HEAT RESISTANT POLYMERS OF OXIDIZED STYRYLPHOSPHINE

Inventors: James C. Fletcher, Administrator of the National Aeronautics and Space Administration, with respect to an invention of Kazimiera Jola Lilianna Paciorek, Corona Del Mar, Calif.

Homopolymers, copolymers and terpolymers of a styrene based monomer are prepared by:

(1) polymerizing at least one oxidized styrylphosphine monomer selected from the group of:

- \((\text{C}_6\text{H}_5\text{O})_2\text{P(O)}\text{N}=\text{P}((\text{C}_6\text{H}_5)_2\text{C}_6\text{H}_4\text{CH}==\text{CH}_2)
- \((\text{C}_6\text{H}_5\text{O})_2\text{P(O)}\text{N}=\text{P}((\text{C}_6\text{H}_5)_2\text{C}_6\text{H}_4\text{CH}==\text{CH}_2)\text{C}_6\text{H}_4\text{CH}==\text{CH}_2)
- \((\text{C}_6\text{H}_5\text{O})_2\text{P(O)}\text{N}=\text{P}((\text{C}_6\text{H}_5)_2\text{C}_6\text{H}_4\text{CH}==\text{CH}_2)\text{C}_6\text{H}_4\text{CH}==\text{CH}_2)\text{C}_6\text{H}_4\text{CH}==\text{CH}_2)

or

(2) polymerizing p-diphenylphosphinestyrene and then oxidizing said polymerized p-diphenylphosphinestyrene monomer with an organoazide selected from the group and

\(-\text{C}_6\text{H}_5\text{N}3\text{N}=\text{P}((\text{C}_6\text{H}_5)_2\text{C}_6\text{H}_4\text{CH}==\text{CH}_2)\text{C}_6\text{H}_4\text{CH}==\text{CH}_2\) and

Copolymers can also be prepared by copolymerizing styrene with at least one oxidized styrylphosphine monomer selected from the group of:

- \((\text{C}_6\text{H}_5\text{O})_2\text{P(O)}\text{N}=\text{P}((\text{C}_6\text{H}_5)_2\text{C}_6\text{H}_4\text{CH}==\text{CH}_2)\text{C}_6\text{H}_4\text{CH}==\text{CH}_2)
- \((\text{C}_6\text{H}_5\text{O})_2\text{P(O)}\text{N}=\text{P}((\text{C}_6\text{H}_5)_2\text{C}_6\text{H}_4\text{CH}==\text{CH}_2)\text{C}_6\text{H}_4\text{CH}==\text{CH}_2)\text{C}_6\text{H}_4\text{CH}==\text{CH}_2)
- \((\text{C}_6\text{H}_5\text{O})_2\text{P(O)}\text{N}=\text{P}((\text{C}_6\text{H}_5)_2\text{C}_6\text{H}_4\text{CH}==\text{CH}_2)\text{C}_6\text{H}_4\text{CH}==\text{CH}_2)\text{C}_6\text{H}_4\text{CH}==\text{CH}_2)\text{C}_6\text{H}_4\text{CH}==\text{CH}_2)

7 Claims, No Drawings

References Cited

U.S. PATENT DOCUMENTS

3,235,536 2/1966 Garner ........................................ 526/13
3,542,752 11/1970 Hoffman ................................... 526/50
3,674,767 7/1972 Lilly et al. .................................. 526/50
3,702,833 11/1972 Rose et al. ................................. 260/2 P
3,708,462 1/1973 McKinley et al. ............................ 526/13
3,826,788 7/1974 Froehlich et al. .......................... 526/50
3,828,024 8/1974 Breslow ..................................... 526/50
3,948,820 4/1976 Reynard et al. ................................ 526/276
HEAT RESISTANT POLYMERS OF OXIDIZED STYRYLPHOSPHINE

ORIGIN OF THE INVENTION

The invention described herein was made in the performance of work under a NASA contract and subject to the provisions of Section 305 of the National Aeronautics and Space Act of 1958, Public Law 85-568 (72 stat 435; 42 USC 2457).

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to flame-resistant, nontoxic vinyl polymers which contain phosphazene groups. The polymers of the present invention do not emit any toxic or corrosive products when they are oxidatively degraded.

2. Description of the Prior Art

Presently, there are available a number of flame resistant materials and materials combinations. The vast majority of these, however, produce unacceptable large amounts of toxic and corrosive substances when subjected to oxidative thermal decomposition even in the absence of a flame. The toxic product formation is as great a hazard as a fire itself in any confined location and is particularly dangerous in space capsules, aircraft, or submarines, where egress or ventilation cannot be readily accomplished. The applicability of the few polymeric compositions which are flame resistant and do not form toxic degradation products, on the other hand, is limited because of cost, often poor processibility, and the fact that they do not lend themselves to modifications to improve deficiencies in physical or mechanical characteristics. These materials are based on highly condensed aromatic structures which during oxidative thermal decomposition form chars in high yields, and thus, release combustible decomposition products at too low a rate to support a flame.

All other flame resistant compositions derive this property from the presence of elements, which are known to act as flame retardants. These are elements of the third, fifth, and seventh main groups of the periodic table, specifically boron, nitrogen, phosphorus, antimony, and the halogens. Of these, only nitrogen, phosphorus, and the halogens are directly bonded in or to the polymer backbone. Boron and antimony normally are physically admixed with the flame resistant compositions, the former usually as a salt of boric acid, the latter either as its oxide or oxychloride. Yet internal bonding is preferable to admixture since additives are subject to removal by physical and chemical processes such as abrasion and washing.

