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Cross-Linking Of Polystyrene by Friedel-Crafts Chemistry: Multifunctional Additives

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Headnote

Various multifunctional aromatic compounds were synthesized and tested to ascertain if they were able to cross-link polystyrene. Catalysis and inhibition at high temperature were studied to achieve control over the cross-linking temperature, in order to develop suitable formulations which may function as flame retardants.

INTRODUCTION

One of the key steps in the burning of most polymeric materials is the release of low-molecularweight degradation products (monomers, dimers, oligomers, etc.) from the bulk polymer to the gas phase (1). Grassie pioneered the strategy of the cross-linking of polystyrene by Friedel-Crafts reactions in order to prevent or postpone this process and thus to achieve stabilization and flame retardancy (2). Further work has been performed, but the cross-linking temperatures of most systems that have been studied are lower than the processing temperature of polystyrene (3-5). To increase the flame retardancy of the system, the optimal cross-linking temperature should be higher than the processing temperature (ca. 200-250degC) to be practical and lower than the degradation temperature (ca. 360degC) to be useful.

Previous work from this laboratory has shown that the incorporation of functional groups (e. g., chloride, alcohol, etc.) by copolymerization is an effective way to stabilize polystyrene (6-9). It has been shown that the stabilization occurs by Friedel-Crafts chemistry (7, 8) and that it leads to a cross-linked product. Furthermore, the temperature at which the reaction occurs can be controlled when the catalyst is 2-ethylhexyldiphenyl phosphate. This phosphate undergoes thermal decomposition at about 240degC to form a phosphoric acid which then functions as a catalyst for the Friedel-- Crafts reaction. Thus, below the decomposition temperature, there is no catalyst, and no cross-linking may occur. When the temperature reaches 240degC, catalyst is formed, and the alkylation reaction, i. e., cross-linking, occurs. Studies using radiative gasification and cone calorimetry have established that the cross-linking leads to the formation of char which effectively insulates the polymer from the heat source so that a significant decrease of heat release rate is observed.

The previous work required the synthesis of the copolymer and its utilization to produce the final product. In this paper we report on recent work which has been directed towards the development of multifunctional additives which may be used in typical processing equipment, together with polystyrene and any other necessary additives, to produce this more thermally stable. The strategy used herein is to carry out the Friedel-Crafts reaction on polystyrene in order to produce functionalized polystyrene which will have enhanced thermal stability.

EXPERIMENTAL

Materials and Instruments

Polystyrene (PS) was obtained from Aldrich Chemical Co., $M_w \sim 280,000$. High-impact polystyrene (HIPS) was supplied by Dow Chemical as Styron 404; acrylonitrile-butadiene-styrene terpolymer (ABS) by Japan Synthetic Rubber Co., Ltd., containing 15 wt % of acrylonitrile, 40 wt % of butadiene, and 45 wt % of styrene; styrene-butadiene-styrene block copolymer (SBS) by Shell as Kraton D 1102, containing about 75% of butadiene; and K-resin by Phillips Petroleum as KRO1, containing about 25% of butadiene. The phosphate was provided by Solutia Inc., under trade name Santicizer 141, which consists of about 92% of 2-ethylhexyldiphenyl phosphate. Most of the other chemicals were obtained from the Aldrich Chemical Co., including 1,4-benzenedimethanol, 4-(chloromethyl)benzoyl chloride, sodium borohydride, ethyl chloroformate, phenyl chloroformate, ethyl chlorooxoacetate, methyl chlorooxoacetate, ar-vinylbenzyl alcohol, 4-vinylbenzyl chloride, chlorotrimethylsilane, terephthalaldehyde, terephthalaldehyde mono(diethyl acetal), 1,4-- diacetylbenzene, 4-acetoxystyrene, dibenzyl carbonate, 2-allyloxybenzaldehyde, ar-vinylbenzaldehyde, alpha,alpha'-dichloro-p-xylene (p-DCP), 4-aminophenol, 1,8diaminooctane, quinoline, 1,4-diazabicyclo[2.2.2]octane, 1,8-diazabicyclo[5.4.0]undec-7-ene, 1,8-bis(dimethylamino)naphthalene ("Proton Sponge"), and 2,2,6,6-tetramethyl-4-piperidinol (TMP).

