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ORIGINAL PAPER

Synthesis of novel polymeric HALS stabilizers and chain transfer effect of hindered amine norbornene derivatives on ring-opening metathesis polymerization

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Abstract Cyclooctadiene (COD) was polymerized via ring-opening metathesis polymerization (ROMP) in the presence of 5-norbornene-*exo*, *endo*-2-carboxylic acid 2,2,6,6-tetramethyl-4-piperidinyl ester (**PN**) or 5-norbornene-2-*exo*-3-*endo*-dicarboxylic acid bis(2,2,6,6-tetramethyl-4-piperidinyl) ester (**2,3-PN**) to prepare a new kind of polymeric hindered amine (HALS) stabilizers. Unexpectedly, hindered amine norbornene derivatives **PN** and **2,3-PN** did not act as comonomer but acted as chain transfer agent (CTA). The resulting polymers were characterized by gel permeation chromatography (GPC) and ^{1}H-NMR. Investigation of polymerization behavior showed that hindered amine groups were introduced into polymer chain by virtue of chain degradation resulted from chain transfer. The molecular weight (M_n) and HALS content of the resulting polymeric HALS stabilizer could be regulated by varying molar ratio of initial monomer to catalyst.

Keywords Hindered amine · Polymeric stabilizer · Chain transfer · Ring-opening · Metathesis polymerization

Introduction

It is well known that hindered amine light stabilizers (HALS) based on 2,2,6,6-tertramethylpiperidine structure are generally the most effective stabilizers for a large number of commercial polymers. Additives bearing HALS were usually added into polymer products to prevent them from degradation caused by oxygen, processing and ultraviolet. However, conventional low molecular weight HALS stabilizers vaporize easily and have poor extraction resistance. Consequently, they

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migrate and leach out from the polymer matrix, emit harmful amine by evaporation or extraction during the processing and end use. In order to achieve long-term stabilizing effect and avoid potential toxicity caused by physical loss of additives, polymeric HALS stabilizers have gained much interest to minimize the physical loss and to enhance compatibility and durability in recent years [1–4]. Various kinds of polymeric HALS were prepared by copolymerization of vinyl monomers containing HALS group [5–7]. Other polymeric HALSs were obtained by polycondensation or addition polymerization [8]. Alternatively, many polymeric HALS can be prepared through graft modification of preformed polymers [9–12]. More general reference covered recent advances in synthesis and stabilization on polymers of HALS [13–15]. There have been many arguments around the optimum molecular weight. In addition, as a special functional polymer, the design of main chain structure playing an important role in compatibility and diffusion of HALS is still imperative. Taking advantage of ring-opening metathesis polymerization (ROMP), a novel polymeric HALS bearing alkene and cycloalkyl in main chain was prepared. 5-norbornene-*exo*, *endo*-2-carboxylic acid 2,2,6,6-tetramethyl-4-piperidinyl ester (**PN**) and 5-norbornene-2-*exo*-3-*endo*-dicarboxylic acid bis(2,2,6,6-tetramethyl-4-piperidinyl) ester (**2,3-PN**) were synthesized and subjected to copolymerization with cyclooctadiene (COD) by sequential addition via ROMP to give polymeric HALS stabilizer. Unexpectedly, **PN** and **2,3-PN** didn't act as cycloolefin monomer to give block copolymer or statistic copolymer but acted as chain transfer agent (CTA) to give random copolymer. Degradation of macromolecule PCOD resulted from CTA not only causes a reduction in the molecular weight but also successfully transfers HALS group from **PN/2,3-PN** to the PCOD's chain. As far as we know, single olefinic compound such as allyl acetate and 1, 4-diacetoxy-2-butene acted as CTA in ROMP to prepare end functional polymers [16–18]. Herein, cycloolefin derivatives **PN** and **2,3-PN** endowed with chain transfer ability were first reported. The procedure described below for the synthesis of polymeric HALS permitted the preparation of polymers with tunable molecular weights.

