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CHEMICAL KINETICS AND CATALYSIS

Kinetics and Structure-Activity Relationship of Dendritic Bridged Hindered Phenol Antioxidants to Protect Styrene against Free Radical Induced Peroxidation[1]

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Abstract—A series of dendritic poly(amido-amine) (PAMAM) bridged hindered phenols antioxidants were synthesized. The active antioxidant group (3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionic acid) was attached to two generations of PAMAM dendrimers, and their structure was verified by nuclear magnetic resonance (NMR) and fourier transform infrared spectra (FT-IR). The antioxidant abilities of the dendritic phenols to inhibit the oxidation of styrene were evaluated and the relationships between the length of core, the generation of dendrimers and the antioxidant activities were established. The reaction kinetics of scavenging peroxyl radicals was followed by oxygen consumption. The inhibition time (t_{inh}) values showed the dendritic phenols had the ability of scavenging peroxyl radicals, and that the antioxidant ability increased with the increasing length of the core and the generation. The kinetic analysis demonstrated that dendritic phenols could slow the rate of styrene peroxidation induced by AIBN, as shown by the number of trapping $ROO^{\bullet}$ (n), and this role was in accordance with that of the t_{inh} values.

Keywords: dendritic phenol, generation, antioxidant ability, kinetic parameter

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INTRODUCTION

Polymer materials, which are commonly hydrocarbon polymers, have a broad range of applications in food packaging, pipeline, and medical equipment due to their excellent mechanical properties, low cost, and superior processability [1–3]. However, polymer materials are susceptible to oxidative degradation during processing or in the presence of light, heat, oxygen, and chemical agents [4]. As a consequence free radicals, produced by oxidation, could lead to a loss of performance. Therefore, hindered phenol antioxidant is an essential additive, due to the presence of a hydroxyl substituent and aromatic structure, which inhibits oxidation by a hydrogen atom competing with the polymer in the formation of peroxy radicals [5, 6]. Several synthetic approaches of hindered phenol antioxidants have been developed to improve the antioxidant properties. These include the grafting of phenolic antioxidants onto the polymer backbone or nanoparticles to increase the molecular weight of phenolic antioxidants [7]. Xue et al. [8] synthesized several norbornene derivatives by attaching sterically hindered phenol to norbornene, and the antioxidant activity of the hindered phenol was investigated by 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical assay. The results showed that polymers bearing 3,5-di-*tert*-butyl-4-hydroxyphenyl-propionate, as side chain, exhibited a higher radical scavenging ability than the polymers bearing 3,5-di-*tert*-butyl-4-hydroxy-benzoate as side chain. Shi et al. [9] synthesized a functionalization of multiwalled carbon nanotubes (MWCNTs) with antioxidant ability by grafting the antioxidant group onto the surface of MWCNTs. The resulting antioxidant activity showed that not only the free radical scavenging ability of functional MWCNTs but also the dispersion and antioxidant efficiency the antioxidants in the polyethylene matrix are increased.

Dendrimer, with its uniform and well-defined size and shape, has attracted great interest. Dendrimer has a large number of surface groups which can be easily tailored to achieve various objects [10]. For their unique architecture and macromolecular characteristics, dendrimers have become one of the research hotspots in areas such as inorganic chemistry, organic chemistry, polymer chemistry, coordination chemistry and bioscience, especially in synthesis, drug delivery, biotechnology, nanotechnology, detection and catalyst [11]. Surface functional dendrimers have been synthesised and their applications have become the primary focus. Malgas et al. [12] synthesised first-gen-

[1] The article is published in the original.

eration and second-generation multinuclear nickel complexes based polypropyleneimine dendrimers, and the use of the corresponding Ni complexes for catalysis were evaluated in the oligomerization of ethylene. The oligomerization results showed these dendritic catalysts exhibited catalysis activity, and that the second-generation dendritic catalyst showed higher activity than that of the first-generation catalyst.

Zarghami et al. [13] successfully synthesized integrated biosorbents for heavy metals, by grafting different generation PAMAM dendrimers to chitosan, and their reactive Pb^{2+} removal potential was evaluated. The results showed that the products with higher generations of dendrimer, have more adsorption capacities than those of products with lower generations of dendrimer and chitosan alone. Phenolic units were attached to 4-aminomethylbenzylamine to form an antioxidant and the ability of the dendritic antioxidant to scavenge DPPH is higher than that of some natural antioxidants [14]. Li et al. [15] synthesized two dendritic antioxidants by grafting 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionic acid to dendritic PAMAM with ammonia as core, and evaluated their antioxidant activity in polyolefins. The results showed that the antioxidant activity of dendritic antioxidants was better than that of antioxidant 3114 and antioxidant 1010 in polyolefin. Later, Li et al. [16] synthesized two dendritic antioxidants by grafting 3-(3,5-di-*tert*-butyl-4-hydroxy-phenyl)-propionic acid to dendritic PAMAM with ethanediamine as core, and evaluated their antioxidant activity using the DPPH assay. The results showed that the scavenging capacities of dendritic hindered phenols were superior to antioxidant 1010 and antioxidant 1098 at the same phenol hydroxyl groups.

The aim of this work is to synthesize a series of dendritic antioxidants by changing the length of the core and the generation of dendritic PAMAM. The influences of the concentration of phenol hydroxyl, structure and the generation of PAMAM on the antioxidant activities by inhibiting styrene oxidation induced by azodiisobutyronitrile (AIBN) were also examined. The synthetic route and the names of these dendritic PAMAM bridged hindered phenol antioxidants are shown in Schemes 1 and 2.

EXPERIMENTAL

Materials

Chloroform, benzene, toluene, styrene, potassium carbonate and azodiisobutyronitrile (AIBN) purchased from Tianjin Kemiou Chemical Reagent Development Center (China), were of an analytical reagent grade and used directly. 3-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-propionyl chloride(3,5-propionyl chloride) was synthesized in our laboratory [17]. A series of the first-generation dendritic poly(amidoamine) (1.0G PAMAM) and the second-generation dendritic poly(amidoamine) (2.0G PAMAM) with different lengths of the core were also synthesized in our laboratory [18]. The structures of the 1.0G and 2.0G dendritic PAMAM bridged hindered phenols were characterized by ^{1}H NMR (NOVA400 MHz spectrometer) and FT-IR (TENSOR27).