The halogenated flame resistant materials such as polytetrafluoroethylene, copolymers of perfluoropropane and vinylidene fluoride, or polyvinylchloride contain the flame retardant bonded to the polymer backbone. Some of these materials exhibit very good flame resistance and have other desirable characteristics such as good mechanical properties and good processibility. However, these materials upon oxidative thermal decomposition produce copious quantities of highly toxic and corrosive gases. Moreover, the thermal decomposition process can take place long before flame temperatures are reached. Polyvinylchloride, for example, was found to lose practically all of the chlorine present (56.7%) in the form of toxic and corrosive hydrogen chloride at about 280° C leaving a residue which was combusted by excess air in a strongly exothermic reaction (Boettner et al.; Organic Coatings and Plastics Chemistry, Preprints, 28, No. 1, 311, April 1968). Polytetrafluoroethylene (Teflon), when exposed to elevated temperature in the presence of air, was shown by K. L. Paciorek et al, Final Report, Part I, Contract NASW-1921, August 1970; CR 114357 and K. L. Paciorek et al., Final Report, Part II, Contract NASW-1921, June 1971 to form carbonyl fluoride, which is hydrolyzed to toxic hydrogen fluoride and carbon dioxide, if water is also present. Fluorinated polymers, which also contain hydrogen, e.g., the copolymer of perfluoropropene and vinylidene fluoride (Viton, Fluorel) release hydrogen fluoride directly if not judiciously compounded. One of the reasons for this behavior is that halogens can be present in a polymer only as singly bonded moieties, and consequently cannot be incorporated into the normally more stable polymer backbone. Accordingly, the fire retarding element can be removed from the material by such simple reactions as dehydrohalogenation. This type of action is unlikely to occur in the case of an element which is either multiply bonded in the backbone or which is a part of an aromatic structure, thus capable of charring without volatilization upon exposure to a flame or elevated temperatures.

The remaining two of the above enumerated elements known to act as flame retardants are nitrogen and phosphorus, both of which are multivalent, thus can be incorporated in a polymer backbone, and are capable of multibonding. The flame retarding capability of triazine type compounds, and especially of phosphorus-nitrogen combinations, has been amply documented. U.S. Pat. No. 2,514,268 (1950); Brit. Pat. No. 638,434 (1950); R. C. Nometz, Ind. Engin. Chem., 59, 99 (1967); G. C. Tesoro et al, 155th ACS Meeting, Organic Coatings and Plastics Chemistry, Preprints, 28, No. 1, 243, April 1968; H. R. Alliceock, C&EN, Apr. 22, 1968, 68-81, and C. E. Miles et al, 155th ACS Meeting, Organic Coatings and Plastics Chemistry, Preprints, 28, No. 1, 237, Apr. 1968. The exact nature of their action as flame retardants either alone or in combination is not known. Either one of the elements would be expected to interfere in the free radical chain reactions propagating the flames. More importantly, however, both are known to form strong chars and accordingly do not contribute fuel to the flame. Such chars, in addition, insulate thermally the lower layers of the polymers thus inhibiting pyrolysis, and depress or prevent the access of oxygen to the subsurface. Phosphorus, when contained in an aromatic structure or when substituted by aromatic moieties such as phenyl groups, forms mechanically particularly strong chars, which have been shown to exhibit the above properties.

Flame-resistant polymers containing phosphazene repeating units in the polymer backbone are known, see for example U.S. Pat. Nos. 3,702,837, 3,888,799 and 3,896,058. However, these polymers lack the mechanical properties and good processibility possessed by vinyl polymers such as polystyrene. As a result, these polymers have a limited field of use.

Accordingly, there exists a need for flame resistant polymers whose degradation products are both nontoxic and non-corrosive which possesses mechanical and processing properties similar to those of known vinyl polymers.
SUMMARY OF THE INVENTION

It is an object of the present invention to provide a process for preparing flame-resistant homopolymers, copolymers and terpolymers. The process involves the preliminary polymerization of a monomer with at least one organoazide and subsequent oxidation of the oxidized monomer, and the second route involves the polymerization of at least one organoazide. The oxidized monomer of the present invention can be prepared by any convenient and acceptable technique. In one embodiment styrylphosphine can be prepared by synthesizing a reactive Grignard agent of chloroostyrene. The Grignard agent is then reacted with diphenyl halophosphine to complete the preparation. In another embodiment an active lithium intermediate can be prepared by reacting the chlorostyrene with an organo lithium compound such as butyllithium, and then reacting the reactant with diphenylhalophosphine.

The oxidized monomer of the present invention can be prepared by mixing stoichiometric quantities of organoazide and styrylphosphine in a solvent. Suitable solvents include dialkyl ethers such as diethyl ether, diisopropyl ether and the like; tetrahydrofuran, acetonitrile; aromatic hydrocarbons such as benzene, toluene and the like; and halohydrocarbons such as chloroform, methylenechloride and the like. The reaction temperature is not critical, but usually ranges from 0°C to ambient temperature depending on the activity of the azide. Slow reacting azides may require temperatures as high as refluxing temperatures. The reaction pressure also is not critical. During the course of the reaction, nitrogen is evolved as evidence of the destruction of the azido compound. The desired oxidized monomer can then be obtained by any suitable precipitation or solvent removal technique. In some instances oxidation of styrylphosphine monomer results directly in the formation of a homopolymer without the isolation of the oxidized monomer. Thus, when styrylphosphine is reacted with diphenylphosphinyl azide, a polymeric material of the formula:

$$\text{R} = \text{N} = \text{P(C_6H_5)_2(C_6H_3)_CH = CH_2}$$

wherein R is an organic moiety selected from the group of:

$$(C_6H_5)_2P(O)--, (C_6H_5)OP(O)--, (C_6H_5)NC_6H_4--,$$

mixtures thereof or by polymerizing a compound having the formula:

$$C_6H_5C_6H_4[N=\text{P(C_6H_3)(C_6H_5)CH=CH_2}]_2$$

or by reacting a polymer of the formula:

$$+\text{CH}--\text{CH}_2$$

with an organic azide selected from the group of:

$$(C_6H_5)_2P(ON)=, (C_6H_5)OP(ON)=, (C_6H_5)NC_6H_4(ON)=,$

$$(C_6H_5)_2C_6H_4(ON)=,$$

mixture thereof, and by polymerizing mixtures of the above azido oxidized styrylphosphine monomers and by polymerizing one or more of these monomers with a vinyl monomer such as styrene. Alternatively, the interpolymer can be prepared by first polymerizing diphenyl-p-styryl phosphate either alone or with another vinyl monomer to prepare a polymer. The resulting polymer is then reacted with an organo azide to introduce phosphazene groups into the resultant polymers.