Proton and ^{13}C NMR spectra were obtained on a General Electric GN-300 spectrometer at 300 MHz and 75 MHz, respectively, Chemical shifts are reported in ppm vs. Me_4Si by using a deuterated solvent peak as reference. Gas chromatography/mass spectrometry (GC/MS) was performed on a Hewlett-Packard 5890 AGC instrument

equipped with a 25 m x 0.25 mm DB-1 column along with a Hewlett-Packard 5970 series mass selective detector. Molecular ion mass (M^+), fragment ion masses (M/e), and relative intensity are reported. Infrared (IR) spectra were obtained on a Nicolet FTIR spectrometer. A Type PL-2 Brabender Plasti-Corder apparatus was used to make some of the blends if there was no common solvent for all the components.

The test for cross-linking, i.e., the presence of gel, was solubility. If the blend of styrenic resin and additives was insoluble in either tetrahydrofuran (THF) or chloroform after treatment at high temperature, then cross-linking was believed to have occurred.

Synthesis of 4-(Hydroxymethyl)benzyl Chloride (P-EMMC)

A 3.09-g (80-mmol) portion of NaBH_4 and 300 mL of ethanol/THF (1/1, v/v) were added slowly to a solution of 3.86 g (20 mmol) of 4-(chloromethyl)benzoyl chloride in 150 mL of anhydrous THF contained in a three-necked round-bottom flask that was equipped with a magnetic stirrer, an addition funnel, and a nitrogen inlet. The mixture was stirred for an additional 3 h at room temperature, then concentrated to about 100 mL. About 400 mL of water and 1 g of NaHCO_3 were added, and the aqueous solution was extracted twice with 400-mL portions of ether. The ether solutions were combined, washed twice with aqueous sodium chloride, and then dried over anhydrous magnesium sulfate overnight. The solution then was concentrated and the residue recrystallized from the mixed solvent ether/cyclohexane to yield 3.54 g (80%), mp 58degC [lit. 60degC (10)] of 4-(hydroxymethyl)benzyl chloride, 98% pure by GC/MS. Mass spectrum: 158 (13, M^+), 156 (48, M^+), 138 (7), 121 (55), 107 (82), 92 (25), 91 (100), 79 (45), 77 (56), 65 (21), 63 (21), 51 (26), and 50 (15); ^1H NMR (CDCl_3) delta 7.3 (m, 4H), 4.70 (s, 2H), 4.59 (s, 2H), and 1.67 (s, 1H); ^{13}C NMR (CDCl_3) delta 141.37, 135.10, 128.88, 127.37, 64.93, and 46.12, results which agree well with the literature (10). The characterization was further confirmed by 2D NMR (^1H - ^1H and ^1H - ^{13}C) and IR analysis.

Synthesis of 3-(Hydroxymethyl)benzyl Chloride (m-HMBC)

The procedures for synthesis and work-up were similar to those used for the para-isomer (see above). The crude product was purified by column chromatography on silica gel, using a mixed solvent consisting of hexanes/ethyl acetate (5/1, v/v), to give 3-(hydroxymethyl)benzyl chloride (55% yield), 96% pure by GC/MS. Mass spectrum: 158 (M^+ , 12), 156 (M^+ , 36), 138 (5), 121 (72), 107 (60), 103 (13), 92 (35), 91 (100), 89 (22), 79 (32), 77 (50), 65 (25), 63 (21), 51 (21), and 50 (11); ^1H NMR (CDCl_3) delta 7.28 (m, 4H), 4.51 (s, 2H), 4.48 (s, 2H), and 3.55 (s, 1H); ^{13}C NMR (CDCl_3) delta 141.51, 137.64, 128.82, 127.62, 126.96, 126.84, 64.41, and 46.14.