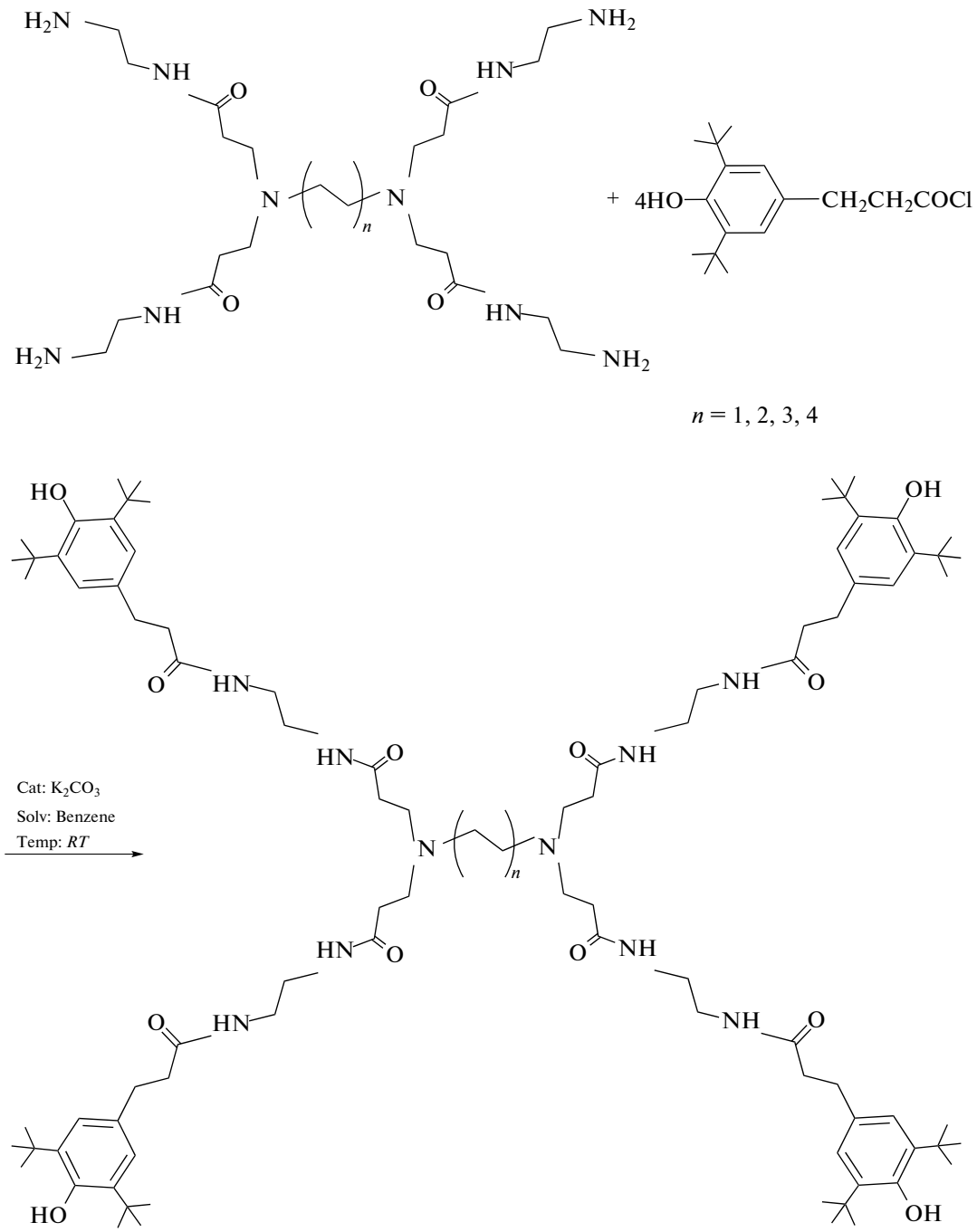
Syntheses of Dendritic PAMAM Bridged Hindered Phenol Antioxidants

Syntheses of 1.0G dendritic PAMAM bridged hindered phenol antioxidants. 1.0G PAMAM (0.003 mol) and anhydrous potassium carbonate (0.024 mol) were dissolved in 20 mL of distilled water at room temperature. A solution of 3,5-propionyl chloride (0.030 mol) in 60 mL toluene was added slowly to the solution of 1.0G PAMAM at 0°C. The mixture was heated slowly to 25°C and was reacted for 24 h at 25°C. The mixture was cooled to 5°C and left for 5 h, then filtered under vacuum pressure. The crude solid was recrystallized twice from benzene-chloroform to obtain a series of 1.0G dendritic PAMAM bridged hindered phenol antioxidants (C2-1.0G dendritic phenol, C4-1.0G dendritic phenol, C6-1.0G dendritic phenol, and C8-1.0G dendritic phenol).

C2-1.0G dendritic phenols. IR spectrum, ν, cm^{-1}: 3633(Ar–OH), 3289(N–H), 3089(=CH from benzene ring), 2955(–CH_2 or –CH_3), 1650(C=O), 1233(–C(CH_3)); ^{1}HNMR spectrum, δ, ppm: 7.30 (s, 8H, –CON<u>H</u>–), 7.05 (d, 8H, Ar–<u>H</u>), 5.07 (s, 4H, Ar–O<u>H</u>), 4.10–4.19 (m, 16H, C<u>H</u>$_2$–CONH–), 3.31–3.37 (s, 8H, Ar–CH_2–C<u>H</u>$_2$–), 2.53–2.58(s, 8H, Ar–C<u>H</u>$_2$–CH_2–), 2.61–2.68 (t, 16H, –CONH –C<u>H</u>$_2$), 2.15–2.27 (m, 4H, N–C<u>H</u>$_2$–C<u>H</u>$_2$–N), 1.45 (s, 72H, –C(C<u>H</u>$_3$)$_3$).

C4-1.0G dendritic phenols. IR spectrum, ν, cm^{-1}: 3632(Ar–OH), 3289(N–H), 3091(=CH from benzene ring), 2958(–CH_2 or –CH_3), 1652(C=O), 1233 (–C(CH_3)); ^{1}HNMR spectrum, δ, ppm: 7.28 (s, 8H, –CON<u>H</u>–), 6.99 (d, 8H, Ar–<u>H</u>), 5.08 (s, 4H, Ar–O<u>H</u>), 4.11–4.17 (m, 16H, C<u>H</u>$_2$–CONH–), 3.29–3.32 (s, 8H, Ar–CH_2–C<u>H</u>$_2$–), 2.54-2.58 (s, 8H, Ar–C<u>H</u>$_2$–CH_2–), 2.59–2.65 (t, 16H, –CONH–C<u>H</u>$_2$), 2.18–2.25 (m, 4H, N–C<u>H</u>$_2$–CH_2–CH_2–C<u>H</u>$_2$–N), 1.89–1.96 (s, 4H, N–CH_2–C<u>H</u>$_2$–C<u>H</u>$_2$–CH_2–N), 1.46 (s, 72H, –C(C<u>H</u>$_3$)$_3$).

