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THERMAL STABILITY OF POLY(STYRENE) CONTAINING PHOSPHORUS IN THE MAINCHAIN

B. A. Howell[*] *and J. Uzibor*

Center for Applications in Polymer Science, Central Michigan University, Mt. Pleasant, MI 48859-0001, USA

For many applications poly(styrene) must be treated to reduce its flammability. This is usually done by incorporating a flame retardant additive, usually an organohalogen compound, into the formulation as the polymer is being processed. A potentially very efficient way of introducing flame retardance would be to incorporate a suitable structural unit directly into the polymer. This can be done by using 2,4,4,5,5-pentaphenyl-1,3,2-dioxaphospholane as an initiator for styrene polymerization. The strained carbon–carbon bond of the phospholane undergoes homolysis at moderate temperatures to generate a diradical which initiates polymerization. The resulting polymer contains an O–P–O unit in the mainchain. Thermogravimetry indicates that the thermal stability of the polymer is quite comparable to that of poly(styrene) generated by conventional methods.

Keywords: *flame retardancy, phospholane polymerization initiator, phosphorus-containing poly(styrene), phospholane-styrene copolymers, thermal stability*

Introduction

Poly(styrene) and copolymers are large volume commodity polymers. Billions of pounds are produced worldwide annually for use in a wide variety of applications. These materials are quite flammable and must be flame-retarded for most applications. The traditional flame retardants for these polymers have been organohalogen compounds [1, 2]. However the development of new, more effective, and environmentally friendly flame retardant strategies for styrenics is of increasing urgency as the criticism of the use of organohalogens, primarily brominated aromatics, becomes more prominent around the world [3–5]. Flame retarding species that can be chemically incorporated into the polymer are particularly attractive since volatility, blooming and loss during processing are not issues of limitation for the use of the retardant [2, 6–8]. A goal of this work was the development of an organophosphorus (phosphate or phosphonate) containing a thermally-labile carbon–carbon bond that might be cleaved homolytically to generate a diradical that could act as an initiator for styrene polymerization. The use of such a compound as initiator would generate a polymer with a phosphorus-containing unit incorporated into the mainchain. The polymer should display desirable flammability properties and be readily processable using standard techniques. It is possible that such a molecule with a strained carbon-carbon bond might also be reactive toward propagating radicals, i.e., it might act as a monomer. In this case, several phosphorus-containing units may be incorporated into the polymer mainchain. In fact, if the compound were to be sufficiently reactive as a monomer, the level of incorporation could be controlled by simply adjusting the concentration of the phosphorus compound in the polymerization mixture.

Experimental

Materials

Syntheses were generally performed in an inert atmosphere (dry nitrogen). The apparatus used for synthesis included a three-necked, round-bottomed flask, of appropriate size, fitted with a condenser bearing a gas-inlet tube, a thermometer and a magnetic stirring bar. Before use, all glassware was thoroughly cleaned and dried overnight in an oven at 120°C and allowed to cool under a stream of prepurified nitrogen. A photoreactor with a mercury lamp with an emission of 345 nm was used to carry out photoreduction of ketones.

1,1,2,2-Tetraphenyl-1,2-ethanediol [10]

In a 5-liter, three-necked photoreaction flask was placed 91.10 g (0.501 moles) of benzophenone followed by the addition of 500 mL of isopropyl alcohol. Then a few drops of glacial acetic acid were added to the mixture. A mercury lamp with an emission wavelength of 345 nm was then inserted into the flask. After 6 h of irradiation, a few crystals had formed in the bottom of the flask. The reaction

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[*] Author for correspondence: bob.a.howell@cmich.edu

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

mixture was left for one week in the photoreactor for higher conversion. The crystals formed were collected by filtration at reduced pressure and washed, successively with three 50-mL portions of hexane and dried at reduced pressure (15 torr) and 30°C. The diol was obtained as a white crystalline solid (89.25 g, 97.3% yield); ^{1}H NMR (δ, $CDCl_3$), 3.03 (s, 2H, exchangeable protons), 7.10–7.60, (m, 20H, aromatic protons); ^{13}C NMR (δ, $CDCl_3$) 83.3 (tertiary carbon atoms bearing hydroxyl groups), 127.2 (substituted aromatic carbon atoms), 127.5 (aromatic carbon atoms at *ortho* positions), 128.4 (aromatic carbon atoms at *meta* positions), 144.4 (aromatic carbon atoms at *para* positions).

