

COPOLYMERIZATION OF PROPYLENE WITH HINDERED PIPERIDINE MONOMER OVER A HIGH ACTIVITY SUPPORTED ZIEGLER-NATTA CATALYST

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ABSTRACT

Copolymerization of propylene and hindered piperidine monomers was carried out over a high activity supported Ziegler-Natta catalyst, using $\text{Al}(\text{C}_2\text{H}_5)_3$ as cocatalyst. Factors which affect the copolymerization were studied. The copolymers exhibited high light stability without adding extra light stabilizers. A self-stabilized polypropylene was prepared.

INTRODUCTION

In order to improve the light stability of plastics, some light stabilizers should be added. But the concentration of the light stabilizers will decrease during the processing and after long time use. The decrease in light stabilizers content caused by physical loss through diffusion with subsequent volatilization, solvent (or water) extraction is more serious than it consumes during the course of stabilization^[1]. Although light stabilizers with high molecular weight can minimize the physical loss, it can not be improved thoroughly^[2-3]. The most effective method to prevent from physical loss is to prepare polymers with chemically bound light stable group. Usually it can be realized by the process of free radical polymerization. But it is difficult to prepare them by high actively complex catalysts, such as Ziegler-Natta catalyst, because the polar moiety of the stabilizer will deactivate the active sites and inhibit the polymerization.

Some patents reported that they had succeeded in the polymerization of α -olefins over Ziegler-Natta catalyst in the presence of sterically hindered piperidine light stabilizer^[4-7], attempts to introduce light stable group into the polymer chain

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were almost not successful. Spitz and Proto et al. used the piperidine compound as external modifier in Ziegler-Natta catalysts, but the excess amount of piperidine compound added depressed the catalyst activity^[8-10].

Recently, Wilen and his co-workers reported their results of copolymerization of propylene and sterically hindered piperidine monomer over a high activity supported Ziegler-Natta catalyst^[11].

In this paper we synthesized the hindered piperidine monomers, such as 4-allyloxy-2,2,6,6-tetramethylpiperidine, 4-allyloxy-1,2,2,6,6-pentamethylpiperidine through a simple way. Copolymers of propylene and those hindered piperidine monomers over a high activity supported Ziegler-Natta catalyst were prepared. The photostabilizing efficiency of the copolymers was examined.

EXPERIMENTAL

1. Materials

Ziegler-Natta catalyst (CS-1) was prepared from $\text{MgCl}_2 \cdot \text{EH}$ (2-ethylhexanol)/PA (phthalic anhydride)/ TiCl_4 /BP (diisobutyl phthalate) according to the reference [12].

4-hydroxy-2,2,6,6-tetramethylpiperidine and 4-hydroxy-1,2,2,6,6-pentamethylpiperidine were industrial grade products and recrystallized with acetone, m.p.: 129—130°C and 79—79.1°C, respectively.

Propylene was commercially obtained and used without further purification.

All other chemicals used for preparation and polymerization were reagent grade and obtained from Beijing Chemical Factory. Heptane and some other chemicals were dried with 0.4 nm molecular sieves.

2. Preparation of 4-allyloxy-1,2,2,6,6-pentamethylpiperidine (M_1) and 4-allyloxy-2,2,6,6-tetramethylpiperidine (M_2)

To a 3-necked 500 ml flask, equipped with magnetic stirrer, reflux condenser and thermometer, 180 ml tetrahydrofuran, 68.5 g (0.4 mol.) 4-hydroxy-1,2,2,6,6-pentamethylpiperidine were charged, and 32 g metal potassium was added in batches. Then the mixture was heated under reflux and stirring for 12 h. After that, 48.4 g (0.4 mol.) allyl bromide was added dropwise over 2 h period. The reaction mixture was stirred for another 2 h under reflux temperature. At the end of the reaction, the mixture was cooled to room temperature and 40 ml ethanol was added dropwise to it for decomposing the unreacted potassium. The white solid (KBr) was filtered off. The solvent and excess of allyl bromide was removed by distillation. 65 g (77%) of 4-allyloxy-1,2,2,6,6-pentamethylpiperidine was obtained by vacuum distillation: bp.

