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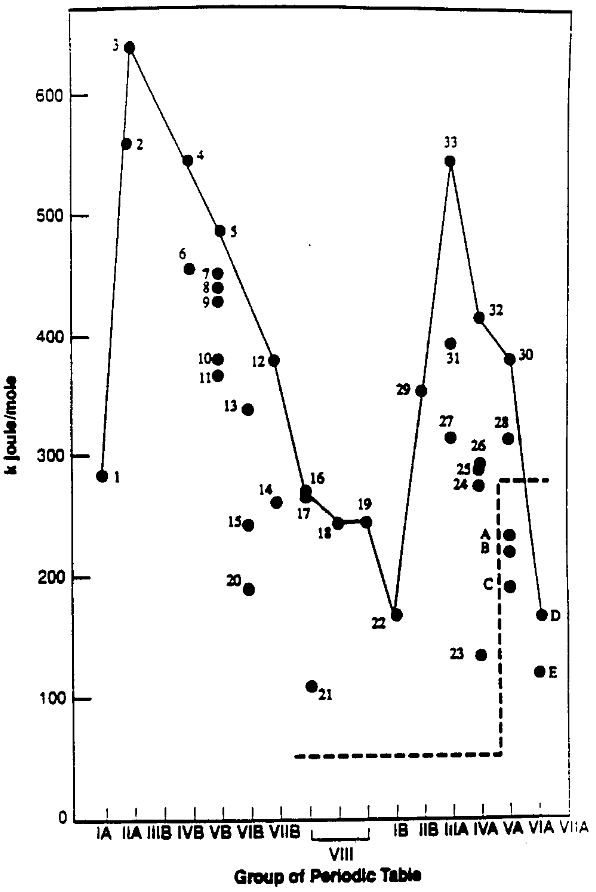
(54) Title: NUCLEATING SYSTEM FOR POLYESTERS AND ARTICLES FORMED THEREFROM

(57) Abstract

This invention relates to a composition comprising (a) at least one polyester and (b) one or more effective nucleating agents having a particle size which is about equal to or more than the lamellar thickness of the polyester, preferably the particle size is about 100 Å to about 500 Å.



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NUCLEATING SYSTEM FOR POLYESTERS AND ARTICLES FORMED THEREFROM

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to novel nucleating agents for polyesters and to polymer based compositions containing the nucleating agents as well as the articles of manufacture formed totally or in part from the polymer based composition of this invention. The invention also relates to a process for preparing the nucleated polymer materials.

2. Description of the Prior Art

The "super" or morphological structure in which the crystalline units are arranged, affects the physical properties of polymers. The crystalline units are arranged in polycrystalline aggregates known as spherulites. These spherulites may be detected by microscopic examination under polarized light. They are characterized by a more or less symmetrical growth in all directions from a nucleus and are composite structures made up of crystalline and amorphous regions. The number and size of the spherulites determines the texture or graininess in the bulk of the material and influences optical as well as physical properties. Physical properties improve with increasing homogeneity and fineness of the spherulitic structure throughout the bulk of the material.

To obtain optimum physical properties in articles fabricated from polymers, it is desirable, therefore, to produce a highly crystalline material, crystallized with an extremely fine, dense and uniform morphological structure.

Among the physical properties affected by increased crystallinity and improved morphological structure are abrasion resistance, heat distortion temperature, inherent stability or resistance to deformation, resistance to hot water, coefficient of expansion, hardness, tensile yield strength and surface hardness.

Nucleation by foreign materials has been extensively studied, especially in the case of polypropylene. For example, H.N. Beck or H.D. Led better, J. Appl. Polym. Sci. 9, 2131 (1965) and H.N. Beck, J. Appl Polym. Sci. 11,673 (1987) checked the nucleation activity of more than two hundred substances by determining the temperature, Tcc, at which the crystallization rate on cooling is the fastest. F.L. Binsbergen, Polymer, 11, 253 (1970) extended these studies in testing two thousand substances for nucleating activity in polyethylene, polypropylene, poly(4-methyl-1-pentene) and poly(styrene). Other working nucleating agents for polyolefin are described by J.P. Mercier, Polymer Engineering and Science, 30, 270 (1990), Wijga, P. W. O. US pat. 3,207,735; -6; -8(1960) Wijga, P. W. O. and Binsbergen, F. L. US Pat. 3,299,029(1961) Wales, M. US Pat. 3,207,737; -(1961-62) Binsbergen, F. L. US Pat. 3,326,880; 3,327,020; -1(1963) Kargin, V. A. et al, Dokl. Akad. Nauk. SSSR 1964, 156, 1156(transl.: Dokl. Phys. Chem. 1964, 156, 621, 644) Doring, C. and Schmidt, H. German Pat.(Federal Rep.) 1,188,279(1963) and Vonk, G.C. Kolloid Z. 1965, 206, 121.

The function of nucleating agents when cooling semi-crystalline polymers from the molten state into the solid form is to increase the number of nuclei formed in a given time interval at a predetermined temperature. The final and overall crystallinity, however, depends not only on the number of nuclei that are formed but also on the spherulitic growth rate from such nuclei. As noted above, spherulites develop with respect to a center, or nucleus, of growth. Addition of the nucleating agents thus provides a large number of sites for growth upon cooling from a melt. In order to be of practical use, such nucleating agents not only must produce a fine spherulitic structure but also must do this under conditions of rapid cooling to a temperature above the glass transition temperature of the polymer, i.e., they must reduce the time that is necessary under a given set of conditions for crystallization to start. This time is usually referred to as "induction time". Subsequent growth from the spherulitic center depends on the polymer chain mobility. Thus, a factor in the spherulitic growth rate is the macroscopic viscosity of the polymer and its temperature dependence. All segmental motion is "frozen in" at the glass transition temperature (Tg) and no additional crystallization occurs even when nuclei are present.

At present, most nucleating agents for polyester contain sodium or potassium ions in a form that makes them mobile in the molten polyester. The nucleation mechanism is still in dispute, but with no exception, nucleation of polyesters by these ions is always associated with substantial chain cleavage, as reflected by dramatic reduction in melt and solution viscosity. The nucleating agents of this invention contain none of the above ions and the nucleation process is not accompanied by chain cleavage. On the contrary, often in our case, molecular weight increases are combined with relatively large increases in T_{∞}, a combination dramtically different from existing systems.

Summary of the Invention

Presently, it has been discovered that the crystallization temperature (T_{∞}) of polyesters can be increased by the addition of one or more effective nucleating agents having a particle size which is about equal to or more than the lamellar thickness of the desired polyester. The crystallization temperature upon cooling reflects the overall crystallization rate due to the combined effects of nucleation and growth of crystallites/spherulites. A non-nucleated polymer would have a lower T_{cc} than a nucleated material, and a polymer crystallizing at a lower rate would have a lower T_{cc} than a faster crystallizing polymer. It is believed that an increase in T_{cc} and the corresponding increase in the crystallization rate cause an improvement in the thermal, optical and/or mechanical properties of the polymer. See "Memory Effects in Polymers II. Processing History vs. Crystallization Rate of Nylon 6-Observation of Phenomenon and Product Behavior", Y.P. Khanna et al. in Polymer Engineering and Science, 24, Vol. 28, pp. 1600-1606, December, 1988, and also "Memory Effects in Polymers III", Y.P. Khanna et al. in Polymer Engineering and Science, 24, Vol. 28, pp. 1607-1611, December 1988, for additional information regarding the effects of increasing the T_{cc} of a polymer.

The composition of this invention comprises (a) at least one polyester and (b) one or more nucleating agents having an effective particle size.

Yet another aspect of this invention relates to a novel process for enhancing the rate of crystallization of a polyester from the melt, which comprises adding to said polymer a nucleating agent of this invention.

Several advantages flow from this invention. For example, by speeding up the rate of crystallization, processing times are decreased.

Brief Description of the Drawings

The invention will be more fully understood and further advantages will become apparent when reference is made in the following detailed description of the invention and the accompanying drawings in which:

FIG. 1 is a graph of the heat of formation of selected oxides of table II as a function of the group of the Periodic Table to which the element forming the oxide belongs.

Description of the Embodiments of the Invention

As an essential ingredient, the composition of this invention comprises one or more polyesters. The polyesters used can vary widely. The particular polyester chosen for use can be homo-polyester, or a random or block copolyester or terpolymer, or mixtures thereof as desired. Many polyesters are generally prepared by the condensation of an organic dicarboxylic acid and an organic diol, and, therefore, illustrative examples of useful polyesters will be described hereinbelow in terms of these diol and dicarboxylic acid precursors.