2,4,4,5,5-Pentaphenyl-1,3,2-dioxaphospholane [11]

A solution of 1.00 g (2.71 mmol) of benzpinacol and 0.553 g (5.50 mmol) of triethylamine in 50 mL of anhydrous diethyl ether was placed into a 100-mL, three-necked, round-bottomed flask fitted with a magnetic stir bar, a pressure-equalizing dropping funnel and an Allihn condenser bearing a gas-inlet tube. Dichloro(phenyl)phosphine (0.49 g, 2.71 mmol) was added dropwise over a period of 0.25 h. The mixture was stirred at solvent reflux for 2 h, allowed to cool to room temperature, and triethylammonium chloride was removed by filtration. The filtrate was subjected to rotary evaporation at reduced pressure to remove the solvent. The solid residue was crystallized twice from hexane to afford 2,4,4,5-pentaphenyl-1,3,2-dioxaphospholane (0.90 g, 70.5% yield) as a white crystalline solid, *m.p.* 72°C (DSC): ^{1}H NMR NMR (δ, $CDCl_3$), 7.01–7.42 (m, 25H, aromatic protons); P-31 NMR (δ, $CDCl_3$), 22.1(s); FTIR (cm^{-1}, NaCl), 3028(vs) (aromatic C–H stretch), 2925(vs) (aliphatic C–H stretch), 1601(vs) (aromatic nucleus), 1059 and 759 (O–P–O stretch and bending); mass spectrum *m*/*z*, (% of base), 77(70), 106(62), 141(21), 182(100), 473(53).

Polymerization of styrene (1% 2,4,4,5,5-pentaphenyl-1,3,2-dioxaphospholane as initiator) at 70°C

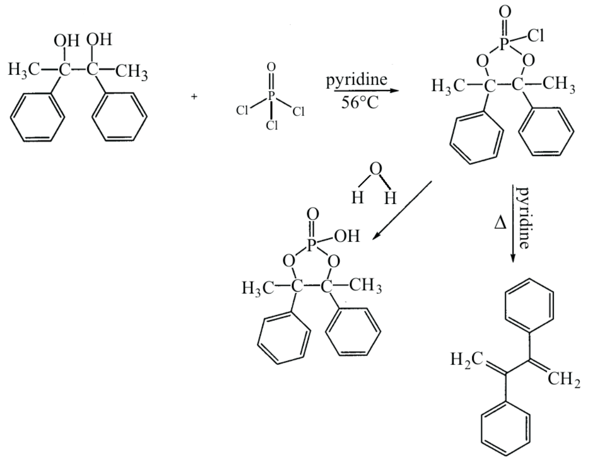
A polymerization tube fitted with a two-way stopcock was charged with inhibitor-free dry styrene monomer (10.0 g, 96.0 mmole) and 2,4,4,5,5-pentaphenyl-1,3,2-dioxaphospholane (0.10 g, 0.21 mmole). The solution was degassed with pure dry nitrogen for 30 min and the tube was placed in a constant temperature oil bath at 70°C for 15 h. SEC analysis of the polymer after purification by repeated dissolution in toluene followed by precipitation with methanol provided the following parameters: M_w $3.65\cdot10^5$, M_n $1.80\cdot10^5$ with a polydispersity of 2.03. Spectral properties: ^{1}H NMR (δ, $CDCl_3$) 1.58 (3H, methylene and methine protons), 6.8–7.5 (aromatic protons); P-31 NMR (δ, $CDCl_3$) 31.4(s); FTIR (cm^{-1}, NaCl), 3025(vs) (aromatic C–H stretch), 2922(vs) (aliphatic C–H stretch), 1601(vs) (aromatic nucleus), 1492, 1452 (characteristic bands for polystyrene), 1059 and 759 (O–P–O stretch).