The polymers of the present invention can be molded into shaped articles and films using conventional techniques.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The polymers of the present invention are vinyl based polymers characterized by containing pendant radicals containing phosphazene groups. The polymers can be prepared by two techniques in which the first route involves the polymerization of at least one organoazide oxidized styrylphosphine monomer, and the second route involves the preliminary polymerization of styrylphosphine monomer and subsequent oxidation of the pendant phosphine moieties in the polymer with at least one organoazide. In the context of the present invention the term styrylpolymer monomer not only includes the ortho, meta and para isomers of styryldiphenylphosphine, but also includes other vinylaromatic diphenyl phosphines such as vinylanthryldiphenylphosphine. Furthermore, each aromatic residue in the monomer can be substituted by one or more substituents such as alkyl, preferably lower alkyl of one to six carbon atoms, nitro, halo such as carbon, bromo and iodo, and the like.

In the first route, the appropriate monomer(s) is prepared by oxidatively reacting a styrylphosphine compound with an organoazide. The type of organoazide selected for the reaction is not critical. Suitable organoazides include diphenylphosphinyl azide, (C_6H_5)_{2}P(ON)=; diphenylphosphoryl-azide, (C_6H_5)_{2}P(ON)_{2}; diphenylphosphoryl-azide, (C_6H_5)_{2}P(ON)_{3}; dibenzylphosphinyl azide, (C_6H_5)C_6H_4N_3; 2,4-diazido-6-phenyl-s-triazine, (C_6H_5)C_6H_3N_2(N_3); trimethylsilylazide, triphenylsilylazide and phenylazide. The reaction of the styrylphosphine with the organoazide results in the oxidation of the trivalent phosphorus atom to the pentavalent state in the form of an unsaturated P= =N linkage known as a phosphazene group.

The basic styrylphosphine monomer of the present invention can be prepared by any convenient and acceptable technique. In one embodiment styrylphosphine can be prepared by synthesizing a reactive Grignard agent of chloroostyrene. The Grignard agent is then reacted with diphenyl halophosphine to complete the preparation. In another embodiment an active lithium intermediate can be prepared by reacting the chlorostyrene with an organo lithium compound such as butyllithium, and then reacting the reactant with diphenylhalophosphine.

The oxidized monomer of the present invention can be prepared by mixing stoichiometric quantities of organoazide and styrylphosphine in a solvent. Suitable solvents include dialkyl ethers such as diethyl ether, diisopropyl ether and the like; tetrahydrofuran, acetonitrile; aromatic hydrocarbons such as benzene, toluene and the like; and halohydrocarbons such as chloroform, methylenechloride and the like. The reaction temperature is not critical, but usually ranges from 0°C to ambient temperature depending on the activity of the azide. Slow reacting azides may require temperatures as high as refluxing temperatures. The reaction pressure also is not critical. During the course of the reaction, nitrogen is evolved as evidence of the destruction of the azido compound. The desired oxidized monomer can then be obtained by any suitable precipitation or solvent removal technique. In some instances oxidation of styrylphosphine monomer results directly in the formation of a homopolymer without the isolation of the oxidized monomer. Thus, when styrylphosphine is reacted with diphenylphosphinyl azide, a polymeric material of the formula:

$$+\text{CH}--\text{CH}_2$$

is obtained, and the oxidized monomer,

$$(C_6H_5)_2P(ON)=P(C_6H_3)C_6H_4$$

is not isolated. Diphenylphosphoryl azide when reacted with styrylphosphine also results in the formation of some polymer material, however, not to the extent obtained with diphenylphosphinylazide. Reaction of styrylphosphine with the other oxidizing agents does not result in the formation of polymer. Only the desired oxidized monomer is obtained. It thus appears that there is a relationship between the ease or rate of oxidation of styrylphosphine by an azide and the ability of the azide to function as a polymerization catalyst. The triazene azides, which promote the oxidation reaction very...
phosphine so that it undergoes polymerization. It may be that during oxidation a transition state exists which activates the double bond of styrylphosphine so that it undergoes polymerization.

The polymerization reaction of the invention as it relates either to the polymerization of an oxidized styrylphosphine monomer or to the polymerization of styrylphosphine monomer which is later oxidized with at least one organozinc, can be conducted by bulk polymerization techniques. An alternative technique can be the homopolymerization or copolymerization of the styrylphosphine monomer in an organic solvent such as benzene or toluene, with a radical initiator such as 2,2'-azobis-(2-methylpropionitrile). This reaction is usually conducted under an inert atmosphere of nitrogen argon or the like at 50°-100° C for 4-200 hours. In conducting the bulk polymerization of either the oxidized or unoxidized styrylphosphine monomer, it is necessary to achieve a polymer product having as high a molecular weight as possible in order to obtain a polymeric material having satisfactory molding and film forming characteristics as well as a satisfactory melting or softening range. While the molecular weight can widely vary the molecular weights of the polystyrylphosphine usually ranges from 10,000 to 100,000. These values, as determined with an osmometer, are number average molecular weights. Any convenient method can be used for the bulk polymerization of both oxidized and unoxidized styrylphosphine monomer. In one embodiment of the bulk polymerization process, a desired quantity of a monomer or desired quantities of more than one monomer are sealed in an enclosed reactor and heated to 60° C to 250° C, preferably 60° C to 250° C to effect polymerization. If necessary, a radical initiator such as 2,2'-azobis-(2-methylpropionitrile) can be used either with or without the presence of an organic solvent. The reaction is normally conducted from }_{\frac{1}{2}} to 288 hours, preferably 0.5 to 24 hours. In many instances, longer reaction times can be used at lower temperatures in the indicated range. Once the reaction is complete, the reaction residue is treated with an appropriate solvent to remove soluble polymer products therefrom. Suitable solvents for the extraction include halohydrocarbons such as chloroform and the like. The precipitated polymer is then isolated by any convenient technique such as filtration and then dried.