Polyesters which are suitable for use in this invention are those which are derived from the condensation of aromatic, cycloaliphatic, and aliphatic diols with aliphatic, aromatic and cycloaliphatic dicarboxylic acids. Illustrative of useful aromatic diols, are those having from about 6 to about 24 carbon atoms. Such aromatic diols include bis-(p-hydroxyphenyl)ether; bis-(p-hydroxyphenyl)thioether; bis-(p-hydroxyphenyl)-sulphone; bis(p-hydroxyphenyl)-methane; 1,2-(bis-(p-hydroxyphenyl)-ethane); 1-phenyl-bis-(p-hydroxy-phenyl)-methane; diphenyl-(bis-(p-hydroxyphenyl)-methane); 2,2-bis(4-hydroxy-dimethylphenyl) propane); 1,1- or 2,2-(bis(p-hydroxyphenyl)-butane); 1,1-dichloro-or 1,1,1-trichloro-2,2-(bis-(p-hydroxyphenyl)-ethane); 1,1-(bis-(p-hydroxyphenyl)-cyclopentane); 2,2-(bis-(p-hydroxyphenyl)-propane (Bisphenol A); 1,1-(bis-(p-hydroxyphenyl)-cyclohexane) (bisphenol C); p-xylene glycol; 2,5-dichloro-p-xylylene glycol; p-xylene-diol; the fluoroalkyl and fluoroalkylene analogues of the above and the like.

Suitable cycloaliphatic diols include those having from about 5 to about 24 carbon atoms. Exemplary of such useful cycloaliphatic diols are 1,4-dihydroxy cyclohexane, 1,4-dihydroxy methylcyclohexane, 1,3-dihydroxy-cyclopentane, 1,5-dihydroxycycloheptane, 1,5-dihydroxycyclooctane, 1,4-cyclo-hexane dimethanol, 2,2-bis(4-hydroxycyclohexane)propane and the like.

Useful and aliphatic diols include those having from about 2 to about 12 carbon atoms, with those having from about 2 to about 6 carbon atoms being particularly preferred. Illustrative of such preferred diol precursors are 1,2-ethylene glycol, 1,3-propylene glycol, 1,2-propylene glycol, 1,8-octanediol, 1,6-nonanediol, neopentyl glycol, pentyl glycol, 1,6-hexanediol, 1,4-butanediol, and the like.

Cycloaliphatic diols and aliphatic diols are preferred for use. Propylene glycol, ethylene glycol, neopentyl diol, 1,4-dihydroxy methylcyclohexane, 1,4-butanediol and 2,2-bis(4-hydroxy cyclohexyl) propane are particularly preferred as diol precursors of polyesters for use in the conduct of this invention.

Suitable dicarboxylic acids for use as precursors in the preparation of useful polyesters are linear and branched chain saturated aliphatic dicarboxylic acids, aromatic dicarboxylic acids and cycloaliphatic dicarboxylic acids. Polyesters containing up to about 80% repeat units of monomer containing both hydroxyl and carboxyl groups, such as hydroxybenzoic acid, vanillic acid, syringic acid and the like, may also be used in the practice of this invention. Illustrative of aliphatic dicarboxylic acids which can be used in this invention are those having from about 2 to about 50 carbons atoms, as for example, malonic acid, dimethylmalonic acid, succinic acid, itanoic acid, octadecylsuccinic acid, pimelic acid, adipic acid, trimethyladipic acid, sebacic acid, suberic acid, azelaic acid and dimer acids (dimerisation products of unsaturated aliphatic carboxylic acids such as oleic acid) and alkylated malonic and succinic acids, such as octadecylsuccinic acid, and the like.

Illustrative of suitable cycloaliphatic dicarboxylic acids are those having from about 6 to about 15 carbon atoms. Such useful cycloaliphatic dicarboxylic acids include 1,3-cyclobutanedicarboxylic acid, 1,2-cyclopentanedicarboxylic acid, 1,3- and 1,4-cyclohexanedicarboxylic acid, 1,3- and 1,4-dicarboxymethylcyclohexane and 4,4-dicyclohexyldicarboxylic acid, and the like.

Polyester compounds prepared from the condensation of a diol and an aromatic dicarboxylic acid are preferred for use in this invention. Illustrative of such useful aromatic carboxylic acids are terephthalic acid and isophthalic acid, 2,6- or 2,7-naphthalenedicarboxylic acid, 4,4'-diphenyldicarboxylic acid, 4,4-diphenylsulphone-dicarboxylic acid, 1,1,3-trimethyl-5-carboxy-3-(p-carboxyphenyl)-indane, diphenyl ether 4,4-dicarboxylic acid bis-p(carboxyphenyl) methane and the like. Of the aforementioned aromatic dicarboxylic acids based on a benzene ring such as terephthalic acid and isophthalic acid are preferred for use and amongst these preferred acid precursors terephthalic acid is particularly preferred. Copolymers and terpolymers prepared from mixtures of the above aromatic diacids are especially preferred.

In the most preferred embodiments of this invention, poly(ethylene terephthalate), poly(butylene terephthalate), poly(ethylene naphthalate) as well as copolymers and terpolymers thereof such as poly(ethylene/terephthalate/2,6-naphthalene dicarboxylate) and poly(tetramethylene/terephthalate/2,6-naphthalene dicarboxylate), are the polyesters of choice. Among these polyesters of choice, poly(ethylene terephthalate) and the copolymers and terpolymers thereof are most preferred.

The molecular weight of the polyester may vary widely, for example, the polyester may be a wax having relatively low molecular weight, i.e. about 1000 to 5000 or more. The polyester may also be a melt-spinnable and of a fiber-forming molecular weight. In other embodiments, the polyester has film-forming molecular weight. Usually the film-forming polyester has a molecular weight of at least about 10000. In preferred embodiments of the invention, the molecular weight of the polyester is from about 1000 to about 200,000 and in particularly preferred embodiments is from about 25,000 to about 150,000. Amongst the particular preferred embodiments, the most preferred are those in which the molecular weight of the polyester is from about 35,000 to about 140,000.

A second essential component of the composition of this invention will include at least one effective nucleating agent. For the practice of this invention, an effective nucleating agent has a particle size which is about equal to or more than the lamellar thickness of the polymer (i.e. effective particle size). The lamellar thickness is the average thickness of the flat polymer crystals plus half of the thickness of the amorphous layers separating such crystals. A common lamellar thickness is about 50Å to 150Å.

In preferred embodiments of the invention, the nucleating agents possess a compound or material having a particle size of about 500Å or less. Preferably, the nucleating agents is at least about 50Å, and more preferably, the particle size of the nucleating agent is about 100Å to about 300Å. In particularly preferred embodiments, the particle size is from about 100Å to about 200Å with from about 100Å to 150Å being the size of choice. By keeping the size of the nucleating agents as close as possible to the lamellar thickness, one can maximize the number of nuclei presented by a fixed volume or weight of nucleating agent.

Selection of nucleating agents is guided by those materials which satisfy the above particle size requirements, processing conditions and end-use properties. Preferably, the nucleating agent is selected from one or more of the elements of groups VA and VIA of the periodic table. Illustrative of such elements are antimony, arsenic, bismuth, tellurium and selenium. These elements are excellent nucleators when present in the polyester in their elemental form (i.e. the valence = 0).

The nucleating agent is added to the polyester in an "effective amount". As used herein, an "effective amount" is an amount which is sufficient to improve the homogeneity and/or fineness of spherulitic structures in the polyester to any extent. Preferably, the amount of nucleating agent used is sufficient to increase the T_{cc} of the nucleated polymer at least 10°C over that of other polyesters prepared without the nucleating agents of this invention. The enhanced crystallization characteristics can be measured by comparing the crystallization temperature upon cooling (T_{cc}). The amount nucleating agent may correspond to amounts of conventional nucleating agents. However, it is noted that lesser amounts of the nucleating agents may be used since the use nucleating sites tends to be maximized by the nucleating agents used herein. In the preferred embodiments of the invention, the amount of nucleating agent employed is in the range of from about 0.001 to about 5 weight percent based on the total weight of polyester and agent, and in the more preferred embodiments of the invention is from about 0.01 to about 3 weight percent on the aforementioned basis. In particularly preferred embodiments, the amount of nucleating agent employed is from about 0.01 to about 2.0 weight percent based on the total weight of agent and polyester. In further preferred embodiments, the amount of nucleating agent is from about 0.01 to about 1.0%. The nucleating agent is uniformly dispersed in the polyester.