Experimental

Matrials

Grubbs 1st generation catalyst was available from Aldrich. Dichloromethane (KOKUSAN CHEMICAL) were dried by standard methods before use. Dicyclopentadiene, 2,2,6,6-tetramethyl-4-hydroxy piperidine, tetraisopropyl orthotitanate, methyl acrylate, fumaric acid dimethyl ester and the other reagents were purchased from TOKYO CHEMICAL and were used without further purification. Dicyclopentadiene was cracked at 180 °C and distilled to prepare cyclopentadiene (CPD). 5-Norbornene-*exo*, *endo*-2-carboxylic acid 2,2,6,6-tetramethyl-4-piperidinyl ester (**PN**) was synthesized via previous literature procedure [19]. Anal. Calcd for $C_{17}H_{27}O_2$ N: C, 73.59; H, 9.82; N, 5.05. Found: C, 73.43; H, 9.81; N, 4.99.

Instruments

^{1}H-NMR spectra were recorded on a JEOL JNM-AL300 spectrometer. Melting point was determined by a SHIMAZU DSC-60 differential scanning calorimeter (DSC). A heating rate of 10 °C/min and nitrogen atmosphere was consistently employed. The number average molecular weights (M_n) and polydispersity index (M_w/M_n) of the polymers were determined with a JASCO gel permeation chromatography (GPC) equipped with a Shodex K-805L chromatograph column and a JASCO RI-2031 detector, using chloroform as an eluent at a flow rate of 1.0 ml/min, calibrated by polystyrene standards at 40 °C.

Synthesis of fumaric acid bis (2,2,6,6-tetramethyl-4-piperidinyl) ester (**FBP**)

2,2,6,6-Tetramethyl-4-hydroxy piperidine (10.9 g; 0.064 mol), fumaric acid dimethyl ester (4.2 g; 0.029 mol) and tetraisopropyl orthotitanate (2.0 ml) were mixed with toluene (100 ml). After being stirred at 90°C for 1 h and then at 120 °C for 8 h under nitrogen atmosphere, the reaction solution was cooled to room temperature and quenched by water (10 ml). After washing with 100 ml of water, the organic phase was separated, dried over anhydrous magnesium sulfate and filtered. Removal of the toluene under reduced pressure left yellow viscous oil. After dilution with 60 ml hexane and warm filtration, the product crystallized from filtrate upon cooling. (8.73 g; 71.3% yield). mp: 116 °C. ^{1}H-NMR ($CDCl_3$, 300 MHz, δ): 6.79 (s, 2H, –HC=CH–), 5.24–5.32 (m, 2H, –OCOCH–), 1.55–1.97 (m, 8H, $-CH_2-$), 1.10–1.19 (m, 12H, CH_3).

Synthesis of 5-norbornene-2-exo-3-endo-dicarboxylic acid bis (2,2,6,6-tetramethyl-4-piperidinyl) ester (**2,3-PN**)

To a solution of **FBP** (2.0 g; 0.005 mol) in 50 ml of toluene, cyclopentadiene (0.67 g; 0.01 mol) was added dropwise with stirring under nitrogen atmosphere at 0–5 °C during a period of 15 min. The reaction mixture was stirred overnight with ice-water bath, and then was stirred at 40 °C for 1 h and refluxed for 4 h in sequence. Removal of the toluene under reduced pressure left yellow viscous oil. Crystallization from hexane upon cooling gave product. (1.6 g; 70.4% yield). mp: 105 °C. ^{1}H-NMR ($CDCl_3$, 300 MHz, δ): 6.26–6.29 (dd, 1H, J = 3 Hz, 3 Hz, olefinic proton in 6 position of norbornene ring), 6.04–6.07 (dd, 1H, J = 3 Hz, 3 Hz, olefinic proton in 5 position of norbornene ring), 5.08–5.22 (m, 2H,—OCOCH–), 3.32–3.34 (m, 1H, –CH– in 4 position of norbornene ring), 3.23 (s, 1H, –CH– in 1 position of norbornene ring), 3.08 (s, 1H, *exo*-CH–), 2.62 (m, 1H, *endo*-CH–), 1.14–1.94 (m, 34H, CH_3, $-CH_2-$ of piperidine and $-CH_2-$ in 7 position of norbornene ring). Anal. Calcd for $C_{27}H_{44}O_4N_2$: C, 70.38; H, 9.63; N, 6.08. Found: C, 70.25; H, 9.80; N, 6.16.