Other polymers were prepared in an analogous manner.

Methods

Nuclear magnetic resonance (NMR) spectra were obtained using 10 to 25% solutions in deuterochloroform and a Varian Mercury 300 MHz Spectrometer. Proton and carbon chemical shifts are reported in parts-per-million (δ) with respect to tetramethylsilane (TMS) as internal reference (δ=0.00). Phosphorus chemical shifts are reported in δ with respect to 85% aqueous phosphorous acid solution as external reference (δ=0.00). Infrared (IR) spectra were obtained using thin films between sodium chloride plates or solid solutions (1%) in anhydrous potassium bromide (as discs) and a Nicolet Magna-IR 560 spectrometer. Absorptions were recorded in wavenumbers (cm^{-1}), and absorption intensities were classified in the usual fashion as very weak (vw), weak (w), medium (m), strong (s) and very strong (vs) relative to the strongest band in the spectrum. Mass spectra were obtained using a Hewlett-Packard 5995A gas chromatography/mass spectrometer with an ionizing potential of 70 electron volts and temperature programmed elution into the spectrometer inlet (90–200°C).

Thermal decomposition temperatures were obtained using a PerkinElmer Pyris 1 Thermogravimetric Analyzer (TG). Samples were analyzed at a heating rate of 10°C min^{-1} in a flow of prepurified nitrogen gas at a rate of 50 mL min^{-1}. Melting points were determined using a PerkinElmer Pyris Diamond differential scanning calorimeter (DSC). All samples were analyzed at a heating rate of 5°C min^{-1} under a stream of prepurified nitrogen at a rate of 50 mL min^{-1}. Size exclusion chromatography (SEC) was used to determine the molecular mass of polymers. A Waters 150-CV chromatograph equipped with mixed bed columns (Polymer Laboratories) was used. Narrow distribution polystyrene standards were used for calibration. Tetrahydrofuran (THF) at 1.0 mL min^{-1} was used as elution solvent. Samples dissolved in THF (0.01 mass%) were filtered through a 0.45 μm Nylon filter prior to injection. Polymerization was carried out in 25×200 mm Pyrex test tubes under dry nitrogen [9]. Samples were thoroughly degassed with a stream of dry nitrogen prior to polymerization.



Scheme 1 Synthesis of a cyclic hydrogen phosphate ester from 2,3-diphenyl-2,3-butanediol

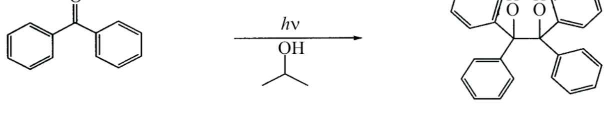
Results and discussion

The synthesis of an appropriate phosphorus compound was based on an earlier observation that when 2,3-diphenyl-2,3-butanediol was treated with phosphoryl chloride at 56°C, a cyclic phosphate which could be isolated and characterized was formed [10]. This is illustrated in Scheme 1. Because this ester contains hydrogen atoms alpha to the ester functionality, it is unstable at higher temperature in the presence of base and readily undergoes elimination of phosphate to form the corresponding diene.

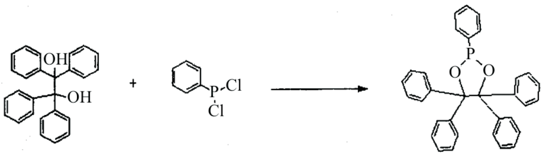
This instability makes it unsuitable for use as described above. However, a similar compound with no alpha hydrogen atoms could not undergo elimination and if the central carbon–carbon bond is sufficiently strained, it might be expected to undergo thermally-induced homolysis. Therefore, 1,1,2,2-tetraphenyl-1,2-ethanediol, or benzpinacol, was selected as the substrate for the synthesis of a phosphorus ester that might function as a polymerization initiator, a reactive monomer, or both.

The diol, benzpinacol, is readily available from reductive photodimerization of benzophenone. Irradiation (354 nm; mercury lamp reactor) of a solution of benzophenone in 2-propanol afforded white needles of benzopinacol in greater than 97% yield.