In any embodiment of the bulk polymerization procedure, a desired quantity of a monomer or desired quantities of more than one monomer are placed in an evacuated reactor. After evacuation of the reactor, usually a glass ampoule, to a suitable pressure of about 10^{-2} mm, the ampoule is then heated to 60° C to 250° C, preferably 150° C to 230° C to effect polymerization over a time period of }_{\frac{1}{2}} to 288 hours, preferably 0.5 to 24 hours. Instead of conducting the reaction under a vacuum the reaction can be conducted under an inert atmosphere such as nitrogen, or the like. After the reaction is complete, the desired polymer product can be isolated as described supra.

By the use of a suitable bulk polymerization procedure, an oxidized styrylphosphine monomer such as

\[ (C_8H_5)C_3N_3[\equiv P(C_6H_5)C_6H_4CH\equiv CH_2] \]

can be polymerized to yield homopolymers having a molecular weight range of 10,000 to 100,000. The polymerization reactions for the homopolymers can be conducted at a temperature ranging from 130° C to 230° C. For the homopolymerization of \((C_8H_5)O=P(C_6H_5)CH_2CH=CH_2\), the polymerization temperature preferably ranges from 150° C to 160° C. If the polymerization temperature is elevated to about 230° C, cross-linking of the polymer product obtained occurs. Polymeric material having a molecular weight range of 50,000 to greater than 100,000 can be obtained. The homopolymer is oxidatively stable up to temperatures of about 275° C. For the homopolymerization of \((C_8H_5)C_3N_3[\equiv P(C_6H_5)C_6H_4CH\equiv CH_2]\), the polymerization temperature preferably ranges from 130° C to 160° C and always provides a cross-linked material because of the difunctionality of the monomer. If the reaction is conducted at a temperature of about 160° C, the resulting product is mostly chloroform insoluble indicating a highly cross-linked polymer product. The polymer product obtained, when heated, starts to thermally decompose at about 300° C. However, the char yield upon decomposition stabilizes at 41% at about 550° C, and does not seem to decrease further at temperatures up to 610° C.

Copolymeric materials can be prepared by reacting two of the oxidized styrylphosphine monomers of the present invention in any suitable bulk polymerization procedure at a temperature ranging from 150° C to 235° C for 0.5 to 5.0 hours at mole ratios ranging from 1:1 to 1:10. Included within the scope of the copolymerization reaction are both styrylphosphine monomer and styrene. From analysis of the soluble fractions of the polymers, the molecular weight ranges from 15,000 to 34,000.

In one embodiment of the copolymerization aspect of the invention diphenyl-p-styrylphosphine can be bulk polymerized with

\[ (C_8H_5)C_3N_3[\equiv P(C_6H_5)C_6H_4CH\equiv CH_2] \]

in any suitable relative amounts to produce a copolymer of good thermal stability. Usually, however, equimolar quantities of reacting monomers are used. In another embodiment of the copolymerization procedure appropriate quantities of

\[ (C_8H_5)C_3N_3[\equiv P(C_6H_5)C_6H_4CH\equiv CH_2] \]

can be reacted with

\[ (C_8H_5)C_3N_3[\equiv P(C_6H_5)C_6H_4CH\equiv CH_2] \]

usually in a mole ratio of 1:20, to form a polymeric residue containing both chloroform soluble and insoluble polymers. Both insoluble and soluble portions of the copolymer can be used in the preparation of molded articles.

Terpolymeric polymeric materials can also be prepared by coreacting three oxidized styrylphosphine monomers by any suitable bulk polymerization procedure at a temperature ranging from 165° C to 230° C. The reacting monomers can be polymerized in any appropriate quantities. However, when the difunctional monomer \((C_8H_5)C_3N_3[\equiv P(C_6H_5)C_6H_4CH\equiv CH_2]\), is used as a reactant, it should not be used in proportional amounts greater than 10 mole %, i.e., no greater than a ratio of 1:10 relative to the other monomers. Difunc-
tional monomer containing polymers can be molded into transparent discs at 350° F and a pressure of about 750 lbs. Since the polymer product obtained when the difunctional monomer is used as a reactant, is solvent insoluble, molecular weights can not be determined. However, the minimum molecular weight is believed to be about 20,000. In a preferred embodiment of the present invention terpolymer can be prepared by reacting 50 to 90 mole % of

\[ (C_6H_5)PO(N=P(C_6H_4)CH=CH_2), \]

...should be also amenable to fabrication of useful articles; however, this type of material would be expected to undergo oxidation to the oxide

\[ (C_6H_5)PO(N=P(C_6H_4)CH=CH_2), \]

Copolymers can be prepared by reacting the preformed polystyrylphosphine with two organoazides in appropriate quantities in much the same manner polystyrylphosphine is reacted with only one organoazide. When two organoazides are reacted with the preformed polystyrylphosphine, they can be reacted in any relative amounts either simultaneously or consecutively. Thus, in a preferred embodiment of this aspect of the invention, from 50 to 90 mole percent of

\[ (C_6H_5)PO(N=NP((C_6H_4)CH=CH_2), \]

In a manner similar to that used above for the preparation of copolymers, terpolymers can be prepared by reacting the desired amounts of three organoazides with a unit amount of polystyrylphosphine. In the terpolymers if monofunctional azides are employed, these can be used in equal mole percent or any other percentages depending on the desired properties of the final polymer. All of the three azides can be added simultaneously. However, if a difunctional azide is employed to yield a crosslinked product, it has to be added after the monoazides have reacted to avoid intramolecular reactions, i.e., joining of adjacent sites on the same polymer chain. An especially useful terpolymer which is amenable to molding and film casting and which has high molecular weight is high melting and yet soluble, can be prepared as follows:

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In a manner similar to that used above for the preparation of copolymers, terpolymers can be prepared by reacting the desired amounts of three organoazides with a unit amount of polystyrylphosphine. In the terpolymers if monofunctional azides are employed, these can be used in equal mole percent or any other percentages depending on the desired properties of the final polymer. All of the three azides can be added simultaneously. However, if a difunctional azide is employed to yield a crosslinked product, it has to be added after the monoazides have reacted to avoid intramolecular reactions, i.e., joining of adjacent sites on the same polymer chain. An especially useful terpolymer which is amenable to molding and film casting and which has high molecular weight is high melting and yet soluble, can be prepared as follows:
(The above reaction sequence is not to be interpreted as meaning that block copolymers are formed by this procedure.)