A preferred process for forming the nucleated polyester compositions of this invention is a process by which not only crystallization properties are enhanced but also the molecular weight of the polyester can be increased. The process for enhancing the crystallization and melt viscosity properties of a polyester by forming an extended chain polyesters and block or graft polyesters or copolyesters, said process comprising the steps of (a) forming an intimate mixture of one or more polyesters, one or more effective nucleating agents and at least one effective chain extension reagent compound; (b) heating said mixture for a time and at a temperature sufficient to form said extended chain, or graft or block copolyester or polyester. In the above process the polymer chain extended or coupled as often referred to in the art. Chain extension or coupling as discussed herein shall both apply coupling polyesters and preparing graft and/or block polyesters and copolyesters. Chain extension reactions of polyesters, such as poly(ethyleneterephthalate) (PET), with a phosphorus (III) chain extension reagent, such as triphenylphosphite (TPP), at effective melt temperatures result in an increase in the molecular weight of the polymer. We have found that the chain extension of polyesters by reaction with one or more phosphorus (III)-containing chain extension reagents, such as aryl phosphites, in the presence of one or more substances which contain at least one element belonging to groups VA and VIA of the periodic table, will produce polyesters having enhanced T_{cc} values. It is noted that the polyester composition, which is melt processed in accordance with this invention, generates a polyester material having not only improved T_{cc} values but also the molecular weight of the polymer, as measured by the I.V., is reduced to a much lesser extent, if it is not maintained or increased when compared with materials prepared in the absence of the chain extension agent and selected nucleating agent. The substances which contain an element belonging to groups VA and VIA of the periodic table can be of many forms, for example inorganic or organic compounds, complexes or salts containing of substances which comprise elements of group VA or VIA. It is noted for example that in the presence of substances like oxides or organic salts or organic coordination compounds of antimony, arsenic, bismuth, tellurium and selenium, or in the presence of residues from polymerization (esterification) catalysts containing one or more of these substances; a reaction with the chain extension reagent takes place in which the valence of the group VA or VIA component(s) is reduced to zero. The elements from group VA and VIA precipitate as very fine particles, e.g. significantly less than 1 micron.

Often substances which comprise elements belonging to group VA and VIA of the periodic table are present in the original polymer as components which serve as polymerization catalysts. In preferred embodiments a catalyst employed for the original polymerization of the polyester is selected from those inorganic and organic catalysts that contain substances which reduce to elemental form by the reaction with the chain extension reagent (e.g. aryl phosphite) at elevated temperatures of the chain extension process. The catalysts employed should also not attack the polymers after their formation. Preferably, the catalyst is selected from catalysts which contain substances belonging to groups VA and VIA. Catalysts from these groups are used to catalyze the initial polymeric condensation for forming polyesters with the added advantage of effecting enhanced crystallization characteristics in the polyester after the chain extension reaction. More preferably, the catalyst is selected from catalysts which contain one or more elements selected from antimony, arsenic, bismuth, tellurium or selenium Illustrative of useful catalysts are antimony triacetate, arsenic triacetate, bismuth triacetate, tellurium oxide, selenium oxide, antimony (III) oxide, arsenic (III) oxide and bismuth (III) oxide. Many of these catalysts are commercially available.

Once a polyester, such as poly(ethylene terephthalate), is obtained commercially or is prepared by polycondensation in the presence of one or more catalysts, the chain extension of the polyester is conveniently carried out in two steps. The first step of the process consists of forming an intimate mixture of one or more appropriate polyesters, one or more chain extension reagent compounds and one or more substances as described above which contain at least one element from group VA or VIA. In the second step of the process, the intimate mixture is heated at a temperature and for a time sufficient to mix the ingredients thoroughly and form the desired extended chain polyester, or block or graft copolyester or polyester, as indicated by an increase in the viscosity of the polymer mixture.

In a preferred embodiment of this invention, an intimate mixture in the first process step is a molten mixture. As used herein, "molten mixture" is an intimate mixture which has been heated to a temperature which is equal to or greater than the melting point of at least one of the polymer components of the mixture. The manner in which the molten mixture is formed is not critical and conventional methods can be employed. For example, the molten mixture can be formed by maintaining the polymer product of the polycondensation in the molten state or through use of conventional polymer and additive blending means, in which the polymeric components are heated to a temperature equal to or greater than the melting point of at least one of the polymers, and below the degradation temperature of each of the polymers. In a particularly preferred embodiment of this invention, the polymers are heated above the melting point of each of the polymers in the mixture. An effective amount of one or more chain extension reagent compounds in a liquid or powdered form is added to the melted polymers while at the same time vigorously stirring the melt, or added prior to melting and mixing. Heating is continued until the desired extended chain, or block and/or graft polyester or copolyester is formed as indicated by an increase in the melt viscosity.

In a more preferred embodiment, the components of the intimate mixture can be granulated, and the granulated components mixed dry in a suitable mixer, as for example, a tumbler or a Banbury Mixer, or the like, as uniformly as possible. Thereafter, the composition is heated in an extruder until the polymer components are melted. As described above, the mixture is heated until the desired extended chain, or block and/or graft copolyester or polyester is formed as indicated by an increase in the melt viscosity. Thereafter the mixture is ejected with cooling. In the most preferred embodiment, one or more effective chain extension reagents are injected directly into the molten stream of polymer formed from the polycondensation reaction wherein the polymer and phosphites are thoroughly mixed prior to subsequent processing.

The order of mixing of the various components of the intimate mixture is not critical. Accordingly, the order of addition of the polymers and chain extension reagent compounds and other optional components to be described in more detail hereinbelow, to form the intimate mixture, can be varied as desired.

The process can be carried out in a batchwise or discontinuous fashion, as for example, carrying out the process in a sealed container. Alternatively, the process can be carried out in a continuous fashion in a single processing zone, as for example, by use of an extruder as described hereinabove, or in a plurality of such reaction zones, in series or parallel.

Reaction temperature can be varied over a wide range. However, it should be appreciated that the process temperature employed in any specific instance will depend on the particular polyesters employed and, in the preferred embodiments should be at least as high as the melting point of semi-crystalline polyesters, and below the degradation temperature of such polyesters. In the preferred embodiments of this invention, the process temperature is such that the polyesters will remain in the molten state at the extended chain polyester, or block or graft polyester or copolyesters are formed. Normally this can be accomplished in one of two ways. Either the process can be carried out at a temperature which is equal to or greater than the melting point of the desired product; or process temperatures can be increased periodically over the course of the conduct of the process so as to maintain the mixture in the molten state. An optimal process temperature is the highest temperature which is below the degradation temperature of the polyester or polyesters. In the particularly preferred embodiments of this invention employing particularly preferred polyesters compositions, the process temperature is at least about 200°C. Amongst these particularly preferred embodiments, most preferred process temperatures are in the range of from about 225°C to about 325°C.

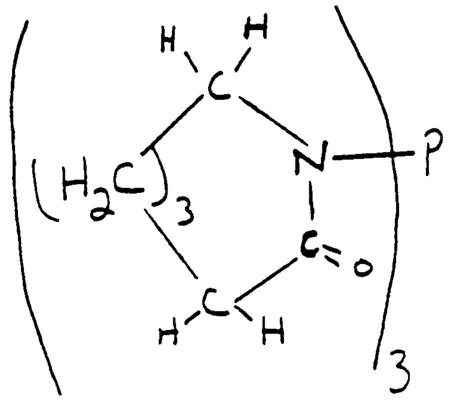
The process is carried out for a time sufficient to form the desired extended chain polyester, or block or graft polyester or copolyester as is indicated by the increase in the viscosity of the mixture. Reaction times can be varied over a wide range. Usually, reaction times will depend on a variety of factors such as the polymeric components, reaction temperatures, chain extension reagent compound and its concentration, and other factors known to those of skill in the art to affect reaction times. In most instances, the reaction time can vary from a few seconds to 24 hours or more. In the preferred embodiments of this invention, reaction times will vary from about 1 min. to about 2 hours and in the particularly preferred embodiments from about 2 min. to about 30 to 60 min.

Best results are obtained when the process of this invention is carried out in the presence of as little water as possible. The process is preferably conducted in the absence of moisture and at atmospheric pressure.

