the solidification time of the polymerization are shown as a function of the concentration of the chain initiator (Ac-CL) at various
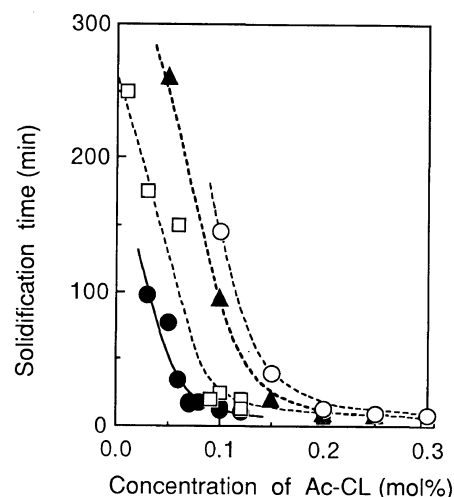
Figure 2. Effects of water content on the solidification time, where the solidification time is plotted against the concentration of the chain initiator (Ac-CL). Polymerization conditions: temperature, 150°C; concentration of catalyst (EtMgBr), 0.5 mol%; water content, 0.013 mol% (●), 0.038 mol% (□), 0.063 mol% (▲), 0.088 mol% (○), respectively.
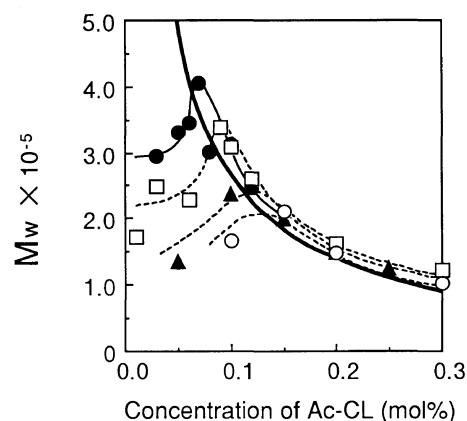

Figure 3. Effects of water content on M_w, where M_w is plotted against the concentration of the chain initiator (Ac-CL). Polymerization conditions: temperature, 150°C; concentration of catalyst (EtMgBr), 0.5 mol%; water content, 0.013 mol% (●), 0.038 mol% (□), 0.063 mol% (▲), 0.088 mol% (○), respectively. The thick solid line (—) is the calculated M_w.

water contents; 0.013, 0.038, 0.063, and 0.088 mol%, respectively. The concentration of catalyst (EtMgBr) was kept constant at 0.5 mol%. As the Ac-CL concentration decreases, the solidification time gradually increases at every water content. Solidification time becomes longer with increasing water content. At low concentration of the chain initiator, the solidification time becomes steeply longer at every water content. Figure 3 shows M_w of the polymer as a function of Ac-CL concentration under the same conditions as Figure 2. The relation between M_w and Ac-CL concentration is shown by a curved plot with a maximum peak. As water content decreases, the maximum M_w increases. M_w (4.0×10^5) was maximum at 0.07 mol% of Ac-CL and 0.013 mol% water content.

The thick solid line in Figure 3 indicates the calculated M_w assuming eq 2.

