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Studies on the catalyst modification in propylene polymerization using ethylene-propylene copolymerization

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SUMMARY

Ethylene-propylene copolymerizations were carried out using conventional and high activity supported Ziegler-Natta catalysts to examine the reduction of Ti(III) to Ti(II) by aluminum alkyls, which has been considered as a main reason for the catalytic activity decay in propylene polymerization. For the catalyst system cocatalyzed with DEAC, the reduction was negligible regardless of the catalyst types, while an irreversible catalyst modification such as the reduction reaction occurred significantly for the catalyst with TEA.

INTRODUCTION

The rate decay of propylene polymerization has been explained with the augmentation of monomer diffusion path owing to the accumulation of polymer layer around the catalyst particles(1). Ray et al.(2,3) simulated the material and heat transfer with multigrain model which corresponds to the morphology of the polymer particles and predicted negligible mass and heat transfer resistances for the conventional Z-N catalysts.

Doi et al.(4) was the first to show experimentally using a $MgCl_2$ supported Z-N catalyst that the rate decrease is not due to the increase in mass transfer resistance. They observed the propylene polymerization rate decreasing even in the absence of monomer after a certain time of polymerization. Same kind of experiment has been done by Choi and Ray(5) with $TiCl_3$ $1/3AlCl_3$ catalyst system. The activity decay has been attributed to an overreduction of Ti(III) to Ti(II) by aluminum alkyls, because the latter is inactive for propylene polymerization. Poluboyarov et al.(6) observed that the peak of ESR spectrum corresponding to Ti(II) became pronounced as the polymerization proceeded.

Many researchers studied on the activity decay of Z-N catalysts(7-13) and reported different results depending on the types of the catalysts. Kashiwa et al.(7) reported that the reaction between triethylaluminum(TEA) and ethylbenzoate(EB) as well as the reduction reaction provoked the rate decrease of propylene polymerization over $MgCl_2$/EB/$TiCl_4$-TEA/EB catalyst system. Tang(8) showed that the rate of decrease in active site concentration of $TiCl_3TiCl_4nBu_2O$/DEAC and $TiCl_31/3AlCl_3$catalysts was similar to that of polymerizing activity decay, from which he concluded the rate decrease was due to the decrease in active site concentration. Yoon and Ray(12) aged $TiCl_31/3AlCl_3$ in 25 wt% DEAC solution at 70°C for 22 hours and showed there was little or no effect of DEAC on the catalyst deactivation in the absence of polymerization. However aging the catalyst with TEA gave rise to a significant rate decay. Therefore it seems that the reduction reaction is important when TEA is used as a cocatalyst, but such a reaction is trivial, if present, when DEAC is employed as a cocatalyst.

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To confirm this point, we performed ethylene-propylene copolymerization because Ti(III) polymerize propylene as well as ethylene, but Ti(II) is active only for ethylene polymerization(14,15). The significance of the reduction of titanium species can be tested by measuring the composition of the copolymers.

EXPERIMENTAL

Ethylene-propylene copolymerizations were carried out in a n-hexane slurry reactor of 2 liter capacity. Propylene was fed into a 2 liter mixing chamber to a certain pressure followed by ethylene introduction so that the final total pressure be 13 kg/cm^2. To keep away from condensation of the monomers, temperature of the mixing chamber was maintained at 95^{o}C. The polymerization time was kept to be less than 10 minutes to minimize the variation of monomer composition. The composition of monomers was calculated using Benedict-Webb-Rubin equation and bubble point calculation method.

Copolymer composition was determined using the ratio of absorbance of IR spectra at 1155 cm^{-1} and 720 cm^{-1} with reference to the calibration curve obtained with proton nmr spectra. Due to the contribution of propylene unit mesodyad to the peaks of the proton nmr spectra, a small error could be present for the copolymers of very high propylene content(16).

For DSC thermograms, samples were heated to 200^{o}C at a rate of 10^{o}C/min and kept at that temperature for 10 minutes. Then the samples were cooled slowly down to room temperature. The thermograms were obtained by reheating the samples at a rate of 10^{o}C/min.

