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Synthesis, Antioxidant Properties, and Reaction Kinetics of Aliphatic Diamine Bridged Hindered Phenols[1]

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Abstract—A series of aliphatic diamine bridged hindered phenols was synthesized. Their antioxidant activity was evaluated for assessing the role of bridging groups in trapping 1,1-diphenyl-2-picrylhydrazyl radical (DPPH$^{\bullet}$) and in 2,2'-azodi(isobutyronitrile) (AIBN) induced oxidation of styrene. The study of reaction kinetics of scavenging of the peroxyl radicals demonstrated that the scavenging ability of the DPPH free radical decreased when length of the bridging groups increased. However, the ability to protect styrene from AIBN-induced oxidation increased with increased length of the bridging groups.

Keywords: hindered phenol, bridged group, antioxidant ability, DPPH, kinetic behavior

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Free radicals, produced by oxidation, act as the main factor of performance loss during service life of many organic synthetic materials [1, 2]. Antioxidants are widely used to stabilize organic compounds as they can provide hydrogen atoms or electrons to terminate free radicals [3, 4]. Activity of phenolic antioxidants depends on the number of phenolic hydroxyl groups, position and kind of substituents [5, 6], and generally increases with the increase in number of phenolic hydroxyl groups [7]. Kajiyama and co-workers [8] studied the effect of *para*-substituents on the activity of phenolic antioxidants and the accumulated data demonstrated that those localize and stabilize the phenoxy radical electron in *p*-position increasing the activity of phenols. Phenolic antioxidants with *tert*-butyl and/or methyl substituents on both *o*-positions exhibited high antioxidant activity [9]. Electron donating substituents increased the antioxidant activity of phenolic antioxidants [10], while electron-withdrawing substituents diminished it. However, effect of length of *para*-substituents on antioxidant activity has not been reported so far. The ideal antioxidant was derived from Irganox 1098, produced by Giba–Geigy (Switzerland). Antioxidant 1098 contains 1,6-hexanediamine as the bridging group.

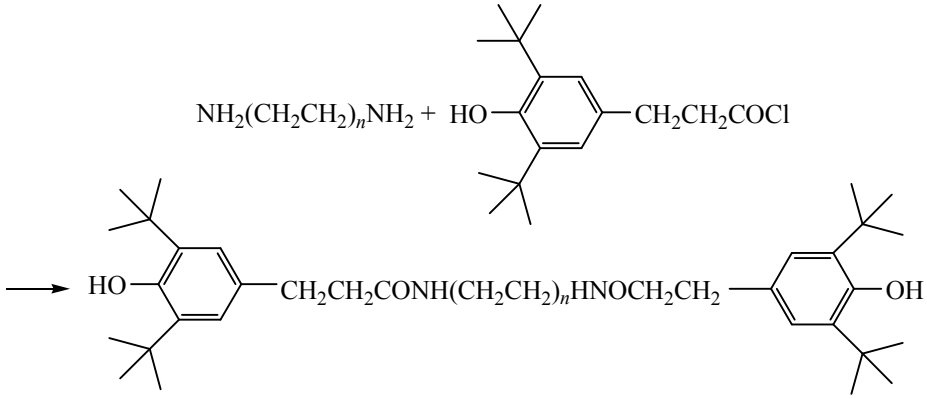
Based on that material and our recent study, four kinds of hindered phenols were synthesized with ethylenediamine, 1,4-butanediamine, 1,6-hexanediamine and 1,8-diaminooctane as the bridging groups. Their structures were characterized by FT-IR, ^{1}H NMR and LC Mass spectra. The effect of length of the bridging groups on the activity of antioxidants was investigated using the DPPH assay [11] and online oxygen consumption determination [12]. Kinetics of scavenging of peroxyl radicals (ROO$^{\bullet}$) produced in the oxidation of styrene was evaluated by calculating the inhibition rate (k_{inh}) and the number of trapping ROO$^{\bullet}$ (n).

RESULTS AND DISCUSSION

Synthesis and characterization of aliphatic diamine bridged hindered phenols. Four kinds of aliphatic diamine bridged hindered phenols were synthesized using ehtylenediamine, 1,4-butanediamine, 1,6-hexanediamine, and 1,8-diamineoctane as the bridging groups (Scheme 1). Those phenols were based on the Irganox 1098. 3-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)propionate (3,5-propionate) was substituted by more active 3,5-propionyl chloride. Concentration of 3,5-propionyl chloride was much higher than that of aliphatic diamine. Unreacted 3,5-propionyl chloride was removed by washing the solid product with toluene. Hindered phenols were characterized by IR, ^{1}H NMR and EI-MS spectra. The spectral characteristics of other hindered phenols were similar.