The proton NMR spectrum of this material is displayed in Fig. 1. The spectrum contains the expected absorption for aromatic protons as well as absorption for exchangeable protons at δ 3.03(s). The compound is a white solid with a melting point of 184°C. The synthesis of a suitable cyclic phosphorus compound was achieved by treatment of the diol with excess (dichloro)phenylphosphine (Scheme 3).



Scheme 2 Synthesis of 1,1,2,2-tetraphenyl-1,2-ethanediol (benzpinacol)



Scheme 3 Synthesis of 2,4,4,5,5-pentaphenyl-1,3,2-dioxaphospholane

In this case, the phosphine served as both reactant and solvent. The cyclic compound, 2,4,4,5,5-pentaphenyl-1,3,2-dioxaphospholane, can be obtained in good yield as a white crystalline solid with a melting point of 72°C (DSC). The proton and phosphorus-31 NMR spectra of this compound are displayed in Figs 1 and 2, respectively. The proton NMR spectrum contains absorption for aromatic protons and the phosphorus spectrum consists of a singlet at δ 22.1 ppm, relative to the absorption for 85% aqueous phosphoric acid as external reference. The infrared spectrum of this material is displayed in Fig. 3.

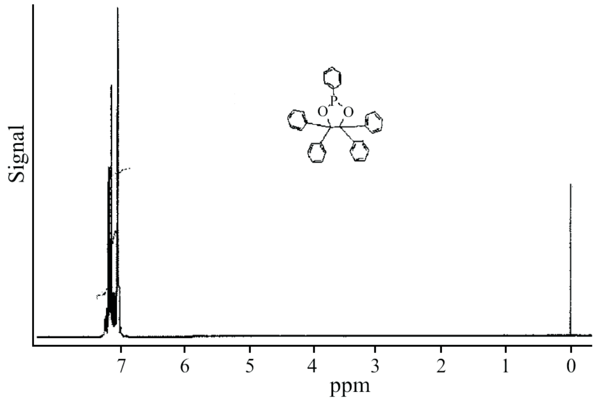


Fig. 1 ^{1}H NMR spectrum of 2,4,4,5,5-pentaphenyl-1,3,2-dioxaphospholane

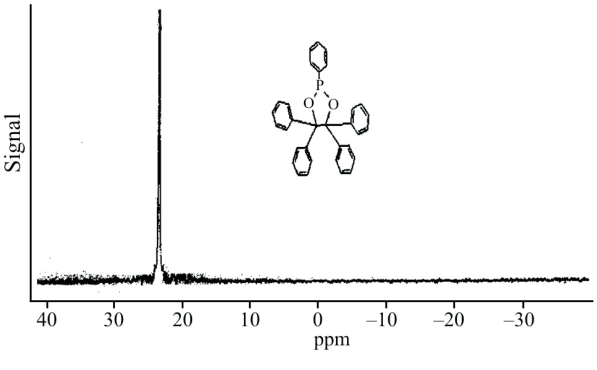


Fig. 2 ^{31}P NMR spectrum of 2,4,4,5,5-pentaphenyl-1,3,2-dioxaphospholane

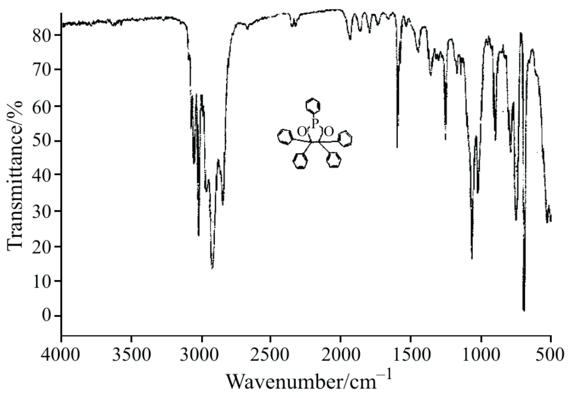
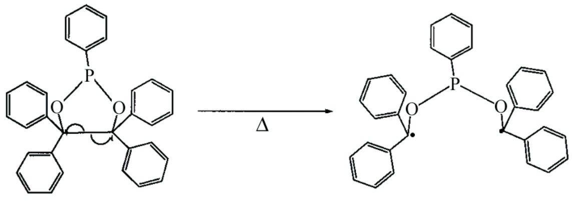


