Synthesis and Performance of Phenolic Polybutadiene-Bound Stabilizers

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ABSTRACT: An antioxidant derivative, 6-sulfanylhexyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propanoate, was synthesized and examined. With a radical initiator, the addition of this compound to pending vinyls of OH-telechelic, low molecular weight liquid polybutadiene (LBH) was performed to various degrees of conversion to form polymeric antioxidants (PAOs) in which the phenolic moiety was separated from the main chain by a spacer [—CH$_2$CH$_2$—S—(CH$_2$)$_6$—O—CO—]. Pure, unstabilized LBH was mixed in several ratios with PAOs, Irganox 1520, and Irganox 1076,

and the oxidation stabilities of these mixtures, determined by thermogravimetric analysis and differential scanning calorimetry, were compared. Probably because of their good compatibility with LBH, PAOs exhibited equal or better effectiveness than commercial antioxidants of the Irganox type. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 87: 885–889, 2003

Key words: antioxidants; polybutadiene; differential scanning calorimetry (DSC); thermogravimetric analysis (TGA)

INTRODUCTION

Ideally, the stabilizers [antioxidants (AOs) and UV stabilizers] of polymers should meet three basic requirements: (1) to effectively protect polymers from various, mostly radical degrading processes; (2) to be compatible with the polymer; and (3) to persist in the polymer. Although the first two requirements are usually satisfied by any modern low molecular weight stabilizer with a single effective stabilizing moiety (or, in some cases, two) in its molecule, the third requirement is generally not fully met, especially under severe conditions, because the concentrations of most classic stabilizers in polymeric materials gradually decrease through evaporation and/or extraction with a liquid. A simple increase in the molecular weight of such single-moiety stabilizers mostly diminishes their relative effectiveness.

As a possible solution to the problem, syntheses of various oligomeric and polymeric stabilizers have been reported in the literature[1–8] for more than a decade. Basically, there are two different synthetic approaches: (1) the attachment of a polymerizable group (mostly vinyl) to the molecule of a stabilizer followed by the copolymerization of the resulting substance with a monomer[9] and (2) the attachment of a

stabilizing moiety to a modified[10] or unmodified[11] (co)polymer chain.

The addition of AO structures directly to main-chain double bonds has already been described (for ABS copolymers, see refs. 12–14). In the first step, a thiol group is introduced onto the AO molecule; then, the resulting substance reacts, through its thiol groups, with C≡C bonds of the copolymer by a free-radical mechanism (a radical initiator is used; see ref. 15).

We used this general idea with two crucial changes: (1) unlike ABS, the butadiene blocks of which contained only main-chain C≡C bonds, our polybutadiene substrate contained about 60% pending vinyls, which were much more sensitive to oxidation, and (2) unlike the polymeric ABS-based stabilizers previously cited, the AO structures of which were attached to the polymer chain directly, a spacer was used in our case (it could be assumed that, with the length and flexibility of the side chain or spacer increasing, the degree of freedom and operation volume of the AO moiety increased). Specifically, we attempted to attach a phenolic AO to C≡C bonds of low molecular weight, OH-telechelic polybutadienes [hydroxylated liquid polybutadiene (LBH)]. For this purpose, it seemed advantageous to introduce the SH (thiol) group into the molecule of the AO so that this group and the effective stabilizing moiety were separated by a relatively long spacer. The radical addition of such modified AOs onto double bonds (mostly pending vinyls) of LBHs through SH groups should yield hydroxy-telechelic, polymeric AOs to be admixed to bulk LBH. We expected that the incorporation of such a mixture

of diols into polyurethanes would give self-stabilized materials.