$$M_w = \frac{P \cdot M_{CL}}{[I]/[M]} \tag{2}$$

Here, [I] is the concentration of the chain initiator

Table I. Reaction mechanisms of the anionic polymerization of ε-caprolactam[3,27,31]
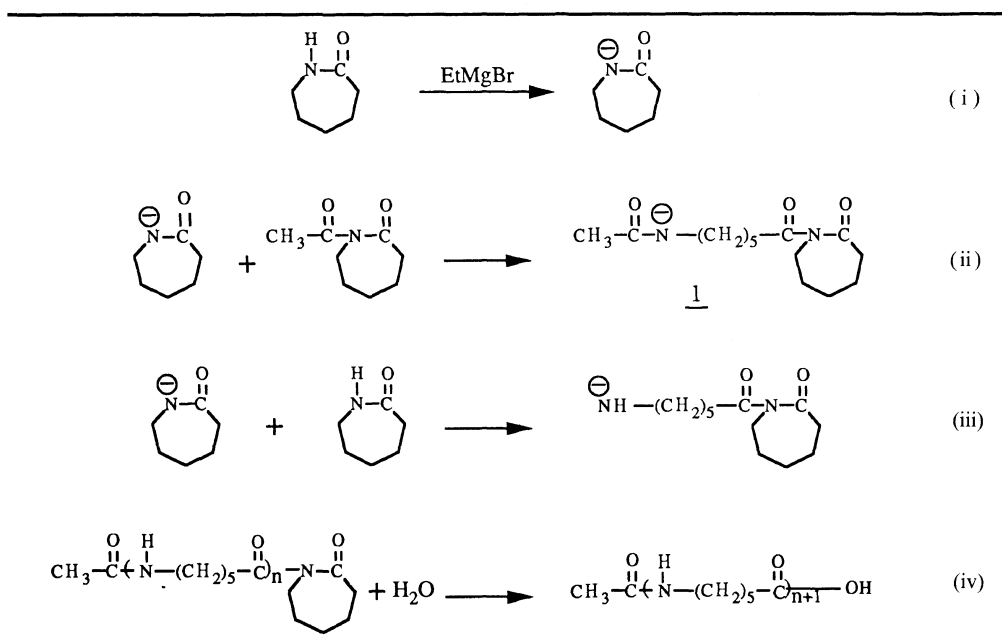
(mol g^{-1}), and [M] is the initial concentration of the monomer (mol g^{-1}), and M_{CL} is the molecular weight of ε-caprolactam. P means polydispersity ($P = M_w/M_n$), the value of which was estimated to be 2.3 by GPC measurements. As for this polymerization, it was proposed that the initiation reaction proceeds according to the eq i and ii in Table I (the main reactions),[3,27,31] and the molecular chains extend with 1 as an initiator. Therefore, if the polymerization proceeds ideally, the number of chains corresponds to the number of initiators, represented by eq 2. The smaller amount of initiator might provide the higher molecular weight.

In Figure 3, the right side of the peak top in each curve closely follows the calculated line. The maximum value of M_w obtained by these experiments (water content 0.013 mol%) is 4.0×10^5, which corresponds to $M_w = 3.7 \times 10^5$ calculated from the concentration of Ac-CL (0.07 mol%). Therefore, it is clarified that the high molecular weight nylon 6 is obtained along with the line by controlling the water content and the concentration of chain initiator Ac-CL.

In Figure 3, the left side of the peak top in each curve deviates appreciably from the calculated line. The solidification time at low Ac-CL concentration (especially below 0.05 mol%) becomes longer such as in Figure 2 even at the water content 0.013 mol%. The conversion reaches only 70—85% in the left side of the peak top. The long solidification time is the result of low concentration of the growing chain end. Consequently, the side reaction like eq iii in Table I with slow reaction rate[3] becomes significant, which is generally ignored in polymerization using a high concentration of the chain initiator. The influence of water is not ignored for the anionic polymerization even at 0.013 mol%, which is comparable with the concentration of Ac-CL (0.03—0.07 mol%). Water causes the side reactions like eq iv in Table I and stops the propagation of the molecular chain. The deviation between the experimental M_w and the calculated M_w is caused by all factors described above.
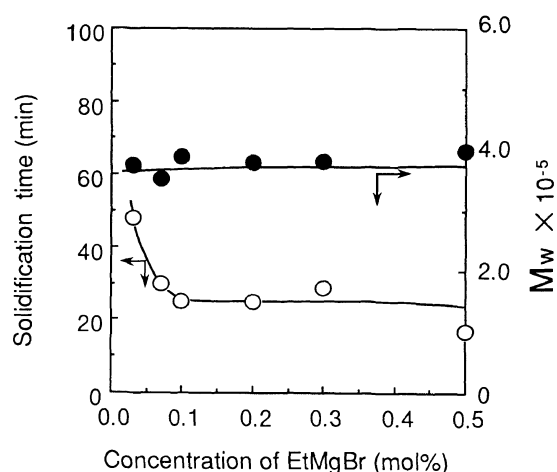

Figure 4. Effects of concerntration of catalyst (EtMgBr) on the solidification time and M_w. Polymerization was carried out at: temperature, 150°C; concentration of chain initiator (Ac-CL), 0.07 mol%; water content, 0.013 mol%.
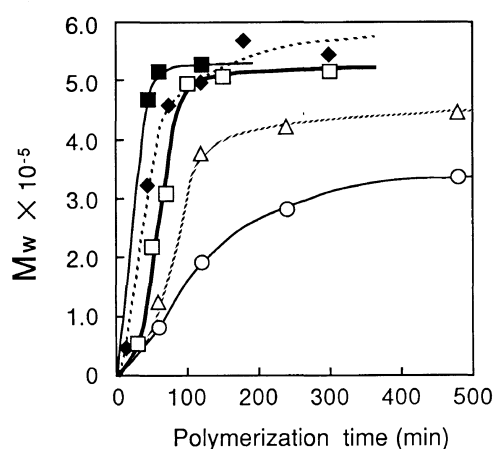
On the anionic polymerization with Grignard reagents, it was revealed the water content and the chain initiator concentration controls the molecular weight of the product.

Effects of Concentration of Catalyst

To clarify the effects of the catalyst, the solidification time and M_w of the product *versus* the concentration of catalyst EtMgBr were investigated in the presence of 0.013 mol% water, which is shown in Figure 4. The initiator Ac-CL concentration was kept constant at 0.07 mol%. Although the solidification time becomes longer below 0.1 mol% of EtMgBr, M_w of the polymer is constant at about 3.9×10^5 ($[\eta] = 6.6$). It is suggested that the molecular weight of the product does not mainly depend on the concentration of the catalyst. To achieve the high molecular weight, however, the polymerization should be ideally initiated by the minimum concentration of 1 formed with molar equivalent of the catalyst EtMgBr

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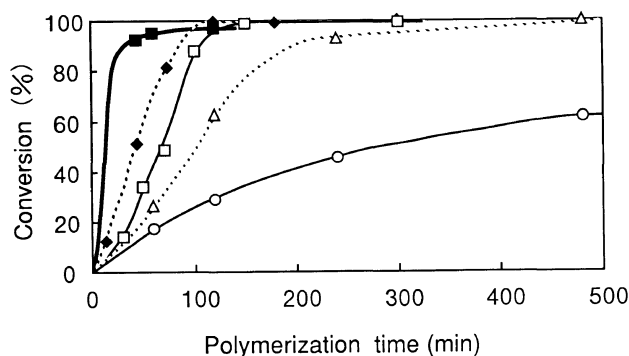
Figure 5. Time–conversion curves at various polymerization temperature. Polymerization conditions: temperature, 130°C (○), 140°C (△), 150°C (□), 170°C (◆), 190°C (■), respectively; concentration of catalyst (EtMgBr), 0.1 mol%; chain initator (Ac-CL), 0.05 mol%; water content, 0.013 mol%.

Figure 6. Effects of the polymerization temperature on M_w, where M_w is plotted against the polymerization time at various temperatures. Polymerization conditions: temperature, 130°C (○), 140°C (△), 150°C (□), 170°C (◆), 190°C (■), respectively; concentration of catalyst (EtMgBr), 0.1 mol%; chain initiator (Ac-CL), 0.05 mol%; water content, 0.013 mol%.

and the chain initiator Ac-CL. Consequently, the concentration of EtMgBr is required to approximate the concentration of Ac-CL closely and not to increase the side reaction or not to decrease the polymerization rate. We conclude the concentration of the catalyst should be reduced to 0.1 mol%. The polymerization was carried out at 0.1 mol% of EtMgBr.

