Notes

Mechanism of Stabilization of Some Polypropylene Ultraviolet Stabilizers

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A number of conflicting reports[1-4] have appeared which attempt to classify polyolefin ultraviolet stabilizers as acting as either ultraviolet light screens or through nonscreening processes. We have determined the relative importance of screening and nonscreening processes by an analysis of the effect of ultraviolet light exposure on the viscosity of polypropylene stabilized with various commercial ultraviolet stabilizers.

Experimental Section

Film Preparation. Films of Eastman isotactic polypropylene having a melt flow of 4.5 containing 0.1% 2,6-di-*tert*-butyl-4-methylphenol, 0.3% dilauryl 3,3′-thiodipropionate and the appropriate concentration (0.01–0.30%) of ultraviolet stabilizer were cast at 120–125° from a 4% (w/v) dope in chlorobenzene. The final concentrations of the additives in the film were determined by ultraviolet spectrophotometry.

Irradiation of Films. Dope-cast films (1- to 3-mils thick) were placed in Pyrex test tubes, mounted in a Rayonet photochemical reactor, and irradiated with 300-nm lamps for 3 days (the time to embrittlement for unstabilized films) at 40°. Viscosities (at 145° in Tetralin tetrahydronaphthalene) were determined before and after irradiation.

Gel Permeation Chromatographic (GPC) Analysis. A Waters Model 100 GPC unit was used for this work. The 0.25% polypropylene (partially photodegraded) solutions in 1,2,4-trichlorobenzene were filtered through a double thickness of 0.2-μ porosity Millipore filter at 140° and analyzed by GPC. The GPC curves were recorded by a strip-chart recorder and a PDP-8I computer. The molecular weights were calculated from the PDP-8I computer tapes by using a polypropylene calibration curve.

Results and Discussion

An ultraviolet stabilizer may stabilize polypropylene by one or more of the following mechanisms: (a) screening out incident light, (b) quenching excited states, (c) trapping radicals, or (d) decomposing hydroperoxides.[5,6] Processes b–d will be termed nonscreening processes (NSP).

When a stabilizer functions as an ultraviolet light screen, the amount of polymer photodegradation should be directly proportional to the quantity (I) of the light absorbed by the polymer; however, if a stabilizer derives its effectiveness by both screening out ultraviolet light and through NSP, the polymer will undergo less degradation than that predicted from the quantity of light absorbed by the polymer. Hence, the effects of NSP and screens on polypropylene photodegradation can be separately estimated by determination of the relationship between the quantity of light absorbed by the polypropylene samples and polypropylene molecular breakdown.

The polypropylene films embrittled when the inherent viscosity [η] dropped to between 0.8 and 0.7 (initial [η] was 1.63). These data agree substantially with photodegradation studies by Adams.[7] There was a uniform loss of number-average molecular weight ($\bar{M}_n$) with loss in [η] (Table I). Although instrument noise caused some scattering of points, a linear log–log plot of [η] *vs.* $\bar{M}_n$ was obtained for the irradiated polypropylene films. Viscosity was converted to the number of polymer bonds broken/polymer molecular ($\bar{B}$) by[8]

Table I
Variation of $\bar{M}_n$[a] and $\bar{M}_w$[b] with [η][c] of Photolyzed Polypropylene

[η]	$\bar{M}_n$	$\bar{M}_w$
1.63	46,600	196,000
1.50	45,500	196,000
1.36	42,100	192,000
1.06	35,300	163,000
0.92	37,000	122,000
0.76	27,600	90,500

[a] Number-average molecular weight. [b] Weight-average molecular weight. [c] Inherent viscosity.

$$(\bar{M}_{n_0}/\bar{M}_n) - 1 = \bar{B} \qquad (1)$$

where $\bar{M}_{n0}$ and $\bar{M}_n$ are the number-average molecular weights of the polymer before and after irradiation, respectively. If we let $\bar{B}_0$ and $\bar{B}$ equal the number of bonds broken for the unstabilized and stabilized films, respectively, and then plot $\bar{B}/\bar{B}_0$ *vs.* L/L_0 (where L and L_0 are the fractions of light absorbed by the stabilized and unstabilized polymer, respectively) a linear plot should be obtained.