RESULTS AND DISCUSSION

Four types of catalysts were employed for the ethylene-propylene copolymerization, which are currently used industrially for polypropylene production.

$TiCl_3$1/3 $AlCl_3$(Stauffer catalyst)-DEAC
$Mg(OEt)_2/DIBP/TiCl_4$(supported catalyst)-DEAC
$TiCl_3$1/3$AlCl_3$(Stauffer catalyst)- TEA
$Mg(OEt)_2/DIBP/TiCl_4$(supported catalyst)-TEA

The variation of activity of the catalysts after a certain time of aging in the aluminum alkyl solution was shown in figure 1. The copolymerization rate decreased significantly with aging time when TEA was used as a cocatalyst, while it was almost invariable in DEAC solution regardless of the types of the catalysts. However as figure 2 demonstrates, the copolymerization rate diminishes with polymerization time irrespective of the catalyst-cocatalyst systems. It could be seen that the catalyst with TEA lost its activity with polymerization time as well as duration of aging. However for the catalyst with DEAC, aging did not modified the activity of the catalyst, while the polymerization rate decreased steadily with reaction time. Yoon and Ray(12) explained the difference in the rate behavior for the Stauffer-DEAC system with competitive absorption of DEAC and the byproduct of chain transfer to DEAC reaction onto the active site. Their model simulated well many experimentally observed results such as rate decrease in the absence of monomer or rate increase with further addition of DEAC after a certain time of polymerization.

Effects of aging time on the propylene contents of the coplymers are drawn in figure 3. Gas phase monomer composition was fixed to be 0.25/0.75 for ethylene/propylene. The copolymer obtained with the supported catalyst had lower propylene content than that with the Stauffer catalyst. Figure 4 exhibits the effect of the polymerization time on the accumulated composition of the copolymers. For each experiment catalyst loading was adjusted to obtain almost same quantity of copolymer irrespective of the duration of

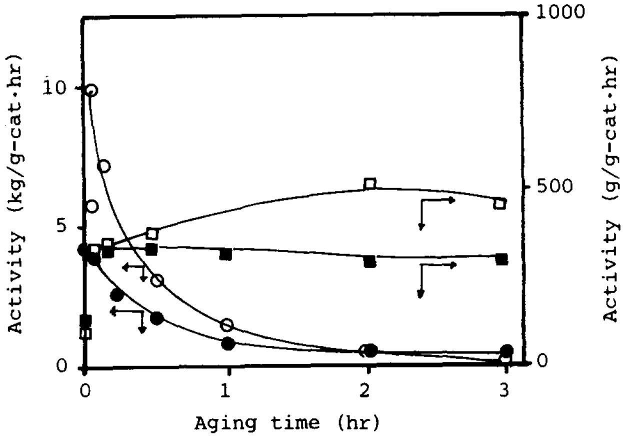

Fig. 1. Effects of aging on the activity of the catalysts.
O–O $Mg(OEt)_2/DIBP/TiCl_4$-TEA; ●–● Stauffer-TEA; □–□ $Mg(OEt)_2/DIBP/TiCl_4$-DEAC; ■–■ Stauffer-DEAC

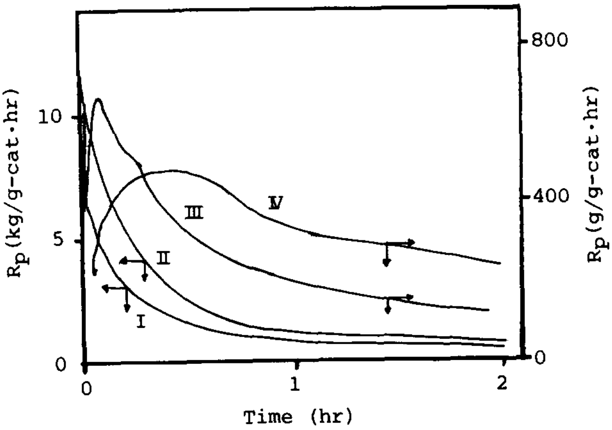

Fig. 2. Variation of polymerization rate with polymerization time.
I Stauffer-TEA;
II $Mg(OEt)_2/DIBP/TiCl_4$-TEA
III Stauffer-DEAC
IV $Mg(OEt)_2/DIBP/TiCl_4$-DEAC