Synthesis of Chloromethyl-4-(1-hydroxyethyl)benzene (p-HEBC)

A 50-mL portion of THF was added to a solution of 16 g (50 mmol) of $\text{Hg}(\text{OAc})_2$ in 50 mL of water, resulting in a yellow precipitate (11). To this vigorously stirred suspension was added 7.6 g (50 mmol) of 4-vinylbenzyl chloride, whereupon the mixture became a colorless clear solution. It was stirred for 3 h and then cooled to about 0degC. A solution of 1.9 g (50 mmol) of NaBH_4 in 100 mL of EtOH was added slowly while the temperature was maintained near 0degC with a Dry Ice/acetone bath. The resultant gray suspension was stirred for an additional 2 h at room temperature. The solution was then saturated with K_2CO_3 and separated, and the aqueous layer was extracted with 300 mL of ether. The organic layers were combined, washed with aqueous sodium chloride three times, and dried over anhydrous MgSO_4 . After concentration, the crude product was purified by column chromatography on silica gel with a mixed solvent consisting of ethyl acetate/hexanes (2/3, v/v) to give 0.72 g (5% yield) of chloromethyl-4-(1-hydroxyethyl)benzene as a viscous oil, 86% pure by GC/MS. Mass spectrum: 170 (M^+ , 6), 155 (48), 117 (17), 91 (100), and 43 (60); ^1H NMR (CDCl_3) delta 7.28 (m, 4H), 4.79 (q, 1H, $J = 6$ Hz), 4.54 (s, 2H), 2.92 (s, 1H), and 1.40 (d, 3H, $J = 6$ Hz); ^{13}C NMR (CDCl_3) delta 146.14, 136.47, 128.67, 125.77, 69.78, 46.00, and 25.10. The characterization was further confirmed by 2D NMR (^1H - ^1H and ^1H - ^{13}C) and IR analysis.

Synthesis of Ethyl (or Phenyl) 4-(Hydroxymethyl)benz Carbonate

A solution of about 20 mmol of ethyl (or phenyl) chloroformate in 100 mL of anhydrous THF was added slowly to a solution of 6.91 g (50 mmol) of 1,4-benzenedimethanol in a mixed solvent consisting of 200 mL of THF and 5 mL of pyridine, with stirring under a nitrogen atmosphere. The turbid mixture was stirred for 3 h at room temperature and then concentrated. After the addition of about 300 mL of ether, the mixture was filtered. The resultant ether solution was washed three times with aqueous sodium chloride and then dried over anhydrous MgSO₄. After concentration, the crude product was extracted with cyclohexane and shown to consist of about a 50% yield of the desired product in 95% purity by GC/MS (for both the ethyl and the phenyl compounds). Mass spectrum (ethyl): 200 (M⁺, 32), 179 (7), 137 (36), 121 (50), 107 (100), 91 (94), 79 (74), and 77 (57); phenyl: 121 (100), 91 (33), 77 (32), and 65 (20).

Synthesis of ar-Vinyl(trimethylsilyloxymethyl)benzene

A solution of 10.9 g (100 mmol) of chlorotrimethylsilane in 10 mL of ether was added slowly to a solution of 2.01 g (15 mmol) of ar-vinylbenzyl alcohol ("ar-" indicates a mixture of regioisomers) in 10 mL of ether contained in a three-necked flask under nitrogen protection. The mixture was stirred for 20 h at room temperature and then concentrated to give 2.06 g (66% yield) of crude product (85% pure by GC/MS). Mass spectrum: 206 (M⁺, 32), 191 (30), 161 (15), 117 (100), 115 (22), 91 (12), 75 (21), 73 (25), and 45 (15).

Synthesis of Methyl ar-Vinylbenzyl Oxalate (DBOX)

A solution of 4.20 g (34 mmol) of methyl chlorooxalate in 10 mL of ether was added slowly to a solution of 4.60 g (34 mmol) of ar-vinylbenzyl alcohol in 10 mL of ether contained in a three-necked flask under a nitrogen atmosphere. The mixture was stirred for 3 h at room temperature, and then the white precipitate was filtered and dried to give 2.6 g (35% yield) of crude product.

Synthesis of Methyl (or Phenyl) ar-Vinylbenzyl Carbonate

A solution of 34 mmol of methyl (or phenyl) chloroformate in 10 mL of ether was added slowly to a solution of 4.60 g (34 mmol) of ar-vinylbenzyl alcohol in 10 mL of ether contained in a three-necked flask under nitrogen protection. The mixture was stirred for 3 h at room temperature and then concentrated to give 4.4 g (67% yield) (or 9.8 g and 90% yield for phenyl) of crude product.

Synthesis of bis(ar-Vinyl) Oxalate

About 5 mL of a 2 M solution of oxalyl chloride in CH₂Cl₂ (10 mmol) was added slowly to 2.68 g (20 mmol) of ar-vinylbenzyl alcohol in a three-necked flask, under nitrogen protection and at about 5°C. The mixture was stirred for 3 h at room temperature, the resultant white precipitate was recrystallized from a mixed solvent consisting of ether/acetone (1/1, v/v) to yield 0.45 g (14%) of product.

Synthesis of 4-(Hydroxymethyl)benzyl Diphenyl Phosphate

In a 50-mL flask, 1.38 g of 1,4-benzenedimethanol was dissolved in 20 mL of anhydrous pyridine. This solution was then cooled to 0°C. A 2.68-g portion of diphenyl chlorophosphate was added dropwise, and a large quantity of white solid precipitated during the addition. The flask was placed in the refrigerator for 12 h. After the solid was filtered off, the filtrate was neutralized with 10% aqueous HCl, then extracted with diethyl ether three times. The ether solution was washed with distilled water and dried with anhydrous Na₂SO₄. About 2 g of crude product was obtained after the ether was removed. This crude product contained both monosubstituted and disubstituted phosphate. About 1 g of 4-(hydroxymethyl)benzyl diphenyl phosphate was obtained after column chromatography with elution by a mixture of ethyl acetate and petroleum ether (1/2, v/v).

Syntheses of ar-Vinylbenzyl Diphenyl Phosphate and 2-(ar-Vinylbenzyl)ethyl Tosylate

Upon replacing 1,4-benzenedimethanol with vinylbenzyl alcohol in the above process, ar-vinylbenzyl diphenyl phosphate was obtained without further purification. By using 2-(4-vinylphenyl)ethanol and TsCl as starting materials, 2-(ar-vinylphenyl)ethyl tosylate was obtained.

Synthesis of ar-Vinylbenzyl Nitrate (DBN)

About 2.0 g of AgNO₃ was dissolved in 15 mL of ethanol, and 1.53 g of ar-vinylbenzyl chloride was added to the solution. This solution was stirred for 12 h at room temperature. Silver chloride precipitated during the reaction. After filtration of AgCl and the removal of ethanol, 1.89 g of ar-vinylbenzyl p-nitrobenzoate was obtained.

Reactions of Additives and Polymers

Blends of the additives and polymer were prepared in solution, if the additive were soluble in either THF or chloroform, or by mixing in a Brabender mixer at 180degC for 10 min. For solution mixing, the additive and polymer were both dissolved in the same solvent, either THF or chloroform, and the solution was stirred with a magnetic stirrer for 10 min. After stirring, the solvent was removed, and the resulting solid was then dried overnight in a vacuum oven at 70degC. These blends of additives and polymers were then placed in a testtube-like container and transferred to a vacuum trap which was maintained by an oil bath at a constant temperature for 30 min under a flowing nitrogen atmosphere. The samples were tested for cross-linking by attempted dissolution in either THF or chloroform.

RESULTS AND DISCUSSION

Difunctional Additives

The difunctional additives that have been studied can be classified into three major groups: (1) those that cannot cross-link polystyrene under any conditions, (2) those that can cross-link polystyrene under all conditions, (3) those that can cross-link polystyrene only under certain controlled conditions. Structures of the difunctional cross-linking additives used in this study are summarized in Table 1.

Compounds in the first group do not contain two active Friedel-Crafts alkylating agents and thus cannot cross-link polystyrene under any conditions tested. Examples of alkylating agents in this category include terephthalaldehyde, terephthalaldehyde mono(diethyl acetal), 1,4-diacetylbenzene, 4-acetoxystyrene, dibenzyl carbonate, 2-allyloxybenzaldehyde, ar-vinylbenzaldehyde, ethyl (or phenyl) 4-(hydroxymethyl)benzyl carbonate, ar-vinyl(trimethylsilyloxymethyl)benzene, 1,4-benzenedimethanol (this diol can cross-link polystyrene at 300degC if catalyzed by zeolites in a sealed vessel; see reference 6), 4-(2-hydroxyethyl)styrene (9), and 4-(3-hydroxypropyl)styrene (9).

