

Multiple Injection Method for Bulk Syndiospecific Polymerization of Styrene with Homogeneous Metallocene Catalyst

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메탈로센 촉매를 이용한 신디오탁틱 폴리스타이렌의 벌크 중합에 관한 연구

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Abstract At the early stage of a bulk syndiotactic polymerization of styrene, the homogeneous reactant mixture transforms to a slurry state consisting of a precipitated solid syndiotactic PS and a liquid reactant mixture. As the reaction proceeds, the slurry transforms into a wet and then a dried powder if proper methods are used to prevent agglomeration. When a large amount of catalyst and co-catalyst is added to the styrene to achieve a high conversion rate, the reactant mixture becomes a lumpy agglomeration and further control of the reaction is impossible. In this study, we introduce a novel approach to avoid such agglomeration while maintaining a high conversion rate. Instead of adding the catalyst and co-catalyst at once, the total amount of the catalyst and co-catalyst is divided into several parts and added successively. This method is found to be very effective to avoid the formation of agglomerate and to maintain a fairly high conversion rate of slurry into powdery product (up to 70 %). It is also observed that this method produces syndiotactic PS of a higher molecular weight.

요약 신디오탁틱 폴리스타이렌의 벌크 중합 시, 반응의 초기단계에서 균일하던 반응혼합물은 반응이 진행됨에 따라 점차 침전된 고휘 sPS와 액체 반응생성물로 형성된 슬러리 상태로 변해간다. 반응이 더 진행되면 고휘 침전물의 양이 많아지고 반응물이 엉겨 붙는 현상을 적절한 방법으로 해소하면 슬러리 상태에서 젖은 분말 형태 더 나가서는 마른 분말 형태의 반응 생성물을 얻게 된다. 전환율을 높이기 위해 촉매와 조촉매의 양을 늘리는 경우 반응생성물은 어느 순간 한 덩어리가 되어 더 이상의 반응 제어가 불가능해진다. 이 연구에서는 이렇게 덩어리로 응집되는 현상을 막고 고 전환율의 반응이 가능하도록 특별한 방법을 사용하였다. 촉매와 조촉매를 한 번에 투입하지 않고 여러 단계로 나누어 투입하는 경우 반응물의 응집을 막고 전환율을 높게 유지할 수 있었다. 또한 이 방법은 sPS의 분자량을 높이는 데도 도움이 되는 것을 알 수 있었다.

Key Words : Syndiotactic Polystyrene, Metallocene Catalyst, Multiple Injection

1. INTRODUCTION

Syndiotactic polystyrene (sPS) is a new engineering thermoplastic having excellent properties, such as high modulus and excellent resistance to heat and chemicals, due to its crystalline nature. Ishihara et al.[1,2] first investigated the syndiospecific polymerization of styrene

by organotitanium compounds with methylaluminum-oxane(MAO) as a cocatalyst. Since then, many studies have been conducted on homogeneous catalysts producing sPS[3]. Several sPS polymerization methods have been introduced including solution polymerization[3], reaction injection molding[4,5], the bulk polymerization process[6,7], and slurry polymerization[8,9]. Solution

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polymerization, generally performed in dilute media, is adequate for the study of intrinsic catalytic behavior in a homogeneous catalytic system.

From a commercial viewpoint, however, bulk polymerization is preferable for several reasons. For example, the reaction apparatus for bulk polymerization is smaller and post treatments such as the solvent recovery process can be eliminated. Additionally, bulk polymerization can produce sPS of a much higher molecular weight because the concentration of monomer is maintained at a higher level than during solution polymerization. The reaction time for bulk polymerization is shorter because of the faster reaction rate. However, a major drawback is that it is not simple to obtain a final product that can be handled easily and conveniently. In sPS bulk polymerization, the whole reaction mixture tends to agglomerate into a global gel beyond the conversion of 10 % [6] and finally becomes a hard lump unless special techniques are employed. Once the gel-like form is produced, mixing and heat transfer are impossible; consequently, further control of the reaction is lost. Therefore, the prevention of the gel-like formation is extremely important in bulk polymerization.