In another aspect of the invention phosphazene group containing styryl polymers can be obtained by copolymerizing styrene with the reactive monomer(s) in either of the polymerization procedures of the invention. Other suitable comonomers include those which are amenable to copolymerization with styrene such as butadiene. Thus, when an oxidized styrylphosphine monomer or more than one oxidized styrylphosphine monomer is reacted with styrene, from 20 to 95 mole % of styrene can be reacted with 80 to 5 mole % of oxidized styrylphosphine monomer(s). In the situations where the object polymers are prepared by oxidizing the pendant phosphine groups of preformed styrylphosphine polymers, from 20 to 95 mole % of styrene can be reacted with from 80 to 5 mole % of styrylphosphine monomer. Preferred embodiments of copolymers derived from the polymerization of styrene with an oxidized styrylphosphine monomer include a copolymer having the formula:

\[ \text{X: } 50-10 \text{ mole percent and } y: 50-90 \text{ mole percent; and a copolymer of the formula:} \]

\[ \text{X: } 50-10 \text{ mole percent and } y: 50-90 \text{ mole percent.} \]

According to thermal gravimetric analysis data, the homopolymers, copolymers and terpolymers of the invention are thermally stable. Some of the homopolymers appear to be thermally stable up to 350 °C. In fact, under conditions which cause polystyrene to explode, i.e. a temperature of 540 °C under a dynamic flow of oxygen preheated to 540 °C, a Nomex cloth impregnated with 32% of \( (\text{C}_6\text{H}_5)Z \) gave an 86% residue.

The melting points of all solid monomers were determined in nitrogen filled sealed melting point capillaries, softening and melting points of the polymers were obtained using a Fisher-Johns apparatus.

**EXAMPLE 1**

**PREPARATION OF 2-CHLORO-4-DIPHENYL-TRIAZINE**

The procedure used was based on the method of Jones et al, AD 229453, Sept. 1959. A stirred mixture of magnesium turnings (24.3 g, 0.935 mol) and a crystal of iodine in ether (150 ml), was added a solution of bromobenzene (155.3 g, 0.985 mol) in ether (100 ml) under a nitrogen atmosphere over a period of 3.75 hr at such a rate as to maintain a gentle reflux. Thereafter, the mixture was refluxed for 2.5 hr. The Grignard reagent thus prepared was then cooled and transferred to an addition funnel and added with stirring to a solution of cyanuric chloride (70 g, 0.38 mol) in benzene (500 ml) at 4°-15° C and possess higher char yields than styrene. The polymeric materials of the present invention can be used in the manufacture of components of systems such as space crafts, air crafts, and the like from which egress in the presence of fire is difficult or impossible. In addition co- and terpolymers obtained by copolymerization of the styrylphosphine oxidized monomer with other conventional monomers can be employed for the same applications, mainly as structural materials, where styrene copolymers are used with the advantage that the presence of the chemically bonded phosphorus will render these materials more flame resistant than is the case usually with styrene based compositions.

Having generally described this invention, a further understanding can be obtained by reference to certain specific examples which are provided herein for purposes of illustration only and are not intended to be limiting unless otherwise specified.

**I. PREPARATION OF ORGANOAZIDE REACTANTS**

All solvents used were reagent grade and were dried and distilled prior to use. All operations involving moisture or air sensitive materials were carried out either in an inert atmosphere enclosure (Vacuum Atmospheres Model HE-93B), under nitrogen by-pass, or in sealed ampoules. The commercially available starting materials were usually purified by distillation, crystallization, or other appropriate means. All molecular weights were determined using a Mechrolab Osmometer Model 302.

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**EXAMPLE 1**

**PREPARATION OF 2-CHLORO-4-DIPHENYL-TRIAZINE**

The procedure used was based on the method of Jones et al, AD 229453, Sept. 1959. A stirred mixture of magnesium turnings (24.3 g, 0.935 mol) and a crystal of iodine in ether (150 ml), was added a solution of bromobenzene (155.3 g, 0.985 mol) in ether (100 ml) under a nitrogen atmosphere over a period of 3.75 hr at such a rate as to maintain a gentle reflux. Thereafter, the mixture was refluxed for 2.5 hr. The Grignard reagent thus prepared was then cooled and transferred to an addition funnel and added with stirring to a solution of cyanuric chloride (70 g, 0.38 mol) in benzene (500 ml) at 4°-15° C and possess higher char yields than styrene. The polymeric materials of the present invention can be used in the manufacture of components of systems such as space crafts, air crafts, and the like from which egress in the presence of fire is difficult or impossible. In addition co- and terpolymers obtained by copolymerization of the styrylphosphine oxidized monomer with other conventional monomers can be employed for the same applications, mainly as structural materials, where styrene copolymers are used with the advantage that the presence of the chemically bonded phosphorus will render these materials more flame resistant than is the case usually with styrene based compositions.