EXPERIMENTAL

Materials

Commercial low molecular weight, 1,2-rich, OH-telechelic polybutadiene, supplied by Kaučuk a.s. (Kralupy nad Vltavou, Czech Republic) under the trademark Krasol LBH (hereafter simply called LBH), was used as a polymer substrate. It was prepared by a living anionic polymerization in polar media that was terminated with propylene oxide, yielding secondary hydroxy groups at both chain ends.[16] Its molecular parameters, given by the manufacturer, were as follows: the number-average molecular weight was 2.37 $\times 10^3$; the weight-average molecular weight/number-average molecular weight ratio was 1.13; the 1,4-cis-, 1,4-trans-, and 1,2-monomer unit contents were 19.6, 18.0, and 62.4%, respectively; and the nonhydroxy-lated, semitelechelic, and telechelic chain contents were 0.1, 1.1, and 98.8%, respectively. For the stabilization of LBH, the manufacturer used Irganox 1520 L, its concentration (ca. 0.03 wt %) being an order of magnitude lower than usual for standard applications.

Irganox 1520 L and Irganox 1076 {i.e., 2-methyl-4,6-bis[(octylsulfanyl)methyl]phenol and octadecyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propanoate, respectively}, both from Ciba Specialty Chemicals, Inc. (Basel, Switzerland), were used as received.

Synthesis of 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propanoic acid (I)

A modified procedure[17] was applied. NaOH (3.20 g, 0.08 mol) was dissolved in a 1/1 (v/v) ethanol/water mixture (400 mL), and this solution was added to Irganox 1076 (21.00 g, 0.041 mol). The mixture was stirred and refluxed under argon for 24 h and then kept at 5°C overnight. The separated octadecanol was filtered off, and the slightly yellowish filtrate was acidified with 25 mL of 20% HCl to precipitate the product. The crystals of **I** were recrystallized from an ethanol/water mixture to yield 7.1 g (60% in theory) of colorless needles (mp = 173–174°C, lit. 172–174°C[18]). The results of an elemental analysis for $C_{17}H_{26}O_3$ were as follows: for carbon, 73.34% was calculated and 72.94% was found, and for hydrogen, 9.41% was calculated, and 10.25% was found. The differences corresponded to 0.55 wt % residual water.

Synthesis of 6-sulfanylhexyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propanoate (II)

Compound **I** (5.00 g, 0.018 mol), 6-sulfanylhexan-1-ol (purum; Fluka (Buchs, Switzerland); 2.59 g, 0.019 mol),

4-methylbenzene-1-sulfonic acid (purum; Fluka; catalytic amount), and benzene (analytical-grade; Lachema, Brno, Czech Republic; 150 mL) were refluxed under argon in a flask equipped with a stirring bar and a special azeotropic adapter designed to prevent the formation of benzene/water emulsions in the distillate.[19] The reaction water was trapped from the circulating solvent with an active molecular sieve outside the reaction mixture. The degree of conversion was checked by liquid chromatography (completed within 24 h). The mixture was then transferred into a separation funnel and washed with saturated aqueous NaCl. The benzene layer was filtered, dried with anhydrous Na_2SO_4, filtered again, and concentrated. The oily residue was freed from volatile impurities via heating at 60°C and 13 Pa for 12 h, and the product (6.87 g, 96% in theory) was stored under argon to prevent oxidation. The purity of the product was checked by gas chromatography/mass spectrometry (GC-MS; 99%). The results of an elemental analysis for $C_{23}H_{38}O_3S$ were as follows: for carbon, 70.01% was calculated and 69.90% was found; for hydrogen, 9.71% was calculated, and 10.02% was found; and for sulfur, 8.12% was calculated, and 8.35% was found.

The formation of an isomeric product, that is, *S*-(6-hydroxyhexyl) 3-(3,5-di-*tert*-butyl-4-hydroxy)propanethioate, was excluded by IR and NMR spectroscopy. In IR spectra, the band of —C(O)—O— (1732 cm^{-1}) was found, whereas that of —C(O)—S— was absent. ^{1}H-NMR spectra showed the presence of OH in the benzene ring but no OH in the aliphatic chain [δ (ppm) = 1.2–1.6 (9H, m), 1.4 (18H, s), 2.43 (2H, q), 2.57 (2H, t), 2.85 (2H, t), 4.03 (2H, t), 5.14 (1H, s), and 6.97 (2H, s)].