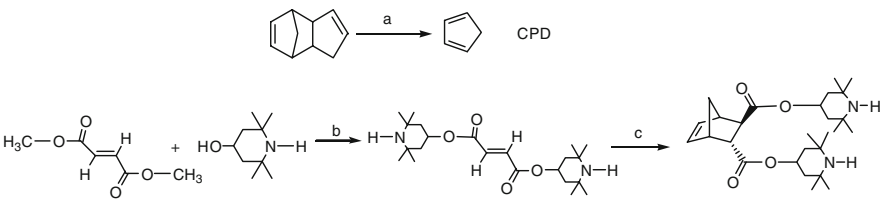
Polymerization

In a typical experiment (Scheme 2), a 25 ml flask was charged with cycloolefin monomer COD (0.26 ml, 2.12 mmol) and 2.34 ml of dichloromethane under nitrogen atmosphere. 1.33 ml of Grubbs 1st catalyst dichloromethane solution (16 mmol/l) was added into the flask by syringe. After being stirred at room temperature for 2 h, 0.5 ml of **PN** dichloromethane solution (0.2 g/ml) was added and stirred for 2 h. Finally, ethyl vinyl ether (0.5 ml) was added to the mixture to quench the reaction. The resulting polymer was precipitated in excess of methanol and purified by reprecipitation from chloroform and methanol. The reprecipitated polymer was collected and then dried under vacuum at 30 °C for 6 h to yield hindered amine functionalized PCOD polymer which was named polymeric HALS in the following sections.

Results and discussion

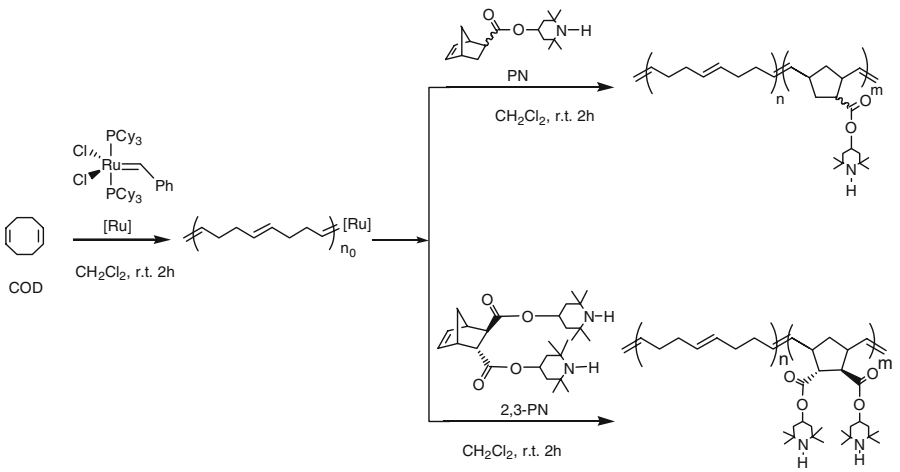
Synthesis of norbornene derivatives

The strategy for norbornene derivatives **PN** and **2,3-PN** was based on Diels-Alder cycloaddition reaction (Scheme 1). Acrylic derivative 2,2,6,6-tetramethyl-4-piperidinyl acrylate [19] and fumaric derivatives **FBP** were synthesized via ester exchange reaction catalyzed by $[(CH_3)_2CHO]_4Ti$, and then they were used as functionalized dienophile for the Diels-Alder cycloaddition reaction with cyclopentadiene (CPD) to give **PN** and **2,3-PN** respectively. Unfortunately, the *exo*-and *endo*- isomer mixture of the **PN** cycloaddition adduct was inseparable by selective recrystallization. The ^{1}H-NMR signals of olefinic proton appeared in the range of 5.90–6.19 ppm as three sequences of peaks overlapped partly, indicating the existence of two isomers in **PN**. However, in the case of **2,3-PN**, olefinic protons appeared as two individual peaks due to the fact that *trans*- symmetric substituent structure of dienophile **FBP** resulted in formation of an *exo*- and *endo*- arrangement during the cycloaddition. It was suggested that a high shielding of the double bond



a) 180°C
b) $[(CH_3)_2CHO]_4Ti$, toluene, 90°C 1h, 120°C 8h
c) CPD, toluene, 0~5°C dropwise, 40°C 1h, reflux 4h

Scheme 1 Synthesis of norbornene derivative 2,3-PN



Scheme 2 Expected polymerization of cyclooctadiene in the presence of PN or 2,3-PN ($n_0 > n$, $m < n$)

could lead to low ROMP reactivity of *endo*-2,3-diester norbornene derivatives [20]. Therefore, maleic acid dimethyl ester resulting in *endo* diester norbornene derivative is unsuitable for being employed as a precursor to prepare ROMP reactive derivatives.