[1] The text was submitted by the authors in English.

Scheme 1. Synthesis of aliphatic diamine bridged hindered phenols.



n = 1–4.

Scavenging the DPPH free radical ability of the aliphatic diamine bridged hindered phenols. With an increase in concentration of hindered phenols, inhibition increased rapidly to a certain level. At the concentration 4×10^{-5} mol/L the maximum rate of inhibition was lower than 100% due to reversible nature of the process [13]. Inhibition decreased with an increase in the length of the bridging groups (Fig. 1).

Inhibition was affected not only by concentration of the phenol hydrogen but also by scavenging time for the hindered phenols [14] (Fig. 2).

The EC_{50}, TC_{50} and AE values of the hindered phenols were estimated on the basis of Figs. 1 and 2 (Table 1).

With the increase in length of the bridging group, EC_{50} and T_{EC50} values also increased, while AE values decreased. The total scavenging ability of ethylenediamine bridged hindered phenol was five times higher than that of 1,8-diaminooctane analogue due to not only donating of H atoms but also the molecular size of the antioxidant. The higher the ability of donating of H atoms the higher was the scavenging ability. The larger molecule size the smaller was the reaction probability between the antioxidant and the DPPH free radical. Total scavenging ability of the hindered phenols decreased with an increase in length of the bridging group.

Scavenging the ROO$^{\bullet}$ ability of the aliphatic diamine bridged hindered phenols. Initiation of AIBN-induced oxidation of styrene led to accumulation of the corresponding radical which combined with oxygen to give the peroxyl radical. The latter abstracted H atom from another styrene molecule. The process of radical

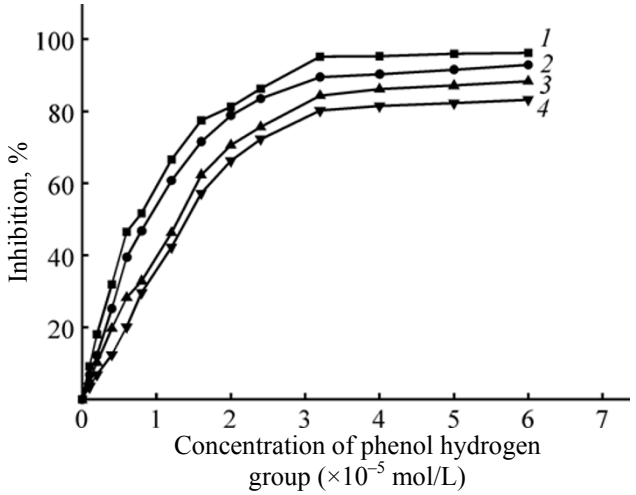


Fig. 1. Effect of aliphatic diamine bridged hindered phenols on scavenging ability: (*1*) C^2-phenol, (*2*) C^4-phenol, (*3*) C^6-phenol, and (*4*) C^8-phenol.

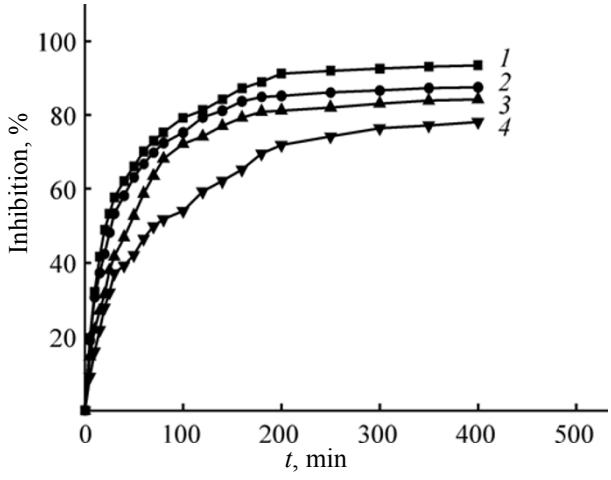


Fig. 2. Effect of time on scavenging ability at concentration 4×10^{-5} mol/L and 30°C: (*1*) C^2-phenol, (*2*) C^4-phenol, (*3*) C^6-phenol, and (*4*) C^8-phenol.

propagation caused oxidation of styrene and peroxide formation. The hindered phenols inhibited oxidation in the course of styrene polymerization. With the increase of molar concentration of phenols the amount of oxygen consumption decreased (Fig. 3).