C6-1.0G dendritic phenols. IR spectrum, ν, cm^{-1}: 3634(Ar–OH), 3293(N–H), 3095(=CH from benzene ring), 2955(–CH_2 or –CH_3), 1655(C=O), 1233(–C(CH_3)); ^{1}HNMR spectrum, δ, ppm: 7.26 (s, 8H, –CON<u>H</u>–), 6.95 (d, 8H, Ar–<u>H</u>), 5.05 (s, 4H, Ar–O<u>H</u>), 4.12–4.18 (m, 16H, C<u>H</u>$_2$–CONH–), 3.26–3.33 (s, 8H, Ar–CH_2–C<u>H</u>$_2$–), 2.51-2.54 (s, 8H, Ar–C<u>H</u>$_2$–CH_2–), 2.56–2.61 (t, 16H, –CONH–C<u>H</u>$_2$), 2.15–2.21 (m, 4H, N–C<u>H</u>$_2$–(CH_2–CH_2)$_2$–C<u>H</u>$_2$–N),

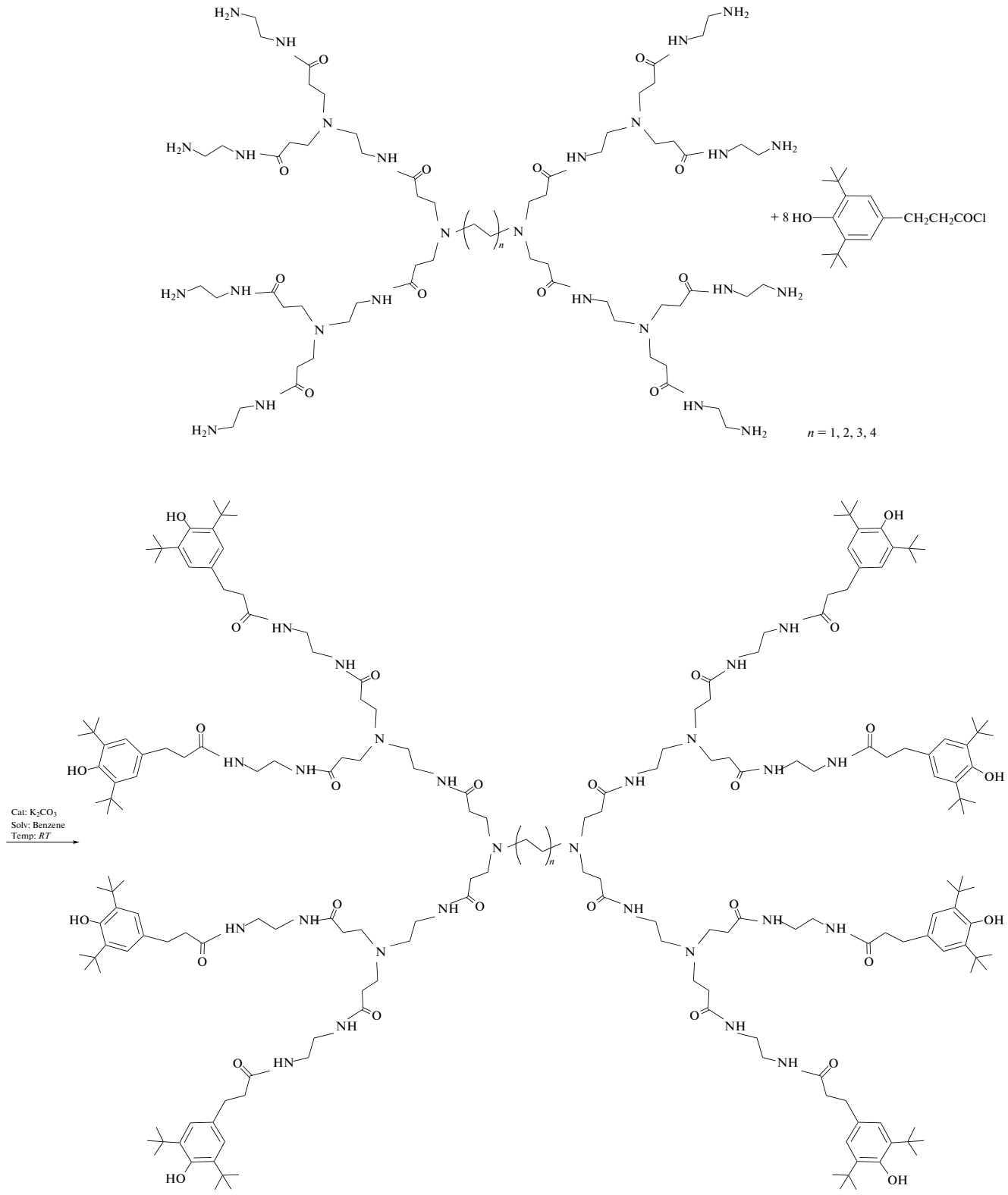


Scheme 1. Synthetic routes of a series of 1.0G dendritic PAMAM bridged hindered phenol antioxidants.

1.94–2.08 (s, 8H, N–CH_2– ($C\underline{H}_2$– $C\underline{H}_2$)$_2$–CH_2–N), 1.42 (s, 72H, –C($C\underline{H}_3$)$_3$).

C8-1.0G dendritic phenols. IR spectrum, ν, cm^{-1}: 3633(Ar–OH), 3330(N–H), 3095(=CH from benzene ring), 2955(–CH_2 or –CH_3), 1648(C=O), 1234(–C(CH_3)); ^{1}HNMR spectrum, δ, ppm: 7.22 (s, 8H, –CON$\underline{H}$–), 6.93 (d, 8H, Ar–$\underline{H}$), 5.03 (s, 4H, Ar–O$\underline{H}$), 4.10–4.13 (m, 16H, $C\underline{H}_2$–CONH–), 3.28–3.32 (s, 8H, Ar–CH_2–$C\underline{H}_2$–), 2.49–2.52 (s, 8H, Ar–$C\underline{H}_2$–CH_2–), 2.55–2.59 (t, 16H, –CONH–$C\underline{H}_2$), 2.11–2.17 (m, 4H, N–$C\underline{H}_2$–(CH_2–CH_2)$_3$–$C\underline{H}_2$–N), 1.92–2.09 (s, 12H, N–CH_2–($C\underline{H}_2$–$C\underline{H}_2$)$_3$–CH_2–N), 1.40 (s, 72H, –C($C\underline{H}_3$)$_3$).

Syntheses of 2.0G dendritic PAMAM bridged hindered phenol antioxidants. 2.0G PAMAM (0.002 mol) and anhydrous potassium carbonate (0.0075 mol) were dissolved in 20 mL of distilled water at room temperature. The solution of 3,5-propionyl chloride



Scheme 2. Synthetic routes of a series of 2.0G dendritic PAMAM bridged hindered phenol antioxidants.

