

Urethane-Based Stabilizers for Radiation-Crosslinked Polyethylene

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Synopsis

Unsaturated urethane-based stabilizers for use in radiation-crosslinked polyethylene were synthesized. Aromatic amine moieties were attached to allylic and acrylic monomers by means of aromatic or aliphatic diisocyanates. The synthesized stabilizers were incorporated in high-density polyethylene films which were subjected to electron beam irradiation. The oxidative stability of the films prior to and after extraction was determined by DTA in the temperature range 185–210°C and compared with samples treated with commercial amine-bearing antioxidants. Tensile strength and gel content were also determined. Best results were obtained with a stabilizer prepared from equimolecular amounts of allyl alcohol, tolylene-2,4-diisocyanate and *N*-phenyl-1,4-phenylenediamine. Estimated lifetimes at 70°C of stabilized irradiated polyethylene samples were calculated.

INTRODUCTION

The suitability of antioxidants for stabilization of polymers depends not only on the rate of inactivation by chemical reactions, but also on the extent of physical loss of the antioxidants from the substrate by diffusion or leaching out processes. The incompatibility of stabilizers with the polymeric substrates accelerates the depletion of the former in the processing stage or during use at relatively high temperatures and upon contact with solvents. These processes cause rapid oxidative destruction of the polymers.

The mobility of the stabilizing agent can be reduced by oligomeric or polymeric stabilizers^{1–8} or alternatively by chemical bonding of stabilizers to the polymer chain.^{9–11} An attempt to develop oxidation inhibitors, such as 2-arylamino-4,6-diallyloxy-*s*-triazine, which combine migration stability and nonvolatility and can impart crosslinking to low density polyethylene by irradiation was reported.¹² The purpose of this investigation was to synthesize a series of stabilizers bearing vinylic or allylic side groups. Irradiation of polyethylene containing such stabilizers was expected to lead to graft copolymerization of the stabilizer onto the polymer and to crosslinking of the substrate. Such processes should ensure high resistance to exudation of the antioxidants and thus increase the effectiveness of protection of polyethylene.

EXPERIMENTAL

Materials

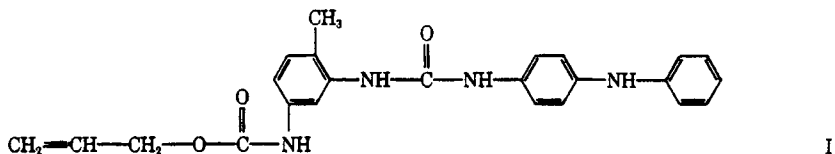
High-density polyethylene (PE) in the form of a white powder without additives, marketed under the trade name of Hostalen GMVP 2250 P (Hoechst, West Germany), was used as received. Tolylene-2,4-diisocyanate (TDI) and 1,6-di-

isocyanatehexane (HDI) from Aldrich, as well as *N*-phenyl-1,4-phenylenediamine (PPDA) from Fluka, were used without further purification. 2-Hydroxyethyl acrylate (HEA) and allyl alcohol (AA) from Fluka were dried prior to use over molecular sieve type 5A pellets. The commercial antioxidant used for comparison was Agerite Resin D(AD)-polymerized 2,2,4-trimethyl-1,2-dihydroquinoline (R. T. Vanderbilt Co.).

Synthesis of Stabilizers

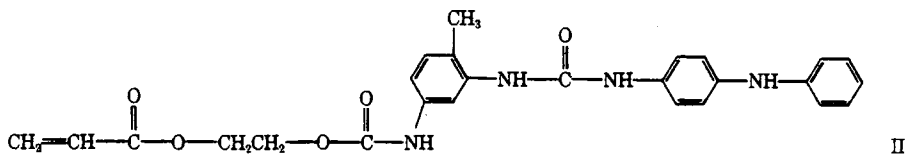
The unsaturated stabilizers were prepared in two steps. First a monoisocyanate was obtained by the reaction of equimolecular quantities of the hydroxyl containing monomer and the diisocyanate. The joining of the aromatic amine to the monoisocyanate was carried out in the second step.