The process of this invention employs one or more chain extension reagents. The reagents are referred to as chain extension reagents since they will extend polymeric chains by coupling the polymeric chains together at reactive sites on the polymer reactants. The reaction of chain extension is the coupling reaction that occurs via the formation of a linking group between reactant polymers. An effective chain extension reagent is a compound containing a trivalent phosphorus atom (phosphorus III) to which is attached at least one effective leaving group, but not more than three leaving groups. The effective leaving group contains a hetero atom bonded to the phosphorus atom, and the hetero atom is bonded to a carbon which is double bonded to an atom other than the hetero atom. Preferably, the hetero atom is nitrogen or oxygen. The hetero atom either forms a conjugated system with the double bonded carbon or the hetero atom is bonded to a carbon of a conjugated system. It is believed that the conjugated system of the leaving group provides the leaving group with the ability to delocalize negative charge and therein the leaving group is a "stable" moiety. The phenomenon of stability as used herein relates to the ability of the leaving group to delocalize negative charge within its structure.

An effective leaving group can be a cyclic aromatic or cyclic non-aromatic. It is noted that cyclic includes monocyclic and polycyclic moieties. Preferably, the leaving group is a cyclic structure; that is the hetero atom of the leaving group is part of a cyclic ring or the carbon to which the hetero atom is bonded is part of a cyclic ring. It is proposed that the cyclic structures can more efficiently delocalize negative charge than a linear leaving group. When the hetero atom is part of the cyclic ring it is preferred that the hetero atom is nitrogen. Chain extension reagents having such nitrogen bonded to the phosphorus atom are referred to herein as phosphinamines.

Illustrative of such phosphinamines are the phosphorus trislactams disclosed in U.S. Patent No. 5,118,805 assigned to Allied-Signal Inc. Such compounds are efficient chain extension reagents and may be used instead of or in combination with any other effective chain extension reagents. Illustrative of such phosphinamines are phosphorus triscaprolactam, phosphorus tris(2-pyrrolidone), phosphorus trislaurolactam and phosphorus triscaprylolactam. The formula for phosphorus triscaprolactam is shown below.



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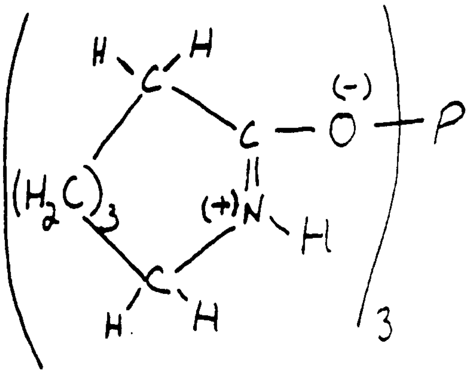
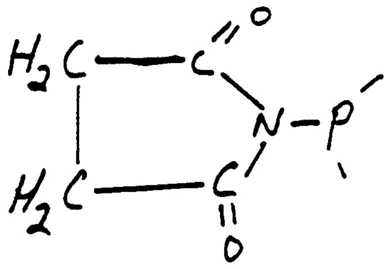
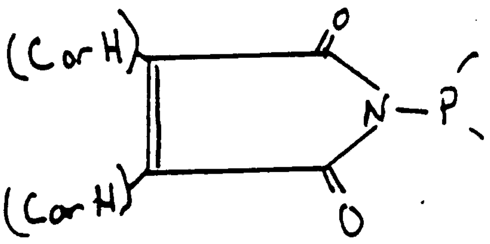


It is noted that phosphorus (III) chain extension reagent need only have one lactam as a leaving group. The remaining moieties attached to the phosphorus atom may be identical or similar lactam leaving groups or other varied leaving groups which are discussed infra.

In alternatively preferred embodiments of the invention, the phosphinamines chain extension reagents are compounds having at least one bond of a trivalent phosphorus atom bonded to the nitrogen of an imide. Basically, the leaving group is an imide such as succinimide, phthalimide and maleimide as shown below.



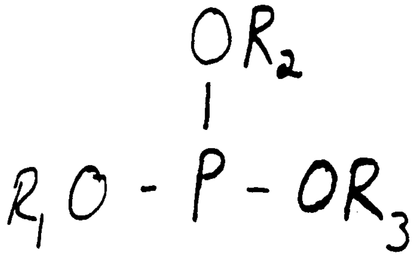


In further preferred embodiments of this invention, the chain extension reagent has (a) one or more aryl containing leaving groups wherein the hetero atom of the chain extension reagent is bound to a carbon atom of the aryl group and/or (b) one or more leaving groups wherein the hetero atom is actually part of a heteroaromatic ring (although the hetero atom is bound to the other ring atoms through single bonds only). Illustrative of heteroaromatic leaving groups are pyrrolyl, indolyl, carbazolyl,imidazolyl and benzimidazolyl.

Of particular interest are the aryl containing chain extension reagents which are phosphites, i.e. a phosphorus atom single bonded directly to three oxygen atoms. Illustrative of effective phosphite chain extension reagents are phosphites having one or more aryloxy groups bound directly through the oxygen of the aryloxy group to the phosphorus atom of the phosphite. Often an effective phosphite is a compound which is commonly referred to as a phosphite ester or polyphosphite ester. More specifically, an aryloxy containing phosphite as described above is referred to as an aryl phosphite ester. The aryloxy moiety of the phosphite can be derived from any aromatic alcohol which contains a hydroxylated aryl group; wherein the aryl group is substituted or unsubstituted yet the aryl ring itself is hydroxylated. Useful aromatic compounds employed in forming the aryloxy groups are mono-, di- and other polycyclic aromatics, which include but are not limited to substituted and unsubstituted benzenes, naphthalenes, anthracenes, biphenyl or polyphenyl compounds, methylene bridged aromatic compounds and the like. Preferably, the aromatic group which forms the arlyoxy is selected such that the aryloxy group is a least hazardous, volatile or toxic material.

Useful phosphite esters, and polyphosphite esters are known compounds. The polyphosphite esters, which may be symmetrical or asymmetrical, have more than one aryl phosphite ester. Such compounds can be conveniently prepared by reacting phosphorus trichloride and one or more alcohols at least one of which is an aromatic alcohol. For example, triphenyl phosphite can be prepared by reacting three moles of phenol with one mole of phosphorus trichloride, and trisnonylphenol phosphite can be prepared by reacting three moles of nonylphenol with one mole of phosphorus trichloride. Mixed phosphites such as diphenyl isodecyl phosphite, diphenyl isooctyl phosphite and phenyl diisodecyl phosphite, can be prepared by reacting an appropriate mixture of aromatic and aliphatic alcohols with phosphorus trichloride. Similarly, useful phosphites containing more than one phosphite ester moiety can be prepared by reacting aromatic and aliphatic alcohols at least one of which is polyhydric with phosphorus trichloride.

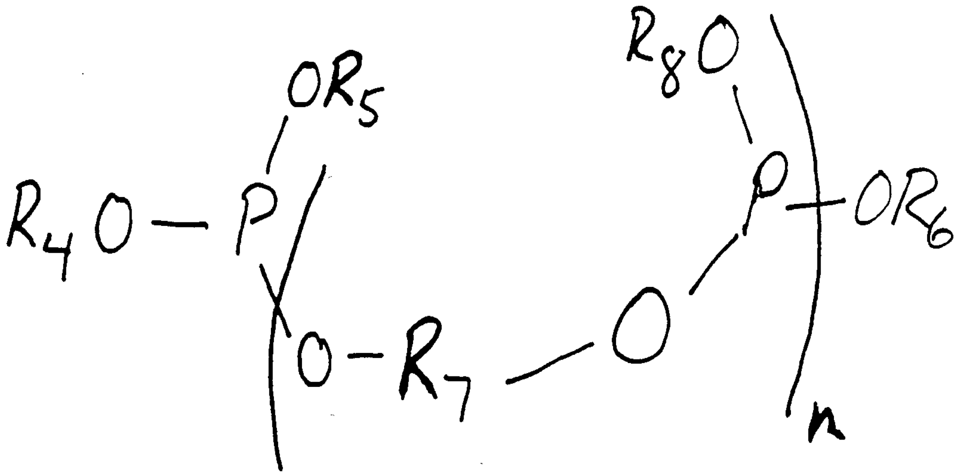
Illustrative of useful phosphite esters and polyphosphite esters are compounds of the formula I:



$$R_1O-\overset{\displaystyle OR_2}{\overset{|}{P}}-OR_3$$

and asymmetrical and symmetrical phosphite derivatives thereof having more than one phosphite ester moiety wherein:

R_1, R_2 and R_3 are the same or different and are hydrogen, metal cations, ammonium radicals, or substituted or unsubstituted aryl or alkyl wherein permissible substituents are one or more alkyl, alkoxy, cyano, nitro or halo groups, or R_1, R_2 and R_3 individually may form a moiety of the formula II:



wherein n is 0 or a positive whole number and R_4, R_5 and R_6 are the same or different and are R_1, R_2 and R_3, R_7 can be a single bond between the two oxygens, or a divalent aromatic or aliphatic group, R_8 can be R_4, R_5, or R_6; and R_5, R_7 and R_8 together can be polyalkoxy group derived from an aromatic or aliphatic polyalcohol; with the proviso that each phosphite moiety includes a substituted or unsubstituted aryl group.