In the bulk polymerization of sPS, the homogeneous reaction mixture (styrene + catalyst + cocatalyst) initially enters a slurry state consisting of precipitated solid sPS (formed by a crystallization process from solution to solid) and liquid reactant mixture. As the reaction proceeds, the slurry becomes a wet and then a dried powder if proper methods are used to prevent the formation of the gel-like product. It is reported that the ratio of the crystallization rate to the reaction rate is a crucial factor in the determination of the final form. When the reaction rate is faster than the crystallization rate (i.e. solidification rate), the reaction product assumes a gel-like form. Therefore, a faster reaction rate is unfavorable in terms of preventing the formation of a lump. A larger amount of catalyst provides a faster reaction rate and thus tends to form a lump. However, a small amount of catalyst leads to only a limited conversion. To overcome this dilemma, several methods have been tried. R. Fan et al. reported that the gel-like form is prevented at higher agitation speeds. They also reported that powdery sPS can be successfully obtained by using a reactor equipped with a two-screw ribbon anchor[7].

In our experiences, these two methods do work, but the improvement is less than satisfactory. Kinetic studies reveal that the reaction rate is the highest for only a very short period of the entire reaction time, generally at the earlier stage[7]. The remainder of the reaction period provides a slow reaction rate. If the peak reaction rate could be lowered while the average reaction rate over the entire reaction time was maintained at relatively high level, the possibility for agglomerate formation would be lowered without sacrifice of the conversion rate.

In this study, we introduce a novel strategy to achieve this goal. In this strategy, the catalyst is divided and injected in stages, rather than being injected at once. It was expected that this method would reduce the peak reaction rate and consequently prevent agglomerate formation while preserving the average reaction and conversion rates. Hereafter, we refer to this method as the multiple injection method.

2. EXPERIMENTAL

1.1 Materials

Styrene, phenylacetylene free grade, was donated from LG Chemicals. Phenylacetylene in styrene is known to reduce catalytic activity by acting as a catalytic poisoner[10]. The styrene was purified by letting it pass through an activated alumina column to eliminate moisture and inhibitors. Toluene was distilled after refluxing over sodium for 48h just before use. Methylaluminoxane(MAO) with 1 M Al in toluene solution was purchased from Tosoh Akzo and used without further purification. The Cp*Ti(OMe)₃ was purchased from Aldrich-Sigma and used in diluted toluene solution (5x10⁻²M Ti in toluene).

1.2 Polymerization

Polymerization experiments were carried out in a 1L glass reactor equipped with a water-circulating jacket for temperature control, a steel anchor-paddle impeller and rubber septums through which the monomer and catalyst were fed (see Fig. 1.(a)). The reactor was first filled with dried N₂ gas at the desired reaction temperature for about one hour. Styrene was bubbled with dried N₂ for several

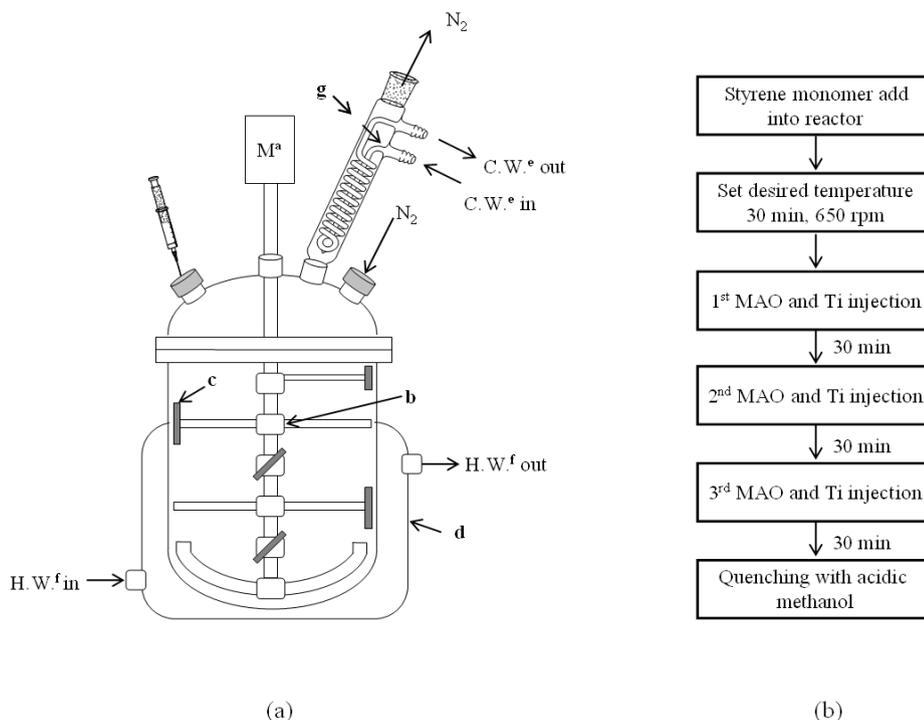
hours to remove any residual moisture before use.