(0.040 mol) in 60 mL toluene was added slowly to the solution of 1.0G PAMAM at 0°C. The mixture was heated slowly to 25°C and was reacted for 24 h at 25°C. The mixture was cooled to 5°C and left for 5 h, then filtered under vacuum pressure. The crude solid was recrystallised twice from benzene-chloroform to

obtain a series of 2.0G dendritic PAMAM bridged hindered phenol antioxidants (C2-2.0G dendritic phenol, C4-2.0G dendritic phenol, C6-2.0G dendritic phenol, and C8-2.0G dendritic phenol).

C2-2.0G dendritic phenols. IR spectrum, ν, cm^{-1}: 3632(Ar–OH), 3296(N–H), 3089(=CH from benzene ring), 2952($-CH_2$ or $-CH_3$), 1652(C=O), 1233($-C(CH_3)$), ^{1}HNMR spectrum, δ, ppm: 7.23 (s, 20H, –CONH–), 6.97 (d, 16H, Ar–H), 5.05 (d, 8H, Ar–OH), 4.11 (m, 40H, $-CH_2-CONH-$), 3.28–3.32 (s, 8H, $Ar-CH_2-CH_2-$), 2.49–2.52 (s, 8H, $Ar-CH_2-CH_2-$), 2.56–2.60 (t, 40H, $-CONH-CH_2$), 2.52–2.63 (s, 8H, $-CH_2$–*tert*–N–), 2.16–2.29 (m, 4H, $N-CH_2-CH_2-N$), 1.42 (s, 144H, $-C(CH_3)_3$).

C4-2.0G dendritic phenols. IR spectrum, ν, cm^{-1}: 3632(Ar–OH), 3288(N–H), 3087(=CH from benzene ring), 2953($-CH_2$ or $-CH_3$), 1651(C=O), 1233($-C(CH_3)$), ^{1}HNMR spectrum, δ, ppm: 7.30 (s, 20H, –CONH–), 6.95 (d, 16H, Ar–H), 5.02 (d, 8H, Ar–OH), 4.10 (m, 40H, $-CH_2-CONH-$), 3.35 (s, 8H, $Ar-CH_2-CH_2-$), 2.33–2.50 (s, 8H, $Ar-CH_2-CH_2-$), 2.54–2.61 (t, 40H, $-CONH-CH_2$), 2.54–2.63 (s, 8H, $-CH_2$–*tert*–N–), 2.18–2.29 (m, 4H, $N-CH_2-CH_2-CH_2-CH_2-N$), 1.89–1.96 (s, 4H, $N-CH_2-CH_2-CH_2-CH_2-N$), 1.41 (s, 144H, $-C(CH_3)_3$).

C6-2.0G dendritic phenols. IR spectrum, ν, cm^{-1}: 3630(Ar–OH), 3286(N–H), 3089(=CH from benzene ring), 2952($-CH_2$ or $-CH_3$), 1645(C=O), 1234($-C(CH_3)$), ^{1}HNMR spectrum, δ, ppm: 7.25 (s, 20H, –CONH–), 6.98 (d, 16H, Ar–H), 5.04 (d, 8H, Ar–OH), 4.10 (m, 40H, $-CH_2-CONH-$), 3.28–3.30 (s, 8H, $Ar-CH_2-CH_2-$), 2.47–2.52 (s, 8H, $Ar-CH_2-CH_2-$), 2.57–2.60 (t, 40H, $-CONH-CH_2$), 2.54–2.63 (s, 8H, $-CH_2$–*tert*–N–), 2.16–2.29 (m, 4H, $N-CH_2-(CH_2-CH_2)_2-CH_2-N$), 1.89–1.95 (s, 8H, $N-CH_2-(CH_2-CH_2)_2-CH_2-N$), 1.41 (s, 144H, $-C(CH_3)_3$).

C8-2.0G dendritic phenols. IR spectrum, ν, cm^{-1}: 3632(Ar–OH), 3288(N–H), 3089(=CH from benzene ring), 2952($-CH_2$ or $-CH_3$), 1647(C=O), 1233($-C(CH_3)$), ^{1}HNMR spectrum, δ, ppm: 7.23 (s, 20H, –CONH–), 6.97 (d, 16H, Ar–H), 5.03 (d, 8H, Ar–OH), 4.11 (m, 40H, $-CH_2-CONH-$), 3.27–3.32 (s, 8H, $Ar-CH_2-CH_2-$), 2.49–2.52 (s, 8H, $Ar-CH_2-CH_2-$), 2.56–2.63 (t, 40H, $-CONH-CH_2$), 2.52–2.60 (s, 8H, $-CH_2$–*tert*–N–), 2.16–2.24 (m, 4H, $N-CH_2-(CH_2-CH_2)_3-CH_2-N$), 1.88–1.96 (s, 12H, $N-CH_2-(CH_2-CH_2)_3-CH_2-N$), 1.37 (s, 144H, $-C(CH_3)_3$).

Styrene Protection Against AIBN-Induced Oxidation by Dendritic PAMAM Bridged Hindered Phenol Antioxidants

The experiment of AIBN-induced oxidation of styrene was performed as described in the literature with a little modification. Briefly, styrene toluene solution and AIBN toluene solution were put into a stainless steel autoclave that had been charged with dry nitrogen three times and then purged by oxygen. The resulting mixture was then stirred for 10 min at 50°C. Dendritic phenol solution was injected into the autoclave and the exhausted oxygen was measured in the reaction process. Every experiment was repeated at least three times and the final result was the average values from the three independent measurements.

RESULTS AND DISCUSSION

Deduction of AIBN-Induced Peroxidation Based on the Oxygen Consumption Determination

The hydrogen atom from the phenolic antioxidants can trap peroxyl radicals to form more stable macromolecular radicals, which couple rapidly with the peroxyl radical to form the non-radical compound. The peroxidation would then effectively be inhibited. In order to study the reaction rate and mechanism of the chemical reaction process, it is necessary to explore the chemical reaction kinetics. One of the more important parameters of evaluating phenolic antioxidants abilities is the rate constant for its reaction with peroxyl radicals. In the experiment the values were obtained by studying the thermally initiated autoxidation of styrene, in the absence and presence of the antioxidant.

The process of peroxidation of styrene by AIBN can be represented by the following equations [19], where k_d, k_p, and k_t are rate constants for decomposition of the initiator, for chain propagation (the value is 238 M^{-1} s^{-1} at 50°C) and for chain termination, respectively.