Having generally described this invention, a further understanding can be obtained by reference to certain specific examples which are provided herein for purposes of illustration only and are not intended to be limiting unless otherwise specified.
PREPARATION OF 2-AZIDO-4,6-DIPHENYL-S-TRIAZINE

A suspension of 2-chloro-4,6-diphenyl-s-triazine (30 g, 0.112 mol), sodium azide (12.86 g, 0.199 mol) and lithium azide (1.24 g, 0.025 mol) in acetonitrile (550 ml) was stirred at room temperature for 11 days. After filtration, the filtrate on evaporation yielded 6.9 g (88% yield). The melting point and infrared spectrum were identical with that of an authentic sample.

PREPARATION OF 2,4-DICHLORO-6-PHENYL-S-TRIAZINE

This compound was prepared via a two-step reaction using a combination of two literature procedures. A mixture of 2,4-diamino-6-phenyl-s-triazine (150 g, 0.802 mol) and 90% sulfuric acid (600 ml) was heated with stirring in an oil bath maintained at 105°-116° C bringing the total yield of 2-azido-4,6-diphenyl-s-triazine to 26.9 g (88% yield). The melting point and infrared spectrum were identical with that of an authentic sample.

PREPARATION OF TRIMETHYLSILYL AZIDE

2-Chloro-4,6-diphenyl-s-triazine was fractioned over a short Vigreaux column, the fraction with bP 128.2°-131° C. Crystallization from heptane gave 12.2 g of 2,4-diazido-6-phenyl-s-triazine, mp 130°-132° C. Total yield of 2,4-diazido-6-phenyl-s-triazine was 20.2 g (85.5% yield). The melting point and infrared spectrum were identical with that of the authentic sample.

PREPARATION OF DIPHENYLPHOSPHINYL CHLORIDE

Diphenylchlorophosphine (200 ml, 246 g, 1.12 mol) was heated with stirring at 100°C and through this solution was bubbled gaseous oxygen dried by passing through towers filled with phosphorus pentoxide and Drierite. This process was performed over a period of 31 hr. The crude product was distilled in vacuo through a short Vigreaux column, the fraction with bP 164°-168° C at 0.02 mm, 212 g (80.3% yield) exhibited an infrared spectrum identical to that of an authentic sample.

PREPARATION OF DIPHENYLPHOSPHINYL AZIDE

Following a previously [Paciorek et al., Inorg. Nucl. Chem. Letters, 2, 39 (1966)] developed procedure, diphenylphosphinyl chloride (14.87 g, 62.96mmol) was introduced into a tube (in the inert atmosphere enclosure). Trimethylsilyl azide (10.45 g, 90.69 mmol) was then condensed onto this material on a vacuum line at liquid nitrogen temperature. The tube was sealed in vacuo through a short Vigreaux column, the fraction with bP 164°-168° C at 0.02 mm, 221 g (80.3% yield), exhibited a quantitative yield of pure diphenylphosphinyl azide was realized.
EXAMPLE 8
PREPARATION OF TRIPHENYLSILYL AZIDE

Following the method of Wiberg et al [Wiberg et al, Angew. Chem. Internat'l Ed. Engl., 1, 355 (1962)] in an inert atmosphere enclosure a solution of triphenylsilyl chloride (73.9 g, 0.251 mol) in tetrahydrofuran (400 ml) was stirred with lithium azide (15.3 g, 0.312 mol) at room temperature over a period of 115 hr. After filtration, the solvent was removed in vacuo. The resulting white solid was boiled with heptane (350 ml), filtered hot and allowed to crystalline. Triphenylsilyl azide, 65.5 g (86.3% yield), mp 82°-84°C was obtained. The melting point and infrared spectrum were identical with that of an authentic sample.

EXAMPLE 9
PREPARATION OF DIPHENYL-P-STYRYLPHOSPHINE

In a 500 ml round bottom flask equipped with stirrer, reflux condenser, thermometer, and nitrogen by-pass were placed 17.74 g (0.741 mol) of magnesium turnings for 1.5 hr at room temperature before being transferred into a dropping funnel inside an inert atmosphere enclosure. To this were added 2.7 ml portions of tetrahydrofuran (a polymerization inhibitor) in tetrahydrofuran (20 ml) over a period of 3 hr, immediate evolution of gas was observed. The solution was then stirred at room temperature for 120 hr. Thereafter, the solvent was removed in vacuo; crystalization from benzene-heptane gave 14.35 g of product (77.3% yield), mp 150°-152°C. Anal. calcd for C32H27PzN03: C, 71.77%; H, 5.08%; P, 11.57%; N, 2.62%; 0, 8.96%; MW 535.53 Found: C, 71.93; H, 5.35; P, 11.51; N, 2.60, MW 569.

ATTEMPTED PREPARATION OF DIPHENYL-P-STYRYLPHOSPHINE

To a stirred solution of diphenyl-p-styrylphosphine (10.0 g, 34.68 mmol) and 0.2g. of 4-t-butylpyrocatechol (a polymerization inhibitor) in tetrahydrofuran (100 ml) under an inert atmosphere was added diethylammonium azide (9.54 g, 34.66 mmol) (which was obtained from Willow Brook Labs., Inc., Waukesha, WI, and used as received) in tetrahydrofuran (100 ml) over a period of 3 hr, immediate evolution of gas was observed. The solution was then stirred at room temperature for 120 hr. Thereafter, the solvent was removed in vacuo; crystallization from benzene-heptane gave 14.35 g of product (77.3% yield), mp 150°-152°C. Anal. calcd for C2,H2,P2N=PGH,CH=CH2: C, 71.77%; H, 5.08%; P, 11.57%; N, 2.62%; O, 8.96%; MW 535.53 Found: C, 71.87; H, 5.35; P, 11.51; N, 2.60, MW 569.

III. BULK POLYMERIZATION OF OXIDIZED STYRYLPHOSPHINE MONOMER

EXAMPLES 12-22

Styrylphosphine monomer oxidized by diphenylphosphorylazide, 2,4-diazido-6-phenyl-s-triazine and 2-azido-4,6-diphenyl-s-triazine (Examples 12-16, 17-18 and 19-22 respectively) were bulk polymerized under the conditions described in Table I below. All of the polymerization reactions were conducted in evacuated ampoules (10⁻³ mmHg) in a vacuum line. After completion of each reaction, the residue in each ampoule was extracted with about 10 ml of chloroform, and the soluble polymer was precipitated by treatment of the chloroform solution with heptane, filtered and dried.