Fig. 3 Infrared spectrum of 2,4,4,5,5-pentaphenyl-1,3,2-dioxaphospholane

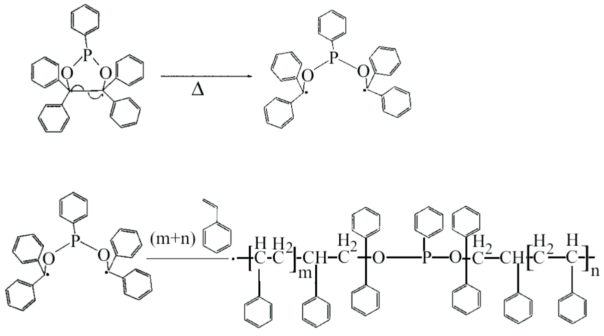
The spectrum contains an aromatic absorption band at 1601 cm^{-1} as well as strong bands for O–P–O absorption at 1059 and 759 cm^{-1}. As noted above this five-membered ring structure contains a sterically strained carbon–carbon bond that might be expected to undergo thermally induced homolysis at modest temperatures. This may be readily demonstrated for 2,4,4,5,5-pentaphenyl-1,3,2-dioxaphospholane using thermogravimetry. The compound readily undergoes thermal decomposition with a maximum rate of degradation at 120°C and a degradation onset temperature of 70°C. Isothermal thermogravimetry was used to determine a half-life for decomposition at various temperatures. For example, the half-life for its decomposition at 72°C is 10 h. The 10-h half-life temperature is a convenient way to classify polymerization initiators. Because of the ease with which the central carbon-carbon bond of this bond undergoes homolysis, it should function as a polymerization initiator.



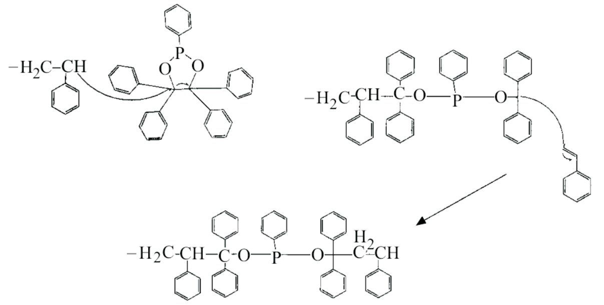
Scheme 4 Homolysis of the carbon–carbon bond in 2,4,4,5,5-pentaphenyl-1,3,2-dioxaphospholane

This is illustrated in Scheme 5 for the polymerization of styrene. If the compound functions as initiator, each polymer chain generated should contain one phosphorus moiety.

Alternatively, it is possible that the phosphorus compound could also function as a comonomer in the polymerization, i.e., the propagating poly(styryl) radical could add to the strained carbon–carbon bond (Scheme 6).



Scheme 5 Initiation of styrene polymerization with 2,4,4,5,5-pentaphenyl-1,3,2-dioxaphospholane



Scheme 6 Copolymerization of styrene and 2,4,4,5,5-pentaphenyl-1,3,2-dioxaphospholane

A series of mixtures was prepared in standard polymerization tubes. The first tube contained pure styrene monomer and was used as a control. The remaining tubes contained solutions of 1, 5 and 10% by mass of 2,4,4,5,5-pentaphenyl-1,3,2-dioxaphospholane in styrene monomer, respectively. Tubes were placed in an oil bath maintained at 70°C. Progress of polymerization was followed by removing aliquots of the mixture as a function of time for viscosity measurement. The aliquots were diluted with benzene (1 g of mixture/100 mL of benzene). The relative viscosity was determined as a function of time to establish the extent of polymerization. The results are displayed in Table 1.