Initiation:

$$R-N=N-R \xrightarrow{k_d} 2R^{\bullet} + N_2, \quad (1)$$

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet}, \quad (2)$$

$$ROO^{\bullet} + Ph-CH=CH_2 \rightarrow ROOH + Ph-CH=CH^{\bullet}. \quad (3)$$

Propagation:

$$Ph-CH=CH^{\bullet} + O_2 \xrightarrow{\text{fast}} Ph-CH_2COO^{\bullet}, \quad (4)$$

$$Ph-CH_2COO^{\bullet} + Ph-CH=CH_2 \xrightarrow{k_p} Ph-CH_2COOH + Ph-\dot{C}H. \quad (5)$$

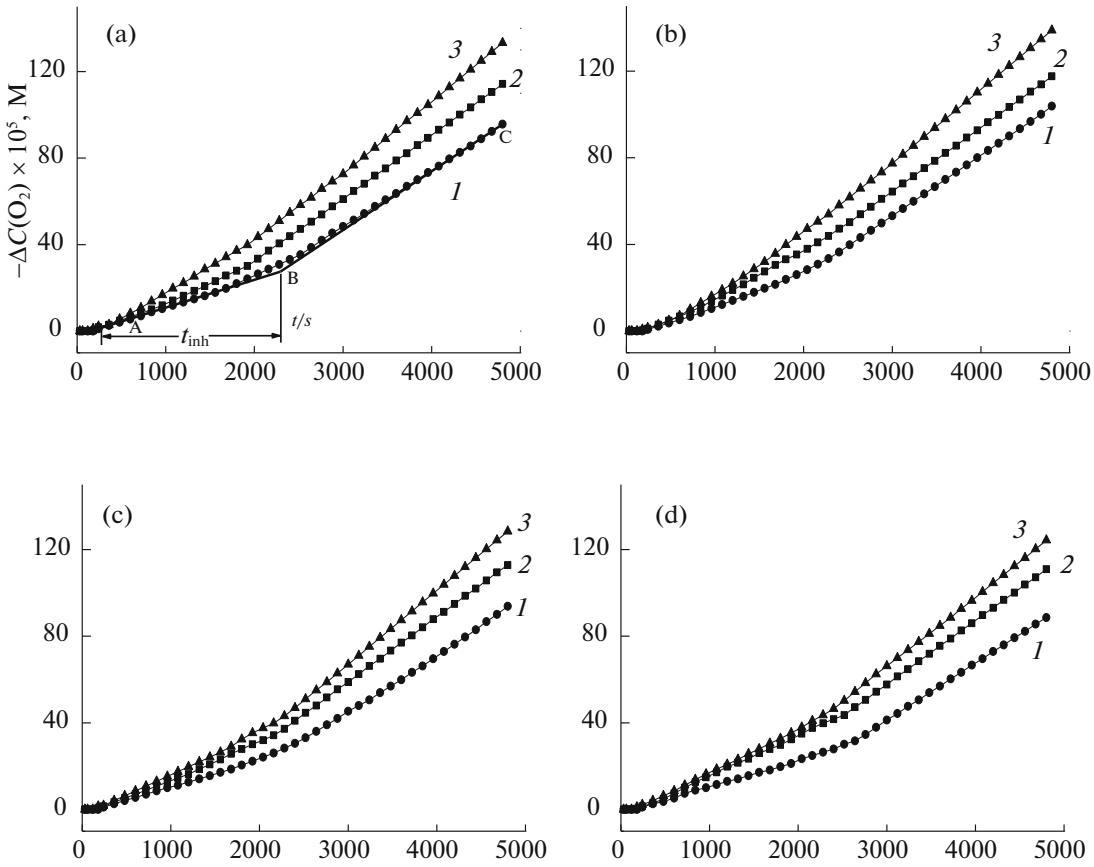


Fig. 1. Oxygen consumption curve of styrene protection against AIBN-induced oxidation by 1.0G dendritic bridged hindered phenol antioxidants; (a) C2-1.0G dendritic phenol, (b) C4-1.0G dendritic phenol, (c) C6-1.0G dendritic phenol, (d) C8-1.0G dendritic phenol; concentrations of antioxidant: (*1*) 8.77, (*2*) 4.38, (*3*) 0.88 μM.

Termination:

$$2\text{Ph}-\text{CH}_2\text{COO}^\bullet \xrightarrow{k_t} \text{Ph}-\text{CH}_2\text{COOOOCCH}_2-\text{Ph}. \quad (6)$$

In the presence of dendritic PAMAM bridged hindered phenol antioxidants, the peroxyl radicals can be trapped rapidly and the peroxidation would be inhibited. The process is showed in equations:

$$2\text{Ph}-\text{CH}_2\text{COO}^\bullet + \text{AH} \rightarrow \text{Ph}-\text{CH}_2\text{COOH} + \text{A}^\bullet, \quad (7)$$

$$2\text{Ph}-\text{CH}_2\text{CO}^\bullet + \text{A}^\bullet \rightarrow \text{Ph}-\text{CH}_2\text{COOA}. \quad (8)$$

In this paper, the oxygen consumption was measured in styrene protection against AIBN-induced oxidation by dendritic phenol antioxidants at different concentrations of antioxidant, and the reaction kinetics in the process were studied by the oxygen consumption at different reaction time (Figs. 1 and 2).

The inhibition rate (R_{inh}) of a series of dendritic phenol antioxidants during the inhibition period can be obtained from the figures and be expressed by equation:

$$-d[\text{O}_2]/dt = R_{inh} = k_p R_i[\text{LH}]/(nk_{inh}[\text{AH}]), \quad (9)$$

where k_{inh}, [LH], and [AH] represent the susceptibility of the peroxy radical to capture the hydrogen atom from antioxidants, and the concentrations of styrene and dendritic phenol, respectively [20]. The stoichiometric factor from equation:

$$n = (R_i t_{inh})/[\text{AH}], \quad (10)$$

where n refers to the number of peroxy free radicals trapped by every antioxidant molecule, t_{inh} stands for the inhibition period of the dendritic phenol in the initiation of AIBN-induced oxidation of styrene. This can be measured by the cross-point from the tangent lines for the inhibition and oxidation periods in Fig. 1a [21]. The inhibition rate, can also be expressed by equation:

$$-d[\text{O}_2]/dt = R_{inh} = k_p[\text{LH}]/(t_{inh}k_{inh}). \quad (11)$$

The free radical is supplied by the decomposition of AIBN at 50°C, where the generation rate of free radical, R_g, can be expressed by equation:

$$R_g = R_i = 2.64 \times 10^{-6}[\text{AIBN}]. \quad (12)$$

After consumption of all the antioxidant at point B, the oxygen consumption rate increased and changed