Addition of II to LBH

Four reaction mixtures containing LBH (0.486 g, 9 mmol, C=C), 2,2-azobisisobutyronitril (0.074 g, 0.45 mmol), compound **II** (various amounts; see Table I), and toluene (up to 9 mL) were introduced into four cylindrical, 12-mL, glass ampules. After degassing by repeated freezing–thawing cycles on a vacuum line, they were sealed and placed in a water thermostat kept at 60°C for various periods of time.

The content of each ampule was then poured into methanol (analytical-grade; Lachema; 50 mL) under argon and vigorous stirring. The nonsedimenting emulsion obtained was centrifuged (2647 g, 30 min). The sediment was dissolved in approximately 5 mL of toluene, and 50 mL of methanol was added under stirring to form an emulsion again. This cycle was repeated five times for the removal of all nonpolymeric substances. Finally, the syrupy sediment was transferred into a small flask, dried at 65°C and 13 Pa for 8 h, and stored under argon. The characteristics of the products are given in the Results and Discussion section.

| Product | II/vinyl (mol/mol) | Reaction time (h) | x_{AO} as determined by | | | x | |
			Analysis C (S)	Gravimetry	^{1}H-NMR	1,2-Isomer	1,4-Isomer
PAO-1	0.050	24	0.060 (0.055)	0.050	0.052	0.534	0.414
PAO-2	0.133	40	0.142 (0.124)	0.160	0.137	0.420	0.443
PAO-3	0.217	56	0.229 (0.252)	0.270	0.256	0.282	0.462
PAO-4	0.300	72	0.295 (0.306)	0.390	0.376	0.221	0.403

x-molar fraction of unreacted units determined by ^{1}H-NMR. For other reaction conditions, see the text.

Removing Irganox 1520 L from the original LBH

A mixture of 10 g of LBH, 5 g of activated carbon black, and 100 mL of *tert*-butyl methyl ether (MTBE) was stirred overnight under argon, filtered, and concentrated. High performance liquid chromatography (HPLC) showed the complete removal of Irganox 1520 L.

Mixing LBH and various AOs [Irganox 1520 L, Irganox 1076, and polymeric antioxidants (PAOs)]

Mixtures of the stabilizer-free LBH sample with commercial Irganox 1520 L, Irganox 1076, PAO-3, or PAO-4 were prepared by the addition of appropriate amounts of stock solutions of the AOs in MTBE. After the evaporation of MTBE from the solutions, the clear, stabilized polymer mixtures were stored under argon.

Measurements and analytical methods

Differential scanning calorimetry (DSC) measurements were performed with a PerkinElmer DSC 7 instrument (Perkin Elmer Corp., Analytical Instruments, Norwalk, CT) at a heating rate of 3°C/min with open aluminum pans in air (50 mL/min).

Thermogravimetric analyses (TGAs) were performed with a PerkinElmer TGA 7 instrument at a heating rate of 3°C/min in air (50 mL/min).

^{1}H-NMR spectra were recorded with a Bruker Avance DPX-300 spectrometer (Bruker Analytik

GmbH, Karlsruhe, Germany) at 300.1 MHz and 25–70°C.

Fourier transform infrared spectra were measured on a PerkinElmer Paragon 1000 PC instrument, at a 4-cm^{-1} resolution within the range 450–4400 cm^{-1}, with polymer films cast onto KBr pellets.

Liquid chromatography was used for the determination of stabilizers in LBHs (ECOM, Prague, Czech Republic; C18 column packing, methanol as a mobile phase, flow rate = 0.3 mL/min, 220 nm] and the analysis of reaction mixtures (CECIL, Cambridge, United Kingdom; C18 column packing, 95/5 v/v methanol/water as an isocratic mobile phase, flow rate = 0.4 mL/min, 210 nm).

GC-MS measurements were carried out on a PerkinElmer Autosystem TurboMass instrument with a PE-MS5 capillary column (20 m × 0.18 mm i.d., 0.18-μm film thickness) operated at 100–260°C and 10°C/min, with the initial temperature held for 5 min. The injector was set at 220°C and was used in a split mode. Mass spectra were recorded under electron ionization (EI) at 70 eV, ranging from 20 to 350 m/z.

RESULTS AND DISCUSSION

Syntheses and characterizations of PAOs

Compound **II**, bearing simultaneously the SH group and the AO moiety, reacted through a radical addition
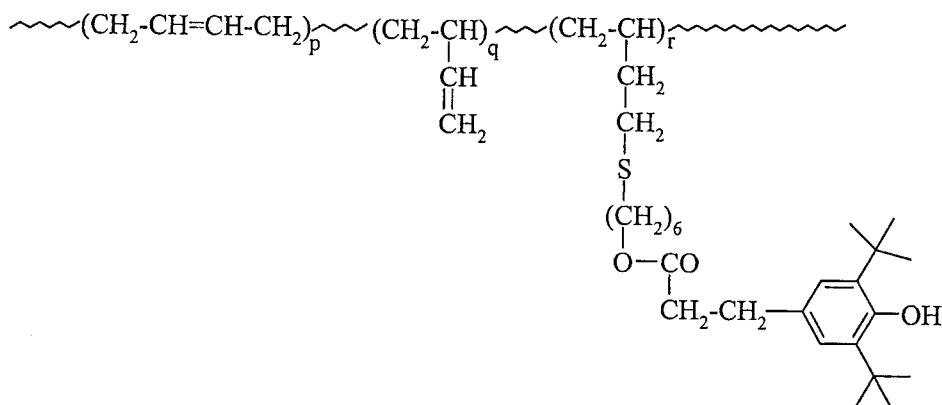
Scheme 1

with the pending vinyls of LBH. The reaction conditions are summarized in Table I.

The resulting product was a statistical terpolymer, its monomer units being (1) the original 1,4-butadiene units (with the cis–trans isomerism disregarded), (2) the original 1,2-butadiene units, and (3) the 1,2-butadiene units modified by the addition of **II** (AO-modified unit), as seen in Scheme 1, in which the subscripts p, q, and r represent the number of the statistically distributed monomer units in the chain.
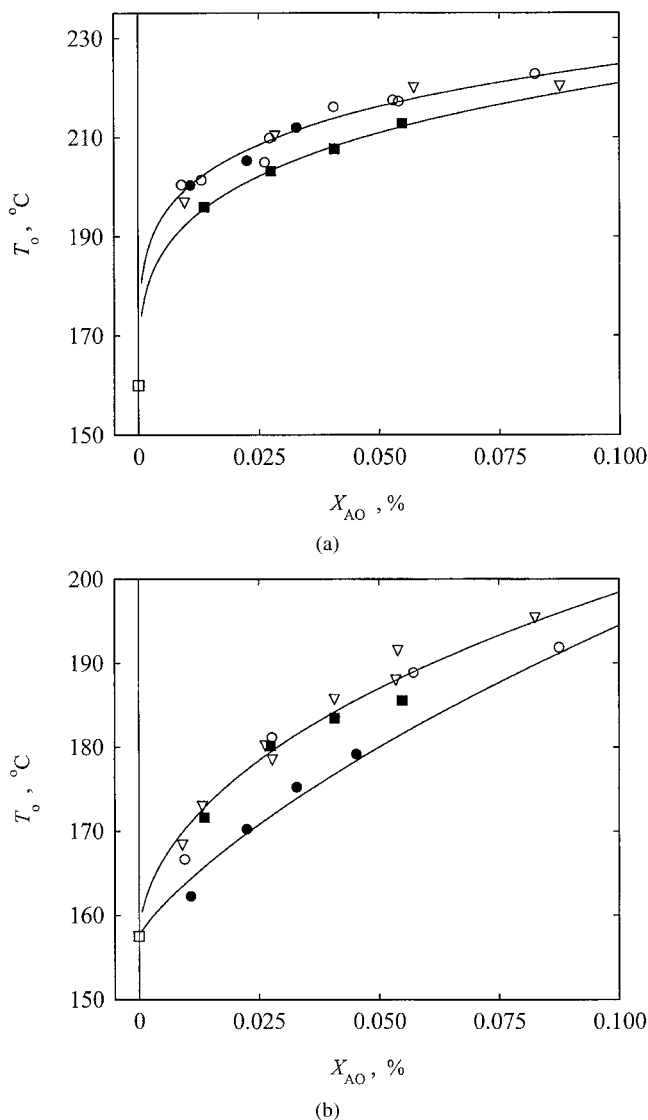
The molar fractions of 1,4-, 1,2, and AO-modified 1,2-units, that is, $x_{1,4} = p/(p + q + r)$, $x_{1,2} = q/(p + q + r)$, and $x_{AO} = r/(p + q + r)$, respectively, could be determined by ^{1}H-NMR spectroscopy (where x_{AO} is the molar fraction of butadiene monomer units modified by the addition of compound **II**). An elemental analysis (C and/or S) yielded only x_{AO} (and the sum $x_{1,4} + x_{1,2}$). The results are given in Table I.