Effects of Temperature

The catalytic system consisting of the catalyst (EtMgBr) and the chain initiator (Ac-CL or Ad-CL) may provide advantageous polymerization at lower temperature. Polymerization temperature is an important factor for controlling the reaction rate of the main reaction and side reaction. The effects of temperature on the polymerization were studied and the results are shown in Figures 5 and 6. Here, the concentration of catalyst (EtMgBr) is 0.1 mol%, the concentration of chain initiator (Ac-CL) is 0.05 mol% and water content is 0.013 mol%. Figure 5 shows the relation between the conversion and the polymerization time at 130—190°C using Ac-CL. The conversion increases monotonously with polymerization time for all temperatures. The time to reach 100% conversion becomes short with increase
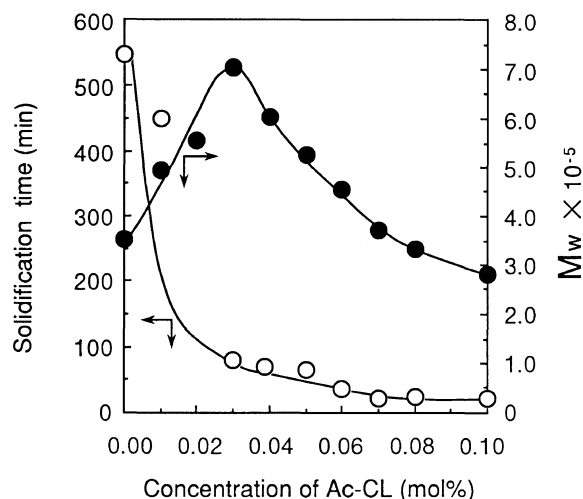
Figure 7. Plots of solidification time and M_w against the concentration of the monofunctional chain initiator (Ac-CL). Polymerization conditions: temperature, 150°C; concentration of catalyst (EtMgBr), 0.1 mol%; water content, 0.013 mol%.

in temperature. This means that the polymerization rate increases with temperature. The conversion at 190°C does not reach 100% (about 97%), since an equilibrium monomer exists probably.[32]

Figure 6 shows M_w of the polymer *versus* the polymerization time at 130—190°C using Ac-CL. The time to reach the steady state of M_w decreases with increase in temperature. M_w of the polymer synthesized at 150—190°C was about 5.0×10^5 and at 130 and 140°C, only 3.3×10^5 and 4.4×10^5 respectively.

In spite of decrease in side reactions at lower temperature (130 and 140°C), it takes a very long time to reach 100% conversion, since the main reaction becomes slower than that at higher temperature. M_w of the polymers synthesized at 170°C and 190°C are same as at 150°C despite the increase in polymerization rate. The increase of M_w after reaching 100% conversion at 170°C is almost within experimental error. It is considered that the lower temperature is favorable to decrease side reactions, so that 150°C is the most suitable temperature of the polymerization.

Maximum M_w by Monofunctional Initiator

To obtain higher molecular weight nylon 6, polymerization was carried out at 0.1 mol% of EtMgBr and 0.013 mol% of water content. The solidification time and M_w of the polymer as a function of the concentration of the chain initiator (Ac-CL) are shown in Figure 7. As the concentration of the chain initiator decreases, M_w of the polymer increases gradually above 0.03 mol% of Ac-CL. M_w maximum is 7.0×10^5 ($[\eta] = 11.2$), at 0.03 mol% of Ac-CL concentration. Below 0.03 mol% of Ac-CL, M_w of the polymer decreases. This is similar to the results in Figure 3. The solidification time increases monotonously and steep increase are observed below the chain initiator 0.03 mol%. This behavior is similar to that in Figure 2. Consequently, by controlling the catalyst concentration, the increase of M_w was more in the region of the lower concentration of the chain initiator than that of Figure 3 (0.07 mol% of Ac-CL).

