

STUDY OF GRAFTING COPOLYMER OF STYRENE AND 2,2,6,6-TETRAMETHYL-4-PIPERIDINYLMETHACRYATE ONTO POLYPROPYLENE DURING HEATING

PAN Jiangqing(潘江庆), ZHANG Can(张 灿) and MA Zhenmin(马振民)

(Institute of Chemistry, Academia Sinica, Beijing)

ABSTRACT

The grafting of copolymer of styrene and 2, 2, 6, 6-tetramethyl-4-piperidiny methacrylate onto polypropylene during heating was studied by IR and ESR. It is found that the graft reaction is going through the stable free radical $>\text{NO}\cdot$ mechanism.

INTRODUCTION

In principle, polymer radical graft reaction can be achieved by forming free radical of vinyl monomer and polymer under high energical irradiation, UV-light, in the presence of initiator or by forming macro-free radical from mechanical-chemical degradation of polymer in the effect of mechanical force(e.g. blend and mastication).

Recently, we have observed that the copolymer of styrene and 2,2,6,6-tetramethyl-4-piperidiny methacrylate(PDS) can be grafted onto PP by forming stable nitroxy free radical during heating. Moreover, it has been known that small molecular hindered amine light stabilizer Tinuvin-770 can be grafted onto PP during light irradiation^[1], but up to now it has not been reported that PDS grafts onto PP during heating. This result can be used as another new method for polymer free radical graft. The main results are as follows:

EXPERIMENTAL

1. Materials

Additive free isotactic PP powder(20—40 mesh) was supplied by Beijing Xiang Yang Chemical Factory. It had been stored in the laboratory for one year. PDS was the synthetic product^[2] and PDSNO $\cdot$ was prepared by oxidation of PDS by using $\text{Na}_2\text{WO}_4\text{--H}_2\text{O}_2$ ^[3].

2. Sample preparation

The PDS and PDSNO $\cdot$ was dissolved in chloroform at given concentration. Then the PP powder was added into the solution. After that, the solvent was removed by strong stirring under reduced pressure and then treated in vacuum for 24 hours.

3. Heat treatment of sample

Heat treatment of sample was carried out in a glass reactor filled with air or argon. The temperature of reaction is $150 \pm 0.5^\circ\text{C}$ either in air oven or in silicone oil bath. After being heated the sample was refluxed in chloroform for 1.5 hour and pressed into a film of about 110μ at 190°C for IR measurement.

4. IR measurement

IR measurement is similar to that in literature^[4]. Pekin Elmer-180 Infrared Spectroscopy is used in the present work. The definition of carbonyl index is similar to that in literature^[4], that is:

$$\text{Carbonyl Index} = \frac{\text{Optical density of carbonyl}}{\text{Thickness of sample}} \times 1$$

The carbonyl absorption presents at 1723cm^{-1} for PDS and 1725cm^{-1} for PDSNO.

5. ESR Measurement

ESR measurement is the same as that in literature^[11], and the ESR Spectrometer used in this work is made by China Mineral Mechanical Factory. The relative $\text{>NO}\cdot$ radical concentration in PP was determined from the height of the central line of nitroxyl spectrum.

RESULTS AND DISCUSSION

The change of carbonyl optical densities of the sample containing PDS with the time of refluxing in chloroform is shown in Fig. 1. It can be seen that all PDS in the sample can be extracted with chloroform within 0.5–1 hour. The carbonyl index retention of sample during heating in air after chloroform refluxed for 1.5 hour is shown in Fig. 2. The carbonyl index increases with heating time, but there may be a bit of interference of air oxidation, especially in the late stage, in spite of PDS or PDSNO is good for inhibiting oxidation of PP. But grafting PDS onto PP can also be confirmed by the difference of carbonyl absorption between oxidizing pure PP and PDS after chloroform refluxed, and carbonyl absorption for pure PP presents at 1710cm^{-1} , PDS at 1723cm^{-1} and PDSNO at 1725cm^{-1} .