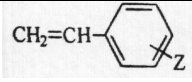
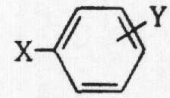
Compounds in the second group contain one or two very active Friedel-Crafts alkylating agents and were found to cross-link polystyrene under all conditions tested. Examples of these very active difunctional alkylating agents include 4-(hydroxymethyl)benzyl diphenyl phosphate, ar-vinylbenzyl diphenyl phosphate, 1,4-benzenedimethanol bis(diphenyl phosphate), 2-(arvinylphenyl)ethyl tosylate, 3-(ar-vinylphenyl)propyl tosylate, and 1,4-butanediol ditosylate.

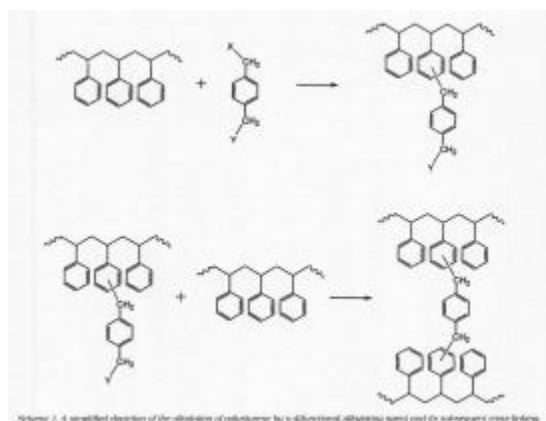
Compounds in the third group contain two somewhat active functional groups which show different activities under different temperature conditions, with or without the presence of catalysts or inhibitors. Compounds in this category include 4-(hydroxymethyl)benzyl chloride (p-HMBC), 3-(hydroxymethyl)benzyl chloride (m-HMBC), chloromethyl-4-(1-hydroxyethyl)benzene (p-HEBC), ar-vinylbenzyl alcohol (VBA), 4-(hydroxymethyl)benzyl p-nitrobenzoate (p-HONB), 1,4-benzenedimethanol di-(p-nitrobenzoate) (p-NBNB), ar-vinylbenzyl nitrate (DBN), methyl (or phenyl) arvinylbenzyl carbonate, methyl ar-vinylbenzyl oxalate (DBO), and alpha,alpha'-dichloro-p-xylene (p-DCP).

Most of the compounds in the third group fall into the category of aromatic difunctional Friedel-Crafts alkylating compounds, X-C₆H₄-Y, where X- or Y- is one of the functionalities, vinyl-, chloromethyl-, and hydroxymethyl- or its esters. Most of the results with additives agree well with those of copolymers that contain alcohol or chloride functional groups (9). The reactivity of these functional groups can be tuned by varying the concentrations of catalysts and/or inhibitors, thus achieving control over the cross-linking temperature. A simplified scheme showing how the reaction proceeds is shown as Scheme 1. In this scheme we show the substituents attached to the aromatic ring through a methylene group: if the substituent were vinyl, there would be no methylene group present, but in most other cases, this is a necessary functionality. More details of the results for the third group are shown in Table 2.

If only p-HMBC is added, even in very low concentration, the blends are found to cross-link at very low temperature (entries 1 and 3 in Table 2). A similar result was obtained for m-HMBC and p-DCPX (entries 7 and 13), with the cross-linking temperature lower than processing temperature. We assume that the HCl released from reaction of the chloride group catalyzes further reaction of the hydroxyl groups and thus leads to cross-linking. Addition of TMP as HCl scavenger was found to raise the cross-linking temperature to above 250degC (entries 3, 9, and 11). Yet the surprising effectiveness of TMP at such a low concentration (~0.05 wt %) indicates that it may act not only as an HCl scavenger after initial reaction and formation of HCl, but also as a Friedel-Crafts reaction inhibitor beforehand. Thus the role of base needs further elucidation. A temperature above 250degC for the onset of cross-linking is higher than is desired in a real fire situation. At this onset temperature the rate of reaction may be too slow for the reaction to be complete before the temperature reaches degradation range (> 360degC), well within one minute in most cases. However, added phosphate (Santicizer 141), which catalyzes reaction above ~ 220degC, was found to override the inhibition of amine at intermediate temperatures, thus initiating reaction of the chloride group, with further HCl evolution driving cross-linking to completion. The final combination of additives giving the desired temperature control of the consecutive Friedel-Crafts reactions is cross-linking additive (10%), Santicizer 141 (5%), and TMP (0.050.10%); see entries 4, 6, 10, and 12 in Table 2.