The fraction (L) of light absorbed by the polymer films exclusive of the stabilizer is given by[1]

$$L = (1 - T)[A_p/(A_p + A_s)] \qquad (2)$$

where T is the fraction of light transmitted by the polymer–stabilizer system, A_p is the absorbance of the unstabilized film, and A_s is the absorbance of the stabilizer in the polymer.

On the $\bar{B}/\bar{B}_0$ *vs.* L/L_0 plot, the unstabilized film would be represented by point 1,1; and as the polymer absorbs less light due to stabilizer absorption, the plot would approach the origin. At the origin, the stabilizer would be absorbing all of the incident light.

To verify the above assumptions, unstabilized polypropylene films were irradiated through ultraviolet filters. The filters were polypropylene films containing a range of concentrations of 4-(dodecyloxy)-2-hydroxybenzophenone. The plot of $\bar{B}/\bar{B}_0$ *vs.* L/L_0 for the filtered films is linear (Figure 1). The scattering of points is probably due to variations in filter film thicknesses and scattering of the light from the six surfaces involved.

If a $\bar{B}/\bar{B}_0$ *vs.* L/L_0 plot of polypropylene films containing an additive lies below the point for pure absorption, then the fraction of bonds broken is less than that anticipated from the amount of light absorbed by the polymer. Hence, the additive is stabilizing by both screening and NSP. If, on the other hand, the plot lies above the absorption line, then the additive is a sensitizer.

All of the stabilizers tested act as ultraviolet light screens and through NSP (Figure 1). There is considerable light scattering in the films used. However, when the values of L and L_0 are close ($L/L_0 > 0.90$), the scattering essentially cancels out. At L/L_0 values <0.90 the scattering, along with a slight decrease in L and L_0 on irradiation, introduces an error in our data of 20–25%. Since the greatest deviation from the screening plot is when $L/L_0 >$ 0.90, the shapes of the curves are not changed appreciably by these errors, but the errors are large enough to prevent

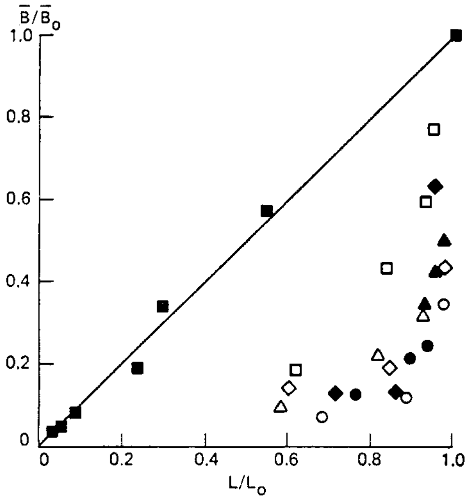

Figure 1. Effect of fraction of light absorbed (L/L_0) by the polymer (polypropylene film) containing ultraviolet stabilizers on the fraction of bonds broken/polymer molecule ($\bar{B}/\bar{B}_0$) for polymer films containing the following ultraviolet light stabilizers: control films with external filters (■), nickel bis(dibutyldithiocarbamate) (○), 2,4-di-*tert*-butyl-6-(5-chloro-2*H*-benzotriazol-2-yl)phenol (△), [2,2′-thiobis[4-(1,1,3,3-tetramethylbutyl)phenolato]]nickel (▲), zinc bis(dibutyldithiocarbamate) (□), 4-(dodecyloxy)-2-hydroxybenzophenone (●), 4,4′-bis(octyloxy)-2-hydroxybenzophenone (◇), and bis(2′-hydroxy-5′-methyllaurophenone oximato)nickel(II) (◆).

the quantitative calculation of the importance of screening and NSP. Furthermore, the relative importances of screening and NSP depend on the concentration of the stabilizer. As the concentration of a stabilizer increases, the depth of penetration of the incident light into the polymer decreases; hence, the screening process increases in importance.

In conclusion, all of the ultraviolet stabilizers tested act as ultraviolet screens and through NSP. The method presented here for determining the relative importance of screening and NSP should be useful in other polymer–stabilizer systems.