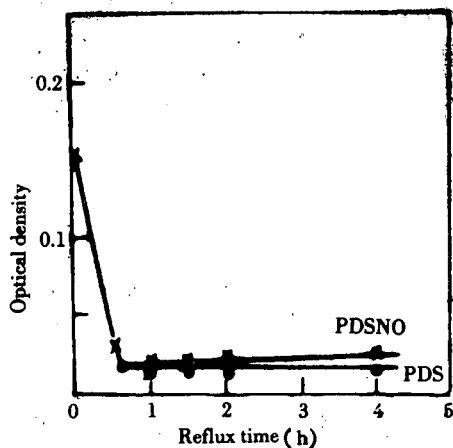


Fig. 1 The change of carbonyl optical density of PP sample (reflux in chloroform, unheating sample)

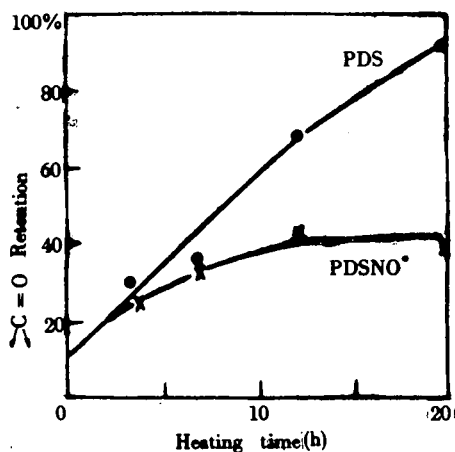


Fig. 2 The change of ester carbonyl retention with heating time in air (reflux in chloroform for 1.5 h.)

In order to avoid the interference of air oxidation, heat-treatment of sample was carried out in a glass reactor filled with argon at 150°C . The result is shown in Fig. 3, from which it can be seen that the graft rate in argon is a bit slower than that in air. It was found that pure PP was not oxidized within 20 h. at 150°C in argon, while in air, oxidation of PP can be found even at 120°C .

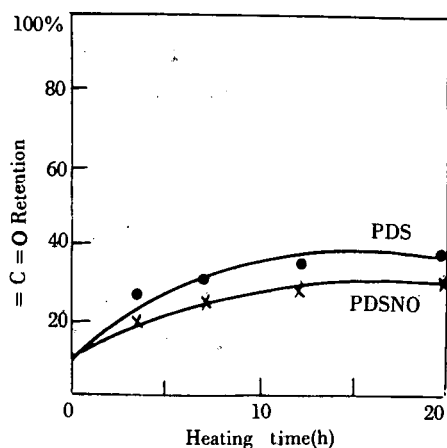


Fig. 3 The change of ester carbonyl retention with heating time in argon (reflux in chloroform for 1.5 h.)

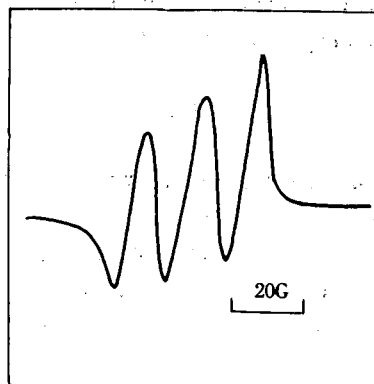
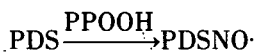


Fig. 4 ESR spectrum of PDS during heating (in toluene solution)

within 7 hours. Therefore, the increase of carbonyl index of PP containing PDS during heating in argon is a result of PDS grafted onto the PP, instead of the interference of oxidation.

The results of ESR measurement are shown in Table 1. There are much more PDSNO· stable free radical which cannot be extracted off from PP because it has been grafted onto PP. This result is analogous to that in the measurement of IR. Furthermore, ESR measurement showed that both samples heat-treated in air or in argon can yield stable nitroxy radical (as shown in Fig. 4). ESR measurement has also showed that the original PDS contains a small amount of PDSNO· (about 0.94×10^{-4} mol/kg), and the concentration of PDSNO· increases by about 30 times during mixing with PP which was stored for one year at room temperature. This may be due to the oxidation of PDS by PP-hydroperoxide which is a main product of oxidation of PP at room temperature:

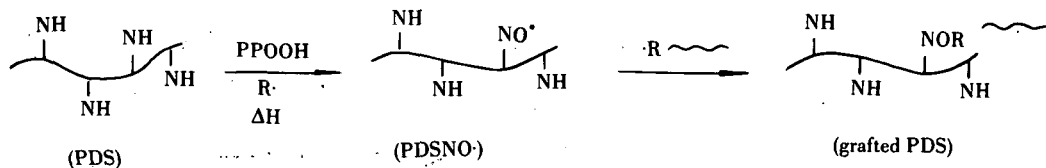


Literatures^[5,6] have shown that the piperidines are readily oxidized to corresponding nitroxyl free radical $\text{>NO}\cdot$ by organic hydroperoxide or oxygen. Therefore, the small amount of PDSNO· in original PDS is the result of PDS oxidation with oxygen.

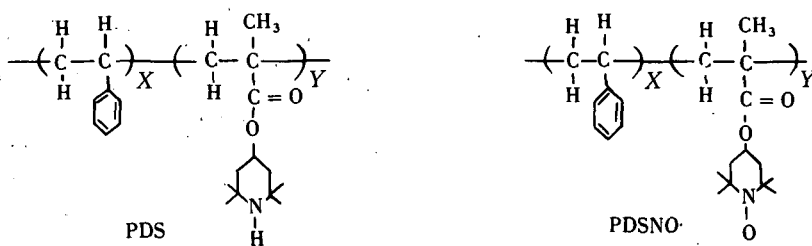
In addition, a pink solution can be obtained when PDS was added into cumenyl hydroperoxide (cumenyl hydroperoxide is a bit yellow; PDS is white; PDSNO· is red). The ESR measurement shows that the concentration of PDSNO· in this pink solution increases about 30% in comparison with the original PDS in accordance with the literature^[5,6]. On the other hand, the PDSNO· signal cannot be obtained when the pure PP and original PDS were mixed (sample 50 mg., PDS 3% in PP); while mixing PDS with PP preoxidized at 120°C for 3 hrs., we can obtain strong signal of $\text{>NO}\cdot$, that means PP-hydroperoxide can oxidize PDS to PDSNO·.

Because hindered amine is easy to form stable free radical $\text{>NO}\cdot$, and is a good scavenger of alkyl radical from heat treatment of PP. It had been reported that small molecular hindered amine can graft onto PP during light irradiation^[1]. Based on the results of measurement of IR, ESR and

the fact of forming $\text{>NO}\cdot$ during heating PDS as well as the consideration of that macro-alkyl radical can be formed during thermal degradation of PP, we propose that the mechanism of grafting PDS onto PP during heating is:



$\cdot\text{R} \sim \sim$ is macro-alkyl radical formed from degradation of PP during heating. PDS is a copolymer of styrene and 2,2,6,6-tetramethyl-4-piperidinyl methacrylate and its structure is as follows:



There are two benefits for grafting PDS onto polypropylene. One of them is a scavenging effect for free radical produced during degradation, and the other is a slightly crosslinking effect^[7,8]. Both make PDS have a good stabilizing action. Literatures^[7,8] have reported that PDS has a good protecting action photo-oxidation^[7,8] and thermal oxidation^[9]. One of the reasons may be related to this grafting action.

Table 1 Relative concentration of $\text{>NO}\cdot$ in PP sample

No.	Additive	Unheating Unreflux	Unheating Reflux*	Heat in argon gon at 150°C for 20 hrs.	Heat in air at 150°C for 20 hrs.
1	PDS	$3.70 \cdot 10^{-4}$	$1.0 \cdot 10^{-5}$	$2.86 \cdot 10^{-4}$	$2.17 \cdot 10^{-3}$
2	PDSNO $\cdot$	$3.71 \cdot 10^{-2}$	$8.2 \cdot 10^{-4}$	$4.63 \cdot 10^{-3}$	$9.23 \cdot 10^{-3}$

Keyword:

Graft of hindered amine; Hindered amine. light stabilizer; Polypropylene; Polymeric hindered amine light stabilizer (PDS)

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