The observed maximum value of M_w (7.0×10^5) is somewhat lower than the calculated value of M_w
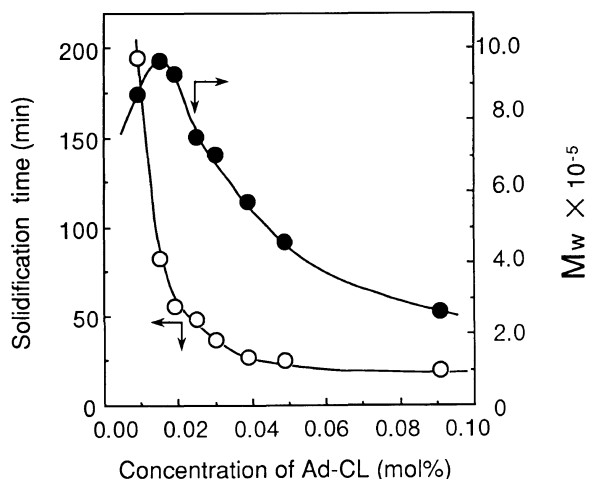
Figure 8. Plots of solidification time and M_w against the concentration of the bifunctional chain initiator (Ad-CL). Polymerization conditions: temperature, 150°C; concentration of catalyst (EtMgBr), 0.1 mol%; water content, 0.013 mol%.

(8.6×10^5) assuming that the concentration of Ac-CL is 0.03 mol%. The reason is attributed to the increase of side reactions like eq iii in Table I. Higher M_w than 7.0×10^5 using the monofunctional chain initiator (Ac-CL) could not be achieved, since water in ε-caprolactam (even 0.013 mol%) and in EtMgBr solution may not be ignored in these low concentration of the catalyst and the chain initiator. It is experimentally difficult to reduce the water content below 0.013 mol%. Therefore, it is recognized that the highest molecular weight of the polymer using the monofunctional chain initiator (Ac-CL) is $M_w = 7.0 \times 10^5$.

Maximum M_w by Bifunctional Initiator

Polymerization using the bifunctional chain initiator (Ad-CL) was carried out to achieve further high molecular weight. Figure 8 shows the solidification time and M_w of the polymer as a function of the concentration of the chain initiator Ad-CL at 0.1 mol% of EtMgBr. As the concentration of the chain initiator decreases, M_w of the polymer increases gradually above 0.015 mol% of Ad-CL. M_w maximum is 9.5×10^5 ($[\eta] = 14.1$), which is achieved at 0.015 mol% of Ad-CL concentration. M_w of the polymer decreases below 0.015 mol% of Ad-CL. This is similar to the results in Figure 7. The solidification time is also similar to that in Figure 7 except that the time is about half.

The concentration of the bifunctional chain initiator (Ad-CL) providing maximum M_w is 0.015 mol%, which is half the monofunctional chain initiator (Ac-CL, 0.03 mol%), since Ad-CL has 2 active molecular chain ends per molecule. Maximum $M_w = 9.5 \times 10^5$ (Ad-CL, 0.015 mol%) obtained from the bifunctional chain initiator is lower than the calculated M_w (1.7×10^6). This considerable deviation between the observed and calculated M_w may be due to the relative increase of side reactions such as eq iii in Table I. The highest molecular weight of the polymer obtained by the bifunctional chain initiator is $M_w = 9.5 \times 10^5$.

CONCLUSION

To obtain high molecular weight nylon 6, the anionic polymerization of ε-caprolactam was explored. Maximum molecular weights of $M_w = 7.0 \times 10^5$ ($[\eta] = 11.2$) using the monofunctional chain initiator (Ac-CL) and $M_w = 9.5 \times 10^5$ ($[\eta] = 14.1$) using the bifunctional one (Ad-CL) were achieved. It was clarified that the molecular weight of the polymer depends on quantities of active molecular chains, and minimizing water content is necessary for maximal molecular weight, since water mainly terminates the propagation of the molecular chains. The essential conditions for maximum M_w are; (1) water content in ε-caprolactam should be below 0.013 mol%, (2) relation between the concentration of the catalyst and the chain initiator is important, and 0.1 mol% of the catalyst (EtMgBr) and 0.03 mol% (monofunctional) or 0.015 mol% (bifunctional) of the chain initiator are required, (3) 150°C is the most suitable polymerization temperature without decrease of the polymerization rate and without increase of side reactions.

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