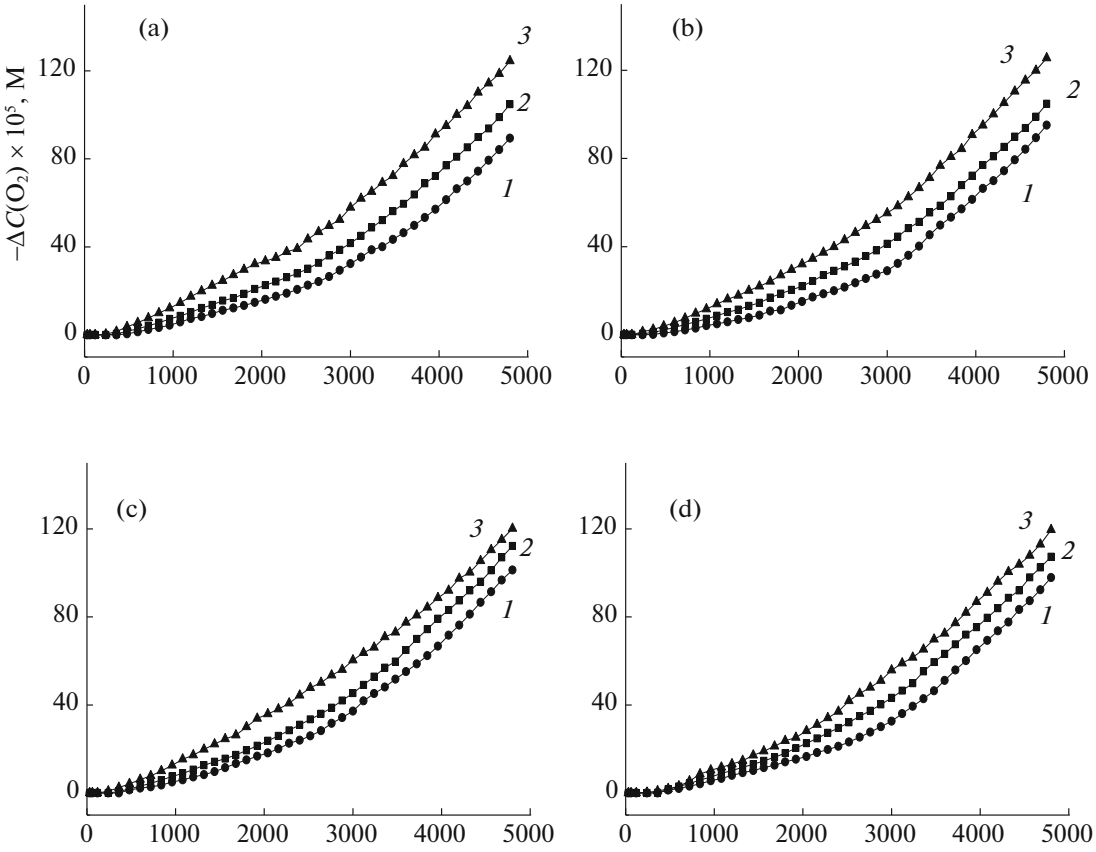


Fig. 2. Oxygen consumption curve of styrene protection against AIBN-induced oxidation by 2.0G dendritic bridged hindered phenol antioxidants; (a) C2-2.0G dendritic phenol, (b) C4-2.0G dendritic phenol, (c) C6-2.0G dendritic phenol, (d) C8-2.0G dendritic phenol; (*1*–*3*) see Fig. 1.

obviously with the increasing concentration of the phenol hydroxyl. Based on the steady-state kinetic treatment, the reaction rate in the period of propagation, R_p, can be expressed by equation:

$$R_p = -d[O_2]/dt = (k_p/(2k_t)^{0.5})R_i^{0.5}[LH], \quad (13)$$

where $k_p/(2k_t)^{0.5}$ is referred to the oxidizability of the substrate, representing the susceptibility of styrene to undergo peroxidation [22]. The kinetic chain length, *kcl*, that defines the number of chain propagation by each initiating radical in the periods of inhibition (kcl_{inh}) and propagation (kcl_p), are shown in equations:

$$kcl_{inh} = R_{inh}/R_i, \quad (14)$$

$$kcl_p = R_p/R_i. \quad (15)$$

Therefore, the kinetic detail of a free radical related reaction can be described by n, k_{inh}, oxidizability, and *kcl*.

Antioxidant Ability of Dendritic PAMAM Bridged Hindered Phenol Antioxidants

It can be seen from Figs. 1 and 2 that dendritic phenol antioxidants were well-behaved antioxidants which showed inhibition periods. The inhibition periods of dendritic phenol antioxidants at different concentrations are shown in Tables 1 and 2. With increasing concentration of dendritic phenol antioxidants, the amount of oxygen consumption decreased while the t_{inh} values increased. The results suggested that dendritic phenol antioxidants played a role in inhibiting oxidation during the styrene polymerization process.

By comparing t_{inh} with the corresponding value in Fig. 3, it is shown that the t_{inh} value of dendritic phenols not only increased with the increase of the length of core but also with the generation of PAMAM. This was because the chance of dendritic phenols coming into contact with the long chain alkyl radical produced during the polymerization, increased with the increasing length of core. For the different generation dendritic phenols, the t_{inh} value of the C8-1.0G phenol was 2614 s, while that of the C8-2.0G phenol was 3290 s. The possible reason was that dendritic phenol antioxidants are an inter-molecular complex phenolic amine antioxidant, and terriary amines could donate electron-pair to terminate free radicals, except for the hydroxyl group in the molecular. When the concentration of phenolic hydroxyl of 1.0G and 2.0G dendritic phenols is the same, the concentration of N atom of

Table 1. Parameters of inhibition of AIBN-induced peroxidation of styrene by 1.0G dendritic PAMAM bridged hindered phenol antioxidants

Antioxidants	c, μM	$R_p \times 10^8$, M s^{-1}	$R_{inh} \times 10^8$, M s^{-1}	t_{inh}, s	$k_p/(2k_t)^{0.5}/10^{-3}$	$k_{inh} \times 10^{-5}$, M^{-1} s^{-1}	kcl_p	kcl_{inh}
C2-1.0G dendritic phenol	0.88	34.11	27.71	2010	0.17	3.27	5.38	4.37
	4.38	29.52	18.05	2092	0.15	4.89	4.66	2.84
	8.77	26.42	12.77	2170	0.13	6.69	4.17	2.01
C4-1.0G dendritic phenol	0.88	34.11	27.75	2064	0.17	3.17	5.38	4.38
	4.38	29.35	20.90	2142	0.15	4.07	4.63	3.29
	8.77	27.91	14.88	2217	0.14	5.52	4.40	2.35
C6-1.0G dendritic phenol	0.88	34.11	28.65	2112	0.17	3.01	5.38	4.52
	4.38	30.06	21.35	2210	0.15	3.86	4.74	3.37
	8.77	27.16	15.03	2351	0.14	5.15	4.28	2.38
C8-1.0G dendritic phenol	0.88	32.57	28.88	2312	0.16	2.73	5.13	4.55
	4.38	29.48	21.85	2496	0.15	3.34	4.65	3.45
	8.77	26.29	15.53	2614	0.13	4.49	4.15	2.45

$R_i = R_g = 2.64 \times 10^{-6}$[AIBN] s^{-1} = 6.34×10^{-8} M s^{-1} when the concentration of AIBN was 2.4 mM. [LH] = 0.765 mol/L.