70°C (20 Pa). NMR spectra was carried out using a EM-360L NMR spectrometer at room temperature, CCl_3 as solvent and TMS as internal standard. IR spectra was obtained using a Perkin Elmer 683 spectrophotometer.

Elementary analysis:

Theoretical C 73.81%, H 11.83%, N 6.62%

Found C 74.14%, H 11.17%, N 6.75%

^1H NMR (ppm) 1.1—1.25; 2.0—2.2; 5.0—5.3

IR (cm^{-1}) 1650; 1080.

For M_2 , the procedure and ingredients were the same as in the preparation of M_1 except that the 4-hydroxy-2,2,6,6-tetramethylpiperidine was used instead. 4-allyloxy-2,2,6,6-tetramethylpiperidine was obtained by vacuum distillation: bp. 64°C (40 Pa), yield: 66%.

Elementary analysis:

Theoretical C 73.05%, H 11.75%, N 7.10%

Found C 73.15%, H 11.84%, N 7.20%

^1H NMR (ppm) 1.1; 2.0; 5.1—5.2

IR (cm^{-1}) 1660; 1080; 3320.

3. Copolymerization of propylene and hindered piperidine monomers

Copolymerization was carried out at 50°C in a 500 ml glass reactor equipped with a mechanical stirrer. The reactor was evacuated and charged with pure and dried nitrogen for three times. Finally, at the propylene atmosphere 50 ml n-heptane, measured amount of hindered piperidine monomer, $\text{Al}(\text{C}_2\text{H}_5)_3$ were added. The mixture was stirred for 3 minutes at 50°C. Then a measured amount of dimethoxydiphenylsilane(DDS), CS-1 catalyst and 50 ml n-heptane were added to start the polymerization. Propylene was supplied continuously and kept the partial pressure of reactor at 53.3 KPa. After 1 h the copolymerization mass was quenched with 100 ml of ethanol.

The formed copolymer was filtered and washed with ethanol and hexane 3 times respectively, then dried in vacuum. The isotacticity index (I.I) was determined as the insoluble fraction in boiling n-heptane.

4. Determination of photostabilizing efficiency

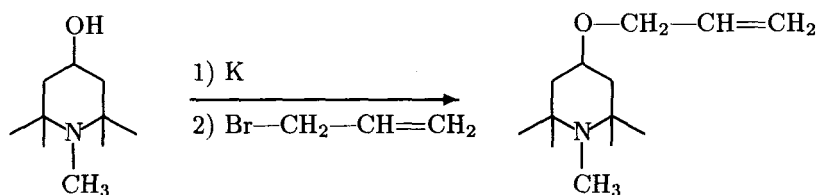
Preparation of sample: antioxidant and calcium stearate was dissolved in acetone. The solution was mixed with copolymer powder. The solvent was removed by evaporation under reduced pressure. The mixture was dried further in vacuum. Then, it was pressed at 180°C into 110 μm thick film.

Photooxidation: The PP film samples were placed on a rotating plate and

exposed under a 375 W high pressure mercury lamp. A Pyrex glass filter was used to cut off light of wavelength shorter than 290 nm. The test temperature was about 50°C. Photooxidation was monitored by using a Perkin Elmer 983G IR spectrometer at wavenumber of 1710 cm^{-1} .

RESULTS AND DISCUSSION

The high activity supported Ziegler-Natta catalyst is easily attacked by the polar moiety of the stabilizer, such as amine group of piperidine. As the active sites are deactivated by the formation of stable complexes between the initiator compounds and the stabilizer molecule, thus the polymerization is inhibited. For the sake of decreasing the electron donating character of the amine, a piperidine monomer containing four methylene group between the double bond and piperidine ring was synthesized by Wilen. But the synthetic process was too complicated and long. There are six steps for preparing the piperidine monomer and the overall yield is only 10% based on 2,2,6,6-tetramethylpiperidone. We consider that the deactivation can be prevented by increasing the steric encumbrance about the heteroatom of piperidine ring. Therefore, a piperidine monomer having high steric encumbrance, 4-allyloxy-1,2,2,6,6-pentamethylpiperidine (M_1), was synthesized and 4-allyloxy-2,2,6,6-tetramethylpiperidine (M_2) was also prepared for comparison. The synthetic route is illustrated in Scheme 1.