N-phenyl-(3-amino-6-methyl-*N*-allyloxy-carbonyl)-*N'*-phenyl-(4-phenyl-amino)urea (I),



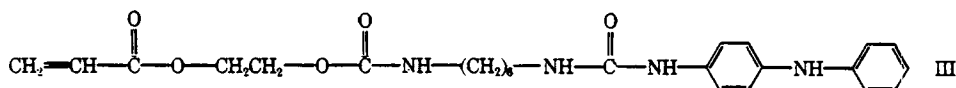
was prepared according to accepted procedures.¹³ TDI (3.48 g) and hexane (4 mL) were placed in a reaction flask and then 1.16 g of AA in 2 mL of hexane was added dropwise over a period of 5 min with stirring. After 30 min the stirring was stopped, and the monoisocyanate precipitated in the form of a viscous liquid. After separation, the monoisocyanate was washed three times with hexane and vacuum dried. The yield was 3.89 g (83.8%). A volumetric determination of the isocyanate groups was carried out by reaction with diethylamine and back-titration with hydrochloric acid¹⁴ (17.5% NCO vs. 18.1% calculated). An equimolecular quantity of PPDA (2.94 g) was introduced into the reactor and dissolved in 100 mL of dibutyl ether. Subsequently, the monoisocyanate, dissolved in 25 mL of the same solvent, was added. The reaction product appeared immediately in a suspended form. The reaction product was filtered off by suction, washed with dibutyl ether until the solvent was colorless, and dried at 50°C under vacuum. The light-grey powder obtained (yield 85%) had a melting point of 146°C.

N-Phenyl-[3-amino-6-methyl-*N*-(2-acryloxyethoxycarbonyl)]-*N'*-phenyl-(4-phenylamino)urea (II),



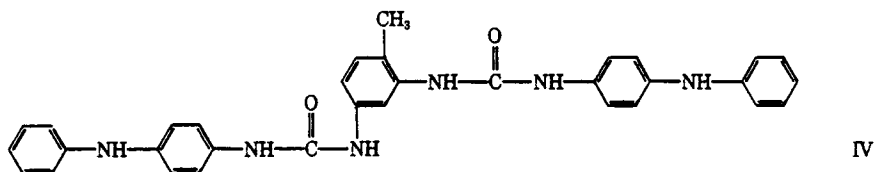
was prepared by a technique similar to that used for I. The monomer in this case was HEA. The solvent for HEA was a mixture of hexane and acetone (3:1 by volume). In the second step of the reaction the reactants were dissolved in methyl ethyl ketone instead of dibutyl ether. The product obtained was grey, melting point 189°C, yield about 80%.

N-6-Aminoethyl-[*N*-(2-acryloxyethoxycarbonyl)]-*N'*-phenyl-(4-phenylamino)urea (III),



was synthesized from HDI, HEA, and PPDA in equimolecular ratio. The solvents and methods were similar to those used in the synthesis of II. In the first step of the reaction, dibutyl tin dilaurate (0.005% of the amount of HDI) catalyst was introduced. The melting point of the product was 165°C.

In addition to the three stabilizers containing olefinic groups, a saturated stabilizer of the same family, *N*-phenyl-[3-amino-6-methyl-*N*-(4-phenylamino phenylamidocarbonyl)]-*N'*-phenyl-(4-phenylamino)urea (IV),



was prepared by a one-step reaction between TDI and PPDA (1:2 mol ratio). Solutions of reactants (10% in dibutyl ether) were introduced into the reaction flask. The product was formed almost immediately after the beginning of the reaction. After filtration through a Büchner filter, washing and drying at 50°C under vacuum, a cream-colored powder was obtained with a melting point of 235°C. The yield was 91.5%.

Preparation of Samples

All stabilizers were incorporated by milling with PE in a ratio of 2 mmol to 100 g of PE mixture. The samples were molded in a Carver laboratory press, at a temperature of 170°C and pressure of 20 atm, into 0.5-mm-thick sheets or 0.1-mm films. The pressure time was 8 min, including 6 min of cooling. The PE samples containing stabilizers were subsequently irradiated at room temperature in air by a commercial electron beam accelerator, High Voltage Model EPS-550-IND. The samples were subjected to electron beam radiation at an accelerating voltage of 550 kV and current of 15 mA by means of a conveyer traveling at a rate of 10.6 m/min. The radiation dose delivered was 20 Mrad.

Oxidative Stability Measurements

Differential thermal analysis (DTA) represents a rapid method for evaluation of the effectiveness of antioxidants at test temperatures far above the expected service temperatures.^{15,16} In this study the stability tests were performed with a DuPont 990 Thermal Analyzer, coupled to a base module and DSC cell, at 185–210°C. The DSC cell was employed since its structure permits good contact between the sensor unit and film samples.