Hindered phenols demonstrated the same trend in oxygen consumption in the course of styrene polymerization. Probably the monomer free radical initiated by AIBN combined with oxygen supporting its consumption [15]. Upon addition of the hindered phenol antioxidants, the phenolic hydroxyl group terminated the free radical and decreased the oxygen consumption rate. With the increase of concentration of hindered phenol the effective phenol hydroxyl number and the ability to provide H atoms increased. Therefore, oxygen consumption decreased indicating that phenols could inhibit styrene chain propagation.

Inhibition period of antioxidants (t_{inh}) in the initiation of AIBN-induced oxidation of styrene could be measured by the cross-point from the tangent lines for inhibition and oxidation periods (Figs. 3a and 4). The t_{inh} values became higher when concentration and bridging group length increased. Inhibition period of ethylenediamine bridged hindered phenol was 2869 s at concentration of 17.55 μM, while that of the 1,8-diaminooctane bridged hindered phenol was 3453 s indicating the higher inhibiting ability of the latter. The effect of inhibiting $ROO^{\bullet}$ oxidation was opposite to that of scavenging the DPPH radical. Possibly styrene generated not only $ROO^{\bullet}$, but also long chain radicals during the polymerization process and probability of hindered phenols contact with the longer chain alkyl radical increased.

Table 1. Scavenging parameters of aliphatic diamine bridged hindered phenols on the DPPH radical

Antioxidant	EC_{50}, mmol/L	TC_{50}, min	$AE\times10^{-3}$
C^2-Phenol	0.0076	21.43	6.14
C^4-Phenol	0.0088	28.04	4.05
C^6-Phenol	0.0124	45.14	1.79
C^8-Phenol	0.0140	70.74	1.01

Reaction kinetics of aliphatic diamine bridged hindered phenols. Reaction kinetics of inhibition of aliphatic diamine bridged phenols (AH) was studied. Inhibition rate (R_{inh}) of aliphatic diamine bridged phenols for the chain propagation reaction could be expressed by Eq. (1), where k_{inh}, k_p, and [LH] represent

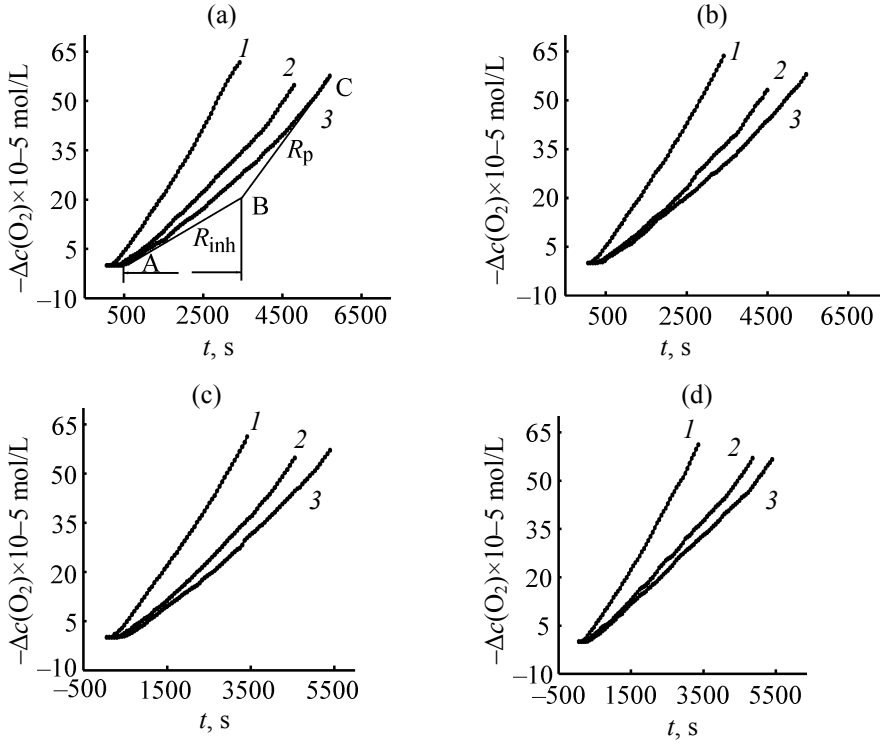


Fig. 3. Oxygen consumption curves [(*1*) 1.75, (*2*) 8.75, (*3*) 17.55 μM] of the initiation of AIBN-induced oxidation of styrene. (a) C^2-phenol, (b) C^4-phenol, (c) C^6-phenol, and (d) C^8-phenol.

