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Kinetic and mechanistic studies on the inhibition of free radical-initiated polymerization of styrene by β-carotene and α-tocopherol

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ABSTRACT: The inhibition of free radical-initiated polymerization of styrene by β-carotene (βC) and α-tocopherol (TOH) was studied by dilatometry. The polymerization was initiated by 2,2′-azobis(isobutyronitrile) at 50 °C in chlorobenzene and inhibited by βC and/or TOH. It was found that βC and TOH could efficiently inhibit the polymerization, either used individually or in combination, and a significant synergistic effect was observed when they were used in combination. It is proposed that retinal, which is the principal oxidation product of βC, may be involved in the synergistic inhibition reaction of βC and TOH. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: polymerization; inhibition; synergsim; styrene; β-carotene; α-tocopherol

INTRODUCTION

α-Tocopherol (TOH), the most effective component of vitamin E, is a well-known lipid-soluble chain-breaking antioxidant which can scavenge chain-propagating peroxyl radicals and protect cellular membranes against oxidative damage both *in vitro*[1,2] and *in vivo*.[3,4] β-Carotene (βC) has been recognized as an unusual lipid-soluble antioxidant.[5] We found recently that βC and TOH exhibited novel synergistic antioxidation and mutual protection effects in the inhibition of linoleic acid peroxidation in homogeneous solution and in micelles.[6–8] In this paper, we report a kinetic study on the inhibition effect of βC and TOH against the 2,2′-azobis(isobutyronitrile) (AIBN)-induced polymerization of styrene by using dilatometry.

EXPERIMENTAL

Materials

D,L-α-Tocopherol (Merck, biochemical regent) and all-*trans*-retinal (Sigma) were used as received and kept under nitrogen in a refrigerator before use. β-Carotene (Merck, biochemical reagent) was purified before use by column chromatography on neutral alumina with carbon tetrachloride as the eluent. 2,2′-Azobis(isobutyronitrile) (AIBN) was purchased from Shanghai 4th Chemicals and recrystallized from absolute ethanol before use. Styrene was purchased from Shanghai 2nd Chemicals and treated with 10% NaOH, dried over anhydrous calcium chloride and distilled in vacuum before use to remove peroxides and inhibitors. Other reagents were treated by conventional methods.

Determination of inhibition period

A chlorobenzene solution containing 6.92 M styrene, 17–20 mM AIBN and different amounts of inhibitors was filled into a dilatometer which was kept in a thermostated bath at 50 ± 0.1 °C. The reaction kinetics were followed by monitoring the liquid levels of the dilatometer. The volume of the dilatometer was 15 ml and the volume of the capillary was about 8×10^{-4} ml mm^{-1}, corresponding to 0.032% conversion of styrene when the level of the solution in the capillary decreased by 1 mm. Each experiment was repeated two or three times and the relative standard deviation was within 10%. The reaction yield, C, can be described by[9]

$$C(\text{wt\%}) = 100\Delta V/V_0 - V_\infty \qquad (1)$$

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The rate of propagation can be represented by[9]

$$R_p = C[\mathrm{M}]_0/100\Delta t \qquad (2)$$

where ΔV is the change of volume observed, V_0 is the initial volume, V_∞ is the final volume when all of the monomer is converted into the polymer and $[\mathrm{M}]_0$ is the initial concentration of styrene.

RESULTS AND DISCUSSION

The free radical polymerization initiated by an azo initiator can be simply described as follows:

Initiation:

$$\mathrm{R{-}N{=}N{-}R} \xrightarrow{k_d} 2e\mathrm{R}^{\cdot} + \mathrm{N_2} + (1-e)\mathrm{R{-}R} \qquad (3)$$

$$\mathrm{R}^{\cdot} + \mathrm{CH_2{=}CHPh} \longrightarrow \mathrm{R{-}CH_2CHPh}^{\cdot} \qquad (4)$$

Propagation:

$$\mathrm{R{-}[CH_2CHPh]}_n^{\cdot} + \mathrm{CH_2{=}CHPh} \xrightarrow{k_p} \mathrm{R{-}[CH_2CHPh]}_{n+1}^{\cdot} \qquad (5)$$

Termination:

$$\mathrm{R{-}[CH_2CHPh]}_n^{\cdot} + \mathrm{R{-}[CH_2CHPh]}_m^{\cdot} \xrightarrow{k_t} \mathrm{R{-}[CH_2CHPh]}_{n+m} \qquad (6)$$

where k_d, k_p and k_t represent rate constants for the decomposition of the initiator, chain propagation and termination, respectively, and e is the efficiency of the initiator.