Polymerization and characterization

A typical polymerization sequence and reaction time were shown in Scheme 2. The decision of reaction time in sequential copolymerization was based on ensuring essentially maximal conversion of monomer **COD** in the first step under molar ratio of **COD** monomer to catalyst ([M]/[C]) varying from 100 to 1,000. The monomer **COD** was subjected to homopolymerization under the catalysis of Grubbs 1st catalyst for 2 h. An intermediate PCOD bearing end living species was formed as shown in Scheme 2. After addition of **PN** or **2,3-PN** solution, the ring-opening and insert reaction of hindered amine norbornene derivatives were initiated by living ruthenium species above mentioned. Table 1 summarized the results of the polymerization of **COD** in the presence of **PN** under various [M]/[C]. The molecular weight (M_n) of resulting intermediate PCOD increased from 4.90×10^3 to 5.13×10^3 when [M]/[C] increased from 100 to 500. Typical GPC profiles of the resulting polymeric HALS and that of the corresponding intermediate PCOD were observed and shown in Fig. 1. Comparing Run1 and Run 2, it was evidently found that the GPC profile of the Run 2 obtained after the addition of **PN** shifted toward the lower molecular weight region. Accompanied by the decline of M_n, M_w/M_n also changed. Likewise for Run 4 and Run 6 obtained under 200 and 500 of [M]/[C] respectively. Although the polymerization was carried out by a sequential addition, the M_n did not increase as we expected. As shown in Fig. 2, the similar phenomenon was observed in the presence of **2,3-PN** Table 2.

Table 1 Polymerization of cyclooctadiene (COD) in the presence of PN

Run	Feed (g)		[M]/[C]	M_n^a (10^3)	M_w/M_n^a	HALS[b] (mol%)
	COD	PN				
1	0.20	0.00	100	4.90	2.37	–
2	0.20	0.10	100	2.04	1.83	12.8
3	0.20	0.00	200	4.94	2.33	–
4	0.20	0.10	200	3.04	8.65	11.5
5	0.20	0.00	500	5.13	3.72	–
6	0.20	0.10	500	2.29	2.32	18.6
7	0.20	0.10	1000	1.99	2.20	35.3

[a] Value measured by GPC, calibrated with polystyrene standards

[b] Determined with ^{1}H-NMR; polymerization conditions: Grubbs 1st generation catalyst, methylene chloride solvent, r.t. 2h + 2h in sequence; polymerization was terminated by adding of excess ethyl vinyl ether. [M]/[C]: molar ratio of COD monomer to catalyst

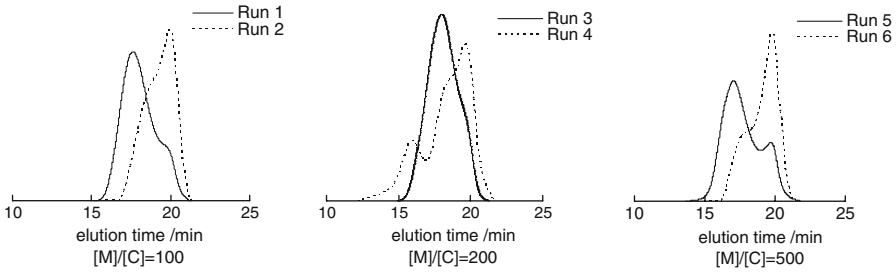
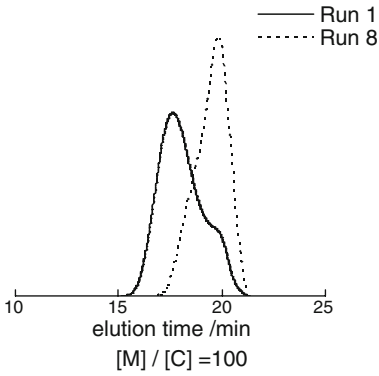


Fig. 1 GPC elution profiles before and after addition of PN

Fig. 2 GPC elution profiles before and after addition of 2,3-PN



The polymerization did not proceed in a block-like way, and some chain degradation reaction occurred presumably. Given the present results, it was concluded that the polymeric HALS appear to have resulted from chain transfer process between high molecular weight intermediate PCOD and the **PN/2, 3-PN**.