Table 1. Structures of the Difunctional Cross-Linking Additives Used in this Study.

| | Group I | Group II | Group III |
|---|---|--|--|
|  | $\left\{ \begin{array}{l} Z = -\text{CH}_2\text{CH}_2\text{OH} \\ -\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \\ -\text{CH}_2\text{OSi}(\text{CH}_3)_3 \\ -\text{CHO} \\ -\text{O}_2\text{CCH}_3 \end{array} \right.$ | $\left\{ \begin{array}{l} Z = -\text{CH}_2\text{O}_2\text{P}(\text{OPh})_2 \\ -\text{CH}_2\text{CH}_2\text{OTs} \\ -\text{CH}_2\text{CH}_2\text{CH}_2\text{OTs} \end{array} \right.$ | $\left\{ \begin{array}{l} Z = -\text{CH}_2\text{OH} \text{ (VBA)} \\ -\text{CH}_2\text{ONO}_2 \text{ (DBN)} \\ -\text{CH}_2\text{OCO}_2\text{CH}_3(\text{Ph}) \\ -\text{CH}_2\text{OCOCO}_2\text{CH}_3 \text{ (DBOX)} \end{array} \right.$ |
|  | $\left[\begin{array}{l} X = Y = -\text{CH}_2\text{OH} \\ -\text{COCH}_3 \\ -\text{CHO} \end{array} \right]_p$ $\left[\begin{array}{l} X = -\text{CHO} \\ Y = -\text{CH}(\text{OCH}_2\text{CH}_3)_2 \end{array} \right]_p$ $\left[\begin{array}{l} X = -\text{CH}_2\text{OH} \\ Y = -\text{CH}_2\text{O}_2\text{COCH}_2\text{CH}_3(\text{Ph}) \end{array} \right]_p$ $\left[\begin{array}{l} X = -\text{CHO} \\ Y = \text{OCH}_2\text{CH} = \text{CH}_2 \end{array} \right]_o$ | $\left[\begin{array}{l} X = Y = -\text{CH}_2\text{OTs} \\ -\text{CH}_2\text{OMs} \\ -\text{CH}_2\text{O}_2\text{P}(\text{OPh})_2 \end{array} \right]_p$ $\left[\begin{array}{l} X = -\text{CH}_2\text{OH} \\ Y = -\text{CH}_2\text{O}_2\text{P}(\text{OPh})_2 \end{array} \right]$ | $\left[\begin{array}{l} X = Y = -\text{CH}_2\text{Cl} (p - \text{DCPX}) \\ X = Y = -\text{CH}_2\text{O}_2\text{CC}_6\text{H}_4\text{NO}_2 (p - \text{NBNB}) \\ \left[\begin{array}{l} X = -\text{CH}_2\text{OH} \\ Y = \text{CH}_2\text{Cl} \end{array} \right] (m - \text{HMBC}) \\ \left[\begin{array}{l} X = -\text{CH}_2\text{OH} \\ Y = \text{CH}_2\text{Cl} \end{array} \right] (p - \text{HMBC}) \\ \left[\begin{array}{l} X = -\text{CH}_2\text{OH} \\ Y = -\text{CH}_2\text{O}_2\text{CC}_6\text{H}_4\text{NO}_2 \end{array} \right] (p - \text{HONB}) \\ \left[\begin{array}{l} X = \text{CH}_2\text{Cl} \\ Y = -\text{CH}(\text{OH})\text{CH}_3 \end{array} \right] (p - \text{HEBC}) \end{array} \right.$ |
| Other | PhCH ₂ OCO ₂ CH ₂ Ph | TsOCH ₂ (CH ₂) ₂ CH ₂ OTs | |



Scheme 1. A simplified depiction of the alkylation of polystyrene by a difunctional alkylating agent and its subsequent cross-linking.