100 ml of purified styrene was first introduced into the reactor. After the reactor was agitated for 30 minutes at 650 rpm, a predetermined amount of MAO was injected into the reactor, and subsequently a predetermined amount of metallocene catalyst ($Cp^*Ti(OMe)_3$) was injected into the reactor to start the polymerization. Total reaction time was 1.5 hours, with the exception of run 9 (2hrs). For all runs, the ratio of MAO to $Cp^*Ti(OMe)_3$ was maintained at a molar ratio of 100:1. For most runs, MAO and the catalyst were added two more times in the same order every 30 minutes (see Fig1.(b)). The molar amount of $Cp^*Ti(OMe)_3$ catalysts used in each polymerization step are described in Tables as experimental conditions. For example, in the case of run 6, the temperature was 70°C, and 6.0ml (equivalent to 6.0×10^{-3} mol Al) of MAO solution and 1.2 ml (6.0×10^{-5} mol Ti) of $Cp^*Ti(OMe)_3$ solution was added at 0 min. 2.0 ml (2.0×10^{-3} mol Al) of MAO solution and 0.4 ml (2.0×10^{-5} mol Ti) of $Cp^*Ti(OMe)_3$ was added again at 30min. Finally, 2.0 ml (2.0×10^{-3} mol Al) of MAO solution and 0.4 ml ($2.0 \times$

10^{-5} mol Ti) of $Cp^*Ti(OMe)_3$ was added at 60 min. Polymerization was then sustained for 30 more minutes. The reaction was terminated by the addition of acidified methanol. The resulting polymer was washed with methanol several times, filtered and dried in a vacuum oven at 80°C overnight. For several runs, the reactant agglomerated and became a lump. In those cases, the lump was ground into small particles (less than 0.2mm in diameter) and post-treated in same way as the powdery product.

1.3 Characterization

The polymer morphology was observed under an optical microscope (model: Olympus BX41) at a magnification of x 40 and a sample picture is shown in Fig. 2. Melting temperature was determined by DSC (model: TA Instruments DSC2010) at a heating rate of 20°C/min. The molecular weight of the polymer was inferred by measuring the viscosity in the apparent shear rate of 5 s^{-1} at 300°C



[Fig 1] (a) A schematic diagram of the polymerization apparatus. a: agitating motor, b : flat paddle type impeller, c: scraper, d: heating water jacket, e: cooling water, f: heating water, g: condenser. (b) A typical scheme of multiple injection method for sPS polymerization

[Table 1] The results of the sPS polymerization using multiple injection method

Run No.	T _r (°C)	Ti (mol) x 10 ⁵				yield _p (g) ^a	yield _l (g) ^b	Conversion _p (g) ^c	Powder form (%) ^d	Activity _p (Kg PS/mol Ti hrs) ^e	t ^f (min)
		1 st	2 nd	3 rd	4 th						
1	50	10	4	0	0	74.2	0.0	0	0	32	
2	50	10	2.5	0	0	35.7	10.8	39.3	76.8	-	
3	50	5	5	0	0	23.5	6.7	25.9	77.8	-	
4	70	7	0	0	0	0	56.1	0.0	0	4	
5	70	6.5	2	0	0	14.5	15.3	15.9	48.6	52	
6	70	6	2	2	0	31.3	0	34.4	100	-	
7	70	2	4	4	0	19.1	0	21.0	100	-	
8	70	1	4	2.5	0	19.3	13.8	21.2	58.2	-	
9*	70	1	4	2.5	2.5	20.5	10.5	22.5	66.6	-	
10	90	8	0	0	0	14.5	61.4	15.9	19	13	
11	90	4	3	3	0	56.5	4.9	73.3	92	-	

Catalyst: Cp*Ti(OMe)₃, Al(MAO)/Ti molar ratio=100, polymerization time=90min(except run9*=120min)

Tr: reaction temperature, yield_p (g)^a: yield for powdery product, yield_l^b: yield for lump product, Conversion_p^c: conversion of powder product, Powder form (%)^d: weight percent of powdery product, Activity_p(Kg PS/mol Ti hrs)^e: activity of powdery product, t^f: agitating stop time due to drastic formation of lump.