The rate of propagation is given by

$$R_p = -\mathrm{d}[\mathrm{PhCH=CH_2}]/\mathrm{d}t = (k_p/2k_t)^{-1/2}[\mathrm{PhCH=CH_2}]R_i^{1/2} \qquad (7)$$

In the presence of an inhibitor (InH) the polymerization is inhibited by the following reactions:

$$\mathrm{R}^{\cdot} + \mathrm{InH} \longrightarrow \mathrm{RH} + \mathrm{In}^{\cdot} \qquad (8)$$

$$\mathrm{R{-}[CH2CHPh]n}^{\cdot} + \mathrm{InH} \longrightarrow \mathrm{R{-}[CH_2CHPh]_nH} + \mathrm{In}^{\cdot} \qquad (9)$$

The rate of chain initiation, R_i, can be determined from Eqn. (3) or by the inhibition method when an inhibitor is used:[10]

$$R_i = n[\mathrm{InH}]_0/\tau \qquad (10)$$

where τ is the induction period produced by the inhibitor and n is the stoichiometric factor which designates the number of radicals trapped by each inhibitor molecule. The n value of TOH has been shown to be 2.0 or very close to it,[11] hence R_i can be easily determined from the induction period of TOH. The ratio of rate constants $k_p/(2k_t)^{1/2}$ represents the polymerizability of the monomer and can be easily obtained by measuring the rate of polymer formation.

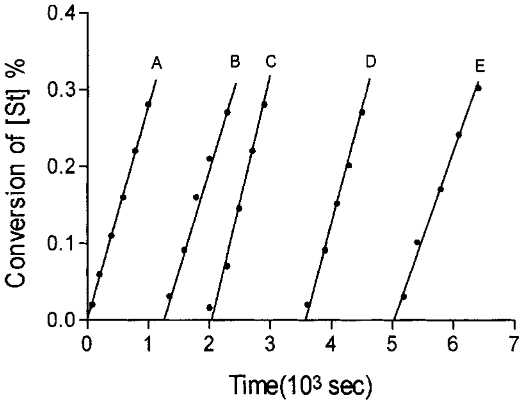


Figure 1. Representative polymerization kinetics as measured by consumption of styrene. The polymerization was initiated by AIBN (20.3 mM) and conducted in chlorobenzene at 50 °C. (A) Uninhibited reaction; (B) inhibited with βC (5.81×10^{-5} M); (C) inhibited with TOH (1.48×10^{-4} M); (D) inhibited with TOH (1.48×10^{-4} M) and βC (1.94×10^{-5} M); (E) inhibited with TOH (1.48×10^{-4} M) and βC (5.81×10^{-5} M)

A dilatometer measures the change in volume accompanying the chain propagation to follow the polymerization kinetics. It is a very accurate method because of the large difference in densities of the monomer and polymer.[9] In the presence of an inhibitor, the chain propagation is suppressed, hence any volume change in the capillary can be observed. When all of the inhibitor has been consumed, the polymerization starts and the volume of the reaction system decreases with a rate similar to that in the absence of the inhibitor, as shown in Fig. 1.

Inhibition of polymerization of styrene by α-tocopherol and β-carotene

Figure 1 shows the polymerization and inhibition kinetics measured by dilatometry. The monomer styrene was converted linearly with time in to polystyrene upon AIBN initiation. Addition of TOH or βC completely inhibited the polymerization, producing an induction period. After the induction period the polymerization took place at a similar rate to that in the absence of the inhibitor, demonstrating the exhaustion of the inhibitor. The time of the induction period, τ, depended linearly on the amount of the inhibitor used (Fig. 2). The slope of this straight line was close to $2.0/R_i$ for TOH and larger than $2.0/R_i$ for βC. The kinetic parameters obtained from a