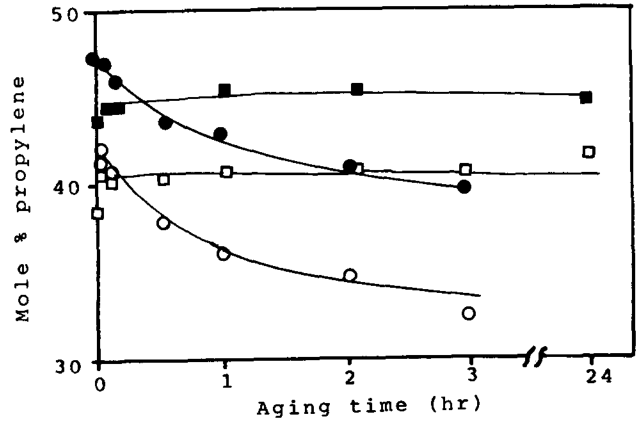

Fig. 3. Effects of Aging time on the propylene content of ethylene-propylene copolymers.
O–O $Mg(OEt)_2/DIBP/TiCl_4$-TEA
●–● Stauffer-TEA
□–□ $Mg(OEt)_2/DIBP/TiCl_4$-DEAC
■–■ Stauffer-DEAC

polymerization. It is to be noted that the propylene content in the copolymer remained constant with even 24 hours of aging and polymerization time, when the catalysts were cocatalyzed with DEAC, while it decreased significantly for the catalyst with TEA. Therefore the rate decrease of polymeriza-

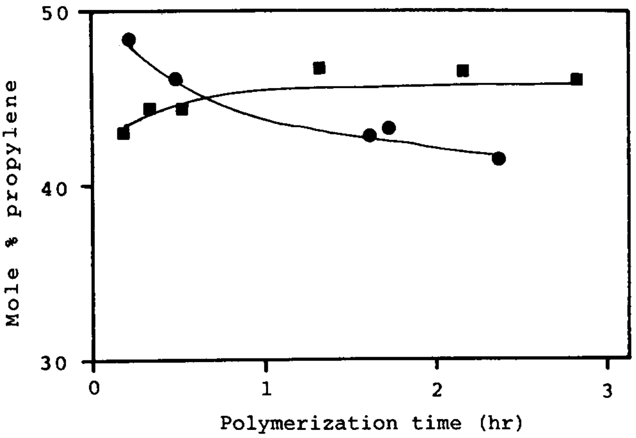

Fig. 4. Variation of the accumulated propylene content of the ethylene-propylene copolymers polymerized over ●—● Stauffer-TEA and ■—■ Stauffer-DEAC catalysts as a function of polymerization time. The quantity of the copolymers produced was kept almost constant for each experiment.

tion with TEA can be thought to be due to the reduction of Ti(III) to Ti(II) reaction. It is also possible that an irreversible redistribution of Ti(III) site having different activity and reactivity ratio toward ethylene and propylene polymerization would cause the rate decrease and change in the copolymer composition as well. However it is clear that such an irreversible catalyst modification is absent during aging and polymerization, when DEAC is employed as a cocatalyst.

The fact that the activity decay of the catalyst with DEAC does not occur during aging period before monomer introduction, in spite that the rate decreased continuously even in the absence of monomer when the polymerization began implies that the initiation of ethylene and propylene polymerization does not proceed in the absence of monomer. Kohara et al.(9) supposed also that the monomer presence is needed for the initiation of propylene polymerization.