Permissible R_1, R_2 and R_3 groups include aliphatic groups such as t-butyl, n-butyl, isopropyl, hexyl, pentyl, 2-chloroethyl, neophentyl, decyl, dodecyl, isodecyl, butoxyethyl, 3-chlorobutyl and the like; aromatic groups such as 2,4-di-tert-butyl-phenyl, 4-tert-butylphenyl, 3-isopropylphenyl, 2,4-dimethylphenyl, 4-nonyl-phenyl, octylphenyl, 4-chlorophenyl, 2,4-dibromophenyl, 4-fluorophenyl, 3,5-dichlorophenyl, 4-cyanophenyl, 2-nitrophenyl, bisphenol methyl and the like; metal cations such as sodium, potassium, zinc, lithium, calcium, aluminum, and the like and groups containing one or more phosphite moieties, as for example, ethylene diphenyl phosphite, or a poly-(dipropylene glycol) phenyl phosphite moiety bonded to the oxygen atom via the dipropylene glycol moiety.

Preferred for use in the practice of this invention are phosphite esters of the above formula I and II in which:

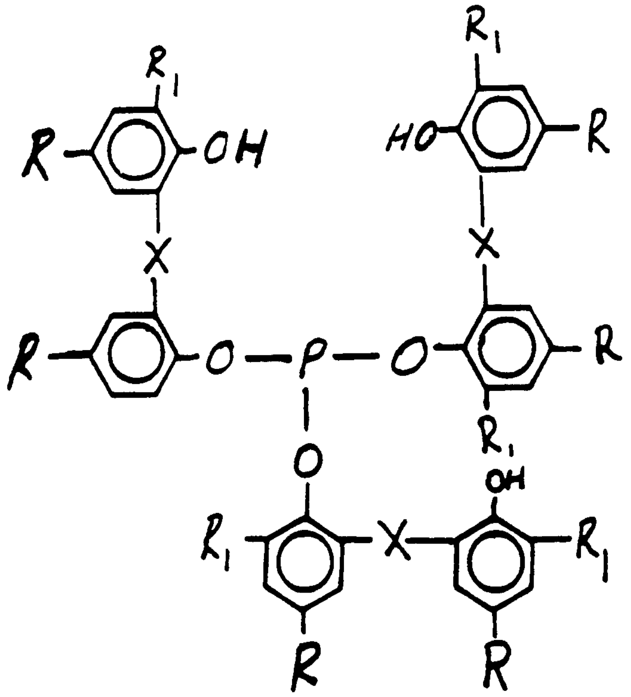
R_1, R_2 and R_3 are the same or different and are a alkyl, aryl or aryl substituted with one or more alkyl groups, with the proviso that at least one of R_1, R_2, and R_3 is aryl or substituted aryl. More preferred for use are such esters in which at least two of R_1, R_2, R_3 are aryl or alkyl substituted aryl, and most preferred for use are those esters in which R_1, R_2, and R_3 are the same or different and are aryl or alkyl substituted aryl, such as nonyl phenyl or 2,4-di-tert butyl phenyl. For many of the preferred embodiments, R_1, R_2, and R_3 are selected from phenyl groups, bisphenyls and "novolac-type" polyphenyls known in the art and described herein infra.

Preferably, R_7 is an alkoxy or polyalkoxy derived from a divalent aromatic alcohol such as bisphenol A or a biphenol. When R_5, R_7 and R_8 together are a polyalkoxy of a polyalcohol, the polyalcohols may be a pentaerythritol, pyrogallol, tetrahydroxybenzophenone, and saccharides, such as galactose, or polyalcohols such as phenol-aldehyde or resorcinol-formaldehyde oligomers and the like.

Illustrative of several useful phosphite esters within the scope of the above-structural formula are triphenyl phosphite, diphenyl phosphite, tris(nonylphenyl) phosphite, di-phenyl isodecyl phosphite, phenyl diisodecyl phosphite, diphenyl isooctyl phosphite, phenyl diisodecyl phosphite, poly(dipropylene glycol) phenyl phosphite, poly(4,4-isopropylidene diphenol neopentyl alcohol phosphite), bis-(2,4-di-t-butylphenyl) phosphite.

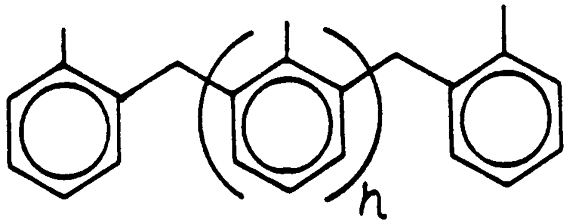
Additional phosphite esters which can be employed in the practice of the invention are disclosed in the following publications: U.S. Patents 3,367,996 to Strauss; 3,697,459 to Dannels et al.; 3,949,024 to Beck et al. and 5,068,388 to Gatto.

Examples of phosphites having biphenyls and polyphenyls in the arlyoxy group are disclosed by Beck et al. and are shown the formula below.



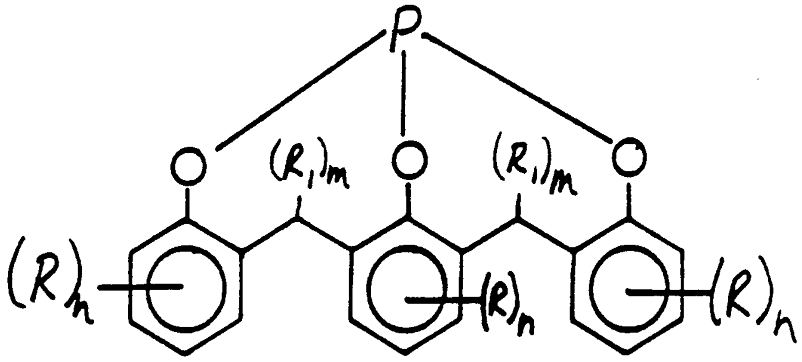
wherein X is sulfur or lower alkylene (e.g. methylene); R is hydrogen or an alkyl radical and R_1 is an alkyl radical.

For novolac phosphites, one or more, preferably three of the oxygens of the phosphite ester are bonded to the same compound, which may be a dimer, oligomer or polymer of a repeating unit as shown below:



wherein n=0 to about 6.

Some of the "novolac-type" phosphites which are disclosed by Gatto are shown below.



wherein each R and R_1 is an independently selected C_1-c_6 alkyl radical, n=1, 2 or 3 and m=0 or 1.

An effective amount of one or more effective chain extension reagents is employed in forming the intimate mixture. As used herein, "an effective amount" is an amount of the chain extension reagents which when added to the polymeric component in accordance with this invention forms a mixture which when heated forms the desired graft copolymer. The formation of the graft copolymer will be accompanied by an increase in the melt viscosity of the mixture. As used herein, "viscosity" denotes the internal friction, i.e. resistance to flow of the polymer mixture, and is well known in the art. A wide variety of viscometers are available for measurement of viscosity, such as capillary, rotational, orifice, falling ball, and oscillatory types. They are described in Barr, "A Monograph of Viscometry", Oxford, N.Y. (1931) and Kirk and Othmer, "Encyclopedia of Chemical Technology", Vol. 14, pp. 756-775 the Interscience Encyclopedia, Inc., New York (1955).

In the preferred embodiments of this invention, the quantity of the one or more chain extension reagents employed is at least about 0.05 weight percent, based on the total weight of the mixture. In the particularly preferred embodiments of this invention, the weight percent of reagent compounds is in the range of from 0.1 to about 10 weight percent, and amongst these particularly preferred embodiments, those in which the quantity of reagent compounds employed is from about 0.4 to about 4 weight percent based on the total weight of the mixture are most preferred.