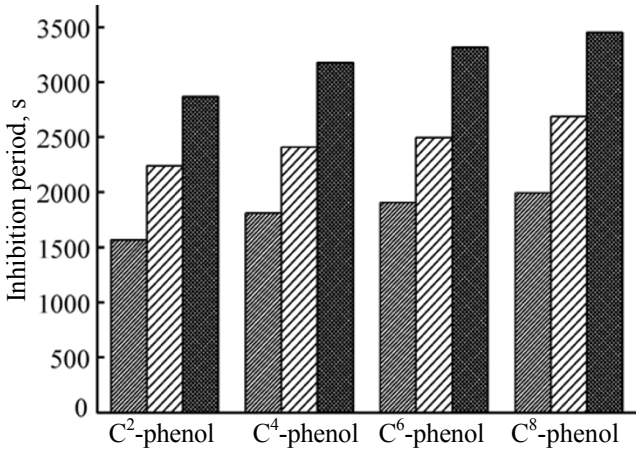


Fig. 4. Inhibition period (t_{inh}) of aliphatic diamine bridged hindered phenols.

the susceptibility of the peroxy radical to capture the hydroxyl atom from antioxidants, the rate constant of chain propagation (238 M^{-1} s^{-1} at 50°C) and concentration of styrene [16, 17]. Inhibition period could be deduced from the AB segment (Fig. 4). The stoichiometric factor, n, refers to the number of peroxy free radicals trapped by every antioxidant molecule and can be expressed by Eq. (2) [18].

$$-d[O_2]/dt = R_{inh} = k_p[LH]/(t_{inh}k_{inh}), \quad (1)$$

$$n = (R_i t_{inh})/[AH], \quad (2)$$

$$R_i = R_g = 2.64\times10^{-6}[AIBN]. \quad (3)$$

Upon depletion of all antioxidants at the point B, oxygen consumption rate increased rapidly. Based on the steady-state kinetic treatment, the rate of oxygen consumption in the period of propagation, R_p, could be expressed by Eq. (4), where $k_p/(2k_t)^{0.5}$ referred to oxidizability of the substrate, representing the susceptibility of styrene to undergo peroxidation. The kinetic chain length, *kcl*, that defined the cycle number of chain propagation in the periods of inhibition (kcl_{inh}) and propagation (kcl_p) was deduced from Eqs. (5) and (6).

$$R_p = -d[O_2]/dt = [(k_p/(2k_t)^{0.5}]R_i^{0.5}[LH], \quad (4)$$

$$kcl_{inh} = R_{inh}/R_i, \quad (5)$$

$$kcl_p = R_p/R_i. \quad (6)$$

For many phenol antioxidants scavenging of free radicals was slow and the mechanism was very complicated. Therefore, it was important to explore scavenging of the peroxy free radical mechanisms by antioxidants.

According to the accumulated data (Table 2) phenols acted as antioxidants with clear inhibition period during which the rate of chain propagation and the kinetic chain length were significantly decreased. Oxygen consumption rate (R_{inh}), kinetic chain length (kcl_{inh}) and oxidizability [$k_p/(2k_t)^{0.5}/10^{-2}$] decreased with increased antioxidant concentration due to the fact that more hydrogen was provided by the phenolic

Table 2. Scavenging parameters of aliphatic diamine bridged hindered phenols on the ROO radical[a]