Table 2. Parameters of inhibition of AIBN-induced peroxidation of styrene by 2.0 G dendritic PAMAM bridged hindered phenol antioxidants

Antioxidants	c, μM	$R_p \times 10^8$, M s^{-1}	$R_{inh} \times 10^8$, M s^{-1}	t_{inh}, s	$k_p/(2k_t)^{0.5}/10^{-3}$	$k_{inh} \times 10^{-5}$, M^{-1} s^{-1}	kcl_p	kcl_{inh}
C2-2.0G phenol	0.44	41.23	17.37	2801	0.21	3.74	6.50	2.74
	2.19	40.89	13.33	2855	0.21	4.80	6.45	2.10
	4.39	40.56	9.13	2930	0.21	6.80	6.39	1.44
C4-2.0G phenol	0.44	41.72	17.09	2875	0.21	3.70	6.58	2.69
	2.19	39.35	12.59	2955	0.20	4.89	6.21	1.99
	4.39	38.54	8.67	3012	0.20	6.97	6.08	1.37
C6-2.0G phenol	0.44	42.98	15.54	2947	0.22	3.98	6.78	2.45
	2.19	42.35	11.98	3023	0.21	5.02	6.68	1.89
	4.39	41.67	8.22	3132	0.21	7.07	6.57	1.61
C8-2.0G phenol	0.44	40.46	14.57	3069	0.20	4.07	6.38	3.09
	2.19	40.22	10.49	3123	0.21	5.56	6.34	2.13
	4.39	39.67	7.69	3290	0.21	7.20	6.26	1.54

$R_i = R_g = 2.64 \times 10^{-6}$[AIBN] s^{-1} = 6.34×10^{-8} M s^{-1} when the concentration of AIBN was 2.4 mM. [LH] = 0.765 mol/L.

2.0G dendritic phenols are higher than that of 1.0G hindered phenols. Therefore, 2.0G dendritic phenols had higher antioxidant ability for protecting styrene against AIBN-induced oxidation.

Reaction Kinetics of Dendritic PAMAM Bridged Hindered Phenol Antioxidants

Kinetics parameters of dendritic phenol antioxidants to protect styrene against free radical induced peroxidation are shown in Tables 1 and 2. The increase of antioxidant concentration, reduced oxygen consumption rate (R_{inh}), kinetic chain length (kcl_{inh}) and oxidizability ($k_p/(2k_t)^{0.5}/10^{-2}$), demonstrating that the styrene was protected more markedly by dendritic phenol antioxidants [23]. This was because the hydroxyl groups of dendritic phenol antioxidants can be hydrogen-abstracted, by either the initiating radical or the propagating radical, and therefore decreasing the peroxidation rate of styrene (Eq. (7)).

Above all, the kinetic discussion on a free radical related reaction is based on knowing R_i. The relation-

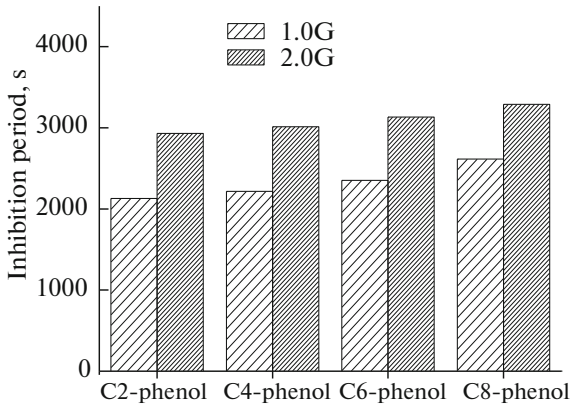


Fig. 3. Inhibition period (t_{inh}) of a series of dendritic bridged hindered phenols.

ship between t_{inh} and [AH] should be established, where the slope, n/R_i, can be obtained from Eq. (10). The equation of t_{inh} ~ [AH] is listed in Table 3. The n values of dendritic phenol antioxidants all increased with increasing of the length of core, and the n values of 2.0G dendritic phenol antioxidants were higher than those of 1.0G dendritic phenol antioxidants. This was in accordance with that of t_{inh} values. As for dendritic phenol antioxidants, a much higher n value implies that it appears to be a strong antioxidant. However, the n value of dendritic phenols was less than the number of hydroxyl groups in the molecular. This implies that the dendritic phenols could effectively trap the peroxy free radicals, (Eq. (7)), but the dendritic phenol radical formed might be subject to side reactions that diminishes the effectiveness of the reaction. See Eq. (8) [24].

Table 3. The equation of t_{inh}, $s = ac+b$ (c is concentration of antioxidant, μM, and $a = n/R_i$) and the stoichiometric factor, n, of hindered phenol antioxidants in protecting styrene against AIBN-induced oxidation

Antioxidant	a	b	r^2	n
C2-1.0G dendritic phenol	15.2	1996.1	0.99	0.96
C4-1.0G dendritic phenol	19.3	2050.7	0.98	1.21
C6-1.0G dendritic phenol	30.3	2082.3	0.98	1.92
C8-1.0G dendritic phenol	37.8	2297.2	0.92	2.39
C2-2.0G dendritic phenol	32.9	2781.6	0.94	2.08
C4-2.0G dendritic phenol	34.3	2867.6	0.99	2.17
C6-2.0G dendritic phenol	46.9	2924.1	0.99	2.97
C8-2.0G dendritic phenol	56.8	3027.7	0.99	3.60

$R = R_g = 6.34 \times 10^{-8}$ M s^{-1}, thus, n = coefficient $\times 6.34 \times 10^{-8}$ M s^{-1}.

We suggest the possible hypotheses to explain the anti-radical efficiencies of 1.0G dendritic phenol antioxidants. After donating hydroxyl atom, 1.0G dendritic phenol radical species could form peroxy radical molecules combined with alkyl radicals as showed in Fig. 4. The same reaction mechanism appeared for 2.0G dendritic phenol antioxidants.