[Fig. 2] Sample picture of an optical microscope for run no. 3.

3. RESULTS AND DISCUSSION

The sPS polymerization results using the multiple injection method are summarized in Table 1. We investigated the polymerization behavior of sPS at three different reaction temperatures, but the majority of experiments were carried out at 70°C. It was not iced that there was a critical catalyst concentration beyond which a lump would be formed. When we injected the catalyst into the reactor with a concentration above the critical value, the reactant assumed a gel-like form and subsequently became a lump. Once the lump was formed, mixing of the reactant was impossible since the torque of the mechanical stirrer became infinite (run1, 4, 5 and

9). Moreover, it is not easy to remove the heat generated by an exothermic reaction. However, even after a lump was formed, we did not terminate the reaction, but allowed the polymerization to continue for a total of 1.5hours of polymerization time without further addition of the catalyst and co-catalyst. When the gel-like products were formed, the polymerization was limited by the diffusion rate of the styrene monomer, which might have been enclosed by the agglomerated sPS. Therefore, the reaction rate was expected to be very low in those circumstances. It was sometimes observed that the powdery form and the lumps coexisted near the critical concentration of the catalyst (e.g. run 2, 3, 5, and 8). The critical concentration was observed to decrease as reaction temperature decreased. As demonstrated by Fan et al., the reaction mixture agglomerates when the reaction rate is faster than the crystallization rate⁷(very relevant to solidification rate or precipitation rate from the sPS + styrene solution). Since the reaction rate of the sPS polymerization increases with rising temperature, it is not surprising that the critical concentration decreases with as reaction temperature decreases.

At 30 min after the first injection of the catalyst/co-catalyst, the second injection of the catalyst/co-catalyst was carried out. For the second injection, catalyst amounts smaller than the critical amounts for the first injection can sometimes still cause agglomeration. When agglomeration occurs at the second or third injection, the whole of the powdery reaction

product formed to that point tends to become encased in the lump, and almost no powdery product is obtained. Sometimes, the powdery product can still be obtained despite formation of a lump (e.g. run 5). It was found that the multiple injection method is an effective way to avoid lump formation. For example, when 10 mol of Cp*Ti(OMe)₃ was added all at once, a lump was formed at 70°C. However, when we divided the 10 mol into 6.0+2.0+2.0 mol or 2.0+4.0+4.0, lump formation could be avoided. It was observed that the conversion to powdery product increases with the total amount of Cp*Ti(OMe)₃ and as reaction temperature increases(compare runs 4, 5 and 6). Therefore, the multiple injection method is very good strategy to avoid lump formation, while maintaining a fairly high conversion rate to powdery product..

It was also found that the multiple injection method provides sPS of higher molecular weight. This is another benefit of the multiple injection method (compare run 4 vs. 5 and run 10 vs. 11 in 4.2.). It is well known that the lower concentration of catalyst in the syndiotactic polymerization of styrene generates higher molecular weight[7]. Thus, it is inferred that the multiple injection method maintains the catalyst concentration at a lower level than that of the whole injection method.

It is somewhat surprising that the total conversion rate is much higher when agglomeration occurs (see run 1, 4, and 10). This is inconsistent with the study by Fan et al.[6,7]. It seems that Fan et al. stopped the reaction as soon as the agglomerate occurred. When agglomeration occurs, the reaction product becomes a gel-like form consisting of amorphous-phase sPS and styrene captured

in the sPS phase, as shown by Fan et al.[6,7]. Because the reaction is exothermic and heat transfer is not easy, the temperature in the lump is high (most probably higher than T_g), so that diffusion of styrene in the amorphous sPS phase is enhanced and reaction can continue. On the other hand, when powdery (crystallized) sPS is formed, part of the catalyst and co-catalyst is captured in the crystalline phase, so that catalytic activity is reduced. Moreover, the temperature of the reactant in this case was much lower than that during lump formation. Although lump formation must be avoided at the mass production scale, it is worth investigating this kind of a solid state polymerization in detail because the research may provide the easiest way to produce sPS at a laboratory scale.