From both the viscosity data and the chromatographic data, it is apparent that thermal decomposition of 2,4,4,5,5-pentaphenyl-1,3,2-dioxaphospholane is effective in initiating styrene polymerization. In fact, when no phospholane was present in the monomer, no polymer was produced at 70°C. In the presence of phospholane, polymer is readily produced under the same conditions. Further, the molecular mass of the polymer formed decreases regularly, as expected, as the concentration of initiator (phospholane) is increased.

The polymerization was repeated at 100°C. Again, the polymer generated was examined using size exclusion chromatography. The results are collected in Table 3. In this case, the temperature was sufficient to promote self-initiation of styrene

Table 1 Relative viscosities of solutions of 2,4,4,5,5-pentaphenyl-1,3,2-dioxaphospholane in styrene monomer at 70°C as a function of time

Concentration of phospholane/mass%	Time/h at 70°C	t_0	t	$t–t_0$	η_r [$(t–t_0)/t_0$]
0	5	32	32	0	0.00
	10	32	33	1	0.03
	15	32	33	1	0.03
	20	32	34	2	0.06
	25	32	35	3	0.09
1	5	32	65	33	1.03
	10	32	90	58	1.81
	15	32	100	68	2.13
	20	32	120	88	2.75
	25	32	170	138	4.31
5	5	32	77	45	1.41
	10	32	122	90	2.81
	15	32	143	111	3.47
	20	32	156	124	3.88
	25	32	194	162	5.06
10	5	32	82	50	1.56
	10	32	134	102	3.19
	15	32	154	122	3.81
	20	32	166	134	4.19
	25	32	206	174	5.44

Table 2 Size exclusion chromatographic characterization of poly(styrene) produced using 2,4,4,5,5-pentaphenyl-1,3,2-dioxaphospholane as initiator at 70°C

Initiator present/ mass%	M_n	M_w	Polydispersity
0	N[1]	N[1]	N[1]
1	180000	365400	2.03
5	120000	302400	2.52
10	90000	273600	3.04

N[1] – no polymer formed.

Table 3 Size exclusion chromatographic characterization of poly(styrene) produced using 2,4,4,5,5-pentaphenyl-1,3,2-dioxaphospholane as initiator at 100°C

Initiator present/ mass%	M_n	M_w	Polydispersity
0	266000	848540	3.19
1	77500	233275	3.01
5	36000	85680	2.38
10	25000	46750	1.87

polymerization and high molecular mass polymer was formed in the absence of initiator. The molecular mass of the polymer formed in the presence of phospholane was much smaller and decreased regularly with an increasing level of phospholane present in the polymerization medium.

It may also be noted that the molecular mass of polymer produced from phospholane initiation at 100°C is significantly smaller than that of polymer produced at 70°C. Again, this is as expected.

At 100°C the initiator undergoes decomposition more rapidly than at 70°C. More propagating chains are initiated as a function of time. Therefore, monomer is consumed more rapidly and the ultimate polymer molecular mass is smaller. Analysis of both sets of polymers by both infrared and phosphorus-31 NMR spectroscopy indicated that phosphorus units were incorporated into the polymer mainchain at a much higher level than can be accounted for by initiation, i.e., the phosphorus moiety probably functions as both initiator and comonomer.

Thermal properties of styrene polymers containing phosphorus units

The thermal stability of the styrene polymers generated using 1, 5 and 10 mass% 2,4,4,5,5-pentaphenyl-1,3,2-dioxaphospholane as initiator was examined using thermogravimetry. The curve for the decomposition of the polymer produced using one mass% phospholane as initiator is shown in Fig. 4.

This polymer undergoes major decomposition at 443.0°C. In contrast, poly(styrene) undergoes decomposition in a single step with degradation onset at 418.6°C. The decomposition data for the polymers produced in the presence of 1, 5 and 10 mass phospholane are collected in Table 4.

From these results, it would appear that the thermal stability of the polymers containing a phospholane unit is similar to that of poly(styrene), i.e., incorporation of the phospholane into the polymer mainchain does not diminish the thermal stability of poly(styrene).