References and Notes

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Upper Molecular Weight Limit for the Characterization of Polystyrene in Gel Permeation Chromatography

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Gel permeation chromatography (GPC) is a widely used tool for characterizing polymeric materials.[1] However, because of the lack of adequate polymer standards, there has been no attempt using such materials to determine, experimentally, the maximum size that current GPC columns can resolve. It is well known that many commercially available polymers have very high molecular weight tails. Also, recent work has shown[2] that very high molecular weight polystyrene, having molecular weights greater than 5×10^6 g/mol, can be made. Consequently the validity of characterizing this range of molecular weights by GPC must be tested. It will be shown in this work that the failure of current GPC columns to resolve high molecular weight polymers is primarily due to shear degradation of the polymer either in the column or in the associated plumbing.

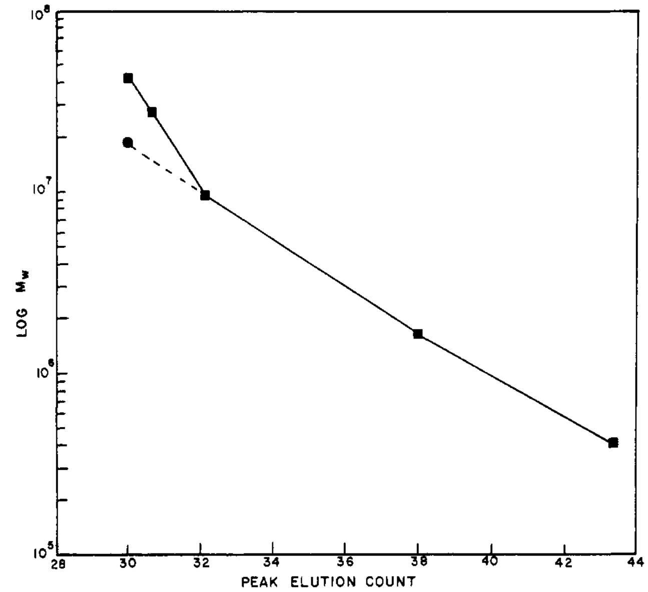

Figure 1. Calibration curve of weight-average molecular weight against peak elution count: (■) molecular weight of sample measured before being put in GPC columns; (●) molecular weight of sample measured after elution through GPC columns.

Experimental Section

Polymer Synthesis. The synthesis of the highest molecular weight polystyrenes (LJF-13 and LJF-18) was accomplished with the aid of a high-vacuum apparatus. The basic details of the use of this equipment have appeared elsewhere.[3,4] Since the attainment of the ultra-high molecular weight polystyrenes requires an extremely low concentration of initiator (10^{-6} to 10^{-7} *M*), precautions must be taken which will ensure the removal of virtually all terminating impurities. To this end a benzene solution[5] of (*sec*-butyl) (*n*-butyl) Mg was used to purify the monomer and also to simultaneously purge the reactor, solvent, and monomer prior to the addition of the initiator.

The solvent used for these polymerizations was tetrahydrofuran, which was purified in the conventional manner.[3,4] The "initiator" was low molecular weight polystyryllithium in benzene prepared by reacting *sec*-butyllithium with styrene.

The polymerization reactor was a 1-l. flask to which was attached another flask of identical size. Following the distillation of the monomer (about 20 g) and solvent (total volume 0.6–0.7 l.), the reactor was sealed off from the vacuum line. When the solution was at room temperature a dilute benzene solution of dibutylmagnesium was added and the mixture was allowed to stand for 1 hr or so. Then the mixture was transferred to the attached 1 l. flask and the solvent and monomer were distilled back into the reactor. This step was repeated at least five times in order to rinse the reactor free from the dibutylmagnesium. It should be mentioned that this organometallic does not cause any significant polymerization of the styrene during this purification procedure.

When the final transfer of the monomer and solvent was achieved, the mixture was frozen with liquid nitrogen and the second flask was removed by sealing off at the glass constriction used to attach the two flasks, one to the other. The mixture was thawed and the dilute initiator solution was added. Since tetrahydrofuran was the solvent, the polymerization was completed in several minutes. The very low chain-end concentration used