Table 2 Polymerization of cyclooctadiene (COD) in the presence of 2,3-PN

Run	Feed (g)		[M]/[C]	M_n^a (10^3)	M_w/M_n^a	HALS[b] (mol%)
	COD	2,3-PN				
8	0.20	0.10	100	1.83	1.59	26.0
9	0.20	0.10	500	–	–	–
10	0.20	0.10	1,000	–	–	–

[a] Value measured by GPC, calibrated with polystyrene standards

[b] Determined with ^{1}H-NMR; polymerization conditions: Grubbs 1st generation catalyst, methylene chloride solvent, r.t. 2h + 2h in sequence; polymerization was terminated by adding of excess ethyl vinyl ether. [M]/[C]: molar ratio of COD monomer to catalyst

Chain transfer resulted from the addition of **PN** increased the number of the chains and concomitantly caused a reduction in the molecular weight. A proposed mechanistic chain transfer was shown in Fig. 3. According to the mechanism of metathesis reaction initiated by $RuCl_2(PCy_3)$(=CHPh) [21], the crucial step is dissociation of bound PCy_3 from species I to form a living species II. Three unfavorable factors should prevent living ruthenium center from coordinating double bonds of **COD** monomer or **PN/2,3-PN**, and then preclude polymer chain from growing. At first, an intramolecular complex (III) between the ruthenium center and the adjacent carbonyl should greatly do harm to reactivity of ruthenium living center [22, 23]. Secondly, after 2 h homopolymerization, COD monomer concentration decreased to equilibrium concentration $[M]_e$. As ROMP is typically a thermodynamically governed process, at a given temperature, there is a certain equilibrium concentration $[M]_e$ below which polymerization to high polymer will not occur [24]. Furthermore, unfavorable thermodynamical factor of **PN** and **2,3-PN**

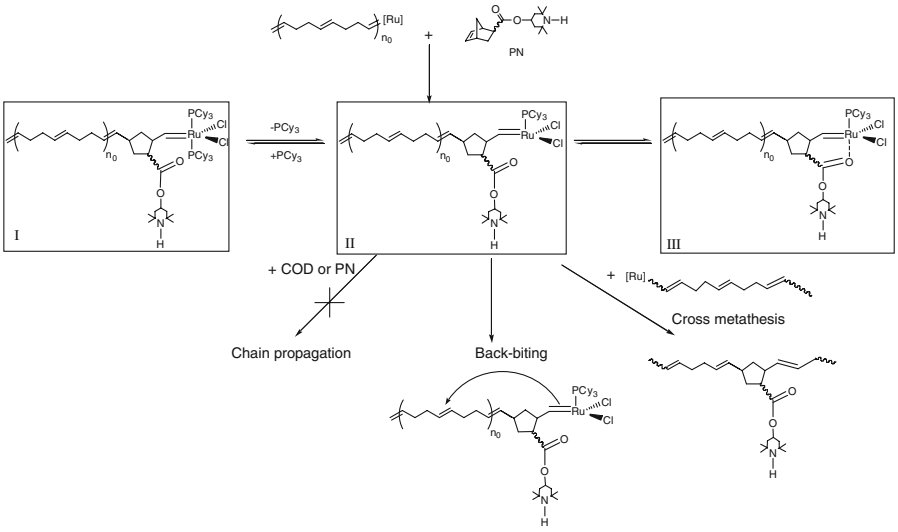


Fig. 3 Proposed mechanistic chain transfer leading to polymeric HALS

accounts for low metathesis reaction reactivity of both HALS functionalized norbornene. In fact, at the beginning of the experimental, we tried to homopolymerize **PN** or **2,3-PN** by using of Grubbs 1st catalyst at the same conditions. Unfortunately, homopolymerization was unfeasible and only got a little of oligomer with so low molecular weight that could not be determined by GPC. Under the influence of above factors, the living ruthenium center was prone to coordinating double bonds of the polymer, leading to secondary metathesis such as back-biting, cross metathesis with another chain. So, herein, due to the low ROMP reactivity of **PN/2,3-PN** and rapid transfer reaction, the **HALS** unit was introduced into polymer chain at the expense of chain degradation. The process could be written formally as:

$$P^* + M \rightarrow PM^* (\text{propagation})$$

$$PM^* + P \rightarrow PMP + P^* (\text{transfer to polymer})$$

where M represents PN or 2, 3-PN, P* represents a living chain, PM* represents a polymer chain with an **M** living terminal.