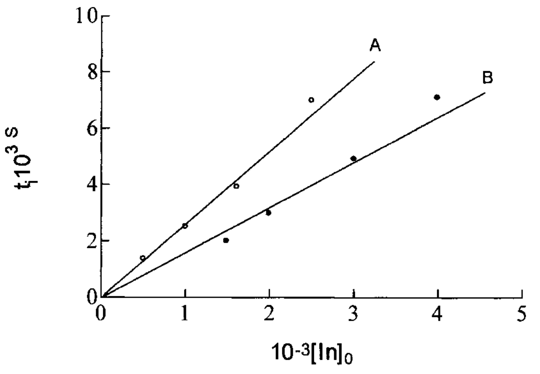


Figure 2. Plot of the induction period versus the concentration of inhibitor in the AIBN-initiated polymerization of styrene in chlorobenzene at 50 °C. The polymerization was initiated by 17.2 mM of AIBN. (A) [βC]; (B) [TOH]

series of experiments are summarized in Tables 1 and 2 where ν is the kinetic chain length, which is defined as the average number of monomer molecules consumed by each initiating radical and can be represented by the following equation:

$$\nu = R_p/R_i \tag{11}$$

Inhibition synergism of α-tocopherol and β-carotene

It can be seen from Fig. 1 that adding TOH and βC together significantly prolonged the induction period of the two inhibitors, and the induction period when the two inhibitors were used together [$\tau_{(T+C)}$] was longer than the sum of when they were used individually ($\tau_T + \tau_C$), demonstrating a synergistic inhibition effect. The synergistic efficiency, *SE* (%) can be represented as shown in Eqn. (12)[12] and the results are summarized in Table 3.

$$SE = [\tau_{(T+C)} - (\tau_T + \tau_C)]/\tau_{(T+C)} \times 100\% \tag{12}$$

It can be seen from Table 3 that the synergistic efficiency depended on the relative concentration of TOH and βC. An increase in the concentration of βC decreased the synergistic efficiency. We have reported previously that TOH and βC exhibited a synergistic antioxidation effect and mutual protection effect against peroxidation of linollic acid. That is, the decay of TOH became slower in the presence of βC, and the decay of βC became much

Table 1. Inhibition of AIBN-initiated polymerization of styrene by TOH in chlorobenzene at 50 °C[a]

[AIBN] (M × 10^2)	[TOH] (M × 10^4)	t_i (s × 10^{-3})	R_p[b] (M s^{-1} × 10^5)	ν[c]	$k_p/(2k_t)^{1/2}$ [(M s)$^{-1/2}$ × 10^3][d]
1.72	–	–	1.85	226	9.63
1.72	1.485	1.98	2.06	138	7.69
1.72	2.121	3.18	2.06	156	8.10
1.72	2.971	4.86	2.31	189	9.65
1.72	3.939	7.08	1.88	170	8.15
2.03	0.619	0.72	2.49	145	8.67
2.03	1.238	1.77	2.96	213	11.47
2.03	1.857	2.52	2.94	200	11.08
2.03	2.476	4.02	2.34	189	9.63
2.03	3.095	4.92	2.72	215	11.07

[a] $R_i = (0.87–1.03) \times 10^{-7}$ and $(1.11–1.50) \times 10^{-7}$ M s^{-1} calculated by Eqns (3) and ((10)), respectively, $k_d = 2.98 \times 10^{-6}$ s^{-1}(50 °C in styrene),[9] $e = 0.85$.[9]
[b] Calculated by Eqns. (1) and (2).
[c] Kinetic chain length after induction period.
[d] Polymerizability $k_p/(2k_t)^{1/2} = R_p/[\mathrm{St}]\, R_i^{1/2}$.

Table 2. Inhibition of AIBN-initiated polymerization of styrene by β-carotene in chlorobenzene at 50 °C[a]

[AIBN] (M × 10^2)	[βC] (M × 10^4)	t_i (s × 10^{-3})	R_p[b] (M s^{-1} × 10^5)	ν[c]	$k_p/(2k_t)^{1/2}$ [(M s)$^{-1/2}$ × 10^3][d]
1.72	–	–	1.85	226	9.36
1.72	0.194	0.072	2.70	330	13.6
1.72	0.404	0.660	2.06	252	10.4
2.03	0.496	0.390	1.58	267	8.04
1.72	0.581	1.260	2.15	202	11.0
1.72	0.807	2.580	1.65	227	8.42
1.72	1.614	3.900	1.85	267	9.42
1.72	2.422	7.080	2.18	193	11.0

[a] $R_i = 0.87–1.03 \times 10^{-7}$ M s^{-1} calculated by Eqn. (3).
[b–d] See footnotes to Table 1.