Antioxidants	Concentration, μM	$R_p\times10^{-8}$, M/s	$R_{inh}\times10^{-8}$, M/s	t_{inh}, s	$k_p/(2k_t)^{0.5}/10^{-2}$	$k_{inh}\times10^5$, M/s	kcl_p	kcl_{inh}
C^2-Phenol	1.75	24.8	16.7	1568	0.128	6.95	3.91	2.63
	8.75	16.7	8.1	2241	0.086	10.03	2.63	1.27
	17.55	15.6	7.3	2869	0.081	8.69	2.47	1.15
C^4-Phenol	1.75	24.5	16.1	1811	0.127	6.24	3.86	2.53
	8.75	17.6	9.0	2412	0.091	8.38	2.77	1.41
	17.55	17.3	8.2	3179	0.089	6.98	2.72	1.29
C^6-Phenol	1.75	23.5	16.3	1908	0.122	5.85	3.71	2.57
	8.75	18.4	9.5	2499	0.095	7.66	2.90	1.49
	17.55	17.5	8.7	3318	0.091	6.30	2.76	1.37
C^8-Phenol	1.75	24.1	16.2	1993	0.125	5.63	3.84	2.55
	8.75	16.1	10.2	2690	0.083	6.63	2.53	1.61
	17.55	14.9	9.4	3453	0.077	5.61	2.35	1.48

[a] $R_i = R_g = 2.64\times10^{-6}[AIBN]$ $s^{-1} = 6.34\times10^{-8}$ M/s at concentration of AIBN = 24 mM, [LH] = 0.765 mol/L.