The ^{1}H-NMR spectra of intermediate PCOD and the corresponding end product polymeric HALS was shown as an example in Fig. 4. The integration of the proton peaks revealed the HALS content of the resulting polymeric HALS. As the polymerization proceeded, new broad olefinic proton of the double bound of the ring-opening polymer chain appeared at 5.3–5.4 ppm. The resonances relating to protons from hindered amine unit clearly appeared in Fig. 4 (Run 2), which showed that the HALS functional groups were successfully bound into the polymer chain to some extent. Decreasing catalyst concentration will lead to a longer PCOD chain, while relative increasing [CTA]/[C] will improve the HALS amount through accelerating the degradation of PCOD chain. Because the proportions of the two components depend on the ratio of the amount of HALS units to the amount of PCOD fragment, the HALS content in the end product is the result of a complex interdependence of [M]/[C] and [CTA]/[C]. Given the obtained M_n and HALS

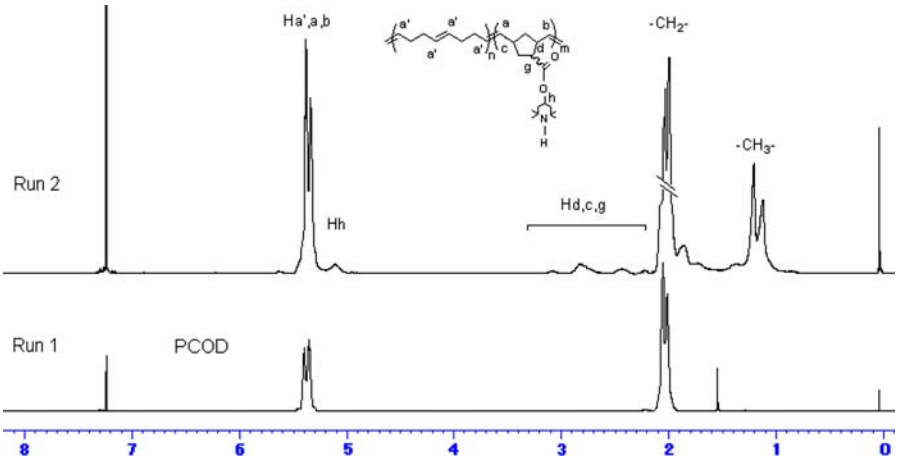


Fig. 4 ^{1}H NMR spectra of intermediate PCOD and the resulting polymeric HALS

content, two reversed trends were found. With the increase of [M]/[C], M_n of the polymeric HALS end product firstly increased and then decreased. When [M]/[C] was 200, M_n reached the maximum value 3.04×10^3. On the contrary, the HALS content in the resulting polymeric HALS declined to a minimum value of 11.5% for [M]/[C] = 200, while it climbed to 35.3% when [M]/[C] increased to 1,000. It should be mentioned that regardless of the structure, polymeric HALS containing a hindered amine moiety in each repeat unit should be more effective due to the high functional group density. From this point of view, the copolymer we proposed was a comparatively worse one. Therefore, alternative method of using **2,3-PN** for improving HALS group density was brought forward here. **2,3-PN** gave rise to double functional density. However, the increasing HALS content made the resulting polymeric HALS to be soluble in methanol. As a result, when Run 9 and Run 10 proceeded under 500 and 1,000 of [M]/[C], no polymer precipitated from the cloudy methanol solution.

Conclusions

Polymeric HALS stabilizers bearing alkene and cycloalkyl structure in main chain were prepared through ring-opening metathesis polymerization of cyclooctadiene (COD) in the presence of 5-norbornene-*exo*,*endo*-2-carboxylic acid 2,2,6,6-tetramethyl-4-piperidinyl ester (**PN**) or 5-norbornene-2-*exo*-3-*endo*-dicarboxylic acid bis(2,2,6,6-tetramethyl-4-piperidinyl) ester (**2,3-PN**). Investigation of polymerization behavior indicated that hindered amine norbornene derivatives **PN** and **2,3-PN** acted as chain transfer agent (CTA). Degradation of macromolecule PCOD resulted from CTA not only causes a reduction in the molecular weight but also successfully transfers HALS group from **PN/2,3-PN** to the PCOD's chain. Tunable molecular weight, HALS content and novel main chain structure confer to this kind of polymeric HALS attractiveness for further study.

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