Polymers which may be employed in the chain extension process of this invention are linear or branched polyesters. The type of polyester is not critical and the particular polyester chosen for use in any particular situation will depend essentially on the physical properties and features, i.e. flexibility, hardness, toughness, desired in the final shaped article of manufacture. Thus, a multiplicity of linear thermoplastic polyesters having wide variations in physical properties are suitable for use in the process of this invention. One important feature of the polyesters employed is that they must have terminal reactive groups which allow coupling between two or more polyesters chains via the formation of a linking group. Each polyester should have at least one terminal reactive group. In alternative embodiments, the polyesters comprise two terminal groups wherein such polyesters may contain the same terminal group or two different terminal groups. When one polyester contains two identical terminal groups, it is chain extended with a second polyester having two terminal groups which allow coupling with the two terminal groups of the other polymer. Often the polyesters are coupled via the formation of an ester as the linking group. For example, useful polyesters are those that are terminated with a hydroxy and/or carboxy group with the proviso that at least one of each of the two terminal groups is present in the polymers selected for chain extension although an individual polymer need not possess both types of terminal groups. Preferably, the total mole ratio of terminal hydroxy groups to carboxy groups present in all polyesters employed ranges from about 10:1 to about 1:10. More preferably, the total mole ratio of terminal hydroxy groups to carboxy groups present in all polyesters employed ranges from about 4:1 to about 1:4. In further preferred embodiments, the total mole ratio of terminal hydroxy groups to carboxy groups present in all polyesters employed ranges from about 6:5 to about 5:6. The aforementioned polyesters are generally useful for the chain extension process.

Since the compositions of this invention are useful in forming molded articles, in addition to the above-described essential components, compositions of this invention can include various optional components which are additives commonly employed with the polymers and copolymers of this invention. Such optional components include additional nucleating agents, viscosity enhancers, fillers, plasticizers, impact modifiers, chain extenders, colorants, mold release agents, antioxidants, ultraviolet light stabilizers, lubricants, antistatic agents, fire retardants, and the like. These optional components are well known to those of skill in the art, accordingly, only the preferred optional components will be described herein in detail.

The composition of this invention can be prepared by blending or mixing the essential ingredients, and other optional components, as uniformly as possible employing any conventional blending means. Appropriate blending means, such as melt extrusion, batch melting and the like, are well known in the art and will not be described here in greater detail. In one useful procedure, the blending procedure can be carried out at elevated temperatures above the melting point of the polymer and the nucleating agent added either alone or as individual components of the agent separately or as a combination of the components in a suitable form as for example, granules, pellets and preferably powders are added to the melt with vigorous stirring. Alternatively, all or a portion of the various components of the nucleating agent can be masterbatched or preblended with the polymer in the melt and this premixed or masterbatch added to the polyolefin in the melt in amounts sufficient to provide the desired amount of nucleating agent in the polyolefin product. Stirring is continued until a homogeneous composition is formed. The nucleating agent can also be added to the melt coated on the surface of small particle inert powders which have a high surface to volume ratios. The use of such inert powders, as for example, fused silica, fused alumina, carbon black and aerogels, and hydrogels of silica or alumina, helps to reduce the amount of nucleating agent required to provide optimum results. Blending pressures, and the order of addition of the various components are not critical and may be varied as desired provided that a substantially homogeneous composition results. The blending procedure can be carried out at elevated temperatures, in which case the polymer component is melted and the solid nucleating agent is admixed therewith by vigorously stirring the melt. Similarly, the various solid components can be granulated, and the granulated components mixed dry in a suitable blender, or for example, a Banbury mixer, as uniformly as possible, then melted in an extruder and extruded with cooling.

Alternatively, the composition of this invention can be formulated by dissolving the components in an appropriate inert solvent, after which the solvent is removed by evaporation, or other conventional solvent removing means are employed to provide the composition. The solvent is not critical, the only requirement being that it is inert to the components of the composition, and it is capable of solubilizing the various components, or at least forming dispersions thereof.

The compositions according to the invention can be partly or highly crystalline, depending on which individual constituents are employed. They are thermoplastic materials from which molded articles of manufacture having valuable properties can be produced by the conventional shaping processes, such as melt spinning, casting, injection molding and extruding. Examples of such moldings are components for technical equipment, apparatus casting, household equipment, sports equipment, components for the electrical and electronics industries and electrical insulations, car components, circuits, fibers, films, piping, gaskets, tank linings, connectors, valve diaphragms, and semi-finished products which can be shaped by machining. The molding compositions according to the invention are outstandingly suitable for specific applications of all types since their spectrum of properties can be modified in the desired direction in many ways.

Several examples are set forth below to illustrate the nature of the invention and a manner of carrying it out. However, the invention should not be considered as being limited to the details thereof.

EXAMPLES

Procedure for Measurement of Tcc

The experiments were carried out to show the superior crystallization characteristics of the composition of this invention as compared to other nucleated polyester compositions and un-nucleated compositions as determined by differential scanning colorimetry (DSC) experiments.

The DSC experiments were carrier out using a DuPont 9900 automated system, in a nitrogen atmosphere. A sample of 10.0±0.2 mg was crimped in an aluminum cup, heated to 300°C at a program rate of 10°C./min, held there for 5 min. and then cooled at 10°C./min to obtain the Tcc (the crystallization temperature).

A. Mixing

PET obtained in the form of 1" (0.3175 cm) pellets was ground into 12 mesh size particles. . After weighing in wide-mouth jars, the PET samples were dried for 16 hours at 100°-110°C in a vacuum oven. This drying step was done prior to blending, and the samples were kept in sealed jars during interim periods to maintain dryness. Weighed amounts of the phosphite additives were added to the polymers and the sealed jars were rotated on a rolling mill for 0.5 hr. This rotation action effectively coated the surface of the pellets with the phosphite additives.

B. Melt Processing

Each time about 60 grams of the mixtures were charged into the cavity of a Haake Rheocord-90 melt blending instrument and processed at preset temperatures in the range of about 270 to 300°C for up to 20 minutes before being discharged. The instrument was set to 50 rpm. After the material was discharged, it was rapidly cooled to ambient temperature (approximately 23°C) upon which it was characterized by solution viscosity to determine its intrinsic viscosity and by repeated heat-cool cycles in the DSC instrument to determine its crystallization temperatures. The torque values of the Haake instrument are a direct indication of the melt viscosity of the polymer during a processing stage. The higher Torque values indicate and increase in the viscosity caused by the chain extension process of this invention (i.e. the chain extension brought about by mixing together the polymeric chain ends with the aryl phosphite.

The determination of the extended chain polyester or block or graft copolyester formation is noted by the relative increases in viscosity. Solution viscosity was measured at 23°C., on 0.5% and lower concentrations of polymer in 60:40 phenol/tetrachloroethane solvent mixture. A description of the materials used for the experiments and their physical properties, i.e. intrinsic viscosity (I.V. or [η]), T_{cc} and torque values measured by the Haake Rheocord-90 are set forth in the TABLE I.

EXAMPLE 1

Table I demonstrates the increases in T_{cc} for polyesters reacted with aryl phosphite. PET's polymerized with Ge or Ti-containing catalyst did not exhibit a similar degree of crystallization upon processing in comparison to PET with Sb-containing catalyst. It was observed that for the PET with Sb-containing catalyst the T_{cc} value increased along with a significant increase in the intrinsic viscosity (i.e. molecular weight) when processed in the presence of the phosphite. This is surprising since generally for PET purchased commercially the increase in T_{cc} is accompanied by a decrease in the intrinsic viscosity (See Table II below). For further information, see also S.M. Aharoni, "Nucleation of PET Crystallization by Metal Hydoxides", Journal of Apllied Polymer Science, **29**, 853-865 (1984).

TABLE I

SAMPLE	**INITIAL IV**	**CATALYST**	**PHOSPHITE TPP**	**HAAKE TORQUE 20 MIN @ 285°C**	**IV AFTER HAAKE PROC.**	**Tcc, °C 1ST CYCLE**	**Tcc, °C 2ND CYCLE**
1	1.01	GeO_2 450 ppm	None	80	0.65	175.6	177.2
2	1.01	GeO_2 450 ppm	1.5%	135	0.70	177.8	178.2
3	0.95	Ti TYZOR-TE 35 ppm	None	110	0.61	182.4	185.7
4	0.95	Ti TYZON-TE 35 ppm	1.5%	300	0.74	183.7	187.4
5	0.90	Sb 450 ppm	None	50	0.73	183.2	187.7
6	0.90	Sb 450 ppm	1.5%	240	1.63	204.7	206.2

(a) ppm is the amount of elemental residues of the catalyst

TABLE II

	T_M	T_{cc}	I.V.
PET I.V=0.20	254.5	218.2	0.20
PET I.V=0.53	258.0	197.5	0.53
PET I.V=0.70	255.3	185.2	0.70
PET I.V=0.91	255.0	173.7	0.91

PET (without nucleating agent) was obtained from Allied-Signal Inc.