Table 4 Comparison of the extrapolated onset and maximum decomposition rate temperature of styrene polymers produced in the presence of 1, 5, 10% 2,4,4,5,5-pentaphenyl-1,3,2-dioxaphospholane at 70°C

Phospholane in polymerization mixture/ mass%	Extrapolated onset temperature for decomposition/°C	Maximum decomposition rate temperature/°C
0	418.1	438.9
1	424.2	443.0
5	429.3	448.3
10	433.2	454.1

Table 5 Flammability behavior of styrene polymers generated by initiation with 2,4,4,5,5-pentaphenyl-1,3,2-dioxaphospholane at 70°C

Observation	Level of phospholane in polymerization mixture/mass/mass%			
	0	1	5	10
Total flaming combustion for each specimen	30s	30s	30s	30s
Total flaming combustion for all 5 specimens of any set	250s	250s	250s	80s
Flaming and glowing combustion for each specimen after second burner	60s	60s	60s	60s
Cotton ignited by flaming drips from any specimen	YES	YES	YES	NO
Glowing or flaming combustion of any specimen to holding clamp	YES	YES	NO	NO
Classification			94V-1	<94V-1

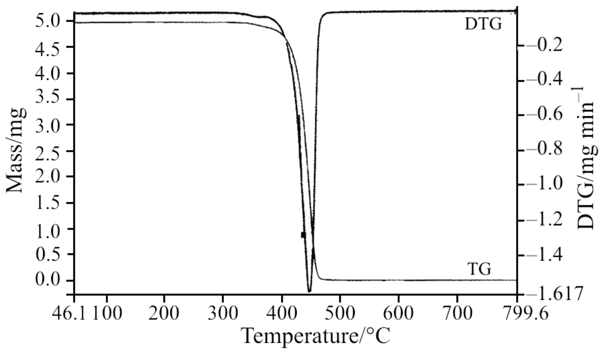


Fig. 4 TG/DTG curves for the degradation of the styrene copolymer produced using 1 mass% 2,4,4,5,5-pentaphenyl-1,3,2-dioxaphospholane as initiator at 70°C

Evaluation of flammability

The flammability of these polymers was evaluated using the UL-94 vertical burn test. In this test a 3.2 mm×12.7 mm×127 mm specimen is held at one end in a vertical position. A burner flame is applied in a vertical direction to the free end of the specimen for two 10-s intervals separated by the time it takes for flaming combustion to cease after the first application. For this test not only the rate at which the flame of the burning polymer is extinguished but also whether or not flaming drips are formed is considered. If flaming drips capable of igniting a cotton sample placed under the test plaque are formed, the effectiveness of the flame retardant is lower than if this is not the case. Of the samples examined here only that containing no additive formed flaming drips. None of those containing flame retardant, even at a three-percent level, formed flaming drips. The presence of any of the flame retardants had a positive effect on the flammability of the polymer. For the UL-94 test, results are presented as a series of designations reflecting the effectiveness of the flame retarding additive.

- V-2: burning stops within 60 s after two applications of 10 s each of a flame to a test bar. Flaming drips ARE allowed.
- V-1: burning stops within 60 s after two applications of ten seconds each of a flame to a test bar. NO flaming drips are allowed.
- V-0: burning stops within 10 s after two applications of ten seconds each of a flame to a test bar. NO flaming drips are allowed.

A V-0 designation is the most desirable and is indicative of effective flame retardation.

The results of the flammability testing are collected in Table 5.

The results presented in Table 5 suggest that, at the level of incorporation, the phospholane imparts a modest flame retardancy to poly(styrene).

Conclusions

2,4,4,5,5-Pentaphenyl-1,3,2-dioxaphospholane undergoes thermally-stimulated homolysis of a carbon–carbon bond at 70°C to generate a diradical which efficiently initiates styrene polymerization. Polymers produced from initiation in this manner contain phosphorus in the mainchain. As assessed by thermogravimetry these polymers display thermal stability comparable to that of conventional poly(styrene), i.e., incorporation of phosphorus moieties into the polymer mainchain does not diminish the thermal stability of the polymer. The presence of phosphorus in the polymer leads to a decreased flammability.

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