Although PAO-1 and PAO-2 were clear, viscous liquids, PAO-3 and particularly PAO-4 were turbid, semisolid substances. This was probably due to the fact that the concentration of polar side chains and, therefore, the influence of their incompatibility with nonpolar main chains increased from PAO-1 to PAO-4. Removing the solvent traces from almost solid PAO-4 was obviously quite difficult, and this manifested itself in nonnegligible differences in x_{AO} determined for this sample by elemental analysis and by NMR (Table I). (Obviously, x_{AO}, determined gravimetrically, was a subject to a relatively large experimental error.) For further calculations, x_{AO}, obtained by NMR, was taken.

It further follows from Table I that, with increasing x_{AO} (i.e., with an increasing degree of conversion), the content of unreacted 1,2-units decreased, whereas that of unreacted 1,4-units remained approximately constant. This was due to the higher reactivity of pending vinyl groups in comparison with the main-chain C=C bonds.

Figure 1 T_o versus X_{AO}: (a) TGA and (b) DSC [(○) PAO-3, (▽) PAO-4, (□) nonstabilized LBH, (●) Irganox 1520, and (■) Irganox 1076].

Performance of PAOs in comparison with some commercial stabilizers

The AO performances of PAO-3, PAO-4, Irganox 1520 L, and Irganox 1076 in LBH were compared on a molar basis [with the molar fraction of the AO moiety in the mixture (X_{AO})]. The calculation of this quantity was trivial for both Irganox-type stabilizers. For PAOs, however, the following procedure had to be applied: the molar fraction x_{AO} given in Table I was converted into the corresponding weight fraction, which was then multiplied by the weight fraction of PAO in its mixture with LBH (obtained by the weighing of the components); the product, which was equal to the weight fraction of AO-modified butadiene units in the mixture, was converted into X_{AO}, the latter quantity representing the axes of abscissas in Figure 1(a,b).

The efficiency of the AOs was measured by the determination of the oxidation onset temperature (T_o) of LBH/AO mixtures by TGA [Fig. 1(a)] and DSC [Fig. 1(b)]. The differences in T_o, as observed with TGA and DSC, were not surprising: they were due to the different physical natures of the two methods. As expected, for both methods, the values obtained for LBH/PAO-3 and LBH/PAO-4 mixtures fit the same curve. [In both figures, the curves serve as guides to the eye only; they were obtained by least-squares fitting with the equation $T_o = \ln(a X_{AO}{}^b + c)$ and were not based on any theory.] Both methods revealed a good stabilizing effect of PAOs (high T_o) in LBH/PAO mixtures in comparison with both low molecular weight AOs. This can be explained by the better compatibility of LBH and PAOs in comparison with that of an LBH/Irganox mixture.

What is rather surprising, however, is that an LBH/Irganox 1520 mixture yielded a higher T_o value than an LBH/Irganox 1076 mixture in TGA, whereas the opposite was true for DSC. Again, the only explanation is that TGA and DSC are sensitive to different structural effects. However, the difference in the T_o values of the nonstabilized LBH sample with TGA and DSC was negligible. Furthermore, the T_o values of neat PAO-1 through PAO-4 (undiluted with LBH) could be measured only by DSC (206.6, 219.1, 223.6, and 225.3°C, respectively), whereas TGA failed (no weight increase due to oxidation was observed).

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