Table 2. Results for Tests of Group III Additives on Polystyrene Cross-Linking.

| Entry | ADD | Wt % ADD | Wt % 141 | Wt % TMP | @ 200°C | @ 250°C | @ 300°C |
|-------|----------------|----------|----------|----------|---------|---------|---------|
| 1 | <i>p</i> -HMBC | 10 | 0 | 0 | Yes | Yes | Yes |

| | | | | | | | |
|----|----------------|-----|---|------|-----|-----|-----|
| 2 | <i>p</i> -HMBC | 0.2 | 0 | 0 | Yes | Yes | Yes |
| 3 | <i>p</i> -HMBC | 10 | 0 | 0.05 | No | No | Yes |
| 4 | <i>p</i> -HMBC | 10 | 5 | 0.05 | No | Yes | Yes |
| 5 | <i>p</i> -HMBC | 10 | 0 | 0.10 | No | No | Yes |
| 6 | <i>p</i> -HMBC | 10 | 5 | 0.10 | No | Yes | Yes |
| 7 | <i>m</i> -HMBC | 10 | 0 | 0 | Yes | Yes | Yes |
| 8 | <i>m</i> -HMBC | 10 | 5 | 0 | No | Yes | Yes |
| 9 | <i>m</i> -HMBC | 10 | 0 | 0.10 | No | No | Yes |
| 10 | <i>m</i> -HMBC | 10 | 5 | 0.10 | No | Yes | Yes |
| 11 | <i>p</i> -DCPX | 10 | 0 | 0.05 | No | No | Yes |
| 12 | <i>p</i> -DCPX | 10 | 5 | 0.05 | No | No | Yes |
| 13 | <i>p</i> -DCPX | 10 | 0 | 0 | Yes | Yes | Yes |
| 14 | <i>p</i> -DCPX | 10 | 5 | 0 | No | No | Yes |
| 15 | VBA | 10 | 0 | 0 | No | No | N/A |
| 16 | VBA | 10 | 5 | 0 | No | Yes | Yes |
| 17 | <i>p</i> -HONB | 10 | 0 | 0 | No | No | N/A |
| 18 | <i>p</i> -HONB | 10 | 5 | 0 | No | Yes | Yes |
| 19 | <i>p</i> -NBNB | 10 | 0 | 0 | No | No | N/A |
| 20 | <i>p</i> -NBNB | 10 | 5 | 0 | No | Yes | Yes |
| 21 | DBN | 10 | 0 | 0 | No | N/A | N/A |
| 22 | DBN | 10 | 5 | 0 | N/A | Yes | N/A |

Catalysts and Inhibitors

The cross-linking of polystyrene is believed to occur by Friedel-Crafts reactions between the additives and the phenyl groups in polystyrene. Theoretically, this reaction can be catalyzed by any acid, but most acids show activity at low temperature, even room temperature. The preferred catalyst, 2-ethylhexyldiphenyl phosphate (Santicizer 141), has been shown to degrade between 220 and 240degC to give an olefin and a phosphoric acid (7). Most amines, such as 4-aminophenol, 1,8-diaminooctane, quinoline, 1,4-diazabicyclo[2.2.2]octane, 1,8-diazabicyclo[5.4.0]undec-7-ene, and 1,8-bis(dimethylamino)naphthalene ("Proton Sponge"), are so active that they completely inhibit cross-linking below 250degC, possibly by nucleophilic substitution reactions. The hindered amine (HALS), 2,2,6,6-tetramethyl-4-piperidinol (TMP), apparently functions only as an acid acceptor and thus increases the temperature at which cross-linking occurs. The amount of added TMP has been optimized at ~0.1 wt %, and it is effective by inhibiting cross-linking up to above 200degC, until it is consumed by the resultant phosphoric acid from the phosphate degradation.

Blends of Styrenic Copolymers

Similar results were obtained on blends of HIPS, ABS, SBS, and K-resin with several of the above crosslinking agents, such as *p*-HMBC and *p*-DCPX

CONCLUSION

Polystyrene was successfully cross-linked at temperatures between 200 and 300degC, by varying the functional additives, catalysts, and/or inhibitors. These results lay the foundation for the development of flame-retardant formulas for styrenic resins. Further work on applications and on the mechanism and kinetics is underway in this laboratory.

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