Structure-Activity Relationship of Dendritic PAMAM Bridged Hindered Phenol Antioxidants

The thermodynamics parameter, n, just indicates an aspect of antioxidant ability, and the authentic reaction behavior should be expressed by an inhibition rate constant (k_{inh}). The k_{inh} of adding 2.0G dendritic phenol antioxidants was much higher than that of adding 1.0G dendritic phenol antioxidants. This demonstrated 2.0G dendritic phenol antioxidants played the more effective role in suppressing radical propagation. This role was in accordance with those of n value and t_{inh} value. This mean the antioxidant ability of dendritic phenol antioxidants were affected by the generation, and increased with an increase of the generation of antioxidants. The possible reason is that the inner space of dendritic phenols molecule increased with an increase in the generation and could accommodate more peroxy radicals to react with tertiary amine groups. Surprisingly, the k_{inh} of adding 2.0G dendritic phenols increased with increasing of the concentration, and the k_{inh} of adding 1.0G dendritic phenols decreased. This was because the k_{inh} value is related to not only the t_{inh} value but also the R_{inh} value, as Eq. (11) shows.

CONCLUSIONS

A number of hindered phenol active group have been covalently grafted onto the first-generation and second-generation dendritic PAMAM by the condensation reaction of the amidation. The antioxidant abilities were assessed by inhibiting AIBN induced oxidation of styrene. Based on the test results, the scavenging ability of the dendritic phenol antioxidants on the peroxy free radicals increased, through both increasing the concentration of hydroxyl groups, and also on increasing the length of the core for the same number of hydroxyl groups. Furthermore, compared with the 1.0G dendritic phenols, 2.0G dendritic phenols antioxidants exhibited higher t_{inh} values and n values and were more efficient in preventing styrene from AIBN-induced oxidation. This was due to more secondary amine groups and tertiary amine groups. A series of

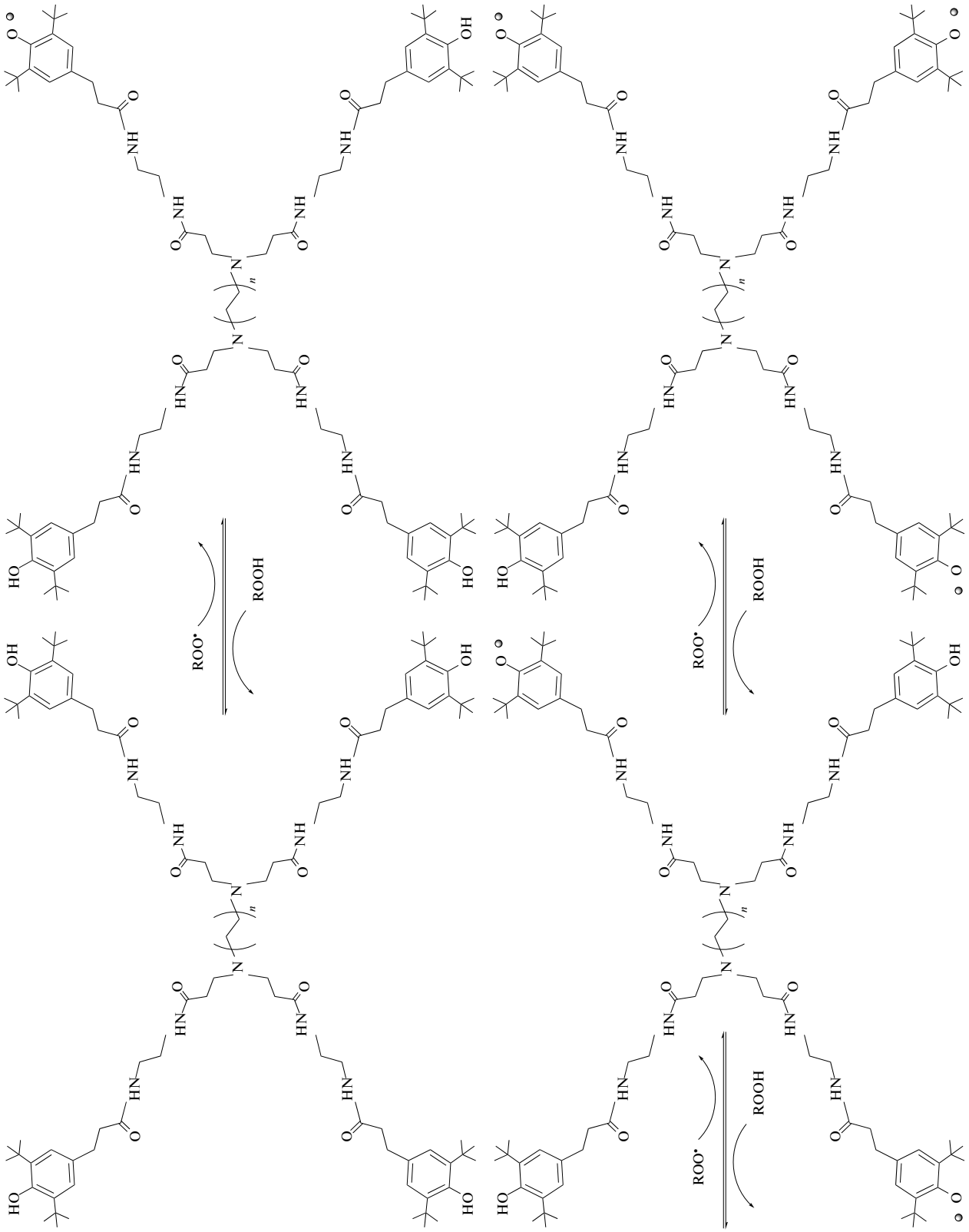


Fig. 4. Proposed mechanism for 1.0G dendritic bridged hindered phenol antioxidants/ROO• reaction.

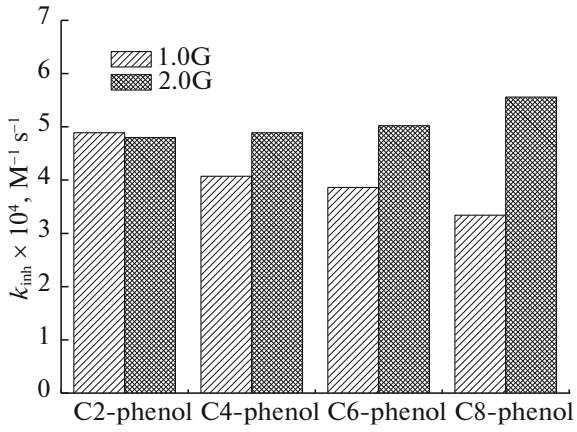


Fig. 5. Relationship between the inhibition rate constant and the different dendritic phenols.

PAMAM dendrimers with phenol ending groups are expected to have many applications. Other properties of these hindered phenols will be studied in our further work.

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