Table 3. Inhibition of AIBN-initiated polymerization of styrene by TOH and βC in chlorobenzene at 50 °C[a]

		Induction period (10^3 s)							
[TOH] (M × 10^4)	[βC] (M × 10^5)	τ_T	τ_C	$\tau_{(T+C)}$	$\tau_{(T+C)}-(\tau_T+\tau_C)$	R_p[b]	ν[c]	*SE* (%)	$k_p/(2k_t)^{1/2}$ [(M s)$^{-1/2}$ × 10^3][d]
1.485	1.937	1.98	0.07	3.66	1.61	2.31	283	78.4	11.7
1.485	4.036	1.98	0.66	4.50	1.86	1.54	188	70.1	7.83
1.485	5.812	1.98	1.26	4.98	1.74	1.96	240	53.7	9.92
1.485	8.072	1.98	2.58	6.12	1.56	1.58	195	34.2	7.97
1.485	16.14	1.98	3.90	9.36	3.48	1.75	214	59.2	8.81
1.485	24.22	1.98	7.08	11.34	2.28	1.38	169	25.2	6.96

[a–d] See footnotes to Table 1.

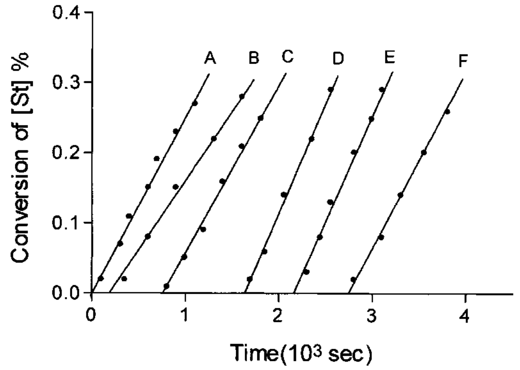


Figure 3. Representative polymerization kinetics as measured by consumption of styrene. The polymerization was initiated with AIBN (20.3 mM) and conducted in chlorobenzene at 50 °C. (A) Uninhibited reaction; (B) inhibited with RCHO (4.96 × 10^{-4} M); (C) inhibited with TOH (6.19 × 10^{-5} M); (D) inhibited with TOH (6.19 × 10^{-5} M) and RCHO (9.40 × 10^{-5} M); (E) inhibited with TOH (6.19 × 10^{-5} M) and RCHO (2.81 × 10^{-4} M); (F) inhibited with TOH (6.19 × 10^{-5} M) and RCHO (4.96 × 10^{-4} M)

slower in the presence of TOH.[6–8] It was also proposed that this novel mutual protection effect may involve retinal, which is a representative oxidative degradation product of βC, as the crucial intermediate. Therefore, the interaction of retinal with TOH in the inhibition of styrene polymerization was also studied.

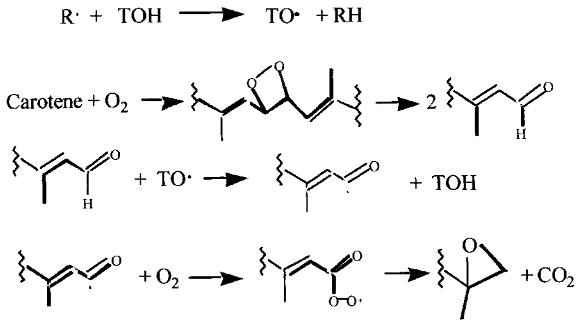
Inhibition synergism of α-tocopherol and retinal

It seems that βC should not be a good antioxidant and/or inhibitor and could not regenerate TOH from α-tocopheroxyl radical since it is a poor hydrogen and electron donor.[12] On the other hand, it was reported that oxidation of βC in pure oxygen produced a series of β-apocarotenals and β-apocarotenones in which all-*trans*-retinal (RCHO) is a representative compound.[13] We also found that about 36% of all-*trans*-retinal was obtained when a benzene solution containing all-*trans*-β-carotene was treated with AIBN at 50 °C for 8 h in air. Therefore, retinal and other apocarotenals may play a role in the inhibition of styrene polymerization when βC and TOH are used as inhibitors. As shown in Fig. 3, addition of retinal appreciably decreased the rate of propagation and produced a clear induction period, demonstrating that retinal could serve as a chain transfer agent and inhibitor to suppress and inhibit the polymerization of styrene. Furthermore, when retinal was used together with TOH the induction period of TOH was substantially increased and the synergistic efficiency was very high and increased with increase in the concentration of retinal. The results are summarized in Table 4.