Example 2

For PET, the effects of melt processing various additives on T_m, T_{cc} and I.V. were examined. The materials were processed in the absence of a chain extension agent. The only increase in T_{cc} is accompanied by a decrease in I.V. (i.e. molecular weight). See Table III. The PET used contains residual amounts (approx 450 ppm) of Sb-containing catalyst.

TABLE III

Effects of the Presence of Various Additives on T_m and T_{cc} of Poly(Ethylene Terephthalate)

Additive	Wt %	T_m °C	T_{cc} °C	[η] dL/g
Sodium pyrophosphate $Na_4P_2O_7$	1.0	254.6	201.5	0.40
Dibasic sodium phosphate Na_2HPO_4	1.0	255.4	202.0	0.32
Disodium salt of phenyl phosphate	1.0	256.1	204.0	0.38
None	None	257.5	192.8	0.49
k-Carrageenan	1.0	254.7	191.8	0.32
i-Carrageenan	1.0	253.2	197.6	0.31
64 K+Carboxylate fractal A2105-82G	1.0	256.2	192.9	0.46
None	None	258.3	191.8	0.61
None	None	256.3	196.7	0.53

Example 3

For PET (which contains approx. 450 ppm of Sb-containing catalyst as in Example 2), the effects of melt processing with and without various additives in the presence of a chain extension agent (e.g. aryl phosphite) were examined. The result show that the Sb-containing PET, which is melt processed with or without additives, generates a PET material having not only improved T_{cc} values but also the molecular weight of the polymer, as measured by the IV is reduced to a much lesser extent, if it is not maintained or increased when compared with materials prepared in the absence of the chain extension agent. See Table IV for the results. Values marked with "b" denote the use of triphenyl phosphite as the chain extension agent.

TABLE IV

Effects of the Presence of 1.5% Triphenyl Phosphite on T_m and T_{cc} of Poly(Ethylene Terephthalate) Melt Blended for 20 minutes at 270° in Haake Rheocord-90

Code	Additives to PET Other than Sb-catalyst	T_m°c	T_{cc}°c	[η]	T_m (b)	T_{cc} (b)	[η] (b)	M.Wt light scatter -ing
1. A2105-82B: PET BLANK	None	257.5	192.8	0.49	252.8	209.4	0.52	43,000
2. PET - Blank	None	256.3	196.7	0.53	255.3	207.6	0.96	200,000
3. A2105-82C	1% A2105-78B: 64 Carboxyl Fractal	257.5	192.2	0.49	255.5	206.2	0.53	
4. A2105-82D	1% A2105-89B: 48 Ester Fractal	256.9	195.8	0.47	242.1	195.9*	0.50	
5. A2105-82K	1% A2105-82G: 64K+Carboxylate fractal	256.2	192.9	0.46	254.3	217.3	0.65	150,000

* Note that for sample 4, the ester containing radical is not expected to react with the phosphite.

SAMPLE PREPARATIONS

SAMPLE 3: Preparation of AB-fractal polyamide with carboxylic acid reactive sites

In 200 ml DMAc there were dissolved 0.00224 mol (0.47g) 1,3,5-benzenetricarboxylic acid. To this there were added 0.25 mol pyridine and 0.20 mol TPP dropwise throughout the condensation reaction. After dissolution, a solution in 200 ml DMAc of 0.1 mol (18.12g) 5-aminoisophthalic acid and 0.1 mol (13.71g) 4-aminobenzoic acid was added dropwise from a separate dropper to the solution containing the 1,3,5-benzenetricarboxylic acid. The addition took six hours and the reaction was allowed to continue for an extra hour, all at 115°C. After completion, the product was worked up as before. This reaction produced a stiff AB-type fractal polyamide with about 64 carboxylic acid end groups per molecule. The intrinsic viscosity of the polymer was 0.17 dL/g and its $M_w = 14200$. Reaction with 4-iodoaniline followed by mass balance and I,C,H,N element analysis confirmed that there exist close to 64 accessible carboxylic acid groups per molecule. The product was coded A2105-78B.

SAMPLE 4: Ester terminated AB-fractal polyamides

A 48-amine AB-type fractal polyamide was prepared as described above using trifunctional nuclei (prepared from 0.5g 1,3,5-benzenetricarboxylic acid and 1.4g 1,4-phenylenediamine) and 0.1 mol (15.25g) 3,5-diaminobenzoic acid and 0.1 mol (13.71g) 4-aminobenzoic acid. When the reaction was completed, a large excess of mono-methylterephthalate was added and the reaction was allowed to continue for 3 additional hours. Work up was as before. NMR analysis indicated that all the free amines were reacted to produce exclusively methyl ester-terminated FPs. From the ratio of methyl to aromatic carbons in the NMR scans, it was found that each polymer molecule is associated with close to 48 ester groups. The product was coded A2105-79B.

SAMPLE 5: Potassium carboxylate terminated AB-fractal polyamides

The carboxyl-terminated FP A2105-78B was dissolved in DMAc at over 80°C. To this solution a slight molar excess of KOH in methanol was added, resulting in gradual precipitation. After workup in methanol and acetone, the dried polymer contained over 16.0% by weight potassium. This product was coded A2105-82G.

Example 4

For examples 1 and 5 of Example 3, the effects of removing the Sb-containing material prior melt processing was also examined. The catalyst was removed by acid wash. The PET dissolved in trifluoroacetic acid, then precipitated in water, neutralized, washed in water & dried. For PET w/o Sb catalyst, the T_{cc} values are lower than for the same material melt processed with Sb catalyst residue. See Table V for results.

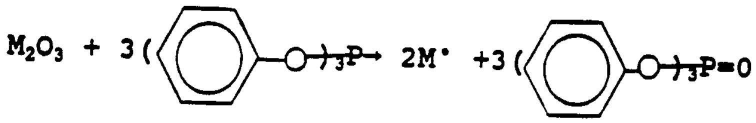
TABLE V

Effects of Removal of Antimony Residues From PET on Tcc of PET

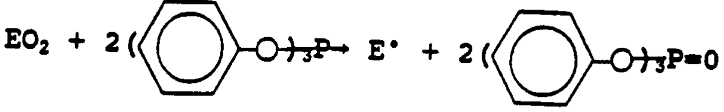
Sample	**Code**	**TPP Content**	**Result After Melt Proc. [η],dL/g. Tcc°C.**		**Results After Wash [η],dL/g. Tcc°C.**		**M.W. by Light Scat.**
Linear PET Control	None	None	0.53	196.7	0.58	-	43,000
PET & Fractal Polyamide Ungrafted	Sample 5	None	0.46	192.9	-	-	-

In addition to reactions in the molten polymer, model reactions were conducted in the absence of polymer or solvent (the TPP serves as solvent when appropriate) at temperatures of 180°C and 240°C. These reactions progress slower with trialkylphosphites (e.g. tributyl phosphite).

Typical reactions are:



where M = As, Sb, Bi.



where E = Se, Te.

The reactions products were determined by ^{1}H and ^{31}P-NMR, IR, XRD and element analyses. No reactions took place between TPP and oxides or organic salts and complexes of elements designated in the Table VI below as inactive. The numbers (1-33) in Figure 1 correspond to the inactive oxides for which color was unchanged. The letters (A-E) in Figure 1 correspond to the active oxides which produce solid elements. Figure 1 graphs the heat of formation of oxide per oxygen atom (in kjoule/mole) vs the groups of the periodic table to which the oxide belongs. It should also be noted that the reactions between the active oxides and TPP take place below their melting points, i.e., the reaction is a solid/liquid reaction. A list of the melting points of tested oxides is given in Table VII.