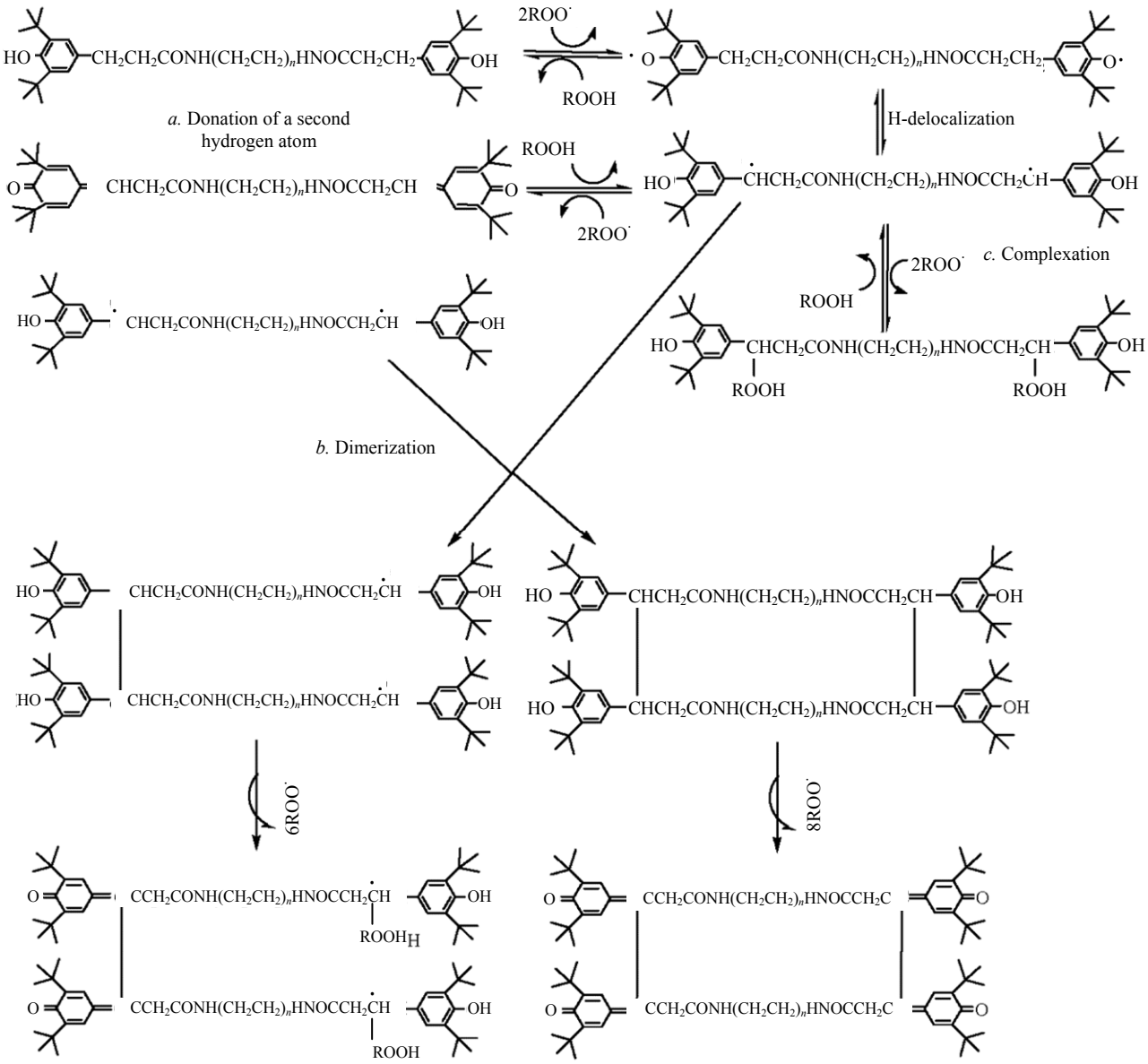


Fig. 5. Proposed mechanism for aliphatic diamine bridged hindered phenols/DPPH· reaction

hydroxyl which could be trapped by the ROO• radical. With the increase in concentration of hindered phenols and the bridged group, the t_{inh} value increased (Table 2). On the basis of R_i data, the relationship between t_{inh} and concentration of hindered phenols could be obtained as listed in Table 3. The n values of the hindered phenols were similar due to their close chemical structures. Generally, one hydroxyl group could trap only one DPPH radical. However, the n value did not correspond to the number of the OH groups hydrogen atoms available for donation and was higher than that of the OH groups of phenols. This was in agreement with the results of presented by Kurechi [19] who determined that compounds with the hydroxyl group, sterically hindered by the *tert*-butyl group, demonstrated high antioxidant ability.

There could be considered three possible approaches to explaining the antioxidant ability of aliphatic diamine hindered bridged phenols [20]. After the first reaction, phenol radicals could form a kenolic compound by donation of two hydrogen atoms or two DPPH molecular radicals combined with two aryl radicals as shown in steps *a* (n = 4) and *b* (n = 4) (Fig. 5). The third approach referred to dimerization between two phenoxyl radicals [21]. Upon dimerization it could

Table 3. The equation of t_{inh} [antioxidant] and n of an antioxidant in protecting styrene against AIBN-induced oxidation[a]

Antioxidant	t_{inh} (s) = (n/R_i) [antioxidant (μM)] + constant	n
C^2-Phenol	t_{inh} = 81.8 [antioxidant] + 1460.4 (r^2 = 0.9853)	5.18
C^4-Phenol	t_{inh} =86.6 [antioxidant] + 1657.5 (r^2 = 0.9997)	5.49
C^6-Phenol	t_{inh} =89.4 [antioxidant] + 1739.1 (r^2 = 0.9985)	5.67
C^8-Phenol	t_{inh} =92.1 [antioxidant] + 1850.2 (r^2 = 0.9968)	5.83

[a] $R_i = R_g = 6.34\times10^{-8}$ M/s.

interact for the second time with DPPH radicals to produce the bi-quinonoid structure, as presented in steps *c* (n =5) and *d* (n = 6).

EXPERIMENTAL

Materials. Analytical reagent grade ethylenediamine, 1,4-butanediamine, 1,6-hexanediamine, 1,8-diaminooctane, and toluene were purchased from Tianjin Kemiou Chemical regent development center (China). Dibutyltin dilaurate was purchased from Changchun Chemical (China). DPPH was purchased from Beijing Jingkehongda Biotechnology Co., Ltd. (China). Antioxidant 1098 was purchased from Ciba Specialty Chemicals (Shanghai, China). 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionyl chloride (3,5-propionyl chloride) was synthesized in our laboratory [22].

Synthesis of the aliphatic diamine bridged hindered phenols. Aliphatic diamine was added to toluene and heated slowly to 25°C and stirred for 10 min under the atmosphere of N_2. Dibutyltin dilaurate (2% of aliphatic diamine) and 3,5-propionyl chloride (the molar ratio of 3,5-propionyl chloride to aliphatic diamine 4 : 1) were added to the above mixture and heated slowly to 40°C. The reaction lasted for 15 h. The solvent and by-product methanol were removed by rotary evaporation at 40°C. The residue was stored at 25°C for 8 h and filtered off as white solid, washed three times with toluene (100 mL) and dried under vacuum for 24 h at 60°C. Four aliphatic diamine bridged hindered phenols were synthesized with ethylenediamine, 1,4-butanediamine, 1,6-hexanediamine, and 1,8-diamineoctane as bridging groups, named C^2-phenol, C^4-phenol, C^6-phenol (Irganox 1098), and C^8-phenol, respectively.