Scheme 1

We can see from scheme 1 that only one step is needed for preparing M_1 and the yield (77%) is high.

The results of propylene polymerization in the presence of hindered piperidine monomer M_1 or M_2 are presented in Table 1. In our system, according to the conditions presented in Table 1, in comparison with that of propylene polymerization the yield is decreased by 46% when in the presence of 0.008 mol/L of M_2 . But in the case of M_1 , a high yield, 6.0 kg/g·Ti·h was obtained which is very close to the yield of propylene polymerization. It is clear that increasing the steric encumbrance

about the heteroatom has a great effect for decreasing the influence of heteroatom on the catalyst activity. The isotacticity of copolymers has no change in both cases.

Table 1 Copolymerization of propylene and piperidine monomers (M)

Type of M	Amount of M in heptane (mol/L)	Yield (kg/g·Ti·h)	I.I (%)
		6.7	98.5
M ₁	0.008	6.0	96.5
M ₂	0.008	3.6	97.0

Polymerization condition: cat. 0.18 g, Al/Ti = 200(mol), Al/DDS = 10 (mol), Temp. 50°C, Time 1h. Propylene was supplied continuously and kept the partial pressure of reactor at 53.3 KPa.

Table 2 Influence of Al/Ti mole ratio on the yield of copolymerization

Type of M	Amount of M in heptane (mol/L)	Al/Ti (mol)	Yield (kg/g·Ti·h)
M ₁	0.008	100	3.6
M ₁	0.008	150	5.0
M ₁	0.008	200	6.0
M ₂	0.008	100	2.2
M ₂	0.008	150	2.7
M ₂	0.008	200	3.6

Polymerization condition: cat. 0.18 g, Al/DDS = 10 (mol), Temp. 50°C, Time 1 h Propylene was supplied continuously and kept the partial pressure of reactor at 53.3 KPa.

Table 2 shows the influence of Al/Ti on the yield of copolymerization. Whether M₁ or M₂, the yield of copolymerization is increased with the raising of the Al/Ti molar ratio. High Al/Ti molar ratio means high concentration of organic aluminum compound in the system, number of active center will increase with the concentration of aluminum compound. At the same time, high concentration of organic aluminum will make it easy to complex with piperidine monomer and decrease the influence of amine group on the catalyst activity as showed by Wilen's work. On the other hand, the yield of copolymerization of M₁ shows a great increase compared with M₂. That is to say, increasing of steric encumbrance about the heteroatom is a more effective method to decreasing electron donating character and to prevent from decreasing the activity of polymerization.

It was found that besides the structure of piperidine monomer and Al/Ti mole ratio, the charging time of piperidine monomers also had notable influence on the yield of copolymerization. The results are shown in Table 3. From Table 3 we can see that even in the case of lower Al/Ti and high concentration of M₁ (0.08 mol/L),

if we added the monomer at the time of 30 or 50 min. after the beginning of copolymerization, a satisfactory yield was obtained. The isotacticity index of copolymer is almost the same as that of the polypropylene.

Table 3 Influence of charging time of piperidine monomer (M_1) on the yield of propylene polymerization

No.	Time (min.)	Amount of M_1 in heptane (mol/L)	Yield (kg/g·Ti·h)	I.I (%)
1	10	0.008	2.7	96.6
2	30	0.008	6.8	97.3
3	50	0.008	6.9	96.3
4	10	0.08	2.4	
5	50	0.08	5.0	

Polymerization condition: cat. 0.18g, Al/Ti=100 (mol), Al/DDS=10 (mol), Temp. 50°C, Time 1h. Propylene was supplied continuously and kept the partial pressure of reactor at 53.3 KPa.