Figure 5 and 6 show DSC thermogram of the copolymers, which are typical thermograms for ethylene-propylene copolymers produced with a stereospecific catalyst. A mixture of ethylene-propylene homopolymer or ethylene-propylene block copolymer exhibits two endothermal peaks of DSC thermogram at around 130 and 160°C. Therefore present copolymers are random ones because there appears only one endothermal peak at around 125°C. These figures also demonstrate that the endothermal peak moved to a higher temperature region for the Stauffer-TEA catalysts, which implies the production of cop-

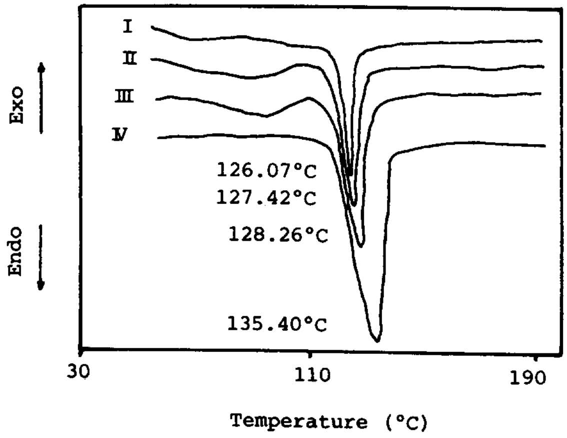

Fig. 5. DSC thermograms of the ethylene-propylene copolymers produced with Stauffer-DEAC catalysts as a function of aging time.

I	24 hours
II	1 hour
III	5 minutes
IV	ethylene homopolymer

olymers progressively rich in ethylene, while the opposite is true for the Stauffer-DEAC catalysts.

Though it is not very clear, because the position of the melting peak of the copolymers does not differ significantly from that of ethylene homopolymer, there does not seem to appear any inflection point of the thermogram at around 130°C even with a catalyst aged in TEA solution for a long time. This seems to be due to the fact that Ti(II) is only weakly active or due to the lowering of melting point of ethylene homopolymer forming polymer blend of ethylene-propylene copolymer and ethylene homopolymer.

The composition of the copolymers obtained with the Stauffer-DEAC catalyst remained unchanged with aging time. However their DSC endothermal peak moved to a lower temperature region as the aging went on. From this observation, the aging of catalysts seemed to affect the active site distribution of the catalysts, because the endothermal peaks of the copolymers depend not only on the copolymer composition but also strongly on its distribution(17).

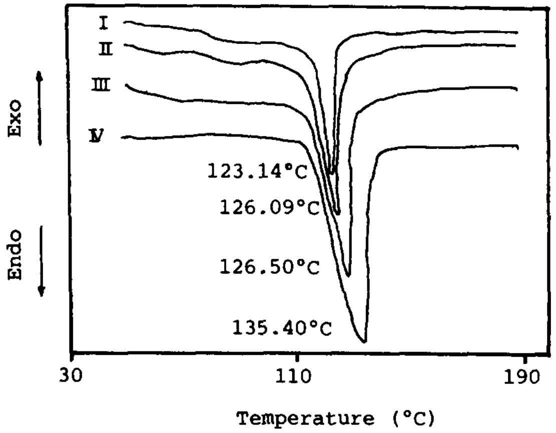

Fig. 6. DSC thermograms of the ethylene-propylene copolymers produced with Stauffer-TEA catalysts as a function of aging time.

I no aging
II 30 minutes
III 3 hours
IV ethylene homopolymer

CONCLUSION

Ethylene-propylene copolymerization rate decreases and the copolymers produced become more rich in ethylene unit with aging time as well as polymerization time regardless of the catalyst type when TEA is used as a cocatalyst, which is a confirmation that an irreversible catalyst modification such as the reduction of Ti(III) to Ti(II) reaction occurs during polymerization.

The copolymerization rate remains unchanged with aging time, while it diminishes as the polymerization proceeds when DEAC is employed as a cocatalyst. The composition of the copolymers remained invariable for both of the supported and the Stauffer catalyst, which implies absence of the reduction reaction in this catalyst system during the polymerization.

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