TABLE VI

FIG. NO./LETTER	OXIDE
1	H_2O
2	BaO
3	CaO
4	ZrO_2
5	V_2O_3
6	TiO_3
7	NbO
8	VO
9	VO_2
10	Nb_2O_5
11	V_2O_5
12	MnO
13	WO_3
14	MnO_2
15	MoO_3
16	FeO
17	Fe_2O_3
18	CoO
19	NiO
20	CrO_3
21	RuO_2
22	Cu_2O
23	PbO_2
24	GeO_2
25	SnO_2
26	SnO
27	In_2O_3
28	P_2O_5
29	ZnO
30	P_2O_3
31	B_2O_3
32	SiO_2
33	Al_2O_3
A	Sb_2O_3
B	As_2O_3
C	Bi_2O_3
D	TeO_2
E	SeO_2

TABLE VII
MELTING POINTS OF TESTED OXIDES, °C[a]

OXIDE	M.P., °C	OXIDE	M.P., °C
Al_2O_3	2015	P_2O_3	23.8
Sb_2O_3	656	P_2O_5	580
As_2O_3	315	RuO_2	1200
BaO	1923	SeO_2	340
Bi_2O_3	820	SiO_2	1610
B_2O_3	460	Ag_2O	230 decomposes
CaO	2580	TeO_2	733
CrO_3	196	SnO	1080
CoO	1935	SnO_2	1127
Cu_2O	1235	TiO_2	1825
GeO_2	1086	WO_3	1473
H_2O	0.00	VO	950
In_2O_3	850	V_2O_3	1970
FeO	1420	VO_2	1967
Fe_2O_3	1565	V_2O_5	690
PbO_2	290	ZnO	1975
MnO	1650	ZrO_2	1715
MnO_2	535		
MoO_3	795		
NiO	1990		
NbO	>240		
Nb_2O_5	1460		
Nb_2O_3	1780		
OsO_4	40		

(a) values from handbook of Chemistry & Physics and Alfa Catalog of Research Chemicals.

WHAT IS CLAIMED IS:

1. A composition comprising (a) at least one polyester and (b) one or more effective nucleating agents having a particle size which is about equal to or more than the lamellar thickness of the desired polyester.

2. The composition of claim 1 wherein at least one nucleating agent is selected from one or more elements of groups VA and VIA of the periodic table.

3. The composition of claim 1 wherein at least one nucleating agent is selected from antimony, arsenic, bismuth, tellurium and selenium.

4. The composition of claim 1 further comprising one or more additives selected from viscosity enhancers, fillers, plasticizers, impact modifiers, chain extenders, colorants, mold release agents, antioxidants, ultraviolet light stabilizers, lubricants, antistatic agents, fire retardants and nucleating agents other than those of claim 1.

5. The composition of claim 1 wherein said amount of nucleating agent or agents is about 0.001 to about 5 weight percent based on the total weight of the polymer.

6. A process for enhancing the rate of crystallization of a polyester which comprises adding to said polyester one or more effective nucleating agents having a particle size which is about equal to or more than the lamellar thickness of the desired polyester.

7. A process for enhancing the crystallization and melt viscosity properties of a polyester by forming an extended chain polyesters and block or graft polyesters or copolyesters, said

process comprising the steps of:

(a) forming an intimate mixture of one or more polyesters, one or more effective nucleating agents and at least one effective chain extension reagent compound;

(b) heating said mixture for a time and at a temperature sufficient to form said extended chain, or graft or block copolyester or polyester.

8. The process of claims 7 wherein the polyester used in step (a) contains at least one element selected group VA or VIA of the periodic table or combination thereof, or a substance having a component selected group VA or VIA of the periodic table or combination thereof, that will be reduced to elemental form under the process conditions.

9. The process of claim 7 wherein the polyester of step (a) is prepared by using a catalyst selected from polyester catalysts containing elements belonging to groups VA, VIA or combination thereof.

10. The process of claims 1 through 9 wherein the polyesters are selected from poly(ethylene terephthalate), poly(butylene terephthalate), poly(ethylene naphthalate), poly(ethylene/terephthalate/2,6-naphthalene dicarboxylate) and poly(tetramethylene/terephthalate/2,6-naphthalene dicarboxylate).

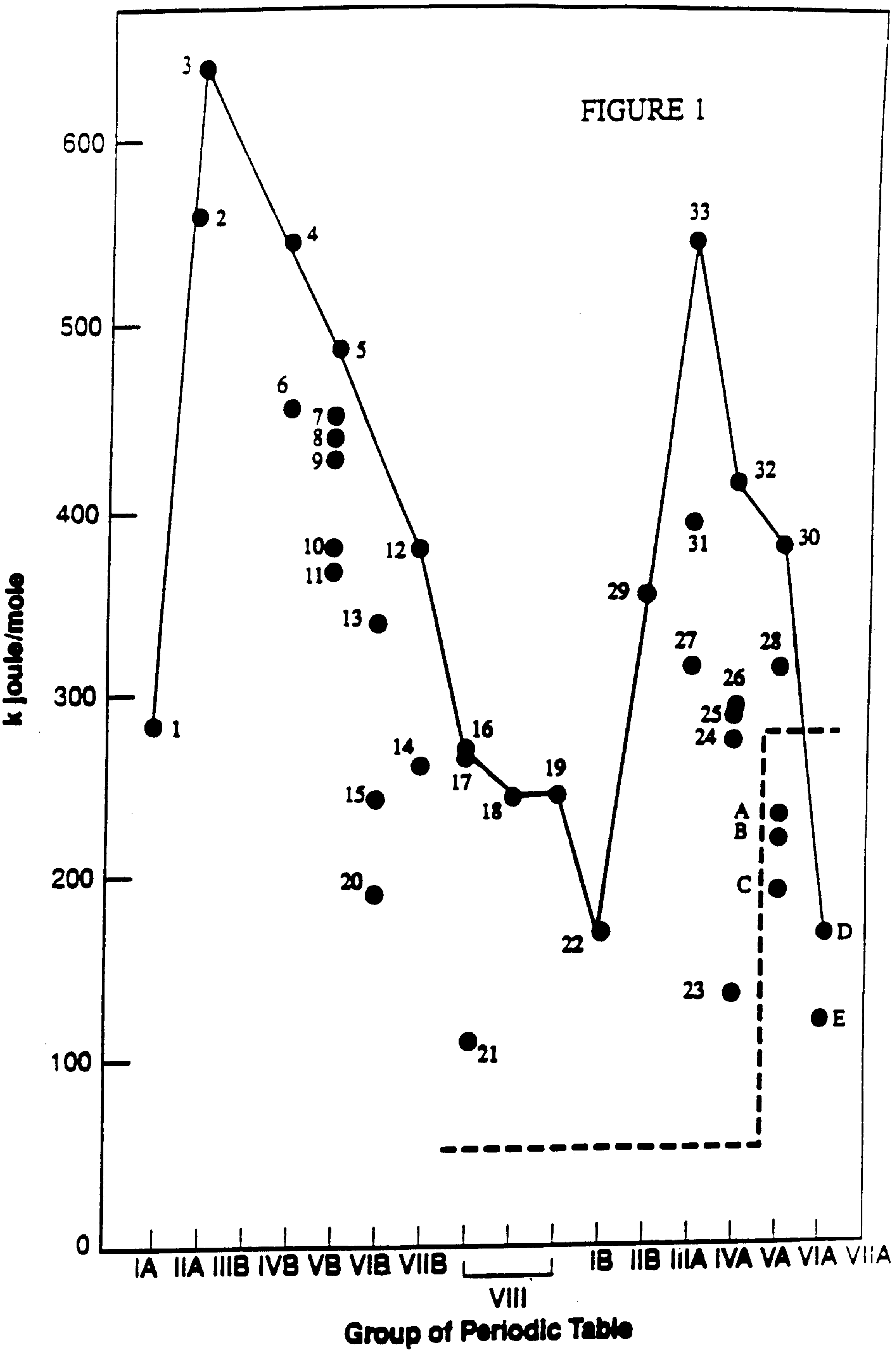


FIGURE 1
k joule/mole
600
500
400
300
200
100
0
1
2
3
4
5
6
7
8
9
10
11
12
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31
32
33
A
B
C
D
E
IA IIA IIIB IVB VB VIB VIIB
VIII
IB IIB IIIA IVA VA VIA VIIA
Group of Periodic Table

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 93/10252

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C08L67/02 C08K3/08 C08G63/692 //(C08K3/08,3:22,5:524)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C08G C08K C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 429 311 (IMPERIAL CHEMICAL INDUSTRIES PLC) 29 May 1991	1-5,10
Y	see page 2, line 27 - page 3, line 38; claims; example 6 ---	1-10
Y	WO,A,92 00305 (ALLIED-SIGNAL INC.) 9 January 1992 cited in the application see page 1, line 10 - page 2, line 9 see page 16, line 4 - line 18; claims ---	1-10
A	DATABASE WPI Week 8814, Derwent Publications Ltd., London, GB; AN 88-094499 & JP,A,63 043 921 (TEIJIN KK) 25 February 1988 see abstract -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1

Date of the actual completion of the international search
11 February 1994

Date of mailing of the international search report
01.03.94

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 93/10252

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0429311	29-05-91	CN-A-	1051922	05-06-91
		JP-A-	3230933	14-10-91
WO-A-9200305	09-01-92	US-A-	5118805	02-06-92
		EP-A-	0536252	14-04-93