

Oligomer of *o*-Xylene as a Heat Stabilizer for Isotactic Polypropylene

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Synopsis

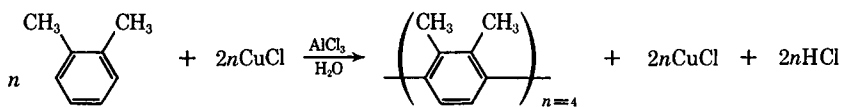
Oligomers of *o*-xylene (molecular weight ~ 400) have been shown to be novel heat stabilizers for isotactic polypropylene film. In contrast to unstabilized films which failed after exposure of 5 hr in a 150°C air oven, a film containing 0.5 and 1.0 wt-% of the *o*-xylene oligomer survived 100 and 226 hr, respectively. Furthermore if 0.25% dilauryl thiodipropionate (DLTP) was also present, only 0.1 wt-% of the *o*-xylene oligomer was necessary to maintain a film intact up to 124 hr. In absence of DLTP, this low level of *o*-xylene oligomer was not effective. Oligomers of toluene, *m*-xylene, *p*-xylene, and 1,2,4-trimethyl benzene were found less effective.

INTRODUCTION

This paper describes our finding that an oligomer of *o*-xylene (molecular weight ~ 400) is a heat stabilizer for isotactic polypropylene. We believe that it represents the first known all-hydrocarbon stabilizer which consists of nonfused aromatic rings, with the possible exception of carbon black. Unlike the latter, the *o*-xylene oligomer is entirely soluble in the polypropylene.

Oligomers of toluene, *m*-xylene, *p*-xylene, and 1,2,4-trimethylbenzene were also examined but were found less effective or inert.

The oligomers were synthesized according to procedures which were disclosed earlier by Kovacic,¹⁻³ e.g., for *o*-xylene:



EXPERIMENTAL

Preparation of Test Sample

The oligomer was deposited on the polypropylene fluff by mixing the polymer and an acetone solution of the oligomer and then evaporating the acetone. This product was first milled, and a sheet was compression molded. Test strips (1 × 2 in. and 6 to 8 mils thick) were simultaneously

TABLE I. Characterization of Soluble Oligomers from Polymerization of Simple Aromatic Molecules^a

Aromatic molecule	Soluble in benzene ^b wt-%	Color ^c	Mol wt ^d	Elemental analysis, %		NMR ^f Ar-CH ₃ Ar-H		Infrared ^g	UV ^h	ESR ⁱ
				Exp.	Calcd ^e	Exp.	Calcd ^e			
Toluene	71	Dark red	C	93.4	92.8	1.5 ^j	0.91 ^j	<0.01	Para subst. 12.3 μ	Peaks at 375, 485, 513 and 620 μ
			H	6.0	7.2					
<i>o</i> -Xylene	91	Brown	C	91.5	91.4			0	Peak at 12.2 μ	Shoulder at 378 μ
			H	7.6	8.6	2.9	2.4			
<i>m</i> -Xylene	100	Pale yellow-green	C	92.1	92.0			0.05	Peak at 12.18 μ	Strongly paramagnetic
			H	7.7	8.0	3.2	2.5			
<i>p</i> -Xylene	100 ^k	Brown	C	91.2	92.0			0.07	---	---
			H	7.8	8.0	3.1	2.5			
1,2,4-Trimethylbenzene	100 ^k	Brown	C	90.9	90.0			<0.02	---	---
			H	8.7	10.0	7.1	5.4			
			Cl	0.06	---					

^a The synthesis of these products followed procedures described by Kovacic and workers.¹⁻³

^b This represents that part of the whole product which is soluble in benzene. For most of the products CCl₄ is also a good solvent. The results reported in this table were obtained with these soluble fractions.

^c This represents the color of the solid product; dilute solutions in benzene were yellow to brown in color.

^d Ebullioscopic determinations in toluene solvent.

^e This value was calculated for a molecule having an average molecular weight as determined by the ebullioscopic method.

^f These were done in deuterated benzene as solvent.

^g The KBr-infrared method was used.

^h Carbon tetrachloride was used as solvent.

ⁱ The ESR determinations were done for us by T. Buckman of this laboratory. Comparable signals were obtained from the soluble and insoluble fractions. The line widths are narrow, e.g., about 5 gauss wide. A few spectra show symmetric lines which are attributed to different radical species. In general, the signal due to the insoluble fraction was larger than that of the soluble fraction.

^j We believe that these higher experimental ratios occur because some postalkylation had taken place on part of the product molecule. This would place excess methyl groups on the product beyond that expected from the parent aromatic molecule.

^k This material is the residue which remained in the pot after all volatiles were removed in a distillation at 1 mm Hg pressure and at temperatures up to 200°C.

TABLE II
Heat Stabilization of Polypropylene Films^a

Exp. no.	Additive, wt-%			Time to failure at 150°C, hr ^a
	Oligomer of <i>o</i> -xylene ^b	Ionox 330 antioxidant ^c	DLTP ^d	
1	0	0	0	5
2	0.1	0	0	5
3	0.1	0	0	5
4	0.50	0	0	100
5	1.00	0	0	226
6	0	0.1	0	320
7	0.1	0	0.25	124
8	0.5	0	0.20	194
9	2.0	0	0.20	220
10	0	0.1	0.25	>462

^a The test film strips were maintained in a 150°C with a constant circulation of air. See experimental procedure for the preparation of samples and procedures used to test heat stability.

^b The sample described in Table II was used.