Aliphatic diamine bridged hindered phenols. mp 211.8–212.4 (C^2-phenol), 205.1–205.6 (C^4-phenol), 161.2–162.0 (C^6-phenol), and 156.0–162.1°C (C^8-phenol). IR spectrum, ν, cm^{-1}: 3500–3650, 1530, 1640, 1240, 1390. ^{1}H NMR spectrum of C^2-phenol, δ, ppm: 5.08 s (2H, Ar-OH), 1.39–1.42 m [36H, $C(CH_3)_3$], 6.97–7.05 m (4H, Ar-H), 3.36–3.41 m (4H, Ar-CH_2), 2.83 s (4H, Ar-C–CH_2), 7.32 t (2H, CONH), 2.42–2.46 t (4H, O=C–N–CH_2–CH_2–N–C=O). The spectral data for other synthesized aliphatic diamine bridged hindered phenols were similar. The chemical shifts of protons of the bridging groups [O=C–N–C–$(CH_2)_n$–C–N–C=O] were in the range of 5.67–5.72. ESI-MS (*m/z*): 581.4 $[M + 1]^+$ (C^2), 609.5 $[M + 1]^+$ (C^4), 637.5 $[M + 1]^+$ (C^6), and 665.5 $[M + 1]^+$ (C^8).

Measurement of the scavenging DPPH free radical. Scavenging capacity of aliphatic diamine bridged hindered phenols on DPPH free radical were determined by the modified method reported by Brand–Williams [23]. DPPH free radical was dissolved in ethanol and the solution was stored in darkness. Ethanol solution of aliphatic diamine bridged hindered phenol was added to the DPPH radical solution and the mixture was equilibrated for 5 min at 25°C. Absorbance at 517 nm was recorded at various time intervals until the reaction reached equilibrium. The scavenging ability of hindered phenols was expressed in terms of % inhibition and antioxidant ability (AE). Percent inhibition was calculated by Eq. (7).

$$\%\ \text{Inhibition} = \left(\frac{A_0 - A_t}{A_0}\right) \times 100, \qquad (7)$$

where A_0 and A_t were the absorbance at 517 nm of the mixture solution at the beginning and at the certain time.

The antioxidant ability was calculated by Eq. (8) [24].

$$\text{AE} = \frac{1}{EC_{50}TC_{50}}, \qquad (8)$$

where EC_{50} was the amount of hindered phenol needed to decrease the initial DPPH radical concentration by 50%, and TC_{50} was the time needed to reach the steady state at EC_{50} concentration.

Measurement of the ROO free radical scavenging ability. Free-radical reactions in the absence and presence of antioxidants were monitored by oxygen uptake determination, and the free-radical resource was

supplied by decomposition of 2,2'-azodi(isobutyronitrile) (AIBN) at 50°C. Briefly, the rate of oxygen uptake was measured under the oxygen atmosphere in a closed stainless steel autoclave. AIBN and the synthesized hindered phenol antioxidants were dissolved directly in toluene. The process of AIBN-induced peroxidation of styrene was monitored by an oxygen consumption apparatus equipped with an oxygen pressure gauge sensitive to oxygen pressure. Styrene in the toluene solution and antioxidant solution were poured into a stainless steel autoclave which had been filled in with dry nitrogen three times and then purged by oxygen. The mixture was stirred for 10 min at 50°C. The AIBN solution was injected to the mixture with a syringe in order to initiate the peroxidation of styrene. Initial concentrations of AIBN and styrene were 24 mM and 0.765 M, respectively. All experiment were repeated not less than three times with the standard deviation within 10% and the final data were calculated as average of three independent measurements.

CONCLUSIONS

Four hindered phenol antioxidants with aliphatic diamines as the bridging groups were synthesized by acylamidation. Radical scavenging activity of antioxidants was tested by stable DPPH$^{\bullet}$ and inhibiting AIBN induced oxidation of styrene. The experimental data indicated that the hindered phenols had high scavenging ability on the DPPH radical that increased with increasing concentration of an antioxidant and decreased with higher length of bridging groups at the same concentration. The scavenging effect of hindered phenols on the ROO$^{\bullet}$ radical was opposite to that of the DPPH radical.

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