<table>
<thead>
<tr>
<th>Example No.</th>
<th>Monomer</th>
<th>Conditions</th>
<th>Polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>(Φ0)2P(ON)=PΦ0CH=CH2</td>
<td>0.41</td>
<td>230</td>
</tr>
<tr>
<td>13</td>
<td>(Φ0)2P(ON)=PΦ0CH=CH2</td>
<td>1.00</td>
<td>150</td>
</tr>
<tr>
<td>14</td>
<td>(Φ0)2P(ON)=PΦ0CH=C6H4OH</td>
<td>1.00</td>
<td>150</td>
</tr>
<tr>
<td>15</td>
<td>(Φ0)2P(ON)=PΦ0CH=CH2</td>
<td>1.50</td>
<td>150</td>
</tr>
<tr>
<td>16</td>
<td>(Φ0)2P(ON)=PΦ0CH=CH2</td>
<td>15.5</td>
<td>165</td>
</tr>
</tbody>
</table>

Table I

SUMMARY OF BULK POLYMERIZATIONS CONDUCTED ON PRE-OXIDIZED MONOMERS

<table>
<thead>
<tr>
<th>Example No.</th>
<th>Monomer</th>
<th>Conditions</th>
<th>Polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>(Φ0)2P(ON)=PΦ0CH=CH2</td>
<td>0.41</td>
<td>230</td>
</tr>
<tr>
<td>13</td>
<td>(Φ0)2P(ON)=PΦ0CH=CH2</td>
<td>1.00</td>
<td>150</td>
</tr>
<tr>
<td>14</td>
<td>(Φ0)2P(ON)=PΦ0CH=C6H4OH</td>
<td>1.00</td>
<td>150</td>
</tr>
<tr>
<td>15</td>
<td>(Φ0)2P(ON)=PΦ0CH=CH2</td>
<td>1.50</td>
<td>150</td>
</tr>
<tr>
<td>16</td>
<td>(Φ0)2P(ON)=PΦ0CH=CH2</td>
<td>15.5</td>
<td>165</td>
</tr>
</tbody>
</table>
The completion of each reaction was extracted with a vacuum line (Exs. below in the quantities shown. All polymerization reactions were conducted in evacuated ampoules either in sealed ampoules (Exs. 'Not determined.

The results in the Table above show that homopolymers of very good molecular weight characteristics were obtained from the styrylphosphine monomer oxidized with diphenylphosphorylazide. These homopolymers (Exs. 12-16) could readily be formed into molded articles and films

**EXAMPLES 23-28**

As shown in Table 2 below, a series of copolymers (Exs. 23-26) and terpolymers (Exs. 27-28) were prepared by the bulk polymerization of the oxidized monomers indicated under the conditions shown. All polymerization reactions were conducted in evacuated ampoules in the manner described for Examples 12-22. The soluble polymer in each example was isolated as 30% chloroform and isolated in the manner described for Examples 12-22.

**TABLE 2**

<table>
<thead>
<tr>
<th>Example No.</th>
<th>Monomer A</th>
<th>Amt</th>
<th>Monomer B</th>
<th>Amt</th>
<th>Monomer C</th>
<th>Amt</th>
<th>Mole Ratio A : B : C</th>
<th>Temp °C</th>
<th>Period h</th>
<th>Yield %</th>
<th>MP °C</th>
<th>MW</th>
<th>TGA Fig. No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>(SO₂)₃NO = P = P = CH = CH₂</td>
<td>2.00</td>
<td>(SO₂)₃NO = P = P = CH = CH₂</td>
<td>0.31</td>
<td>n.a.</td>
<td>0.75</td>
<td>230 0.75</td>
<td>69</td>
<td>140-165</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>(SO₂)₃NO = P = P = CH = CH₂</td>
<td>1.03</td>
<td>(SO₂)₃NO = P = P = CH = CH₂</td>
<td>2.00</td>
<td>n.a.</td>
<td>1.5</td>
<td>230 1.5</td>
<td>80</td>
<td>130-140</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>(SO₂)₃NO = P = P = CH = CH₂</td>
<td>2.07</td>
<td>(SO₂)₃NO = P = P = CH = CH₂</td>
<td>0.15</td>
<td>n.a.</td>
<td>2.0</td>
<td>230 2.0</td>
<td>81</td>
<td>125-146</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>(SO₂)₃NO = P = P = CH = CH₂</td>
<td>1.92</td>
<td>(SO₂)₃NO = P = P = CH = CH₂</td>
<td>1.23</td>
<td>n.a.</td>
<td>2.0</td>
<td>230 2.0</td>
<td>18000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>(SO₂)₃NO = P = P = CH = CH₂</td>
<td>2.24</td>
<td>(SO₂)₃NO = P = P = CH = CH₂</td>
<td>0.74</td>
<td>(SO₂)₃NO = P = P = CH = CH₂</td>
<td>0.53</td>
<td>230 0.5</td>
<td>77</td>
<td>16000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>(SO₂)₃NO = P = P = CH = CH₂</td>
<td>2.00</td>
<td>(SO₂)₃NO = P = P = CH = CH₂</td>
<td>0.17</td>
<td>n.a.</td>
<td>2.0</td>
<td>230 2.0</td>
<td>70</td>
<td>130-150</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**IV. BULK POLYMERIZATION OF DIPHENYL-p-STYRYLPHOSPHINE**

**EXAMPLES 29-43**

Diphenyl-p-styrylphosphine was polymerized by a bulk procedure under the conditions shown in Table 3 below in the quantities shown. All polymerization reactions were conducted in evacuated ampoules either in sealed ampoules (Exs. 29-34) or in ampoules attached to a vacuum line (Exs. 35-43). The polymeric material at the completion of each reaction was extracted with chloroform and isolated in the manner described for Examples 12-22.
V. PREPARATION OF PHOSPHAZENE GROUP CONTAINING POLYMERS BY OXIDATION OF PREFORMED POLYMERS OF STYRYLPHOSPHINE

The following procedures are representative of those employed for the synthesis of substituted ("oxidized") homopolymers and copolymers shown in Table 4. The styrylphosphine polymers prepared in Examples 29-43 were used in the oxidation reactions.