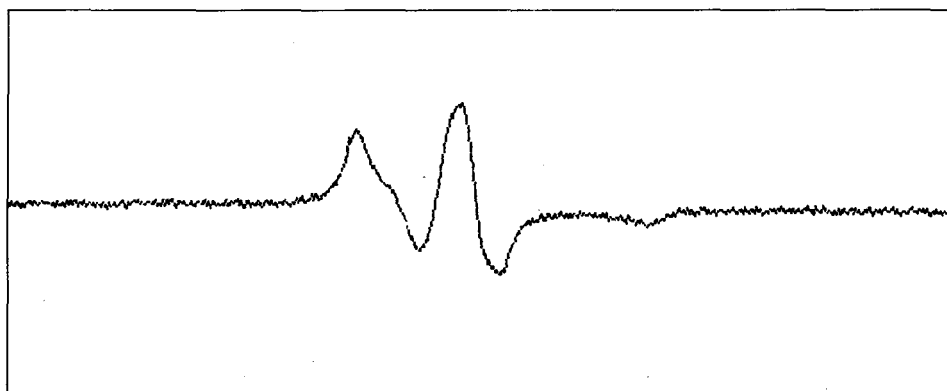


Fig. 1 ESR signal of copolymer of propylene and M_1 (Sample No. 1 in Table 3)

Wilen reported that the contents of HALS (hindered amine light stabilizer) in the copolymer were 1.9% (wt.) determined by Kjeldahl method. Since the N% (wt.) for piperidine monomer, 4-(hex-5-enyl)-2,2,6,6-tetramethylpiperidine, is 6.27% (wt.), a copolymer contains 1.9% (wt.) HALS means that the N% (wt.) in the copolymer is only 0.12% (wt.). It may be impossible to determine such a small amount of nitrogen by Kjeldahl method. In fact, only about 0.3—0.5% (wt.) HALS is needed for stabilizing polypropylene. It is difficult to determine the stabilizing group bound in polypropylene by usual method. We have tried to determine it by ESCA, NMR and Element analysis. But unfortunately, they were unsuccessful. Therefore, we have made a qualitative analysis by ESR method. At first, the copolymer (sample

No. 1 in Table 3) oxidized with aqueous hydroperoxide in the presence of sodium tungstate.^[13] Then the oxidized copolymer was determined by ESR. Fig. 1 showed the ESR signal of copolymer in the solid state. Because the copolymer was washed for several times at the end of polymerization and the hydroperoxide oxidation process with heptane, ethanol and other organic solvent, so we believe that the nitroxyl radical signal represents the nitrogen of piperidine ring bound in the copolymer. Fig. 2 shows the photostabilizing efficiency of copolymer. We can see from Fig. 2 that copolymer without adding extra light stabilizers exhibits excellent photostabilizing efficiency. The oxidative induction period (carboxyl index=0.5) of the copolymer is nearly 3 times more than polypropylene. It is shown that the copolymer has self-stabilized function and is a self-stabilized polypropylene.

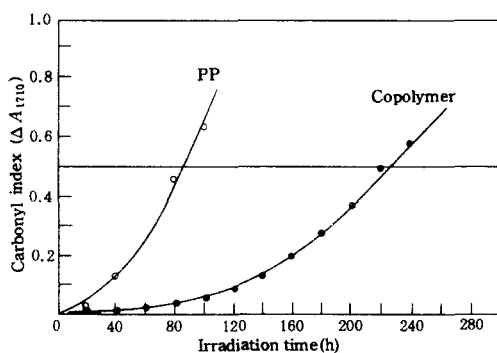


Fig. 2 Photostabilizing efficiency of copolymer of propylene and M₁ (sample No. 1 in Table 3)

CONCLUSION

1. Copolymerization of propylene and hindered piperidine monomer over a high activity supported Ziegler-Natta catalyst was carried out with high yield even in the presence of high concentration of hindered piperidine monomer (M₁), such as 0.08 mol/L. The isotacticity index of copolymer is almost the same as that of the polypropylene.

2. According to our results, it is shown that increasing steric encumbrance about the heteroatom of piperidine ring is a more effective method to decreasing electron donating character and to prevent from decreasing the activity of polymerization.

3. The copolymer without adding extra light stabilizers exhibits excellent photostabilizing efficiency. A self-stabilized polypropylene was obtained.

Keywords:

Ziegler-Natta catalyst; Propylene copolymerization; Hindered piperidine; Chemically bound stabilizer; Self-stabilized polypropylene

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