The average particle size and the standard deviation of the powdery product were obtained from optical microscopy observation and are presented in Table 2. The crucial factor affecting morphology was observed to be the reaction temperature. The multiple injection method seems not to alter the polymer morphology much. The average size of the powdery sPS tends to decrease with the reaction temperature.

In this study, it was found that the multiple injection of the catalyst and co-catalyst provides several benefits. Due to experimental limitations, our multiple injections of the catalyst/co-catalyst were constrained to four portions. We think that more frequent injections of the catalyst/co-catalyst divided in many parts would produce better results. Ultimately, a continuous feeding of the catalyst/co-catalyst during the whole polymerization period would be the best way. This may be possible in

[Table 2] The characterizations of produced sPS using multiple injection method

Run No.	T _r (°C)	Ti (mol) x 10 ⁵				d _n ^a (μm)	σ ^b	η (kPa.s) ^c		T _m (°C) ^d	
		1 st	2 nd	3 rd	4 th			powder	lump	powder	lump
1	50	10	4.0	0.0	0.0	16.5	1.3	-	38.3	-	271.5
2	50	10	2.5	0	0	18.4	9.7	76.4	86.9	269.3	268.0
3	50	5	5	0	0	17.4	9.4	83.7	n. m.	269.9	271.1
4	70	7	0	0	0	-	-	-	13.4	-	270.1
5	70	6.5	2	0	0	n. m.	n. m.	29.3	24.7	269.9	269.3
6	70	6	2	2	0	n. m.	n. m.	20.0	-	269.0	-
7	70	2	4	4	0	n. m.	n. m.	15.2	-	269.0	-
8	70	1	4	2.5	0	21.9	10.6	8.8	11.8	270.9	270.3
9	70	1	4	2.5	2.5	15.9	4.1	24.3	28.4	269.2	269.1
10	90	8	0	0	0	13.5	4.7	0.96	1.05	271.8	271.7
11	90	4	3	3	0	10.6	2.3	8.13	15.3	270.6	271.3

T_r: reaction temperature, d_n^a: average particle size, σ^b: standard deviation of particle size distribution, η^c: viscosity at 5 s⁻¹, T_m^d: melting point. n.m. means not measured.

mass production using a well-controlled metering pump.

The absolute molecular weights of the sPS prepared in this study were not measured. However, they can be inferred by measuring the viscosity of the sPS melts. The results are shown in Table 2. First of all, it was noted that the molecular weight of the sPS was much affected by the reaction temperature. Higher polymerization temperature produced sPS of lower molecular weight. This is consistent with many studies¹¹. The molecular weight is not relevant to the protocols for the injection of the catalyst. Interestingly, the molecular weights of the lump and the powdery product do not show a large difference when the lump and powdery product are formed at the same time. Also, the molecular weight of the lump itself is fairly high. Given this result, we do not agree with the previous studies[6,7] that the polymerization reaction cannot proceed once the gel-like product is formed. As discussed above, it was observed that the reaction proceeds even after the gel-like products are formed. According to Schellenberg's work[12], the syndiotacticity is linearly correlated with the melting temperature(T_m) of the sPS, and the T_m of sPS having 100% syndiotacticity is about 270°C. Syndiotacticities of the sPSs synthesized in this study were, most likely, at least higher than 97% since the melting temperatures were mostly near 270°C.

3. CONCLUSIONS

We successfully synthesized sPS by bulk polymerization through a novel multiple injection method. This novel approach was intended to avoid agglomeration, while maintaining a fairly high conversion rate. Rather than adding the catalyst and co-catalyst at once, the total amount of the catalyst and co-catalyst was divided into several parts and added successively. This method was found to be very effective for preventing the formation of agglomerate and maintaining a fairly high conversion to powdery product. It was also observed that this method produces syndiotactic PS of a higher molecular weight.

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