EXAMPLE 44

PREPARATION OF

\[
\left[ \text{C}_6\text{H}_4\text{O}_2\text{P(O)}\text{N=Ph-P(Ph)CH} = \text{CH}_2 \right]_{1.0 \times 10^3}
\]

To a stirred solution of polydiphenyl-p-styrylphosphine (2.00 g, 6.936 mmol) in tetrahydrofuran (40 ml) was added diphenylphosphoryl azide (1.91 g, 6.934 mmol) in tetrahydrofuran (40 ml) over a period of 1 hr under an inert atmosphere. Nitrogen gas evolution was observed immediately. The solution was then stirred overnight at room temperature. Subsequently, the polymer was precipitated from solution with heptane (250 ml), filtered and dried in vacuo for 7 hr at 103°C affording 3.31 g (89% yield) of product, mp 142°-166°C; MW > 50000.

EXAMPLE 45

PREPARATION OF

\[
\phi, \text{C}_6\text{N}=\text{PPh}_2\text{CH} = \text{CH}_2
\]

EXAMPLE 49

PREPARATION OF CANDIDATE TERPOLYMER

To polydiphenyl-p-styrylphosphine (2.00 g, 6.936 mmol) in tetrahydrofuran (20 ml) was added diphenylphosphoryl azide (1.527 g, 5.549 mmol) in tetrahydrofuran (20 ml) under an inert atmosphere. The resulting solution was stirred at room temperature for 5 days. Then to the solution was added 2-azido-4,6-diphenyl-s-triazine (190 mg, 0.694 mmol). After 2 hr this was followed by 2,4-diazido-G-phenyl-s-triazine (41.3 mg, 0.173 mmol). Subsequently, after stirring for 14 hr at room temperature, an additional quantity of 2-azido-4,6-diphenyl-s-triazine (95.0 mg, 0.347 mmol) was introduced. The resulting solution, following stirring at room temperature for 6 hr, was poured onto heptane (203 ml). The precipitated product was filtered and dried in vacuo at 90°-93°C for 9 hr giving 3.39 g (93% yield) of polymer, mp 153°-170°C; MW 91300.
<table>
<thead>
<tr>
<th>Example</th>
<th>Composition</th>
<th>MP °C</th>
<th>MW</th>
<th>No. Units</th>
<th>TGΔ FIG.</th>
<th>Starting Material</th>
<th>No. Units</th>
</tr>
</thead>
</table>
| 44      | \[[\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Phi\Ph
In the formation of the terpolymers (Exs. 46-52) not all of the 2-azido-4,6-diphenyl-s-triazine was added in the second step of the oxidation sequence. This is described in detail above for Example 49. The reason for this was to ensure that when the diazide oxidizing agent was added, that a sufficient number of sites remained to permit interchain linking to take place (scheme I); not intramolecular reaction (scheme II).

It can be readily determined from the data in Table 4 that terpolymers of very substantial molecular weight and good processing properties were obtained by oxidation of preformed polystyrylphosphine.

VI. TOXICOLOGICAL TESTING

The toxicological effects of the thermal degradation products of three representative styrylphosphine polymers of the present invention were tested. Samples of polymers of Examples 16, 26 and 45 were formed into 20-27 washers of 0.709 outside diameter with a center hole of inner diameter 0.25 and 0.08 average thickness. The amounts of materials submitted for testing varied between 9.25g and 13.10g. In the test, rats were subjected to thermal degradation products of each polymer material, and no mortalities were observed.

VII. MOLDING STUDIES

A number of polymeric compositions as shown in Table 6 below were compressed in a molding device in combination with a Carver Laboratory Press, Model C. All polymer samples in Table 6 below were ground in a mortar before being placed into the mold.

Having now fully described the invention, it will be apparent to one of ordinary skill in the art that many changes and modifications can be made there to without departing from the spirit or scope of the invention as set forth herein.

What is claimed as new and intended to be secured by Letters Patent is:

1. A process for treating homopolymers, copolymers and terpolymers of styrene based monomers, which comprises:
   - polymerizing or copolymerizing p-diphenylphosphinestyrene by bulk or solvent polymerization procedures; and
   - oxidizing said polymerized p-diphenylphosphinestyrene with at least one organoazide selected from the group consisting of (C₆H₅)₂P(0)N₃, (C₆H₅O)₂P(0)N₃, (C₆H₅)C₆N₃(N₃)₂ and (C₆H₅)₂C₆N₃(N₃).

2. The process of claim 1 wherein said p-diphenylphosphinestyrene is polymerized at a temperature of 100° to 230° C.
3. The process of claim 1, which comprises: reacting diphenylphosphoryl azide with polydiphenylstyrlylphosphine. 

4. A polymeric composition prepared by oxidizing said p-diphenylphosphinestyrene with any two of said organoazides as set forth in claim 1. 

5. The polymeric composition of claim 3, prepared by sequentially reacting 50 to 90 mole % of \((\text{C}_6\text{H}_5\text{O})_2\text{P(O)N}_2\) with a unit amount of polydiphenylstyrlylphosphine and then reacting 50 to 10 mole % of \((\text{C}_6\text{H}_5\text{)}_2\text{C}_2\text{N}_3\text{N}_3\) with the partially oxidized polydiphenylstyrlylphosphine. 

6. A polymeric composition prepared by oxidizing said p-diphenylphosphinestyrene with any three of said organoazides as set forth in claim 1. 

7. The polymeric composition of claim 6, which has the formula: 

\[
\text{CHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCHCH