ISSN 0965-5441, Petroleum Chemistry, 2019, Vol. 59, No. 9, pp. 1037–1042. © Pleiades Publishing, Ltd., 2019.
Published in Russian in Neftekhimiya, 2019, Vol. 59, No. 5, pp. 589–594.

Synthesis and Anti-Oxidative Properties of Poly(diphenylamine) Derivative as Lubricant Antioxidant

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Received August 11, 2017; revised November 17, 2017; accepted May 13, 2019

Abstract—The poly(diphenylamine) derivative (PDPA) as amine antioxidant was synthesized via diphenylamine, styrene, and formaldehyde. The steps of the synthesis were discussed in detail, and the structure of PDPA was fully characterized with multiple analysis techniques. Furthermore, the anti-oxidative properties of PDPA were evaluated through oxidation—corrosion tests and differential scanning calorimetry. It was found that PDPA significantly improved the oxidation stability of base oils, especially pentaerythritol ester when it was added at concentrations of only 0.5 wt % to 0.8 wt %. Thermogravimetric analysis shows that anti-oxidation behavior of PDPA is better than traditional additive p, p-dioctylphenylamine. The synthesized PDPA antioxidant is a potential alternate additive in high-temperature conditions.

Keywords: poly(diphenylamine) derivative, antioxidant, base oils, oxidative stability

DOI: 10.1134/S0965544119090081

INTRODUCTION

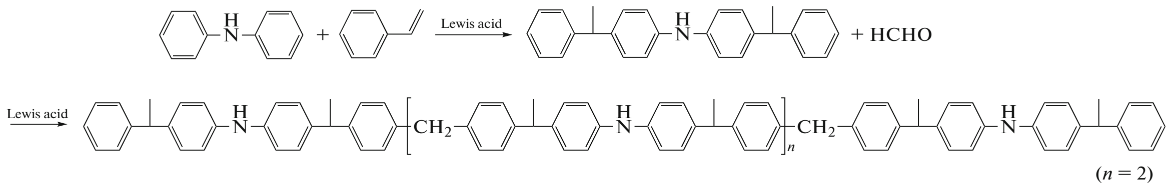
Thermal oxidation stability is an important property of lubricants. Lubricating oils are influenced by water, oxygen, sulfur compounds and metal catalysis during oxidation, and result in a series of chemical products, including coke, glial, sludge, and other substances [1, 2]. These oxidation products are harmful to lubricant, losing lubricity and undergoing lubrication failure thereat. Thus the service life and working efficiency of engines are evidently affected, so high-performance lubricating oils are developed to cope with the elevated temperature and pressure environment [3–6]. The high-temperature oxidation resistance of lubricating oils depends on the quality of base oils and the performance of additives [7, 8]. Therefore, selecting suitable antioxidants is important to improve the anti-oxidation capacity of lubricating oils at high temperatures and extend the working life of the lubricants.

Various antioxidants are currently applied to enhance the anti-oxidation capacity of lubricating oils. Among these antioxidants, phenolic antioxidants are mainly utilized in low-temperature conditions, including universal machine, turbine, hydraulic, and transformer oils. However, meeting the needs of high-temperature and high-pressure environments is difficult [9, 10]. Amine antioxidants, which are suitable for high temperatures, are widely applied in high-temperature lubricating environment. They are mainly divided into four types, namely, p-phenylenediamine, ketone/amine compound, diphenylamine derivatives, and naphthylamine [11]. These amine antioxidants, especially alkylated diphenylamine and N-phenyl-alpha-aniline, are widely used in aviation lubricating oils. However, they demonstrate limited performance in the volatilization and inhibition of carbon sludge [12, 13]. Thus, an excellent antioxidant is required to improve the performance of lubricating oils elevated temperature.

Macromolecular amine antioxidants are increasingly drawing attention, since they have a molecular weight of 1000 or above and exhibit low volatility as well as thermal stability. Its structure possesses excellent anti-oxidation ability and nearly produces no sludge in application [14]. This paper aims to synthesize poly diphenylamine derivative (PDPA) substituted by aromatic alkyl. Its structure was examined through various characterization methods, and its anti-oxidation properties as a specific additive were evaluated.

EXPERIMENTAL

Base oils and additives. The mineral base oil 500 SN, synthetic base oil pentaerythritol ester (PE) and dioctyldiphenylamine antioxidant (DODPA) were purchased from a commercial source. PDPA was synthesized in the laboratory according to the pathway outlined in Scheme 1.



Scheme 1. Reaction pathway of PDPA.

The ideal mass and optimum proportions were optimized through the orthogonal array testing, the steps were as follows. First, diphenylamine (16.9 g, 0.1 mol) was placed in a round-bottom flask and heated to melt. Activated clay treated by alkali was combined with diphenylamine in the flask. The mixture was immediately heated to 220°C. Afterward, styrene (43.2 g, 0.41 mol) was added to the content drop by drop in a period of 2 h, and the reaction mixture was refluxed for 2 h at 220°C. Intermediate products were obtained after hot filtration (yield of 80.1%). Second, toluene (200 ml), potassium hydroxide (14 g, 0.25 mol), and the intermediate products (37.7 g, 0.10 mol) were added to a 500 ml three-necked bottle and stirred at 70°C. Then formaldehyde (2.25 g, 0.075 mol) was added and the mixtures were stirred for 1.5 h. After complete reaction, the reaction mixtures were washed with water, distilled, and dried over anhydrous sodium sulphate. The brown viscous product PDPA was finally obtained (yield of 98.4%). The typical properties of antioxidant PDPA are listed in Table 1.

Characterization of PDPA. The structure of PDPA was confirmed through infrared spectroscopy spectrum (IR) with a PerkinElmer Fourier Transform Spectrum BX instrument, proton nuclear magnetic resonance spectroscopy (NMR) with FX-90Q, mass spectrum (MS) with a MALDI-TOF mass spectrometer, and elementary analysis with JB-750. The synthesized compounds of PDPA were isolated through chromatography and its structure was identified through the methods described.

The stretching vibration absorption band of N-H bonds during FTIR at 3400 cm^{-1} was observed in the product. The bending vibration absorption band of C-N bonds was detected at 1513 cm^{-1} and confirmed the formation of amidogen in the aromatic secondary amine compound. The formation of asymmetric and symmetric stretching vibration absorption bands of C-H was observed at 2965 and 2902 cm^{-1}, respectively. These results indicated the existence of methyl in the product. The same C-H bands were observed at 2929 and 2872 cm^{-1}, which were the characteristic peak of methene. A strong band from 3000–3100 cm^{-1}, a band that includes 1597, 1513, and 1450 cm^{-1}, and a characteristic band for benzene were observed in the spectrum. In addition, the absorption band of C–C bonds belonging to 1,4-substituted benzene was confirmed by the peak at 826 cm^{-1}. The absorption spectrum of the frequency zone at 1650–2000 cm^{-1} was a typical characteristic of the substituent counterpoint in benzene. The analysis of infrared spectra revealed the presence of methyl, methylene, and substituted benzene in the molecules, and the benzene substituents were likely alkyl and amino which had obvious alignment characteristics.

Table 1. Typical properties of PDPA

Item	PDPA
Color	Brown liquid
Nitrogen content	4.1%
Kinematic KV (40°C)	650 mm^2/s
Density (20°C)	1.09 g/mL
Flash point (opening)	230°C

The ^{1}H NMR spectrum showed peaks at 6.82–7.57 ppm, which indicated benzene formation. The appearance of peaks at 4.20–4.24 ppm corresponding to hydrogen atoms in amino and peaks at 4.30–4.38 ppm corresponding to methylene groups between singlet-connected benzene was detected. The protons of the methyl groups were observed at 0.88 ppm adjacent to alkyl. These protons belonging to aminobenzene, benzyl and benzene were all detected. Furthermore, the ratio of hydrogen in benzene to hydrogen in methyl and methylene was about 9 : 4 according to the values of the peaks in the spectrum. We can obtain additional information from the ^{13}C NMR spectrum. The peaks at 117.1–147.1 ppm indicated the presence of benzene carbon. The peaks at 22.0–22.5 ppm and those at around 39.8–44.8 ppm suggested the presence of methyl and methylene, respectively.

The proportion of each element in the elementary analysis was (wt %): C—87.58 (87.26); H—7.16 (7.24) and N—4.09 (4.16). Furthermore, the mass spectrum data showed that molecular weights were about 1516, which confirmed the product structures.

Oxidation–corrosion tests. Oxidation degradation of lubricants usually results in chemical composition changes in oils and further affects physical and chemical properties. The thermal oxidation stability of PDPA added to 500 SN and PE was evaluated by kinematic viscosity (KV) according to ASTM D445-06 and total acid number (TAN) according to ASTM D664-06 after the oxidation–corrosion tests. All experiments were repeated in triplicate. Oxidation–

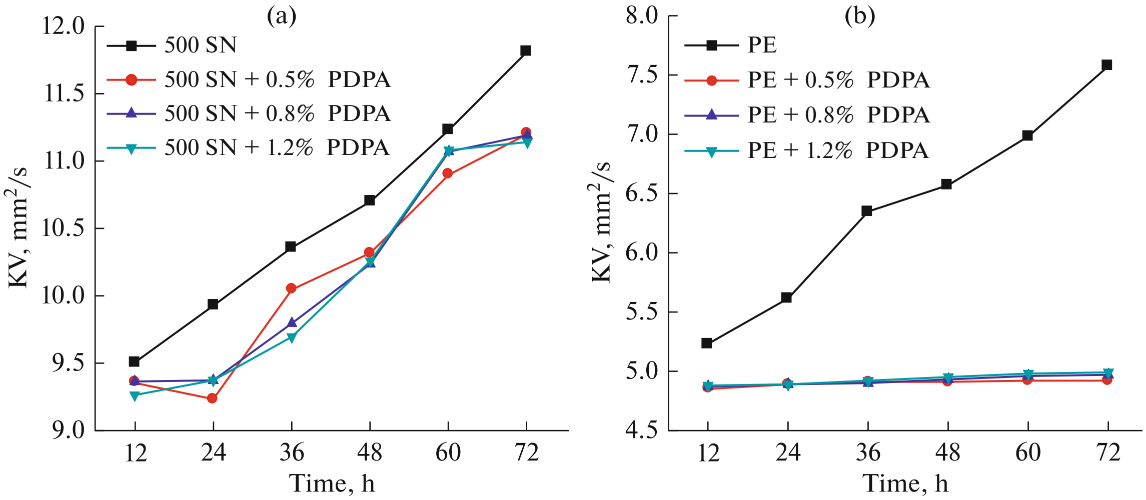


Fig. 1. Variation in KV of 500 SN (a) and PE (b) at 175°C.

corrosion tests were conducted at 175°C according to the Federal Test Method Standard 791b Method 5307. Dry air at 167 mL/min passed through 250 ml of oil in the presence of six metals, Cu, Fe, Al, Ag, Mg, and Ti. Oxidation was indicated by increases in the KV and TAN of the oil.

Differential scanning calorimetry tests (DSC). DSC is utilized to evaluate the anti-oxidation performance of the additives in base oils at different proportions. The results were recorded on a PerkinElmer 8 instrument according to ASTM E 2009–2008. A 2.0 mg weighed sample was placed in open aluminum pans with the oxygen flow maintained at 60 ml/min. The temperature was increased from 50 to 300°C at a heating rate of 10°C/min. DSC provided the initial oxidation temperature (IOT), which characterized the oxidative stability of the samples. The higher temperature was, the better thermal stability was. IOT was obtained through a temperature-programmed experiment.

Thermogravimetric tests (TGA). TGA is used to evaluate the oxidation stability of the antioxidants according to ASTM D 6375-2009. It was carried out with a NETZSCH STA 449C instrument. A small amount of antioxidants (2.0 mg) was placed in the TGA sample holder. The antioxidants were heated from an initial temperature of 0 to 400°C at a rate of 10°C/min in air. Weight loss was monitored in the instrument. The procedure for mixing the antioxidants with the base oils was followed. The base oils were doped with additives at 0.5, 0.8, and 1.2 wt % at room temperature. Afterward, the mixture was mechanically stirred at 60°C for 10 min and the antioxidants were mixed with different base oils.

RESULTS AND DISCUSSION

Analysis of the oxidation-corrosion tests. Different proportions of antioxidant PDPA were added to 500 SN and evaluated by oxidation–corrosion tests at 175°C. The changes in KV of 500 SN (a) and PE (b) are shown in Fig. 1. The changes in TAN of 500 SN (a) and PE (b) are shown in Fig. 2.

Figure 1a shows that the KV of the oil samples increases with the increase of oxidative time, which is in accordance with the rules of oil oxidation. Furthermore, a substantial increase occurred after 36 h. When antioxidants were added to the 500 SN, the KV of oils decreases in varying degrees comparing with base oil, which shows that antioxidants exhibit better thermal stability properties. When the oxidative time is increased from 12 to 72 h, the KV of 500 SN increases from 9.51 to 11.81 mm^2/s, with an increment of 2.3 mm^2/s. The increases in other samples successively added to the different proportions of antioxidant PDPA are 1.84, 1.82, and 1.87 mm^2/s.

Figure 2a shows that the change trends of TAN are same with KV of oils. The addition of PDPA antioxidant can improve the TAN of 500 SN. After 36 h the increase rate of TAN rapidly changes, which is associated with the decay of KV. The TAN of 500 SN can be improved by addition of PDPA. However, increasing the proportions of PDPA doesn't enhance the thermal stability properties comparing to oils containing different proportions of antioxidants. Therefore, the addition of 0.5 wt % PDPA can efficiently improve the changes in KV and TAN of 500 SN.

Figure 1b shows that the KV of PE can be significantly improved by antioxidant PDPA. The KV of the PE increases from 5.24 to 7.57 mm^2/s at a percentage of 44.5% from 12 to 72 h. Under the same experimental conditions, when 0.5 wt % PDPA antioxidants was added to PE base oil, the KV of it increases from 4.86 to 4.93 mm^2/s at a rate of 1.4%. Similarly, Fig. 2b shows that the TAN of PE base oil significantly increases from 1.62 mg KOH/g at 12 h to 10.52 mg KOH/g at 72 h. However, the TAN of PE containing different proportions of PDPA antioxidants is almost unchanged after

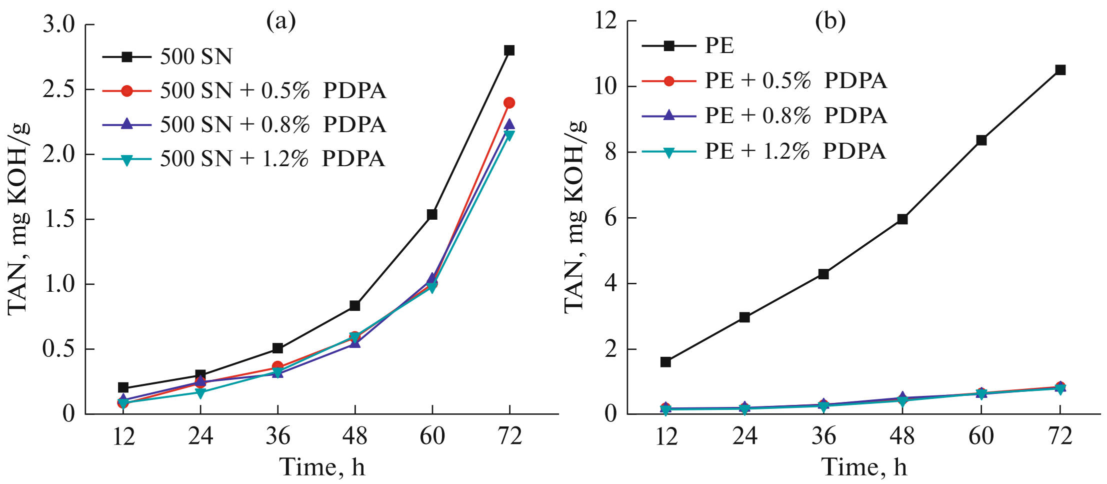


Fig. 2. Variation in TAN of 500 SN (a) and PE (b) at 175°C.

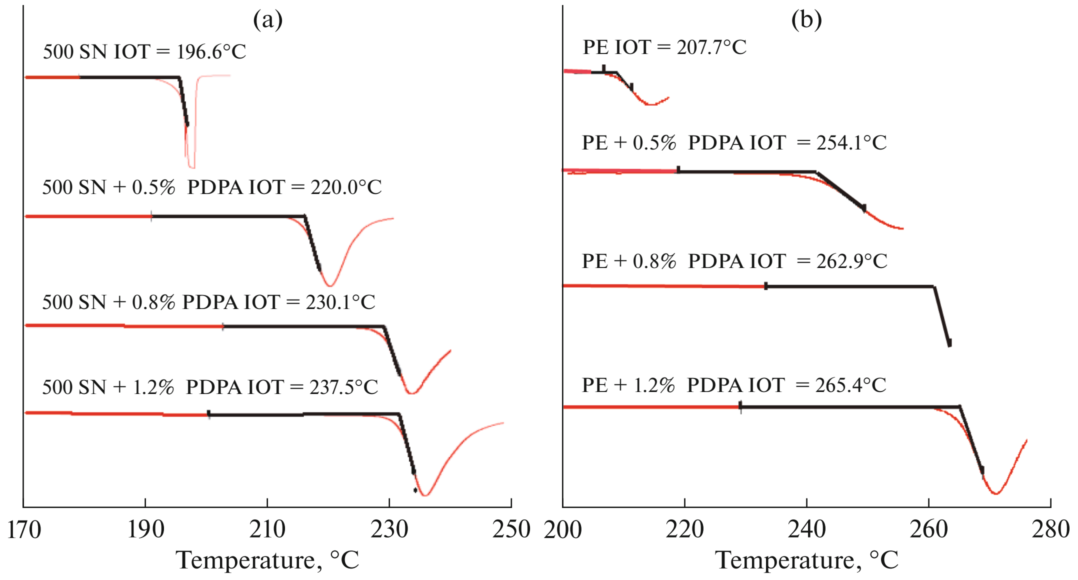


Fig. 3. The IOT of 500 SN (a) and PE (b) containing different contents of PDPA.

different oxidative time, which only increases from 0.18 mg KOH/g at 12 h to 0.85 mg KOH/g at 72 h. These results show that PDPA exhibits better antioxidative adaptability in PE.

Analysis of DSC tests. To understand the effects of antioxidants on the properties of 500 SN, the oxidation process of base oils should be considered. Given that the oxidation of base oils, along with the breakdown and formation of chemical bonds, is an exothermic process, DSC is utilized to evaluate the thermal stability property of 500 SN with different proportions of PDPA antioxidants, the results are shown in Fig. 3a. The IOT obtained from the DSC curve is set as the measurement of the oxidative stability of oils, a high initial oxidation temperature indicates good oil oxidative stability.

The DSC curve clearly indicates the thermal oxidative degradation of 500 SN. The oxidation stability of the samples without antioxidants is fairly poor, with an IOT of 196.6°C. IOT increases as the antioxidant contents increase, because antioxidants significantly influence thermal–oxidative decomposition. Results suggest that the proportion of 0.8% possesses outstanding oxidation resistance. And the thermal stability property of typical mineral base oils can be improved by PDPA antioxidant.

Figure 3b shows that the IOT of PE without any antioxidant is only 207.7°C. When PE was combined with 0.5 wt % PDPA antioxidant, the IOT increases from 207.7 to 254.1°C at the proportion of 22.3%. The addition of PDPA at 0.5 wt % results in a relatively good IOT improvement. However, when the additive dosage is increased to 0.8 wt %, it only contributes

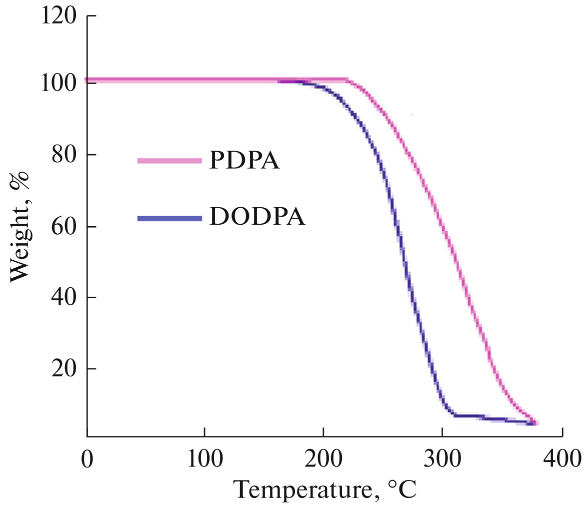
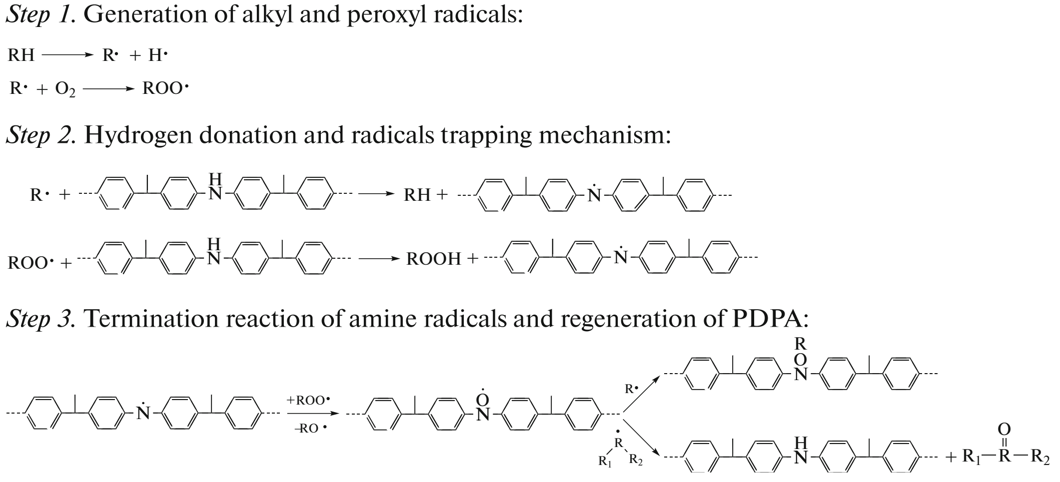


Fig. 4. The TGA curves of PDPA and DODPA.

8.8°C to IOT, which is a 0.3% increase that failed to yield highly positive results. When PE was combined with 1.2 wt % PDPA antioxidant, the IOT is 265.4°C, its thermal stability is not greatly improved. Therefore, the antioxidant PDPA is highly effective in enhancing the IOT of the base oils. However, the increased mass of antioxidants added to the oils doesn't necessarily lead to good thermal stability. Thus, it can be concluded that the thermal stability of base oils can be significantly improved by antioxidant PDPA. The best result is acquired at 0.5 to 0.8 wt %, which indicates that antioxidant PDPA has a better effect on ester-based oils than on mineral-based oils.

Analysis of TGA tests. TGA is employed to compare the anti-oxidation behaviors of the novel antioxidant PDPA and DODPA in base oils. The TGA curves of the antioxidants are shown in Fig. 4. This figure clearly demonstrates that addition of the novel additives at a concentration of 0.5 wt % doesn't result in any weight loss when the temperature is less than 225°C. The addition of the commercial antioxidant DODPA at the same concentration results in a relatively low temperature of 190°C. Furthermore, the temperature of the novel antioxidant PDPA for total decomposition is approximately 400°C, indicating that it has high thermal stability. However, the decomposition temperature for DODPA is 310°C, which is lower by about 90°C than that of the PDPA.

Anti-oxidation mechanism of PDPA. Arylamine antioxidants are known to act as radical scavengers by donating hydrogen atoms to terminate alkoxy and alkyl peroxy radicals, thus interrupting the radical chain mechanism of the auto-oxidation process [15, 16]. Generally, arylamine antioxidants, especially PDPA, display excellent antioxidant properties at elevated temperatures. The outstanding anti-oxidation performance of PDPA can be explained by two reasons. First, the volatilization of PDPA is significantly lower than that of other amine antioxidants because of its high molecular weight. Thus, it exhibits excellent thermal stability. Second, the structure of PDPA is a long chain with an aromatic ring. This structure provides more stable resonance intermediates and more hydrogen atoms to terminate alkoxy and alkyl peroxy radicals compared with other traditional amine antioxidants. As shown in Scheme 2, antioxidant PDPA participates in three steps of chemical reactions to inhibit the oxidation of base oils. At first step, hydrocarbons are oxidized to alkyl radicals at the initial stage of chain reactions and peroxyl radicals are generated when parts of alkyl radicals reacted with oxygen. At second step, PDPA provides alkyl radicals and peroxyl radicals with hydrogen to stable oxidation products. At third step, parts of formed aryloxyl radicals could react with alkyl radicals to terminate the chain reaction, due to their conjugation effects, and the others combined with alkyl radicals to regenerate the antioxidant. In other words, the novel antioxidant PDPA exhibits excellent anti-oxidation to inhibit the oxidation of the base oils and is an ideal alternative for the traditional amine antioxidants.


Step 1. Generation of alkyl and peroxyl radicals:

$RH \longrightarrow R\cdot + H\cdot$

$R\cdot + O_2 \longrightarrow ROO\cdot$

Step 2. Hydrogen donation and radicals trapping mechanism:

Step 3. Termination reaction of amine radicals and regeneration of PDPA:

Scheme 2. Anti-oxidation mechanism of PDPA.

CONCLUSIONS

A novel poly(diphenylamine) derivative (PDPA) antioxidant was successfully synthesized and found to exhibit superior antioxidant properties for base oils, especially ester oil. The oxidative stability of PE was improved with different concentrations of antioxidants, especially from 0.5 to 0.8 wt %. Besides, TGA tests demonstrate that novel additive PDPA performs better than traditional antioxidant DODPA. To some extent, the synthesized additive PDPA is a promising high-temperature antioxidant in lubricants.

FUNDING

This work was subsidized by funds from the National Natural Science Foundation of China (Grant 51575525) and the Natural Science Foundation of Jiangsu Province (Grant BK20151157 and BK20161188). The project was also supported by the Tribology Science Fund of the State Key Laboratory of Tribology (Grant SKLTKF14B10).

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