The samples, in the form of 5-mm discs with an approximate thickness of 0.1 mm and weight of 2.5–3.0 mg, were heated to the test temperature at a rate of 10°C/min under nitrogen, introduced with a flow rate of 100 mL/min. When the test temperature was reached, the nitrogen was turned off and oxygen was introduced at the same flow rate and the experiment was continued under isothermal conditions. The oxidation induction period (τ) is defined as the time necessary to initiate the degradation process.

The thermal stability tests were performed on samples which were subjected to solvent extraction with methanol and dimethyl sulfoxide (DMSO), as well as on unextracted samples. The extractions in methanol were carried out in a Soxhlet apparatus equipped with coarse thimbles. When using DMSO the PE samples were placed in 80-mesh stainless steel baskets and extracted at 80°C. In all tests the extraction time was 32 h.

Gel Fraction Determination

Polymer samples of about 300 mg were placed in a stainless steel basket (80-mesh) and extracted with boiling xylene (stabilized with 0.5% 2,6-di-*t*-butyl-*p*-cresol) for 48 h. The samples were then vacuum-dried at 80°C for 24 h and weighed. The percent gel present in the irradiated specimens was calculated as $(w/w_0) \times 100$, where w_0 and w represent the weights of the irradiated dried sample and nonextractable fraction, respectively.

Tensile Strength Measurements

Tensile strength (TS) and elongation measurements at 100°C were performed according to ASTM D882-67. A table Instron Model 1026 tensile tester, equipped with a temperature cabinet Model 3111, was used. The selected testing speed was 5 mm/min. The elongation measurements were limited to 700% by the internal height of the temperature cabinet.

RESULTS AND DISCUSSION

The synthesized stabilizers exhibit comparable effectiveness to that afforded by the commercial stabilizers AD and PPDA (see Table I). Exposure to ionizing radiation reduces the induction time of stabilized samples by about 50% in the case of I, II, and AD. Stabilizer IV loses about 90% of its effectiveness, while PPDA demonstrates inertness to radiation. However, the irradiated PPDA treated samples exhibit strong exudation: After some hours at room temperature the surface of the PE film was covered with the amine. One-year storage decreased the protective ability of the PPDA considerably, i.e., the induction period fell 15-fold, from 390 to 27 min at 190°C.

TABLE I
DTA Induction Period for Stabilized Polyethylene Films^a

Stabilizer	Wt % stabilizer	Induction period (min)				
		Nonextracted				
		Non-irradiated	Irradiated		Extracted in DMSO ^b	
			Immediately after preparation	After 1 year storage	Non-irradiated	Irradiated
I	0.83	340	173	153	43	124
II	0.94	322	150	151	—	109
III	0.93	257	69	59	—	36
IV	0.54	303	31	34	—	9
PPDA	0.37	400	390	27	24	13
AD	0.34	375	150	100	—	65
Nonstabilized	0	12	0	—	—	—

^a The DTA tests were carried out at 190°C. Irradiation dose = 20 Mrad, extraction time = 32 h.

^b Extraction with methanol yielded almost identical results to those obtained with DMSO.

A visual examination of the PE films, stabilized with I–IV and AD, did not show any exudation of the stabilizer. After 1-year storage at room temperature, practically no diminution in the stability properties of the films, treated with I–IV, was observed. The residual stability of the irradiated stabilized PE samples after 1-year storage decreases in the following order: I > II > AD > III > IV > PPDA.

The effect of radiation treatment on the bonding of stabilizers can be deduced from the data in the last column of Table I. PE samples, stabilized with I and II, show the least effect of extraction on induction times (~20% decrease), while PPDA-stabilized samples show very strong reduction in properties. The somewhat higher stability of PE samples treated with I over II after extraction could be ascribed to a higher extent of radiation induced bonding by the former. Allylic monomers are known to be more effective than acrylates in enhancing radiation-induced crosslinking in PE.^{17,18}

The low radiation stability of PE treated with unsaturated stabilizer III, in which the amine group is linked to the acrylic moiety by HDI, as well as of that stabilized by the saturated IV, is somewhat surprising.

The temperature dependence of the DTA induction period for PE, stabilized with the synthesized and commercial materials, is represented by an Arrhenius-type temperature relationship, as shown in Figure 1. The slope and intercept of the plots were used to evaluate the apparent activation energies of the oxidation process, as well as induction periods at 70°C and temperatures at which the PE films undergo immediate oxidation ($\tau = 1$ min). These data are shown in Table II. The correlation coefficients of the experimental plots were in the range of 0.986–0.997.

From data in Table II one can see that there are no significant differences in the activation energies of induction periods in the oxidation of the PE samples. The values 33.0–34.9 kcal/mol are in satisfactory agreement with literature data on other stabilizers obtained by differential thermal analysis.^{15,19} The estimated lifetime (DTA induction period), calculated from the Arrhenius equation, is 85 years for the PE sample stabilized with I and is the highest among the samples tested (Table II).

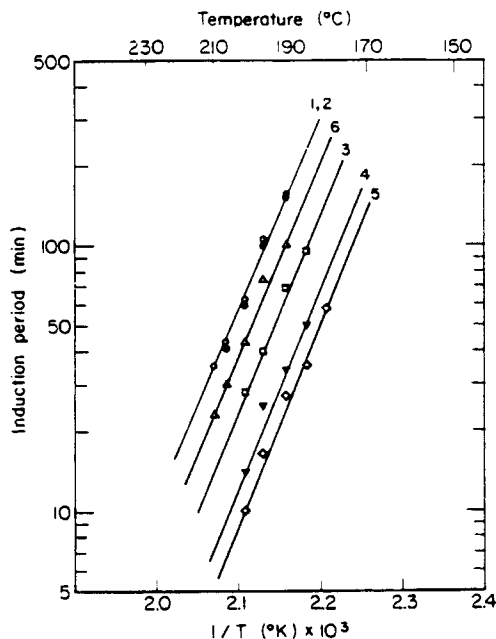


Fig. 1. Arrhenius-type plot of DTA induction period for stabilized polyethylene. Curves 1-6 are for stabilizers I-IV, PPDA and AD, respectively.

The data on mechanical properties and gel fraction measurements of the irradiated stabilized PE samples, as well as the untreated film, are reported in Table III. It is of interest to note that the gel fraction measurements indicate that there is little interference of the stabilizers used with the electron-beam-induced crosslinking. This observation may reflect the fact that, in the case of high-density PE subjected to high flux radiation, large stabilizer molecules do not significantly affect the dimerization of radicals within the short time of irradiation. The data in Table III indicate that stabilizers I, II, and III are more effective in enhancing crosslinking than the three saturated stabilizers. This can be seen from gel fraction and especially from TS data. It should be noted that stabilizer I has a small effect on the color of the PE sample.

TABLE II
Apparent Activation Energy and DTA Induction Period for Stabilized Irradiated PE, Calculated from the Arrhenius-Type Equation

Stabilizer	E (kcal/mol)	Induction period at 70°C (years)	Temperature at $\tau = 1$ min (°C)
I	33.0	85	266
II	33.5	83	262
III	34.2	57	249
IV	34.5	34	238
PPDA	34.9	28	233
AD	33.3	63	258

TABLE III
Mechanical Properties and Gel Content of Irradiated Stabilized PE Samples^a

Stabilizer	Gel fraction (%)	TS at yield (kg-cm ⁻²)	Elongation at yield (%)	TS at elongation of 700% (kg-cm ⁻²)	Sample color
I	67.6	64.6	50.8	91.7	Light-grey
II	68.7	62.3	58.8	90.0	Grey
III	65.2	64.5	58.8	92.9	Light-grey
IV	64.2	62.4	61.2	84.5	Grey
PPDA	63.2	60.4	57.2	73.6	Dark-brown
AD	62.3	63.5	56.0	85.7	Yellow
PE ^b	62.8	61.8	58.8	85.6	White
PE ^c	0.6	56.6	65.2	62.4	White

^a Irradiation dose approx 20 Mrad (520 kV, 15 mA); speed of testing 5 mm/min.

^b Unstabilized, irradiated PE.

^c Unstabilized, nonirradiated PE.

SUMMARY

PE stabilizers containing vinyl or allylic moieties were synthesized. The incorporation of the stabilizers into PE films afforded slightly lower oxidation protection than that obtained by using commercially available PPDA and AD stabilizers. Electron beam irradiation of stabilized compounds leads to a decrease in oxidation stability for all samples except PPDA. However, the latter loses its effectiveness after a period of storage of 1 year. Prolonged storage time of irradiated PE samples treated with I or II has no effect on the oxidative properties. The strong bonding of stabilizers I and II to PE following irradiation manifested itself also by the fact that extraction of irradiated samples leads to only a small (ca. 20%) decrease in the effectiveness. Thus it appears that stabilizers I and II may provide adequate stabilization properties to radiation-crosslinked polyolefines.

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