Table 4. Inhibition of AIBN-initiated polymerization of styrene by TOH and retinal (RCHO) in chlorobenzene at 50 °C[a]

		Induction period (10^3 s)							
[TOH] (M × 10^4)	[RCHO] (M × 10^4)	τ_T	τ_R	$\tau_{(T+R)}$	$\tau_{(T+R)}-(\tau_T+\tau_R)$	R_p[b]	ν[c]	*SE* (%)	$k_p/(2k_t)^{1/2}$ [(M s)$^{-1/2}$ × 10^3][d]
6.19		0.72				2.04	119		7.14
	0.94		0.14			1.73	179		8.04
	2.81		0.18			1.79	185		8.32
	4.96		0.16			1.78	184		8.28
6.19	0.94	0.72		1.68	0.82	1.89	196	93.5	8.78
6.19	2.81	0.72		2.19	1.29	2.00	207	143	9.29
6.19	4.96	0.72		2.70	1.82	1.75	181	209	8.14

[a–d] See footnotes to Table 1.



Scheme 1. Proposed mechanism for the inhibition synergism of *β*C and TOH

We have reported previously[6–8] that retinal may reduce α-tocopheroxyl radical to regenerate TOH similarly to the reaction of ascorbic acid with α-tocopheroxyl radical.[14,15] The reaction between ratinal and α-tocopheroxyl radical has been confirmed recently by ESR spectroscopy.[16] Therefore, it is reasonable to assume that the synergistic inhibition of styrene polymerization by TOH and *β*C proceeds with a mechanism similar to that shown in Scheme 1.

CONCLUSIONS

TOH and *β*C can act as free radical inhibitors to inhibit AIBN-initiated polymerization of styrene. *β*C is more efficient than TOH with a stoichiometric factor, $n_{\beta C}$, closing to 4. When the two inhibitors are used together they show a significant synergistic inhibition effect with retinal as the active intermediate.

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REFERENCES

1. Niki E, Saito T, Kawakami A, Kamiya Y. *J. Biol. Chem.* 1984; **259**: 4177–4182.
2. Barclay LRC, Bailay AMH, Kong D. *J. Biol. Chem.* 1985; **260**: 15809–15814.
3. Buring JE, Hennekens CH. *J. Cell Biochem.* 1995; Suppl 22: 226–230.
4. Packer L, Maquire JJ, Melhorn RJ, Serbinova E, Kagan VE. *Biochem. Biophys. Res. Commun.* 1989; **159**: 229–235.
5. Burton GW, Ingold KU. *Science* 1984; **224**: 569–573.
6. Li Z-L, Wu L-M, Ma L-P, Liu Y-C, Liu Z-L. *J. Phys. Org. Chem.* 1995; **8**: 774–780.
7. Liu Z-L, Li Z-L, Ma L-P, Liu Y-C. In *Proceedings of the International Symposium on Natural Antioxidants*, Packer L, Traber MG, Xin WJ (eds). JAOCS Press: Champaign, IL, 1996; chapt. 21, 196–216.
8. Li Z-L, Wu L-M, Ma L-P, Liu Y-C, Liu Z-L. *Chem. J. Chin. Univ.* 1997; **11**: 1814–1819.
9. Allcock HR, Lampe FW. *Contemporary Polymer Chemistry*, Prentice Hall: Englewood Cliffs, NJ, 1981; 280–282.
10. Howard JA, Ingold KU. *Can J. Chem.* 1967; **45**: 785–792; 1967; **45**: 793–803; 1964; **42**: 1044–1056.
11. (a) Walling C. *J. Am. Chem. Soc.* 1969; **91**: 7590–7594; (b) Burton GW, Ingold KU. *Acc Chem. Res.* 1986; **19**: 194–201; (c) Burton GW, Ingold KU. *J. Am. Chem. Soc.* 1981; **103**: 6472–6477.
12. Yi OY, Han D, Skin HK. *J. Am. Oil Chem. Soc.* 1991; **11**: 881–883.
13. Hardelman GJ, Frederik JGM, Kurk V, Chatterjee A. *Free Rad. Biol. Med.* 1991; **10**: 427–437.
14. Packer JE, Slater TF, Willson RL. *Science* 1979; **218**: 737–738.
15. Liu Z-L, Han Z-X, Yu K-C, Zhang Y-L, Liu Y-C. *J. Phys. Org. Chem.* 1992; **5**: 33–38.
16. Zhu B, Chen Z-H, Chen Y-D, Jia Z-S, Jia Y, Wu L-M, Yang L, Liu Z-L. *Appl. Magn. Reson.* 2000; **18**: 397–406.