^c Trademark for Shell commercial stabilizer.

^d A commercially available sample (American Cyanamid Company) was used.

cut from this large sheet in a specially designed cutter. The samples were suspended in an air oven at 150°C by means of metal clamps; these test strips were insulated from the metal clamp by highly stabilized polypropylene film. At regular intervals the samples were removed from the oven, cooled, and then tested as now described.

The Hand Tensile Test for Measuring Thermal Stability

A portion of the film was grasped between the thumbs and the index fingers of both hands, and using the ends of the fingers as a fulcrum while at the same time moving both hands away from each other, the film was stretched. The test sample was considered to fail when it tore when subjected to this test. A fresh part of the test sample was used each time. Three test strips were used for each experiment. The basis for this test is the experimental observation that the film tears easily upon stretching when the degradation process lowers the sample molecular weight to a critically low value. Thus, when degradation lowered the molecular weight to an intrinsic viscosity of 0.7 dl/g, the film tore very easily when stretched.

RESULTS AND DISCUSSION

Table I collects the characterization data on the various oligomers of aromatic compounds tested as potential stabilizers. Table II collects the data on the ability of the *o*-xylene oligomer, Ionox 330 antioxidant, and dilauryl thiodipropionate (DLTP) to stabilize isotactic polypropylene against thermal degradation when used alone or in various combinations.

Unstabilized polypropylene films had oven lifetimes of about 5 hr at 150°C; usually the test samples deteriorated completely in less than 12 hr. Test samples containing only dilauryl thiodipropionate have been found to survive up to about 20 hr.

The following salient features characterize an oligomer of *o*-xylene as a heat stabilizer at 150°C:

1. At a concentration level of 0.1 wt-%, the sample failed at about 5 hr.
2. Polypropylene test strips containing 0.5 and 1.0 wt-% of the *o*-xylene oligomer remained intact for about 100 and 226 hr, respectively (experiments 4 and 5 in Table II). In comparison, a control film which contained 0.1 wt-% Ionox 330 antioxidant survived up to about 320 hr (experiments 6 in Table II).
3. Incorporating DLTP into the test strip greatly enhanced the heat stabilizing ability of the *o*-xylene oligomer (compare experiments 7, 8, and 9 with experiments 2 and 4). In the presence of DLTP, *o*-xylene oligomer was effective at a 0.1 wt-% concentration level (cf. experiments 2 and 7). This synergism was demonstrated by others earlier for hindered alkylphenol-type stabilizers and DLTP, and these results are confirmed in experiments 6 and 10 of Table II.
4. In comparison to oligomers of other aromatic compounds, the oligomer of *o*-xylene was most effective, as shown in Table III. These oligomers were added in 0.5 wt-% concentrations to polypropylene by the evaporation method.

The mechanism by which the oligomers of *o*-xylene function as heat stabilizers was not established in this investigation. Three speculative schemes are proposed:

1. Conventional heat stabilizers (SH) are said to delay to chain-type degradation of polypropylene by furnishing hydrogen atoms to the radical species R \cdot and ROO \cdot , e.g., R \cdot and/or ROO \cdot + SH \rightarrow RH + ROOH + S \cdot . The radical species R \cdot and ROO \cdot are said to be the active participants in the degradation of polypropylene, as follows:

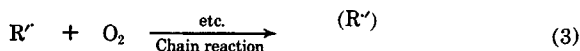
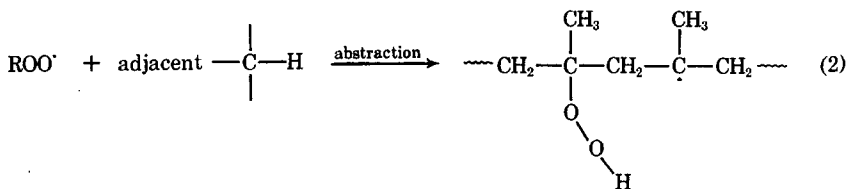
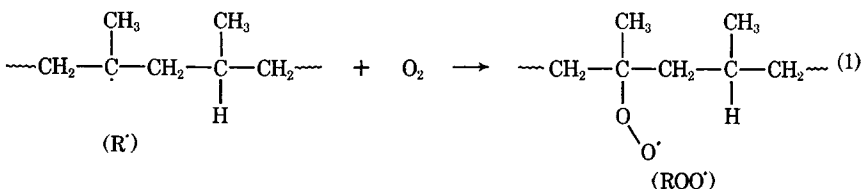


TABLE III
Heat Stabilizing Ability of Aromatic Oligomers

Oligomer	Hours to failure at 150°C
None	5
Toluene	4
<i>m</i> -Xylene	8
<i>p</i> -Xylene	24
1,2,4-Trimethylbenzene	48
<i>o</i> -Xylene	100

The stabilizing effect of the oligomer of *o*-xylene may similarly be due to the sacrificial donation of benzylic hydrogen atoms to these radicals ($R\cdot$ and $ROO\cdot$), thus preventing or diminishing the above chain reaction.

2. The polyaromatic may delay the chain degradation by stabilizing the polypropylene radical $R\cdot$ or $ROO\cdot$ through the interaction of the free-radical and the π -electron system of the aromatic.

3. The polyaromatic, according to a proposal of Bell,⁴ is oxidized to a phenolic-type stabilizer during the test. This proposal is unique in that a part of the oxygen would be consumed in the formation of the heat stabilizer from the precursor polyaromatic.

References

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4. E. R. Bell, private communication.

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